THE STRUCTURE DETERMINATION OF

BICYCLO [2.2.2] OCTYL-2 p-BROMOBENZENESULFONATE

IN THE SOLID PHASE

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

By

Patricia Westbrook Mueller

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

Georgia Institute of Technology

March, 1973

THE STRUCTURE DETERMINATION OF

BICYCLO [2.2.2] OCTYL-2 p-BROMOBENZENESULFONATE

IN THE SOLID PHASE

Approved:

C. L. Liotta, Chairman

J. W. Bertrand

R. H. Felton

Date approved by Chairman: 3/12/73

ACKNOWLEDGMENTS

The author would like to thank Dr. C. L. Liotta for suggesting the problem and especially Dr. J. A. Bertrand whose guidance and patience made this study possible. The author gratefully acknowledges the assistance of the members of the research groups of Dr. Bertrand and Dr. Liotta. The author also wishes to thank Dr. R. H. Felton for reading the final manuscript.

The author wishes to express appreciation to her husband Heinz for his love and understanding during the course of her graduate studies.

The author would also like to thank the Georgia Institute of Technology for financial assistance.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

The molecular structure of crystalline bicyclo [2.2.2]
octyl-2 p-bromobenzenesulfonate has been studied by examin-
ation of x-ray diffraction data collected using zirconium
filtered molybdenum Kα radiation with the object of dis-
covering if the bicycloöctane group was twisted about the
bridgehead-bridgehead axis. The molecule crystallized in
space group P2$_1$ with four molecules per unit cell. The
best model attained indicated some twist, although problems
in the data set did not allow sufficiently accurate refine-
ment for the angle of twist to be determined conclusively.

CHAPTER I

INTRODUCTION

In the past decade there has been considerable interest in the conformation of bicyclo [2.2.2] octane and its derivatives. Studies of the parent compound itself and of bicyclo [2.2.2] octane systems substituted at one or both bridgehead carbons have been undertaken but nothing has been reported concerning the conformation of bridge substituted bicyclo [2.2.2] octane systems. One reason for interest in such systems is their usefulness in the study of electrostatic effects in organic molecules. A system whose geometry is accurately known is advantageous in the study of the transmission of the effect of a dipole upon a reaction center through space because the distance, $\vec{R}$, from the center of a dipole to the reaction center and the angle (θ) which $\vec{R}$ makes with the direction of the bond moment must be known in order to calculate the log of the ratio of the dissociation constant of the substituted compound to that of the parent hydrocarbon [log (K_X/K_H)] according to the expression:

$$\log \frac{K_X}{K_H} = \frac{e\mu \, \cos \, \theta}{2.3 \, kTR^2 D_E}$$

where e is the electronic charge, μ the difference in group or bond moment between the substituent and hydrogen, D_E is the effective dielectric and KT has its usual meaning.

The studies which have been carried out on bicyclo [2.2.2] octane and related bridgehead substituted compounds have differed in their conclusions. Some favored a rigid molecule with the cis hydrogens on each bridge eclipsed. Some favored a molecule twisted about the bridgehead - bridgehead axis. Still others concluded that there are two energy minimums corresponding to the twisted conformations separated by an energy hump which is much lower than the energy available at room temperature. The results are inconclusive and still a matter for argument.

One of the earliest conformational studies of a bicyclo [2.2.2] octane compound was the analysis of the microwave spectrum of 1-bromo and 1-chlorobicyclo [2.2.2] octane by Nethercot and Javan[1]. They concluded that if there were an angle of twist about the symmetry axis, it was small, 0° ± 4°. Somewhat later Turner, Meador, and Winkler[2] determined the heats of hydrogenation of bicyclo [2.2.2] octadiene and bicyclo [2.2.2] octene. They considered the heat of hydrogenation of bicyclooctene to bicyclooctane (-28.3 kcal/mole) to be suprisingly high in view of the two 1:2- and two 1:3- eclipsed hydrogen interactions which are introduced. One explanation which they

suggested was that a twist about the central axis accompanied the hydrogenation process, and thus somewhat relieved the interactions and accounted for a larger total energy change. They favored, however, an alternative explanation in light of the heat of hydrogenation of bicyclooctadiene to bicyclooctene (28.0 kcal/mole) which they considered also abnormally high. They suggested that if twisting of bicyclooctene were also permitted there would be an increase in torsional strain of the double bond which would cause an increase in the heat of hydrogenation of this substance. There would also be an increase in the heat of hydrogenation of bicyclooctadiene to bicyclooctene because the twisting in the product would relieve the two 1:2- and two 1:3- hydrogen-hydrogen interactions introduced. In either case they favored some degree of twisting about the central axis of bicyclooctane. They maintained that twisting to about 10° could be accommodated without distortion of bond angles.

Macfarlane and Ross[3] then analyzed the vibrational spectrum of bicyclo [2.2.2] octane. They predicted eight fundamentals active in both the infrared and the Raman region for bicyclooctane with D_{3h} symmetry (cis hydrogens eclipsed), and sixteen active in both regions for bicyclooctane with D_3 symmetry (twisted). They found only eight coincidences between Raman and vapour or solution infrared frequencies. They concluded that the agreement of the

number of coincidences and the comparative simplicity of the spectrum were compatable with the D_{3h} conformation. However, they recognized that if the skeletal twisting were slight the breakdown of selection rules would be inconsiderable and the spectral consequences would be difficult to recognize. They, therefore, concluded that if there is twisting it must be slight.

The first attempt to evaluate angle strain effects by implicit calculation and thus determine the conformation of bicyclo [2.2.2] octane was made by Gleicher and Schleyer[4]. Using the Westheimer approach the total strain energy was considered to be the sum of various independent strain-producing mechanisms, as expressed in terms of energy according to the following equation:

$$E_{total\ strain} = E_{bond\ length\ strain}$$

$$+ E_{bond\ angle\ strain} + E_{torsional\ strain}$$

$$+ E_{nonbonded\ interaction\ strain}$$

An initial geometry was assumed for the molecule, the strain energy was calculated for this geometry, and then the coordinates of each atom were varied until an energy minimum was reached. Contrary to the conclusions which Turner, Meador, and Winkler[2] drew from their heats of hydorgenation data,

Gleicher and Schleyer's calculations favored the conformation having D_{3h} symmetry. They also stated that rather than helping the torsional strain as Turner, Meador, and Winkler proposed, twisting about the central axis might increase the strain. Gleicher and Schleyer also considered the bridgehead-bridgehead nonbonded repulsion to be of importance. They concluded that if the molecule were twisted the internuclear distance between bridgeheads would be shorter, thus increasing the already appreciable nonbonded repulsions.

One of the first important x-ray analyses carried out on a bicyclo [2.2.2] octane system was done by Ermer and Dunitz[5] on bicyclo [2.2.2] octane-1, 4-dicarboxylic acid. They found that the crystals were monoclinic, in space group $P2_1/c$ and had four molecules per unit cell. They observed about 1150 reflections and refined to R = 0.066. Their final structure indicated no significant deviation from D_{3h} symmetry in the carbon skeleton, and they found good agreement with the chemically equivalent bond distances from the calculations of Gleicher and Schleyer[4]. The conclusion that the D_{3h} symmetry arises neigher from rapid interconversion of the two D_3 enantiomers nor from disorder caused by random occupation of the molecular sites by D_3 enantiomers was supported by nearly spherical electron-density maxima corresponding to the methylene carbon atoms. Also, the absolute entropy calculations of Amzel, Cucarella and Becka[6] indicate that there is no residual entropy, "thus excluding the possibility

of a diffraction D_{3h} symmetry being due to the coexistence

of the two twisted D_3 forms at low temperatures[6]." However,

the results of the x-ray analysis of 1-p-bromobenzenesulpho-

nyloxymethylbicyclo [2.2.2] octane (I) carried out by

R — 1 ⟨ 2 3 / 6 5 ⟩ 4 / 7 8
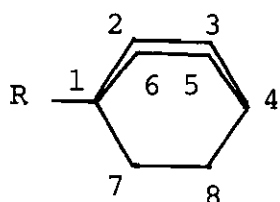
I, R = Br · $C_6H_4SO_2$ O CH_2

II, R = H

Cameron, Ferguson, and Morris[7] indicated D_3 rather than D_{3h}

symmetry. The group of atoms C(2) C(6) C(7) was rotated 3°

about the C(1) . . . C(4) axis with respect to the C(3) C(5)

C(8) group. This twist results in the following torsional

angles: 4.7° at C(2) - C(3), 5.1° at C(5) - C(6), and 5.4°

at C(7) - C(8), all significantly non-zero. The fact that

the 1,4 non-bonded distances, C(2) . . . C(5), C(3) . . .

