STACKED CONJUGATED OLIGOMERS AS MOLECULAR MODELS TO EXAMINE INTERCHAIN INTERACTIONS IN CONJUGATED MATERIALS

A Dissertation Presented to The Academic Faculty

by

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To my wife, Dawson

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LIST OF SYMBOLS AND ABBREVIATIONS

δ	Chemical shift
λ	Wavelength
3	Molar absorptivity
J	Coupling constant
Hz	Hertz
ppm	Parts per million
d	Doublet
dd	Doublet of doublets
t	Triplet
S	Singlet
b s	Broad singlet
MP	Melting point
BP	Boiling point
dppp	diphenylphosphinopropane
RT	Room temperature
CV	Cyclic Voltammetry
DPV	Differential Pulse Voltammetry
IR	Infrared
NMR	Nuclear Magnetic resonance
ESR	Electron Spin Resonace
OLED	Organic light emitting diode
OFET	Organic field effect transistor

NIR	Near infrared
DMF	Dimethyl foramide
THF	Tetrahydrofuran
NBS	N-bromosuccinimide
BPO	Benzoyl peroxide
TMEDA	N,N,N,N-Tetramethyl ethylene diamine
НОМО	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital
SOMO	Singly Occupied Molecular Orbital
СТ	Charge transfer
HRMS	High resolution mass spectrometry
p-TSA	Para-toluene sulfonic acid
Bz	Benzene
EI	Electron Ionization
Th	Thiophene
EA	Elemental Anaylsis
RC	Radical cation
DC	Dication
D1	Dimer
E _{1/2}	Oxidation potential
BE	Bulk electrolysis
СР	Conductive polymer
DME	Dimethoxyethane

SUMMARY

Conjugated oligomers and polymers have attracted attention for their potential use in organic field effect transistors and light emitting diodes by virtue of their semiconducting properties. However, the movement of delocalized charge carriers along individual conjugated chains (i.e., a one dimensional pathway) does not provide for a complete understanding of conduction in the solid state. The importance of interchain hopping in conjugated materials led us to propose an extension of one-dimensional models into the second dimension by preparation and analysis of well-defined oligomers held in permanent cofacial arrangements. Thieno-fused bicyclo[4.4.1]undecanes provide a convenient scaffold to prepare oligomers that are held in a covalent π -stack, affording control of the distance and orientation of the conjugated segments and the study of the nature of charge transport by UV-vis-NIR spectroscopy and electrochemical measurements.

We have substituted the bis(thieno)fused bicyclo[4.4.1]undecane core to prepare a series of stacked oligothiophenes including terthiophene and a quinquethiophene, along with their linear (unstacked) analogs. Preparation of this first series of compounds provided insights into synthetic methodology as well as preliminary understanding of the π -stacking effects the electronic structure of radical cations and dication. With this series we were able to determine trends in the spectroscopic and electrochemical behavior of conjugated molecules and relate the influence of π -stacking to the stability of delocalized radical cations, and the potential role for π -dimers in charge transport.

Expanding this synthetic methodology, we were able to devise compounds that were covalently stacked with phenyl-capped oligothiophenes and a stacked ferrocene hybrid compound. Although less electron rich and with slightly higher oxidation potentials, the phenyl-capped series allowed us to examine the formation of π -dimers of conjugated radical cations. The stacked ferrocene compound and its unstacked model also demonstrated effective stacking by through space charge delocalization illustrated in electrochemistry measurements.

With this bis(thieno)fused bicyclo[4.4.1]undecane core, numerous other types of π -stacked derivatives may be synthesized to provide further insight into organic semiconducting materials (i.e. alkyne substituted oligomers, 3,4-ethylenedioxy-thiophenes, and n-dopable substituents). Varying the degree of π -overlap of terthiophene also may allow us to examine the stability of radical cations held in different orientations by use of the bis(thieno)fused bicyclo[4.4.1]undecane core.

CHAPTER 1

INTRODUCTION

1.1. π -Conjugated Materials

The electronic properties of π -conjugated materials are important in many aspects of chemistry. Over the last 25 years new classes of π -conjugated polymers such as oligo(phenylene vinylene)s,³ oligo(isothianaphthene)s⁴ oligothiophenes,^{1,2} and $oligo(phenylene ethynylene)s^5$ have been synthesized and studied for their intrinsic abilities to conduct electricity, Figure 1.1. The appreciation for Heeger, MacDiarmid, and Shirakawa were honored with a Nobel Prize in Chemistry in 2000 for their work in the field originating with a published observation of conductivity of polyacetylene in the 1970s.⁶ The revolutionary discovery of the conductivity of polyacetylene provided a foundation for studying broad classes of organic conjugated polymers as "synthetic metals".^{7,8} Among the incentives for the development of these conjugated materials are the potential for light, flexible, devices with characteristics that can be optimized by molecular design such as field effect transistors (FETs),⁹⁻¹³ light emitting diodes (LEDs),¹⁴ solar cells,¹⁵ and lasers,^{16,17} and other devices for energy storage such as supercapacitors¹⁸ and fuel cells.¹⁹



Figure 1.1. Examples of some π -conjugated oligometric polymers.

1.2. Charge Carriers in Conductive Materials

As the conjugation length of a molecule is extended, a density of states develops leading to the formation of a band gap. Ideally, a π -conjugated system with equal bond lengths should produce a band gap that diminishes as conjugation length increases, causing the material to become more metallic. However, the coupling of electrons and lattice vibrations, known as Peierl's distortion, leads to the formation of a gap between valence and conducting bands, Figure 1.2. Extrapolation of the optical and electrochemical properties of model oligomers to an infinite length can be used to predict the intrinsic properties of conjugated polymers. **1D ATOMIC CHAIN**



Figure 1.2. Schematic diagram for Peierl's distortion.

Longer conjugation lengths of π -conjugated polymers increases the ease of oxidation or reduction (processes known as doping), which greatly increases their conductivity. In the case of polymers with non-degenerate ground states, a low level of oxidation leads to polarons as charge carriers which give rise to new optical absorptions and an ESR signal. A positive polaron in polythiophene, for example, is created when an electron is removed by chemical doping with FeCl₃. The charge (+1) and spin are localized over several thiophene rings with a geometrical change to a quinoid structure. A positive polaron corresponds to a radical cation in chemical terminology. Further oxidation leads to bipolarons which are spinless and ESR-silent.²⁰⁻²² The positive charge (+2) localized on the polymer chain is known as a dication, Figure 1.3.



Neutral polymer

Radical cation (polaron) *ESR active*

Dication (bipolaron) ESR inactive

Figure 1.3. Doping of a π -conjugated polyene.

1.3. Fates of Radical Cations in Doped π-Conjugated Oligomers

A radical cation, formed upon one-electron oxidation, is delocalized along the π conjugated chain. If we concentrate on the radical cation species only, it can interact in several ways, Figure 1.4. The first example illustrates radical cations located on two separated molecules (denoted 'M') where one becomes oxidized and the other reduced known as disproportionation. The process has been ovserved for rigid thienylene vinylene systems for which UV-vis-NIR and ESR analysis suggests gives rise to formed a neutral and dicationic species.²³

DISPROPORTIONATION $M^{+\cdot} + M^{+\cdot} \rightarrow M^{2+} + M^0$

BIS(RADICAL CATION) COMBINATION $M^{2(+.)} \rightarrow M^{2+}$

 $\sigma\text{-DIMERIZATION} \\ M^{++} + M^{++} \rightarrow M^{+} - M^{+}$

 $\begin{array}{l} \textbf{\pi-DIMERIZATION} \\ \textbf{M}^{+\cdot} & - \textbf{M}^{+\cdot} \rightarrow \ \textbf{(M} & - \textbf{M})^{2 + \prime 0} \end{array}$

Figure 1.4. Schematic representation of the fates of radical cations.

Similarly, a secong e- oxidation of a radical cation to form a bis(radical cation) on a single subunit may result in combination of the two radical cations form a dication, as depicted first in Figure 1.3 and in Figure 1.4. Orthogonally fused thiophene oligomers²⁴ were probed electrochemically and exhibit this behavior.

Reversible σ -dimerization of two radical cations or anions is plausible where a σ bond between two oligomers forms by alignment of the sp^2 orbitals. 1,3,5-Tripyrrolidinobenzene has been shown to be a redox switch when two of these molecules join to form a sigma bond,²⁵ and electroreduction of 9-fluoro-10-cyanoanthracene²⁶ showed similar reversible dimerization. In another study of diphenylpolyene radical anions,²⁷ argument against σ -bond dimerization was that such bond formation was energetically favored because of the relative orientation of the chains.

Analysis of alkylated oligothiophenes²⁸ by Miller²⁹ and others^{30,31} indicates that the oligomeric radical cations associate in solution to form π -dimers, Figure 1.5. The dimers give rise to a new absorption band in the near IR and are ESR-silent, and serve as models for spinless bipolarons. These spectral characteristics are also noted for a polyester

containing isolated tetrathiophene units.³² This four-ring system is too short for the formation of stable dications (bipolarons). However, one-electron oxidation of the conjugated units in the polyester (*i.e.*, to the radical cation) leads to a strong optical absorption spectrum and a weak ESR signal consistent with dimerization of the polarons to form spinless charge carriers in aggregates of the arene units.



Figure 1.5. π -Dimer formation by aggregation of radical cations.

Whereas the structure of the π -dimers formed in solution or in the polyester are not well defined, the effects are observed in the crystalline state. Direct evidence for π -dimers comes from X-ray analysis of electro-crystallized oligothiophene radical cation salts³³ which display a conductivity of 10⁻² Scm⁻¹ in spite of their short conjugation length, Figure 1.6.



Figure 1.6. X-ray structural analysis of radical cation salt (from reference 33).

The concept of π -dimers is also illustrated by new UV-vis-NIR absorbances attributed to association of bis(radical cations of terthiophenes, quarterthiophenes, and β -methoxy- α -methyl capped oligothiophenes.^{29,34-37} The solid-state structural analysis of 3',4'-dibutyl-2,5"-diphenyl-5,2':5',2"-terthiophene radical cation salt³³ provided additional insight into the idea of that spinless charge carries can be models for polarons and bipolarons in polymer systems such as poly(p-phenylene)oligomers.³⁸

Mimicking through-space delocalization of charge carriers in conjugated organic oligomers and polymers requires the ability to control the orientation and degree of interactions between adjacent chains. Studies of linear interchain electronic interactions in the development of new functional materials often ignore aggregation of oligomers in solution.³⁹⁻⁴³

1.4. Two-Dimensional Compounds: π-Stacking Interactions

The movement of delocalized charge carriers along π -conjugated chains within a one dimensional unit does not provide complete understanding of conductivity in conjugated polymers. Conductivity over macroscopic distances in polymers requires interactions between chains, which are absent in the isolated linear oligomers in solution. The fact that organic semiconductor materials tend to be highly processable, flexible, and less costly favor the continued development of such materials.

The influence of π -stacking on the electronic structure of *neutral* arenes is apparent in the photophysical behavior resulting from their self-association as excimers and Jaggregates. Monomolecular analogs of such assemblies have been studied extensively by the preparation of compounds in which two stilbene chromophores are held in a cofacial arrangement by a [2.2]paracyclophane unit.^{44,45} Others have used crystal engineering to examine the spectroscopy of neutral oligomers assembled into well-defined stacks in the solid state.⁴⁶ In addition to investigations of stacked aggregates, other recent studies have addressed approaches to non-planar arrangements of oligomers (tetrahedral,⁴⁷ dendritic⁴⁸) to gain control over interchain interactions.

Cofacial stacking of oligomeric units into a permanent π -stack by covalent bonds would provide control of the distance and orientation of the conjugated systems, allowing us to study the nature of charge transport by spectroscopy and electrochemical measurements. Cyclophanes constitute an important class of organic molecules in which two or more arenes are fused on a single macrocycle.^{49,50} Small meta- and paracyclophanes adopt a face-to-face geometry in which the arenes are held at a short distance from one another. Orthocyclophanes are generally flexible and adopt nonstacked geometries. However, judicious choice of a bridging unit leads to the formation of stacked π -systems.⁵¹ This approach can also be used to prepare multi-layered orthocyclophanes⁵² which are relatively simple to prepare relative to multilayered paracyclophanes. Thus, preparation of stacked orthocyclolphanes which hold π conjugated oligomers in close proximity will allow for examination of the through space π - π interactions and effect on stabilizing charged species which might serve as charge carriers in conjugated polymers. The through-space interaction of the π -systems has also been studied by substitution of the rings with various electroactive, electron-donating and electron-withdrawing substituents,⁵³ and by UV-visible spectroscopy.

Approaches to compounds in which fused- or oligo- arenes are held in stacks include preparation of benzo-annelated bicyclo [4.4.1] undecanes,⁵⁴⁻⁵⁶ quadruple-layered orthonaphthophanes,⁵² and thieno[3.3]orthocyclophanes.⁵⁷ Whereas benzene undergoes oxidation at a relatively high potential to form poorly defined polymers,⁵⁸ these tripleand quadruple-decker analogs undergo oxidation to the radical cation and dication at relatively low potentials. Collard et. al. has previously synthesized oligothienylsubstituted [2.2]paracyclophanes illustrating the effect of through space delocalization of charges.^{59,60} Other studies demonstrate the electronic communication of oligothiophenes through the paracyclophane subunit with shorter oligomer subunits.⁶¹⁻⁶⁴ These studies have also been extrapolated to other classes of conjugated polymers such as polyfluorenes,⁶⁵ where the anion radicals can be kinetically controlled by solvation.⁶⁵

The electrochemistry and photophysics of conjugated oligomers continues to be an area of intense interest as models for conjugated polymers and for the development of new functional materials. Computational studies systematically compare effects such as orbital splitting, internal reorganization energies, and molecular packing motifs.^{66,67} Other studies provide a wealth of information to clues evolution of electronic structure of individual conjugated molecules as they are incorporated into a 3D molecular material.⁶⁸⁻⁷⁰ Other studies try to determine which theoretical theory is best for radical cation molecular geometry.⁷¹ There are few model systems to corroborate the output from these calculations. Ideally, a combination of experimental results and theoretical calculations should be used to examine the electronic structure of conjugated materials.⁷²

1.5. Scope of Work

The importance of interchain hopping of charge carriers in doped conjugated polymers led us to propose an extension of one-dimensional models into the second dimension by synthesis of novel compounds and analysis of well-defined charged oligomers held in a permanent cofacial arrangement. We can exert control over the distance, orientation and overlap of conjugated units to determine the influence of molecular packing on the behavior of charge carriers, Figure 1.7.



Figure 1.7. Unstacked linear analog (left) and π -stacked analog (right). Each box denotes a central thiophene unit attached at the α -positions to another heterocycle or aromatic compound.

To explore the effect of interacting conjugated systems on charged carriers in conjugated polymers we set out to vary the extent of interaction between conjugated oligothiophene by: (i) design of a framework to hold the oligomers in close proximity, (ii) variation of the length of the conjugated substituents, (iii) examination of the spectroscopy of different redox states by level of doping, and (iv) installation of substituents onto the oligomers. The design of models for polythiophene using this approach allows us to vary the extent of π -overlap and compare the properties of these π -dimers to unstacked model oligomers.

A combination of synthetic chemistry, electrochemistry, and spectroscopy will allow us to develop models for charge carriers in doped conjugated polymers, and to explore the evolution of electronic structure in materials consisting of close-packed π -electronrich molecules. In particular it allows us to examine the electronic structure of various states shown in Figure 1.8.



Figure 1.8. Redox states arising from oxidation of π -stacked oligomers.

Whereas, Otsubo recently reported a series of dimeric quinquethiophenes held together by bridges at the termini and examined them as π -dimers models of

polythiophene,⁷³⁻⁷⁵ here, we prepare extended π -conjugated oligomers held together in the center. A divergent synthesis allows us to vary the length of the oligomers to explore the effect of chain length on charge delocalization. Extended conjugated oligomers based on a dithieno-fused bicyclo[4.4.1]undecone core show promise for further investigations to the nature of charge transport in organic materials.

The dithieno-fused bicyclo[4.4.1]undecane **1.4** can be prepared as a heteroarene analog of Mataka's work⁷⁶ thereby providing us with access to stacked oligomers consisting entirely of thiophene rings. In analogy to the reaction of α , α '-dibromo-o-xylene,⁷⁶ treatment of 3,4-Bis(bromomethyl)thiophene⁷⁷ **1.1** with dimethyl 1.3-acetonedicarboxylate (dimethyl oxaglutarate, **1.2**) under phase transfer conditions, followed by saponification, decarboxylation, and ketalization with ethylene glycol provides the dithieno-fused bicyclo[4.4.1]undecane **1.4** in which the arenas are held in a cofacial arrangement, Figure 1.9.



Figure 1.9. Synthesis of dithieno-fused π -stacked orthocyclophane with ethylene glycol.

Conjugated arms to be tethered to the framework core can be prepared by carboncarbon bond forming reactions (Stille, Negishi, or Suzuki reactions) at the unblocked α thienyl positions These arms include: (i)oligothiophenes, (ii) phenyl-terminated
oligothiophene analogs, and (iii) ferrocene. This versatile framework is applicable to a wide variety of π -linear systems and allow us to demonstrate the infuence of permanent π -stacking on cofacial oligomers.

In Chapter 2, the synthesis of 3,4-bis(bromomethyl)thiophene, the dithieno-fused bicyclo[4.4.1]undecanone core, and π -stacked analogs is described. This is elaborated in Chapter 3 where the synthesis of extended terthiophene and quinquethiophene π -stacked compounds and their respective linear model compounds is discussed. In Chapter 4, the photophysical and electrochemical characterization of the π -stacked oligothiophenes and linear model is explored. Exploring other π -conjugated systems by varying the termini of oligothiophenes with phenyl-capped and ferrocene-capped substituents is synthesized and explored in Chapters 5 and 6. Other π -conjugated compounds and varying the degree of overlap is mentioned in Chapter 7.

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CHAPTER 2

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF DITHIENO-FUSED BICYCLO[4.4.1]UNDECANES

2.1. Introduction

In covalently linking two π -conjugated oligomers together in a stacked arrangement, we chose a rigid dithieno-fused bicyclo[4.4.1]undecane framework. Such fused-arene bicycles were previously prepared by Shuntaro Mataka at Kyushu University from 1986-2000.¹⁻¹⁰ Incorporation of fused-dithieno rings according to the methodology of Mataka would provide control over the orientation of the two thiophenes stacked on top one another to allow charged carriers (*i.e.* radical cations, dications) to hop through space when oxidized chemically or electrochemically.

Early work by Mataka⁸ examined the synthesis and conformational rigidity of a series of bicyclic compounds. Symmetrical fused dibenzo[3,4;8,9]bicyclo[4.4.1] undeca-3,8-dienes, dinaphtho-[3,4-*b*;8,9-*b'*]bicyclo[4.4.1]undeca-3,8-dienes and dinaphtho[3,4,5-*de*;-9,10,11-*d'e'*]bicyclo[5.5.1]trideca-3,9-dienes, and asymmetrically fused naphtha-[3,4,5-*de*]benzo[9,10]bicyclo[5.4.1] dodeca-3,9-dien-12-one compounds, **2.1-2.4**, exist in different conformations depending on the temperature, as shown by ¹H and ¹³C NMR spectroscopy, Figure 2.1. The methylene groups of **2.1c** give a coalesced signal in the ¹H NMR spectrum and one signal in the ¹³C NMR spectrum at room temperature. Upon

cooling to -40 °C, the ¹³C NMR exhibits two types of methylene peaks and two sets of aromatic signals (3 carbons each).⁸



Figure 2.1. Conformational benzo-annelated bicylo[4.4.1]undecanes (from reference 8).

The plausible conformations for these compounds are illustrated in Figure 2.2. The boat-boat form (**B**₁) and chair-chair (**C**₁) conformations are not formed according to the NMR characterization for 2.1c, 2.1f, 2.2a, and 2.2c. The A_1/A_1^* chair-boat conformations exist in equilibrium at room temperature, and one conformation is preferred at low temperature. One single crystal structure analysis of 2.1a confirmed the chair-boat conformation in the solid state. Comparisons of ΔG values calculated from dynamic ¹³C NMR spectra (kinetic data from ring inversions calculated by signal widths

and activation energies calculated from Eyring $plots^{11}$ indicate that the conversion between chair-boat conformations (*i.e.* A₁ and A₁^{*}) is stepwise.



Figure 2.2. Possible dynamic conformations (from reference 8).

Expanding on his previous work, Mataka showed that the arenes fused to the bicyclo[4.4.1]undecane core could be forced into a stacked orientation, *i.e.* C₁ (chair-chair) conformation, by ketalizing the ketones 2.1-2.3c.⁹ Several ketalizing groups were used: ethylene glycol, neopentyl glycol, and dithioketal to afford compounds 2.5 and 2.6, Figure 2.3. Face-to-face stacking was shown by an upfield shift for the aromatic signals in ¹H NMR spectra of ketals by 0.3-0.5 ppm compared to the ketone precursors. In addition, the methylene protons exhibited geminal and vicinal splitting (*i.e.*, a pair of

doublet of doublets for the ketal). The X-ray crystal structures of some of the compounds showed close arene-arene contact of 3.03 to 4.1 Å.



Figure 2.3. Orthocyclophanes with benzene and naphthalene (from reference 9). B and N indicate benzo and 2,3-naphtho annelation.

Mataka expanded his previous synthetic methodology to prepare arene-fused multi-decker orthocyclophanes to study the electronic properties of such compounds. One such compound was a triple-layered orthocyclophane³ in which Mataka demonstrated π - π -communication from one naphthalene unit through the benzene core, to the other naphthalene unit by electrochemical investigations, Figure 2.4. Upfield shifts were apparent for this compound as well as the coupling of methylene protons consistent with a chair-chair conformation.



Figure 2.4. Triple-Deckered Orthocyclophane (from reference 3).

The π -stacking effect were also apparent in a quadruple decker⁶ reported by Mataka in 1998, Figure 2.5. There was an pronounced upfield proton shift for the two inner benzene units (δ 5.77 ppm) and a less dramatic upfield shift for the outer benzene units (δ 6.4-6.62 ppm).



Figure 2.5. Quadruple Decker Orthocyclophane (from reference 6).

Here we report a roadmap to the efficient synthesis of a *dithieno*-fused bicyclo[4.4.1]undecane scaffold, and the ketalization of this core to provide a π -stacked core for π -conjugated oligomers to examine charge distribution in doped π -conjugated materials. Structural characterization was performed by variable temperature NMR and X-ray crystallography.

2.2. Experimental

2.2.1. General Procedures

All reagents and catalysts were purchased from Aldrich, TCI, or Strem Chemicals and used without further purification. THF and diethyl ether were distilled from benzophenone-sodium ketyl. Dichloromethane was distilled from calcium hydride and anhydrous DMF was purchased from Aldrich. ¹H and ¹³C NMR spectra were recorded from a 300 or 400 MHz Varian Mercury spectrophotometer. Infrared spectra were recorded on a Nicolet 4700 FTIR. Mass spectra were collected on a VG-70SE instrument. Elemental analyses were obtained from Atlantic Microlabs, Inc. Gravity and flash column chromatographies were carried out with silica gel (32-63 mesh, 60 Å from Sorbent Technologies). TLC plates were visualized by a UV lamp or iodine vapor.

2.2.2. Synthetic Procedures



2,5-*Dichloro-3,4-diiodothiophene*.¹² Iodine (41 g, 0.16 mol) was added to a solution of 2,5-dichlorothiophene (30 g, 0.2 mol), periodic acid (20 g, 0.09 mol), acetic acid (110 mL), H₂O (22 mL), and H₂SO₄ (3.4 mL), and the mixture was heated at 90 °C for 18 h. The reaction mixture was cooled and a saturated aq. solution of Na₂SO₃ (300 mL) was added, and the mixture was stirred for 10 min. CHCl₃ (100 mL) was added, and the organic layer was separated. The aqueous layer was extracted with CHCl₃ (2 x 75 mL) and the organic layers were combined, washed with H₂O (5 x 100 mL), 0.2 M NaOH (2 x 50 mL), H₂O again (2 x 50 mL), dried over MgSO₄, and the solvent was removed under reduced pressure. The crude product was recrystallized in ethanol (300 mL) to afford 2,5-dichloro-3,4-diiodothiophene as a white crystalline solid (30 g, 80%). MP = 78-80 °C (Lit. MP = 80-81 °C). ¹³C NMR (75 MHz, CDCl₃): δ 128.3 (Th-3,4), 94.7 (Th-2,5). MS (EI): *m/z* (%) 403.7 (M⁺, 100), 276 (M⁺-I, 24), 149 (M⁺-2I, 30).



2,5-*Dichloro-thiophene-3,4-dicarboxylic acid.*¹² A 2.5 M solution of *n*-BuLi in hexanes (0.28 mol, 110 mL) was added dropwise to a cooled solution of 2,5-dichloro-3,4-diiodothiophene (50 g, 0.12 mol) in dry ether (200 mL) at -78 °C. The mixture was allowed to stir for 1 h and then CO₂ gas was bubbled through the reaction for 12 h. Crushed ice (200 g) was added, and the aqueous layer was separated. The organic layer was washed with 10% aqueous NaOH (3 x 50 mL), and the combined aqueous layers were acidified with 12 M HCl to pH = 1. The aqueous layer was then slowly cooled to 4 °C overnight, and the precipitated needles were filtered and washed with cold water to afford 2,5-dichlorothiophene-3,4-dicarboxylic acid (14 g, 46%) MP = 204-206 °C (Lit. MP = 205-206 °C). ¹³C NMR (75 MHz, CDCl₃): δ 161.9 (C=O), 131.7 (Th-2,5), 127.8 (Th-3,4).



2,5-Dichloro-3,4-bis(hydroxymethyl)thiophene.¹³ LiAlH₄ (8.3 g, 0.2 mol) was added to a solution of 2,5-dichlorothiophene-3,4-dicarboxylic acid (13 g, 50 mmol) in dry Et₂O (300 mL) at 0 °C, warmed slowly to reflux, and stirred for 18 h. The reaction was quenched with H₂O, and the product collected in ether. The solvent was removed under reduced pressure. Recrystallization from ethanol provided the title compound as a white solid

(10.2 g, 89%). MP = 132-134 °C (Lit. MP = 134-135 °C). ¹H NMR (300 MHz CDCl₃): δ 4.80 (b s, 2H, -OH), 4.61 (s, 4H, -CH₂-). ¹³C NMR (75 MHz, CDCl₃): δ 136.6 (Th-3,4), 124.5 (Th-2,5), 56.7 (methylene). IR (KBr) 3470 (-OH), 2900, 1045, 825 cm⁻¹. MS (EI): m/z (%) 211.9 (M⁺, 100).



3,4-Dicyanothiophene.^{14,15} 3,4-Dibromothiophene (10 g, 41 mmol) was added to a suspension of copper cyanide (10.7 g, 120 mmol) in DMF (15 mL) and refluxed for 4 h. The mixture was cooled and poured into a solution of ferric chloride (42 g) in 1.7 M HCl (100 mL). The mixture was stirred for 30 min at 60 °C, cooled and extracted with CH₂Cl₂ (3 x 100 mL). The organic layers were combined, washed with 2 M HCl, H₂O (200 mL), aqueous Na₂CO₃ (3 x 50 mL), and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was sublimed and the residue then recrystallized from acetonitrile to afford 3,4-dicyanothiophene as a yellow solid (700 mg, 12%). MP = 168-169 °C (Lit. MP = 169-171 °C). ¹H NMR (300 MHz, CDCl₃): δ 8.1 (s, 2H, Th-2,5). IR (KBr) 3018, 2235, 2230 cm⁻¹.



Thiophene-3,4-dicarboxylic acid.^{14,16} A solution of 3,4-dicyanothiophene (1.4 g, 10 mmol) and NaOH (2.7 g, 68 mmol) in ethylene glycol (15 mL) was heated to reflux, and the mixture was stirred for 18 h, cooled, and poured onto ice (100 g). The solution was washed with Et₂O (50 mL), and the organic layer discarded. The aqueous layer was acidified with 12 M HCl to pH = 1. The round bottom was placed in the freezer overnight, and the precipitated crystals were separated by filtration and washed with cold H₂O to afford thiophene-3,4-dicarboxylic acid as colorless needles (340 mg, 19%). MP = 226-228 °C (Lit. MP = 227-229 °C). ¹H NMR (300 MHz, CDCl₃): δ 8.10 (s, 2H, Th-2,5), 10.90 (-OH). ¹³C NMR (75 MHz, CDCl₃): δ 163.9 (C=O), 137.4 (Th-3,4), 125.1 (Th-2,5). IR (KBr) 3320, 3018, 1203, 1040, 976 cm⁻¹.



3,4-Bis(hydroxymethyl)thiophene.^{13,17} LiAlH₄ (3.15 g, 0.09 mol) was added to a solution of thiophene-3,4-dicarboxylic acid (1.5 g, 8.7 mmol) in dry THF (150 mL) and heated at reflux for 18 h. The reaction was cooled to 0 °C and a saturated NH₄Cl solution (100 mL) was added dropwise over 45 min. The solution was vigorously stirred and acidified with 12 M HCl to pH = 1. The organic layer was separated and the aqueous extracted with CH₂Cl₂ (3 x 50 mL). The combined organic layers were washed with H₂O (100 mL), and the solvent removed under reduced pressure to afford 3,4-

bis(hydroxymethyl)thiophene as an white solid (1.1 g, 88%). MP = 64-65 °C (Lit MP = 65-66 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.1 (s, 2H, Th-2,5), 4.5 (s, 4H, -CH₂-), 4.2 (b s , 2H, -OH). ¹³C NMR (75 MHz, CDCl₃): δ 140.2 (Th-3,4), 124.8 (Th-2,5), 59.3 (methylene). IR (KBr) 3295 (-OH), 3098, 2966, 2910, 1050, 1000 cm⁻¹.



3,4-Bis(bromomethyl)-2,5-dichlorothiophene.¹³ 2,5-dichlorothiophene (5.1 g, 33 mmol) was added to a solution of 48% aq. HBr (100 mL) and 36.8% aqueous formaldehyde (27.5 mL). The mixture was stirred at room temperature for 24 h, H₂O (100 mL) was added, and the aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with 10% aq. NaHCO₃ (2 x 100 mL), and H₂O (3 x 100 mL), and dried over MgSO₄. The solvent was removed under reduced pressure to afford 3,4-bis(bromomethyl)-2,5-dichlorothiophene as a white crystalline solid (8.3 g, 73%). ¹H NMR (300 MHz, CDCl₃): δ 4.5 (s, 4H, -CH₂-). ¹³C NMR (75 MHz, CDCl₃): δ 132.8 (Th-3,4), 126.8 (Th-2,5), 21.9 (-CH₂-). IR (KBr) 2970, 2904, 1411, 975 cm⁻¹. MS (EI): *m/z* (%) 337.8 (M⁺, 15), 259 (100), 178 (80), 143 (15). HRMS (EI): *m/z* Calcd. for C₆H₄Cl₂Br₂S, 337.77570; found, 337.77593, Δ = 0.6 ppm.



1,1'-Thiodipropan-2-one.¹⁸ A solution of $Na_2S \cdot 9H_2O$ (52 g, 0.22 mol) in H_2O (200 mL) was added dropwise to a solution of chloroacetone (40 g, 34 mL, 0.43 mol) in acetone (400 mL) at room temperature over a period of 1 h. The yellow solution was allowed to

stir for an additional 1 h, after which the acetone was removed under reduced pressure. The residue solution was extracted with methylene chloride (10 mL), and the aqueous layer was extracted with methylene chloride (2 x 50 mL). The combined organic layers were washed with 10% Na₂CO₃ (2 x 50 mL), H₂O (2 x 50 mL), and dried over MgSO₄. Evaporation of the solvent under reduced pressure afforded 1,1'-thiodipropan-2-one as orange crystals (25 g, 80%). MP = 43-45 °C. IR (neat) 2932, 1690, 1436, 1200, 1106 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 2.26 (s, 6H, -CH₃), 3.29 (s, 4H, -CH₂-).



2,3,4,5-*Tetrabromothiophene*.¹⁹ Br₂ (220 mL, 4.0 mol) was added dropwise to solution of thiophene (84.0 g, 1.0 mole) in CHCl₃ (35 mL) at 0 °C over 3 h. The last 50 mL of Br₂ were added without external cooling. The mixture was heated for an additional 4 h. 2M NaOH (150 mL) was cautiously added and the mixture was heated at reflux for an additional 1 h. The mixture was transferred to a large evaporating dish and allowed to cool to room temperature. The large crystalline mass was filtered and washed with H₂O (1 L). Recrystallization from CHCl₃ afforded 2,3,4,5-tetrabromothiophene as a white crystalline solid (315 g, 80%). MP = 113-115 °C (Lit. MP = 112-114 °C). ¹³C NMR (75 MHz, CDCl₃): δ 116.9 (Th-C-3,4), 110.3 (Th-C-2,5). IR (KBr) 1491, 1406, 1291, 866, 761 cm⁻¹.



3,4-Dibromothiophene.^{19,20} A 2.5 M solution of *n*-butyllithium in hexanes (100 mL, 0.25 mol) was added to a solution of tetrabromothiophene (50.0 g, 0.13 mol) in dry Et₂O (200 mL) at 0 °C. The resulting suspension was stirred for 2 h at 0 °C, poured onto crushed ice (350 g), and extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with water (3 x 150 mL), dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was distilled to provide 3,4-dibromothiophene as a colorless liquid (25 g, 81%). BP = 96-99 °C/11 mmHg. (Lit. BP = 220 °C/760 torr.) ¹H NMR (300 MHz, CDCl₃): δ 7.41 (s, 2H, Th-H). ¹³C NMR (75 MHz, CDCl₃): δ 123.6 (Th-H), 113.8 (Th-Br). IR (neat) 3112, 1415, 1394, 1208, 1155, 900, 702 cm⁻¹.



3,4-Dimethylthiophene.^{19,21} A 2.5 M solution of methylmagnesium bromide (200 mL) in hexanes was cannulated into a solution of 3,4-dibromothiophene (50 g, 0.21 mol) and Ni(dppp)Cl₂ (5.6 g, 11 mmol) in dry Et₂O (250 mL) at 0 °C under N₂. After 30 min, the mixture was heated to reflux and stirred for 24 h. The flask was cooled to 0 °C and carefully poured onto crushed ice (300 g), and a 2M HCl (50 mL) solution was added. The organic layer was separated, and the aqueous phase was extracted with Et₂O (4 x 100 mL). The combined organic layers were washed with saturated aq. NaHCO₃ (2 x 150 mL), H₂O (3 x 100 mL), and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was distilled to afford 3,4-dimethylthiophene as a colorless liquid (20 g, 87%). BP = 142-144 °C/760 torr. ¹H NMR (300 MHz, CDCl₃): δ 6.88 (s, 2H, Th-2,5), 2.21 (s, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 137.6, (Th-C-3,4), 127.6 (Th-C-2,5), 14.6 (-CH₂-). IR (neat) 3110, 2948, 2875, 1413, 1394, 1228, 1155, 900, 750 cm⁻¹. HRMS (EI): *m/z* Calcd. for C₆H₈S, 112.01498; found, 112.01532, Δ = 3.1 ppm.



3,4-Bis(bromomethyl)-2,5-dimethylthiophene.²² 2,5-dimethylthiophene (5.0 g, 45 mmol) was added to a solution of 48% aq. HBr (100 mL) and 37% aqueous formaldehyde (27.5 mL). The mixture was stirred at room temperature for 24 h, H₂O (100 mL) was added, and the aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with 10% aq. NaHCO₃ (2 x 100 mL), H₂O (3 x 100 mL), and dried over MgSO₄. The solvent was removed under reduced pressure to afford 3,4-bis(bromomethyl)-2,5-dimethylthiophene as a pale green crystalline solid (11.02 g, 83%). MP = 76-78 °C. ¹H NMR (300 MHz, CDCl₃): δ 4.52 (s, 4H, -CH₂-), 2.37 (s, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 135.9 (Th-C-3,4), 131.7 (Th-C-2,5), 24.6 (-CH₂-), 13.0 (-CH₃). IR (KBr) 3113, 2914, 2880, 1412, 1380, 1201, 1145, 905, 750 cm⁻¹. MS (EI): *m/z* (%) 297.9 (M⁺, 9), 219 (M⁺-Br, 45), 138 (M⁺-2Br, 100). HRMS (EI): *m/z* Calcd. for C₆H₁₀Br₂S, 297.88495; found, 297.88461, Δ = 1.1 ppm.



Tetramethylthiophene.²³ LiAlH₄ (3.5 g, 93 mmol) was added to a solution of 3,4bis(bromomethyl)-2,5-dimethy-thiophene (11.0 g, 37 mmol) in dry THF (150 mL) at 0 °C under N₂. The mixture was heated to reflux for 18 h, cooled to 0 °C, and saturated aq. NH₄Cl (100 mL) was added. The aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with H₂O (150 mL), dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was vacuum distilled to afford tetramethylthiophene as a colorless liquid (3.2 g, 60%). BP = 80-85 °C/20 mm (Lit. BP = 74-79 °C/15 mm). ¹H NMR (300 MHz, CDCl₃): δ 2.37 (s, 6H, Th-2,5-CH₃), 2.08 (s, 6H, Th-3,4-CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 132.8 (Th-C-3,4), 127.6 (Th-C-2,5), 13.0 (-CH₃), 12.7 (-CH₃). IR (neat) 2911, 2858, 1438, 1383, 1156, 1043, 954.



*3,4-bis(bromomethyl)-thiophene.*¹⁷ *N*-bromosuccinimide (6.4 g, 36 mmol) and benzoyl peroxide (200 mg, 0.8 mmol) were added to a solution of 3,4-dimethylthiophene (2.0 g, 18 mmol) in CCl₄ (100 mL). The solution was slowly warmed to reflux at which time a W lamp was placed against the flask for 30 min. After 2 h the solution was cooled to 0 °C, and the succinimide was removed by filtration. The solvent was removed under reduced pressure to produce an orange oil which was subjected to column chromatography (100 % hexanes) to afford 3,4-bis(bromomethyl)thiophene as a colorless solid (1.9 g, 40%). MP = 81-82 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.4 (s, 2H, Th-2,5), 4.6 (s, 4H, -CH₂-). ¹³C NMR (75 MHz, CDCl₃): δ 136.4 (Th-C-3,4), 127.0 (Th-C-2,5),

25.7 (-CH₂-). IR (KBr) 3100, 2950, 1412, 1200, 610 cm⁻¹. MS (EI): *m/z* (%) 269.9 (M⁺,
17). HRMS (EI): *m/z* Calcd. for C₆H₆Br₂S, 267.85569; found, 267.85354, Δ = 8 ppm.



Dimethyl 11-oxo-dithieno[3,4-c:8,9-c']*bicyclo*[4.4.1]*undeca-3*,8-*diene-1*,6-*dicarboxylate*. Tetra-n-butylammonium bromide (1.05 g, 3.2 mmol) was added to a solution of 3,4bis(bromomethyl)thiophene (3.1 g, 11 mmol) in CH₂Cl₂ (30 mL) analogous to literature procedures.^{4-7,9} A 25% aq. NaOH solution (25 mL) was added, and the resulting biphasic mixture was vigorously stirred at room temperature. A solution of dimethyl 1,3acetonedicarboxylate (1.13 g, 6.50 mmol) in CH₂Cl₂ (30 mL) was added dropwise over 1 h. After stirring for 24 h, H₂O (50 mL) was added and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with a 5% aqueous HCl solution (2 x 50 mL) and H₂O (3 x 75 mL), and dried over MgSO₄. Removal of solvent under reduced pressure afforded a yellow oil, which was purified by flash chromatography (30% ethyl acetate/70% hexanes) to give the title compound as a white solid (1.9 g, 74%). MP = 162-164 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.01-7.1 (b s, 4H, Th-H), 3.71 (s, 6H, -OCH₃), 2.65-3.32 (m, 8H,-CH₂-). ¹H NMR (CDCl₃, -60 °C): δ 7.0 (s, 2H, Th), 7.2 (s, 2H, Th) 3.61 (s, 6H, -OCH₃), 3.70 (d, 2H, J = 15.4 Hz, -CH₂-), 3.40 (d, 2H, J = 15.4 Hz, -CH₂-), 3.01 (d, 2H, J = 14.8 Hz, -CH₂-), 2.45 (d, 2H, J = 14.8 Hz, -CH₂-). ¹³C NMR (75 MHz, CDCl₃) δ 209.6 (ketone

C=O), 172.4 (ester C=O), 136.6 (Th-C-3,4), 124.0 (Th-C-2,5), 64.5 (-CH-), 52.3 (-OCH₃), 31.02 (-CH₂-). IR (KBr) 3158, 3098, 3006, 2960, 2848, 1738, 1697, 1433, 1275, 1235, 1104, 1071, 919, 748, 694 cm⁻¹. MS (EI): m/z (%) 390.2 (M⁺, 100). HRMS (EI): m/z Calcd. for C₁₉H₁₈O₅S₂, 390.05957; found, 390.06095, Δ = 3.5 ppm.



11-Oxo-dithieno[*3*,*4-c:*8,*9-c'*]*bicyclo*[*4*.*4*.*1*]*undeca-3*,*8-diene-1*,*6-dicarboxylic* acid.^{4-7,9} A solution of the dimethyl-11-oxo-dithieno[3,*4-c:*8,*9-c'*]*bicyclo*[4.4.1]*undeca-3*,*8-diene-1*,*6-dicarboxylate* (2.0 g, 5.5 mmol) and KOH (3.1 g, 54 mmol) in ethanol/H₂O (30 mL/5 mL) was heated at reflux for 18 h. The solvent was evaporated, and water (25 mL) was added. The mixture was acidified to pH = 1 with concentrated HCl, and the precipitated white solid was collected by filtration and recrystallized from ethanol to give the title compound as colorless needles (1.5 g, 80%). MP = >300 °C (decomp). ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.2 (s, 4H, Th-2,5), 3.2 (b s, 1H, -OH), 2.71-3.02 (m, 8H, -CH₂-). ¹³C NMR (75MHz, DMSO-*d*₆): δ 207.3 (ketone C=O), 173.0 (diacid C=O), 137.3 (Th-C-3,4), 124.1 (Th-C-2,5), 63.7 (-CH-), 32.0 (-CH₂-). IR (KBr) 3420, 3011, 2952, 1702, 1695, 1241, 1040, 918, 830, 715 cm⁻¹. MS (EI): *m/z* (%) 362.0 (M⁺, 100). HRMS (EI): *m/z* Calcd. for C₁₅H₁₄OS₂, 362.02827; found, 362.02908, Δ = 2.2 ppm.



Dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one.^{4-7,9} 11-Oxo-dithieno[3,4c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylic acid (200 mg, 550 µmol) was heated at 300 °C in a pyrex tube under N₂ until the evolution of gas ceased (approx. 5-10 min). After the reaction was complete, CH₂Cl₂ (25 mL) and a 10 % aq. NaOH solution (10 mL) were added. The organic layer was separated, dried over MgSO₄, and the solvent was removed under reduced pressure. The aqueous layer was reacidified with 12 M HCl to pH = 1, extracted with Et₂O, dried over MgSO₄, and resubjected to pyrolysis. The residue was extracted with CH_2Cl_2 (30 mL), and the solvent was removed. The combined residues were subjected to column chromatography on silica gel (30% ethyl acetate/70% hexanes) to give a white solid (115 mg, 76 %). MP = 180-181 °C. ¹H NMR (300 MHz, CDCl₃): δ 6.99-7.01 (br s, 4H, Th-H), 3.00-3.25 (m, 2H, -CH-), 2.70-2.90 (m, 8H, -CH₂-). ¹³C NMR (75MHz, CDCl₃): δ 215.4 (ketone C=O), 138.3 (Th-C-3,4), 123.0 (Th-C-2,5), 53.7 (-CH-), 30.2 (-CH₂-). IR (KBr) 3151, 3098, 2934, 2848, 1690, 1216, 1104, 908, 740 cm⁻¹. MS (EI): m/z (%) 274.0 (M⁺, 100), 163 (59), 135 (15), 111 (46). HRMS (EI): m/z Calcd. for C₁₅H₁₄OS₂, 274.04861; found, 274.04744, $\Delta = 4.2$ ppm.



Ethylene acetal of dithieno[3,4-c:8,9-c']*bicyclo*[4.4.1]*undeca-3*,8-*diene-11-one*. ^{4-7,9} A solution of the dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one (50 mg, 0.18 mmol), ethylene glycol (113 mg, 1.82 mmol), and *p*-toluenesulfonic acid (2 mg) in

benzene (10 mL) was heated at reflux for 18 h with a Dean-Stark trap. The solvent was evaporated under reduce pressure, and the residue was subjected to column chromatography on silica gel (10% ethyl acetate/90% hexanes) to give the title compound as colorless crystalline solid (55 mg, 95%). MP = 214-215 °C (decomp). ¹H NMR (300 MHz, CDCl₃): δ 6.51 (s, 4H, Th-H), 4.06 (s, 4H, -OCH₂CH₂O-), 3.17 (dd, 4H, *J* = 3.3, 15 Hz, -CH₂-), 2.80 (dd, 4H, *J* = 5, 15Hz, -CH₂-), 2.16-2.25 (m, 2H, -CH-). ¹³C NMR (75 MHz, CDCl₃): δ 140.2 (Th-C-3,4), 121.5 (Th-C-2,5), 113.8 (ketal), 64.7 (-OCH₂CH₂O-), 42.5 (bridgehead), 31.2 (-CH₂-). IR (KBr) 3125, 2920, 1430, 1250, 1170, 100, 990, 945 cm⁻¹. MS (EI): *m/z* (%) 318.1 (M⁺, 100), 273 (5), 232 (10), 207 (84), 163 (21), 135 (16), 110 (12). HRMS (EI): *m/z* Calcd. for C₁₇H₁₈O₂S₂, 318.07482; found, 318.07665, Δ = 5.7 ppm. Anal. calcd. for C₁₇H₁₈O₂S₂: C, 64.11; H, 5.78; S, 20.14. Found: C, 64.10; H, 5.69; S, 20.08.



Dimethyl 11-oxo-(2,2',5,5'-tetramethyl)dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8diene-1,6-dicarboxylate.²⁴ Tetra-n-butylammonium bromide (3.09 g, 9.6 mmol) was added to a solution of 3,4-bis(bromomethyl)-2-5-dimethylthiophene (10 g, 34 mmol) in CH₂Cl₂ (50 mL). A 25% aq. NaOH solution (50 mL) was added, and the resulting biphasic mixture was vigorously stirred at room temperature. A solution of dimethyl 1,3acetonedicarboxylate (3.36 g, 19 mmol) in CH₂Cl₂ (50 mL) was added dropwise over 1 h. After stirring for 24 h, H₂O (50 mL) was added and the organic layer was separated. The

aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic layers were washed with a 5% aqueous HCl solution (2 x 50 mL) and H₂O (2 x 25 mL), and dried over MgSO₄. Removal of solvent under reduced pressure afforded a yellow oil, which was purified by flash chromatography (20% ethyl acetate/80% hexanes) to give the title compound as a white solid (3.8 g, 50%). MP = 221-222 °C (Lit. MP = 215-216 ° C). ¹H NMR (300 MHz, CDCl₃): 3.75 (s, 6H, -OCH₃), 2.70-3.32 (m, 8H,-CH₂-), 2.32 (s, 12H, methyl). ¹³C NMR (75 MHz, CDCl₃) δ 207.0 (ketone C=O), 172.9 (ester C=O), 132.5 (Th-C-3,4), 124.0 (Th-C-2,5), 64.6 (bridgehead), 52.6 (-OCH₃), 29.0(methylene), 13.1 (methyl). IR (KBr) 2953, 2914, 2839, 1736, 1446, 1229, 1235, 1071, 913, 742, 657 cm⁻¹. MS (EI): *m/z* (%) 446.1 (M⁺, 52), 428.2 (25), 369.1 (14), 138.3 (100). HRMS (EI): *m/z* Calcd. for C₂₃H₂₆O₅S₂, 446.12217; found, 446.12406, Δ = 4.2 ppm.



11-Oxo-(2,2',5,5'-tetramethyl)dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-1,6dicarboxylic acid.²⁴ A solution of the dimethyl 11-oxo-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (1.6 g, 3.6 mmol) and KOH (2.5 g, 63 mmol) in ethanol/H₂O (40 mL/10 mL) was heated at reflux for 18 h. The solvent was evaporated, and H₂O (25 mL) was added. The mixture was acidified to pH = 1 with concentrated HCl, and the precipitated white solid was collected by filtration and recrystallized from ethanol to give the title compound as colorless needles (1.4 g, 93%).

MP = 315-316 °C (decomp) (Lit. MP = 322-324 °C). ¹H NMR (300 MHz, DMSO- d_6): δ 2.5-2.65 (m, 8H, methylene), 3.02 (m, 2H, bridgehead), 2.21 (s, 12H, methyl). ¹³C NMR (75MHz, DMSO- d_6): δ 215.3 (ketone C=O), 173.0 (diacid C=O), 133.3 (Th-C-3,4), 130.1 (Th-C-2,5), 63.5 (bridgehead), 27.0 (methylene), 12.8 (methyl). IR (KBr) 3420, 2852, 1680, 1415, 1241, 1130, 1040, 924, 850, 715 cm⁻¹.



2,2',5,5'-*Tetramethyl-dithieno*[3,4-*c*:8,9-*c*']*bicyclo*[4.4.1]*undeca-3*,8-*diene-11-one*.²⁴ 11-Oxo-(2,2',5,5'-tetramethyl)dithieno[3,4-*c*:8,9-*c*']*bicyclo*[4.4.1]*undeca-3*,8-*diene-1*,6-*dicar*boxylic acid (1.4 g, 3.3 mmol) was heated at 300 °C in a pyrex tube under N₂ until the evolution of gas ceased (approx. 5-10 min). After the reaction was complete, CH₂Cl₂ (25 mL) and a 10 % aq. NaOH solution (10 mL) were added. The organic layer was separated, dried over MgSO₄, and the solvent was removed under reduced pressure. The aqueous layer was reacidified with 12 M HCl to pH = 1, extracted with Et₂O, dried over MgSO₄, and resubjected to pyrolysis. The residue was extracted with CH₂Cl₂ (30 mL) and the solvent was removed. The combined residues were subjected to column chromatography on silica gel (30% ethyl acetate/70% hexanes) to give a white solid (960 mg, 81%). MP = 255-256 °C (Lit. MP = 252-253 °C). ¹H NMR (300 MHz, CDCl₃): δ 3.0 (m, 2H, bridgehead), 2.40-2.70 (m, 8H, methylene), 2.20 (s, 12H, methyl). ¹³C NMR (75MHz, CDCl₃): δ 215.9 (ketone C=O), 133.9 (Th-C-3,4), 129.8 (Th-C-2,5), 53.3 (bridgehead), 27.4 (methylene), 13.0 (methyl). IR (KBr) 2954, 2920, 2855, 1690, 1459, 1388, 1144, 1098, 908, 657 cm⁻¹. MS (EI): m/z (%) 330.2 (M⁺, 100), 191.1 (58), 138.1 (68). HRMS (EI): m/z Calcd. for C₁₉H₂₂OS₂, 330.11121; found, 330.11016, Δ = 3.2 ppm.



Ethylene acetal of 2,5,2',5'-tetramethyl-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8diene-11-one.²⁴ А solution of the 2,5,2',5'-tetramethyldithieno[3,4-c:8,9c']bicyclo[4.4.1]undeca-3,8-diene-11-one (270 mg, 0.81 mmol), ethylene glycol (300 mg, 5.2 mmol), and *p*-toluenesulfonic acid (2 mg) in benzene (10 mL) was heated at reflux for 18 h with a Dean-Stark trap. The solvent was evaporated under reduce pressure, and the residue was subjected to column chromatography on silica gel (10% ethyl acetate/90% hexanes) to give the title compound as colorless crystalline solid (260 mg, 85%). MP = 275-276 °C, decomp. (Lit. MP = 273 °C). ¹H NMR (300 MHz, CDCl₃): δ 4.01 (s, 4H, $-OCH_2CH_2O_-$), 2.80-2.90 (dd, 4H, J = 3 Hz, J = 15 Hz, $-CH_2-$), 2.65- 2.75 (dd, 4H, J = 5 Hz, J = 15 Hz, $-CH_{2}$ -), 2.19-2.23 (m, 14H, $-CH_{2}$ + $-CH_{3}$). ¹³C NMR (75) MHz, CDCl₃): δ 135.8 (Th-C-3,4), 126.8 (Th-C-2,5), 114.2 (ketal), 64.6 (-OCH₂CH₂O-), 42.6 (bridgehead), 28.1 (-CH₂-), 13.3 (-CH₃). IR (KBr) 2961, 2917, 1448, 1257, 1109, 1048, 1000, 913, 787, 730 cm⁻¹. MS (EI): m/z (%) 374.1 (M⁺, 100), 312 (30), 235 (40), 138 (36). HRMS (EI): m/z Calcd. for C₂₁H₂₆O₂S₂, 374.13742; found, 374.13597, $\Delta = 3.9$ ppm.

2.3. Results and Discussion

2.3.1. Synthetic Approaches for a Key Intermediate: 3,4-bis(bromomethyl)thiophene

3,4-Bis(bromomethyl)thiophene is a intermediate in out multi-step synthesis of π stacked oligothiophenes. According to the literature, it was first prepared in the early
1970's from the reaction of PBr₃ in dry ether with 3,4-bis(hydroxymethyl)-thiophene.¹⁷
The bis(hydroxy)thiophene compound was prepared by reduction of 3,4-thiophene
dicarboxylate (for which a convenient synthesis is not reported). Consequently, our first
attempt to prepare 3,4-bis(bromomethyl)thiophene made use of 2,5-dichlorothiophene
(Aldrich) as a starting material. It was envisioned that carboxylic and aldehyde
functional groups could be installed at the 3- and 4- positions and that the ring could then
be dechlorinated to afford thiophene-3,4-dialdehyde. The iodination of 2,5dichlorothiophene¹² with molecular iodine in strong oxidizing conditions (potassium
periodate, sulfuric acid) provided 2,5-dichloro-3,4-diiodo-thiophene in reasonable yields
after isolation and recrystallization from ethanol, Figure 2.6. However, subsequent
lithiation with *n*-butyllithium followed by reaction with dimethyl formamide did not
produce the desired product dialdehyde in reasonable or reproducible yields.¹²



Figure 2.6. Synthetic approach to make thiophene-3,4-dialdehyde.

Modification to the above procedure by quenching the lithiated intermediate with carbon dioxide instead of DMF followed by acidification with 12 M HCl produced the desired 2,5-dichlorothiophene-3,4-dicarboxylic acid¹² in moderate yields (45-60%),

Figure 2.7. Reduction of the dicarboxylic acid with LiAlH₄ in dry THF afforded 2,5dichloro-3,4-bis(hydroxymethyl)thiophene in good yields (85-95%). However, attempted dehalogenation of the 2- and 5- positions following a known literature procedure,¹³ proved to be irreproducible and decomposition of the starting material was evident by NMR analysis (poisoning of the catalyst with sulfur). While attempts were made to optimize reaction conditions (Pt catalyst, reaction time, reaction pressure, solvent) none of these were particularly successful this route was terminated.



Figure 2.7. Attempt to prepare 3,4-bis(hydroxymethyl)thiophene by reductive dechlorination of 3,4-bis(hydroxymethyl)-2,5-dichlorothiophene.

Attempts to dehalogenate with and zinc metal in acetic acid following a literature procedure¹³ gave he desired product in milligram amounts. Byproducts including monochlorinated thiophenes and acetate esters of the bis(hydroxymethyl) starting material, Figure 2.8. Thus, this route again proved to be inefficient for the synthesis of suitable substituted thiophenes.



Figure 2.8. Attempted Zn/AcOH dechlorination of 3,4-bis(hydroxymethyl)-2,5dichlorothiophene to synthesize 3,4-bis(hydroxymethyl)thiophene.

Another attempted route for the synthesis of 3,4-bis(hydroxymethyl)thiophene is shown in Figure 2.9. Tetrabromination of thiophene with molecular bromine in chloroform under gentle reflux afforded tetrabromothiophene¹⁹ in good vield after recrystallization from chloroform in an evaporating dish and washing the crystals with a copious amount of H₂O (1-2 L), Figure 2.9. Lithiation of the 2,5- positions with 2 equivalents of *n*-butyllithium in diethyl ether at 0 °C provided 3,4-dibromothiophene^{19,20} as a colorless liquid after vacuum distillation. The conversion of 3,4-dibromothiophene to 3,4-dicyanothiophene was best accomplished by modification of a literature procedure.¹⁴ However, this only low yields of product due to losses during the exhaustive extraction with aqueous HCl, water washings, sublimation, and recrystallization from acetonitrile (yield 12%). The subsequent hydrolysis of the cyano groups with hydroxide in ethylene glycol followed by acidification provided thiophene-3,4-dicarboxylic acid in another low yielding step (19%). Reduction of the dicarboxylic acid (LAH, dry THF at reflux) provided 3,4-bis(hydroxymethyl)thiophene in satisfactory yield (74%). The last step in this synthetic route was bromination with phosphorus tribromide in dry ether which produced 3,4-bis(bromomethyl)thiophene in a reasonable yield after column chromatography and recrystallization from methanol (yield, 80%). This overall scheme proved to be cumbersome, with two low yielding steps which did not provide an adequate supply of 3,4-bis(bromomethyl)thiophene.



Figure 2.9. Successful, albeit low yielding, synthesis of 3,4-bis(bromomethyl)thiophene.

Another possible precursor for the synthesis of 3,4-bis(bromomethyl)thiophene could be 3,4-dimethylthiophene. A large scale synthesis to provide ample 3,4-dimethylthiophene was attempted on a modified literature procedure which contained neopentyl groups on thiophene instead of methyl groups.²⁵ The reaction of 1-chloropropan-2-one with sodium sulfide in acetone gave 1,1'-thiodipropan-2-one in good yields (80-90 %). However, cyclization by a the McMurry reaction²⁶ was problematic and pure product could not be obtained after many attempts with various conditions (temperature, concentration, metal reducing agent), Figure 2.10.



Figure 2.10. Approach to prepare 3,4-dimethylthiophene on a larger scale by McMurry reaction.

Our favored route to synthesize 3,4-dimethylthiophene from thiophene in three steps is illustrated in Figure 2.11. This involved the Kumada coupling of 3,4dibromothiophene with MeMgX, (X = Br or Cl) in the presence of 1,3bis(diphenylphosphino) propane dichloronickel (II) in dry ether and distillation to produce 3,4-dimethylthiophene in a yield of 96%.



Figure 2.11. Efficient route to synthesize 3,4-dimethylthiophene from 3,4-dibromothiophene.

Several attempts to perform radical bromination of 3,4-dimethyl-thiophene with *N*-bromosuccinimide and catalytic azobisisobutyronitrile (AIBN) in benzene were unsuccessful. The major products of this reaction were the monobrominated material and products resulting from the mono and dibromination of the 2,5-positions of the thiophene ring. Various parameters were modified (concentration, mode of addition, stoichiometry, and reaction times) with no success.

The use of different solvents and catalyst *i.e.*, benzoyl peroxide (BPO) are reported in the literature for the radical bromination of 3-methylthiophene in CCl₄ with NBS.²⁷ Optimization of these conditions led us to the use of BPO added to solutions of 2-g of 3,4-dimethylthiophene with 2.0 equivalents of NBS in CCl_4 (100 mL), Figure 2.12. However, one equivalent of NBS was added initially then another equivalent added 10 min later while the reaction mixture was at reflux. The mixture was irradiated with a mercury lamp at the start of the reaction and removed when the reaction mixture become faint orange. After stirring the mixture until the orange color turned light yellow (< 1 h), the reaction mixture was cooled in an ice bath, and succinimide was removed by filtertration and washed with cold CCl₄. The solvent was removed by rotary evaporation. The crude product from other batches was combined at this stage. Recrystallization from various solvents (cyclohexane, hexanes) were moderately successful, removing starting material ($R_f = 0.85$) in hexanes and mono-reacted material ($R_f = 0.7$). Flash chromatography used immediately after workup to prevent hydrolysis of the unstable product. After careful fractionation, the desired product was obtained as a white crystalline solid ($R_f = 0.2$ in hexanes) with yields ranging from 20-40%. Almost immediately above this spot on TLC is residual BPO which becomes discolored on silica plates, and was discarded.



Figure 2.12. Successful radical bromination of 3,4-dimethylthiophene to 3,4-bis(bromomethyl)thiophene.
2.3.2. Synthesis of Dithieno-Fused Bicyclo[4.4.1]undecanone

Once an adequate supply of 3,4-bis(bromomethyl)thiophene was obtained, we used to used it to alkylate dimethyl 1,3-acetonedicarboxylate under phase transfer condition. Tetrabutylammonium bromide was used as the phase transfer reagent in the presence of hydroxide anion in a vigorously stirred solution of dichloromethane and aq. NaOH. Dimethyl 1,3-acetonedicarboxylate in dichloromethane was added dropwise to a solution of 3,4-bis(bromomethyl)thiophene over 20 min, Figure 2.13. The reaction was performed at room temperature and stirred fro 18 h. After workup and purification by column chromatography (30% ethyl acetate/70% hexanes) gave the resulting bicyclic diester, **2.1**.



Figure 2.13. Synthesis of bisthieno-fused bicyclo[4.4.1]undecanone.

The saponification of the diester was performed by reaction with excess base (KOH or NaOH) in refluxing aqueous ethanol, Figure 2.13. Careful workup included removal of ethanol prior to acidification with 12 M HCl to pH = 1. The resulting aqueous solution was placed in the freezer overnight. The resulting crystalline solid was

recrystallized from H₂O, filtered, and dried in under reduced pressure to afford the diacid 2.2 in good yield (90%). In 10-30% ethyl acetate/hexanes, the R_f value of the 2.2 was zero, so it was easily distinguished from the starting material. The dithieno-fused bicyclo[4.4.1]undecanone core 2.3 was synthesized by decarboxylation of 2.2 at elevated temperatures. Large scale pyrolysis resulted in a large amount of char and only low yields of product due to poor heat transfer. Accordingly, this process was performed on a small scale. The small scale reaction of diacid 2.2 (>250 mg) provided best results upon heating to temperatures of 250-300 °C. The major byproduct in the reaction was the mono-decarboxylated material. While this byproduct was present in most reaction mixtures the material could be recovered and re-pyrolyzed. A simple base wash (5-10%) aqueous NaOH) removed the monoacid after it was taken back up in CH₂Cl₂. Reacidification of the basic extract to pH = 1, extraction into Et₂O, removal of the solvent under reduced pressure, and resubjecting the residue to decarboxylation provided more desired crude product. Purification was performed by passing a solution (10% ethyl acetate/90% hexanes) of crude product through a short silica plug with to afford the desired ketone 2.3 as a white solid in good yields (65-76%).

2.3.3. Ketalization of the Dithieno-Fused Bicyclo[4.4.1]undecanone

The ketalization of the dithieno-fused ketone **2.3** provides a suitable scaffold to examine through-space interactions between adjacent thiophenes stacked on top one another. Initial attempts to ketalize with neopentyl glycol were unsuccessful; the predominant material obtained was the hemiacetal. Reaction of ketone **2.3** in a small

round bottom flask with excess ethylene glycol, benzene, and *para*-toluenesulfonic acid (*p*-TSA) afforded the ethylene ketal **2.4**, Figure 2.14.



Figure 2.14. Ketalization of the dithieno-fused ketone, 2.3.

Careful precautions were taken to avoid decomposition of the acid sensitive product. The solvent was evaporated to less than 15% of the original volume and the residual solution was immediately placed on a column for flash chromatography. NMR analysis of the ketal was performed in deuterated chloroform that had been distilled onto molecular sieves and sodium bicarbonate. Typical yields for the ketalization step were >90%.

2.3.4. Synthesis of the Tetramethylated π -Stacked Analog

The tetramethylated π -stacked analog **2.8** was synthesized in an analogous route.²⁴ This analog was important in our study for charge migration of doped π -stacked oligothiophenes. 2,5-Dimethyl-3,4-bis(bromomethyl)thiophene was synthesized in one step from 2,5-dimethylthiophene, aqueous formaldehyde, and aqueous HBr, Figure 2.15. Reaction with dimethyl 1,3-acetonedicarboxylate followed by saponification, decarboxylation, and ketalization with ethylene glycol gave the π -stacked tetramethylated analog **2.8** in good yield, Figure 2.14. The two dithieno-fused bicyclo[4.4.1] undecanes

provide suitable scaffolds to elucidate the properties of conjugated oligomers arising from π -stacking interactions.



Figure 2.15. Synthesis of methylated π -stacked analog, **2.8**.

The dithieno-fused bicycle[4.4.1]undecanone **2.3** as a core in the development of extended oligomers for studies of charge migration in doped conjugated materials. To prepare analogous stacked oligomers, we explored the synthesis of a bisthieno-diester halogens installed in the thiophene 2,5- positions. This would allow us to install aromatic units on the central thiophenes to prepare conjugated chains. Reaction of 2,5- dichlorothiophene with aqueous formaldehyde and aqueous HBr produced 2,5-dichloro-3,4-bis(chloromethyl)thiophene, Figure 2.16. However, this material failed to undergo

reaction with dimethyl 1,3-acetonedicarboxylate under phase transfer conditions, and it decomposes readily.



Figure 2.16. Attempt to alkylate with 3,4-bis(bromomethyl)2,5-dichlorothiophene.

Similarly, the alklylation of dimethyl 1,3-acetonedicarboxylate with 2,5-dibromo-3,4-bis(bromomethyl)thiophene was not successful under various reaction condition modifications, Figure 2.17. Variation of the reaction with temperature, mode of addition, and concentration also did not provide any desired product. The majority of the starting material was recovered in this reaction with no desired product.



Figure 2.17. Attempt to alkylate with 3,4-bis(bromomethyl)2,5-dibromothiophene.

2.3.5. Synthesis of Unstacked Linear Model 2,3,4,5-Tetramethylthiophene

In order to determine the effect of stacking on the electronic structure of conjugated oligomeric polythiophene it was important to have analogous unstacked model linear analogs. The electrophilic aromatic substitution at the 3- and 4- positions of 2,5-dimethylthiophene with aqueous HBr and aqueous formaldehyde provided 3,4-

bis(bromomethyl)2,5-dimethylthiophene. Reduction of 3,4-bis(bromomethyl)2,5dimethylthiophene with LiAlH₄ in dry THF provided the model linear compound 2,3,4,5tetramethylthiophene as a colorless liquid after distillation (BP = 80-85 °C/20 mm) in good yield (90%), Figure 2.18.



Figure 2.18. Synthesis of 2,3,4,5-tetramethylthiophene.

2.3.6. Structural Characterization: Variable Temperature ¹H and ¹³C NMR Spectroscopy

The successful synthesis of π -stacked ethylene acetals **2.4** and **2.8** are conformational rigid compared to their respective ketone/diester precursors which was confirmed by variable temperature ¹H NMR. The ¹H NMR spectrum of the diester **2.1** at room temperature is illustrated in Figure 2.19. The conformational flexibility between chair-boat, chair-chair, and boat-boat conformations exhibits a broadened, coalesced multiplet (2.6-3.4 ppm) for the methylene protons. A broadened singlet (7.0 ppm) for the aromatic protons is representative of coalesced signals for the different conformations. The methyl ester protons are not affected by the conformation flexibility, therefore are equivalent (singlet at δ 3.7 ppm).



Figure 2.19. ¹H NMR (300 MHz, CDCl₃) of diester 2.1 at room temperature.

Upon cooling to -60 °C, **2.1** adopts one chair-boat conformation, Figure 2.20. This conformation is thermodynamically favored at lower temperature with methylene protons being decoalesced into four doublets (2.70, 2.95, 3.15, 3.30 ppm; J = 15 Hz). Two sharp singlets for the four aromatic protons (7.0, 7.2 ppm) confirm the chair-boat conformation (the two thiophene protons closest to the ketone give a different signal from the other thiophene ring further away from the ketone).



Similarly, the room temperature ¹H NMR spectrum of the tetramethylated diester **2.5** exhibits a coalesced signal for the methylene protons (2.8-3.2 ppm) and a broad singlet for the twelve methyl protons (2.3 ppm), Figure 2.21. Upon cooling -40 °C, the methylene protons decoalesced to four distinct doublets (2.51, 2.90, 3.10, 3.15 ppm, J = 15 Hz), and the methyl protons decoalesced into two singlets (2.3-2.4 ppm) confirming conformation rigidity at low temperature and conformational flexibility at room temperature.



Figure 2.21. ¹H NMR (400 MHz, CDCl₃) of 2.5 at RT (top) and -40 °C (bottom).

The ¹H NMR spectrum of ketone **2.3** exhibits similar conformational flexibility at room temperature. The eight methylene protons are coalesced into a broad multiplet (2.7-2.9 ppm) at room temperature due to the signal averaging from different conformations, Figure 2.22. The two bridgehead protons appear as a multiplet (3.1 ppm), and the four aromatic protons appear as a broad singlet at 7.0 ppm. Upon cooling to -60 °C, the chair-boat conformation is thermodynamically favored at displaying four distinct multiplets (2.5, 2.7, 2.8, 3.1 ppm) for the methylene protons (one set coincidental with the bridgehead protons at 3.1 ppm), as well two singlets for the aromatic protons (6.9 and 7.2 ppm), Figure 2.23.

Similarly, the ¹H NMR spectrum of tetramethylated ketone **2.5** exhibited a coalesced signal for the eight methlyne protons (2.51-2.78 ppm), Figure 2.24. The two bridgehead protons gave a signal at 3.0 ppm, and the twelve methyl protons gave a sharp singlet at 2.3 ppm. Upon cooling to -60 °C, the ¹H NMR spectrum exhibited decoalesced signals for the methylene protons, and two singlets for the methyl protons.







The ¹H NMR spectrum of π -stacked compound **2.4** at room temperature warmed to 100 °C was unchanged and consistent with the compound existing in a single chairchair conformation. There is an upfield shift for the aromatic protons (6.51 ppm) compared to 3,4-dimethylthiophene (6.88 ppm), and the methylene protons are a pair of doublet of doublets (2.8 ppm, J = 3, 15 Hz; 3.15 ppm, J = 5, 15 Hz), Figure 2.25. The two bridgehead protons give a multiplet and are shifted upfield (2.2 ppm) compared to that of the bridgehead protons of the ketone **2.3** (3.1 ppm). Similarly, the methylated π stacked compound **2.8** exhibited similar splitting for the methylene protons, and an upfield shift for the bridgehead protons (2.2 ppm) coincidental with the twelve methyl protons, Figure 2.26.

The upfield shift due to π -stacking can be ascribed to the relationship of the protons in the circulating magnetic field of the thiophene rings (induced field) to the external magnetic field, commonly known as anisotropy. In this case, the positions where the aromatic protons and bridgehead protons are located actually oppose the magnetic external field and are shielded (upfield). Similarly, the coupling constants for the methylene protons can be approximated by the Karplus Equation:²⁸

$$J_{HH'} = A + B \cos \theta + \cos 2 \theta$$

where A, B, and C are approximately constant for an sp³ hybridized carbon bond and θ is the angle between the two protons measured. These theoretical values are in good agreement with the experimental results observed for π -stacked compounds **2.4** and **2.8**.



Figure 2.25. ¹H NMR (300 MHz, CDCl₃) of ketal 2.4 at room temperature.



The 13 C NMR spectrum of the diester **2.1** exhibits conformational flexibility in the aromatic carbon signal (125 ppm, Th-C-2,5) and methylene carbons (30 ppm). These

carbon signals are broadened, because they are influenced by the conversion between different conformations at room temperature, Figure 2.27. In the case of the ¹³C NMR spectrum of ketone **2.3**, these carbon signals are sharpened but are still broadened more than other carbon signals in the spectrum, Figure 2.28. The bridgehead carbon signals in the diester **2.1** and ketone **2.3** both appear at 52 and 55 ppm, respectively.



Figure 2.27. ¹³C NMR (75 MHz, CDCl₃) of diester 2.3 at room temperature.



Figure 2.28. ¹³C NMR (75 MHz, CDCl₃) of ketone 2.3 at room temperature.

Upon ketalization with ethylene glycol, the ¹³C NMR spectrum of π -stacked compound **2.4** at room temperature exhibits sharp signals for all carbon signals consistent with one conformation, Figure 2.29. The ketone signal (215 ppm) disappears as the ethylene glycol peak (65 ppm) replaces it upon ketalization, and a ketal peak (tertiary carbon) appears at 155 ppm. The bridgehead carbon signal shifts upfield (44 ppm) due to π -stacking the thiophene rings together and forcing the compound in a chair-chair conformation.



Figure 2.29. ¹³C NMR (75 MHz, CDCl₃) of ketal 2.4 at room temperature.

The ¹³C NMR spectrum of tetramethylated ketone **2.7** and ketalization to the π -stacked compound **2.8** exhibited similar behavior, Figure 2.30.



Figure 2.30. ¹³C NMR (75 MHz, CDCl₃) of ketone 2.7 (top) and ketal (bottom) at RT.

Heteronuclear Multiple Bond Correlation (HMBC) was used to identify proton nuclei with carbon nuclei that are separated by more than one bond. The connectivity in the bicyclo[4.4.1]undecane framework was demonstrated with the diacid **2.2**, Figure 2.31. Selective excitation at δ 3.0 ppm on the methylene protons shows that the carbonyl

ketone, carbonyl ester, bridgehead, and thiophene 3,4- carbons are all connected to one another.





Figure 2.31. Heteronuclear Multiple Bond Correlation (HMBC) for diacid 2.2.

¹H-¹H correlation (COSY) experiment were used to confirm the coupled protons in the π -stacked compound **2.4**. Protons labeled C, D, and B correspond to the methylene and bridgehead protons and all are coupled to each other according to the COSY

spectrum, Figure 2.32. There are no other coupled protons in the compound. The π -stacked compound **2.8** exhibited similar behavior in its COSY spectrum.



Figure 2.32. ¹H-¹H NMR correlation (COSY) of π -stacked compound **2.4**.

Signals arising in a ¹H-¹³C NMR correlation (HETCOR) spectrum determined which proton signal was associated with each carbon signal. This shows conclusive evidence for the assigned ¹H NMR signals, Figure 2.33.



Figure 2.33. ¹H-¹³C NMR correlation (HETCOR) of π -stacked compound **2.4**.

2.3.7. X-ray Structural Analysis

The X-ray structural analysis of π -stacked compound **2.4** confirms a rigid cofacial chair-chair arrangement. The distance between the centroid positions of each thiophene ring is 359 pm apart, Figure 2.34. The furthest distance for the two thiophene rings is 429 ppm between the two sulfur atoms of each ring. The angle of coplanarity between the two thiophene units is 28°, comparable to that of the methyl-capped analog **2.8** with angle deviation of 28.9°.²⁴ Another ORTEP view of **2.4** is illustrated in Figure 2.35. The packing diagram in the unit cell for **2.4** is illustrated in Figure 2.36.



Figure 2.34. X-ray structural analysis of 2.4 (sideview).





Figure 2.35. X-ray structural analysis of 2.4 (sideview).



Figure 2.36. Packing diagram of π -stacked compound 2.4.

The calculated HOMO and LUMO orbitals²⁹ illustrate the electron densities for the π -stacked compound, Figure 2.37. The 2,5-positions of each thiophene contain the larger proportion of electron density, similar to that of thiophene for the HOMO level. A large portion of electron density resides on the sulfur atoms in the LUMO model. The proximity of the orbitals demonstrates that this framework will be ideal for through-space electronic communication of other oligothiophene compounds with this bicyclo[4.4.1]undecanone core.



Figure 2.37. HOMO (left) and LUMO (right) of 2.4.

2.4. Conclusion

In conclusion, this chapter explored various synthetic routes to produce the key starting material 3,4-bis(bromomethyl)thiophene, the continued synthesis to the dithieno-fused bicyclo[4.4.1]undecane π -stacked compounds, and the structural characterization of these compounds. Variable temperature ¹H NMR spectroscopy demonstrated the tendencies compounds to exist in flexible conformations at room temperature and rigid conformations at low temperature. The X-ray structural analysis, COSY, and HETCOR all chair-chair conformation of the dithieno-fused bicyclo[4.4.1]undecanone framework upon ketalization with ethylene glycol. The dithieno-fused bicyclo[4.4.1]undecanone the tendencies compounds to the further explore of other π -stacked compounds by expansion at the available unblocked α -thiophene positions.

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CHAPTER 3

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF EXTENDED DITHIENO-FUSED BICYCLO[4.4.1]UNDECANES

3.1. Introduction

The dithieno-fused bicyclo[4.4.1]undecane scaffold described in Chapter 2 provides a π -stacked orientation of the thiophene rings. In this chapter, the stacked thiophene core is elaborated to provide π -stacked terthiophene and quinquethiophene oligomers by installation of arenes. There are numerous studies of linear oligothiophenes that provide insight into the electronic structure of conjugated radical cations and dications.

Detailed studies of radical ions look at the preparation, optical, and electrochemical properties of 3,4-ethylenedioxythiophene oligomers (EDOTn, n = 1-4)¹. Solutions of radical cations were cooled down and formed a new species which was reversible and called a π -dimer. An FT-Raman study of a chemical doped methyl-capped quinquethiophenes² offered an useful technique to explain these charged species formed in solution. Furukawa demonstrated that polarons are the major species existing in doped polythiophene³. New oligothiophenes recently characterized with cyano- and hexyl-terminated ends of quarterthiophene and terthiophene have been studied as thin films of oligothiophenes fabricated by vacuum deposition.⁴ Recent work also on α , α '-

bis(diphenylamino)-capped oligothiophenes in situ spectroelectrochem⁵ has been explored for their oxidized species which strongly depend on the number of thiophene units. The new idea that quarterthiophene potassium salt may serve as models for polaron aggregation (ie. π -dimers)⁶ between two oligomers opened the idea up that carefully designed systems can be synthesized and studied for the inherent electrocnic conduction capabilities.

The continued interest on linear π -conjugated oligomers is important for developing an understanding of how charged species within a conjugated chain migrate (*i.e.* intramolecularly), and also how intermolecular interactions between aggregated chains effect charge carriers. The identity and role of radical cations, dications, and π -dimers on charge migration can be explored by the methodology outlined here.

3.2. Experimental

3.2.1. General Procedures

All reagents and catalysts were purchased from Aldrich, TCI, or Strem Chemicals and used without further purification. NBS was recrystallized from H₂O. THF and diethyl ether were distilled from benzophenone-sodium ketyl. Dichloromethane was distilled from calcium hydride and anhydrous DMF was purchased from Aldrich. ¹H and ¹³C NMR spectra were recorded from a 300 or 400 MHz Varian Mercury spectrophotometer. Infrared spectra were recorded on a Nicolet 4700 FTIR. Mass spectra were collected on a VG-70SE instrument. Elemental analyses were obtained from Atlantic Microlabs, Inc. Gravity and flash column chromatographies were carried out with silica gel (32-63 mesh, 60 Å from Sorbent Technologies).

3.2.2. Synthetic Procedures



2,5-*Dibromo-3,4-dimethylthiophene*. *N*-Bromosuccinimide (6.4 g, 36 mmol) was added to a solution of 3,4-dimethylthiophene (2.0 g, 18 mmol) in CHCl₃ (20 mL) at 0 °C under N₂. The flask was covered in foil, warmed to room temperature, and the mixture was stirred for 18 h. The mixture was cooled to 0 °C, succinimide was removed by filtration, and the organic layer was washed with 5% aq. NaOH (2 x 50 mL). The aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL) and the combined organic layers were dried over MgSO₄. The solvent was removed under reduced pressure to afford 2,5-dibromo-3,4dimethylthiophene as a colorless liquid (4.70 g, 99%). ¹H NMR (300 MHz, CDCl₃): δ 2.10 (s, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 136.9 (Th-C-3,4), 107.3 (Th-C-2,5), 14.9 (-CH₃). MS (EI): *m/z* (%) 269.9 (M⁺, 100), 191.0 (M⁺-Br, 45), 110.1 (M⁺-2Br, 36). HRMS (EI): *m/z* Calcd. for C₆H₆SBr₂, 267.85569; found, 267.85525, Δ = 1.6 ppm.



5-Methyl-2-tri-n-butylstannylthiophene.^{7,8} A 2.5 M solution of *n*-BuLi in hexanes (140 mL, 56 mmol) was added dropwise to solution of 2-methylthiophene (5.0 g, 51 mmol) in dry Et₂O (80 mL) at 0 °C, and the mixture was stirred for 1 h. A solution of tri-*n*-butyltin chloride (17 g, 53 mmol) in Et₂O (20 mL) was added dropwise over 10 min, and the mixture was stirred for and additional 12 h. A saturated aq. solution of NaHCO₃ (80 mL) was added and the mixture was stirred for 30 min. The aqueous layer was separated,

extracted with Et₂O (2 x 100 mL), and the combined organic layers were washed with H₂O (3 x 100 mL) and dried over MgSO₄. The solvent was removed under reduce pressure to afford 5-methyl-2-tri-*n*-butylstannyl-thiophene as an orange oil (19.0 g, 96%) that was used without further purification. ¹H NMR (300 MHz, CDCl₃): δ 7.01 (d, 1H, *J* = 2 Hz, Th-3), 6.90 (dq, 1H, *J* = 1 Hz, Th-4), 2.6 (d, 3H, *J* = 1 Hz, -CH₃), 1.53-1.65 (m, 6H, -CH₂CH₂CH₂CH₃), 1.25-1.40 (m, 6H, -CH₂CH₂CH₂CH₃), 1.13-1.17 (m, 6H, -CH₂CH₂CH₂CH₃), 0.89-0.95 (m, 9H, -CH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 145.1, 135.3, 134.1, 126.53 (aromatic), 29.4 (-CH₂CH₂CH₂CH₂CH₃), 29.1 (-CH₂CH₂CH₂CH₃), 15.1 (-CH₃), 10.8 (-CH₂CH₂CH₂CH₃), 8.9 (-CH₂CH₂CH₂-CH₃).



*5-Methyl-2,2'-bithiophene.*⁹ 2-Tri-*n*-butylstannylthiophene (16 g, 42 mmol) was added to a solution of 2-bromo-5-methylthiophene (5.0 g, 28 mmol), Pd(PPh₃)₄ (330 mg, 300 µmol), and LiCl (3.6 g, 85 mmol) in dry DMF (25 mL) and the mixture heated at 65 °C for 18 h. The mixture was cooled and a saturated aq. solution of KF (10mL) was added and stirred for 2 h at room temperature. The aq. layer was discarded and the organic solution was passed through celite and a silica plug and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (100% hexanes) to afford 5-methyl-2,2'-bithiophene as a colorless liquid (2.8 g, 55%). ¹H NMR (300 MHz, CDCl₃): δ 7.10-7.20 (m, 2H, Th), 7.00-7.10 (m, 2H, Th), 6.67-6.70 (m, 1H, Th), 2.50 (s, 3H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 138.8, 137.7, 134.9, 127.5, 125.7, 123.5, 123.4, 122.8 (aromatic), 15.3 (-CH₃). IR (KBr) 2974, 2944, 2917, 2865, 1439, 1108, 1102, 983, 909, 857, 778 cm⁻¹. MS (EI): m/z (%) 180.0 (M⁺, 100). HRMS (EI): m/z Calcd. for C₉H₈S₂, 180.00674; found, 180.00615, Δ = 3.3 ppm.



