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Crystal and Molecular Structure

of 7-(p-Iodobenzenesulfonyl)-7-azabicyclo 4.1.0 heptane

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The structure of 7-(p-iodobenzenesulfonyl)-7-azabicyclo[4.1.0]heptane has been determined by a three dimensional single-crystal x-ray diffraction study. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell dimension $a_0 = 10.35 \pm .005$, $b_0 = 16.33$, $c_0 = 8.22$ Å and a monoclinic angle, $\beta = 99°40' \pm 5'$. The aziridine ring is fused cis to the cyclohexane ring with fusion angles of 122°. The cyclohexane ring is flattened appreciably, although still in the chair conformation. Bond distances within the cyclohexane ring are shortened to an average value of 1.49 Å. The p-iodobenzenesulfonate group is at an angle of 98.3° to the bicyclic system containing the aziridine and cyclohexane fused rings. A final value of $R = 0.115$ was obtained for the 1272 independent reflections.

INTRODUCTION

The study of the structure of 7-(p-iodobenzenesulfonyl)-7-azabicyclo[4.1.0]heptane was undertaken as part of a continuing program of determining the structures of bicyclic ring systems containing an aziridine ring. Crystals of the compound were kindly furnished to us by P. E. Fanta (1). The interest in this compound centered upon the distortion of the cyclohexane ring to be anticipated when it is fused to an aziridine ring. In the case of alicyclic medium-sized rings, these distortions are more easily accommodated by changes in conformation (2,3) and a general widening of bond angles in the medium-sized ring. Also of interest, is the resultant angles when these two rings are fused.

CRYSTAL DATA

The sample furnished to us had been previously recrystallized from benzene and contained white plate-like single crystals suitable for the structure determination. The space group ($P2_1/n$) and the cell dimensions ($a_0 = 10.35 \pm .005$, $b_0 = 16.33$, $c_0 = 8.22$ Å, $\beta = 99°40' \pm 5'$) were determined from precession photographs taken with filtered Mo-K_α radiation. The calculated density of 1.76 g. cm^{-3} assuming four molecules per unit cell was in good agreement with the density of 1.75 g. cm^{-3} measured by flotation techniques.

Intensity data were collected from the precession pictures of the zero and first four levels about the [001] axis, the zero and first five levels about the [010] axis and the h, k, k zero level. The intensities were estimated visually, using scales made from timed exposures of selected "typical" reflections. Because of the difference in spot shapes of reflections taken about the [001] axis and the [010] axis, a separate scale, using a reflection typical of the spots observed in each direction, was used.

All reflections which were observable, but too light to be accurately compared to the scales, were arbitrarily assigned the minimum value on the scale. Lorentz and polarization corrections were made in the usual manner (4). The common reflections in the h, k, k zero level were then used to correlate the two sets of data and thus put all reflections on the same relative scale. A list of 1272 independent reflections was finally obtained.

Extinction of all h0l reflections with h + l odd and all 0k0 reflections with k odd led to the space group $P2_1/n$. With four molecules in the unit cell, the asymmetric unit thus consisted of one molecule.

Patterson projections made the location of the iodine atom readily apparent. Using the coordinates thus obtained and an initial isotropic temperature factor of 4.5 Å^2, structure factor calculations were carried out resulting in a value of 0.34 for the reliability index (R). Two additional cycles of least-squares refinements resulted in values of r = .378, R = .329 (5). A three dimensional Fourier map, using the magnitudes of the F_O from our observed data and the phases from the last least-squares cycle, was calculated.