C(7), and C(6) . . . C(8), are all approximately equal and

significantly shorter than the analogous 1,4 non-bonded dis-

tances, C(2) . . . C(8), C(3) . . . C(6), and C(5) . . .

C(7), also supports D_3 symmetry. The crystals were monoclinic,

in space group $P2_1/c$, and had four molecules per unit cell.

There were 1715 data and the refinement was carried out to

R = 0.104. The observation was made that the structure was

determined for a solid and the probable low energy barrier

to bridge flipping in the bicyclooctane part of the molecule

would lead to a conformational mixture in solution. Ermer

and Dunitz[8] then calculated a potential energy surface for

bicyclo [2.2.2] octane using semi-empirical potential functions, assuming D_3 symmetry. Their calculations indicated that the energy minimum might be slightly displaced from D_{3h} symmetry, but with a barrier between the two minima of only approximately 0.1 kcal/mole. They then concluded effective D_{3h} symmetry at all temperatures as far as diffraction methods were concerned.

Wong and Westrum[9] calculated the enthalpies of (hypothetical) hydrogenation of bicyclo [2.2.2] octane to ethylcyclohexane and of ethylcyclohexane to n-octane from the standard enthalpies of formation of the compounds. From these values they calculated the strain energy of bicyclo [2.2.2] octane (liquid) to be approximately 9.2 kcal/mole. They suggested that this strain energy can be explained by three pairs of eclipsed hydrogens as approximated from the internal rotation energy barrier of ethane to be 8.7 kcal/mole[9]. This would be the case in a molecule of the compound possessing D_{3h} symmetry.

A gas electron diffraction study of bicyclo [2.2.2] octane was carried out by Yokozeki, Kuchitsu, and Morino[10]. Their results supported the semiempirical calculation of Ermer and Dunitz[8]. They found that the shape of the potential energy function derived from their analysis was significantly dependant on assumptions about the force constant for the torsional motion about the C(2) - C(3), C(5) - C(6), and

C(7) - C(8) bonds of II. The most realistic of the potential functions used gave a potential hump of 75 ± 100 cal/mole at the D_{3h} position and a broad double minimum at about $\phi = 11°$, where ϕ is the dihedral angle between the C(1) - C(2) - C(3) and C(2) - C(3) - C(4) planes. The analysis showed a class-ical turning point (the angle at which the potential energy is comparable with thermal energy at room temperature) of 21.5° ± 0.5° and a rms angle of 12.0° ± 1.5° in terms of ϕ, and a classical turning point of 12.8° ± 0.3° and a rms angle of 7.2° ± 0.9° in terms of the angle of twist τ (the dihedral angle between the C(1) - C(2) - C(4) and C(1) - C(3) - C(4) planes). In general the study concluded that the molecule has a "floppy structure in thermal equilibrium as regards the twisting motion,[10]" and because the potential hump at the D_{3h} position is probably much lower than the thermal energy at room temperature the "molecule may be said to have a 'quasi-D_{3h} structure'[10]."

This view of bicyclo [2.2.2] octane is supported by the microwave spectrum of 1-fluorobicyclo [2.2.2] octane and the review of the microwave spectrum of 1-chlorobicyclo [2.2.2] octane analyzed by Horota[11]. The analysis of the spectrum of the fluoro compound indicated that there were two nearly equally intense strong lines and there was a progression, which was regular on the high-frequency side of the strong lines, and which became irregular near the ground-state line. These features indicated to Hirota that the spectrum was

indicative of a double-minimum potential. The final value of the potential hump between the two minima, V_O, was determined to be 191 ± 52 cal/mole and the equilibrium torsional angle, ϕ_O, to be $16.4° \pm 2.6°$. The spectrum of the chloro compound was reanalyzed and a double minimum potential for the torsional motion was also indicated. The calculated values for V_O and ϕ_O based on the spectrum of the chloro compound were respectively 134 ± 67 cal/mole and $16.2° \pm 4°$. The values for the two compounds agreed within experimental error although the chloro potential barrier seemed to be somewhat lower.

In conclusion, studies have been carried out which provide evidence for each of the three possible conformations of bycyclo [2.2.2] octane to the exclusion of the others, although the evidence does seem to favor either D_{3h} symmetry or a double minimum with the twisted conformers in thermal equilibrium. Also, there has been little definitive work done at all on bridge-substituted derivatives of bicyclo [2.2.2] octane. To date the matter remains unsettled and it was the purpose of this study to shed more light on the subject.

CHAPTER II

INSTRUMENTATION

Melting points were taken with an instrument from Mel-Temp. A Roto-Vac-Flash Evaporator from Buchler Instruments was used for solvent evaporation.

Initial crystal alignment and orientation were achieved using a Mark II Precession Camera and a Picker X-Ray Generator with a Dunlee molybdenum fine focus x-ray tube. The intensity data was collected with a Picker Four Circle Automated Diffractometer coupled with a modified IBM 026 Keypunch. Zirconium filtered molybdenum $K\alpha$ radiation ($\lambda = 0.7107$) was used in the collection of intensity data. For the final data set, a crystal was placed in a glass capillary which was sealed and mounted on a STOE Eucentric Goniometer Head, 63.97 mm, with locks. The Burroughs 5500 and the Univac 1108 computers were used for computations.

CHAPTER III

EXPERIMENTAL

Preparation of Compound and Analysis

Preparation of Bicyclo [2.2.2] octyl-2 p-bromobenzenesulfonate

Bicyclo [2.2.2] octanol-2 was synthesized by the method of Brown and Geoghegan[12]. In a 125 ml erlenmeyer flask, fitted with a magnetic stirrer, was placed 2.94 g (9.24 mmoles) of mercuric acetate. To this flask was added 9.24 ml of water, followed by 9.24 ml of tetrahydrofuran. At this point a yellow suspension formed; 0.976 g of bicyclŏoctene (9.24 mmoles) was then added. The yellow color faded after the mixture stirred five minutes; 9.24 ml of 3.0 M sodium hydroxide were added, followed by 9.24 ml of 0.5 M sodium borohydride in 3.0 M sodium hydroxide. Upon addition of the sodium hydroxide, the yellow color returned, and upon addition of the sodium borohydride mixture, a dark gray-black color formed indicating the formation of mercury. The mercury was allowed to settle and the tetrahydrofuran and water layers were then decanted. Sodium chloride was added to saturation and the two layers separated in a separatory funnel. The tetrahydrofuran layer was then dried over magnesium sulfate, and filtered. The solvent evaporated leaving a crude crystalline solid. After one recrystallization from pentane a

melting point of 178.5° - 179.5°C was obtained for the alcohol, corresponding to a yield of 0.6067 g.

According to the procedure of Walborsky, Baum, and Youssef[13], 1.30 g of recrystallized p-bromobenzenesulfonyl-chloride was added to 0.60 g of bicyclo [2.2.2] octanol-2 dissolved in 3 ml of anhydrous pyridine while stirring and cooling in an acetone-water-ice bath. The reaction mixture was placed in a freezer for fifty minutes and then moved to the warmer compartment of the refrigerator for approximately 64.5 hours. The mixture was then poured over ice (10 ml) and water (5 ml) and stirred in a acetone-water-ice bath. When the ice had amost melted the mixture was filtered and the solid filtrate was placed in a dessicator to dry. This procedure yielded 0.3352 g of crude product with a melting point of 78° - 79.5°C. The crude bicyclo [2.2.2] octyl-2 p-bromobenzenesulfonate was recrystallized from petroleum ether by slow growth from solvent evaporation over a period of six days. The pure crystals used in the final collection of x-ray data gave a melting point of 83° - 84°C.