2-Methyl-5'-tri-n-butylstannyl-5,2'-bithiophene.¹⁰ A 1.6 M solution of n-BuLi in hexanes (26 mL, 16 mmol) was added dropwise to solution of 5-methyl-2,2'-bithiophene (2.6 g, 15 mmol) in dry Et₂O (50 mL) at 0 °C and the mixture was stirred for 2 h. A solution of tri-n-butyltin chloride (5.7 g, 53 mmol) in Et₂O (20 mL) was added dropwise over 20 min., and the mixture was stirred for an additional 18 h. A saturated aq. solution of NaHCO₃ (50 mL) was added and the mixture was stirred for 30 min. The aqueous layer was separated, extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with saturated aq. NaHCO₃ (50 mL) and dried over MgSO₄. The solvent was removed under reduce pressure to afford 2-methyl-5'-tri-n-butylstannyl-5,2'-bithiophene as an orange oil (6.8 g, 99%) without further purification. ¹H NMR (300 MHz, CDCl₃): δ 7.19 (d, 1H, J = 3.3 Hz, Th), 7.04 (d, 1H, J = 3.3 Hz, Th), 6.9 (d, 1H, J = 3.5 Hz, Th), 6.63 (dq, 1H, J = 3.5 Hz, 1.1Hz, Th), 2.5 (d, 3H, J = 1 Hz, -CH₃), 1.53-1.62 (m, 6H, -CH₂CH₂CH₂CH₃), 1.26-1.41 (m, 6H, -CH₂CH₂CH₂CH₃), 1.12-1.18 (m, 6H, -CH₂CH₂CH₂CH₃), 0.88-0.94 (m, 9H, -CH₂CH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 143.1, 138.5, 135.8, 135.6, 135.3, 125.7, 124.1, 123.2 (aromatic), 29.5 (-CH₂CH₂CH₂CH₃), 27.4 (-CH₂CH₂CH₂CH₃), 15.6 (-CH₃), 13.9 (-CH₂CH₂CH₂CH₂CH₃), 11.1 (-CH₂CH₂CH₂-CH₃). IR (neat) 2953, 2922, 2870, 2852, 1517, 1461, 1413, 1370, 1070, 948, 865, 796, 687, 670, 596, 474 cm⁻¹.



3',4'-Dimethyl-2,2':5'2''-terthiophene.¹¹⁻¹³ 2-Tri-n-butylstannylthiophene (1.2 g, 7.4 mmol) was added to a solution of 2,5-dibromo-3,4-dimethylthiophene (0.5 g, 2 mmol), $Pd(PPh_3)_4$ (100 mg, 100 µmol), and LiCl (30 mg, 0.7 mmol) in dry DMF (5mL), and the mixture was heated at 75 °C for 18 h. The mixture was cooled and a saturated aq. solution of KF (10mL) was added and the mixture was stirred for 1 h. The aqueous layer was discarded, and the organic solution was passed through celite and silica, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (10% ethyl acetate/90% hexanes) followed by recrystallization from hexanes to afford 3',4'-dimethyl-2,2':5'2"-terthiophene as a yellow crystalline solid (330 mg, 63%). MP = 116-118 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.30 (dd, 2H, J = 5 Hz, 1 Hz, Th-5), 7.13 (dd, 2H, J = 1 Hz, 3.3 Hz, Th-3), 7.07 (dd, 2H, J = 5 Hz, 3.3 Hz, Th-4), 2.30 (s, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 136.2, 135.0, 129.4, 127.3, 125.9, 125.2, (aromatic), 14.4 (-CH₃). IR (KBr) 3157, 2987, 2900, 1530, 1439, 1378, 1213, 1156, 1091, 735 cm⁻¹. MS (EI): m/z (%) 276.0 (M⁺, 100). HRMS (EI): m/z Calcd. for $C_{14}H_{12}S_3$, 276.01012; found, 276.01300, $\Delta = 10$ ppm. Anal. calcd. for $C_{14}H_{12}S_3$: C, 60.82; H, 4.38; S, 34.80. Found: C, 60.79; H, 4.36; S, 34.59.



2,3',4',5"-Tetramethyl-5,2':5',2"-terthiophene.¹¹⁻¹³ 5-Methyl-2-tri-*n*-butylstannyl thiophene (4.3 g, 11 mmol) was added to a solution of 2,5-dibromo-3,4dimethylthiophene (1.0 g, 2.7 mmol), Pd(PPh₃)₄ (260 mg, 0.16 mmol), and LiCl (48 mg, 1.1 mmol) in dry DMF (5mL), and the mixture was heated at 70 °C for 18 h. The mixture was cooled and a saturated aq. solution of KF (10mL) was added, and the mixture was stirred for 1 h. The aqueous layer was discarded and the organic solution was passed through celite and a silica plug, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (10% ethyl acetate/ 0% hexanes) followed by recrystallization from hexane to afford the product as yellow crystalline solid (750 mg, 66%). MP = 80-82 °C. ¹H NMR (300 MHz, CDCl₃): δ 6.89 (d, 2H, J = 3 Hz, Th-3), 6.70 (dd, 2H, J = 1 Hz, 3 Hz, Th-4), 2.49 (d, 6H, J = 1 Hz, 2.5" - 100 Hz, 2.49 (d, 6H, J = 1 Hz, 2.5)CH₃), 2.26 (s, 6H, 3',4' -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 139.8, 134.4, 133.9, 129.4, 125.7, 125.5 (aromatic), 15.4 (-CH₃), 14.4 (-CH₃). IR (KBr) 3070, 2978, 2913, 2852, 1530, 1439, 1378, 1213, 1044, 787 cm⁻¹. MS (EI): m/z (%) 304.1 (M⁺, 100), 289 (5), 152 (10), 59 (3). HRMS (EI): m/z Calcd. for C₁₆H₁₆S₃, 304.04142; found, 304.04137, Δ = 0.2 ppm. Anal. calcd. for $C_{16}H_{16}S_3 = C$, 63.19; H, 5.30; S, 31.63. Found: C, 62.39; H, 5.31; S, 31.28.



2,3",4",5""-Tetramethyl-5,2':5',2":5",2":5",2""-quinquethiophene.^{14,15} 2-Methyl-5'-tri*n*-butylstannyl-5,2'-bithiophene (3.7 g, 8.0 mmol) was added to a solution of 2,5dibromo-3,4-dimethyl-thiophene (0.5 g, 1.9 mmol), Pd(PPh₃)₄ (215 mg, 0.19 mmol). LiCl (42 mg, 1.0 mmol) in dry DMF (10mL) was added and the mixture was heated at 70 °C for 18 h. The mixture was cooled, a saturated aq. solution of KF (10mL) was added and the mixture was stirred for 1 h. The aqueous layer was discarded, the organic solution was passed through celite and a silica plug, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (20%) dichloromethane/80% hexanes) followed by recrystallization from toluene to afford 2,3",4",5""-tetramethyl-5,2':5',2":5",2"'-quinquethiophene as an orange solid (600 mg, 69%). MP = 165-166 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.03 (d, 2H, J = 3.8 Hz, Th-4'), 7.00 (d, 2H, J = 3.8 Hz, Th-3'), 6.97 (d, 2H, J = 3.3 Hz, Th-4), 6.64-6.68 (m, 2H, Th-3), 2.48 (d, 6H, J = 1.0 Hz, -CH₃), 2.32 (s, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 139.2, 137.5, 135.1, 134.7, 134.5, 129.3, 126.3, 125.9, 123.5, 123.2 (aromatic), 15.5 (-CH₃), 14.6 (-CH₃). IR (KBr) 3065, 2904, 2852, 1504, 1430, 1069, 796 cm⁻¹. MS (EI): m/z (%) 468.1 (M⁺ 100), 454 (4), 234 (15), 217 (3), 141 (3), 45 (3). HRMS (EI): m/zCalcd. for $C_{24}H_{20}S_5$, 468.01686; found, 468.01416, $\Delta = 5.8$ ppm. Anal. calcd. for C₂₄H₂₀S₅ = C, 61.58; H, 4.31; S, 34.24. Found: C, 61.32; H, 4.32; S, 34.08.



Dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one. 11-Oxo-dithieno[3,4c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylic acid (200 mg, 550 µmol) was heated at 300 °C in a pyrex tube under N₂ until the evolution of gas ceased (approx. 5-10 min). After the reaction was complete, CH₂Cl₂ (25 mL) and 10 % aq. NaOH solution (10 mL) were added. The organic layer was separated, dried over MgSO₄, and the solvent was removed under reduced pressure. The aqueous layer was acidified with 12 M HCl to pH = 1, extracted with Et₂O (3 x 25 mL), dried over MgSO₄, and resubjected to pyrolysis. The residue was extracted with CH_2Cl_2 (30 mL) and the solvent was removed. The combined residues were subjected to column chromatography on silica gel (30%) ethyl acetate/70% hexanes) to give the title compound as a white solid (115 mg, 76 %). MP = 180-181 °C. ¹H NMR (300 MHz, CDCl₃): δ 6.99-7.01 (br s, 4H, Th-H), 3.00-3.25 (m, 2H, -CH-), 2.70-2.90 (m, 8H, -CH₂-). ¹³C NMR (75MHz, CDCl₃): δ 215.4 (ketone C=O), 138.3 (Th-C-3,4), 123.0 (Th-C-2,5), 53.7 (-CH-), 30.2 (-CH₂-). IR (KBr) 3151, 3098, 2934, 2848, 1690, 1216, 1104, 908, 740 cm⁻¹. MS (EI): *m/z* (%) 274.0 (M⁺, 100), 163 (59), 135 (15), 111 (46). HRMS (EI): m/z Calcd. for C₁₅H₁₄OS₂, 274.04861; found, 274.04744, $\Delta = 4.2$ ppm.



Tetrabromodithieno[*3*,*4-c*:*8*,*9-c'*]*bicyclo*[*4.4.1*]*undeca-3*,*8-diene-11-one*. *N*-Bromosuccinimide (1.33 g, 7.5 mmol) was added to a solution of dithieno[3,*4-c*:*8*,*9*c']bicyclo[4.4.1]undeca-3,*8*-diene-11-one (500 mg, 1.8 mmol) in DMF (10 mL) at 0 °C in the dark, and the mixture was stirred for 18 h. A solution of 10% aq. HCl (25 mL) was added and the mixture was extracted with CH₂Cl₂ (3 x 100 mL). The combined organic layers were washed with 0.1 M HCl (4 x 100 mL), 0.1 M NaOH (4 x 100 mL), H₂O (3 x 100 mL), and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was triturated with methanol to afford the title compound as a white solid (1.0 g, 93%). MP = 244-246 °C (decomp). ¹H NMR (300MHz, DMSO-*d*₆): δ 3.12-3.17 (m, 2H, -CH-), 2.7-3.0 (m, 8H,-CH₂-). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 212.7 (C=O), 137.4 (β-Th), 109.8 (α-Th), 52.2 (bridgehead), 29.6 (methylene). IR (KBr) 2929, 2849, 1704, 1434, 1259, 1105, 1031, 803 cm⁻¹. MS (EI): *m/z* (%) 589.7 (M⁺, 100), 510.8 (M⁺-Br, 24). HRMS (EI): *m/z* Calcd. for C₁₅H₁₀OBr₄S₂, 585.69065; found, 585.69360, Δ = 5 ppm.


Tetra-(2-thienyl)-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one. Pd(PPh₃)₄ (24 mg, 20 µmol) was added to a solution of 2,5,2',5'-tetrabromo-dithieno[3,4-c:8,9c']bicyclo[4.4.1]undeca-3,8-diene-11-one (200 mg, 0.34 mmol) and LiCl (25 mg, 0.58 mmol) in dry THF (7 mL), and the mixture was stirred at 0 °C for 10 min. 2-Tri-nbutylstannylthiophene (750 mg, 2.01 mmol) was added dropwise, and the solution was heated at 65 °C for 3 d. The resulting mixture was cooled, and the solvent was removed under reduced pressure. A saturated aq. solution of KF (10 mL) was added and the mixture was extracted with Et₂O (3 x 50 mL). The combined organic extracts were washed with H₂O (2 x 50 mL), dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (30% ethyl acetate/70% hexanes) followed by recrystallization from hexanes to provide the title compound as a pale yellow crystalline solid, (112 mg, 55%). MP = 263-265 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.35 (m, 4H, Th), 7.05 (m, 8H, Th), 2.8-3.25 (m, 10H, -CH- and -CH₂-). ¹³C NMR (75 MHz, CDCl₃): δ 214.5 (C=O), 136.4, 135.1, 134.7, 127.7, 127.1, 126.3 (aromatic), 53.6 (-CH-), 29.4 (-CH₂-). IR (KBr) 2934, 2862, 1697, 1453, 1098, 919, 841, 696 cm⁻¹. MS (EI): *m/z* (%) 602 (M⁺, 100), 275 (M⁺-4Th). HRMS (EI): m/z Calcd. for C₃₁H₂₂OS₆, 601.99950; found, 601.99752, $\Delta = 3.3$ ppm.



Ethylene acetal of tetra-(2-thienyl)-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one. A solution of the tetra-(2-thienyl)-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8diene-11-one (100 mg, 170 µmol), ethylene glycol (100 mg, 1.60 mmol), and ptoluenesulfonic acid (1 mg, 5 mmol) in benzene (7 mL) was heated at reflux for 18 h with a Dean-Stark trap. The solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (10% ethyl acetate/90% hexanes) followed by recrystallization from 10% ethyl acetate/90% hexanes to give the title compound (105 mg, 97%) as a yellow crystalline solid. MP = 264-266 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: δ 7.11 (dd, 4H, J = 1.1 Hz, J = 5.1 Hz, Th-5), 6.86 (dd, 4H, J = 3.6, 5.1 Hz, Th-4), 6.80 (dd, 4H, J = 1.1, 3.5 Hz, Th-3), 4.01 (s, 4H, -OCH₂CH₂O-), 3.34 (dd, 4H, J = 5.6, 15.5 Hz, -CH₂-), 3.10 (dd, 4h, J = 3.4, 15.5 Hz, -CH₂-), 2.32 (m, 2H, bridgehead). ¹³C NMR (75 MHz, CDCl₃): δ 138.0, 136.1, 129.6, 127.0, 126.1, 125.0 (aromatic), 113.4 (ketal), 64.7 (-OCH₂CH₂O-), 42.7 (bridgehead), 28.6 (-CH₂-). IR (KBr) 2927, 2855, 1433, 1104, 1038, 906, 834, 703 cm⁻¹. MS (EI): *m/z* (%) 646.1 (M⁺, 100), 564 (M⁺-Th). HRMS (EI): *m/z* Calcd. for C₃₃H₂₆O₂S₆, 646.02571; found, 646.02561, $\Delta = 0.2$ ppm. Anal. calcd. for $C_{33}H_{26}O_2S_6 = C$, 61.27; H, 4.05; S, 29.74. Found: C, 61.04; H, 4.10; S, 29.57.



Tetra-(5-methyl-2-thienyl)-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one. $Pd(PPh_3)_4$ (35 mg, 30 µmol) was added to a solution of tetrabromo-dithieno[3,4-c:8,9c']bicyclo[4.4.1]undeca-3,8-diene-11-one (200 mg, 0.34 mmol)and LiCl (30 mg, 0.71 mmol) in dry THF (7 mL), and the mixture was stirred at 0 °C for 10 min. 5-Methyl-2-tri*n*-butylstannylthiophene (1.1 g, 2.7 mmol) was added dropwise, and the solution was heated at 65 °C for 3 d. The mixture was cooled, and the solvent was removed under reduced pressure. A saturated aq. solution of KF (10 mL) was added, and the mixture was extracted with Et₂O (3x 50mL). The combined organic extracts were washed with H₂O (2 x 75 mL), dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (30% ethyl acetate/70% hexanes) followed by recrystallization from hexanes to provide the title compound as a pale yellow crystalline solid (105 mg, 47%). MP = 257-259 °C. ¹H NMR (300 MHz, CDCl₃): δ 6.6-6.8 (m, 8H, Th), 2.4-3.2 (m, 10H, -CH- and -CH₂-), 2.2-2.4 (m, 12H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 215.0 (C=O), 141.0, 135.9, 132.5, 126.9, 125.8, 122.8 (aromatic), 53.3 (bridgehead), 29.4 (methylene), 15.34 (methyl). IR (KBr) 3006, 2973, 2927, 1723, 1374, 1229, 1098, 913, 742, 650 cm⁻¹. MS (EI): m/z (%) 658.1 (M⁺, 100). HRMS (EI): m/z = Calcd. for C₃₅H₃₀OS₆, 658.06210; found, 658.05948, $\Delta = 4.0$ ppm.



Ethylene acetal of tetra-(5-methyl-2-thienyl)-dithieno[3,4-c:8,9-c']bicyclo[4.4.1] undeca-3,8-diene-11-one. A solution of 2,5,2',5'-tetra-(5-methyl-2-thienyl)-dithieno[3,4-c:8,9c']bicyclo[4.4.1]undeca-3,8-diene-11-one (105 mg, 160 µmol), ethylene glycol (317 mg, 5.11 mmol), and p-toluenesulfonic acid (5 mg, 30 mmol) in benzene (7 mL) was heated at reflux for 18 h with a Dean-Stark trap. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (10%) ethyl acetate/90% hexanes) followed by recrystallization from the eluent system to give the title compound as pale yellow crystalline solid (100 mg, 89%). MP = 214-216 °C. ¹H NMR (300 MHz, CDCl₃): δ 6.60 (d, 4H, J = 3.8 Hz, Th), 6.50-6.54 (m, 4H, Th), 4.03 (s, 4H, -OCH₂CH₂O-), 3.29 (dd, 4H, J = 5 Hz, J = 15Hz, -CH₂-), 3.02 (dd, 4H, J = 3 Hz, J = 15 Hz, -CH₂-), 2.38 (d, 12H, J = 1.0 Hz, -CH₃), 2.28-2.35 (m, 2H, -CH-). ¹³C NMR (75 MHz, CDCl₃): δ 139.2, 137.2, 134.2, 129.5, 125.7, 124.9 (aromatic), 113.5 (C=O), 64.6 (-OCH₂CH₂O-), 42.7 (bridgehead), 28.5 (-CH₂-), 15.2 (-CH₃). IR (KBr) 3074, 2961, 2913, 2887, 1435, 1252, 1100, 1039, 1000, 904, 783, 717 cm⁻¹. MS (EI): *m/z* (%) 702.1 (M^+) , 640 (4), 351 (5), 287 (6), 141 (7). HRMS (EI): m/z Calcd. for $C_{37}H_{34}O_2S_6$, 702.08831; found, 702.08240, $\Delta = 8.4$ ppm. Anal. calcd. for C₃₇H₃₄O₂S₆: C, 63.21; H, 4.88; S, 27.37. Found: C, 63.04; H, 4.86; S, 27.12.



Tetra-[2-(5'-methyl-2',5-bithienyl)]-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-

diene-11-one. 2-Methyl-5'-tributylstannyl-5,2'-bithiophene (1.60 g, 3.4 mmol) was added to a solution of tetrabromodithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one (200 mg, 340 µmol), Pd(PPh₃)₄ (100 mg, 80 µmol), and LiCl (45 mg, 1.1 mmol) in dry DMF (6 mL), and the solution was heated at 65 °C for 18 h. The mixture was cooled and a saturated aq. solution of KF (15 mL) was added, and the mixture was stirred for 1 h. The aqueous layer was discarded and the organic solution was passed through celite and a silica plug, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (70% CHCl₃/30% hexanes) to afford the product as a golden brown solid (180 mg, 54%). MP = 254-256 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.01 (d, 4H, *J* = 3 Hz, Th-H), 6-94-6.97 (m, 8H, Th-H), 6.60-6.62 (m, 4H, Th-H), 2.80-3.20 (m, 10H, methylene, bridgehead), 2.45-2.50 (bs, 12H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 139.2, 137.5, 135.1, 134.7, 134.5, 129.3, 126.3, 125.9, 123.5, 123.2 (aromatic), 53.2 (bridgehead), 29.5 (-CH₂-), 15.5, (-CH₃). IR (KBr) 3069, 2956, 2908, 2852, 1704, 1517, 1434, 1199, 1055, 781, 473 cm⁻¹.



Tetra-[2-(5'-methyl-2',5-bithienyl)]-dithieno[3,4-c:8,9-Ethylene acetal of c']bicyclo[4.4.1]undeca-3,8-diene-11-one. A solution of tetra-[2-(5'-methyl-2',5bithienyl]-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one (150 mg, 100 µmol), ethylene glycol (100 mg, 1.61 mmol), and *p*-toluenesulfonic acid (2 mg, 10 mmol) in benzene (7 mL)was heated at reflux for 18 h with a Dean-Stark trap. The solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (70% CHCl₃/30% hexanes) followed by recrystallization from toluene to give the title compound as an orange solid (70 mg, 45%). MP = 260-261 °C (decomp). ¹H NMR (300 MHz, CDCl₃): δ 6.65-6.78 (m, 12H, Ar), 6.48-6.53 (m, 4H, Ar), 4.10 (s, 4H, ethylene), 3.5 (dd, 4H, J = 5, 15 Hz, methylene), 3.09 (dd, 4H, J = 3, 15 Hz, methylene), 2.30-2.50 (m, 14H, bridgehead, methyl). ¹³C NMR (75 MHz, CDCl₃): δ 138.57, 137.8, 137.2, 134.8, 134.5, 129.5, 128.2, 126.30, 125.5, 122.8 (aromatic), 113.4 (ketal), 64.8 (-OCH₂CH₂O-), 42.6 (bridgehead), 28.72 (-CH₂-), 15.5 (-CH₃). IR (KBr) 3065, 2961, 2917, 1448, 1257, 1109, 1048, 1000, 913, 787, 730 cm⁻¹. MS (FAB): m/z (%) 1029.8 (M⁺, 100). HRMS (EI): m/z = Calcd. for C₅₃H₄₂O₂S₁₀, 1030.03920; found, 1030.03553, $\Delta = 3.6$ ppm. Anal. calcd. for C₅₃H₄₂O₂S₁₀: C, 61.71; H, 4.10; S, 31.09. Found: C, 61.58; H, 3.94; S, 30.87.

3.3. Results and Discussion

3.3.1. Synthesis of π -Stacked Oligothiophenes

 π -Stacked Terthiophene. The successful synthesis and characterization of the dothieno-fused bicyclo[4.4.1[undecanone **2.3** provided a route to extended π -conjugated systems which are in close proximity to each other (3-4 Å), typical for electronic communication in π -conjugated chains in sold state materials. Bromination of the reactive 2- and 5- positions on **2.3** with 4.1 eq. *N*-bromosuccinimide provided the tetrabromo derivative **3.1**, Figure 3.1. Multiple attempts to couple 2-thiophene boronic acid under basic conditions with Pd(PPh₃)₄ in THF or DME were unsuccessful, Figure 3.1. Use of the neopentyl borate ester to increase solubility and reactivity also yielded no coupled product in THF or DME.



Figure 3.1. Synthesis of 3.1 and attempts to synthesize 3.2 via Suzuki coupling.

The Stille reaction was then attempted to install thienyl units on the dithienofused bicyclo[4.4.1]undecanone **3.1**. Treatment of **3.1** with excess (6-8 eq.) commercially available 2-tri-*n*-butylstannylthiophene with LiCl (to aid in transmetallation), and Pd(PPh₃)₄ in anhydrous DMF at 65 °C for 3d gave ketone **3.2** in good yield, 55% (corresponding to 86% conversion of thienylic bromides), Figure 3.2. In order to lock the conformation on the bicyclo[4.4.1]undecanone into a chair-chair arrangement for π - π communication between the terthiophene units, the ketalization was performed with ethylene glycol, benzene and p-toluenesulfonic acid fitted with a Dean-Stark trap Ketal **3.3** was obtained as a yellow crystalline solid after column chromatography (yield, 97%), Figure 3.2.



Figure 3.2. Synthesis of ketone **3.3** and π -stacked ketal **3.4**.

The methyl-capped terthiophene compound was syntheisized in a similar fashion. 2-Methyl-5-tri-*n*-butylstannylthiophene was prepared according to analogous literature procedures^{7,8} and was coupled to **3.1** in the presence of Pd(PPh₃)₄,and LiCl in anhydrous DMF. The ketone **3.4** was attained as a pale yellow crystalline solid a 47% yield (83% conversion per thienylic bromide) after column chromatography and recrystallization from hexanes, Figure 3.3. Ketalization with ethylene glycol afforded the π -stacked compound **3.5** as a pale yellow crystalline solid (yield, 89%), Figure 3.3.



Figure 3.3. Synthesis of ketone **3.5** and π -stacked ketal **3.6**.

Linear Model Terthiophenes. Model compound **3.6** was synthesized in two steps from 3,4-dimethylthiophene. Bromination with 2.1 eq. *N*-bromosuccinimide in CHCl₃ afforded 2.5-dibromo-3,4-dimethylthiophene in almost quantitative yield after aqueous workup and extraction with hexanes. The Suzuki reaction yielded some material on a small scale, but the Stille reaction conditions yielded more material on a larger scale. Column chromatography followed by recrystallization from hexanes afforded 3',4'dimethyl-2,2':5'2"-terthiophene, **3.6**, as yellow crystalline solid, Figure 3.4.



Figure 3.4. Synthesis of linear model terthiophene 3.6.

The methyl-capped model terthiophene **3.7** was prepared in a similar fashion Reaction of 2,5-dibromo-3,4-dimethylthiophene with 2-methyl-5-tri-*n*-butylstannylthiophene in the presence of $Pd(PPh_3)_4$, and LiCl in anhydrous DMF at 60 °C provided **3.7** as yellow crystalline solid (yield, 66%), Figure 3.5.



Figure 3.5. Synthesis of linear, methyl-capped model terthiophene 3.7.

Quinquethiophene π -Stacked and Linear Model Compounds. A key intermediate bithiophene **3.8** was synthesized to extend the conjugation length of the stacked oligomers and linear models up to the quinquethiophene. 2-Bromo-5-methylthiophene, was coupled to 2-tri-*n*-butylstannylthiophene in the presence of Pd(PPh₃)₄, and LiCl in dry DMF to provide 2-methyl-5:2'-bithiophene in good yield (55%), Figure 3.6.⁹ Lithiation with *n*-butyllithium (1.1 eq.) in dry Et₂O followed by addition of tri-*n*butylstannyl chloride provided **3.8** as an orange oil in high yield (99%) after workup.¹⁰



Figure 3.6. Synthesis of intermediate 2-methyl-5:2'-bithiophene, 3.8.

Synthesis of the quinquethiophene ketone **3.9** was accomplished by the Stille coupling of ketone **3.1** to bithiophene **3.8**. Purification by column chromatography (afforded **3.9** as a golden brown solid (yield, 54%), Figure 3.7. Ketalization of ketone **3.9** with ethylene glycol provided π -stacked ketal **3.10** as an orange solid, Figure 3.7. While the solubility of **3.10** was low in CDCl₃ at room temperature, this did not present a problem for spectroscopic and electrochemical characterization.



Figure 3.7. Synthesis of quinquethiophene ketone 3.9 and ketal 3.10.

The model quinquethiophene was synthesized by the Stille reaction of 2,5dibromo-3,4-dimethylthiophene with stannylated bithiophene **3.8**. Purification by column chromatography followed by recrystallization from toluene afforded the desired quinquethiophene, **3.11**, as an orange solid (yield, 69%), Figure 3.8. The major byproduct isolated from this reaction was 2,5"'-dimethyl-5,2':5',2":5",2"'-quarterthiophene from the homocoupling of the stannane. The solubility of **3.11** was considerably higher than that of **3.10**.



Figure 3.8. Synthesis of linear model quinquethiophene 3.11.

3.3.2. Structural Characterization: ¹H NMR Spectroscopy

The influence of π -stacking of oligothiophenes can be observed by ¹H NMR spectroscopy as a change in the chemical shift of signals in the aromatic region of the spectrum. Model terthiophene **3.6** gives three distinct doublet of doublets (B, C, D) each representing two protons (7.3, 7.13, and 7.07 ppm), Figure 3.9. The coupling constants for D are 1 and 5 Hz; 1 and 3 Hz for B; and 3 and 5 Hz for C which are consistent with coupling of 2-thienyl substituents. The methyl signal at δ 2.30 ppm is a singlet for six identical protons.ⁱ The signals for the aromatic protons of π -stacked terthiophene **3.3** are all shifted upfield in its aromatic protons compared to that of the model linear **3.6**. The aromatic signals (7.11, 6.86, and 6.80 ppm) each represents four protons (B, C, D) indicating an upfield shift due to shielding in the magnetic field from a π -stacked orientation, Figure 3.10.

ⁱ The ¹³C NMR spectrum (not shown) for **3.6** displayed six aromatic carbon signals and one methyl signal in CDCl₃.



Figure 3.9. Aromatic region of ¹H NMR spectrum (300 MHz, CDCl₃) of model terthiophene **3.6**.



Figure 3.10. Aromatic region of ¹H NMR spectrum (300 MHz, CDCl₃) of π -stacked terthiophene **3.3**.

The methylene protons of **3.3** (3.34, 3.10 ppm) were each four proton doublet of doublets with coupling constants of 3 or 5, and 15 Hz.ⁱⁱ These coupling constants are consistent with the formation of a chair-chair conformation demonstrating that the face to face packing of the central thiophene rings connected to the bicyclo[4.4.1]undecane framework with ethylene glycol is sufficient for π -stacking. The ketone precursor **3.2** displayed two multiplets in the aromatic region unlike the linear model and stacked compounds because of its conformational flexibility, Figure 3.11.



Figure 3.11. ¹H NMR (300 MHz, CDCl₃) of ketone **3.2**.

It should be noted that there is no slipping (thiophene rings are not offset with respect the ring opposite it) allowed for the thiophene subunits stacked atop one another

ⁱⁱ The ¹³C NMR spectrum contains six aromatic protons and four signals for the methylene, ethylene,

and anti/syn conformations may both give upfield shifts as seen in literature.¹⁶ The conformations are related to the energy of the oligomer where the thiophene rings can rotate accordingly to the lowest ground state energy level. In these examples, the upfield shifts in aromatic protons is due to π -stacking and are can coincidental when the oligomers are in different conformations.

The methyl-capped terthiophene model **3.7** exhibited two different types of aromatic protons at δ 6.89 and 6.70 ppm, Figure 3.12 (top). Proton labeled B was a doublet (J = 3Hz) representing two identical protons from each thiophene unit. The other proton labeled C is a doublet of quartets (J = 1, 3 Hz), as it is split with the other β -proton and three protons of the methyl group by long-range coupling. One methyl signal at δ 2.49 ppm is a doublet (J = 1 Hz).ⁱⁱⁱ

The methylene protons and bridgehead of the intermediate ketone **3.4** are a coalesced multiplet between δ 2.8-3.2 ppm due to the flexibility of the compound, Figure 3.12 (middle). The chemical shifts of aromatic protons of **3.4** are similar to that of **3.7** consistent with an unstacked conformation. Upon ketalization with ethylene glycol, the two terthiophene units of **3.5** are forced over into a stacked conformation and the aromatic protons exhibit an upfield shift due to π -stacking (6.60 and 6.52 ppm). Both exhibited similar coupling constants. The methylene peaks (pair of doublet of doublets, *J* = 3 or 5, 15 Hz) of **3.5** confirm a chair-chair conformation which is stable to 100 °C, and the bridgehead protons are shifted upfield and are nearly coincidental with the twelve methyl protons (*J* = 1 Hz) at 2.4 ppm, Figure 3.12 (bottom).^{iv}

bridgehead, and C-11 carbons (not shown).

ⁱⁱⁱ The ¹³C NMR spectrum of **3.7** has six aromatic signals and two different methyl signals.

^{iv} The ¹³C NMR spectrum for **3.5** displayed six aromatic, one methylene, one bridgehead, one ethylene glycol, and tertiary ketal carbon signals.



Figure 3.12. ¹H NMR (300 MHz, CDCl₃) of methyl-capped model terthiophene, 3.7 (top), ketone 3.4 (middle), ketal 3.5 (bottom).

In the case of the linear model quinquethiophene compound, **3.11**, the ¹H NMR spectrum displays four different aromatic signals for the β -thiophene protons (δ 7.03, 7.00, 6.97, and 6.66 ppm) each of which each integrate to two signals each (eight protons total). Protons labeled B, and C were coupled to each other with a coupling constant of 3 Hz. Protons labeled E and F had coupling constants of 3 Hz, and 3 and 5 Hz, respectively. The two different methyl signals appear at δ 2.48 ppm (doublet, J = 1 Hz) and δ 2.32 ppm (singlet), Figure 3.13 (top). The spectrum of ketone **3.9** is similar to the linear model quinquethiophene **3.11** with very similar chemical shifts for the aromatic

protons, Figure 3.13, (middle). The bridgehead and methylene proton signals are coincident in chemical shift, appearing as a broad multiplet at 2.8-3.2 ppm.



Figure 3.13. ¹H NMR (300 MHz, CDCl₃) of model quinquethiophene **3.11** (top), ketone **3.9** (middle), and ketal **3.10** (bottom).

In the case of π -stacked compound **3.10**, the aromatic protons are shifted upfield with three distinct multiplets (6.77, 6.70, 6.51 ppm). The furthest downfield signal corresponds to the four protons labeled B. The middle aromatic multiplet corresponds to two sets of coincidental proton signals labeled C and E. The other signal at δ 6.51 ppm corresponds to protons labeled F. The bridgehead protons are coincident with the methyl protons (2.3-2.5 ppm), showing coupling to the thienylic protons in the COSY spectrum. There is also a slight upfield shift of the methyl protons of **3.10** compared to model **3.11** (0.1 ppm). The set of doublet of doublets (δ 3.50 and 3.09 ppm) is consistent with the ethylene glycol clipping unit forcing the bicyclo[4.4.1]undecane framework into a chairchair conformation, Figure 3.13 (bottom). ¹³C NMR spectrum of **3.10** shows ten aromatic signals, four signals for the undecane framework and one methyl signal consistent with a single conformation.

A summary of the aromatic and methyl end group protons of the model π conjugated oligothiophenes and π -stacked analogs is illustrated in Table 3.1.

Table 3.1. NMR Chemical Shifts (δ) for aromatic and methyl protons of stacked and unstacked compounds in CDCl₃^{*a*}.

Compound	Ha	H _b	H _c	H _d	H _e	H _f	-CH ₃
tetramethylthiophene	6.88						
stack 2.4	6.51						
model 3.6		7.30	7.06	7.14			
stack 3.3		7.12	6.86	6.79			
model 3.7		6.90	6.70				2.50
stack 3.5		6.62	6.51				2.40
model 3.11		7.03	7.01		6.97	6.66	2.45
stack 3.10		6.77	6.70		6.70	6.51	2.40

^{*a*} Protons are labeled from inner thiophene unit to outer thiophene unit for each symmetrical oligomer.

3.3.3. X-ray Structural Analysis

A suitable single crystal of **3.4** was attained for X-ray structural analysis by slow evaporation of a 4:1 mixture of ethyl acetate/hexanes over two weeks. The X-ray structural analysis confirmed chair-boat conformation for the undecane framework, consistent with the low temperature ¹H NMR, Figure 3.14. The carbonyl at C-11 is not bulky enough to force the bicycle into a chair-chair conformation.



Figure 3.14. ORTEP diagrams of 3.4 illustrating chair-boat conformation (sideview).

Upon ketalization, the terthiophene oligomers stack on top one another in a rigid conformation. Compound **3.3** was dissolved in a 1:6 ethyl actetate/hexanes mixture and the solution was evaporated to obtain a suitable single crystal. The crystal structure of **3.3** shows one terthiophene oligomer in a transoid-cisoid conformation and the other terthiophene oligomer is in a cisoid-cisoid conformation. The stacked ketal **3.3** central core thienyl sulfur atoms are 414 pm apart, Figure 3.15. The closest distance between the central thiophene core is 301 ppm between C9-C13. The closest distance between these outer rings is 352 ppm for C23-S5 and 363 ppm for C31-S3. The terthiophenes are slightly twisted from planarity to facilitate π -stacking. The packing diagram of **3.3** illustrates the arrangement of the stacked compound in the solid state, Figure 3.16.



Figure 3.15. ORTEP diagrams of π -stacked terthiophene **3.3**.



Figure 3.16. Packing diagram of 3.3. Hydrogen atoms excluded.

Methylated terthiophene π -stack **3.5** was slowly crystallized from a 1:9 mixture of ethyl acetate and hexanes over two weeks to obtain a suitable crystal. The sulfur-sulfur

distance of the central thiophenes is 418 pm, and the distance between the β -carbons is 304 ppm (C6-C16), Figure 3.17. Similar to the case of the unmethylated analog **3.3**, one terthiophene oligomer is in a cisoid-transoid conformation, while the other is a cisoid-cisoid π -stacked terthiophene oligomer. Two thiophene rings stacked on top one another adjacent to the central thiophenes are closest at atoms S1-C27 with a distance of 374 ppm. On the opposite side of the molecule, the two thiophene rings π -stacked ontop one another are closest between atoms C23-C31 with a value of 327 ppm. The crystal structure analyses confirm the conformational rigidity in solid state, owing to the compounds existing in one conformation.



Figure 3.17. ORTEP diagrams of 3.5.

The crystal packing diagram of **3.5** illustrates how the rotations of the attached thiophenes to the undecane core are effected by neighboring rings, Figure 3.18. This compound adopts a partial herringbone motif with the sulfur of one thiophene ring oriented perpendicular to the ring of an adjacent molecule. The central thiophene units attached to the undecane core are still held in a π -stacked motif due to the ethylene glycol

unit preventing conformational flexibility, but a contribution from both effects should be noted. The quinquethiophene π -stacked compound, **3.10** did not form X-ray quality crystals in multiple solvents.



Figure 3.18. Crystal packing diagram of 3.5.

3.4. Conclusion

The dithieno-fused bicyclo[4.4.1]undecanone core **2.3** is an ideal candidate to covalently link two π -conjugated oligomers together in a cofacial arrangement. Structural characterization supported the notion that the extended π -stacked oligomers are in close proximity of one another with the potential to influence one another's electronic structure. The influence of π -stacking on neutral and charge species (radical cation, dications) can further be studied through the use of spectroscopy (UV-vis-NIR), doping with chemical oxidants, and electrochemistry (Chapter 4).

3.5. References

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CHAPTER 4

PHOTOPHYSICAL AND ELECTROCHEMICAL CHARACTERIZATION OF π-STACKED OLIGOTHIOPHENES



4.1. Introduction

To identify the nature of the charge carries in p-doped conducting polymers and explore interchain charge transfer of closely held oligomers, we designed twodimensional π -stacked oligothiophenes, Chapters 2 and 3. We focus now on determining the electronic structure of these compounds by UV-vis-NIR spectroscopy, electrochemistry, and ESR.

The electronic states of polarons and bipolarons have been discussed mainly in the framework of theories involving electron-lattice interactions which have been well studied extensively by Bredas¹⁻⁴ and others.^{5,6} The polaron/bipolaron model for charge carriers in doped conjugated polymers serves to explain the observed paramagnetism at low levels of doping and diamagnetism at higher doping levels in materials with nondegenerate ground states. According to a theoretical study by Shimoi,⁷ a polaron gives rise to two absorption peaks, and a bipolaron gives rise to one peak. π -Dimers (formed at low temperature by aggregation of radical cations) show two subgap absorptions, which are characteristic to radical cations at room temperature but with new energy transitions in UV-vis-NIR. However, these π -dimers are ESR silent and establish a possible role for another charge transport mechanism of doped conjugated polymers.

Here we report the physical properties of both π -stacked and linear oligomers model. Comparison of the UV-vis absorbance and fluorescence spectra of the neutral compounds demonstrate the effects of π -stacking two conjugated oligomers together using the bicyclo[4.4.1]undecane framework. Oxidation with FeCl₃ along with electrochemistry allow us to determine how stacking facilitates π -dimer formation and thereby effects the stability of cjarge carriers in doped conjugated polymers. The characterization of these π -dimers provide further understanding of the nature of charge carriers in doped π -conjugated polymers.

4.2. Experimental

Absorbance and fluorescence spectra were recorded on a Shimadzu 2401PC UVvis spectrophotometer and RF5301PC spectrofluorophotometer. UV-vis-NIR spectra were recorded on a Perkin Elmer Lambda 19 spectrophotometer. Specially designed four sided quartz cuvettes fitted with a 14/20 female joint sealed with a rubber septum were used in order to titrate stock solutions of FeCl₃/CH₂Cl₂ via syringe into known concentrations of analyte (1-2 mM). Spectra were typically recorded upon addition of every 0.25 equivalents analyte. FeCl₃ was dried at 100 °C under vacuum for 4 h prior to dissolution in CH_2Cl_2 (1-2 mM). CH_2Cl_2 was distilled from CaH_2 onto molecular sieves prior to use.

Electrochemical measurements were carried out under nitrogen and recorded on a BAS 100B Electrochemical Analyzer with a three electrode cell equipped with a 2 mm gold working electrode, a platinum counter electrode, and a Ag/Ag⁺ reference electrode with 3M NaCl solution end capped with a vycor tip. Substrates (1-2 mM) were dissolved in CH₂Cl₂ containing 0.1 M n-Bu₄NPF₆ which was purchased from Fluka. The ferrocene/ferrocenium couple is +0.45 V under these conditions. Bulk electrolysis was performed in a specially designed cell enclosing a carbon mesh wire as the working electrode. The auxiliary electrode was enclosed in a fritted tube to prevent decomposition of material over typically extended run times.

ESR measurements were recorded on a Bruker EMX EPR with a 4131VT nitrogen temperature controller. ESR tubes were purchased from Wilmad. Typical analyte concentrations were 10^{-3} to 10^{-4} M and a stock solution of FeCl₃/CH₂Cl₂ (1-2.5 mM) was titrated into the tube and measured. Typical power was 0.6 mW-1mW and center fields were 3480-3520 Gauss. The modulation phase was set to 260 degrees in all experiments.