Figure I shows a composite drawing of the peaks observed and assumed to belong to the molecule. Excluding carbon atoms for the moment, all of the peaks showed up quite well with relative heights (obtained by arbitrarily assigning a peak height of 51.0 to the iodine peak) as follows: sulfur 13.4; oxygen 3.6 and 3.8; nitrogen 3.8. With the exception of atoms C_4, C_5, and C_{10}, all of the carbon atom peaks showed up with heights ranging from 2.4 to 4.1. Thus all but three of the peaks to be expected turned up with reasonable relative heights. This was sufficient to allow us to estimate the approximate vicinity of the three remaining peaks, and a closer examination of the Fourier maps revealed smaller peaks very near the estimated location for each of these atoms. These peaks had heights of
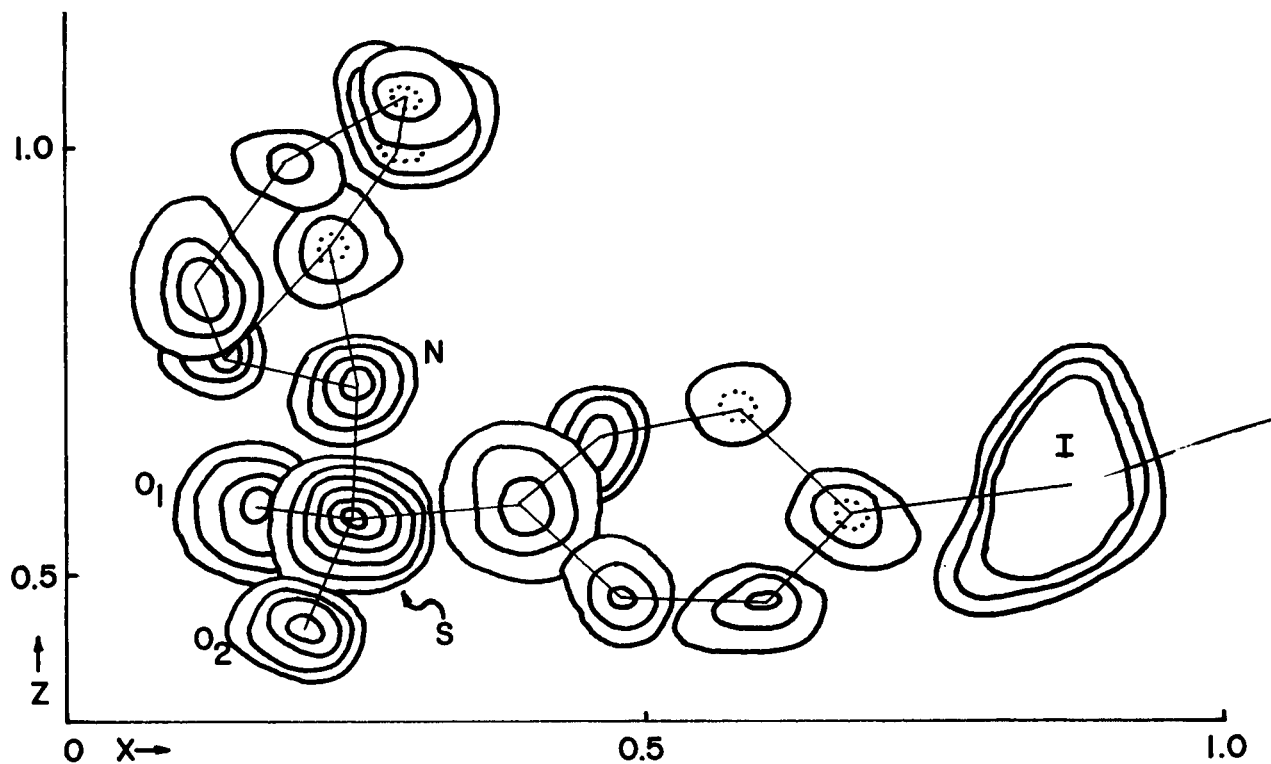
Figure I. Composite drawing of electron density peaks in one molecule, projected down the y-axis. Contours in arbitrary units; with every second contour drawn for the sulfur; the first three contours only for the iodine; and half-unit contours dotted. Fourier Map based on iodine parameters only.
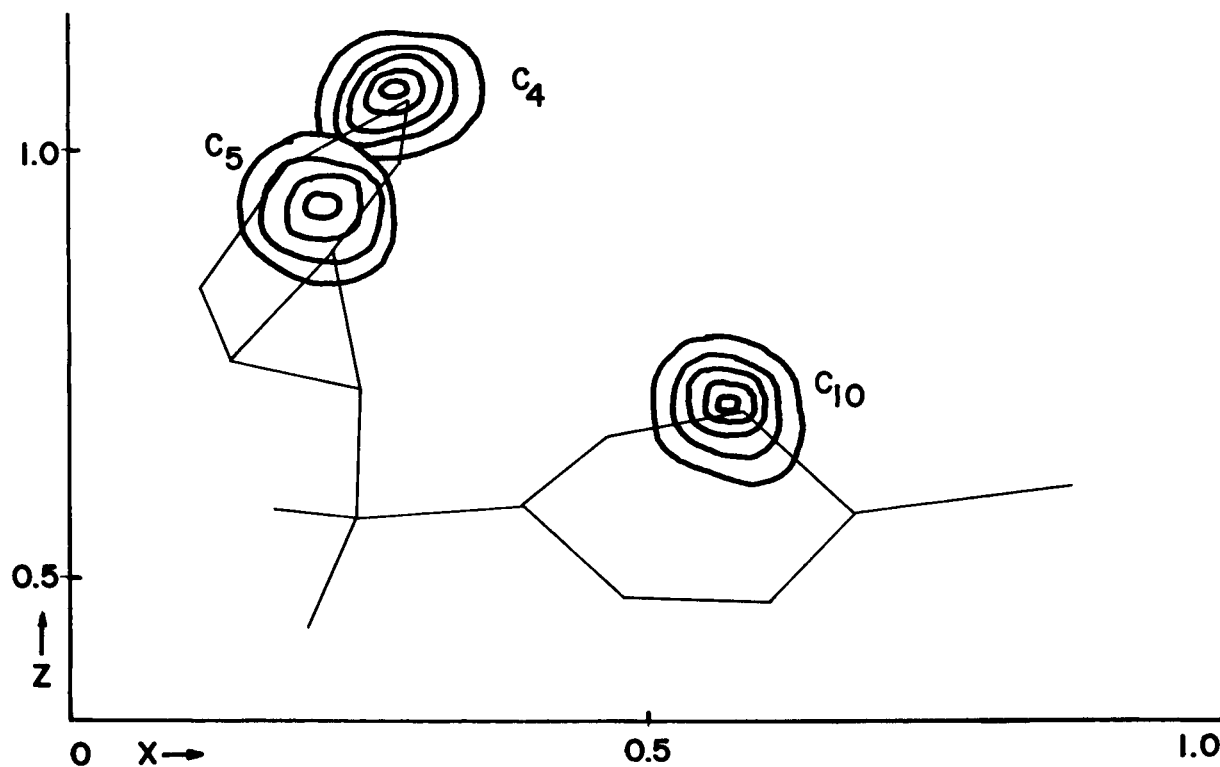