Carbon, Hydrogen, Sulfur Analysis

A carbon, hydrogen, and sulfur analysis was conducted on the crystals by Atlantic Microlab, Inc., Atlanta, Georgia. The calculated weight per cents were %C = 48.70 per cent, %H = 4.93 per cent, and %S = 9.28 per cent. The experimental weight per cents were %C = 48.66 per cent, %H = 4.94 per cent,

and %S = 9.31 per cent.

Crystallographic Study

Calculations

The calculations were carried out with the aid of several computer programs including modified versions of F. L. Carter's program for calculating diffractometer settings[14]; Zalkin's FORDAP Fourier summation program[15]; a direct rewrite of the Ibers/Doedens program RBANG[16]; BECLS(6)[17], a locally modified version of the Ibers/Doedens program NUCLS5, which is a highly modified version of ORFLS[18]; Busing – Martin – Levy's ORFFE[19]; Johnson's ORTEP thermal ellipsoid plotting program[20]; and locally written programs for data reduction. The program RBANG defines a set of orthogonal axes from the crystal axes and provides the orientation angles phi, theta, and rho for a group of atoms to be refined as a rigid body to be used as input for BECLS(6). BECLS(6) allows refinement of individual atoms and/or rigid groups.

Structure Elucidation of Bicyclo [2.2.2] octyl-2 p-bromobenzenesulfonate

The crystals grown in petroleum ether were cut to adequate size for the space group determination and the data collection. The space group was determined using a crystal mounted on a glass rod attached to the goniometer head so that the b* axis was coincident with the spindle axis of the precession camera. The space group indicated by the precession photographs, $P2_1/c$, No. 14[21], (0k0, k = 2n; h0l, l = 2n),

was later found to be in error because the h0l reflections

where l ≠ 2n were weak and were not visible on the photo-

graphs. The space group was later found to be $P2_1$, No. 4^{21},

(0k0, k = 2n), from diffractometer data. It was discovered

that the crystal reacted both with the ethyl acetate in cer-

tain glues and with the water vapor in the air at room temp-

erature. Therefore, the crystal was mounted in a sealed

glass capillary of approximately 0.5 mm diameter. This capil-

lary was then mounted on the goniometer head. Under these

conditions the crystal still decomposed slowly at room temp-

erature in the x-ray beam. Three sets of data were collected

or partially collected because of mounting problems and instru-

ment malfunction. The final set, Data III, was used for

the solution of the structure. The nearly cubical crystal

used in collecting Data III had been cut from a larger cry-

stal and had dimensions of 0.45 x 0.50 x 0.35 mm. The b*

axis was coincident with the φ-axis of the diffractometer.

After approximate alignment on the precession camera the cry-

stal was realigned on the Picker four-circle diffractometer

according to published instructions[22]. The four angles (φ,

×, ω and 2θ) which define the position of the crystal and

detector so that the intensity of a reflection can be meas-

ured were determined for 10 reflections and the angle set-

tings for the data collection were calculated. The limits

set on the Carter program were H from -10 to 10, K from zero

to 12, L from zero to 12. However, all peaks of significant

intensity were found to be within a range of θ from zero to 25°, or diffractometer angle 2θ from 180° to 230°. The cell parameters calculated by least squares treatment of the defining angles of 22 reflections, using the crystal aligned first (Data I), were a = 10.150(3) Å, b = 12.415(3) Å, c = 13.060(4) Å, α = 90.00°, β = 117.11(1)°, γ = 90.00°, and the cell volume = 1465.06 Å^3 at 25°C using molybdenum Kα radiation (λ = 0.7107 Å). The density calculated from the cell volume assuming four molecules per unit cell, 1.56 g/cm^3, agreed well with the density calculated by the flotation method, 1.54 g/cm^3.

The intensities were measured with a scintillation counter mounted 26 cm from the crystal, and they were collected by the θ-2θ scan technique at a scan rate of 1° per minute. A symmetrical 2° scan was taken about the calculated 2θ angle for each reflection, and stationary background counts of 20 seconds were taken at the beginning (B1) and the end (B2) of the 2° scan. The scan of each reflection was monitored by a strip recorder, and in some cases Kβ peaks were observed. When it was possible to exclude the Kβ peak, 0.5 degree was removed from the scan and the background counts were reduced to 15 seconds each. Calibrated copper attenuators were used in the data collection and the threshold point was set so that the counting rate would not exceed 10^4 counts per second. The pulse height analyzer was set for approximately a 90 per cent window, centered on the

molybdenum Kα peak. Two standard reflections (3 3 0 and 0
11 0) were scanned approximately every 35 reflections. Reflec-
tion 3 3 0 was used to monitor the alignment and the decom-
position of the crystal, and 0 11 0 (a systematically absent
reflection) was used to check for false intensity caused by
electrical noise; these reflections, which were repeated dur-
ing the data collection, were averaged. The intensity of
the standard reflection, 3 3 0, decreased significantly dur-
ing the data collection period due to decomposition. The
data set was corrected for this loss of intensity by multi-
plying the intensity of each reflection (corrected for back-
ground) by a correction factor, which was equal to the inten-
sity (corrected for background) of the initial standard
reflection (3 3 0) divided by the intensity (corrected for
background) of the standard (3 3 0) immediately preceding.
The correction for background was made according to the fol-
lowing formula:

$$I = CT - 0.5(t_c/t_b)(B1 + B2)$$

where I is the corrected intensity, CT is the total integrated
peak count, t_c is the scan time, and t_b is the counting time
of each background (either B1 or B2). A standard deviation
for each reflection was calculated according to the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B1 + B2) + (pI)^2]^{1/2}$$

where $\sigma(I)$ is the standard deviation and p, which accounts for unknown random errors, equals 0.02. Initially, 771 reflections were accepted on the basis that the intensity (I) was greater than three times the standard deviation. Later, four reflections were rejected because of irregular, or very high backgrounds. The intensities were corrected for lorentz and polarization effects, but not for absorption effects. The linear absorption coefficient, μ, was calculated to be 31 cm^{-1} according to the formula

$$\mu = \frac{n}{V} \sum_{i=1}^{N} [(\mu_a)A]_i$$

where n is the number of molecules per unit cell, V is the volume of the unit cell, N is the number of different types of atoms in the molecule, μ_a is the atomic absorption coefficient, and A is the number of atoms of type a.

The two independent bromine atoms and the two independent sulfur atoms were located from a three dimensional Patterson synthesis using Data I. The reflections collected in Data I were found to have incorrect intensities due to an instrument malfunction which caused electrical noise to

be recorded as intensity. The remaining structure was derived from suceeding electron density maps based on Data III. The carbon atoms in the two phenyl rings were located and refined as rigid groups; the oxygen atoms were located and their coordinates refined. Atoms in the vicinity of the bicyclo-öctanes were found and were refined as rigid groups. The structure was refined with weights equal to one resulting in a conventional R_1 value ($R_1 = \Sigma ||F_O| - |F_C||/\Sigma |F_O|$) of 0.200. A weighting scheme based on counting statistics (w = $4I/[\sigma(I)]^2$) was introduced and R_1 and R_2 ($R_2 = [\Sigma w(|F_O| - |F_C|)^2/\Sigma w(|F_O|)^2]^{1/2}$) reached values of 0.116 and 0.122 respectively. Each bicycloöctane group was then refined as two groups, each consisting of a bridgehead carbon and the three bonded carbons; R_1 and R_2 then equaled 0.111 and 0.112 respectively. The bicycloöctane atoms were then allowed to refine individually and bond distances were calculated. When the bond distances were found to be unsatisfactory disorder was suspected. Peaks were found in the electron density map in the vicinity of one of the bicycloöctane groups (BIC2) and one in the vicinity of the oxygens of the same molecule. The structure was refined, assuming disorder, with fractional atoms at the positions observed, and although the R values were lower ($R_1 = 0.096$, $R_2 = 0.090$), the bond distances did not improve and no alternate (disordered) group could be clearly seen. Different sets of eight carbon atoms were

chosen for BIC2 and they refined to essentially the same positions. The structure was then refined with the normal number of carbon atom positions in the bicycloöctane groups and one of the three oxygen positions in BIC2 split between two positions. The refinement of scale factor, the coordinates of each atom, and the individual isotropic temperature factors (122 variable parameters) was continued until no parameter varied more than 22.2 per cent of the estimated standard deviation; R_1 and R_2 converged to values of 0.0984 and 0.0929 respectively (Run 21A). When the structure had been refined with only one position for each atom (118 variable parameters), R_1 and R_2 converged to values of 0.1016 and 0.0975 respectively, and no parameter varied more than 67.6 per cent of the estimated standard deviation (Run 24A).