4.3. Results and Discussion

4.3.1. UV-vis Spectroscopy of Neutral Compounds

The model linear π -conjugated oligothiophenes described in Chapters 2 and 3 are denoted as **R-Th_n-R** (R = H or Me, n = 1, 3, 5), and the stacked analogs as *st*-[**R-Th_n-R**]₂ (R = H or Me, n = 1, 3, 5). The electronic spectra of model neutral oligothiophenes and

π-stacked oligothiophene series show π - π^* absorption bands and vibronic emission bands in the visible region. The comparison between the linear and stacked analog is a good starting point to illustrate how oligothiophenes affect the electronic structure of conjugated systems. The stacked compound *st*-[**H**-**Th**₁-**H**]₂ ($\lambda_{max} = 238$ nm) shows a small hypsochromic shift (2 nm) in absorbance upon stacking compared to its model 3,4dimethylthiophene, **H**-**Th**₁-**H**, ($\lambda_{max} = 240$ nm), Figure 4.1 (top). A small bathochromic shift in fluorescence ($\lambda_{max} = 308$ nm, 1 nm) for *st*-[**H**-**Th**₁-**H**]₂ compared to 3,4dimethylthiophene, **H**-**Th**₁-**H**, ($\lambda_{max} = 307$ nm) suggests that stacking does not have a dramatic effect on the electronic structure of arenas, Figure 4.1 (bottom). The Stokes shift is 67 nm for the model and 70 nm for the π -stacked compound.

Similarly, the methyl terminated π -stacked compound *st*-[Me-Th₁-Me]₂ ($\lambda_{max} = 241 \text{ nm}$) shows a small hypsochromic shift (1 nm) in absorbance compared to tetramethylthiophene, Me-Th₁-Me, ($\lambda_{max} = 242 \text{ nm}$), Figure 4.1 (bottom). Again, there is only a small bathochromic shift in fluorescence ($\lambda_{max} = 310 \text{ nm}$, 2 nm) for *st*-[Me-Th₁-Me]₂ compared to tetramethylthiophene, Me-Th₁-Me, ($\lambda_{max} = 308 \text{ nm}$). The Stokes shift for the model compound is 66 nm and for the π -stacked compound is 69 nm.



Figure 4.1. Absorbance fluorescence spectrum of *st*-[**H**-**Th**₁-**H**]₂ (top). Absorbance and fluorescence spectrum of *st*-[**Me**-**Th**₁-**Me**]₂ (bottom). Models not shown.

The absorbance band of model terthiophene **H-Th₃-H** appears at $\lambda_{max} = 333$ nm. Upon excitation at this wavelength the emission band appears at $\lambda_{max} = 431$ nm with a small higher energy peak at $\lambda = 412$ nm, Figure 4.2. The Stokes shift for the model compound is 98 nm. The effect of varying the excitation wavelength is illustrated in Figure 4.3.



Figure 4.2. Absorbance and fluorescence spectrum of H-Th₃-H.



Figure 4.3. Fluorescence spectrum of H-Th₃-H at variable excitations.

For *st*-[**H**-**Th**₃-**H**]₂, the absorbance band at $\lambda_{max} = 324$ nm is blue shifted by 9 nm compared to the model **H**-**Th**₃-**H** ($\lambda_{max} = 333$ nm). Conversely, the fluorescence of *st*-[**H**-**Th**₃-**H**]₂ is red shifted by 9 nm ($\lambda_{max} = 421$ nm) to that of **H**-**Th**₃-**H** ($\lambda_{max} = 412$ nm, 431

nm), and there is a broad shoulder at 500 nm, Figure 4.4. Excitation wavelengths of *st*-**[H-Th₃-H]**₂ at wavelengths from 220-350 nm is illustrated in Figure 4.5.



Figure 4.4. Absorbance and fluorescence spectrum of *st*-[H-Th₃-H]₂.



Figure 4.5. Fluorescence spectrum of *st*-[H-Th₃-H]₂ at variable excitations.

As for the methyl-capped terthiophene π -stacked compound *st*-[**Me-Th**₃-**Me**]₂, it shows a ref shift in fluorescence and a blue shift in absorbance compared to model compound **Me-Th**₃-**Me**. The absorbance band of *st*-[**Me-Th**₃-**Me**]₂ is blue shifted by 10 nm to $\lambda_{max} = 335$ nm and the emission band is red shifted by 21 nm ($\lambda_{max} = 444$ nm, 505 shoulder), compared to **Me-Th**₃-**Me** ($\lambda_{max} = 345$ nm, Fl = 423 shoulder, 442 nm), Figures 4.6 and Figure 4.7.



Figure 4.6. Absorbance and fluorescence spectrum of Me-Th₃-Me.



Figure 4.7. Absorbance and fluorescence spectrum of *st*-[Me-Th₃-Me]₂.

The series of spectra of **Me-Th₃-Me** shown in Figure 4.8 illustrate similar peaks with weakened intensity at wavelengths other than the λ_{max} due to one absorbing species contributing to the emission spectra. *St-*[**Me-Th₃-Me**]₂ exhibits similar behavior with broadened peaks at weaker intensities upon excitation at different wavelengths, Figure 4.9. The Stokes shift increases from 97 nm to 170 nm upon π -stacking the two terthiophene oligomers together.



Figure 4.8. Fluorescence spectrum of Me-Th₃-Me at variable excitations.



Figure 4.9. Fluorescence spectrum of *st*-[Me-Th₃-Me]₂ at variable excitations.

The quinquethiophene model compound **Me-Th₅-Me** absorbs at a longer wavelength due to its greater conjugation length ($\lambda_{max} = 400$ nm). Excitation at 400 nm gives a maximum at $\lambda_{max} = 492$ nm with shoulder at $\lambda = 520$ nm, Figure 4.10. The Stokes shift for this compound is 23 nm larger than the model terthiophene **Me-Th₃-Me**. The quinquethiophene π -stacked compound, *st*-[**Me-Th₅-Me**]₂, ($\lambda_{max} = 386$ nm) is blue shifted in its absorbance by 14 nm compared to its linear model **Me-Th₅-Me** ($\lambda_{max} = 400$ nm), and the fluorescence is red shifted by 16 nm ($\lambda_{max} = 500$, 526 shoulder), Figure 4.11. The Stokes shift for this compound is 140 nm which is not as large as that of the terthiophene π -stacked compound. Variable excitation spectra of **Me-Th₅-Me** and *st*-[**Me-Th₅-Me**]₂ are illustrated in Figures 4.12 and 4.13.



Figure 4.10. Absorbance and fluorescence spectrum of Me-Th₅-Me.



Figure 4.11. Absorbance and fluorescence spectrum of *st*-[Me-Th₅-Me]₂.



Figure 4.12. Fluorescence spectrum of Me-Th₅-Me at variable excitations.


Figure 4.13. Fluorescence spectrum of *st*-[Me-Th₅-Me]₂ at variable excitations.

A summary of UV-vis and fluorescence data is provided in Table 4.1. The extinction coefficients for the π -stacked compounds were less than twice the values for their linear analogs. This measurement is related to how well a conjugated material absorbs a photon upon excitation. If the photon penetrates the compound as would be the case in the π -stacked compounds, the extinction coefficient is lower. Conversely, if the photon hardly penetrates the material as in the linear model compounds and quickly becomes "extinct", the extinction coefficient is higher. However, this is a subtle difference in this series of π -stacked compounds and can also be attributed to the increased degree of overlap between the two chromophores facilitating the photon to become extinct at a faster rate.

	Absorbance $\lambda_{max} / nm (\epsilon^b)$	Fluorescence (nm) λ_{max} (shoulder)	Stokes Shift (nm)
Linear Models			
$H-Th_1-H^c$	$240 (7.3 \times 10^3)$	307	67
Me-Th ₁ -Me ^c	242 (7.4 x 10 ³)	308	66
H-Th ₃ -H	333 (2.1 x 10 ⁴)	(412) 431	98
Me-Th ₃ -Me	345 (2.2 x 10 ⁴)	(423) 442	97
Me-Th ₅ -Me	400 (4.3 x 10 ⁴)	492 (520)	120
Stacked Oligomers			
$st-[H-Th_1-H]_2^c$	238 (1.2 x 10 ⁴)	308	70
st-[Me-Th ₁ -Me] ₂ ^c	241 (1.3 x 10 ⁴)	310	69
st-[H-Th ₃ -H] ₂	324 (4.1 x 10 ⁴)	421 (500)	176
st-[Me-Th ₃ -Me] ₂	335 (4.2 x 10 ⁴)	444 (505)	170
st-[Me-Th ₅ -Me] ₂	386 (8.5 x 10 ⁴)	(500) 526	140

Table 4.1. Electronic Spectral Data^a of Models and Stacked Oligothiophenes

^{*a*}Electronic absorption and emission spectra were measured in CH₂Cl₂, $c = 10^{-5}$ M. Stacked compounds were half as concentrated for molar absorbance comparisons. ^{*b*}Molar absorptivity coefficients are in parentheses. ^{*c*} Measured in CHCl₃.

Stokes shifts are presented graphically as a function of oligomer length in Figure 4.14. The absorbance maxima and emission maxima both increase to lower energy upon extending the conjugation length for the linear model compounds and the Stokes shift increases concomitantly (extending oligomer length stabilizes photon absorption). The larger Stokes shift seen in the three-ring π -stacked compounds compared to the five ring system *st*-[Me-Th₅-Me]₂ can be attributed to the formation of a "phane state." This state (referred to as an excimer) only forms when one of the dimer components is in an excited state. The wavelength of an excimer's emission is longer than that of the excited monomer's emission, because the excimer is stabilized compared to the excited monomer. Similar behavior has previously been noted by Bazan for styryl-substituted paracyclophanes.⁸ The large Stokes shift can be explained in terms of adsorption by a

single oligomer acting as the chromophore, followed by energy transfer to a so called "phane state" which is responsible for emission at significantly lower energy. The lower energy associated with the excited state of the longer oligomer *st*-[Me-Th₅-Me]₂ means that there is less driving force for energy transfer such that a single oligomer is responsible more for both absorption and emission. In the case of the stacked compounds *st*-[R-Th₁-R]₂, the Stokes Shift is not as dramatic. This is attributed to the lack of degree of overlap from only one aromatic ring stacked on top itself providing a negligible driving force for photon relaxation.



Figure 4.14. Stokes shifts of model and stacked oligothiophenes versus the number of aromatic rings.

The change in vibronic structure for the linear model oligothiophenes is characteristic of the Franck-Condon Principle.⁹ There is a symmetrical carbon-carbon stretching vibration that arises from excitation that is a combination of the single and double bonds; therefore there are two energy peaks present in the emission spectra for linear oligothiophenes. As conjugation length increases, the relative intensity of the high energy peak increases. Geometrical relaxation in the excited state takes place on more carbons causing the relative change per bond to diminish. This phenomenon results in the lower energy transition to weaken in intensity upon increasing conjugation length.

4.3.2. Electrochemistry

The effect of stacking on the oxidation potential pf conjugated oligomers was determined by electrochemical characterization. Tetramethylthiophene, **Me-Th₁-Me**, exhibits an irreversible oxidation potential ($E_p = +1.39$ V), Figure 4.15. On the other hand, the π -stacked compound *st*-[**Me-Th₁-Me**]₂ gives a reversible one-electron oxidation ($E_{1/2} = +1.09$ V), which is significantly lower than the peak of the model compound, Figure 4.16. The mono(radical cation) formed upon one-electron oxidation is stabilized by through-space π - π interactions of the thiophene core units. Removal of the second electron at $E_{1/2} = +1.59$ V to form a dication is an irreversible process. The second oxidation process is +0.5 V higher than the first oxidation process, a difference that can be explained by Coulombic destabilization of the highly oxidized species with cationic charge localized on each thiophene ring. The overlaid differential pulse voltammogram (DPV) of **Me-Th₁-Me** (dotted line) and *st*-[**Me-Th₁-Me**]₂ (solid line), Figure 4.17, illustrate the lowering of the first redox peak for the π -stacked compound relative to that of the linear model.



Figure 4.15. CV of **Me-Th₁-Me**. c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.



Figure 4.16. CV of *st*-[Me-Th₁-Me]₂. c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.



Figure 4.17. DPV of **Me-Th₁-Me** and *st*-[**Me-Th₁-Me**]₂. c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The terthiophene model **Me-Th₃-Me** displays a reversible one-electron wave ($E_{1/2}$ = +0.96 V) and an irreversible second oxidation wave (E_p = +1.23 V) by cyclic voltammetry, Figure 4.18. The π -stacked terthiophene analog *st*-[**Me-Th₃-Me**]₂ gives two reversible one-electron waves (1 F/mol for each wave) at $E_{1/2}$ = +0.70 V and $E_{1/2}$ = +0.90 V which are *both* lower than the first oxidation of the model terthiophene compound **Me-Th₃-Me**, Figure 4.19. This splitting of the first oxidation and lowering of the oxidation potentials compared to the terthiophene model is due to increased delocalization of the charged species and stability of the dicationic state. A further 2F/mol oxidation occurs at $E_{1/2}$ = +1.49 V.



Figure 4.18. CV of **Me-Th₃-Me**. c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.



Figure 4.19. CV of **st-[Me-Th₃-Me]**₂. c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

Differential pulse voltammetry of the terthiophene model **Me-Th₃-Me** and π stacked compound **st-[Me-Th₃-Me]**₂ are shown in Figure 4.20. Well resolved oxidations of the π -stacked compound take place at lower potentials than the first oxidation of the linear terthiophene, suggesting that both the mono(radical cation) and dication are stabilized by π -stacking. The lowering of the second oxidation to form the dication to a value lower than the first oxidation of the linear model suggests that the π -stacked dication is stabilized in such a way that it overcomes the destabilization expected to arise from Coulombic repulsion.



Figure 4.20. DPV of **Me-Th₃-Me** (dotted line) and **st-[Me-Th₃-Me]₂** (solid line). c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The model quinquethiophene **Me-Th₅-Me** gives two reversible one-electron oxidations in the CV at $E_{1/2} = +0.79$ V and $E_{1/2} = +1.03$ V, Figure 4.21. Two reversible one-electron processes for the stacked analog *st*-[**Me-Th₅-Me**]₂ at $E_{1/2} = +0.67$ V and $E_{1/2} = +0.73$ V (2 F/mol) are *both* lower than the first oxidation of the model compound **Me**-

Th₅-**Me**, CV in Figure 4.22 and DPV in Figure 4.23. A further oxidation (2F/mol) for *st*-[**Me-Th**₅-**Me**]₂ occurs at $E_{1/2} = +1.22$ V to give the tetracation, which is at a higher potential than the second oxidation of the model compound **Me-Th**₅-**Me**. This higher potential for removal of the third and fourth electrons is due to the stabilization of the π stacked dicationic state and the destabilization of the tetracation by Coulombic repulsion.



Figure 4.21. CV of **Me-Th₅-Me**. c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.



Figure 4.22. CV of *st*-[**Me-Th**₅-**Me**]₂. c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The stacked DPV spectra of **Me-Th₅-Me** and *st*-[**Me-Th₅-Me**]₂ are plotted in Figure 4.23, illustrated the splitting previously discussed.



Figure 4.23. DPV of **Me-Th₅-Me** (dotted line) and *st*-[**Me-Th₅-Me**]₂ (solid line). c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The redox potentials of model and π -stacked oligothiophenes are summarized in Table 4.2. As expected, the ease of oxidation increases upon extending the conjugation length. π -Stacking of two oligomers also results in a lowering of the oxidation potential and splitting of the potential at which two electrons are removed from the stacked oligomers. The difference between the first and second redox processes in the π -stacked compounds (ΔE_I) decreases as oligomer chain length increases ($T_1 = +0.5$; $T_3 = +0.20$, $T_5 = +0.06$ V).

able 112. Oxidation I otentials of ensuened and Stateked engotinophenes					
	$E_l / V (\text{no } e)$	$\Delta E_l / \mathrm{V}$	E_2 / V (no e^{-})	ΔE_{2-1} / V	
Me-Th ₁ -Me	$1.39(1)^{b}$	-	-	-	
st-[Me-Th ₁ -Me] ₂	1.09 (1), 1.59 (1) ^b	0.5	-	-	
Me-Th ₃ -Me	0.96 (1)	-	1.23 (1)	0.27	
st-[Me-Th ₃ -Me] ₂	0.70 (1), 0.90 (1)	0.20	1.49 (2)	0.59	
Me-Th ₅ -Me	0.79 (1)	-	1.02 (1)	0.23	
st-[Me-Th ₅ -Me] ₂	0.67 (1), 0.73 (1)	0.06	1.22 (2)	0.49	

Table 4.2. Oxidation Potentials of Unstacked and Stacked Oligothiophenes

 $\overline{a} c = 2 \text{ mM}, v = 100 \text{ mV/s}; \text{ Ag/Ag}^+ \text{ reference electrode; Au working electrode, platinum auxiliary; Fc / Fc}^+ = +0.45 \text{ V}.$ \overline{b} irreversible. 0.1 M Bu₄NPF₆ supporting electrolyte in CH₂Cl₂ used in all samples.

Plots of the oxidation potentials versus number of aromatic rings (or reciprocal of # rings) for the series of methyl-capped oligothiophenes illustrates these tendencies, Figure 4.24. The first oxidation potentials of the stacked analogs are all lower than their respective unstacked analogs. This can be attributed to the stacking of monomers upon one another, allowing for better charge stabilization. There is localized Coulombic repulsion upon removal of the second electron (+1.59 V) from *st*-[Me-Th₁-Me]₂, but as oligomer conjugation length increases there is an increase in stability of the dicationic state that overcomes Coulombic repulsion, resulting in particularly lower oxidation potential. The second oxidation for the stacked terthiophene (+0.90 V) and stacked

quinquethiophene (+0.73 V) become *lower* than the first oxidation of their linear models (+0.96 V and +0.79 V, respectively).



Figure 4.24. Oxidation potentials of oligothiophenes.

4.3.3. Chemical Oxidation of Neutral Oligothiophenes to Radical Cations



RADICAL CATIONS

Treatment of oligothiophenes, Th_n , with $FeCl_3$ results in chemical oxidation illustrated in the general equation:

$$Th_n + 2FeCl_3 \longrightarrow Th_n^+ + FeCl_4^- + FeCl_2$$

Oxidiation by titration of model terthiophene **Me-Th₃-Me** with a stock solution of FeCl₃ in CH₂Cl₂ of, formed new absorbance bands ($\lambda_{max} = 563$ and 884 nm) with two equivalents of FeCl₃, Figure 4.25. This is consistent with the formation of a radical cation species. Further addition of FeCl₃ (2-4 eq.) does not form the dicationic species due to the high oxidation potential of the cation and instability of the dicationic form.



Figure 4.25. UV-vis-NIR spectrum of Me-Th₃-Me doped with FeCl₃ (0-2 eq.).

For model quinquethiophene **Me-Th₅-Me** one electron oxidation (2 eq. FeCl₃) produces two new energy transitions, Figure 4.26. Peaks at 716 nm (1.73 eV) and 1322

nm (0.94 eV) correspond to a radical cation of **Me-Th₅-Me**. Upon further addition of FeCl₃ (up to 4 eq.), the radical cation peaks diminish and a new absorbance grows in at 915 nm (1.36 eV). This peak is attributed to the dicationic species of this oligomer which is stable at room temperature in CH₂Cl₂. A stacked plot of the radical cations of the terthiophene and quinquethiophene models is shown in Figure 4.27.



Figure 4.26. UV-vis-NIR spectrum of Me-Th₅-Me doped with FeCl₃ (0-4 eq.).



Figure 4.27. UV-vis-NIR spectrum radical cations of Me-Th₃-Me (dashed) and Me-Th₅-Me (solid).

The π -stacked terthiophene *st*-[**Me-Th**₃-**Me**]₂ readily forms the radical cation with two equivalents of FeCl₃. The π - π * transition neutral peak at 335 nm is red shifted to 362 nm upon oxidation and three new energy transitions (437, 591, and 869 nm) appear in Figure 4.28. There is a red shift of peaks for the radical cation of the stacked compound *st*-[**Me-Th**₃-**Me**]₂ compared to peaks for the model **Me-Th**₃-**Me**. Peaks for the stacked compound appear at 437/591/869 nm whereas they are at 563/884 nm for the linear analog.

The π - π * transition of the π -stacked *st*-[Me-Th₅-Me]₂ at 386 nm (3.21 eV) is red shifted to 440 nm (2.82 eV) and is weakened upon one-electron oxidation, Figure 4.28. Two new peaks at higher energies 560 nm (2.21 eV) and 760 nm (1.63 eV) are similar in intensity and the low energy peak at 1307 nm (0.95 eV) is broadened.



Figure 4.28. UV-vis-NIR spectrum of mono(radical cation) species of *st*-[**Me-Th₃-Me**]₂ (dashed line), *st*-[**Me-Th₅-Me**]₂ (solid line). Absorbances are normalized for each neutral unit.

4.3.4. Formation of Dications and π -Dimers

 π -Dimer formation by association of linear radical cations. π -Dimer formation between radical cation is favored at lower temperatures and in more polar solvent such as acetonitrile, which lowers Coulombic repulsion between the two charged species.¹⁰ Weak absorbance peaks at 460 nm (2.58 eV) and 725 nm (1.64 eV) in the spectrum of the radical cation of **Me-Th₃-Me** are increase in intensity as the temperature is lowered in acetonitrile, Figure 4.29 (top). This behavior is consistent with formation of a π -dimer previously reported.¹¹ Similarly, small peaks at 620 nm (1.99 eV) and 1085 nm (1.14 eV) in the spectrum of **Me-Th₅-Me** become predominant upon cooling the radical cation species in acetonitrile, Figure 4.29 (bottom).



Figure 4.29. UV-vis-NIR spectra of radical cation of **Me-Th₃-Me** and π -dimer formed upon cooling radical cation to -30 °C (top). UV-vis-NIR spectra of radical cation of **Me-Th₅-Me** and π -dimer of formed upon cooling radical cation to -30 °C (bottom).

Spectral characterization of dications of stacked oligomers. Upon removal of the second electron from st-[Me-Th₃-Me]₂ at room temperature (4 eq. FeCl₃), new peaks arise at 506 nm (2.58 eV), 778 nm (1.53 eV), and 970 nm (1.22 eV), Figure 4.30. These transitions are red shifted compared to the model terthiophene (460 nm abd 725 nm), and

the new 970 nm absorbance is attributed to a low energy intrachain charge transfer (CT) peak.¹² Upon formation of the dication of *st*-[Me-Th₅-Me]₂, new peaks arise at 654 nm (1.90 eV) and 1123 nm (1.10 eV) and are assigned to π -dimer optical transitions. Again, these peaks are red shifted relative to the π -dimer formed upon association of two linear radical cations.



Figure 4.30. Absorbance spectra of dication (π -dimer) species of *st*-[**Me-Th₃-Me**]₂ (dashed line), *st*-[**Me-Th₅-Me**]₂ (solid line). Absorbances are normalized for each neutral unit.

A combined spectrum for the neutral, radical cation, and π -dimer species for linear model compound **Me-Th₅-Me** is illustrated in Figure 4.31 (top). The π -stacked analog *st*-[**Me-Th₅-Me**]₂ is depicted in Figure 4.31 (bottom).



Figure 4.31. Absorbance spectra of neutral, radical dication, and π -dimer species of **Me-Th₅-Me** (top). Absorbance spectra of neutral, radical dication, and π -dimer species of *st*-[**Me-Th₅-Me**]₂ (bottom). Absorbances are normalized for each neutral unit.

The absorbances of the neutral, radical cation, dication, and π -dimers of the linear model ands π -analogs is shown in Table 4.3. The relative intensities of the bands are labeled as weak, medium, or strong. In summary, stacking two oligothiophenes together causes a blue shift in the absorbance relative to the unstacked oligomer. Oxidation to form a radical cation takes place at lower potential for the stacked compounds. Removal of a second electron from the stacked oligomer provides a dication which has characteristics of a π -dimer formed by aggregation of the two linear radical cations formed at low temperature.

Compound	Neutral	Radical Cation	π-Dimer	Dication
Me-Th ₃ -Me	345 (3.59)	563 s (2.10) 884 s (1.40)	^a 460 (2.70) 725 (1.71)	
st-[Me-Th ₃ -Me] ₂	335 (3.70)	362 s (3.42) 437m (2.84) 591 m (2.10) 869 s (1.43)		506 s (2.45) 778 s (1.59) 970 w (1.28) ^b
Me-Th ₅ -Me	400 (3.10)	731 s (1.69) 1322 s (0.94)	^a 620 s (1.99) 1085 s (1.14)	816 w (1.52) 915 s (1.36) ^a 800 w (1.55) ^a 890 s (1.39)
st-[Me-Th ₅ -Me] ₂	386 (3.21)	440 s (2.82) 560 w (2.21) 760 m (1.63) 1307 s (0.95)		654 s (1.90) 1123 s (1.10)

 Table 4.3.
 UV- Vis-NIR Data for Charged Species

 λ_{max} (eV). Band intensity: strong, medium, weak (s,m,w). ^{*a*} Measured in acetonitrile. ^{*b*} Charge transfer peak.

4.3.5. ESR Spectroscopy: Formation of \pi-Dimers

Addition of two equivalents of FeCl₃ to **Me-Th₅-Me** (c = 2 mM in CH₂Cl₂) forms a mono(radical cation) at room temperature in CH₂Cl₂. A strong ESR spectrum corroborates formation of a spin-active species, Figure 4.32. However, upon cooling the solution down, π -dimer formation is favored especially in acetonitrile. The ESR signal diminishes upon cooling the solution of mono(radical cation), Figure 4.32. This process is reversible, the signal intensified back to the original spin-active spectrum upon warming the solution back to room temperature. Similar, behavior was illustrated with the π -stacked terthiophene compound, *st*-[**Me-Th₃-Me**]₂ (not shown). Subsequent oxidation with two more equivalents of FeCl₃ does form the spinless dicationic species as confirmed by UV-vis-NIR absorbance and disappearance of the ESR signal. We ascribe this behavior to the formation of an intermolecular π -dimerization with formation of a spin-inactive species.



Figure 4.32. ESR spectra of Me-Th₅-Me radical cation formed upon addition of 2 equivalents of FeCl₃ then cooling down gradually to form the π -dimer in acetonitrile.

Upon titration of *st*-[Me-Th₅-Me]₂ with FeCl₃, new absorbance bands exhibited in the UV-vis-NIR spectrum are characteristic of a radical cation. The ESR spectrum demonstrates the formation of a spin active mono(radical cation). The signal intensifies to a maximum upon addition of two equivalents of FeCl₃, Figure 4.33 (black line). This signal then diminishes upon addition of more FeCl₃ with the formation of a spinless dication which possesses the electronic characteristics of a π -dimer in the UV-vis-NIR spectra, Figure 4.33. The stacked dication π -dimer is stable at room temperature and low concentrations because the oligomers are held permanently by the undecane framework.



Figure 4.33. ESR spectra of *st*-[Me-Th₅-Me]₂ radical cation formed upon addition of 2 equivalents of FeCl₃ and continued titration up to 4 equivalents total) to form the dicationic π -dimer.

4.3.6. Electronic Structure

Energy diagrams for a linear oligomer in various oxidation states are provided in Figure 4.34 A. Upon oxidation of a linear oligomer, lattice distortion leads to the formation of two new levels in the band gap, labeled P1 and P2 (used from literature¹³) corresponding to the SOMO and LUMO levels. Thus, whereas the neutral oligomer has a single high energy optical transition, the radical cation has two absorptions corresponding to HOMO-SOMO (C1) transition and the SOMO-LUMO (C2) transition. Upon oxidation to the dication, the new HOMO and LUMO levels of the bipolaron give rise to a new transition (C4). Another possibility for a one-chain radical cation is to associate in solution at low temperature, forming a two-chain aggregate characteristic of a π -dimer energy diagram, Figure 4.34 A.



Figure 4.34. Schematic diagram of various redox states of a single chain (A) and two π -stacked oligomers (B).

The energy diagram for a two oligomers in a stacked arrangement (Figure 4.34 B) displays a splitting of all energy levels into symmetry orbital molecular pairs. For the π - π^* transition in the stacked oligomers, the blue shift is attributed to the interaction between transition dipole moments from adjacent chains (known as Davydov Shift¹⁴). Since the transition dipoles are next to one another, for an intramolecular transition of a two-chain oligomer, the interaction is repulsive. Therefore, the energy required to excite one molecule is blue shifted to higher energy.

In the case of a single radical cation on two chains, the C1 transition is allowed from the HOMO to SOMO (P1') but the C2 transition is now symmetry-forbidden.¹³ Two new transitions C3 and C3' are possible and can form constructive coupling or destructive interference. If the amplitudes of transition dipoles have the same sign (either both positive or both negative), they will add together to form a wave with a larger amplitude, *i.e.* constructive coupling. If the two amplitudes have opposite signs, they will subtract to form a combined wave with lower amplitude, *i.e.* destructive interference. Two new B_u excited states result from this configuration mixing in a singly charged dimer and can be observed spectroscopically. Upon removal of the second electron, there are three transitions HOMO-LUMO (C1), HOMO-LUMO+1 (C2), and a charge transfer band (P1), Figure 4.31B.

Optical Transitions in Context of Electronic Structure. FeCl₃-oxidation of model terthiophene **Me-Th₃-Me** forms the radical cation species at room temperature with values of 563 nm and 884 nm. The peak at 563 (2.10 eV) is due to the C2 transition (P1-P2) and the lower energy peak at 884 (1.40 eV) is HOMO-SOMO (C1) excitation. The shoulders at 460 nm and 725 nm are consistent with π -dimer formation which becomes more predominate at high concentrations and low temperature in acetonitrile (and can be assigned to the C3 and C1 transitions, respectively. ESR measurements confirm this π -dimerization at lower temperature with diminishing of the intensity of the signal by 80%. This signal gave back to the original intensity upon warming.

st-[Me-Th₃-Me]₂ readily forms the radical cation species with two equivalents of FeCl₃. The peak of the radical cation at 362 nm (3.42 eV) is assigned to the π - π^* transition of a neutral chain being influenced by a radical cation π -stacked aggregate (C3-

C3'). The next two peaks at 437 nm (2.72 eV) and 591 nm (2.01 eV) are may be due to configuration mixing between electronic states i.e. deconstructive coupling (C3'-C3). There is a larger splitting for this mixed-transition compared to the AM1/FCI calculations performed.¹³ The transition at 869 nm (1.43 eV) for *st*-[Me-Th₃-Me]₂ is a C1 transition between HOMO-SOMO levels. There are similar C1 transitions in the π -stacked compound *st*-[Me-Th₃-Me]₂ compared to that of the model terthiophene compound Me-Th₃-Me between respective radical cation peaks (884 nm to 869 nm). The weaker lattice relaxation in the two-chain aggregate polaronic levels, which normally causes a red-shift of the absorption band, is negligible here.

Upon removal of the second electron from π -stacked compound *st*-[Me-Th₃-Me]₂ new peaks arise at 506, 778, and 970 nm. These are characteristic of π -dimers in which the electronic structure is a consequence of a combination of the two stacked oligomers, rather than dication-neutral or bis(radical cation) redox states. The 970 nm peak is a low energy intrachain charge transfer (CT) peak P1-P1'. The higher energy 506 nm (2.45 eV) peak is a strong optical excitation due to the two chains held together cofacially as a P1-P2 transition (C2). The lower energy peak at 778 nm (1.59 eV) is a HOMO-SOMO' (C1) transition.

As for the terthiophene, one-electron oxidation of the model quinquethiophene **Me-Th₅-Me** produces two new energy transitions. The first peak at 716 nm (1.73 eV) is the C2 (P1-P2) transition for a single chain radical cation. The lower energy peak at 1322 nm (0.94 eV) is the C1 transition between HOMO-SOMO levels. At room temperature this compound more readily forms a π -dimer in acetonitrile when the corresponding model terthiophene. The shoulder observed at 640 nm is now

predominant at 620 nm (1.99 eV) and is assigned to the C2 transition of the intermolecular π -dimer. The low energy peak at 1085 nm (1.14 eV) is the HOMO-SOMO (C1) transition. Further oxidation of the radical cation in CH₂Cl₂ produces a new intense band at 915 nm (1.36 eV) while the radical cation bands are diminished. The two isosbectic points illustrate the change from neutral, radical cation, and dication species. The new band at 915 nm (1.36 eV) is assigned to the C4 transition for a dication.

The π - π^* peak at 386 nm (3.21 eV) for neutral π -stacked compound *st*-[Me-Th₅-Me]₂ is red shifted to 440 nm (2.82 eV) and is weakened in intensity upon one electron oxidation. Two new peaks at higher energies 560 nm (2.21 eV) and 760 nm (1.63 eV) become apparent. The low energy peak at 1307 nm (0.95 eV) is assigned to the HOMO-SOMO transition (C1) of the mono(radical cation). Upon removal of the second electron, new peaks appear at 654 nm (1.90 eV) and 1123 nm (1.10 eV) and are assigned to interoligomer π -dimer, with a concomitant disappearance the radical cation bands. The higher energy band is assigned to a C3 transition and C1 transition for the lower energy band. The π -dimer bands are red shifted compared to those of the model quinquethiophene, Me-Th₅-Me, due to larger π -stacking interactions in the inherent structure of *st*-[Me-Th₅-Me]₂. Note that the charge transfer band observed for the stacked terthiophene is not observed for the corresponding quinquethiophene due to better delocalization in the longer oligomer.

Combination of data from electrochemistry and electronic spectrea of neutral compounds, Table 4.4, allows us to determine the energy of the HOMOs and LUMOs of the linear models and stacked oligothiophenes, which are illustrated in Figure 4.35.

Compound	E _p (V)	E^{ox}_{onset} (V) ^b	$\lambda_{onset} (nm)^{c}$ (eV)	HOMO (eV) ^d	LUMO (eV) ^e
st-[MeTh ₅ -Me] ₂	+0.67, +0.73, +1.22 ^a	+0.50	486 2.55	-4.94	-2.39
Me-Th ₅ -Me	+0.79, +1.02	+0.65	500 2.48	-5.09	-2.61
st-[Me-Th ₃ -Me] ₂	+0.70,+0.90, +1.49 ^a	+0.60	395 3.14	-5.04	-1.90
Me-Th ₃ -Me	+0.96, +1.23	+0.80	405 3.06	-5.24	-2.18

Table 4.4. Cyclic Voltammetry and UV-vis Absorption Data

^a Two electron process. ^bOnset from electrochemical oxidation. ^cHOMO-LUMO gap measured according to onset of UV absorbance ($E_g=1240/\lambda_{onset}$ eV). ^dHOMO calculated according to the equation by de Leeuw¹⁵. ^eOnset from E_g^{opt} .



Figure 4.35. HOMO-LUMO energy levels determined by cyclic voltammetry and UV absorption.

The HOMO energy levels of the π -stacked compounds are lowered compared to that of the linear model oligomers due to π -orbital overlap. The extrapolated LUMO levels of the stacked compounds are also lower in energy. As the conjugation length increases, the absolute values of the HOMO levels are lowered and the HOMO-LUMO gap diminishes, in model and π -stacked compound alike.

4.4. Conclusion

Arene-fused bicyclo[4.4.1]undecanes provide a versatile scaffold to explore the effects of π -stacking on the electronic structure of a variety of conjugated oligomers to provide models for conjugated polymers. Examination of the π -stacked oligomers and their linear (i.e., unstacked) models by spectroscopy and voltammetry establishes the stabilization of mono- and bis(radical cation)s by interaction of the conjugated oligomeric subunits. *The fact that the two 1e- oxidations of the \pi-stacked analogue take place at lower potentials than the 1e- oxidation of the linear analogue suggests that both the mono(radical cation) and dication are stabilized by the \pi-stacking interaction. In particular, lowering of the second 1e- oxidation potential to form the dication suggests that the stacked dication is stabilized in such a way that it overcomes the destabilization that might be expected to arise from Coulombic repulsion.*

The linear terthiophene and quinquethiophene undergo a second oxidation to form corresponding dications; the π -stacked analogues also undergo subsequent oxidation to form tetracations. This latter process takes place without splitting of voltammetric waves and at higher potential than for the linear analogues, which again may be ascribed to

stabilization of the stacked dication and to destabilization of the tetracation through Coulombic repulsion.

The electronic structure of the stacked dication and origin of this stabilization become apparent from UV-vis-near-IR and ESR spectroscopies. Oxidation of linear model oligomers affords the corresponding radical cation that gives rise to absorptions at low temperatures that are characteristic of the radical cation π -dimers. The electron oxidation of the stacked analogs provides direct access to a dication with the electronic structure of a π -dimer. The accessibility and stability of both the mono- and dicationic states of the stacked analogues arise from the stabilizing influence of interchain interactions between conjugated radical cations. Splitting of the first two oxidations of the stacked oligomers gets progressively smaller as the conjugation length increases, consistent with the formation of a spinless charge carrier delocalized over a number of chains in a p-doped polymer film. The stacked mono(radical cation)s and dications serve as better models for polarons and bipolarons, respectively, than linear unstacked oligomers.

4.5. References

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CHAPTER 5

PHENYL-CAPPED OLIGOTHIOPHENES: SYNTHESIS, STRUCTURAL CHARACTERIZATION, AND PHOTOPHYSICAL/ELECTROCHEMICAL PROPERTIES

5.1. Introduction

Polythiophene and its countless derivatives have continued to attract considerable interest over the past twenty years for potential applications in electronic and opticalelectronic devices. On the basis of such potentially promising aspects of organic semiconducting materials, further development of new high-performance organic materials will increasingly be desired in the near future. Following a simple guiding principle of molecular design, extension of the π -conjugation in the backbone and substituents can be used to tune a material's properties. While there is great interest in use of oligothiophenes in optical and electronic materials, chemical stability remains a concern because of the reactivity of terminal α -positions of the rings. Placing chemically stable substituents at these positions may serve to increase the stability of π -conjugated materials. Phenyl-capped oligothiophenes¹ can be synthesized where both ends of a particular thiophene oligomer have well-defined molecular size and a higher chemical stability. Studies with linear phenyl-capped oligothiophenes²⁻⁵ offer insights into the optical and electrochemical properties of conjugated materials. Theoretical investigations of phenyl-substituted EDOT materials⁶ offer explanations to the molecular packing of such materials in the solid state which can be used as a tool to develop new functional materials. Molecular dynamics have been investigated to show the planarity of charge species,⁷ and phenyl groups were shown to contribute to the stabilization of the charged defects by Raman spectroelectrochemical measurements.⁸ This body of literature provides us with knowledge of linear π -conjugated materials in solution and solid state with little emphasis on the aggregation of oxidized oligomers. Hence, we set out to explore the effects of π -dimerization of two cofacially held phenyl-capped oligothiophenes.

Although phenyl-capped oligothiophenes are less electron rich than corresponding oligothiophenes, they may serve as suitable models to examine charge migration in new π -stacked compounds and as potential new organic semiconductors. We can correlate the findings regarding the phenyl-capped compounds to the thiophene analogs and thereby provide greater understanding for the trends in π -stacked oligomers as it relates to semiconducting materials.

5.2. Experimental

5.2.1. General Procedures

All reagents and catalysts were purchased from Aldrich, TCI, or Strem Chemicals and used without further purification. NBS was recrystallized from H₂O. THF and diethyl ether were distilled from benzophenone-sodium ketyl. Dichloromethane was distilled from calcium hydride and anhydrous DMF was purchased from Aldrich. ¹H and ¹³C NMR spectra were recorded from a 300 or 400 MHz Varian Mercury spectrophotometer. Infrared spectra were recorded on a Nicolet 4700 FTIR. Mass spectra were collected on a VG-70SE instrument. Elemental analyses were obtained from Atlantic Microlabs, Inc. Gravity and flash column chromatographies were carried out with silica gel (32-63 mesh, 60 Å from Sorbent Technologies).

Absorbance and fluorescence measurements were measure on Shimadzu 2401PC UV-vis recording spectrophotometer and RF5301PC spectrofluorophotometer, and a Perkin Elmer Lambda 19 spectrophotometer for doping experiments in the near IR region. Specially designed four sided quartz cuvettes fitted with a 14/20 female joint sealed with a rubber septum were used in order to titrate stock solutions of FeCl₃/CH₂Cl₂ via syringe into know concentrations of analyte. Typical titration were performed every 0.25 eq. analyte, which was anywhere between 20 μ L-200 μ L. FeCl₃ was dried at 100 °C under vacuum for 4 prior to dilution in CH₂Cl₂ (1-2 mM). CH₂Cl₂ was distilled from CaH₂ onto molecular sieves prior to use.

Electrochemical measurements were carried out under nitrogen and recorded on a BAS 100B Electrochemical Analyzer with a three electrode cell equipped with a 2 mm gold working electrode, a platinum counter electrode, and a Ag/Ag^+ reference electrode with 3M NaCl solution end capped with a vycor tip. Substrates (0.5 – 2 mM) were dissolved in CH₂Cl₂ containing 0.1 M *n*-Bu₄NPF₆ or [*n*-Bu₄N][B(C₆F₅)₄]. The ferrocene/ferrocenium couple appears at 0.45 V / 0.47 V in these electrolyte solutions, respectively. Bulk electrolysis was performed in a specially designed cell enclosing a

carbon mesh wire as the working electrode. The auxiliary electrode was enclosed in a fritted tube to prevent decomposition of material over typically extended run times.

ESR measurements were recorded on a Bruker EMX EPR with nitrogen temperature controller 4131VT accessory. ESR tubes were purchased from Wilmad. Typical analyte concentrations were 10^{-3} to 10^{-4} M and a stock solution of FeCl₃/CH₂Cl₂ was titrated into the tube and measured. Typical power was 0.6 mW-1mW and center fields were 3480-3120 Gauss for 9.849 GHz. The modulation phase was set to 260 degrees in all experiments.

5.2.2. Synthetic Procedures



2-Phenylthiophene. A 2.5 M solution of *n*-BuLi in hexanes (100 mL, 0.25 mol) was added dropwise to a solution of thiophene (0.25 mol) in THF (200 mL) at -40 °C. The mixture was stirred for 1 h at -30 °C, then cooled at -40 °C, and a solution of fluorobenzene (0.125 mol) in THF (100 mL) was added dropwise over 20 min. The resulting mixture was warmed to room temperature for 30 min and heated to 60 °C for 18 h. The reaction mixture was allowed to cool to room temperature and H₂O (100 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et₂O (2 x 100 mL). The organic layers were combined and washed with H₂O (2 x 100 mL), dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (100% hexanes) followed by recrystallization from MeOH to afford 2-phenylthiophene as a colorless solid, (10.8 g,

54%). MP = 36-37 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.70-7.75 (m, 2H, Ph), 7.44-7.75 (m, 2H, Ph), 7.40 (dd, 1H, J = 1, 3 Hz, Th-3), 7.34-7.38 (m, 2H, Ph, Th), 7.16 (dd, 1H, J = 5, 3 Hz, Th-4). ¹³C NMR (75 MHz, CDCl₃): δ 144.3, 134.3, 128.8, 128.0, 127.4, 125.9, 124.7, 123.0. IR (KBr) 3147, 3070, 3036, 1596, 1523, 1486 cm⁻¹. MS (EI): m/z (%) 160.1 (M⁺, 100). HRMS (EI): m/z Calcd. for C₁₀H₈S, 160.03367; found, 160.03467, $\Delta = 6.2$ ppm.