Figure II. Difference Fourier Map subtracting out all peaks (except those due to carbon atoms C_4, C_5, C_{10}). Only peaks of height greater than 3.0 e/$\overset{\circ}{A}^3$ are drawn, with contours at 1.0 e/$\overset{\circ}{A}^3$. The outline of the structure based on the initial Fourier Map is indicated for comparative purposes.
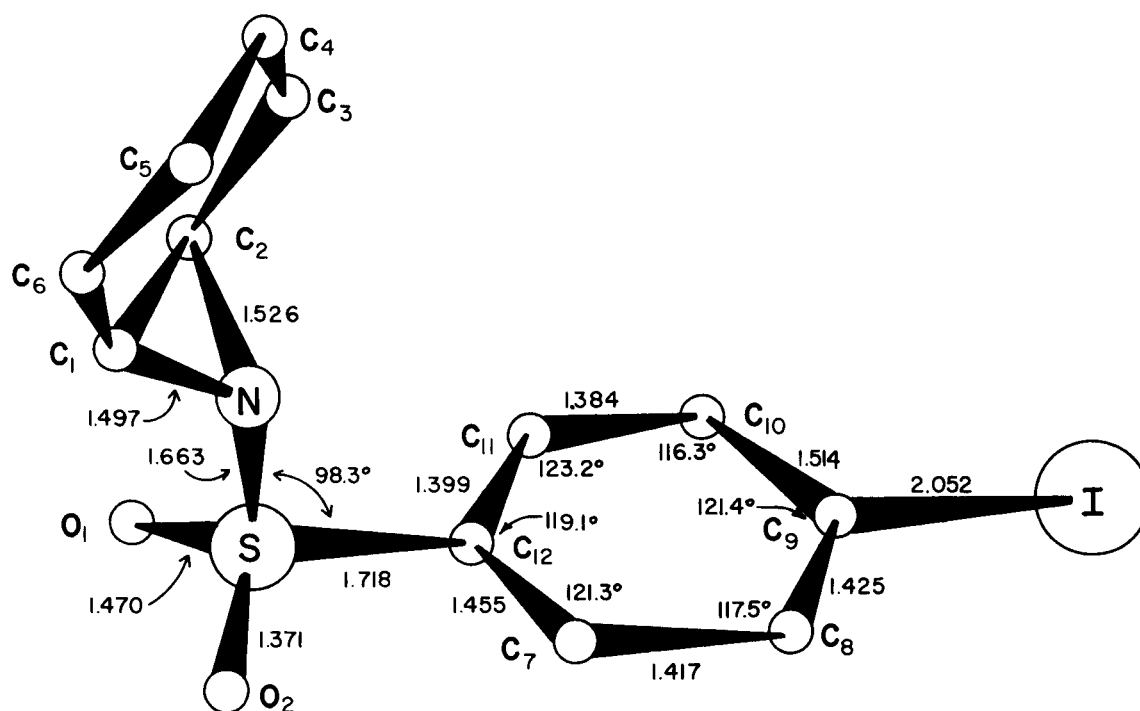
Figure III.   Three-dimensional perspective drawing of the molecule.