The scattering factors tabulated by Ibers[21] were employed for all atoms in the structure factor calculations.

CHAPTER IV

RESULTS

The observed and calculated structure factors for the 767 nonzero, unique reflections are given in Table 1.

The positional and isotropic thermal parameters with their standard deviations in parentheses are listed in Table 2. These values are taken from the last cycle of least-squares refinement with one position per atom (Run 24A). Group isotropic thermal parameters are listed for the phenyl groups. The standard deviations listed for the phenyl carbons are the group origin standard deviations.

Table 1. Observed and Calculated Structure Factors for Bicyclo [2.2.2] octyl-2 p-bromobenzenesulfonate

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
L= 0				L= 1				5	4	35	36	-3	11	17	15
								6	4	16	21	-1	11	19	20
2	0	222	209	-7	0	25	21	7	4	15	12	2	12	13	10
6	0	23	23	-5	0	32	31	-9	5	15	13	L= 2			
7	0	10	8	-1	0	45	83	-7	5	12	9	-8	0	24	23
8	0	21	24	1	0	24	11	-4	5	22	20	-4	0	66	63
10	0	13	12	3	0	62	49	-3	5	58	56	-2	0	17	22
1	1	35	37	5	0	35	33	-2	5	71	66	0	0	106	103
2	1	9	28	7	0	14	14	-1	5	70	68	2	0	105	92
3	1	103	101	-5	1	13	17	0	5	54	48	4	0	21	24
4	1	15	16	-4	1	48	42	1	5	54	52	-7	1	26	25
5	1	57	59	-3	1	19	24	2	5	84	73	-6	1	12	16
6	1	14	13	-2	1	49	50	3	5	26	28	-5	1	46	46
0	2	29	32	-1	1	24	27	4	5	28	28	-4	1	29	30
2	2	91	87	0	1	40	45	-7	6	15	15	-3	1	56	54
3	2	52	56	1	1	79	65	-6	6	22	23	-2	1	54	56
4	2	47	46	2	1	23	22	-5	6	40	41	-1	1	11	15
5	2	13	10	3	1	10	12	-4	6	51	47	0	1	31	37
6	2	11	12	6	1	23	25	-3	6	15	18	1	1	12	7
7	2	15	14	7	1	12	11	-2	6	62	59	2	1	19	21
1	3	55	54	-8	2	12	17	0	6	14	16	3	1	32	34
2	3	39	31	-7	2	30	31	1	6	44	44	5	1	32	34
3	3	92	89	-6	2	10	9	3	6	21	22	7	1	12	16
4	3	59	53	-5	2	55	53	4	6	33	31	-7	2	19	23
5	3	38	40	-4	2	26	28	5	6	12	8	-4	2	11	13
6	3	26	26	-3	2	65	63	6	6	20	18	-3	2	13	13
0	4	27	30	-2	2	40	45	-7	7	12	10	-2	2	77	84
1	4	87	70	-1	2	10	12	-3	7	33	31	-1	2	27	27
2	4	46	39	0	2	8	19	-1	7	49	50	0	2	84	87
3	4	34	36	1	2	94	98	0	7	14	10	1	2	29	31
4	4	11	11	2	2	78	63	1	7	56	52	2	2	63	63
1	5	43	42	3	2	71	71	3	7	27	26	3	2	34	34
2	5	63	56	5	2	25	27	5	7	13	17	4	2	28	25
4	5	39	34	7	2	16	19	-6	8	31	29	-9	3	11	12
6	5	18	14	-8	3	19	20	-5	8	16	16	-7	3	27	29
0	6	36	40	-5	3	21	26	-4	8	27	24	-4	3	47	41
1	6	25	28	-4	3	61	56	-3	8	26	27	-3	3	10	11
3	6	14	16	-2	3	110	121	-2	8	26	26	-2	3	37	44
6	6	11	8	-1	3	16	20	-1	8	19	14	-1	3	23	24
7	6	12	7	0	3	128	121	1	8	13	11	0	3	42	41
2	7	33	29	3	3	26	24	2	8	35	32	1	3	48	45
4	7	21	22	4	3	23	24	4	8	22	18	4	3	15	13
5	7	16	20	5	3	28	27	-4	9	15	11	5	3	35	37
0	8	41	39	6	3	15	22	-3	9	18	17	6	3	19	21
1	8	45	46	-7	4	11	9	-2	9	11	13	-6	4	18	21
2	8	33	30	-6	4	11	10	-1	9	24	23	-4	4	46	40
3	8	19	21	-5	4	39	39	0	9	10	12	-2	4	58	61
1	9	15	7	-4	4	49	46	1	9	31	25	-1	4	61	63
2	9	12	12	-3	4	68	63	2	9	20	20	0	4	59	47
3	9	10	11	-2	4	12	12	3	9	13	15	1	4	34	38
4	9	19	21	-1	4	56	55	-2	10	11	14	2	4	39	31
6	9	18	15	1	4	33	29	-1	10	20	18	6	4	13	18
2	11	17	16	2	4	18	21	0	10	19	16				
4	11	14	14	4	4	27	28	4	10	13	11				

Table 1.   (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
8	4	13	15	3	0	82	80	1	5	60	61	-1	1	38	42
-8	5	14	15	5	0	42	43	2	5	18	12	0	1	13	8
-7	5	12	12	-5	1	14	13	5	5	27	19	1	1	86	85
-6	5	25	26	-4	1	70	74	7	5	14	11	2	1	12	14
-4	5	11	7	-2	1	176	201	-6	6	12	9	3	1	33	35
-2	5	12	22	0	1	134	136	-3	6	25	25	5	1	19	20
0	5	71	59	1	1	31	32	-2	6	22	26	-6	2	32	32
1	5	50	52	2	1	39	41	0	6	51	43	-5	2	12	12
2	5	74	59	3	1	19	21	1	6	9	11	-4	2	42	48
3	5	35	38	4	1	18	19	2	6	31	25	-3	2	38	38
4	5	20	20	6	1	16	17	3	6	26	29	-2	2	48	57
5	5	19	20	-8	2	17	22	-3	7	19	20	-1	2	34	42
-6	6	22	24	-7	2	24	25	-2	7	31	29	0	2	48	51
-5	6	19	19	-6	2	22	24	-1	7	31	30	2	2	14	19
-4	6	32	29	-5	2	61	64	0	7	26	21	3	2	30	30
-3	6	54	56	-4	2	15	22	2	7	13	7	5	2	32	31
-2	6	13	12	-3	2	55	54	3	7	16	14	-8	3	12	11
-1	6	43	41	-2	2	11	12	-6	8	20	20	-7	3	26	29
0	6	19	17	1	2	83	73	-4	8	18	19	-6	3	15	11
1	6	47	43	2	2	38	31	0	8	13	11	-5	3	69	74
2	6	25	20	3	2	69	64	2	8	22	21	-3	3	45	49
-6	7	23	26	4	2	26	26	3	8	10	12	-1	3	19	26
-4	7	14	19	5	2	22	26	4	8	25	24	0	3	46	53
-3	7	16	18	6	2	20	25	5	8	17	13	1	3	37	38
-1	7	14	12	-6	3	21	16	-3	9	33	35	2	3	51	52
0	7	18	19	-5	3	38	43	-2	9	12	12	3	3	42	43
1	7	26	17	-4	3	38	37	-1	9	43	39	4	3	13	13
2	7	38	35	-3	3	73	85	0	9	27	25	5	3	15	16
4	7	51	49	-2	3	50	41	1	9	35	31	-4	4	52	53
5	7	18	16	-1	3	73	64	2	9	15	13	-3	4	19	23
6	7	14	13	0	3	102	89	3	9	11	12	-2	4	51	53
-5	8	15	19	1	3	9	7	-6	10	12	12	-1	4	45	47
-3	8	34	36	2	3	32	30	-4	10	13	13	0	4	50	43
1	8	23	22	4	3	11	17	2	10	22	20	2	4	36	30
-6	9	13	9	5	3	12	9	4	10	14	12	4	4	25	22
-4	9	12	10	6	3	12	11	-3	11	12	11	-8	5	12	12
-2	9	10	13	8	3	11	7	-1	11	28	25	-7	5	22	24
-1	9	20	16	-8	4	11	10	0	11	16	22	-5	5	17	20
0	9	11	12	-7	4	14	10	1	11	20	17	-4	5	39	38
1	9	29	23	-6	4	23	23	3	11	12	6	-3	5	22	23
3	9	10	13	-5	4	14	14					-2	5	18	16
-4	10	10	15	-4	4	47	45		L=	4		-1	5	17	19
-2	10	11	12	-3	4	31	37					2	5	32	30
-1	10	14	15	-1	4	20	23	-6	0	9	9	3	5	16	15
1	10	21	20	0	4	25	23	-4	0	65	67	4	5	21	23
0	11	16	13	1	4	54	52	-2	0	163	161	-6	6	12	8
				2	4	64	52	0	0	51	49	-4	6	29	29
	L=	3		3	4	22	24	4	0	36	31	-3	6	44	43
				4	4	24	25	6	0	22	21	-2	6	33	34
-9	0	22	27	-5	5	19	18	-9	1	18	16	-1	6	34	32
-7	0	40	39	-3	5	39	40	-7	1	31	27	0	6	30	27
-5	0	58	59	-2	5	19	19	-5	1	31	32	1	6	39	38
-3	0	27	41	-1	5	52	50	-3	1	16	17	3	6	24	25
1	0	91	89	0	5	30	32	-2	1	68	62	-6	7	31	30