2-Phenyl-5-tri-n-butylstannylthiophene. A solution of 2.5 M n-BuLi in hexanes (75 mmol, 30 mL) was added dropwise to solution of 2-phenylthiophene (11 g, 67 mmol) in dry Et₂O (100 mL) at 0 °C, and the mixture was stirred for 1.5 h. A solution of tri-*n*-butyltin chloride (24 g, 74 mmol) in dry Et₂O (20 mL) was added dropwise over 20 min, and the mixture was stirred for 18 h. A saturated aq. solution of NaHCO₃ (50 mL) was added and stirred for 30 min. The aqueous layer was separated, extracted with Et₂O (2 x 50 mL), and the combined organic layers were washed with a saturated aq. solution of NaHCO₃ (50 mL) and dried over MgSO₄. The solvent was removed under reduce pressure to afford 2-phenyl-5-(tri-*n*-butylstannyl)thiophene as a dark orange oil that was used without further purification (24 g, 80%). ¹H NMR (300 MHz, CDCl₃): δ 7.61-7.65 (m, 2H, *J* = 1.3 Hz, 7.1 Hz, Ph), 7.43 (d, 1H, *J* = 3.3 Hz, Th-4), 7.32-7.38 (m, 2H, *J* = 1.3 Hz, 7.7 Hz, Ph), 7.20-7.26 (m, 1H, *J* = 7.3 Hz, 1.3Hz, Ph), 7.15 (d, 1H, *J* = 3.3 Hz, Th-3), 1.54-1.66 (m, 6H, -CH₂CH₂CH₂CH₃), 1.25-1.41 (m, 6H, -CH₂CH₂CH₂CH₃), 1.12-1.18
(m, 6H, -CH₂CH₂CH₂CH₃), 0.88-0.95 (m, 9H, -CH₂CH₂CH₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 145.0, 136.7, 136.4, 134.6, 128.8, 127.0, 125.9, 124.2 (aromatic), 29.0 (-CH₂CH₂CH₂CH₃), 27.3 (-CH₂CH₂CH₂CH₃), 13.7 (-CH₂CH₂CH₂CH₃), 10.8 (-CH₂CH₂CH₂CH₃). IR (KBr) 2953, 2922, 2870, 2852, 1517, 1461, 1413, 1370, 1070, 948, 865, 796, 687 cm⁻¹. MS (EI), *m/z* (%) = 450.1 (M⁺, 100). HRMS (EI): *m/z* Calcd. for C₂₂H₃₄SnS, 450.14032; found, 450.13702, Δ = 7.3 ppm



2,5-Diphenyl-3,4-dimethylthiophene. Tri-n-butylphenyltin (5.8 g, 16 mmol) was added to a solution of 2,5-dibromo-3,4-dimethylthiophene (1.74 g, 6.5 mmol), Pd(PPh₃)₄ (750 mg, 0.65 mmol), and LiCl (840 mg, 20 mmol) in dry DMF (30 mL), and the mixture was heated to 70 °C for 18 h. The mixture was cooled to room temperature, and a saturated aq. solution of KF (10 mL) was added, and the mixture was stirred for 1 h. The aqueous layer was discarded and the organic layer was eluted though celite and silica with Et₂O (150 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (100 % hexanes) followed by recrystallization from methanol to afford 2,5-diphenyl-3,4-dimethylthiophene as a white solid (1.20 g, 70%). MP = 162-164 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.47-7.51 (m, 4H, *ortho* Ph), 7.39-7.46 (m, 4H, *meta* Ph), 7.28-7.36 (m, 2H, *para* Ph), 2.25 (s, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 136.7, 134.9, 134.1, 129.3, 128.4, 127.2 (aromatic), 14.1 (-CH₃). IR (KBr) 3152, 3061, 3022, 2978, 2917, 1383, 1096, 904, 739 cm⁻¹. MS (EI): *m/z* (%) 264.1 (M⁺, 100). HRMS (EI): *m/z* Calcd. for C₁₅H₁₆S, 264.09727; found, 264.09694, Δ = 1.2 ppm. Anal. calcd. for C₁₈H₁₆S: C, 81.77; H, 6.10; S, 12.13. Found: C, 81.70; H, 6.27; S, 12.10.



2,5"-Diphenyl-3',4'-dimethyl-5,2':5',2"-terthiophene. 2-Phenyl-5-tri-n-butylstannylthiophene (5.8 g, 16 mmol) was added to a solution of 2,5-dibromo-3,4dimethylthiophene (1.70 g, 6.5 mmol), $Pd(PPh_3)_4$ (750 mg, 0.65 mmol), and LiCl (840 mg, 20 mmol) in dry DMF (30 mL), and the mixture was heated at 60 °C for 18 h. The mixture was cooled and a saturated sq. solution of KF (10 mL) was added, and the mixture was stirred for 1 h at reflux. The aqueous layer was discarded and mixture was eluted though celite and silica with CHCl₃ (200 mL), and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (75%) hexanes/25% dichloromethane) followed by recrystallization from toluene (3 times) to afford 2,5"-diphenyl-3',4'-dimethyl-5,2':5',2"-terthiophene as an orange solid (1.20 g, 70%). MP = 228-229 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.58-7.64 (m, 4H, J = 8.2 Hz, Ph), 7.33-7.41 (m, 4H, *J* = 7.2 Hz, Ph), 7.23-7.30 (m, 4H, *J* = 3.0 Hz, 7.7 Hz, Ph, Th-3), 7.10-7.14 (d, 2H, J = 3.3 Hz, Th-4), 2.39 (s, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 144.3, 136.0, 135.3, 134.3, 129.9, 129.0, 127.6, 126.9, 125.8, 123.5 (aromatic), 14.4 (-CH₃). IR (KBr) 3148, 2978, 2952, 2926, 2900, 2848, 1457, 1387, 2269, 1091, 1009, 908, 733cm⁻¹. MS (EI): m/z (%) 428.1 (M⁺, 100). HRMS (EI): m/z Calcd. for C₂₆H₂₀S₃, 428.07272; Found, 428.07295, $\Delta = 0.5$ ppm. Anal. calcd. for $C_{26}H_{20}S_3 = C$, 72.86; H, 4.70; S, 22.44. Found: C, 72.96; H, 4.79; S, 22.54.



Tetraphenyldithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one. Tri-n-butyl phenyltin (5.78 g, 16 mmol) was added to a solution of tetrabromodithieno[3,4-c:8,9c']bicyclo[4.4.1]undeca-3,8-diene-11-one (0.6 g, 1.0 mmol), Pd(PPh₃)₄ (116 mg, 100 µmol) and LiCl (129 mg, 2.93 mmol) in dry DMF (20 mL), and the mixture was heated to 65 °C for 36 h. The mixture was cooled and a saturated aq. solution of KF (10 mL) was added and stirred for 1 h. The aqueous layer was discarded, the mixture was eluted though celite and silica with Et₂O (150 mL), and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (1:1 CH₂Cl₂/hexanes) followed by recrystallization from hexanes/CH₂Cl₂ (4:1) to afford the title compound as a white solid (275 mg, 47%). MP = 265-266 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.23-7.45 (m, 20H, Ph), 2.65-3.30 (m, 10H, -CH- + -CH₂-). ¹³C NMR (75 MHz, CDCl₃): δ 215.49 (C=O), 134.87, 134.81, 134.077, 129.49, 128.70, 127.75 (aromatic) 53.92 (bridgehead), 29.02 (-CH₂-). IR (KBr) 3156, 3061, 3021, 2983, 2952, 2900, 2843, 1730, 1686, 1596, 1487, 1457, 1439, 1161, 1096, 1048 cm⁻¹. MS (EI): *m/z* (%) 578.3 (M⁺), 502.2 (M⁺- phenyl). HRMS (EI): m/z Calcd. for C₃₉H₃₀S₂O, 578.17381; Found, 578.17525, $\Delta = 2.5$ ppm.



Ethylene acetal of tetraphenyldithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11one. A solution of tetraphenyldithieno[3,4-c:8,9-c']bicyclo[4.4.1] undeca-3,8-diene-11one (275 mg, 470 µmol), ethylene glycol (400 mg, 6.50 mmol), and p-toluenesulfonic acid (6.0 mg, 32 µmol) in benzene (8 ml), and the mixture was heated at reflux for 18 h with a Dean-Stark trap. The solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (40% ethyl acetate/60% hexanes) followed by recrystallization from methanol to give the title compound as white crystalline solid (265 mg, 92%). MP = 145-146 °C (decomp). ¹H NMR (300 MHz, pyridine-d₆): δ 7.40-7.45 (m, 8H, Ph), 7.21-7.35 (m, 12H, Ph), 3.90 (s, 4H, -OCH₂CH₂O-), 3.38 (dd, 4H, J = 3.3, 15 Hz, -CH₂-), 3.16 (dd, 4H, J = 5, 15Hz, -CH₂-), 2.40-2.45 (m, 2H, -CH-). ¹³C NMR (75 MHz, pyridine-d₆): δ 137.02, 136.78, 134.80, 129.71, 128.26, 126.88 (aromatic), 113.54 (ketal), 64.42 (-OCH₂CH₂O-), 43.35 (bridgehead), 28.26 (-CH₂-). IR (KBr) 3156, 3052, 3021, 2961, 2900, 1465, 1378, 1261, 1096, 1000, 539 cm⁻¹. MS (EI): m/z (%) 622.1 HRMS (EI): m/z Calcd. for C₄₁H₃₄O₂S₂, 622.20002; found, 622.19559, $\Delta = 7.4$ ppm.



Tetra-(5-phenyl-2-thienyl)-dithieno[3,4-c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene -11-one. A 2.5 M solution of *n*-BuLi in hexanes (5.0 mL, 12.5 mmol) was added to a solution of 2phenylthiophene (2.0 g, 12 mmol) and TMEDA (2.0 mL, 12 mmol) in dry THF (10 mL) at 0 $^{\circ}$ C. The mixture was heated at reflux for 2 h and cooled to room temperature. A 0.5 M solution of ZnCl₂ in THF (25 mL, 12 mmol) was added, and the mixture was stirred for another 2 h. This mixture was cannulated to a solution of tetrabromo-dithieno[3,4c:8,9-c']bicyclo[4.4.1]undeca-3,8-diene-11-one (0.6 g, 1.0 mmol) and Pd(PPh₃)₄ (300 mg, 260 µmol) in dry THF (20 mL) and heated to 60 °C for 48 h. After the reaction was cooled to room temperature, a 0.5 M solution of HCl (40 mL) was added. The organic layer was collected, and the aqueous layer was extracted with methylene chloride (3 x 40 mL). The organic layers were combined and washed with H_2O (2 x 75 mL), and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (1:2 CHCl₃/hexanes) to afford the title compound as a yellow solid, (200 mg, 22 %). MP = 293-294 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.23-7.45 (m, 28H, Ar), 2.65-3.30 (m, 10H, -CH- + -CH₂-). IR (KBr) 3055, 3017, 2959, 2913, 2854, 1703, 1599, 1490, 1441, 1254, 1070, 1007, 856 cm⁻¹. MS (MALDI-TOF): *m/z* 907.1 (M+H).



Ethylene acetal of Tetra-(5-phenyl-2-thienyl)-dithieno[3,4-c:8,9-c']bicyclo[4.4.1 undeca-3,8-diene-11-one. А solution of tetra-(5-phenyl-2-thienyl)-dithieno[3,4-c:8,9c']bicyclo[4.4.1]undeca-3,8-diene-11-one (200 mg, 220 µmol), ethylene glycol (250 mg, 5.4 mmol), and p-toluenesulfonic acid (5.0 mg, 26 µmol) in benzene (20 mL) was heated at reflux for 48 h with a Dean-Stark trap. The solvent was evaporated under reduce pressure, and the residue was subjected to column chromatography on silica gel (10%) hexanes/90% chloroform) followed by triturating from toluene to give the title compound as yellow solid, (205 mg, 97%). MP = 305-306 °C (decomp). ¹H NMR (300 MHz, CDCl₃): δ 7.25-7.32 (m, 8H, Ph), 7.11-7.19 (m, 12H, Ph), 7.85-7.89 (d, 4H, J = 3.5 Hz, Th), 6.83 (d, 4H, J = 3.5 Hz, Th), 4.10 (s, 4H, -OCH₂CH₂O-), 3.58 (dd, 4H, J = 5 Hz, 15 Hz, -CH₂-), 3.16 (dd, 4H, J = 2.2 Hz, 15Hz, -CH₂-), 2.42-2.50 (m, 2H, bridgehead). ¹³C NMR (75 MHz, CDCl₃): δ 143.57, 138.03, 135.87, 133.88, 129.85, 128.59, 127.04, 126.90, 125.30, 122.86 (aromatic), 113.56 (ketal), 64.83 (-OCH₂CH₂O-), 42.54 (bridgehead), 28.69 (-CH₂-). IR (KBr) 3056, 3024, 2912, 2848, 1597, 1484, 1444, 1396, 1261, 1095, 1071, 1003, 947 cm⁻¹. MS (MALDI-TOF): *m/z* 950.2 [M+H⁺]. HRMS (EI): m/z Calcd. for C₅₇H₄₂O₂S₆, 950.1509; found, 950.1389, $\Delta = 12.6$ ppm. Anal. calcd. for C₅₇H₄₂S₆·2H₂O: C, 69.34; H, 4.70. Found: C, 69.25; H, 4.85.

5.3. Results and Discussion

5.3.1. Synthesis

The phenyl-capped linear model compounds were prepared by coupling 2,5dibromo-3,4-dimethylthiophene to the corresponding stannylated arene. Tri-*n*butylphenyltin is commercially available and 2-phenyl-5-tri-*n*-butylstannyl-thiophene⁹ was prepared in two steps. Reaction of fluorobenzene with 2-lithiothiophene via a benzyne intermediate afforded 2-phenylthiophene, **5.1**, Figure 5.1. Lithiation of **5.1** followed by quenching with tributylstannyl chloride afforded 2-phenyl-5-tri-*n*butylstannylthiophene, **5.2**, in 80% yield.



Figure 5.1. Synthesis of 2-phenyl-5-tri-*n*-butylstannylthiophene, 5.2.

Coupling tri-*n*-butyltin benzene to 2,5-dibromo-3,4-dimethylthiophene via Stille reaction afforded 2,5"-diphenyl-3',4'-dimethyl-5,2':5',2"terthiophene, **5.3**, as a white crystalline solid (55% yield), Figure 5.2.



Figure 5.2. Synthesis of model 2,5-diphenyl-3,4-dimethylthiophene, 5.3.

Coupling **5.2** to 2,5-dibromo-3,4-dimethylthiophene afforded the extended phenyl-capped oligothiophene 2,5"-diphenyl-3',4'-dimethyl-5,2':5',2"-terthiophene, **5.4**, as an orange solid (70 %), after recrystallization several times from toluene, Figure 5.3.



Figure 5.3. Synthesis of model 2,5"-diphenyl-3',4'-dimethyl-5,2':5',2"-terthiophene, 5.4.

Previously reported tetrabomoketone¹⁰ **3.1** (from Chapter 3) was treated with excess tri-*n*-butylphenyl tin using Stille coupling conditions to produce phenyl-capped ketone **5.5** in a 47% overall yield, Figure 5.4. Ketalization with ethylene glycol afforded the π -stacked compound **5.6** in 92% yield. Several attempts to couple 2-phenyl-5-tri-*n*-butylstannylthiophene to **3.1** using Stille conditions were unsuccessful. However, utilization of Negishi coupling conditions by *in situ* formation of 2-phenyl-5-thienylzinc chloride and coupling it to **3.1**, afforded the phenyl-capped ketone **5.7** in a 22% yield. Subsequent ketalization with ethylene glycol afforded π -stacked compound **5.8** (97% yield), Figure 5.4.



Figure 5.4. Synthesis of phenyl-capped, π -stacked oligothiophenes, 5.6, and 5.8.

5.3.2. Structural Characterization: ¹H and ¹³C NMR Spectroscopy

The ¹H NMR spectrum of 2,5-diphenyl-3,4-dimethylthiophene, 5.3, displays a six proton singlet for the methyl protons (2.3 ppm), Figure 5.5. The aromatic protons of the benzene rings give rise to three distinct multiplets. The downfield signal corresponds to the four *ortho* protons. The next four proton multiplet corresponds to the *meta* protons on each benzene ring, while the two *para* protons give the multiplet signal furthest upfield in the aromatic region.



Figure 5.5. ¹H NMR (300 MHz, CDCl₃) of model 5.3 at room temperature.

The ¹³C NMR spectrum of **5.3** displays six distinct aromatic signals corresponding to four different benzene carbons and two different thiophene carbons, Figure 5.6. There is one carbon signal for the two identical methyl carbons in the alipathic region.



Figure 5.6. ¹³C NMR (300 MHz, CDCl₃) of model 5.3 at room temperature.

Upon ketalization with ethylene glycol to the π -stacked compound, 5.6, variable temperature ¹H NMR illustrated no change in conformation up to 100 °C, indicating the stability of this π -stacked compound, Figure 5.7. For the aromatic protons, the *ortho* protons exhibited an eight proton multiplet (7.40-7.45 ppm), while the *meta* and *para* protons appear at 7.21-7.35 ppm. There is a small upfield shift in aromatic protons of 5.6 when compared to the model 5.3 due to π -stacking. The bulkier benzene molecules cause less significant magnetic shielding of the aromatic protons in each benzene ring. The ethylene glycol signal appeared at 3.9 ppm as a singlet. As previously seen upon π stacking, the chair-chair conformation is confirmed by the appearance of a pair of doublet of doublets for the methylene protons. This is also seen for the phenyl-capped compound, **5.6**, with an eight proton pair of doublet of doublets (3.38 and 3.16 ppm) with coupling constants consistent with a chair-chair conformation of the bicyclo[4.4.1]undecane framework. The two bridgehead protons appeared furthest upfield in the spectrum as a multplet (2.43 ppm), Figure 5.7.





Figure 5.7. Variable temperature ¹H NMR (300 MHz, Pyridine-*d6*) of **5.6**. Room temperature (black), 40 °C (red), 60 °C (blue), 80 °C (green), and 100 °C (purple).

The ¹³C NMR spectrum of π -stacked compound **5.6** confirms the presence of one distinct conformation at room temperature. The aromatic carbons provide six distinct signals: four for the benzene rings and two for the thiophene rings, Figure 5.8. The ketal tertiary carbon is present at δ 113 ppm. The ethylene glycol, bridgehead, and methylene carbon signals each appear as separate one carbon signals.



Figure 5.8. ¹³C NMR (300 MHz, CDCl₃) of 5.6 at room temperature.

The phenyl-capped terthiophene model compound **5.4** exhibited four distinct signals in the aromatic region for its ¹H NMR spectrum. The highest downfield multiplet corresponds to the four *ortho* protons on the benzene rings. The next multiplet at 7.4 ppm corresponds to the four *meta* protons on the benzene rings. The multiplet at 7.25 ppm corresponds to the two *para* protons on the benzene ring and two protons on the thiophene rings. The doublet (7.1 ppm) corresponds to the other thiophene proton signal. The singlet at δ 2.35 ppm corresponds to the methyl protons. The ¹³C NMR spectrum of model **5.4** at room temperature exhibited ten aromatic carbon proton signals and one methyl carbon signal, Figure 5.10.



Figure 5.9. ¹H NMR (300 MHz, CDCl₃) of **5.4** at room temperature.



Figure 5.10. ¹³C NMR (300 MHz, CDCl₃) of 5.4 at room temperature.

The π -stacked compound **5.8** exhibits upfield shifts in the aromatic protons compare to that of its model compound, Figure 5.11. The methylene protons exhibit splitting consistent with a chair-chair conformation. The ¹³C NMR spectrum displays ten aromatic carbons, an ethylene glycol peak, and the other bicyclo[4.4.1]undecane framework signals which have been seen in the other π -stacked compounds, Figure 5.11.



Figure 5.11. ¹H NMR (300 MHz, CDCl₃) of **5.8** (top). ¹³C NMR (300 MHz, CDCl₃) of 5.8 (bottom).

A summary of the influence of π -stacking aromatic protons for the phenyl-capped model and π -stacked compounds is shown in Table 5.1.

and it statistical compounds.					
Compound	$\mathrm{H_1}^a$	$H_2^{\ a}$	$H_3^{\ b}$	$H_4^{\ b}$	$H_5^{\ b}$
Model 5.3			7.48	7.44	7.34
Stack 5.6			7.45	7.27	7.27
Model 5.4	7.45	7.21	7.61	7.76	7.47
Stack 5.8	6.91	6.82	7.18	7.29	7.29

Table 5.1. ¹H NMR Chemical Shifts (δ) for aromatic protons of phenyl-capped model and π -stacked compounds.

^{*a*} Thiophene protons. ^{*b*} Benzene protons.

5.3.3. Structural Characterization: Molecular Modeling

Molecular modeling was performed on the π -stacking compound **5.6** to examine the preferred orientation for the benzene rings. The benzene rings are out of plane from the thiophene rings, because the methylene protons are proximal to one set of *ortho* protons on the benzene ring. The steric repulsion does not hinder the compound from being in a chair-chair conformation because the benzene rings can adopt a non-planar orientation of each oligomer upon stacking, Figure 5.12.



Figure 5.12. Optimized geometry for 5.1 performed at the B3LYP-6-31G* level.

The HOMO energy orbitals for π -stacked compound **5.6** lies mostly on the central thiophene rings and the LUMO level is extended partially on the thiophene-phenyl linkage, Figure 5.13.



Figure 5.13. HOMO (left) and LUMO (right) levels of 5.6.

5.3.4. UV-vis and Fluorescence Spectroscopy

Model compound **5.3** has an absorbance peak at $\lambda_{max} = 302$ nm and fluorescence peak at $\lambda_{max} = 391$ nm, Figure 5.14. The π -stacked analog **5.6** shows a slight blue shift in absorbance ($\lambda_{max} = 297$ nm) and broadened red shift in fluorescence ($\lambda_{max} = 396$ and a shoulder at 432 nm), Figure 5.14. The broadened fluorescence peak is ascribed to intersystem crossing to a lower energy state, or "phane" state. The extended phenylcapped oligothiophene **5.4** has a absorbance peak at $\lambda_{max} = 381$ nm and fluorescence peak at $\lambda_{max} = 471$ nm and shoulder peak at 496 nm. The extended π -stacked analog **5.8** exhibits a blue shifted neutral absorbance ($\lambda_{max} = 376$ nm) and broadened, red shifted fluorescence ($\lambda_{max} = 501$, 538 nm shoulder), Figure 5.14.



Figure 5.14. Absorbance/Emission Spectra of model **5.3** (black); extended model **5.4** (green); π -stacked compound **5.6** (red); extended π -stacked compound **5.8** (blue).

Variable excitations of the extended model **5.4** and π -stacked compound **5.8** illustrated in the emission spectra show contributions from one absorbing species, Figure 5.15. The other compounds **5.3/5.6** exhibit similar behavior in emission spectroscopy.



Figure 5.15. Emission spectra of 5.4 (left) and 5.8 (right).

A summary of the absorbance and emission peaks is displayed in Table 5.2. As conjugation length increases, the absorbance and fluorescence peaks are red shifted. Upon π -stacking the general trend, also seen with oligothiophenes, is that there is a blue shift in absorbance when compared to the model compound, and a red shift in fluorescence. The molar absorption values of the π -stacked compounds are less than two times the value of their model compounds due to nonbonding electronic interactions relating to excimer formation.

	Absorbance	Fluorescence (nm)	Stokes Shift (nm)	
	$\lambda_{\max} / \operatorname{nm}(\varepsilon^b)$	λ_{max} (shoulder)	Largest difference	
Unstacked				
5.3	302 (1.8 x 10 ⁴)	391	89	
5.4	381 (4.0 x 10 ⁴)	471 (496)	115	
Stacked				
5.6	297 (3.4 x 10 ⁴)	396 (432)	135	
5.8	376 (7.8 x 10 ⁴)	501 (538)	162	

Table 5.2. Electronic Spectral Data^a of Models and Stacked Oligothiophenes

^{*a*}Electronic absorption and emission spectra were measured in CH₂Cl₂, $c = 10^{-5}$ M.

The Stokes shift of the phenyl-capped oligothiophene model and π -stacked compounds can be compared to the previously discussed compounds in Chapter 4. The π -stacked compounds exhibit larger Stokes shifts than their model compounds due to increased stability by π -stacking two oligomers (blue and red lines), Figure 5.16. Interestingly, the π -stacked three ring system here has more of a similar excited state emission between the absorbing chromophore to the phane state emission. There is not as a much of a driving force for migration of the photon through space to the other chromophore as seen in the π -stacked terthiophene compound, *st*-[Me-Th₃-Me]₂. Extending the conjugation length to the five ring system promotes a similar driving force for emission from the phane state of the molecule as seen in the shorter stacked

oligomers. This behavior correlated to the oligothiophene substituted compounds may be attributed to the steric effects of the phenyl group on the excited state characteristics.



Figure 5.16. Stokes shifts of model and stacked oligothiophenes versus # of aromatic rings.

5.3.5. Electrochemistry of Phenyl-Capped Oligothiophenes

The unstacked phenyl-capped model **5.3** exhibited a $1e^{-1}$ reversible oxidation wave at $E_{1/2} = +1.38$ V, and the removal of a second electron was not plausible in this electrolyte, >2.0 V, Figure 5.17. The π -stacked analog **5.6** exhibited two sharp reversible oxidation waves (both $1e^{-1}$ each) for the oxidation to the radical cation, and then to the dicationic (π -dimer) species, at $E_{1/2} = +1.19$ V and $E_{1/2} = +1.48$ V, respectively, Figure 5.17 . Further oxidation to the tricationic or tetracationic species was not possible under these conditions. DPV in the same electrolyte also gave two resolved peaks at similar oxidation potentials for the π -stacked compound and one for the model compound, Figure 5.18.



Figure 5.17. CV of model **5.3** (dashed) and π -stacked compound **5.6** (solid). c = 2 mM in CH₂Cl₂; 0.1 M *n*-Bu₄NPF₆/CH₂Cl₂; Au working electrode auxiliary, Ag/Ag⁺ reference electrode; v = 100 mV/s.



Figure 5.18. DPV of model compound **5.3** (dotted line) and π -stacked compound **5.6** (solid line). c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuN₄PF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The cyclic voltamogram of model compound **5.4** in the supporting electrolyte *n*-Bu₄NPF₆ gave two sharp, reversible 1 e^- oxidation waves for the formation of a radical cation species to the dicationic species ($E_{1/2} = +0.84$ V and $E_{1/2} = +1.20$ V, respectively, Figure 5.19. The π -stacked compound **5.8** exhibited a 1 e^- reversible oxidation for a radical cation stacked ontop a neutral oligomer at $E_{1/2} = +0.70$ V, followed by another 1 e^- reversible oxidation wave to the dicationic species (π -dimer) at $E_{1/2} = +0.82$ V. At higher oxidation potential, another 2 e^- reversible process occurred concurrently at $E_{1/2} =$ +1.44 V, for the formation of a tetra-cationic species. The DPV of the model **5.4** and π stacked compound **5.8** more easily illustrate the redox peaks of both compounds, Figure 5.20.



Figure 5.19. CV of model **5.4** (dotted line) and π -stacked compound **5.8** (solid line). c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuN₄PF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.



Figure 5.20. DPV of model, **5.4**, (dotted line) and π -stacked compound, **5.8**, (black line). c = 2 mM in CH₂Cl₂; 0.1 M *n*-BuN₄PF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The electronic communication and the nature of the charged species can be influenced by the use of a different supporting electrolyte, such as $[n-Bu_4N][B(C_6F_5)_4]$ which contains weakly ion-pairing anions This particular electrolyte should decrease Coulombic repulsion and increase the solubility of highly charged cations, allowing the charge to become delocalized more freely over the length conjugated oligomer. Using $[Bu_4N][B(C_6F_5)_4]$ and focusing on the extended conjugated compounds, the cyclic voltammetry and the DPV of **5.4** show two reversible redox waves, $E_{1/2} = +0.90$ V and $E_{1/2} = +1.37$ V, Figure 5.21. Compared to the use of the smaller, tightly binding anion PF₆⁻, both oxidation potentials are slightly increased (+60 mV and +117 mV, respectively). The peak splitting increases by +110 mV between the two electron oxidation waves in the bulky electrolyte due to the increased solubility of the charged radical cation.



Figure 5.21. DPV of model, **5.4**, (blue dotted line) and π -stacked compound, **5.8**, (black line). c = 2 mM in CH₂Cl₂; 0.1 M [*n*-Bu₄N][B(C₆F₅)₄]/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

In the $[Bu_4N][B(C_6F_5)_4]$ electrolyte, the voltamogram of **5.8** exhibits different oxidation waves to that of PF₆⁻, first oxidation at $E_{1/2} = +0.76$ V, second oxidation at $E_{1/2}$ = +0.96 V, and simultaneous 3rd and 4th oxidations at $E_{1/2} = +1.70$ V, Figure 5.21 The oxidation potentials are +60 mV, +140 mV, and +260 mV higher than in the smaller anion electrolyte. The splitting between the first and second oxidation waves (+200 mV) is larger than the splitting in the PF₆⁻ (+120 mV), due to the increased charge migration. A summary of the electrochemical data is illustrated in Table 5.3.

	E_1 / V (no e^{-})	$\Delta E_1 / \mathrm{V}$	E_2 / V (no e^{-})	$\Delta E_{2-1} / \mathrm{V}$
Me-Th ₁ -Me	$1.39(1)^{b}$	-		-
st-[Me-Th ₁ -Me] ₂	1.09 (1), 1.59 (1) ^b	0.5	-	-
Me-Th ₃ -Me	0.96	-	1.23 (1)	0.27
st-[Me-Th ₃ -Me] ₂	0.70 (1), 0.90 (1)	0.20	1.49 (2)	0.59
Me-Th ₅ -Me	0.79	_	1.02 (1)	0.23
st-[Me-Th ₅ -Me] ₂	0.67 (1), 0.73 (1)	0.06	1.22 (2)	0.49
5.3	1.38 (1)	-	>2	-
5.6	1.19 (1), 1.48 (1)	0.29	>2	-
5.4	0.84 (1)	-	1.20 (1)	0.36
	$0.90(1)^{c}$	-	$1.37(1)^{c}$	0.47
5.8	0.70 (1), 0.82 (1)	0.12	1.44 (2)	0.62
	$0.76(1), 0.96(1)^{c}$	0.20	$1.70(2)^{c}$	0.74

 Table 5.3. Oxidation Potentials of Unstacked and Stacked Oligothiophenes^a.

 $\overline{}^{a}$ c = 1-2 mM, 0.1 M Bu₄NPF₆ as supporting electrolyte in CH₂Cl₂v = 100 mV/s; Ag/Ag⁺ reference; Au working electrode, platinum auxiliary; Fc / Fc⁺ = 0.45 V. ^b irreversible. ^cSupporting electrolyte = 0.1 M Bu₄N[B(C₆F₅)₄] in CH₂Cl₂; Fc / Fc⁺ = 0.47 V.

 π -Stacked compounds **5.6** and **5.8** are permanently held together by the covalent linkage of a bicyclo[4.4.1]undecane core, with an ethylene glycol clipping unit. In the neutral state, each oligomer acts as an electron donor, and lowers the oxidation potential for the first oxidation wave. This is illustrated with **5.6** (-190 mV) and **5.8** (-140 mV) when compared to each model compound. In the case of the removal of the second electron for **5.6**, ($E_{1/2} = +1.48$ V), there is an energy cost for stable π -dimer formation, +100 mV above the first oxidation of model **5.3**, contributed by an electron-withdrawing

effect of a singly charged oligomer. The highly charged cation of **5.6** exhibits larger Coulombic repulsion than that of **5.8**, due to its decreased conjugation length and more localized charge.

In the case of **5.8**, the removal of the second electron ($E_{1/2} = +0.82$ V) is -20 mV lower than that of the model **5.4**'s first oxidation wave. The electron withdrawing effect is substantially diminished due to the increased charge delocalization of the extended oligomer. Thus, the π -dimer formed upon two electron removal in **5.8** is readily accessible at room temperature under these conditions. The coincidental third and fourth oxidations at $E_{1/2} = +1.44$ V imply that once the π -dimer is formed, it is stable, and undergoes further oxidation higher than that of its second oxidation wave (+620 mV), causing this two electron process to happen together.

5.3.6. Chemical Oxidation of Phenyl-Capped Oligothiophenes

The phenyl-capped model oligothiophene **5.4** undergoes chemical oxidation to the radical cation species with the appearance of new energy transitions at 650 nm (1.91 eV) and 1095 nm (1.13 eV) in its UV-vis-NIR spectrum, Figure 5.22. Cooling the solution down to -30 °C partially formed the π -dimer aggregate with new absorbance bands. The radical cation peaks diminished as peaks at 584 nm (2.12 eV), 975 nm (1.27 eV), 1250 nm (0.99 eV) increased, Figure 5.22. Further oxidation to the dication at room temperature (4 eq. FeCl₃) gave a new peak at 803 nm (1.54 eV) with the absence of the radical cation peaks. Model **5.13** did not form a radical cation spectrum due to its higher oxidation potential (+160 mV higher than FeCl₃).



Figure 5.22. Absorbance spectrum of **5.4.** Neutral (black line), addition of 2eq. FeCl₃ (red line), cooling solution to -30 °C (blue line) in acetonitrile.

For the π -stacked compound **5.6** the radical cation species can be generated chemically, forming new energy transitions (322 nm (3.85 eV), 443 nm (2.80 eV), 569 nm (2.18 eV), and 868 nm (1.43 eV) similar to the oligothiophenes in Chapter 4. Further oxidation to the π -dimer species could not be seen with this oxidant. The longer phenyl-capped oligothiophene **5.8** undergoes 1 e- oxidation to the radical cation species with new energy transitions at 400 nm (3.10 eV), 495 nm (2.51 eV), 665 nm (1.86 eV), and 1105 nm (1.12 eV), Figure 5.23. The two electron oxidation of **5.8** forms new peaks at 590 nm (2.10 eV), 965 nm (1.28 eV), and 1290 nm (0.96 eV) while the radical cation peaks disappear, Figure 5.23.



Figure 5.23. Absorbance spectrum of **5.4.** Neutral (black line), addition of 2 eq. FeCl₃ (red line), addition of 4 eq. FeCl₃ (blue line) in dichloromethane at room temperature. Absorbances are normalized for each neutral unit.

The ESR spectrum corroborated the spin active radical cation species or the spinless π -dimer species. Upon formation of the radical cation species of the model compound **5.4** with two equivalents FeCl₃, a large ESR signal forms. Further titration to four eq. forms an ESR inactive signal, Figure 5.24 (top). For the linear model compound **5.4**, the spin-active radical cation species diminished upon π -dimer formation at lower temperature in acetonitrile, Figure 5.24 (bottom). The color changes by visible inspection of the solutions are apparent by formation of the different species.



Figure 5.24. ESR spectra of 5.4 (bottom) and 5.8 (top).

5.3.7. Correlations in Electronic Structure

The onset of oxidation by electrochemical measurements was correlated to the HOMO energy level as calculated by de Leeuw.¹¹ The onset of optical absorbances for each molecule was used to determine the energy difference between the HOMO and LUMO levels, Table 5.4. For the phenyl-capped oligothiophenes, band gap estimation to the vacuum level is illustrated for models **5.3/5.4** and π -stacked compounds **5.6/5.8** in Figure 5.25.

Compound	$E_p(\mathbf{V})$	E^{ox}_{onset} $(V)^{b}$	λ_{onset} (nn (eV)	n) ^c HOMO (eV) ^d	LUMO (eV) ^e
5.8	+0.70, +0.82, +1.44 ^a	0.60	477 2.60	-5.04	-2.44
5.4	+0.84, +1.20	0.74	466 2.66	-5.18	-2.52
5.6	+0.19, +1.48	1.06	350 3.54	-5.50	-1.96
5.3	+1.38	1.24	372 3.33	-5.68	-2.35

Table 5.4. Cyclic Voltammetry and UV-vis Absorption Data

^a Two electron process. ^bOnset from electrochemical oxidation. ^cHOMO-LUMO gap measured according to onset of UV absorbance ($E_g=1240/\lambda_{onset}$ eV). ^dHOMO calculated according to the equation by de Leeuw¹¹. ^eOnset from E_g^{opt} .



Figure 5.25. HOMO-LUMO energy levels deduced from cyclic voltammetry and UV absorption.

As two oligomers become cofacially aligned, the HOMO energy level (absolute value) decreases which facilitates ejection of an electron to the LUMO level more easily for the π -stacked compounds **5.6** and **5.8**. Upon extended the conjugation length for the phenyl-capped oligothiophenes, the band gap diminishes imparting more semiconductor behavior. The E_g^{opt} values for model and π -stacked compounds changes slightly, but of more interest is the ability of the π -stacked compounds to be oxidized more. The π -stacked compounds can readily form π -dimers which stabilize the dicationic species, and subsequent oxidation to the tetra-cationic species is reversible.

5.4. Conclusion

Phenyl-capped π -stacked oligothiophenes have been synthesized and structural characterized by NMR spectroscopy. The neutral absorbance and emission fluorescences of the π -stacked compounds are characteristic of excimer formation in the excited states, and the larger Stokes shifts and broadened emission spectra are attributed to the intersystem crossing of a photon to a more energetically favored phane state. Electrochemical measurements and FeCl₃ doping of this series of phenyl-capped oligothiophenes provides evidence for stable π -dimer formation of two oligomers held in a cofacial arrangement.

5.5. References

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CHAPTER 6

FERROCENYL-CAPPED OLIGOTHIOPHENES: SYNTHESIS AND PHYSICAL PROPERTIES

6.1. Introduction

Metallocene and ferrocene substituents when coupled to oligothiophenes are interesting as novel organic-organometallic hybrid compounds,¹ where applications include sensors, storage devices, and electroluminescent devices. Oligothiophenes facilitate charge delocalization along a π -conjugated backbone, and attaching a metal center to the system increases charge hopping between metal centers and bridging units, allowing for potential stabilization of the system via another tier. Ferrocene is an ideal candidate for electronic conductivities and magnetic properties, and it can form a 17 electron ferrocenium ion, which has stable mixed valence Fe^{II} and Fe^{III} oxidation states.

Charge delocalization in *linear* π -conjugated model polyenes^{2,3} and poly-ynes^{4,5} has been studied extensively by substitution of the termini of conjugated oligomers with such electroactive groups (binuclear metal complexes). The π -conjugated chain can mediate electron transfer between the terminal groups with the formation of mixed valence states. Ferrocenyl-substituted polyenes with up to twelve methines display peak separation for oxidation of the two redox centers.⁶ In comparison, complexes with saturated bridges with larger than two carbons show a single voltammetric peak for oxidation of the two iron atoms. These studies have been extended to odd-alternate analogs like α, ω diphenylpolymethine anions,⁷ α, ω -bis(*N*-methylpyridinium)polymethine cations,⁸ and α, ω -bis(ferrocenyl)-polymethine cations⁹) which provide added evidence for charge migration in a one-dimensional conjugated chain. These studies of linear π -conjugated materials do not, however, address interchain hopping of these charge carriers when in close proximity to one amother.

A recent study of oligomeric ferrocene-phenothiazine compounds¹⁰ have been shown to adopt an eclipsed conformation by *partial* intramolecular π -stacking, as illustrated with splitting in cyclic voltammetry. We can couple ferrocene by Negishi coupling conditions and study the electronic communication in a *fully* π -stacked system. The comparison of this end-capped ferrocenyl system can be compared to its synthesized linear, unstacked analog. The effect of π -stacking on neutral, cofacial oligomers can be monitored by NMR spectroscopy and UV-vis spectroscopy, white the extent and nature of charge migration by delocalization/charge hopping can be measured by cyclic voltammetry.

6.2. Experimental



2,5-diferrocenyl-3,4-dimethylthiophene. To a solution of ferrocene (4.0 g, 21.4 mmol) and TMEDA (9.7 mL, 64.3 mmol) in a mixture of dry THF (25 mL) and hexanes (15 mL) was added 2.5 M *n*-BuLi in hexanes (8.6 mL, 21.4 mmol) at 0 °C. The reaction mixture was heated at reflux for 2 h and cooled to room temperature. A solution of $ZnCl_2$
(8.76 g, 64.3 mmol) in dry THF (20 mL) was adde,d and the mixture was stirred for another 2 h. The reaction mixture was cannulated to a solution of 2,5-diiodo-3,4dimethylthiophene (2.6 g, 7.2 mmol) and Pd(PPh₃)₄ (100 mg, 0.09 mmol) in dry THF (20 mL) and heated to 50 °C for 72 h. After the reaction was cooled to room temperature, it was quenched with 0.5 M HCl (25mL). The organic layer was collected, and the aqueous layer was extracted with methylene chloride ($3 \times 50 \text{ mL}$). The organic layers were combined and washed with water (2 x 50 mL) and dried over MgSO₄. The solvent was removed under reduced pressure to give the crude product as a brownish red solid. The crude material was purified by column chromatography on silica gel (1:1 hexane/CH₂Cl₂) to afford the title compound as an orange solid, (1.20 g, 35%) after recrystallization from a solution of hexane / CH₂Cl₂ (3:1). MP = 179-180 °C. ¹H NMR (300 MHz, CDCl₃): δ 4.48-4.52 (t, 4H, J = 1.8 Hz), 4.25-4.25 (t, 4H, J = 1.8 Hz), 2.10 (s, 6H). ¹³C NMR $(75MHz, CDCl_3)$: δ 133.9, 133.1, 81.9, 69.7, 68.8, 68.0, 14.0. IR (NaCl) = 3148, 2983, 2896, 1817, 1800, 1643, 1470, 1378, 1169, 1091 cm⁻¹. MS (EI): m/z (%) 479.9 (M⁺, 100). HRMS (EI): $m/z = \text{calc. for } C_{26}H_{24}SFe_2$, 480.02975; found, 480.02983. $\Delta = 0.17$ ppm. Anal. Calc. for C₂₆H₂₄SFe₂·0.5H₂O: C, 63.83; H, 5.05; S, 6.55. Found: C, 63.60; H, 5.09; S, 6.45.