Table 1. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-4	7	37	41	-2	3	60	55	-2	0	139	132	0	7	12	13
-3	7	14	8	-1	3	11	15	0	0	58	61	1	7	14	12
-1	7	12	19	0	3	21	22	4	0	12	13	2	7	22	21
0	7	22	22	6	3	16	17	-9	1	19	22	3	7	21	16
1	7	11	20	-7	4	20	19	-8	1	16	19	-5	8	21	25
2	7	22	19	-6	4	16	16	-7	1	39	41	-4	8	18	19
4	7	20	18	-2	4	24	26	-5	1	43	47	-3	8	22	23
-5	8	16	17	-1	4	37	44	-3	1	12	16	-2	8	21	19
-4	8	13	13	1	4	51	50	-2	1	15	13	-1	8	16	13
-3	8	29	33	2	4	12	19	-1	1	36	38	0	8	20	13
-1	8	41	39	3	4	37	34	0	1	25	28	2	8	14	10
1	8	25	21	4	4	14	25	1	1	67	66	5	8	12	5
4	8	12	16	5	4	12	14	2	1	20	23	-2	9	11	11
-3	9	21	25	-7	5	13	16	3	1	43	45	0	9	18	14
-1	9	18	15	-6	5	18	21	4	1	12	14	2	9	13	15
0	9	19	19	-5	5	36	38	5	1	18	20	-3	10	25	22
2	9	16	13	-4	5	42	43	-6	2	23	22	-1	10	31	31
-5	10	11	9	-3	5	51	55	-5	2	29	31				
-3	10	26	25	-2	5	26	25	-4	2	61	73		L=	7	
-1	10	17	13	-1	5	30	29	-3	2	70	73				
0	10	15	16	0	5	39	32	-2	2	52	56	-9	0	13	5
-2	11	14	13	5	5	12	9	-1	2	18	20	-3	0	57	59
0	11	15	9	-8	6	12	15	0	2	34	32	-1	0	62	61
4	12	13	7	-7	6	14	16	4	2	17	14	1	0	23	19
				-6	6	13	13	-7	3	10	13	3	0	13	14
	L=	5		0	6	51	47	-6	3	33	37	-7	1	13	13
				2	6	47	41	-5	3	20	21	-6	1	26	27
-9	0	11	9	3	6	25	29	-4	3	22	23	-4	1	65	64
-7	0	24	23	4	6	13	12	-2	3	18	16	-3	1	45	43
-5	0	17	27	-7	7	13	20	-1	3	23	28	-2	1	46	48
-3	0	48	46	-5	7	33	36	0	3	26	22	2	1	20	19
-1	0	29	21	-3	7	28	29	1	3	32	32	3	1	12	10
-5	1	10	13	-1	7	28	29	2	3	35	32	4	1	17	20
-4	1	25	25	2	7	13	8	3	3	11	14	-9	2	16	16
-3	1	52	42	-6	8	12	12	4	3	22	24	-7	2	25	28
-2	1	53	51	-4	8	11	10	-7	4	10	13	-6	2	14	15
0	1	46	50	-3	8	13	13	-5	4	15	23	-2	2	20	19
1	1	37	37	-2	8	14	14	-4	4	10	9	-1	2	41	43
2	1	35	37	-1	8	18	11	-2	4	21	21	0	2	22	25
-9	2	17	19	0	8	23	18	-1	4	43	46	1	2	43	48
-7	2	22	23	1	8	13	10	0	4	23	27	3	2	12	13
-5	2	23	22	2	8	18	16	3	4	17	13	-7	3	19	22
-3	2	14	16	3	8	13	13	4	4	11	10	-6	3	25	22
-2	2	21	17	4	8	13	15	-6	5	11	8	-5	3	19	17
-1	2	29	28	-3	9	11	11	-1	5	24	26	-4	3	26	26
1	2	33	36	-1	9	17	14	0	5	32	33	-3	3	21	24
2	2	17	16	1	9	13	11	1	5	11	14	-2	3	42	44
3	2	24	31	2	9	11	6	-5	6	11	11	0	3	18	16
4	2	13	10	-1	10	17	11	-4	6	10	11	1	3	16	14
5	2	20	23					-3	6	10	11	3	3	20	21
-8	3	12	16		L=	6		-2	6	15	14	-7	4	24	29
-6	3	45	43					-1	6	10	18	-6	4	17	22
-4	3	68	67	-8	0	16	14	0	6	11	5	-5	4	36	35
-3	3	30	26	-6	0	42	44	-4	7	10	17	-2	4	20	21

Table 1. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-1	4	14	16	0	1	18	16	-3	8	17	15	-1	6	12	9
0	4	37	34	1	1	25	23	-1	9	15	12	0	6	12	12
1	4	23	23	2	1	10	6		L =	9		-4	7	10	12
2	4	17	17	-7	2	11	15					-2	7	16	15
3	4	13	15	-6	2	19	20	-9	0	25	27	0	7	15	7
-5	5	15	17	-5	2	14	13	-7	0	28	28	1	7	11	7
-4	5	27	31	-4	2	49	45	-3	0	16	18	-2	9	12	12
-3	5	25	26	-2	2	25	23	-1	0	38	38				
-2	5	22	20	-7	3	14	15	1	0	28	28		L=10		
-1	5	26	27	-6	3	10	12	3	0	11	17				
0	5	23	22	-4	3	14	12	-8	1	13	12	-6	0	11	9
1	5	17	20	-1	3	17	18	-6	1	25	29	-4	0	21	29
2	5	16	17	1	3	18	19	-4	1	55	55	2	0	15	14
-8	6	14	16	3	3	16	19	-3	1	30	27	-5	1	15	20
-6	6	24	26	-8	4	12	20	-2	1	35	32	-4	1	16	23
-5	6	11	15	-7	4	11	14	-1	1	21	23	-3	1	21	24
-4	6	20	18	-6	4	32	33	0	1	14	17	2	2	12	11
-2	6	12	12	-5	4	15	17	-8	2	18	19	1	4	14	12
0	6	20	16	-3	4	17	15	-7	2	14	19	-6	7	14	17
2	6	20	18	-2	4	17	18	-6	2	9	8				
-5	7	19	24	0	4	11	6	-1	2	20	22		L=11		
-3	7	23	24	-3	5	11	14	0	2	13	13				
-2	7	11	14	-2	5	12	12	1	2	21	20	-9	0	11	6
-1	7	23	25	-1	5	25	28	-6	3	15	16	-8	3	11	12
-5	8	15	19	0	5	18	22	-5	3	28	32	0	4	17	8
0	8	12	14	1	5	29	29	-3	3	21	26	-2	6	14	16
-5	9	11	15	-7	6	15	18	-1	3	13	15	0	6	14	20
-3	9	18	17	-6	6	12	16	2	3	14	15	-7	7	13	17
-1	9	15	13	-5	6	29	31	-4	4	10	9				
0	9	11	10	-4	6	11	13	-3	4	19	21		L = 12		
-2	10	15	18	-3	6	17	21	-2	4	13	18				
				-2	6	17	11	-1	4	21	20	-8	0	10	9
	L =	8		-1	6	14	18	0	4	21	20	-4	0	19	20
				3	6	11	5	2	4	16	11	-2	0	17	17
-8	0	10	4	-4	7	11	11	5	4	12	6	-3	1	13	12
-6	0	12	6	-2	7	26	24	-5	5	13	11	-2	1	11	5
0	0	25	22	0	7	21	19	-8	6	12	1	-6	2	15	18
-7	1	13	17	2	7	20	21	-2	6	22	18	-5	2	17	20
-4	1	18	14	-5	8	12	16					-3	2	11	11

Table 2. Positional and Thermal Parameters for
Bicyclo [2.2.2] octyl-2 p-bromobenzene-
sulfonate From Run 24A

Atom	x	y	z	$B(\overset{o}{A}{}^2)$
Brl[a]	-0.0531(10)	0.0000	0.2235(8)	8.2(3)
S1	0.4646(15)	0.3465(12)	0.4084(11)	2.9(3)
S101[b]	0.5431(30)	0.3230(22)	0.3324(26)	5.7(7)
S102	0.4189(32)	0.4608(23)	0.3954(24)	5.2(8)
S103	0.5817(32)	0.3140(22)	0.5242(25)	4.9(7)
B1C1[c]	0.5598(50)	0.3932(35)	0.1686(40)	4.8(1.0)
B1C2	0.4642(64)	0.3190(44)	0.2002(45)	5.8(1.5)
B1C3	0.4262(57)	0.2159(41)	0.1609(44)	5.7(1.2)
B1C4	0.4468(49)	0.2100(32)	0.0310(36)	4.2(1.0)
B1C5	0.5852(75)	0.2392(53)	0.0520(54)	7.6(1.6)
B1C6	0.6775(48)	0.3312(34)	0.1430(37)	4.7(1.0)
B1C7	0.4176(61)	0.4281(48)	0.0302(47)	5.8(1.4)
B1C8	0.3367(89)	0.3112(62)	-0.0182(66)	9.9(2.3)
R1C1[d]	0.1240(34)	0.1067(25)	0.2962(25)	7.7(9)
R1C2	0.2677(34)	0.0780(25)	0.3734(25)	7.7(9)
R1C3	0.3796(34)	0.1550(25)	0.4132(25)	7.7(9)
R1C4	0.3479(34)	0.2607(25)	0.3758(25)	7.7(9)
R1C5	0.2042(34)	0.2894(25)	0.2985(25)	7.7(9)

Table 2.   (Continued)

Atom	x	y	z	B($\overset{O}{A}{}^{2}$)
R1C6	0.0922(34)	0.2124(25)	0.2587(25)	7.7(9)
Br2	0.4601(10)	0.4429(5)	0.7269(8)	8.0(3)
S2	-0.0375(27)	0.0767(21)	0.8949(22)	9.4(7)
S2O1	0.9413(37)	0.0552(27)	0.7671(31)	7.3(8)
S2O2	0.0882(42)	0.1213(30)	0.9749(35)	8.2(1.1)
S2O3	0.8895(37)	-0.0062(32)	0.9223(29)	7.4(9)
B2C1	0.0471(98)	0.0237(71)	0.6146(82)	12.3(2.5)
B2C2	0.0160(94)	0.1099(61)	0.7369(75)	10.3(2.2)
B2C3	-0.1302(54)	0.1912(35)	0.6282(39)	4.8(1.1)
B2C4	-0.0635(74)	0.2139(47)	0.5729(64)	8.4(1.7)
B2C5	-0.1270(75)	0.1244(60)	0.4668(62)	8.3(1.9)
B2C6	-0.0668(124)	0.0386(86)	0.5203(99)	12.6(2.8)
B2C7	0.1681(63)	0.1240(45)	0.6935(54)	7.7(1.5)
B2C8	0.0971(90)	0.2276(63)	0.5824(64)	9.8(2.3)
R2C1	0.5922(20)	0.3435(14)	0.7791(15)	2.4(4)
R2C2	0.5567(20)	0.2381(14)	0.7416(15)	2.4(4)
R2C3	0.6662(20)	0.1593(14)	0.7799(15)	2.4(4)
R2C4	0.8114(20)	0.1859(14)	0.8558(15)	2.4(4)
R2C5	0.8470(20)	0.2913(14)	0.8934(15)	2.4(4)

Table 2.   (Continued)

Atom	x	y	z	B($\overset{o}{A}^2$)
R2C6	0.7374(20)	0.3701(14)	0.8550(15)	2.4(4)

[a]Br1 and S1 refer to BIC1; Br2 and S2 refer to BIC2.

[b]S10 refers to an oxygen atom in BIC1; S20 refers to an oxygen atom in BIC2.

[c]B1 refers to a bicyclooctane carbon in BIC1; B2 refers to a bicyclooctane carbon in BIC2.

[d]R1 refers to a phenyl carbon in BIC1; R2 refers to a phenyl carbon in BIC2.

CHAPTER V

DISCUSSION OF RESULTS

After initial positions for all atoms had been chosen
and their parameters refined, the bond distances were cal-
culated. The values varied as much as 0.5 $\overset{\circ}{A}$ from accepted
values. Because of the problem of phasing in an asymmetric
space group, the reliability of the electron density maps
was questioned. In order to choose the best atom positions,
each of the two independent bicyclo [2.2.2] octane groups
was then refined as a rigid body. Next, each bicyclooctane
was refined as two groups, each consisting of a bridgehead
and the three carbon atoms bonded to it. Finally, the atoms
in the bicyclooctane groups were refined individually. The
bond distances improved somewhat, but still varied as much
as 0.25 $\overset{\circ}{A}$ from accepted values in BIC1 and as much as 0.45 $\overset{\circ}{A}$
in BIC2 (Run 24A). R_1 and R_2 converged to values of 0.1016
and 0.0975 respectively. At this point disorder was suspected
and fractional atoms were introduced in one of the bicyclo-
octane groups (BIC2) in the hope of finding definite enantio-
meric disorder. Such disorder was found in the crystal struc-
ture of a similar compound, racemic 2-exo-norbornanol p-
toluenesulfonate, by Altona and Sundaralingam[23]. The dis-
order in that structure caused by approximately a 3:1 ratio

of the two enantiomeres occupying the same area in the unit cell. The same type of disorder was possible with the two enantiomeres of bicyclo [2.2.2] octyl-2 p-bromobenzenesulfo-nate. After several cycles of refinement one of the fractional positions developed an unusually low temperature factor indi-cating more electron density than usual for a carbon atom. Since this position was in the vicinity of the BIC2 oxygen atoms, it was refined as a fractional oxygen position. Refin-ing the atoms in this manner gave the lowest R_1 and R_2 values attained, 0.096 and 0.090 respectively. However, the bond distances were worse and no alternate group of atoms gave a better set of bicycloöctane bond distances. The structure was then refined with the normal number of carbon atom posi-tions, the only fractional positions being two positions for one BIC2 oxygen atom. The bond distances then varied as much as 0.65 $\overset{\mathrm{o}}{\mathrm{A}}$ from accepted values, and R_1 and R_2 refined to 0.0984 and 0.0929 respectively (Run 21A).