Tetraferrocenyl-dithieno-bicyclo[4.4.1]undecane-11-one. To a solution of ferrocene (1.31 g, 7.05 mmol) in dry THF (10 mL) and hexanes (10 mL) was dropwise added 1.7 M t-BuLi in pentanes (5.5 mL, 9.4 mmol) at 0 °C over 10 min. The reaction mixture was heated at reflux for 2 h and cooled to room temperature. A 0.5 M solution of ZnCl₂ in THF (18.8 mL, 9.4 mmol) was added, and the mixture was stirred for another 2 h. The reaction mixture was cannulated to a solution of 3.2 (0.52 g, 0.89 mmol) and Pd(PPh₃)₄ (400 mg, 0.35 mmol) in dry THF (20 mL) and heated to 50 °C for 72 h. After the reaction was cooled to room temperature, it was quenched with 0.5 M HCl (25mL). The organic layer was collected, and the aqueous layer was extracted with methylene chloride (3 x 50 mL). The organic layers were combined and washed with water (2 x 50 mL) and dried over MgSO₄. The solvent was removed under reduced pressure to afford the crude material as a brownish red solid. The crude material was purified by column chromatography on silica gel (10% ethyl acetate/hexanes) to afford the title compound as an orange powder, (250 mg, 28%) after recystallization from a solution of hexane/CH₂Cl₂ (3:1). MP = 210-212 °C. ¹H NMR (300 MHz, CDCl₃): δ 4.44-4.48 (m, 4H, Cp), 4.38-4.44 (m, 4H, Cp), 4.23-4.34 (m, 8H, Cp), 4.18-4.22 (s, 20H, Cp), 2.4-2.8 (m, 10H,

methylene/bridgehead). IR (NaCl) = 3140, 2975, 2875, 1690, 1465, 1372, 1270, 1165, 1091, 908, 735 cm⁻¹.



Tetraferrocenyl-dithieno[*c*,*h*]*bicyclo*[*4.4.1*]*undecan-11-ethylene glycol.* A solution of the tetraferrocennyl ketone (275 mg, 0.47 mmol), ethylene glycol (400 mg, 6.5 mmol), and p-toluene sulfonic acid (6 mg) in benzene (15 mL) was heated at reflux for 48 h with a Dean-stark trap. The solvent was evaporated under reduce pressure, and the residue was subjected to column chromatography on silica gel (25% dichloromethane/75% hexanes) to give the title compound as orange solid, (160 mg, 32%). MP = 235-237 °C decomp. ¹H NMR (300 MHz, CDCl₃): δ 4.00-4.32 (m, 20 H, Cp), 4.32-4.40 (m, 4H, Cp), 4.40-4.48 (m, 4H, Cp), 3.88-3.90 (s, 4H, ethylene), 2.86-3.02 (dd, *J* = 5 Hz, J = 15 Hz, 4H, methylene), 2.66-2.80 (dd, *J* = 6 Hz, *J* = 15Hz, 4H, methylene), 2.12-2.28 (m, 2H, bridgehead). ¹³C NMR (75 MHz, CDCl₃): δ 137.32, 133.22, 113.38, 81.17, 69.60, 68.88, 67.95, 67.88, 64.03, 42.83, 28.10. IR (KBr): 3156, 3052, 3021, 2961, 2900, 1465, 1378, 1261, 1096, 1000, 539 cm⁻¹. MS (MALDI-TOF): *m/z* (%) = 1054.0 (M⁺, 100). HRMS (EI): *m/z* = calc. for C₅₇H₅₀O₂S₂Fe₄, 1054.06498; found, 1054.07010. Δ = 4.8

ppm. Anal. Calc. for C₅₇H₅₀O₂S₂Fe₄·1.5H₂O: C, 63.32; H, 4.80; S, 5.93: found: C, 63.22; H, 4.75; S, 6.03.

6.3. Results and Discussion

6.3.1. Synthesis of Ferrocenyl Compounds

Iodination of 3,4-dimethylthiophene with mercurous oxide, molecular iodine, and benzene provided 3,4-diiodo-3,4-dimethylthiophene in good yield (95%), Figure 6.1. The synthesis of the model 2,5-diferrocenyl-3,4-diemethyl-thiophene was attempted by the Palladium catalyzed Stille and Suzuki reactions using the appropriate reagents, but these attempts were unsuccessful. The Negishi coupling with zinc-chloro-ferrocene was successful which provided **6.1** as an orange solid (75%) after purification, Figure 6.1.





The synthesis of the π -stacked anolog, **6.2**, was synthesized in two steps from previously synthesized tetrabromo-ketone **3.2**. The reaction of ketone **3.2** in THF and

Pd(PPh₃)₄ with excess zinc-chloro- ferrocene formed *in situ* afforded the tetra-substituted ferrocennyl ketone in good yield (66%), Figure 6.2. Ketalization of this intermediate compound with ethylene glycol in benzene with p-TSA afforded the π -stacked compound, **6.2**, in a good yield (90%) as an orange solid after purification, Figure 6.2.



Figure 6.2. Synthesis of tetra-ferrocennyl-capped π -stacked compound **6.2**.

6.3.2. Structural Characterization: ¹H and ¹³C NMR Spectroscopy

The ¹H NMR spectrum of model compound **6.1** illustrated three distinct proton cyclopentadienyl signals, Figure 6.3. Two multiplets (four protons each) corresponding to the two different types of protons on the cyclopentadienyl ring adjacent to the thiophene ring were seen (δ 4.35 and 4.5 ppm). The other ten protons on the bottom cyclopentadienyl ring correspond to a singlet at 4.2 ppm. The six methyl protons on the thiophene ring correspond to a singlet at δ 2.1 ppm. The ¹³C NMR spectrum of **6.1** exhibited two types of aromatic carbon signals for the thiophene ring, Figure 6.4. The next four carbon signals upfield correspond to the four types of cyclopentadienyl carbon

signals (three from the top ring and one from the bottom ring). The methyl carbon was consistent with one carbon signal further upfield in the alipathic region.



Figure 6.3. ¹ H NMR (300 MHz, CDCl₃) of model **6.1** at room temperature.



Figure 6.4. ¹³ C NMR (300 MHz, CDCl₃) of model 6.1 at room termperature.

The ¹H NMR spectrum of π -stacked compound, **6.2**, is illustrated in Figure 6.5. The cyclopentadienyl rings attached directly to the thiophene ring exhibited two multiplet signals (δ 4.44 and 4.36 ppm). One set of protons is distinctly more upfield than the corresponding linear compounds, **6.1**, due to the effect of π -stacking the ferrocene compounds on top one another. The large singlet for the twenty protons of the cyclopentadienyl rings not attached to the thiophene rings is broadened due to the proximity of ethylene glycol unit to the top rings of ferrocene, and small shoulder peaks (δ 4.0-4.2 ppm) may be attributed to the spatial arrangement of protons next to the ethylene glycol clipping unit. The next peak upfield is attributed to the ethylene glycol signal (singlet at δ 3.9 ppm). The methylene protons for the bicyclo[4.4.1]undecane core (δ 2.7 and 2.9 ppm) is consistent with a chair-chair conformation displaying two sets of doublet of doublets, Figure 6.5. The two bridgehead protons upfield are a multiplet (δ 2.2 ppm) as previously seen in other π -stacked analogs.



Figure 6.5. ¹H NMR (300 MHz, CDCl₃) of π -stacked compound **6.2** at room temperature.

The ¹³C NMR spectrum of π -stacked compound, **6.2**, is illustrated in Figure 6.6. The aromatic carbons consistent for one thiophene ring conformation, and the bicyclo[4.4.1]undecane framework carbons are consistent with a chair-chair conformation. The cyclopentadienyl carbons show up as four different signals (three from the ring attached to thiophene and one for the other ring).



Figure 6.6. ¹³ C NMR (300 MHz, CDCl₃) of **6.2**.

6.3.3. UV-vis Spectroscopy of Ferrecene Substituted Compounds

The model compound, **6.1**, exhibited a π - π^* absorbance band at $\lambda_{max} = 323$ nm (ϵ = 2.1 x 10⁴ M⁻¹cm⁻¹) and Fe^{II} d-d transition absorbance band at $\lambda = 452$ nm (1.8 x 10³ M ⁻¹cm⁻¹) in CH₂Cl₂, Figure 6.7.



Figure 6.7. UV-vis spectrum of model compound **6.1**. $c = 8.12 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2$; 323 nm, $\varepsilon = 2.1 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$; 452 nm, $\varepsilon = 1.8 \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$.

Upon π -stacking the oligomer, there is a slight blue shift (3 nm) for the π - π * absorbance band at $\lambda_{max} = 320$ nm ($\epsilon = 1.8 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$), and the Fe^{II} d-d transition absorbance band at $\lambda = 452$ nm (1.7 x 10⁻³ M⁻¹ cm⁻¹) is similar, Figure 6.8. The molar absorptivity is slightly lower in the π -stacked compound due to excimer formation, as seen in other compounds.



Figure 6.8. UV-vis spectrum of π -stacked compound **6.2**. $c = 4.17 \times 10^{-5}$ M in CH₂Cl₂; 320 nm, $\epsilon = 1.8 \times 10^{-5}$ M $^{-1}$ cm⁻¹; 452 nm, $\epsilon = 1.7 \times 10^{-3}$ M $^{-1}$ cm⁻¹.

6.3.4. Electrochemistry

The cyclic voltammogram of model compound **6.1** and ferrocene was performed with the supporting electrolyte 0.1 M *n*-BuNPF₆/CH₂Cl₂, Figure 6.9. Ferrocene exhibits a 1*e*⁻ reversible redox wave at $E_{1/2} = 0.45$ V, while model **6.1** exhibits two 1*e*⁻ reversible redox waves at $E_{1/2} = 0.35$ V and $E_{1/2} = 0.50$ V. The DPV of model compound, **6.1**, is depicted where the peak difference between radical cation and dication potentials in this electrolye is $\Delta E = 150$ mV, Figure 6.1.



Figure 6.9. CV of model compound **6.1** (solid line) and ferrocene (dashed line). c = 1 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/CH₂Cl₂; Au working electrode; Pt auxillary, Ag/Ag⁺ reference electrode; v = 100 mV/s.



Figure 6.10. DPV of model compound **6.1**. c = 1 mM in CH₂Cl₂; 0.1 M *n*-BuNPF₆/ CH₂Cl₂; Au working electrode; Pt auxiliary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

A bulky electrolyte solution of 0.1 M $[n-\text{BuN}][B(C_6F_5)_4 / \text{CH}_2\text{Cl}_2 \text{ was used to}]$ examine the redox behavior of model compound, **6.1**.¹¹ The removal of 1*e*⁻ occurred higher (+70 mV) at $E_{1/2} = 0.42$ V, while the removal of a second electron was +170 mV higher at $E_{1/2} = 0.67$ V, both of which were reversible processes, Figure 6.11. The peak separation of the two processes illustrated by DPV was larger (+250 mV) due to the better solubility of the charge species in a bulky, weakly anion binding electrolyte, Figure 6.12. The different scan rated used helped determine that the redox process was not diffusion controlled due to the linearity in the slope when plotting oxidation potential versus 1/n (not shown).



Figure 6.11. CV of model compound, **6.1**. c = 1 mM in CH₂Cl₂; bulky electrolyte: 0.1 M [*n*-BuN][B(C₆F₅)₄]/CH₂Cl₂; Au working electrode; Pt auxiliary, Ag/Ag⁺ reference electrode; v = 25-350 mV/s.



Figure 6.12. CV of model compound, **6.1**. c = 1 mM in CH₂Cl₂; bulky electrolyte: 0.1 M [*n*-BuN][B(C₆F₅)₄]/CH₂Cl₂; Au working electrode; Pt auxiliary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The π -stacked compound, **6.2**, exhibited two reversible redox waves in the smaller electrolyte solution. Each wave corresponded to two electrons each, therefore the effects of π -stacking were hard to distinguish due to the destabilized charge migration in a tightly anion binding electrolyte. In the bulkier electrolyte solution, the charge stability was greatly enhanced and splitting was observed. The first $1e^{-}$ process to form radical cation occurred at $E_{1/2} = 0.38$ V, and the bis(radical cation) species formed upon removal of a second electron at $E_{1/2} = 0.47$ V, bothe of which were reversible, Figure 6.13. The first electron in the π -stacked compound, **6.2**, was lower than that of its model, **6.1**, by -40 mV due to the effect of π -stacking. The second electron process was stabilized by the bulkier electrolyte solution and at higher potential. Therefore, π -dimerization was slightly impeded by the charge delocalization of the charged species to the extended cyclopentadienyl tiers in the ferrocene moieties. Further redox processes at higher potential was also exhibited in the π -stacked compound, **6.2**. A 2*e*⁻ reversible wave at $E_{1/2} = 0.75$ V corresponded to the formation of the tetra-cationic species. The larger splitting between the second oxidation process and the coincidental two electron process is due to the stabilization of the π -dimer formed in this electrolyte solution and Coulombic repulsion of the unstable tricationic species to form a less destabilized tetracationic species.



Figure 6.13. CV of π -stacked compound, **6.2**. c = 1 mM in CH₂Cl₂; bulky electrolyte: 0.1 M [*n*-BuN][B(C₆F₅)₄]/CH₂Cl₂; Au working electrode; Pt auxiliary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

The splitting of redox waves and influence of π -stacking oligothiophene-ferrocene compounds can be illustrated also in the DPV voltammogram of **6.2**, Figure 6.14. The peak difference between the first two peaks is +90 mV and between the second and third peaks is +280 mV. The π -stacked oligothiophene **5.8** (*st*-[**Ph-Th₃-Ph**]₂), exhibited splitting between its similar peaks of +200 mV and +740 mV. The demonstrates the facile conversion of the ferrocene π -stacked compound to form a π -dimer due to the inceased delocalization/hopping though the compound. The splitting for the tetracationic species is less than 2.6 times than that of the phenyl-capped π -stacked compound also explaining how the addition of another tier increases the stability of the entire charge compound.



Figure 6.14. DPV of π -stacked compound, **6.2**. c = 1 mM in CH₂Cl₂; bulky electrolyte: 0.1 M [*n*-BuN][B(C₆F₅)₄]/CH₂Cl₂; Au working electrode; Pt auxiliary, Ag/Ag⁺ reference electrode; v = 100 mV/s.

6.4. Conclusion

In conclusion, a ferrocene substituted, hybrid π -stacked compound was synthesized and characterized by NMR and UV-vis spectroscopy of the neutral material and electrochemistry for its redox behavior. The stability of the doped material was enhanced in a bulky electrolyte, where the influence of π -stacking and charge transfer in metal centers could be ascertained. Further synthesis of extended oligothiophenes capped with ferrocene or other metal centers like Ru, Os, or Mn may potentially be synthesized and explored for their role as molecular wires, sensors, or other devices.

6.5. References

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CHAPTER 7

FUTURE WORK

7.1. Future Directions in Research

Designing new π -conjugated materials for uses in electrical devices can be further developed through new synthetic routes systematically modified with the intermediate compound 3.1 previously synthesized. The detailed experiments performed in this thesis have demonstrated the tendencies of charge migration and delocalization in π -stacked oligothiophenes, specifically stable π -dimer formation being a key for bis(radical cation) stability at room temperature, low concentration, and a moderately polar solvent like dichloromethane. The p-dopable, cofacial oligomers oriented in a π -stacked conformation were in a fully stacked oriention for each thiophene ring (each position of the thiophene rings on the undecane core were substitued with the same group). A continuation of thiophene π -stacked oligomers would be to vary the degree of overlap for each tier. Initial attempts to synthesize cis/trans terthiophene π -stacked compounds 7.1 and 7.2 were unsuccessful, Figure 7.1. Bromination of 3.2 with two equivalents of NBS in DMF at low temperature produced an inseperable byproduct which was thought to not be formed. Bromination at one thiophene position deactivated the ring but, in this case, the purification could not be attained for the cis/trans dibrominated materials. Subsequent palladium catayzed Negishi coupling to the ketone followed by ketalization with ethylene glycol should be straight forward.

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Figure 7.1. Synthesis of terthiophene π -stacked compounds **7.1** and **7.2**.

Synthesis of a model terthiophene compound, **7.3**, was achieved by the bromination of 3,4-dimethylthiophene with one equivalent of NBS followed by the Stille coupling of 2-methyl-5'-tri-*n*-butylstannyl-5:2'-bithiophene to produce **7.3** in a 75% overall yield, Figure 7.2. This compound is important for its neutral state properties when compared to the π -stacked compounds, *i.e.* NMR, UV-vis, and emission spectra.



Figure 7.2. Synthesis of model terthiophene 7.3.

However, the unblocked α -position on one thiophene ring will dimerize with another molecule upon doping to the radical cation species forming a sexithiophene compound. To circumvent this homo-coupling process, the α -position was methylcapped in two steps: bromination with NBS followed by a Kumada coupling with methylmagnesium bromide in a 75% overall yield to produce model compound, **7.4**.



Figure 7.3. Synthesis of model methyl-capped terthiophene 7.4.

A large body of work focuses on the study of alkyne spacers in conjugated materials.¹⁻⁸ Recent work devoted to synthesis of interlocking π -conjugated macrocycles with terminal acetylene spacers⁹ provides comparisons to the studying of larger extended compounds, which is plausible with our intermediate compounds. Uncomplexed bis(alkynyl)oligothiophenes with transition metals¹⁰ has been extensively studied for their electronic communication by electrochemistry, and we can correlate some of these results with new one undiscovered yet. Another extension to study the effects of charge migration in our conjugated materials might be to couple ethynyl aromatic compounds to the brominated ketone, **3.2**, via Sonogashira reaction conditions to form **7.5** after ketalization, Figure 7.4.



Figure 7.4. Synthesis of alkyne spacer in terthiophene π -stacked compound 7.5.

The alkyne spacers in between the terthiophene oligomers may facilitate charge delocalization better in the π -stacked compound and should be further studied. The analogous model terthiophene, **7.6**, was synthesized in two steps from 3,4-dimethylthiophene. Iodination of the 2,5-positions with molecular iodine with the oxidant potassium periodate followed by the Sonogashira coupling with a TMS acetylated thiophene formed the terthiophene model compound, **7.6**, in a 57% overall yield, Figure 7.5. Other compounds can be coupled in similar fashion to study the effects of π -stacking the π -conjugated oligomers.



Figure 7.5. Synthesis of alkyne substituted model compound 7.6.

Another branch of research in π -conjugated materials focuses on the synthesis and characterization of new functional materials containing Poly(3,4ethylenedioxythiophenes), of PEDOT materials.¹¹⁻¹⁶ One characteristic that can be beneficial for our studies would be to attached this p-dopable compound to the bicyclo[4.4.1]undecane core in order to increase the ease of oxidation of the material. Terthiophene EDOT and quinquethiophene EDOT π -stacked compounds **7.7** and **7.8** can be envisioned by coupling the corresponding thiophene or bithiophene EDOT to ketone **3.2**, followed by ketalization with ethylene glycol Figure 7.6.



Figure 7.6. Ethylenedioxy-substituted terthiophene 7.7 and quinquethiophene 7.8.

One concern with this approach that should be addressed is the steric strain that may be imposed upon stacking the EDOT terthiophene or quinquethiophene together. Synthesis, structural characterization, and electrochemical investigations will provide evidence for or against the effective π -stacking of such compounds. Modification of the clipping unit to neopentyl glycol may facilitate the π -stacking better if the ethylene glycol unit is not sufficient enough.

A broad spectrum of studies has been performed on thiazoles¹⁷⁻²¹ which are ndopable materials, an this π -stacking motif can facilitate the design of such compounds. It can be envisioned to couple a 5-methyl-thiazole or bithiazole with an appropriate palladium catalyzed reaction to ketone **3.2** to afford π -stacked compounds **7.9** and **7.10** after ketalization with ethylene glycol, Figure 7.7.



Figure 7.7. Thiazole-substituted π -stacked compounds **7.9** and **7.10**.

Raman spectroscopy, not explored, can be another useful technique for studying the electronic and vibrational states of self-localized excitations for doped poly(p-phenylenevinylene)²² and poly(p-phenylene).²³ Similarly, SbF₆⁻ radical cation salt formation of these compounds can be a useful technique to determining the solid state structure of doped π -conjugated oligomers.

7.2. References

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APPENDIX A

X-RAY STRUCTURAL ANALYSIS

A suitable crystal of *st*-[**H**-**Th**₁-**H**]₂ was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated MoK α (0.71073Å) radiation. Data was measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART¹ software. Frame integration and final cell refinements were done using SAINT² software. The final cell parameters were determined from least-squares refinement on 3398 reflections. The SADABS³ program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).⁴ Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least-squares with isotropic Uij's related to the riding atom. The C-H distances were fixed at 0.93 Å (aromatic and amide), 0.98 (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.⁵ Structure solution, refinement, graphics and generation of publication materials were performed using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Tables A.1-A.6.

The crystals were all intimately twinned to some degree so data was collected on one clean sample that contained approximately equal contributions of the two components. The unit cells for each component were determined by using a beta test program written by George Sheldrick called Cell_Now. The reflection data was processed with SAINT, taking into account the overlapping of reflections from the two components and were corrected for absorption effects S9 by using TWINABS, a version of SADABS. The structure was solved using only the data that was generated by component 1; however the final refinements used all the data and included the contributions from both components.

Empirical formula	C17 H18 O2 S2		
Formula weight	318.43		
Temperature	173(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/c		
Unit cell dimensions	a = 7.537(1) Å	α = 90°.	
	b = 15.690(2) Å	$\beta = 100.987(3)^{\circ}$.	
	c = 12.4552(16) Å	$\gamma = 90^{\circ}$.	
Volume	1445.9(3) Å ³		
Z	4		
Density (calculated)	1.463 Mg/m ³		
Absorption coefficient	0.370 mm ⁻¹		
F(000)	672		
Crystal size	0.80 x 0.35 x 0.11 mm ³		
Theta range for data collection	2.11 to 28.36°.		
Index ranges	-10<=h<=9, 0<=k<=20, 0	<=l<=16	
Reflections collected	7109		
Independent reflections	7134 [R(int) = 0.0000]		
Completeness to theta = 28.36°	99.4 %		
Absorption correction	Semi-empirical from equi	valents	
Max. and min. transmission	0.9605 and 0.7565		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	7134 / 0 / 190		
Goodness-of-fit on F ²	1.034		
Final R indices [I>2sigma(I)]	R1 = 0.0638, wR2 = 0.132	20	
R indices (all data)	R1 = 0.0844, wR2 = 0.14	11	
Largest diff. peak and hole	0.496 and -0.281 e.Å ⁻³		

Table A.1. Crystal data and structure refinement for *st*-[H-Th₁-H]₂.

	X	у	Z	U(eq)	
S (1)	4470(1)	5804(1)	7618(1)	27(1)	
S(2)	3490(1)	3718(1)	5358(1)	28(1)	
O(1)	-1419(2)	3987(1)	9430(1)	21(1)	
O(2)	-2041(2)	2835(1)	8291(1)	22(1)	
C(1)	-904(3)	3583(1)	8503(2)	18(1)	
C(2)	-1423(3)	4191(1)	7538(2)	18(1)	
C(3)	-603(3)	5085(1)	7761(2)	19(1)	
C(4)	1409(3)	5183(1)	7838(2)	17(1)	
C(5)	2152(3)	5800(1)	7296(2)	21(1)	
C(6)	4460(3)	4962(1)	8494(2)	21(1)	
C(7)	2766(3)	4687(1)	8535(2)	18(1)	
C(8)	2378(3)	3988(1)	9290(2)	20(1)	
C(9)	1061(3)	3274(1)	8811(2)	17(1)	
C(10)	1666(3)	2721(1)	7924(2)	20(1)	
C(11)	1996(3)	3172(1)	6909(2)	19(1)	
C(12)	3586(3)	3138(2)	6537(2)	23(1)	
C(13)	1269(3)	3992(1)	5348(2)	23(1)	
C(14)	662(3)	3671(1)	6218(2)	20(1)	
C(15)	-1222(3)	3807(1)	6429(2)	20(1)	
C(16)	-2066(3)	3329(1)	10052(2)	23(1)	
C(17)	-2971(3)	2728(2)	9166(2)	30(1)	

Table A.2. Atomic coordinates $(x \ 10^4)$ and equivalent isotropic displacement parameters $(\mathring{A}^2x \ 10^3)$ for *st*-[**H**-**Th**₁-**H**]₂. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

S(1)-C(6)	1.713(2)	C(13)-H(13)	0.9500
S(1)-C(5)	1.716(2)	C(14)-C(15)	1.507(3)
S(2)-C(12)	1.717(2)	C(15)-H(15A)	0.9900
S(2)-C(13)	1.727(2)	C(15)-H(15B)	0.9900
O(1)-C(16)	1.431(3)	C(16)-C(17)	1.512(3)
O(1)-C(1)	1.433(2)	C(16)-H(16A)	0.9900
O(2)-C(17)	1.413(3)	C(16)-H(16B)	0.9900
O(2)-C(1)	1.447(2)	C(17)-H(17A)	0.9900
C(1)-C(2)	1.526(3)	C(17)-H(17B)	0.9900
C(1)-C(9)	1.536(3)	C(6)-S(1)-C(5)	91.05(11)
C(2)-C(3)	1.538(3)	C(12)-S(2)-C(13)	91.21(11)
C(2)-C(15)	1.540(3)	C(16)-O(1)-C(1)	106.78(15)
C(2)-H(2)	1.0000	C(17)-O(2)-C(1)	108.59(15)
C(3)-C(4)	1.509(3)	O(1)-C(1)-O(2)	105.34(15)
C(3)-H(3A)	0.9900	O(1)-C(1)-C(2)	106.83(16)
C(3)-H(3B)	0.9900	O(2)-C(1)-C(2)	107.99(16)
C(4)-C(5)	1.360(3)	O(1)-C(1)-C(9)	109.54(16)
C(4)-C(7)	1.437(3)	O(2)-C(1)-C(9)	107.44(16)
C(5)-H(5)	0.9500	C(2)-C(1)-C(9)	118.91(17)
C(6)-C(7)	1.359(3)	C(1)-C(2)-C(3)	113.23(16)
C(6)-H(6)	0.9500	C(1)-C(2)-C(15)	114.11(17)
C(7)-C(8)	1.509(3)	C(3)-C(2)-C(15)	114.44(17)
C(8)-C(9)	1.540(3)	C(1)-C(2)-H(2)	104.5
C(8)-H(8A)	0.9900	C(3)-C(2)-H(2)	104.5
C(8)-H(8B)	0.9900	C(15)-C(2)-H(2)	104.5
C(9)-C(10)	1.541(3)	C(4)-C(3)-C(2)	117.95(17)
C(9)-H(9)	1.0000	C(4)-C(3)-H(3A)	107.8
C(10)-C(11)	1.509(3)	C(2)-C(3)-H(3A)	107.8
C(10)-H(10A)	0.9900	C(4)-C(3)-H(3B)	107.8
C(10)-H(10B)	0.9900	C(2)-C(3)-H(3B)	107.8
C(11)-C(12)	1.367(3)	H(3A)-C(3)-H(3B)	107.2
C(11)-C(14)	1.427(3)	C(5)-C(4)-C(7)	111.86(19)
C(12)-H(12)	0.9500	C(5)-C(4)-C(3)	123.02(19)
C(13)-C(14)	1.352(3)	C(7)-C(4)-C(3)	125.00(18)

Table A.3. Bond lengths [Å] and angles $[\circ]$ for *st*-[H-Th₁-H]₂.

C(4)-C(5)-S(1)	112.58(17)	C(13)-C(14)-C(11)	112.4(2)
C(4)-C(5)-H(5)	123.7	C(13)-C(14)-C(15)	124.1(2)
S(1)-C(5)-H(5)	123.7	C(11)-C(14)-C(15)	123.47(18)
C(7)-C(6)-S(1)	112.77(17)	C(14)-C(15)-C(2)	117.94(17)
C(7)-C(6)-H(6)	123.6	C(14)-C(15)-H(15A)	107.8
S(1)-C(6)-H(6)	123.6	C(2)-C(15)-H(15A)	107.8
C(6)-C(7)-C(4)	111.75(19)	C(14)-C(15)-H(15B)	107.8
C(6)-C(7)-C(8)	123.34(19)	C(2)-C(15)-H(15B)	107.8
C(4)-C(7)-C(8)	124.77(19)	H(15A)-C(15)-H(15B)	107.2
C(7)-C(8)-C(9)	118.32(18)	O(1)-C(16)-C(17)	101.97(17)
C(7)-C(8)-H(8A)	107.7	O(1)-C(16)-H(16A)	111.4
C(9)-C(8)-H(8A)	107.7	C(17)-C(16)-H(16A)	111.4
C(7)-C(8)-H(8B)	107.7	O(1)-C(16)-H(16B)	111.4
C(9)-C(8)-H(8B)	107.7	C(17)-C(16)-H(16B)	111.4
H(8A)-C(8)-H(8B)	107.1	H(16A)-C(16)-H(16B)	109.2
C(1)-C(9)-C(8)	112.81(16)	O(2)-C(17)-C(16)	105.53(18)
C(1)-C(9)-C(10)	113.69(17)	O(2)-C(17)-H(17A)	110.6
C(8)-C(9)-C(10)	115.46(17)	C(16)-C(17)-H(17A)	110.6
C(1)-C(9)-H(9)	104.5	O(2)-C(17)-H(17B)	110.6
C(8)-C(9)-H(9)	104.5	C(16)-C(17)-H(17B)	110.6
C(10)-C(9)-H(9)	104.5	H(17A)-C(17)-H(17B)	108.8
C(11)-C(10)-C(9)	117.08(17)		
C(11)-C(10)-H(10A)	108.0		
C(9)-C(10)-H(10A)	108.0		
C(11)-C(10)-H(10B)	108.0		
C(9)-C(10)-H(10B)	108.0		
H(10A)-C(10)-H(10B)	107.3		
C(12)-C(11)-C(14)	112.29(19)		
C(12)-C(11)-C(10)	124.1(2)		
C(14)-C(11)-C(10)	123.57(19)		
C(11)-C(12)-S(2)	111.92(17)		
C(11)-C(12)-H(12)	124.0		
S(2)-C(12)-H(12)	124.0		
C(14)-C(13)-S(2)	112.15(17)		
C(14)-C(13)-H(13)	123.9		
S(2)-C(13)-H(13)	123.9		

	U ¹¹	U ²²	U33	U ²³	U13	U ¹²
S (1)	25(1)	25(1)	32(1)	1(1)	10(1)	-6(1)
S(2)	29(1)	35(1)	24(1)	-2(1)	13(1)	-1(1)
O (1)	26(1)	19(1)	19(1)	-3(1)	9(1)	-2(1)
O(2)	24(1)	21(1)	23(1)	-6(1)	8(1)	-6(1)
C(1)	20(1)	16(1)	18(1)	-3(1)	5(1)	-2(1)
C(2)	13(1)	20(1)	20(1)	-3(1)	3(1)	0(1)
C(3)	20(1)	18(1)	19(1)	1(1)	3(1)	3(1)
C(4)	22(1)	15(1)	15(1)	-4(1)	4(1)	0(1)
C(5)	24(1)	19(1)	20(1)	0(1)	2(1)	-1(1)
C(6)	20(1)	19(1)	23(1)	-2(1)	3(1)	0(1)
C(7)	22(1)	16(1)	17(1)	-4(1)	4(1)	-2(1)
C(8)	19(1)	21(1)	19(1)	0(1)	0(1)	1(1)
C(9)	21(1)	14(1)	17(1)	1(1)	5(1)	-1(1)
C(10)	19(1)	18(1)	22(1)	2(1)	4(1)	4(1)
C(11)	22(1)	17(1)	18(1)	-6(1)	4(1)	-1(1)
C(12)	21(1)	29(1)	21(1)	-2(1)	3(1)	2(1)
C(13)	28(1)	23(1)	19(1)	-3(1)	5(1)	4(1)
C(14)	24(1)	17(1)	18(1)	-7(1)	4(1)	-2(1)
C(15)	21(1)	23(1)	16(1)	-2(1)	1(1)	0(1)
C(16)	26(1)	23(1)	20(1)	1(1)	7(1)	-2(1)
C(17)	36(1)	31(1)	27(1)	-5(1)	17(1)	-11(1)

Table A.4. Anisotropic displacement parameters $(Å^2 x \ 10^3)$ for *st*-[H-Th₁-H]₂. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}U^{11}$ + ... + 2 h k a* b* U¹²]

	Х	у	Z	U(eq)	
H(2)	-2753	4278	7474	21	
H(3A)	-1214	5468	7174	23	
H(3B)	-903	5292	8456	23	
H(5)	1464	6186	6795	26	
H(6)	5526	4715	8906	25	
H(8A)	1900	4258	9895	24	
H(8B)	3544	3718	9616	24	
H(9)	1062	2874	9437	20	
H(10A)	2795	2424	8260	24	
H(10B)	734	2279	7696	24	
H(12)	4622	2831	6888	28	
H(13)	556	4330	4795	28	
H(15A)	-1850	3250	6350	24	
H(15B)	-1869	4184	5845	24	
H(16A)	-2939	3555	10482	27	
H(16B)	-1059	3046	10551	27	
H(17A)	-2874	2132	9430	36	
H(17B)	-4265	2874	8933	36	

Table A.5. Hydrogen coordinates (x 10⁴) and isotropic displacement parameters ($Å^2x$ 10³) for *st*-[**H**-**Th**₁-**H**]₂.
Table A.6.	Torsion	angles	[°]	for st-[H-	$-Th_1-H]_2.$
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C(16)-O(1)-C(1)-O(2)	28.3(2)
C(16)-O(1)-C(1)-C(2)	142.96(17)
C(16)-O(1)-C(1)-C(9)	-87.01(19)
C(17)-O(2)-C(1)-O(1)	-9.3(2)
C(17)-O(2)-C(1)-C(2)	-123.17(18)
C(17)-O(2)-C(1)-C(9)	107.43(19)
O(1)-C(1)-C(2)-C(3)	55.1(2)
O(2)-C(1)-C(2)-C(3)	167.99(16)
C(9)-C(1)-C(2)-C(3)	-69.4(2)
O(1)-C(1)-C(2)-C(15)	-171.63(16)
O(2)-C(1)-C(2)-C(15)	-58.8(2)
C(9)-C(1)-C(2)-C(15)	63.9(2)
C(1)-C(2)-C(3)-C(4)	70.3(2)
C(15)-C(2)-C(3)-C(4)	-62.9(2)
C(2)-C(3)-C(4)-C(5)	131.8(2)
C(2)-C(3)-C(4)-C(7)	-52.7(3)
C(7)-C(4)-C(5)-S(1)	-0.5(2)
C(3)-C(4)-C(5)-S(1)	175.51(15)
C(6)-S(1)-C(5)-C(4)	0.12(17)
C(5)-S(1)-C(6)-C(7)	0.33(17)
S(1)-C(6)-C(7)-C(4)	-0.7(2)
S(1)-C(6)-C(7)-C(8)	-176.43(16)
C(5)-C(4)-C(7)-C(6)	0.8(3)
C(3)-C(4)-C(7)-C(6)	-175.16(19)
C(5)-C(4)-C(7)-C(8)	176.45(19)
C(3)-C(4)-C(7)-C(8)	0.5(3)
C(6)-C(7)-C(8)-C(9)	-132.6(2)
C(4)-C(7)-C(8)-C(9)	52.2(3)
O(1)-C(1)-C(9)-C(8)	-54.0(2)
O(2)-C(1)-C(9)-C(8)	-167.96(16)
C(2)-C(1)-C(9)-C(8)	69.1(2)
O(1)-C(1)-C(9)-C(10)	172.05(16)
O(2)-C(1)-C(9)-C(10)	58.1(2)
C(2)-C(1)-C(9)-C(10)	-64.8(2)

C(7)-C(8)-C(9)-C(1)	-70.1(2)
C(7)-C(8)-C(9)-C(10)	63.0(2)
C(1)-C(9)-C(10)-C(11)	73.3(2)
C(8)-C(9)-C(10)-C(11)	-59.4(2)
C(9)-C(10)-C(11)-C(12)	123.7(2)
C(9)-C(10)-C(11)-C(14)	-57.5(3)
C(14)-C(11)-C(12)-S(2)	0.6(2)
C(10)-C(11)-C(12)-S(2)	179.56(16)
C(13)-S(2)-C(12)-C(11)	-1.15(18)
C(12)-S(2)-C(13)-C(14)	1.41(18)
S(2)-C(13)-C(14)-C(11)	-1.3(2)
S(2)-C(13)-C(14)-C(15)	179.82(16)
C(12)-C(11)-C(14)-C(13)	0.4(3)
C(10)-C(11)-C(14)-C(13)	-178.5(2)
C(12)-C(11)-C(14)-C(15)	179.32(19)
C(10)-C(11)-C(14)-C(15)	0.4(3)
C(13)-C(14)-C(15)-C(2)	-124.8(2)
C(11)-C(14)-C(15)-C(2)	56.5(3)
C(1)-C(2)-C(15)-C(14)	-71.9(2)
C(3)-C(2)-C(15)-C(14)	60.8(2)
C(1)-O(1)-C(16)-C(17)	-34.7(2)
C(1)-O(2)-C(17)-C(16)	-11.9(2)
O(1)-C(16)-C(17)-O(2)	28.4(2)

Symmetry transformations used to generate equivalent atoms:

A suitable crystal of **3.5** was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated MoK α (0.71073Å) radiation. Data was measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART¹ software. Frame integration and final cell refinements were done using SAINT² software. The final cell parameters were determined from least-squares refinement on 6168 reflections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).⁴ Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least-squares with isotropic Uij's related to the riding atom. The C-H distances were fixed at 0.93 Å (aromatic and amide), 0.98 (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.⁵ Structure solution, refinement, graphics and generation of publication materials were performed using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Tables A.7-A.12.

Empirical formula	C35 H30 O S6				
Formula weight	658.95				
Temperature	173(2) K				
Wavelength	0.71073 Å				
Crystal system	Monoclinic				
Space group	P2(1)/n				
Unit cell dimensions	a = 13.8734(12) Å	<i>α</i> = 90°.			
	b = 12.6812(11) Å	$\beta = 98.282(2)^{\circ}.$			
	c = 17.7401(15) Å	γ= 90°.			
Volume	3088.5(5) Å ³				
Z	4				
Density (calculated)	1.417 Mg/m ³				
Absorption coefficient	0.472 mm ⁻¹				
F(000)	1376				
Crystal size	0.36 x 0.35 x 0.16 mm ³				
Theta range for data collection	1.75 to 28.32°.				
Index ranges	-18<=h<=18, -16<=k<=16, -23<=l<=21				
Reflections collected	29539				
Independent reflections	7658 [R(int) = 0.0493]				
Completeness to theta = 28.32°	99.6 %				
Absorption correction	None				
Refinement method	Full-matrix least-squares	on F ²			
Data / restraints / parameters	7658 / 0 / 383				
Goodness-of-fit on F ²	1.030				
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.098	83			
R indices (all data)	R1 = 0.0658, wR2 = 0.102	33			
Largest diff. peak and hole	0.487 and -0.254 e.Å ⁻³				

 Table A.7. Crystal data and structure refinement for 3.5.