The bicycloöctane sulfur-oxygen bond distances, the oxygen-carbon bond distances and the carbon-carbon bond dis-tances derived from Runs 21A and 24A for BIC1 and BIC2 are compared in Table 3 with standard deviations in parentheses. In both runs the bond distances in BIC1 were usually closer to accepted values than the bond distances in BIC2. In Run 24A the sulfur-oxygen bond distances in BIC1 are quite reason-able, S1-S101 being slightly longer than S1-S102 and S1-S103
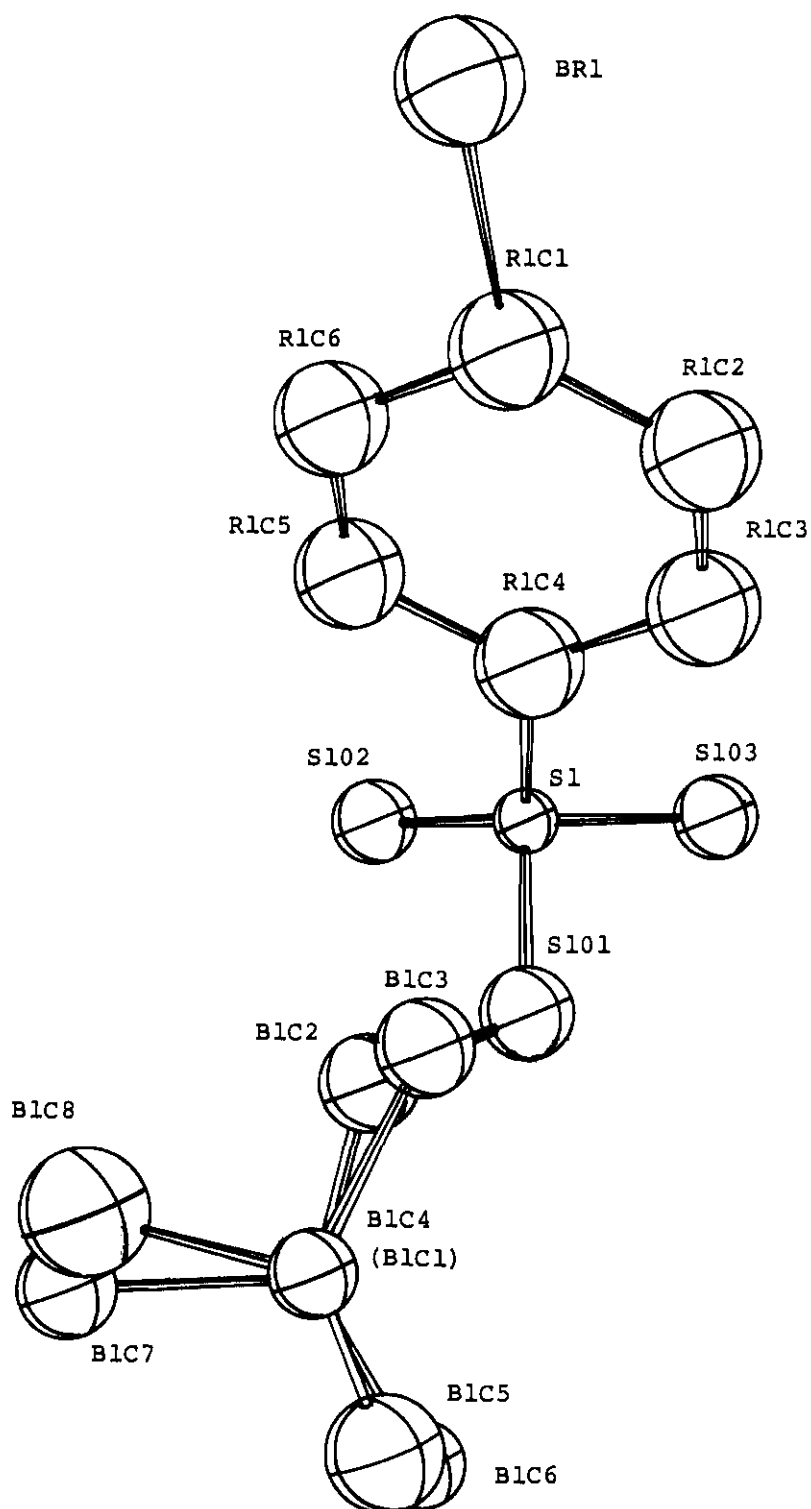
Figure 1.   Bicyclo [2.2.2] octyl-2 p-bromobenzene-
sulfonate (BIC1)

Table 3. Comparison of Interatomic Distances
From Run 21A and Run 24A

Atoms	Distance, Å (Run 21A)	Distance, Å (Run 24A)
S1-S101	1.052(4)	1.558(6)
S1-S102	1.467(1)	1.478(1)
S1-S103	1.460(14)	1.491(14)
S101-B1C2	1.639(2)	1.537(11)
B1C1-B1C2	1.730(3)	1.525(3)
B1C1-B1C6	1.584(2)	1.580(3)
B1C1-B1C7	1.654(17)	1.777(18)
B1C2-B1C3	1.432(8)	1.368(2)
B1C5-B1C6	1.457(3)	1.606(8)
B1C7-B1C8	1.635(5)	1.646(4)
B1C4-B1C3	1.889(2)	1.804(2)
B1C4-B1C5	1.485(14)	1.352(3)
B1C4-B1C8	1.682(5)	1.608(5)
S2-S201	1.622(2)	1.605(3)
S2-S20A	1.748(7)	
S2-S202	1.434(13)	1.346(12)
S2-S203	1.382(2)	1.407(2)
S201-B2C2	1.155(2)	1.210(3)

Table 3. (Continued)

Atoms	Distance, Å (Run 21A)	Distance, Å (Run 24A)
S20A-B2C2	1.314(11)	
B2C1-B2C2	2.208(6)	2.062(3)
B2C1-B2C6	1.127(12)	1.261(14)
B2C1-B2C7	1.850(12)	1.722(9)
B2C2-B2C3	1.515(8)	1.822(14)
B2C5-B2C6	1.371(3)	1.268(4)
B2C7-B2C8	2.072(9)	1.824(7)
B2C4-B2C3	1.382(5)	1.228(5)
B2C4-B2C5	1.640(7)	1.660(6)
B2C4-B2C8	1.536(2)	1.587(2)
S1-R1C4		1.503(35)
Br1-R1C1		2.081(31)
S2-R2C4		1.934(32)
Br2-R2C1		1.719(19)

because S101 is bonded to B1C2 (see Figure 1). In Run 21A

the S1-S102 and S1-S103 distances are also reasonable but

the S1-S101 bond distance (1.052(4) $\overset{o}{A}$) is much too short.

The S101-B1C2 bond distance is also better in Run 24A

(1.537(11) $\overset{o}{A}$) than in Run 21A (1.639(2) $\overset{o}{A}$). A comparison

of the other bond distances in Run 24A to those in Run 21A

indicates that the number of bond distances which improve

approximately equals the number of bond distances which

become worse; however, the extremes are not as great in Run

24A. The agreement between the observed and the calculated

structure factors in Run 21A (R_1 = 0.0984 and R_2 = 0.0929)

is better than the agreement in Run 24A (R_1 = 0.1016 and

R_2 = 0.0975). The difference in refinement between 21A and

24A has better than a 99.5 per cent probability of being

significant (21A supposedly being the better model) according

to the Hamilton R-factor test[25] which takes into account the

increased number of variables in Run 21A. However, the fact

that the bond distances are less reasonable in Run 21A pro-

bably indicates problems in the data set due to decomposition

and/or instrumental problems. Also, a small absorption error

could have been introduced due to irregularities in the glass

capillary or to the x-ray beam passing through varying thick-

ness of glass because of changing orientation of the detector

with respect to the capillary. Another possible explanation

is inconsistent crystal disorder which cannot be accounted

for in the least squares refinement.

The bicyclooctane group in the molecule with the most reasonable bond distances was determined to be B1C1 using the positions taken from Run 24A. This bicyclooctane group was the closest to D_3 symmetry. The dihedral angles between the B1C1-B1C2-B1C4 and the B1C1-B1C3-B1C4 planes (P), between the B1C1-B1C6-B1C4 and the B1C1-B1C5-B1C4 planes (Q), and between the B1C1-B1C7-B1C4 and the B1C1-B1C8-B1C4 planes (R) were calculated; P = 10.4(1)°, Q = 8.3(0)°, and R = 17.8(2)° with a standard deviation equal to 5.0°. These angles indicate twisting about the bridgehead-bridgehead axis; however, it must be remembered that these angles are very sensitive to variation in atom positions. Also, the calculations from other runs showed the group deviating from D_3 symmetry to the extent that different bridges appeared twisted in different directions.

The bond angles for B1C1 and B1C2 from Run 24A are listed in Table 4.

Table 4. Bond Angles for Bicyclo [2.2.2]
          octyl-2 p-bromobenzenesulfonate
          From Run 24A

| Atoms	Angle, degrees	Atoms	Angle, degrees
Br1-R1C1-R1C2	124.78(4)	B1C5-B1C4-B1C8	109.87(28)
Br1-R1C1-R1C6	115.35(4)	B1C4-B1C5-B1C6	122.84(44)
S1-R1C4-R1C3	122.99(5)	B1C5-B1C6-B1C1	105.07(36)
S1-R1C4-R1C5	115.97(4)	B1C1-B1C7-B1C8	101.98(43)
R1C4-S1-S101	104.59(4)	B1C7-B1C8-B1C4	113.63(49)
R1C4-S1-S102	118.83(3)	Br2-R2C1-R2C2	120.48(3)
R1C4-S1-S103	104.89(3)	Br2-R2C1-R2C6	119.61(3)
S103-S1-S102	116.09(3)	S2-R2C4-R2C3	118.50(3)
S102-S1-S101	109.32(3)	S2-R2C4-R2C5	121.41(3)
S103-S1-S101	101.14(8)	R2C4-S2-S201	97.34(3)
S1-S101-B1C2	124.43(32)	R2C4-S2-S202	105.89(3)
S101-B1C2-B1C1	102.40(46)	R2C4-S2-S203	97.67(4)
S101-B1C2-B1C3	111.40(19)	S203-S2-S202	121.73(12)
B1C2-B1C1-B1C6	113.54(16)	S202-S2-S201	120.45(52)
B1C2-B1C1-B1C7	95.78(34)	S203-S2-S201	107.85(37)
B1C6-B1C1-B1C7	104.21(31)	S2-S201-B2C2	116.00(44)
B1C1-B1C2-B1C3	124.62(17)	S201-B2C2-B2C1	107.53(32)
B1C2-B1C3-B1C4	104.94(16)	S201-B2C2-B2C3	98.95(20)

Table 4. (Continued)

Atoms	Atom, degrees	Atoms	Atom, degrees
B1C3-B1C4-B1C5	110.67(73)	B2C2-B2C1-B2C6	106.54(24)
B1C3-B1C4-B1C8	89.22(42)	B2C2-B2C1-B2C7	58.73(24)
B2C6-B2C1-B2C7	124.40(42)	B2C5-B2C4-B2C8	97.55(58)
B2C1-B2C2-B2C3	92.41(37)	B2C4-B2C5-B2C6	101.30(51)
B2C2-B2C3-B2C4	96.51(2)	B2C5-B2C6-B2C1	131.19(19)
B2C3-B2C4-B2C5	103.27(16)	B2C1-B2C7-B2C8	96.81(62)
B2C3-B2C4-B2C8	143.29(42)	B2C7-B2C8-B2C4	90.31(58)

CHAPTER VI

RECOMMENDATIONS

Almost every bicyclo [2.2.2] octane compound whose
crystal structure has been studied using x-ray diffraction
has belonged to the centric space group $P2_1/c$. The only
exception found, omitting this study, was the study of com-
pound III[24].

CH$_3$ OC(CH$_3$)$_3$

H$_3$OOC

HO

H

H

H

III
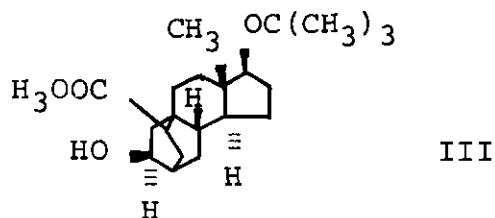
It seems likely, therefore, that if other bridge-substituted
bicyclo [2.2.2] octanes were chosen, one could be found which
crystallized in a centric space group. If this compound were
found free of disorder, then atoms could be chosen more
accurately from a more reliable electron density map.

Solvents other than petroleum ether or different cry-
stallization conditions could be used in the crystallization
of bicyclo [2.2.2] octyl-2 p-bromobenzenesulfonate. In either
case crystals might be produced free from the problems of
disorder.

LITERATURE CITED

1. A. H. Nethercot and A. Jarvan, _J. Chem. Phys._, _21_, 363 (1953).

2. R. B. Turner, W. R. Meador and R. E. Winkler, _J. Am. Chem. Soc._, _79_, 4116 (1957).

3. J. J. MacFarlane and I. G. Ross, _J. Chem. Soc._, 4169 (1960).

4. G. J. Gleicher and P. von R. Schleyer, _J. Am. Chem. Soc._, _89_, 582 (1967).

5. O. Ermer and J. D. Dunitz, _Chem. Comm._, 567 (1968).

6. L. M. Amzel, Martha C. M. Cucarella, and L. N. Becka, _J. Phys. Chem._, _75_, 1073 (1971).

7. A. F. Cameron, G. Ferguson and D. G. Morris, _J. Chem. Soc. B_, 1249 (1968).

8. J. D. Dunitz and O. Ermer, _Acta Cryst._, _A25_, S126 (1969).

9. Shaio-wen Sun Wong and Edgar F. Westrum, Jr., _J. Am. Chem. Soc._, _93_, 5317 (1971).

10. Akimichi Yokozeki, Kozo Kuchitsu and Yonezo Morino, _Bull. Chem. Soc. Jap._, _43_, 2017 (1970).

11. Eizi Hirota, _J. Mol. Spectry._, 38, 367 (1971).

12. H. C. Brown and Philip Geoghegan, Jr., _J. Am. Chem. Soc._, _89_, 1522 (1967).

13. H. M. Walborsky, M. E. Baum and A. A. Youssef, _ibid._, _83_, 988 (1961).

14. F. L. Carter, "Master Card Program for the Picker Four-Angle Programmer," Picker Instruments, Cleveland, Ohio, (1967).

15. A. Zalkin, Fortran Fourier Analysis Program, FORDAP.

16. Robert Doedens, Ph.D. Thesis, University of Wisconsin, (1965).

17. S. J. LaPlaca and J. A. Ibers, _Inorg. Chem._, <u>5</u>, 405 (1966).

18. W. R. Busing, K. O. Martin and H. A. Levy, Fortran Crystallographic Least Squares Program, ORFLS, Oak Ridge National Laboratories.

19. W. R. Busing, K. O. Martin and H. A. Levy, Fortran Function and Error Program, ORFFE, Oak Ridge National Laboratories (1965).

20. C. K. Johnson, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, Oak Ridge National Laboratories (1965).

21. _International Tables for X-Ray Crystallography_, The Kynoch Press, Birmingham, England, (1965).

22. "Full Circle Goniostat Alignment," Picker Instruments, Cleveland, Ohio, (1968).

23. C. Altona and M. Sundaralingam, _Acta Cryst._, <u>B28</u>, 1806 (1972).

24. J. W. Scott, W. Vetter, W. E. Oberhänsli and A. Fürst, _Tetrahedron Letters_, 1719 (1972).

25. Walter C. Hamilton, _Acta Cryst._, <u>18</u>, 502 (1965).