	X	у	Z	U(eq)	
C(1)	9538(1)	1423(2)	8784(1)	22(1)	
C(2)	9560(1)	1932(2)	8014(1)	21(1)	
C(3)	9850(1)	3105(2)	8062(1)	23(1)	
C(4)	10507(1)	3398(2)	8779(1)	23(1)	
C(5)	10143(1)	3407(2)	9499(1)	21(1)	
C(6)	9107(1)	3067(2)	9522(1)	24(1)	
C(7)	8911(1)	1890(2)	9336(1)	22(1)	
C(8)	7818(1)	1673(2)	9034(1)	22(1)	
C(9)	7382(1)	2391(2)	8399(1)	20(1)	
C(10)	7746(1)	2446(2)	7680(1)	20(1)	
C(11)	8566(1)	1761(2)	7502(1)	22(1)	
C(12)	10807(1)	3794(2)	10080(1)	23(1)	
C(13)	10768(1)	3983(2)	10890(1)	23(1)	
C(14)	11497(2)	4372(2)	11418(1)	27(1)	
C(15)	11238(2)	4457(2)	12158(1)	29(1)	
C(16)	10317(2)	4142(2)	12208(1)	28(1)	
C(17)	9784(2)	4155(2)	12881(1)	42(1)	
C(18)	11446(1)	3767(2)	8832(1)	25(1)	
C(19)	12035(1)	3987(2)	8234(1)	27(1)	
C(20)	12564(2)	4880(2)	8144(1)	35(1)	
C(21)	13035(2)	4856(2)	7484(1)	38(1)	
C(22)	12883(2)	3965(2)	7076(1)	32(1)	
C(23)	13235(2)	3678(2)	6343(1)	45(1)	
C(24)	6586(1)	3031(2)	8417(1)	22(1)	
C(25)	5957(2)	3205(2)	9003(1)	26(1)	
C(26)	4973(2)	3367(2)	8892(1)	36(1)	
C(27)	4591(2)	3563(2)	9576(2)	41(1)	
C(28)	5262(2)	3565(2)	10204(1)	33(1)	
C(29)	5117(2)	3747(2)	11010(1)	47(1)	
C(30)	7234(1)	3132(2)	7177(1)	21(1)	

Table A.8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å²x 10^3) for **3.5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

C(31)	7344(2)	3422(2)	6395(1)	23(1)
C(32)	6628(2)	3648(2)	5807(1)	30(1)
C(33)	6990(2)	3943(2)	5127(1)	36(1)
C(34)	7972(2)	3950(2)	5190(1)	35(1)
C(35)	8604(2)	4210(2)	4599(2)	59(1)
O(1)	9980(1)	609(1)	8940(1)	32(1)
S (1)	9753(1)	3728(1)	11326(1)	33(1)
S(2)	11887(1)	4129(1)	9756(1)	29(1)
S(3)	12150(1)	3116(1)	7503(1)	38(1)
S(4)	8475(1)	3606(1)	6104(1)	38(1)
S(5)	6286(1)	3706(1)	7566(1)	25(1)
S(6)	6400(1)	3320(1)	9960(1)	37(1)

		L J		
C(1)-O(1)	1.212(2)	C(15)-C(16)	1.354(3)	
C(1)-C(2)	1.516(3)	C(15)-H(15)	0.9500	
C(1)-C(7)	1.520(3)	C(16)-C(17)	1.493(3)	
C(2)-C(3)	1.540(3)	C(16)-S(1)	1.727(2)	
C(2)-C(11)	1.553(3)	C(17)-H(17A)	0.9800	
C(2)-H(2)	1.0000	C(17)-H(17B)	0.9800	
C(3)-C(4)	1.500(3)	C(17)-H(17C)	0.9800	
C(3)-H(3A)	0.9900	C(18)-C(19)	1.456(3)	
C(3)-H(3B)	0.9900	C(18)-S(2)	1.726(2)	
C(4)-C(18)	1.375(3)	C(19)-C(20)	1.371(3)	
C(4)-C(5)	1.439(3)	C(19)-S(3)	1.728(2)	
C(5)-C(12)	1.370(3)	C(20)-C(21)	1.422(3)	
C(5)-C(6)	1.507(3)	C(20)-H(20)	0.9500	
C(6)-C(7)	1.544(3)	C(21)-C(22)	1.342(3)	
C(6)-H(6A)	0.9900	C(21)-H(21)	0.9500	
C(6)-H(6B)	0.9900	C(22)-C(23)	1.498(3)	
C(7)-C(8)	1.558(3)	C(22)-S(3)	1.729(2)	
C(7)-H(7)	1.0000	C(23)-H(23A)	0.9800	
C(8)-C(9)	1.505(3)	C(23)-H(23B)	0.9800	
C(8)-H(8A)	0.9900	C(23)-H(23C)	0.9800	
C(8)-H(8B)	0.9900	C(24)-C(25)	1.468(3)	
C(9)-C(24)	1.375(3)	C(24)-S(5)	1.732(2)	
C(9)-C(10)	1.439(3)	C(25)-C(26)	1.366(3)	
C(10)-C(30)	1.370(3)	C(25)-S(6)	1.728(2)	
C(10)-C(11)	1.501(3)	C(26)-C(27)	1.415(3)	
C(11)-H(11A)	0.9900	C(26)-H(26)	0.9500	
C(11)-H(11B)	0.9900	C(27)-C(28)	1.345(3)	
C(12)-C(13)	1.466(3)	C(27)-H(27)	0.9500	
C(12)-S(2)	1.733(2)	C(28)-C(29)	1.490(3)	
C(13)-C(14)	1.367(3)	C(28)-S(6)	1.725(2)	
C(13)-S(1)	1.732(2)	C(29)-H(29A)	0.9800	
C(14)-C(15)	1.414(3)	C(29)-H(29B)	0.9800	
C(14)-H(14)	0.9500	C(29)-H(29C)	0.9800	

 Table A.9.
 Bond lengths [Å] and angles [°] for 3.5.

C(30)-C(31)	1.463(3)	C(5)-C(6)-H(6A)	108.7
C(30)-S(5)	1.732(2)	C(7)-C(6)-H(6A)	108.7
C(31)-C(32)	1.364(3)	C(5)-C(6)-H(6B)	108.7
C(31)-S(4)	1.737(2)	C(7)-C(6)-H(6B)	108.7
C(32)-C(33)	1.422(3)	H(6A)-C(6)-H(6B)	107.6
C(32)-H(32)	0.9500	C(1)-C(7)-C(6)	114.51(16)
C(33)-C(34)	1.350(3)	C(1)-C(7)-C(8)	109.15(16)
C(33)-H(33)	0.9500	C(6)-C(7)-C(8)	112.12(16)
C(34)-C(35)	1.499(3)	C(1)-C(7)-H(7)	106.9
C(34)-S(4)	1.726(2)	C(6)-C(7)-H(7)	106.9
C(35)-H(35A)	0.9800	C(8)-C(7)-H(7)	106.9
C(35)-H(35B)	0.9800	C(9)-C(8)-C(7)	114.64(16)
C(35)-H(35C)	0.9800	C(9)-C(8)-H(8A)	108.6
		C(7)-C(8)-H(8A)	108.6
O(1)-C(1)-C(2)	119.50(18)	C(9)-C(8)-H(8B)	108.6
O(1)-C(1)-C(7)	120.22(18)	C(7)-C(8)-H(8B)	108.6
C(2)-C(1)-C(7)	120.16(17)	H(8A)-C(8)-H(8B)	107.6
C(1)-C(2)-C(3)	113.59(16)	C(24)-C(9)-C(10)	112.16(18)
C(1)-C(2)-C(11)	109.67(16)	C(24)-C(9)-C(8)	125.29(18)
C(3)-C(2)-C(11)	111.69(16)	C(10)-C(9)-C(8)	122.50(17)
C(1)-C(2)-H(2)	107.2	C(30)-C(10)-C(9)	113.15(17)
C(3)-C(2)-H(2)	107.2	C(30)-C(10)-C(11)	124.59(18)
C(11)-C(2)-H(2)	107.2	C(9)-C(10)-C(11)	122.16(17)
C(4)-C(3)-C(2)	114.08(16)	C(10)-C(11)-C(2)	115.57(16)
C(4)-C(3)-H(3A)	108.7	C(10)-C(11)-H(11A)	108.4
C(2)-C(3)-H(3A)	108.7	C(2)-C(11)-H(11A)	108.4
C(4)-C(3)-H(3B)	108.7	C(10)-C(11)-H(11B)	108.4
C(2)-C(3)-H(3B)	108.7	C(2)-C(11)-H(11B)	108.4
H(3A)-C(3)-H(3B)	107.6	H(11A)-C(11)-H(11B)	107.4
C(18)-C(4)-C(5)	112.66(18)	C(5)-C(12)-C(13)	132.91(19)
C(18)-C(4)-C(3)	126.68(19)	C(5)-C(12)-S(2)	110.94(15)
C(5)-C(4)-C(3)	120.39(17)	C(13)-C(12)-S(2)	116.14(15)
C(12)-C(5)-C(4)	112.78(17)	C(14)-C(13)-C(12)	127.04(19)
C(12)-C(5)-C(6)	128.48(18)	C(14)-C(13)-S(1)	109.30(16)
C(4)-C(5)-C(6)	118.64(18)	C(12)-C(13)-S(1)	123.65(15)
C(5)-C(6)-C(7)	114.22(16)	C(13)-C(14)-C(15)	113.66(19)

C(13)-C(14)-H(14)	123.2	C(9)-C(24)-S(5)	111.40(15)
C(15)-C(14)-H(14)	123.2	C(25)-C(24)-S(5)	116.77(15)
C(16)-C(15)-C(14)	114.0(2)	C(26)-C(25)-C(24)	127.2(2)
C(16)-C(15)-H(15)	123.0	C(26)-C(25)-S(6)	109.60(17)
C(14)-C(15)-H(15)	123.0	C(24)-C(25)-S(6)	123.05(15)
C(15)-C(16)-C(17)	129.1(2)	C(25)-C(26)-C(27)	113.2(2)
C(15)-C(16)-S(1)	109.82(17)	C(25)-C(26)-H(26)	123.4
C(17)-C(16)-S(1)	121.06(17)	C(27)-C(26)-H(26)	123.4
C(16)-C(17)-H(17A)	109.5	C(28)-C(27)-C(26)	114.2(2)
C(16)-C(17)-H(17B)	109.5	C(28)-C(27)-H(27)	122.9
H(17A)-C(17)-H(17B)	109.5	C(26)-C(27)-H(27)	122.9
C(16)-C(17)-H(17C)	109.5	C(27)-C(28)-C(29)	128.5(2)
H(17A)-C(17)-H(17C)	109.5	C(27)-C(28)-S(6)	109.99(17)
H(17B)-C(17)-H(17C)	109.5	C(29)-C(28)-S(6)	121.56(19)
C(4)-C(18)-C(19)	129.8(2)	C(28)-C(29)-H(29A)	109.5
C(4)-C(18)-S(2)	111.04(16)	C(28)-C(29)-H(29B)	109.5
C(19)-C(18)-S(2)	118.78(15)	H(29A)-C(29)-H(29B)	109.5
C(20)-C(19)-C(18)	127.5(2)	C(28)-C(29)-H(29C)	109.5
C(20)-C(19)-S(3)	109.35(16)	H(29A)-C(29)-H(29C)	109.5
C(18)-C(19)-S(3)	123.13(16)	H(29B)-C(29)-H(29C)	109.5
C(19)-C(20)-C(21)	113.3(2)	C(10)-C(30)-C(31)	131.46(18)
C(19)-C(20)-H(20)	123.3	C(10)-C(30)-S(5)	111.05(15)
C(21)-C(20)-H(20)	123.3	C(31)-C(30)-S(5)	117.47(15)
C(22)-C(21)-C(20)	114.0(2)	C(32)-C(31)-C(30)	127.87(19)
C(22)-C(21)-H(21)	123.0	C(32)-C(31)-S(4)	109.48(16)
C(20)-C(21)-H(21)	123.0	C(30)-C(31)-S(4)	122.54(15)
C(21)-C(22)-C(23)	128.8(2)	C(31)-C(32)-C(33)	113.4(2)
C(21)-C(22)-S(3)	110.15(17)	C(31)-C(32)-H(32)	123.3
C(23)-C(22)-S(3)	121.04(18)	C(33)-C(32)-H(32)	123.3
C(22)-C(23)-H(23A)	109.5	C(34)-C(33)-C(32)	113.9(2)
C(22)-C(23)-H(23B)	109.5	C(34)-C(33)-H(33)	123.0
H(23A)-C(23)-H(23B)	109.5	C(32)-C(33)-H(33)	123.0
C(22)-C(23)-H(23C)	109.5	C(33)-C(34)-C(35)	128.9(2)
H(23A)-C(23)-H(23C)	109.5	C(33)-C(34)-S(4)	110.10(17)
H(23B)-C(23)-H(23C)	109.5	C(35)-C(34)-S(4)	120.96(19)
C(9)-C(24)-C(25)	131.80(19)	C(34)-C(35)-H(35A)	109.5

C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(16)-S(1)-C(13)	93.22(10)
C(18)-S(2)-C(12)	92.56(10)
C(19)-S(3)-C(22)	93.15(11)
C(34)-S(4)-C(31)	93.02(11)
C(30)-S(5)-C(24)	92.23(10)
C(28)-S(6)-C(25)	92.99(11)

Symmetry transformations used to generate equivalent atoms:

	T111	1122	1133	1123	U13	L112	
	U	U	U	U	U	U	
C(1)	16(1)	23(1)	25(1)	-1(1)	-2(1)	-4(1)	
C(2)	17(1)	25(1)	21(1)	-3(1)	3(1)	3(1)	
C(3)	19(1)	27(1)	22(1)	0(1)	1(1)	-2(1)	
C(4)	21(1)	22(1)	24(1)	1(1)	1(1)	0(1)	
C(5)	20(1)	22(1)	22(1)	0(1)	1(1)	1(1)	
C(6)	20(1)	29(1)	23(1)	-3(1)	3(1)	-1(1)	
C(7)	21(1)	26(1)	19(1)	6(1)	2(1)	1(1)	
C(8)	22(1)	23(1)	22(1)	-1(1)	4(1)	-2(1)	
C(9)	18(1)	22(1)	21(1)	-2(1)	0(1)	-3(1)	
C(10)	19(1)	22(1)	19(1)	-4(1)	2(1)	-2(1)	
C(11)	22(1)	23(1)	20(1)	-2(1)	1(1)	2(1)	
C(12)	20(1)	23(1)	24(1)	1(1)	3(1)	1(1)	
C(13)	24(1)	22(1)	24(1)	1(1)	2(1)	2(1)	
C(14)	23(1)	28(1)	29(1)	-1(1)	-1(1)	3(1)	
C(15)	32(1)	29(1)	23(1)	-3(1)	-6(1)	8(1)	
C(16)	37(1)	26(1)	20(1)	1(1)	0(1)	4(1)	
C(17)	49(2)	49(2)	29(1)	2(1)	8(1)	0(1)	
C(18)	23(1)	29(1)	23(1)	2(1)	3(1)	-1(1)	
C(19)	20(1)	35(1)	25(1)	1(1)	1(1)	-2(1)	
C(20)	34(1)	39(1)	33(1)	-5(1)	8(1)	-12(1)	
C(21)	35(1)	40(1)	40(2)	2(1)	11(1)	-13(1)	
C(22)	28(1)	37(1)	31(1)	7(1)	9(1)	1(1)	
C(23)	52(2)	47(2)	42(2)	2(1)	23(1)	4(1)	
C(24)	18(1)	26(1)	21(1)	-3(1)	1(1)	-2(1)	
C(25)	23(1)	27(1)	27(1)	-2(1)	6(1)	-2(1)	
C(26)	26(1)	50(2)	33(1)	-2(1)	4(1)	5(1)	
C(27)	26(1)	52(2)	48(2)	-3(1)	15(1)	6(1)	
C(28)	31(1)	34(1)	37(1)	-5(1)	16(1)	-5(1)	
C(29)	54(2)	54(2)	40(2)	-9(1)	28(1)	-10(1)	
C(30)	17(1)	23(1)	23(1)	-3(1)	1(1)	-3(1)	

Table A.10. Anisotropic displacement parameters $(Å^2x \ 10^3)$ for **3.5**. The anisotropic displacement factor exponent takes the form: $-2\Box^2[h^2 a^{*2}U^{11} + ... + 2h k a^* b^* U^{12}]$

C(31)	24(1)	22(1)	23(1)	-1(1)	1(1)	0(1)	
C(32)	27(1)	30(1)	32(1)	5(1)	-4(1)	-4(1)	
C(33)	47(2)	35(1)	22(1)	5(1)	-8(1)	-5(1)	
C(34)	46(1)	38(1)	22(1)	3(1)	5(1)	6(1)	
C(35)	69(2)	77(2)	37(2)	19(2)	23(2)	17(2)	
O (1)	31(1)	29(1)	36(1)	6(1)	1(1)	9(1)	
S (1)	32(1)	42(1)	26(1)	-3(1)	6(1)	-9(1)	
S(2)	20(1)	40(1)	26(1)	-2(1)	1(1)	-6(1)	
S(3)	45(1)	32(1)	42(1)	-4(1)	20(1)	-7(1)	
S(4)	27(1)	60(1)	27(1)	12(1)	5(1)	7(1)	
S(5)	21(1)	26(1)	27(1)	1(1)	2(1)	4(1)	
S(6)	26(1)	58(1)	27(1)	-8(1)	7(1)	-3(1)	

	X	у	Z	U(eq)	
H(2)	10065	1553	7768	25	
H(3A)	10180	3282	7620	27	
H(3B)	9250	3537	8026	27	
H(6A)	8669	3498	9153	29	
H(6B)	8941	3213	10036	29	
H(7)	9068	1494	9826	27	
H(8A)	7752	935	8851	27	
H(8B)	7438	1744	9462	27	
H(11A)	8657	1885	6965	26	
H(11B)	8373	1014	7545	26	
H(14)	12119	4567	11299	33	
H(15)	11672	4712	12582	35	
H(17A)	10254	4159	13350	63	
H(17B)	9372	3525	12873	63	
H(17C)	9376	4787	12863	63	
H(20)	12611	5457	8489	42	
H(21)	13423	5420	7344	45	
H(23A)	13775	4143	6262	68	
H(23B)	12701	3760	5920	68	
H(23C)	13459	2944	6367	68	
H(26)	4585	3351	8405	44	
H(27)	3917	3683	9591	49	
H(29A)	4437	3940	11028	71	
H(29B)	5544	4320	11227	71	
H(29C)	5275	3102	11306	71	
H(32)	5954	3612	5847	36	
H(33)	6578	4120	4669	43	
H(35A)	8212	4198	4093	89	
H(35B)	9129	3689	4618	89	
H(35C)	8886	4914	4698	89	

Table A.11. Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å²x 10³) for **3.5**.

O(1)-C(1)-C(2)-C(3)	-128.27(19)	
C(7)-C(1)-C(2)-C(3)	55.9(2)	
O(1)-C(1)-C(2)-C(11)	106.0(2)	
C(7)-C(1)-C(2)-C(11)	-69.9(2)	
C(1)-C(2)-C(3)-C(4)	28.9(2)	
C(11)-C(2)-C(3)-C(4)	153.53(16)	
C(2)-C(3)-C(4)-C(18)	116.5(2)	
C(2)-C(3)-C(4)-C(5)	-69.9(2)	
C(18)-C(4)-C(5)-C(12)	0.7(3)	
C(3)-C(4)-C(5)-C(12)	-173.75(18)	
C(18)-C(4)-C(5)-C(6)	177.43(18)	
C(3)-C(4)-C(5)-C(6)	2.9(3)	
C(12)-C(5)-C(6)-C(7)	-117.5(2)	
C(4)-C(5)-C(6)-C(7)	66.4(2)	
O(1)-C(1)-C(7)-C(6)	129.4(2)	
C(2)-C(1)-C(7)-C(6)	-54.8(2)	
O(1)-C(1)-C(7)-C(8)	-104.0(2)	
C(2)-C(1)-C(7)-C(8)	71.8(2)	
C(5)-C(6)-C(7)-C(1)	-30.9(2)	
C(5)-C(6)-C(7)-C(8)	-155.91(17)	
C(1)-C(7)-C(8)-C(9)	-78.1(2)	
C(6)-C(7)-C(8)-C(9)	49.9(2)	
C(7)-C(8)-C(9)-C(24)	-121.9(2)	
C(7)-C(8)-C(9)-C(10)	60.6(2)	
C(24)-C(9)-C(10)-C(30)	1.0(2)	
C(8)-C(9)-C(10)-C(30)	178.68(18)	
C(24)-C(9)-C(10)-C(11)	-175.49(17)	
C(8)-C(9)-C(10)-C(11)	2.2(3)	
C(30)-C(10)-C(11)-C(2)	120.9(2)	
C(9)-C(10)-C(11)-C(2)	-63.0(2)	
C(1)-C(2)-C(11)-C(10)	76.1(2)	
C(3)-C(2)-C(11)-C(10)	-50.7(2)	
C(4)-C(5)-C(12)-C(13)	178.1(2)	

Table A.12. Torsion angles [°] for **3.5**.

C(6)-C(5)-C(12)-C(13)	1.8(4)
C(4)-C(5)-C(12)-S(2)	-1.0(2)
C(6)-C(5)-C(12)-S(2)	-177.30(17)
C(5)-C(12)-C(13)-C(14)	179.5(2)
S(2)-C(12)-C(13)-C(14)	-1.5(3)
C(5)-C(12)-C(13)-S(1)	-0.2(3)
S(2)-C(12)-C(13)-S(1)	178.78(11)
C(12)-C(13)-C(14)-C(15)	-179.57(19)
S(1)-C(13)-C(14)-C(15)	0.2(2)
C(13)-C(14)-C(15)-C(16)	-0.2(3)
C(14)-C(15)-C(16)-C(17)	-177.6(2)
C(14)-C(15)-C(16)-S(1)	0.1(2)
C(5)-C(4)-C(18)-C(19)	-172.9(2)
C(3)-C(4)-C(18)-C(19)	1.2(4)
C(5)-C(4)-C(18)-S(2)	-0.1(2)
C(3)-C(4)-C(18)-S(2)	173.95(16)
C(4)-C(18)-C(19)-C(20)	131.2(3)
S(2)-C(18)-C(19)-C(20)	-41.1(3)
C(4)-C(18)-C(19)-S(3)	-47.9(3)
S(2)-C(18)-C(19)-S(3)	139.78(14)
C(18)-C(19)-C(20)-C(21)	-178.1(2)
S(3)-C(19)-C(20)-C(21)	1.1(3)
C(19)-C(20)-C(21)-C(22)	-0.5(3)
C(20)-C(21)-C(22)-C(23)	178.0(2)
C(20)-C(21)-C(22)-S(3)	-0.3(3)
C(10)-C(9)-C(24)-C(25)	177.4(2)
C(8)-C(9)-C(24)-C(25)	-0.3(3)
C(10)-C(9)-C(24)-S(5)	-0.5(2)
C(8)-C(9)-C(24)-S(5)	-178.16(15)
C(9)-C(24)-C(25)-C(26)	-142.7(2)
S(5)-C(24)-C(25)-C(26)	35.1(3)
C(9)-C(24)-C(25)-S(6)	41.9(3)
S(5)-C(24)-C(25)-S(6)	-140.28(14)
C(24)-C(25)-C(26)-C(27)	-176.9(2)
S(6)-C(25)-C(26)-C(27)	-1.0(3)
C(25)-C(26)-C(27)-C(28)	0.7(3)

C(26)-C(27)-C(28)-C(29)	179.7(2)
C(26)-C(27)-C(28)-S(6)	-0.1(3)
C(9)-C(10)-C(30)-C(31)	-179.50(19)
C(11)-C(10)-C(30)-C(31)	-3.1(3)
C(9)-C(10)-C(30)-S(5)	-1.0(2)
C(11)-C(10)-C(30)-S(5)	175.40(15)
C(10)-C(30)-C(31)-C(32)	144.0(2)
S(5)-C(30)-C(31)-C(32)	-34.5(3)
C(10)-C(30)-C(31)-S(4)	-40.1(3)
S(5)-C(30)-C(31)-S(4)	141.41(13)
C(30)-C(31)-C(32)-C(33)	177.6(2)
S(4)-C(31)-C(32)-C(33)	1.3(2)
C(31)-C(32)-C(33)-C(34)	-0.3(3)
C(32)-C(33)-C(34)-C(35)	179.6(2)
C(32)-C(33)-C(34)-S(4)	-0.9(3)
C(15)-C(16)-S(1)-C(13)	-0.02(17)
C(17)-C(16)-S(1)-C(13)	177.96(19)
C(14)-C(13)-S(1)-C(16)	-0.11(16)
C(12)-C(13)-S(1)-C(16)	179.68(18)
C(4)-C(18)-S(2)-C(12)	-0.38(17)
C(19)-C(18)-S(2)-C(12)	173.28(17)
C(5)-C(12)-S(2)-C(18)	0.80(16)
C(13)-C(12)-S(2)-C(18)	-178.43(16)
C(20)-C(19)-S(3)-C(22)	-1.09(18)
C(18)-C(19)-S(3)-C(22)	178.17(18)
C(21)-C(22)-S(3)-C(19)	0.81(19)
C(23)-C(22)-S(3)-C(19)	-177.7(2)
C(33)-C(34)-S(4)-C(31)	1.34(19)
C(35)-C(34)-S(4)-C(31)	-179.1(2)
C(32)-C(31)-S(4)-C(34)	-1.49(17)
C(30)-C(31)-S(4)-C(34)	-178.03(17)
C(10)-C(30)-S(5)-C(24)	0.56(16)
C(31)-C(30)-S(5)-C(24)	179.34(16)
C(9)-C(24)-S(5)-C(30)	-0.02(16)
C(25)-C(24)-S(5)-C(30)	-178.26(16)
C(27)-C(28)-S(6)-C(25)	-0.46(19)

C(29)-C(28)-S(6)-C(25)	179.7(2)
C(26)-C(25)-S(6)-C(28)	0.86(18)
C(24)-C(25)-S(6)-C(28)	176.96(18)

Symmetry transformations used to generate equivalent atoms:

A suitable crystal of *st*-[H-Th₃-H]₂ was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART 1000 CCD sealed tube diffractometer with graphite monochromated CuK α (1.54178 Å) radiation. Data was measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART¹ software. Frame integration and final cell refinements were done using SAINT² software. The final cell parameters were determined from least-squares refinement on 3846 reflections. The SADABS³ program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).⁴ Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least-squares with isotropic Uij's related to the riding atom. The C-H distances were fixed at 0.93 Å (aromatic and amide), 0.98 (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.⁵ Structure solution, refinement, graphics and generation of publication materials were performed using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Tables A.13-A.17.

Empirical formula	C33 H26 O2 S6		
Formula weight	646.90		
Temperature	173(2) K		
Wavelength	1.54178 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 8.7052(6) Å	$\alpha = 78.705(3)^{\circ}$.	
	b = 11.1163(7) Å	$\beta = 85.048(3)^{\circ}$.	
	c = 15.8390(8) Å	$\gamma = 70.247(3)^{\circ}$.	
Volume	1414.27(15) Å ³		
Z	2		
Density (calculated)	1.519 Mg/m ³		
Absorption coefficient	4.725 mm ⁻¹		
F(000)	672		
Crystal size	0.38 x 0.33 x 0.12 mm ³		
Theta range for data collection	2.85 to 66.78°.		
Index ranges	-7<=h<=9, -9<=k<=11, -17<=l<=16		
Reflections collected	5174		
Independent reflections	3220 [R(int) = 0.0329]		
Completeness to theta = 66.78°	64.0 %		
Absorption correction	Semi-empirical from equi	ivalents	
Max. and min. transmission	1.00 and 0.557226		
Refinement method	Full-matrix least-squares	on F ²	
Data / restraints / parameters	3220/0/370		
Goodness-of-fit on F ²	1.040		
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1396		
R indices (all data)	R1 = 0.0558, wR2 = 0.14	38	
Largest diff. peak and hole	0.484 and -0.478 e.Å ⁻³		

 Table A.13. Crystal data and structure refinement for *st*-[H-Th₃-H]₂.

	Х	у	Z	U(eq)	
C(1)	7362(5)	3402(4)	2611(2)	26(1)	
C(2)	6408(7)	1918(5)	2176(3)	47(1)	
C(3)	7711(8)	1220(5)	2775(5)	76(2)	
C(4)	8360(5)	3995(4)	1910(2)	24(1)	
C(5)	7334(5)	5287(4)	1365(2)	26(1)	
C(6)	6592(5)	6488(4)	1770(2)	23(1)	
C(7)	6645(5)	7685(4)	1365(2)	25(1)	
C(8)	5012(5)	7775(4)	2730(2)	23(1)	
C(9)	5642(5)	6542(4)	2551(2)	22(1)	
C(10)	5224(5)	5400(4)	3073(3)	25(1)	
C(11)	6651(5)	4144(4)	3349(2)	24(1)	
C(12)	7939(5)	4316(4)	3891(3)	27(1)	
C(13)	8809(5)	5258(4)	3491(2)	25(1)	
C(14)	8803(5)	6314(4)	3829(2)	27(1)	
C(15)	10444(5)	6091(4)	2449(2)	24(1)	
C(16)	9751(5)	5135(4)	2712(2)	25(1)	
C(17)	9935(5)	4025(4)	2254(3)	26(1)	
C(18)	7345(5)	8074(4)	528(3)	28(1)	
C(19)	7160(5)	7727(4)	-285(2)	21(1)	
C(20)	7999(6)	8354(5)	-945(3)	40(1)	
C(21)	8680(7)	9133(5)	-677(3)	50(1)	
C(22)	3829(5)	8286(4)	3391(2)	24(1)	
C(23)	3751(5)	7812(4)	4269(2)	26(1)	
C(24)	2350(6)	8596(4)	4672(3)	30(1)	
C(25)	1408(6)	9623(4)	4126(3)	30(1)	
C(26)	8016(5)	6802(4)	4599(3)	27(1)	
C(27)	7709(5)	6136(4)	5404(2)	27(1)	
C(28)	6919(6)	7009(5)	5984(3)	35(1)	
C(29)	6639(6)	8268(5)	5633(3)	39(1)	
C(30)	11446(5)	6387(4)	1696(2)	25(1)	

Table A.14. Atomic coordinates $(x \ 10^4)$ and equivalent isotropic displacement parameters (Å²x 10^3) for *st*-[**H-Th₃-H**]₂. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

C(31)	12147(6)	7336(4)	1554(3)	32(1)	
C(32)	13003(6)	7430(5)	761(3)	33(1)	
C(33)	12951(7)	6552(5)	294(3)	42(1)	
O(1)	6031(3)	3245(3)	2212(2)	28(1)	
O(2)	8375(4)	2112(3)	2964(2)	29(1)	
S (1)	5562(1)	8886(1)	1945(1)	26(1)	
S(2)	9968(1)	7150(1)	3186(1)	28(1)	
S(3)	8409(2)	9138(1)	390(1)	53(1)	
S(4)	2168(1)	9674(1)	3101(1)	29(1)	
S(5)	7324(2)	8463(1)	4590(1)	39(1)	
S(6)	11827(2)	5615(1)	814(1)	53(1)	

C(1)-O(2)	1.437(5)	C(13)-C(16)	1.425(6)
C(1)-O(1)	1.442(5)	C(14)-C(26)	1.454(6)
C(1)-C(11)	1.528(6)	C(14)-S(2)	1.737(4)
C(1)-C(4)	1.535(6)	C(15)-C(16)	1.372(6)
C(2)-O(1)	1.410(6)	C(15)-C(30)	1.467(6)
C(2)-C(3)	1.446(7)	C(15)-S(2)	1.745(4)
C(2)-H(2A)	0.9900	C(16)-C(17)	1.507(6)
C(2)-H(2B)	0.9900	C(17)-H(17A)	0.9900
C(3)-O(2)	1.392(6)	C(17)-H(17B)	0.9900
C(3)-H(3A)	0.9900	C(18)-C(19)	1.451(6)
C(3)-H(3B)	0.9900	C(18)-S(3)	1.706(4)
C(4)-C(17)	1.532(6)	C(19)-C(20)	1.428(6)
C(4)-C(5)	1.545(5)	C(19)-H(19)	0.9500
C(4)-H(4)	1.0000	C(20)-C(21)	1.348(7)
C(5)-C(6)	1.514(6)	C(20)-H(20)	0.9500
C(5)-H(5A)	0.9900	C(21)-S(3)	1.687(5)
C(5)-H(5B)	0.9900	C(21)-H(21)	0.9500
C(6)-C(7)	1.373(6)	C(22)-C(23)	1.391(5)
C(6)-C(9)	1.428(6)	C(22)-S(4)	1.736(4)
C(7)-C(18)	1.459(6)	C(23)-C(24)	1.421(6)
C(7)-S(1)	1.731(4)	C(23)-H(23)	0.9500
C(8)-C(9)	1.370(6)	C(24)-C(25)	1.352(6)
C(8)-C(22)	1.460(6)	C(24)-H(24)	0.9500
C(8)-S(1)	1.730(4)	C(25)-S(4)	1.697(4)
C(9)-C(10)	1.509(5)	C(25)-H(25)	0.9500
C(10)-C(11)	1.538(6)	C(26)-C(27)	1.396(6)
C(10)-H(10A)	0.9900	C(26)-S(5)	1.735(4)
C(10)-H(10B)	0.9900	C(27)-C(28)	1.431(7)
C(11)-C(12)	1.551(5)	C(27)-H(27)	0.9500
C(11)-H(11)	1.0000	C(28)-C(29)	1.348(7)
C(12)-C(13)	1.505(6)	C(28)-H(28)	0.9500
C(12)-H(12A)	0.9900	C(29)-S(5)	1.706(5)
C(12)-H(12B)	0.9900	C(29)-H(29)	0.9500
C(13)-C(14)	1.381(6)	C(30)-C(31)	1.361(6)

 Table A.15.
 Bond lengths [Å] and angles [°] for st-[H-Th₃-H]₂.

C(30)-S(6)	1.731(4)	C(4)-C(5)-H(5B)	107.3
C(31)-C(32)	1.408(6)	H(5A)-C(5)-H(5B)	106.9
C(31)-H(31)	0.9500	C(7)-C(6)-C(9)	112.7(4)
C(32)-C(33)	1.350(6)	C(7)-C(6)-C(5)	122.0(4)
C(32)-H(32)	0.9500	C(9)-C(6)-C(5)	124.9(3)
C(33)-S(6)	1.713(5)	C(6)-C(7)-C(18)	130.3(4)
C(33)-H(33)	0.9500	C(6)-C(7)-S(1)	111.4(3)
		C(18)-C(7)-S(1)	118.1(3)
O(2)-C(1)-O(1)	105.7(3)	C(9)-C(8)-C(22)	130.3(4)
O(2)-C(1)-C(11)	108.9(3)	C(9)-C(8)-S(1)	111.7(3)
O(1)-C(1)-C(11)	107.9(3)	C(22)-C(8)-S(1)	117.4(3)
O(2)-C(1)-C(4)	108.0(3)	C(8)-C(9)-C(6)	112.5(3)
O(1)-C(1)-C(4)	108.7(3)	C(8)-C(9)-C(10)	123.4(4)
C(11)-C(1)-C(4)	117.1(3)	C(6)-C(9)-C(10)	123.8(4)
O(1)-C(2)-C(3)	106.1(4)	C(9)-C(10)-C(11)	117.2(4)
O(1)-C(2)-H(2A)	110.5	C(9)-C(10)-H(10A)	108.0
C(3)-C(2)-H(2A)	110.5	С(11)-С(10)-Н(10А)	108.0
O(1)-C(2)-H(2B)	110.5	C(9)-C(10)-H(10B)	108.0
C(3)-C(2)-H(2B)	110.5	C(11)-C(10)-H(10B)	108.0
H(2A)-C(2)-H(2B)	108.7	H(10A)-C(10)-H(10B)	107.2
O(2)-C(3)-C(2)	107.8(4)	C(1)-C(11)-C(10)	113.0(3)
O(2)-C(3)-H(3A)	110.2	C(1)-C(11)-C(12)	114.6(4)
C(2)-C(3)-H(3A)	110.2	C(10)-C(11)-C(12)	113.9(3)
O(2)-C(3)-H(3B)	110.2	C(1)-C(11)-H(11)	104.6
C(2)-C(3)-H(3B)	110.2	C(10)-C(11)-H(11)	104.6
H(3A)-C(3)-H(3B)	108.5	C(12)-C(11)-H(11)	104.6
C(17)-C(4)-C(1)	112.4(3)	C(13)-C(12)-C(11)	118.1(3)
C(17)-C(4)-C(5)	114.7(3)	C(13)-C(12)-H(12A)	107.8
C(1)-C(4)-C(5)	113.6(4)	C(11)-C(12)-H(12A)	107.8
C(17)-C(4)-H(4)	105.0	C(13)-C(12)-H(12B)	107.8
C(1)-C(4)-H(4)	105.0	C(11)-C(12)-H(12B)	107.8
C(5)-C(4)-H(4)	105.0	H(12A)-C(12)-H(12B)	107.1
C(6)-C(5)-C(4)	120.2(3)	C(14)-C(13)-C(16)	112.7(4)
C(6)-C(5)-H(5A)	107.3	C(14)-C(13)-C(12)	124.8(4)
C(4)-C(5)-H(5A)	107.3	C(16)-C(13)-C(12)	122.5(4)
C(6)-C(5)-H(5B)	107.3	C(13)-C(14)-C(26)	131.3(4)

C(13)-C(14)-S(2)	110.8(3)	C(24)-C(25)-H(25)	124.0
C(26)-C(14)-S(2)	117.9(3)	S(4)-C(25)-H(25)	124.0
C(16)-C(15)-C(30)	133.5(4)	C(27)-C(26)-C(14)	130.3(4)
C(16)-C(15)-S(2)	110.2(3)	C(27)-C(26)-S(5)	110.4(3)
C(30)-C(15)-S(2)	116.3(3)	C(14)-C(26)-S(5)	119.3(3)
C(15)-C(16)-C(13)	113.9(4)	C(26)-C(27)-C(28)	111.5(4)
C(15)-C(16)-C(17)	125.4(4)	C(26)-C(27)-H(27)	124.2
C(13)-C(16)-C(17)	120.7(4)	C(28)-C(27)-H(27)	124.2
C(16)-C(17)-C(4)	115.7(4)	C(29)-C(28)-C(27)	113.6(4)
C(16)-C(17)-H(17A)	108.3	C(29)-C(28)-H(28)	123.2
C(4)-C(17)-H(17A)	108.3	C(27)-C(28)-H(28)	123.2
C(16)-C(17)-H(17B)	108.3	C(28)-C(29)-S(5)	112.2(4)
C(4)-C(17)-H(17B)	108.3	C(28)-C(29)-H(29)	123.9
H(17A)-C(17)-H(17B)	107.4	S(5)-C(29)-H(29)	123.9
C(19)-C(18)-C(7)	127.2(4)	C(31)-C(30)-C(15)	126.5(4)
C(19)-C(18)-S(3)	111.1(3)	C(31)-C(30)-S(6)	109.3(3)
C(7)-C(18)-S(3)	121.5(3)	C(15)-C(30)-S(6)	124.2(3)
C(20)-C(19)-C(18)	108.6(4)	C(30)-C(31)-C(32)	114.4(4)
C(20)-C(19)-H(19)	125.7	C(30)-C(31)-H(31)	122.8
C(18)-C(19)-H(19)	125.7	C(32)-C(31)-H(31)	122.8
C(21)-C(20)-C(19)	114.6(4)	C(33)-C(32)-C(31)	112.5(4)
C(21)-C(20)-H(20)	122.7	C(33)-C(32)-H(32)	123.7
C(19)-C(20)-H(20)	122.7	C(31)-C(32)-H(32)	123.7
C(20)-C(21)-S(3)	112.7(4)	C(32)-C(33)-S(6)	111.4(4)
C(20)-C(21)-H(21)	123.6	C(32)-C(33)-H(33)	124.3
S(3)-C(21)-H(21)	123.6	S(6)-C(33)-H(33)	124.3
C(23)-C(22)-C(8)	130.3(4)	C(2)-O(1)-C(1)	108.5(3)
C(23)-C(22)-S(4)	110.2(3)	C(3)-O(2)-C(1)	109.1(3)
C(8)-C(22)-S(4)	119.4(3)	C(7)-S(1)-C(8)	91.7(2)
C(22)-C(23)-C(24)	111.7(4)	C(14)-S(2)-C(15)	92.4(2)
C(22)-C(23)-H(23)	124.2	C(21)-S(3)-C(18)	92.9(2)
C(24)-C(23)-H(23)	124.2	C(25)-S(4)-C(22)	92.4(2)
C(25)-C(24)-C(23)	113.7(4)	C(29)-S(5)-C(26)	92.3(2)
C(25)-C(24)-H(24)	123.2	C(33)-S(6)-C(30)	92.4(2)
C(23)-C(24)-H(24)	123.2		
C(24)-C(25)-S(4)	112.0(4)		

	U ¹¹	U ²²	U ³³	U23	U ¹³	U ¹²	
C(1)	29(3)	20(2)	27(2)	-1(2)	-6(2)	-8(2)	
C(2)	61(4)	25(3)	59(3)	-13(2)	-17(3)	-13(2)	
C(3)	90(5)	24(3)	123(5)	-2(3)	-61(4)	-21(3)	
C(4)	31(3)	18(2)	23(2)	-7(2)	0(2)	-7(2)	
C(5)	36(3)	23(3)	19(2)	-1(2)	-2(2)	-10(2)	
C(6)	25(3)	21(3)	20(2)	-1(2)	-4(2)	-5(2)	
C(7)	30(3)	26(3)	19(2)	-4(2)	-1(2)	-8(2)	
C(8)	24(3)	30(3)	14(2)	-2(2)	2(2)	-9(2)	
C(9)	24(3)	22(2)	17(2)	-3(2)	-2(2)	-5(2)	
C(10)	27(3)	25(3)	24(2)	-4(2)	6(2)	-9(2)	
C(11)	31(3)	25(2)	19(2)	0(2)	0(2)	-14(2)	
C(12)	34(3)	28(3)	22(2)	-2(2)	-3(2)	-15(2)	
C(13)	25(3)	24(3)	24(2)	-3(2)	-6(2)	-6(2)	
C(14)	28(3)	30(3)	23(2)	-3(2)	-2(2)	-10(2)	
C(15)	21(3)	27(3)	24(2)	-8(2)	-1(2)	-5(2)	
C(16)	28(3)	22(3)	25(2)	-4(2)	-4(2)	-9(2)	
C(17)	26(3)	21(2)	27(2)	-5(2)	5(2)	-6(2)	
C(18)	33(3)	18(2)	30(2)	0(2)	1(2)	-5(2)	
C(19)	30(3)	14(2)	13(2)	-1(2)	10(2)	-2(2)	
C(20)	53(4)	31(3)	25(2)	0(2)	6(2)	-2(2)	
C(21)	50(4)	45(3)	48(3)	8(2)	10(3)	-19(3)	
C(22)	28(3)	21(2)	24(2)	-4(2)	-2(2)	-7(2)	
C(23)	26(3)	30(3)	19(2)	-8(2)	2(2)	-2(2)	
C(24)	36(3)	34(3)	19(2)	-3(2)	4(2)	-11(2)	
C(25)	33(3)	27(3)	26(2)	-9(2)	6(2)	-6(2)	
C(26)	25(3)	30(3)	27(2)	-8(2)	-2(2)	-10(2)	
C(27)	22(3)	33(3)	24(2)	-7(2)	-7(2)	-7(2)	
C(28)	35(3)	49(3)	28(2)	-7(2)	-4(2)	-21(2)	
C(29)	48(3)	41(3)	38(3)	-20(2)	9(2)	-21(2)	

Table A.16. Anisotropic displacement parameters $(Å^2 x \ 10^3)$ for *st*-[H-Th₃-H]₂. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h² a*²U¹¹ + ... + 2 h k a* b* U¹²]

C(30)	26(3)	27(3)	22(2)	-6(2)	-2(2)	-7(2)
C(31)	39(3)	37(3)	27(2)	-12(2)	-1(2)	-19(2)
C(32)	35(3)	39(3)	30(2)	-4(2)	-2(2)	-20(2)
C(33)	55(4)	47(3)	31(3)	-12(2)	13(2)	-25(3)
O (1)	32(2)	25(2)	32(2)	-6(1)	-8(1)	-12(1)
O(2)	36(2)	18(2)	33(2)	1(1)	-9(1)	-9(1)
S (1)	35(1)	20(1)	22(1)	-3(1)	2(1)	-8(1)
S(2)	35(1)	27(1)	27(1)	-8(1)	2(1)	-14(1)
S(3)	68(1)	58(1)	41(1)	4(1)	-4(1)	-38(1)
S(4)	35(1)	26(1)	20(1)	-3(1)	-1(1)	-4(1)
S(5)	53(1)	32(1)	37(1)	-12(1)	10(1)	-19(1)
S(6)	86(1)	56(1)	39(1)	-26(1)	25(1)	-47(1)

	Х	У	Z	U(eq)	
H(2A)	6766	1756	1586	56	
H(2B)	5442	1639	2344	56	
H(3A)	7281	800	3308	92	
H(3B)	8559	538	2515	92	
H(4)	8729	3368	1500	29	
H(5A)	8032	5504	873	32	
H(5B)	6428	5120	1124	32	
H(10A)	4472	5193	2734	31	
H(10B)	4620	5673	3600	31	
H(11)	6144	3567	3755	29	
H(12A)	7390	4589	4429	32	
H(12B)	8776	3454	4055	32	
H(17A)	10421	3200	2656	31	
H(17B)	10717	4060	1765	31	
H(19)	6578	7174	-365	25	
H(20)	8071	8232	-1526	48	
H(21)	9252	9627	-1049	60	
H(23)	4537	7057	4562	32	
H(24)	2100	8415	5270	36	
H(25)	436	10242	4296	35	
H(27)	7988	5218	5548	32	
H(28)	6621	6727	6561	42	
H(29)	6120	8967	5932	47	
H(31)	12066	7888	1955	38	
H(32)	13556	8043	575	39	
H(33)	13472	6464	-254	51	

Table A.17. Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters(Å²x 10 ³) for *st*-[H-Th₃-H]₂.

A suitable crystal of *st*-[Me-Th₃-Me]₂ was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART 1000 CCD sealed tube diffractometer with graphite monochromated CuK α (1.54178 Å) radiation. Data was measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART¹ software. Frame integration and final cell refinements were done using SAINT² software. The final cell parameters were determined from least-squares refinement on 3996 reflections. The SADABS³ program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).⁴ Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least-squares with isotropic Uij's related to the riding atom. The C-H distances were fixed at 0.93 Å (aromatic and amide), 0.98 (methine), 0.97 Å (methylene), or 0.96 Å (methyl). Only the S and O atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.⁵ Structure solution, refinement, graphics and generation of publication materials were performed using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Tables A.18-A.22.

Empirical formula	C37 H34 O2 S6	
Formula weight	703.00	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.4911(11) Å	$\alpha = 105.859(4)^{\circ}$.
	b = 15.5222(11) Å	$\beta = 91.158(4)^{\circ}.$
	c = 16.5506(13) Å	$\gamma = 96.297(4)^{\circ}$.
Volume	3309.3(4) Å ³	
Z	4	
Density (calculated)	1.411 Mg/m ³	
Absorption coefficient	4.083 mm ⁻¹	
F(000)	1472	
Crystal size	0.28 x 0.23 x 0.02 mm ³	
Theta range for data collection	2.78 to 58.93°.	
Index ranges	-14<=h<=13, -16<=k<=17	7, -18<=l<=15
Reflections collected	15680	
Independent reflections	8373 [R(int) = 0.1144]	
Completeness to theta = 58.93°	88.1 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	1.00 and 0.566295	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	8373 / 0 / 466	
Goodness-of-fit on F ²	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.1510, wR2 = 0.334	41
R indices (all data)	R1 = 0.1877, wR2 = 0.359	94
Largest diff. peak and hole	1.290 and -0.687 e.Å ⁻³	

 Table A.18. Crystal data and structure refinement for st-[Me-Th₃-Me]₂.

	Х	У	Z	U(eq)	
C(1)	3866(7)	6235(6)	1110(6)	18(2)	
C(2)	3544(12)	7345(10)	517(9)	65(4)	
C(3)	4234(10)	6803(8)	-15(8)	51(3)	
C(4)	3119(7)	5437(6)	1177(6)	20(2)	
C(5)	3527(8)	4525(6)	895(6)	23(2)	
C(6)	4254(7)	4334(6)	1489(6)	17(2)	
C(7)	4158(7)	3538(6)	1734(6)	21(2)	
C(8)	5751(7)	4533(6)	2285(6)	19(2)	
C(9)	5163(7)	4886(6)	1809(5)	13(2)	
C(10)	5493(8)	5769(6)	1618(6)	23(2)	
C(11)	4760(7)	6496(6)	1712(6)	21(2)	
C(12)	4504(8)	6911(6)	2626(6)	24(2)	
C(13)	4107(7)	6257(6)	3114(6)	17(2)	
C(14)	4515(7)	6204(6)	3848(6)	22(2)	
C(15)	2974(8)	5119(7)	3343(6)	25(2)	
C(16)	3207(7)	5640(6)	2810(6)	22(2)	
C(17)	2607(8)	5613(7)	2037(6)	24(2)	
C(18)	6720(7)	4852(6)	2710(6)	19(2)	
C(19)	7583(8)	5254(7)	2429(7)	29(3)	
C(20)	8392(9)	5450(7)	3015(6)	32(3)	
C(21)	8216(8)	5191(7)	3720(7)	32(3)	
C(22)	3395(7)	2745(6)	1507(6)	20(2)	
C(23)	2375(8)	2699(7)	1538(6)	32(3)	
C(24)	1921(9)	1778(7)	1325(6)	32(3)	
C(25)	2560(8)	1171(7)	1175(7)	32(3)	
C(26)	5313(8)	6768(7)	4389(6)	29(3)	
C(27)	6267(8)	7061(7)	4232(7)	33(3)	
C(28)	6810(10)	7668(8)	4967(7)	42(3)	
C(29)	6275(8)	7819(7)	5662(7)	32(3)	
C(30)	2151(8)	4410(7)	3312(6)	26(2)	

Table A.19. Atomic coordinates $(x \ 10^4)$ and equivalent isotropic displacement parameters (Å²x 10^3) for *st*-[Me-Th₃-Me]₂. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

C(31)	2221(9)	3626(7)	3550(7)	39(3)
C(32)	1263(9)	3093(8)	3464(7)	39(3)
C(33)	516(9)	3436(8)	3176(7)	39(3)
C(34)	-547(11)	3081(10)	3015(9)	63(4)
C(35)	6587(10)	8432(8)	6533(7)	49(3)
C(36)	2356(10)	154(9)	990(8)	55(4)
C(37)	8910(10)	5309(9)	4480(8)	50(3)
O (1)	3345(5)	6993(4)	1195(4)	26(2)
O(2)	4180(5)	6010(4)	257(4)	26(2)
S (1)	6991(2)	4720(2)	3689(2)	36(1)
S(2)	5171(2)	3494(2)	2363(2)	23(1)
S(3)	3769(2)	1686(2)	1225(2)	31(1)
S(4)	5107(2)	7226(2)	5457(2)	42(1)
S(5)	3830(2)	5367(2)	4197(2)	27(1)
S(6)	945(2)	4473(2)	3007(2)	36(1)
C(1B)	10107(9)	7025(8)	376(7)	38(3)
C(2B)	10725(16)	6636(14)	-914(13)	111(7)
C(3B)	10313(12)	5795(10)	-732(9)	67(4)
C(4B)	9258(8)	7579(7)	419(7)	35(3)
C(5B)	8336(9)	7233(8)	868(7)	40(3)
C(6B)	8449(9)	7559(7)	1799(7)	37(3)
C(7B)	7856(8)	8114(7)	2316(6)	29(3)
C(8B)	9273(8)	7721(7)	3113(6)	29(3)
C(9B)	9258(8)	7323(7)	2261(6)	26(2)
C(10B)	9969(8)	6693(7)	1808(6)	29(3)
C(11B)	10664(8)	7046(7)	1200(7)	34(3)
C(12B)	11307(8)	7937(7)	1599(7)	29(3)
C(13B)	10826(8)	8766(7)	1994(6)	26(2)
C(14B)	11121(8)	9342(7)	2759(6)	26(2)
C(15B)	9733(8)	9857(6)	2081(6)	23(2)
C(16B)	10016(8)	9058(6)	1591(6)	22(2)
C(17B)	9574(9)	8612(7)	723(7)	36(3)
C(18B)	6984(9)	8506(8)	2131(7)	38(3)
C(19B)	6274(10)	8800(8)	2684(8)	51(3)
C(20B)	5569(12)	9247(10)	2322(10)	71(4)
C(21B)	5725(11)	9257(10)	1539(9)	62(4)

C(22B)	9934(7)	7675(6)	3806(6)	22(2)
C(23B)	9830(9)	8075(8)	4643(7)	41(3)
C(24B)	10613(9)	7948(8)	5162(8)	42(3)
C(25B)	11313(9)	7475(7)	4754(7)	35(3)
C(26B)	11913(10)	9304(8)	3351(8)	43(3)
C(30B)	8950(8)	10387(7)	1925(6)	32(3)
C(31B)	8768(6)	10729(5)	1240(5)	10(2)
C(32B)	7998(11)	11209(10)	1330(10)	68(4)
C(33B)	7546(11)	11274(10)	2025(9)	63(4)
C(34B)	6689(14)	11789(13)	2369(11)	100(6)
C(36B)	5144(13)	9685(12)	998(11)	89(5)
C(37B)	12269(10)	7241(9)	5084(8)	49(3)
O(1B)	10855(7)	7304(5)	-154(4)	49(2)
O(2B)	9719(7)	6106(5)	-53(4)	50(2)
S(1B)	8298(2)	8374(2)	3357(2)	34(1)
S(2B)	11017(2)	7172(2)	3684(2)	32(1)
S(3B)	6755(2)	8746(2)	1193(2)	52(1)
S(4B)	8106(3)	10722(2)	2643(2)	52(1)
S(5B)	10447(2)	10251(2)	3015(2)	32(1)
S(6B)	12970(20)	8988(16)	3220(20)	39(3)
C(27B)	11750(60)	9630(50)	4260(40)	110(30)
C(28B)	12580(20)	9573(15)	4773(17)	35(6)
C(29B)	13370(20)	9196(17)	4328(19)	29(7)
C(35B)	14340(20)	8960(20)	4588(18)	67(8)
S(6X)	11917(9)	9699(6)	4341(5)	27(2)
C(27X)	12980(80)	8900(60)	3220(70)	20
C(28X)	13510(20)	9044(15)	3824(19)	38(6)
C(29X)	13050(30)	9440(20)	4538(19)	37(7)
C(35X)	13630(30)	9670(20)	5420(20)	87(10)

C(1)-O(1)	1.412(11)	C(13)-C(16)	1.450(13)
C(1)-O(2)	1.442(11)	C(14)-C(26)	1.433(14)
C(1)-C(11)	1.495(13)	C(14)-S(5)	1.744(10)
C(1)-C(4)	1.540(13)	C(15)-C(16)	1.371(14)
C(2)-O(1)	1.393(16)	C(15)-C(30)	1.464(14)
C(2)-C(3)	1.465(17)	C(15)-S(5)	1.736(11)
C(2)-H(2A)	0.9900	C(16)-C(17)	1.488(13)
C(2)-H(2B)	0.9900	C(17)-H(17A)	0.9900
C(3)-O(2)	1.417(14)	C(17)-H(17B)	0.9900
C(3)-H(3A)	0.9900	C(18)-C(19)	1.408(14)
C(3)-H(3B)	0.9900	C(18)-S(1)	1.725(10)
C(4)-C(5)	1.532(12)	C(19)-C(20)	1.396(14)
C(4)-C(17)	1.563(13)	C(19)-H(19)	0.9500
C(4)-H(4)	1.0000	C(20)-C(21)	1.352(15)
C(5)-C(6)	1.484(13)	C(20)-H(20)	0.9500
C(5)-H(5A)	0.9900	C(21)-C(37)	1.511(16)
C(5)-H(5B)	0.9900	C(21)-S(1)	1.727(12)
C(6)-C(7)	1.394(13)	C(22)-C(23)	1.373(14)
C(6)-C(9)	1.419(13)	C(22)-S(3)	1.717(9)
C(7)-C(22)	1.473(13)	C(23)-C(24)	1.438(15)
C(7)-S(2)	1.721(10)	C(23)-H(23)	0.9500
C(8)-C(9)	1.364(13)	C(24)-C(25)	1.325(14)
C(8)-C(18)	1.442(13)	C(24)-H(24)	0.9500
C(8)-S(2)	1.752(10)	C(25)-C(36)	1.515(16)
C(9)-C(10)	1.513(13)	C(25)-S(3)	1.727(11)
C(10)-C(11)	1.558(13)	C(26)-C(27)	1.371(15)
C(10)-H(10A)	0.9900	C(26)-S(4)	1.757(10)
C(10)-H(10B)	0.9900	C(27)-C(28)	1.445(16)
C(11)-C(12)	1.537(13)	C(27)-H(27)	0.9500
C(11)-H(11)	1.0000	C(28)-C(29)	1.351(15)
C(12)-C(13)	1.522(14)	C(28)-H(28)	0.9500
C(12)-H(12A)	0.9900	C(29)-C(35)	1.515(15)
C(12)-H(12B)	0.9900	C(29)-S(4)	1.713(12)
C(13)-C(14)	1.350(13)	C(30)-C(31)	1.389(15)

 Table A.20.
 Bond lengths [Å] and angles [°] for st-[Me-Th₃-Me]₂.

C(30)-S(6)	1.715(11)	C(6B)-C(7B)	1.375(15)
C(31)-C(32)	1.438(16)	C(6B)-C(9B)	1.456(15)
C(31)-H(31)	0.9500	C(7B)-C(18B)	1.447(15)
C(32)-C(33)	1.329(16)	C(7B)-S(1B)	1.736(11)
C(32)-H(32)	0.9500	C(8B)-C(9B)	1.375(14)
C(33)-C(34)	1.470(18)	C(8B)-C(22B)	1.460(14)
C(33)-S(6)	1.746(12)	C(8B)-S(1B)	1.735(11)
C(34)-H(34A)	0.9800	C(9B)-C(10B)	1.507(13)
C(34)-H(34B)	0.9800	C(10B)-C(11B)	1.556(15)
C(34)-H(34C)	0.9800	C(10B)-H(10C)	0.9900
C(35)-H(35A)	0.9800	C(10B)-H(10D)	0.9900
C(35)-H(35B)	0.9800	C(11B)-C(12B)	1.521(15)
C(35)-H(35C)	0.9800	C(11B)-H(11B)	1.0000
C(36)-H(36A)	0.9800	C(12B)-C(13B)	1.499(13)
C(36)-H(36B)	0.9800	C(12B)-H(12C)	0.9900
C(36)-H(36C)	0.9800	C(12B)-H(12D)	0.9900
C(37)-H(37A)	0.9800	C(13B)-C(14B)	1.358(13)
C(37)-H(37B)	0.9800	C(13B)-C(16B)	1.445(14)
C(37)-H(37C)	0.9800	C(14B)-C(26B)	1.453(16)
C(1B)-O(2B)	1.443(13)	C(14B)-S(5B)	1.722(10)
C(1B)-O(1B)	1.456(14)	C(15B)-C(16B)	1.381(13)
C(1B)-C(4B)	1.497(15)	C(15B)-C(30B)	1.469(14)
C(1B)-C(11B)	1.534(16)	C(15B)-S(5B)	1.727(10)
C(2B)-O(1B)	1.39(2)	C(16B)-C(17B)	1.493(14)
C(2B)-C(3B)	1.47(2)	C(17B)-H(17C)	0.9900
C(2B)-H(2B1)	0.9900	C(17B)-H(17D)	0.9900
C(2B)-H(2B2)	0.9900	C(18B)-C(19B)	1.366(16)
C(3B)-O(2B)	1.401(15)	C(18B)-S(3B)	1.721(12)
C(3B)-H(3B1)	0.9900	C(19B)-C(20B)	1.448(19)
C(3B)-H(3B2)	0.9900	C(19B)-H(19B)	0.9500
C(4B)-C(17B)	1.551(15)	C(20B)-C(21B)	1.321(19)
C(4B)-C(5B)	1.581(16)	C(20B)-H(20B)	0.9500
C(4B)-H(4B)	1.0000	C(21B)-C(36B)	1.50(2)
C(5B)-C(6B)	1.484(15)	C(21B)-S(3B)	1.708(15)
C(5B)-H(5B1)	0.9900	C(22B)-C(23B)	1.372(14)
C(5B)-H(5B2)	0.9900	C(22B)-S(2B)	1.721(10)

C(23B)-C(24B)	1.413(16)	S(6X)-C(29X)	1.68(4)
C(23B)-H(23B)	0.9500	C(27X)-C(28X)	1.17(12)
C(24B)-C(25B)	1.338(15)	C(27X)-H(27X)	0.9500
C(24B)-H(24B)	0.9500	C(28X)-C(29X)	1.37(4)
C(25B)-C(37B)	1.509(16)	C(28X)-H(28X)	0.9500
C(25B)-S(2B)	1.731(11)	C(29X)-C(35X)	1.57(4)
C(26B)-C(27B)	1.49(7)	C(35X)-H(35D)	1.4458
C(26B)-S(6B)	1.56(3)	C(35X)-H(35G)	0.9800
C(26B)-S(6X)	1.585(15)	C(35X)-H(35H)	0.9800
C(26B)-C(27X)	1.63(10)	C(35X)-H(35I)	0.9800
C(30B)-C(31B)	1.404(13)		
C(30B)-S(4B)	1.682(11)	O(1)-C(1)-O(2)	105.5(7)
C(31B)-C(32B)	1.332(16)	O(1)-C(1)-C(11)	108.8(7)
C(31B)-H(31B)	0.9500	O(2)-C(1)-C(11)	109.9(8)
C(32B)-C(33B)	1.297(19)	O(1)-C(1)-C(4)	108.3(7)
C(32B)-H(32B)	0.9500	O(2)-C(1)-C(4)	106.5(7)
C(33B)-C(34B)	1.51(2)	C(11)-C(1)-C(4)	117.3(8)
C(33B)-S(4B)	1.713(15)	O(1)-C(2)-C(3)	108.5(11)
C(34B)-H(34D)	0.9800	O(1)-C(2)-H(2A)	110.0
C(34B)-H(34E)	0.9800	C(3)-C(2)-H(2A)	110.0
C(34B)-H(34F)	0.9800	O(1)-C(2)-H(2B)	110.0
C(36B)-H(36D)	0.9800	C(3)-C(2)-H(2B)	110.0
C(36B)-H(36E)	0.9800	H(2A)-C(2)-H(2B)	108.4
C(36B)-H(36F)	0.9800	O(2)-C(3)-C(2)	103.6(11)
C(37B)-H(37D)	0.9800	O(2)-C(3)-H(3A)	111.0
C(37B)-H(37E)	0.9800	C(2)-C(3)-H(3A)	111.0
C(37B)-H(37F)	0.9800	O(2)-C(3)-H(3B)	111.0
S(6B)-C(29B)	1.83(5)	C(2)-C(3)-H(3B)	111.0
C(27B)-C(28B)	1.42(7)	H(3A)-C(3)-H(3B)	109.0
C(27B)-H(27B)	0.9500	C(5)-C(4)-C(1)	113.4(8)
C(28B)-C(29B)	1.39(4)	C(5)-C(4)-C(17)	114.5(8)
C(28B)-H(28B)	0.9500	C(1)-C(4)-C(17)	113.4(7)
C(29B)-C(35B)	1.49(4)	C(5)-C(4)-H(4)	104.7
C(35B)-H(35D)	0.9800	C(1)-C(4)-H(4)	104.7
C(35B)-H(35E)	0.9800	C(17)-C(4)-H(4)	104.7
C(35B)-H(35F)	0.9800	C(6)-C(5)-C(4)	116.5(8)

C(6)-C(5)-H(5A)	108.2	C(14)-C(13)-C(12)	125.3(9)
C(4)-C(5)-H(5A)	108.2	C(16)-C(13)-C(12)	120.2(8)
C(6)-C(5)-H(5B)	108.2	C(13)-C(14)-C(26)	130.5(10)
C(4)-C(5)-H(5B)	108.2	C(13)-C(14)-S(5)	110.6(8)
H(5A)-C(5)-H(5B)	107.3	C(26)-C(14)-S(5)	118.5(8)
C(7)-C(6)-C(9)	112.3(9)	C(16)-C(15)-C(30)	131.5(10)
C(7)-C(6)-C(5)	122.9(9)	C(16)-C(15)-S(5)	112.1(8)
C(9)-C(6)-C(5)	124.5(9)	C(30)-C(15)-S(5)	116.4(8)
C(6)-C(7)-C(22)	131.5(9)	C(15)-C(16)-C(13)	110.9(9)
C(6)-C(7)-S(2)	111.1(7)	C(15)-C(16)-C(17)	125.4(9)
C(22)-C(7)-S(2)	117.3(7)	C(13)-C(16)-C(17)	123.7(9)
C(9)-C(8)-C(18)	132.3(9)	C(16)-C(17)-C(4)	119.2(8)
C(9)-C(8)-S(2)	110.4(7)	C(16)-C(17)-H(17A)	107.5
C(18)-C(8)-S(2)	117.3(7)	C(4)-C(17)-H(17A)	107.5
C(8)-C(9)-C(6)	114.0(8)	C(16)-C(17)-H(17B)	107.5
C(8)-C(9)-C(10)	121.7(9)	C(4)-C(17)-H(17B)	107.5
C(6)-C(9)-C(10)	124.2(8)	H(17A)-C(17)-H(17B)	107.0
C(9)-C(10)-C(11)	120.1(8)	C(19)-C(18)-C(8)	129.5(9)
C(9)-C(10)-H(10A)	107.3	C(19)-C(18)-S(1)	109.1(8)
C(11)-C(10)-H(10A)	107.3	C(8)-C(18)-S(1)	121.4(7)
C(9)-C(10)-H(10B)	107.3	C(20)-C(19)-C(18)	112.7(10)
C(11)-C(10)-H(10B)	107.3	C(20)-C(19)-H(19)	123.7
H(10A)-C(10)-H(10B)	106.9	C(18)-C(19)-H(19)	123.7
C(1)-C(11)-C(12)	113.3(8)	C(21)-C(20)-C(19)	114.9(10)
C(1)-C(11)-C(10)	115.3(7)	C(21)-C(20)-H(20)	122.6
C(12)-C(11)-C(10)	113.5(8)	C(19)-C(20)-H(20)	122.6
C(1)-C(11)-H(11)	104.4	C(20)-C(21)-C(37)	128.9(11)
C(12)-C(11)-H(11)	104.4	C(20)-C(21)-S(1)	110.1(9)
C(10)-C(11)-H(11)	104.4	C(37)-C(21)-S(1)	120.9(9)
C(13)-C(12)-C(11)	116.7(8)	C(23)-C(22)-C(7)	129.7(9)
C(13)-C(12)-H(12A)	108.1	C(23)-C(22)-S(3)	111.0(8)
C(11)-C(12)-H(12A)	108.1	C(7)-C(22)-S(3)	119.1(7)
C(13)-C(12)-H(12B)	108.1	C(22)-C(23)-C(24)	111.1(10)
C(11)-C(12)-H(12B)	108.1	C(22)-C(23)-H(23)	124.4
H(12A)-C(12)-H(12B)	107.3	C(24)-C(23)-H(23)	124.4
C(14)-C(13)-C(16)	114.5(9)	C(25)-C(24)-C(23)	114.7(11)
C(25)-C(24)-H(24)	122.7	C(29)-C(35)-H(35B)	109.5
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C(23)-C(24)-H(24)	122.7	H(35A)-C(35)-H(35B)	109.5
C(24)-C(25)-C(36)	129.1(11)	C(29)-C(35)-H(35C)	109.5
C(24)-C(25)-S(3)	110.6(8)	H(35A)-C(35)-H(35C)	109.5
C(36)-C(25)-S(3)	120.2(9)	H(35B)-C(35)-H(35C)	109.5
C(27)-C(26)-C(14)	131.7(10)	C(25)-C(36)-H(36A)	109.5
C(27)-C(26)-S(4)	109.3(8)	C(25)-C(36)-H(36B)	109.5
C(14)-C(26)-S(4)	119.0(8)	H(36A)-C(36)-H(36B)	109.5
C(26)-C(27)-C(28)	113.0(10)	C(25)-C(36)-H(36C)	109.5
C(26)-C(27)-H(27)	123.5	H(36A)-C(36)-H(36C)	109.5
C(28)-C(27)-H(27)	123.5	H(36B)-C(36)-H(36C)	109.5
C(29)-C(28)-C(27)	113.4(11)	C(21)-C(37)-H(37A)	109.5
C(29)-C(28)-H(28)	123.3	C(21)-C(37)-H(37B)	109.5
C(27)-C(28)-H(28)	123.3	H(37A)-C(37)-H(37B)	109.5
C(28)-C(29)-C(35)	128.0(11)	C(21)-C(37)-H(37C)	109.5
C(28)-C(29)-S(4)	111.3(9)	H(37A)-C(37)-H(37C)	109.5
C(35)-C(29)-S(4)	120.6(8)	H(37B)-C(37)-H(37C)	109.5
C(31)-C(30)-C(15)	125.7(10)	C(2)-O(1)-C(1)	108.5(8)
C(31)-C(30)-S(6)	111.0(8)	C(3)-O(2)-C(1)	107.7(7)
C(15)-C(30)-S(6)	123.2(8)	C(18)-S(1)-C(21)	93.2(5)
C(30)-C(31)-C(32)	111.0(11)	C(7)-S(2)-C(8)	92.2(5)
C(30)-C(31)-H(31)	124.5	C(22)-S(3)-C(25)	92.5(5)
C(32)-C(31)-H(31)	124.5	C(29)-S(4)-C(26)	93.0(5)
C(33)-C(32)-C(31)	115.1(12)	C(15)-S(5)-C(14)	91.9(5)
C(33)-C(32)-H(32)	122.4	C(30)-S(6)-C(33)	92.6(5)
C(31)-C(32)-H(32)	122.4	O(2B)-C(1B)-O(1B)	106.4(8)
C(32)-C(33)-C(34)	129.8(12)	O(2B)-C(1B)-C(4B)	106.9(9)
C(32)-C(33)-S(6)	110.2(10)	O(1B)-C(1B)-C(4B)	109.0(9)
C(34)-C(33)-S(6)	120.0(10)	O(2B)-C(1B)-C(11B)	109.1(9)
C(33)-C(34)-H(34A)	109.4	O(1B)-C(1B)-C(11B)	106.4(9)
C(33)-C(34)-H(34B)	109.5	C(4B)-C(1B)-C(11B)	118.4(9)
H(34A)-C(34)-H(34B)	109.5	O(1B)-C(2B)-C(3B)	107.3(15)
C(33)-C(34)-H(34C)	109.5	O(1B)-C(2B)-H(2B1)	110.3
H(34A)-C(34)-H(34C)	109.5	C(3B)-C(2B)-H(2B1)	110.3
H(34B)-C(34)-H(34C)	109.5	O(1B)-C(2B)-H(2B2)	110.3
C(29)-C(35)-H(35A)	109.5	C(3B)-C(2B)-H(2B2)	110.3

H(2B1)-C(2B)-H(2B2)	108.5	H(10C)-C(10B)-H(10D)	107.4
O(2B)-C(3B)-C(2B)	102.5(13)	C(12B)-C(11B)-C(1B)	113.4(9)
O(2B)-C(3B)-H(3B1)	111.3	C(12B)-C(11B)-C(10B)	115.0(9)
C(2B)-C(3B)-H(3B1)	111.3	C(1B)-C(11B)-C(10B)	112.3(9)
O(2B)-C(3B)-H(3B2)	111.3	C(12B)-C(11B)-H(11B)	105.0
C(2B)-C(3B)-H(3B2)	111.3	C(1B)-C(11B)-H(11B)	105.0
H(3B1)-C(3B)-H(3B2)	109.2	C(10B)-C(11B)-H(11B)	105.0
C(1B)-C(4B)-C(17B)	114.1(10)	C(13B)-C(12B)-C(11B)	120.0(9)
C(1B)-C(4B)-C(5B)	112.9(10)	C(13B)-C(12B)-H(12C)	107.3
C(17B)-C(4B)-C(5B)	114.5(9)	C(11B)-C(12B)-H(12C)	107.3
C(1B)-C(4B)-H(4B)	104.6	C(13B)-C(12B)-H(12D)	107.3
C(17B)-C(4B)-H(4B)	104.6	C(11B)-C(12B)-H(12D)	107.3
C(5B)-C(4B)-H(4B)	104.6	H(12C)-C(12B)-H(12D)	106.9
C(6B)-C(5B)-C(4B)	113.1(10)	C(14B)-C(13B)-C(16B)	112.4(9)
C(6B)-C(5B)-H(5B1)	109.0	C(14B)-C(13B)-C(12B)	123.9(10)
C(4B)-C(5B)-H(5B1)	109.0	C(16B)-C(13B)-C(12B)	123.7(9)
C(6B)-C(5B)-H(5B2)	109.0	C(13B)-C(14B)-C(26B)	129.6(10)
C(4B)-C(5B)-H(5B2)	109.0	C(13B)-C(14B)-S(5B)	112.4(8)
H(5B1)-C(5B)-H(5B2)	107.8	C(26B)-C(14B)-S(5B)	118.0(8)
C(7B)-C(6B)-C(9B)	112.6(10)	C(16B)-C(15B)-C(30B)	130.3(9)
C(7B)-C(6B)-C(5B)	126.2(11)	C(16B)-C(15B)-S(5B)	111.6(8)
C(9B)-C(6B)-C(5B)	121.2(10)	C(30B)-C(15B)-S(5B)	118.1(7)
C(6B)-C(7B)-C(18B)	131.3(10)	C(15B)-C(16B)-C(13B)	111.9(9)
C(6B)-C(7B)-S(1B)	110.7(9)	C(15B)-C(16B)-C(17B)	122.4(9)
C(18B)-C(7B)-S(1B)	118.0(8)	C(13B)-C(16B)-C(17B)	125.5(9)
C(9B)-C(8B)-C(22B)	131.8(10)	C(16B)-C(17B)-C(4B)	121.5(10)
C(9B)-C(8B)-S(1B)	110.5(8)	C(16B)-C(17B)-H(17C)	107.0
C(22B)-C(8B)-S(1B)	117.7(7)	C(4B)-C(17B)-H(17C)	107.0
C(8B)-C(9B)-C(6B)	113.0(9)	C(16B)-C(17B)-H(17D)	107.0
C(8B)-C(9B)-C(10B)	126.4(10)	C(4B)-C(17B)-H(17D)	107.0
C(6B)-C(9B)-C(10B)	120.6(9)	H(17C)-C(17B)-H(17D)	106.7
C(9B)-C(10B)-C(11B)	116.2(9)	C(19B)-C(18B)-C(7B)	125.5(11)
C(9B)-C(10B)-H(10C)	108.2	C(19B)-C(18B)-S(3B)	110.5(10)
C(11B)-C(10B)-H(10C)	108.2	C(7B)-C(18B)-S(3B)	123.8(8)
C(9B)-C(10B)-H(10D)	108.2	C(18B)-C(19B)-C(20B)	111.0(12)
C(11B)-C(10B)-H(10D)	108.2	C(18B)-C(19B)-H(19B)	124.5

C(20B)-C(19B)-H(19B)	124.5	C(33B)-C(32B)-H(32B)	122.5
C(21B)-C(20B)-C(19B)	114.7(14)	C(31B)-C(32B)-H(32B)	122.5
C(21B)-C(20B)-H(20B)	122.7	C(32B)-C(33B)-C(34B)	130.5(15)
C(19B)-C(20B)-H(20B)	122.7	C(32B)-C(33B)-S(4B)	111.1(12)
C(20B)-C(21B)-C(36B)	127.6(14)	C(34B)-C(33B)-S(4B)	118.3(12)
C(20B)-C(21B)-S(3B)	110.7(12)	C(33B)-C(34B)-H(34D)	109.5
C(36B)-C(21B)-S(3B)	121.6(11)	C(33B)-C(34B)-H(34E)	109.5
C(23B)-C(22B)-C(8B)	125.7(10)	H(34D)-C(34B)-H(34E)	109.5
C(23B)-C(22B)-S(2B)	109.6(8)	C(33B)-C(34B)-H(34F)	109.5
C(8B)-C(22B)-S(2B)	124.5(7)	H(34D)-C(34B)-H(34F)	109.5
C(22B)-C(23B)-C(24B)	112.7(11)	H(34E)-C(34B)-H(34F)	109.5
C(22B)-C(23B)-H(23B)	123.7	C(21B)-C(36B)-H(36D)	109.5
C(24B)-C(23B)-H(23B)	123.7	C(21B)-C(36B)-H(36E)	109.4
C(25B)-C(24B)-C(23B)	115.1(11)	H(36D)-C(36B)-H(36E)	109.5
C(25B)-C(24B)-H(24B)	122.5	C(21B)-C(36B)-H(36F)	109.5
C(23B)-C(24B)-H(24B)	122.5	H(36D)-C(36B)-H(36F)	109.5
C(24B)-C(25B)-C(37B)	130.3(11)	H(36E)-C(36B)-H(36F)	109.5
C(24B)-C(25B)-S(2B)	109.4(9)	C(25B)-C(37B)-H(37D)	109.5
C(37B)-C(25B)-S(2B)	120.2(8)	C(25B)-C(37B)-H(37E)	109.5
C(14B)-C(26B)-C(27B)	118(3)	H(37D)-C(37B)-H(37E)	109.5
C(14B)-C(26B)-S(6B)	131.9(16)	C(25B)-C(37B)-H(37F)	109.5
C(27B)-C(26B)-S(6B)	110(4)	H(37D)-C(37B)-H(37F)	109.5
C(14B)-C(26B)-S(6X)	125.3(10)	H(37E)-C(37B)-H(37F)	109.5
C(27B)-C(26B)-S(6X)	9(4)	C(2B)-O(1B)-C(1B)	105.0(12)
S(6B)-C(26B)-S(6X)	102.6(15)	C(3B)-O(2B)-C(1B)	108.3(10)
C(14B)-C(26B)-C(27X)	132(4)	C(8B)-S(1B)-C(7B)	93.2(5)
C(27B)-C(26B)-C(27X)	110(5)	C(22B)-S(2B)-C(25B)	93.2(5)
S(6B)-C(26B)-C(27X)	5(5)	C(21B)-S(3B)-C(18B)	93.1(7)
S(6X)-C(26B)-C(27X)	102(4)	C(30B)-S(4B)-C(33B)	92.0(6)
C(31B)-C(30B)-C(15B)	130.5(9)	C(14B)-S(5B)-C(15B)	91.7(5)
C(31B)-C(30B)-S(4B)	108.3(8)	C(26B)-S(6B)-C(29B)	98(2)
C(15B)-C(30B)-S(4B)	121.1(8)	C(28B)-C(27B)-C(26B)	112(6)
C(32B)-C(31B)-C(30B)	113.6(10)	C(28B)-C(27B)-H(27B)	123.9
C(32B)-C(31B)-H(31B)	123.2	C(26B)-C(27B)-H(27B)	123.9
C(30B)-C(31B)-H(31B)	123.2	C(29B)-C(28B)-C(27B)	115(4)
C(33B)-C(32B)-C(31B)	114.9(14)	C(29B)-C(28B)-H(28B)	122.7

C(27B)-C(28B)-H(28B) 122.7 C(28B)-C(29B)-C(35B) 133(3) C(28B)-C(29B)-S(6B)105(2) C(35B)-C(29B)-S(6B)122(2)C(29B)-C(35B)-H(35D) 109.3 C(29B)-C(35B)-H(35E) 109.6 H(35D)-C(35B)-H(35E) 109.5 C(29B)-C(35B)-H(35F) 109.5 H(35D)-C(35B)-H(35F) 109.5 H(35E)-C(35B)-H(35F) 109.5 C(26B)-S(6X)-C(29X)95.7(13) C(28X)-C(27X)-C(26B) 116(8) C(28X)-C(27X)-H(27X) 121.8 C(26B)-C(27X)-H(27X) 121.8 C(27X)-C(28X)-C(29X) 112(6) C(27X)-C(28X)-H(28X) 124.0 C(29X)-C(28X)-H(28X) 124.0 C(28X)-C(29X)-C(35X) 120(3) C(28X)-C(29X)-S(6X)113(2) C(35X)-C(29X)-S(6X)127(3) C(29X)-C(35X)-H(35D) 99.0 C(29X)-C(35X)-H(35G) 109.6 H(35D)-C(35X)-H(35G) 67.8 C(29X)-C(35X)-H(35H) 109.3 H(35D)-C(35X)-H(35H) 150.3 H(35G)-C(35X)-H(35H) 109.5 C(29X)-C(35X)-H(35I) 109.5 H(35D)-C(35X)-H(35I) 50.0 H(35G)-C(35X)-H(35I) 109.5 H(35H)-C(35X)-H(35I) 109.5

Symmetry transformations used to generate equivalent atoms:

	U ¹¹	U ²²	U ³³	U ²³	U13	U12
O(1)	32(5)	25(4)	28(4)	16(3)	10(3)	11(3)
O(2)	31(5)	24(4)	28(4)	12(3)	7(3)	13(3)
S (1)	28(2)	54(2)	30(2)	22(1)	-2(1)	-2(1)
S(2)	19(2)	25(1)	30(2)	16(1)	-1(1)	2(1)
S(3)	29(2)	23(1)	42(2)	13(1)	5(1)	3(1)
S(4)	40(2)	52(2)	25(2)	2(1)	5(1)	-6(2)
S(5)	30(2)	31(2)	24(2)	13(1)	3(1)	-2(1)
S(6)	27(2)	33(2)	50(2)	20(1)	5(1)	-3(1)
O(1B)	80(7)	41(5)	23(4)	1(4)	-1(4)	19(5)
O(2B)	101(8)	20(4)	26(4)	-1(3)	-5(4)	16(4)
S(1B)	22(2)	40(2)	48(2)	23(1)	8(1)	6(1)
S(2B)	32(2)	34(2)	32(2)	10(1)	2(1)	11(1)
S(3B)	33(2)	51(2)	81(2)	38(2)	-15(2)	1(2)
S(4B)	38(2)	44(2)	70(2)	11(2)	4(2)	8(2)
S(5B)	29(2)	21(1)	44(2)	5(1)	-7(1)	3(1)
S(6B)	29(4)	30(8)	58(4)	9(5)	7(3)	9(5)
S(6X)	31(4)	27(3)	22(4)	2(2)	-3(3)	5(3)

Table A.21. Anisotropic displacement parameters $(Å^2 x \ 10^3)$ for *st*-[Me-Th₃-Me]₂. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}$]

	Х	У	Z	U(eq)	
H(2A)	3848	7981	723	78	
H(2B)	2917	7325	189	78	
H(3A)	4019	6661	-617	61	
H(3B)	4921	7122	72	61	
H(4)	2566	5399	752	24	
H(5A)	2955	4043	782	27	
H(5B)	3851	4487	357	27	
H(10A)	5704	5623	1032	28	
H(10B)	6096	6055	1985	28	
H(11)	5151	7004	1551	25	
H(12A)	5112	7277	2935	29	
H(12B)	4000	7329	2623	29	
H(17A)	2332	6196	2136	29	
H(17B)	2033	5140	1973	29	
H(19)	7611	5377	1898	35	
H(20)	9019	5744	2925	38	
H(23)	2017	3209	1681	38	
H(24)	1218	1619	1295	39	
H(27)	6543	6883	3696	40	
H(28)	7477	7936	4961	50	
H(31)	2822	3464	3744	47	
H(32)	1172	2536	3603	47	
H(34A)	-612	2424	2786	95	
H(34B)	-848	3346	2609	95	
H(34C)	-890	3237	3542	95	
H(35A)	7299	8652	6555	74	
H(35B)	6467	8094	6950	74	
H(35C)	6197	8945	6656	74	
H(36A)	2684	-40	1433	83	
H(36B)	2618	-130	446	83	
H(36C)	1635	-25	972	83	

Table A.22. Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters(Å²x 10³) for *st*-[Me-Th₃-Me]₂.

H(37A)	9514	5706	4445	75
H(37B)	9092	4719	4497	75
H(37C)	8574	5576	4992	75
H(2B1)	11372	6561	-1181	133
H(2B2)	10260	6800	-1302	133
H(3B1)	9908	5386	-1221	81
H(3B2)	10850	5476	-575	81
H(4B)	9012	7463	-180	42
H(5B1)	7725	7437	676	48
H(5B2)	8247	6565	696	48
H(10C)	9572	6124	1482	35
H(10D)	10393	6544	2235	35
H(11B)	11147	6593	1033	40
H(12C)	11757	7837	2036	35
H(12D)	11734	8073	1160	35
H(17C)	10061	8761	328	43
H(17D)	8975	8907	654	43
H(19B)	6247	8721	3232	61
H(20B)	5036	9513	2623	85
H(23B)	9290	8402	4851	50
H(24B)	10642	8181	5757	50
H(31B)	9157	10627	759	12
H(32B)	7794	11484	917	82
H(34D)	6941	12323	2826	150
H(34E)	6202	11400	2584	150
H(34F)	6367	11977	1920	150
H(36D)	5068	9291	421	133
H(36E)	5504	10270	1002	133
H(36F)	4484	9772	1220	133
H(37D)	12428	7617	5662	73
H(37E)	12813	7350	4728	73
H(37F)	12186	6603	5076	73
H(27B)	11152	9859	4480	135
H(28B)	12605	9774	5370	42
H(35D)	14563	9349	5149	100
H(35E)	14844	9044	4186	100

H(35F)	14268	8327	4600	100	
H(27X)	13164	8555	2690	24	
H(28X)	14180	8907	3818	45	
H(35G)	13718	9116	5564	130	
H(35H)	13236	10044	5843	130	
H(35I)	14279	10010	5398	130	

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VITA

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