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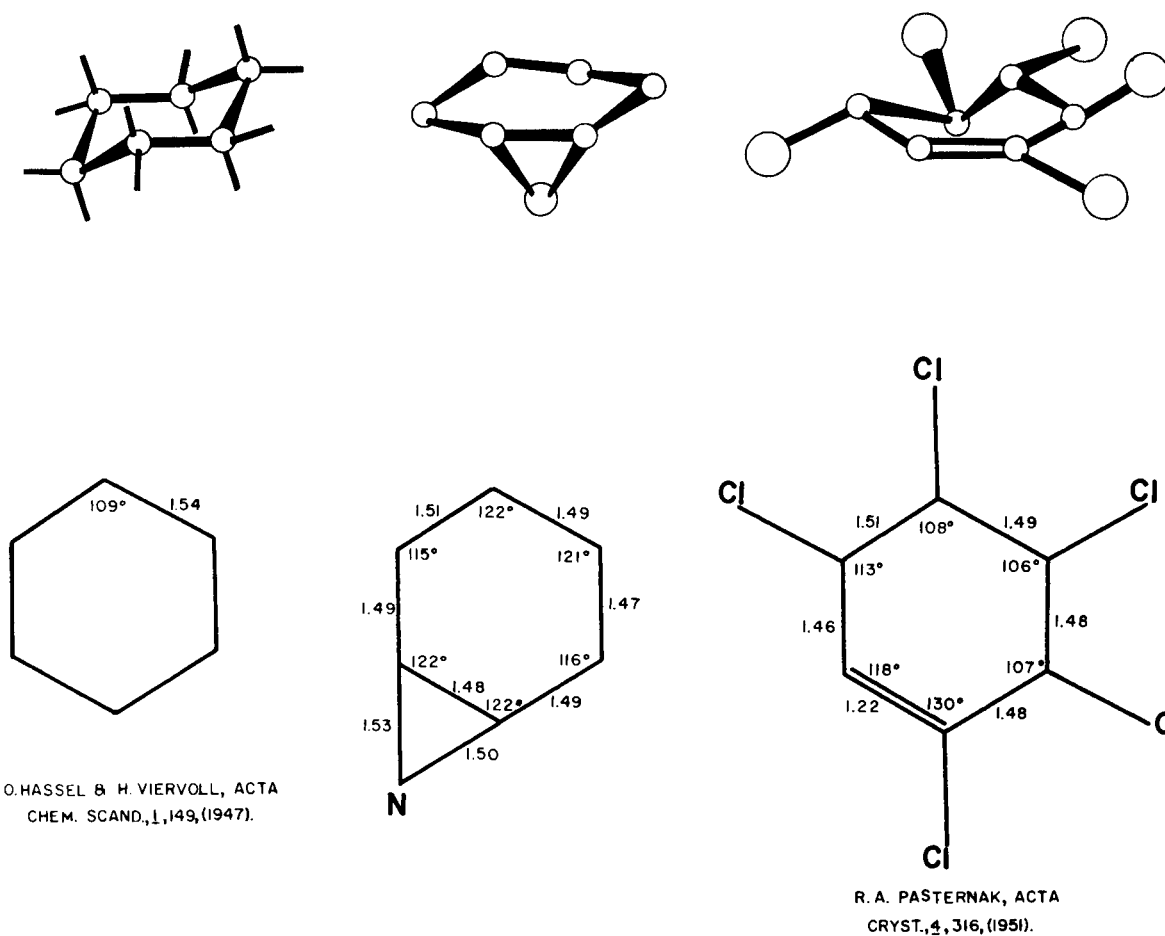CRYST.,4,316,(1951).

Figure IV.   Comparison of the bicyclic portion of this molecule with cyclohexane and cyclohexene.
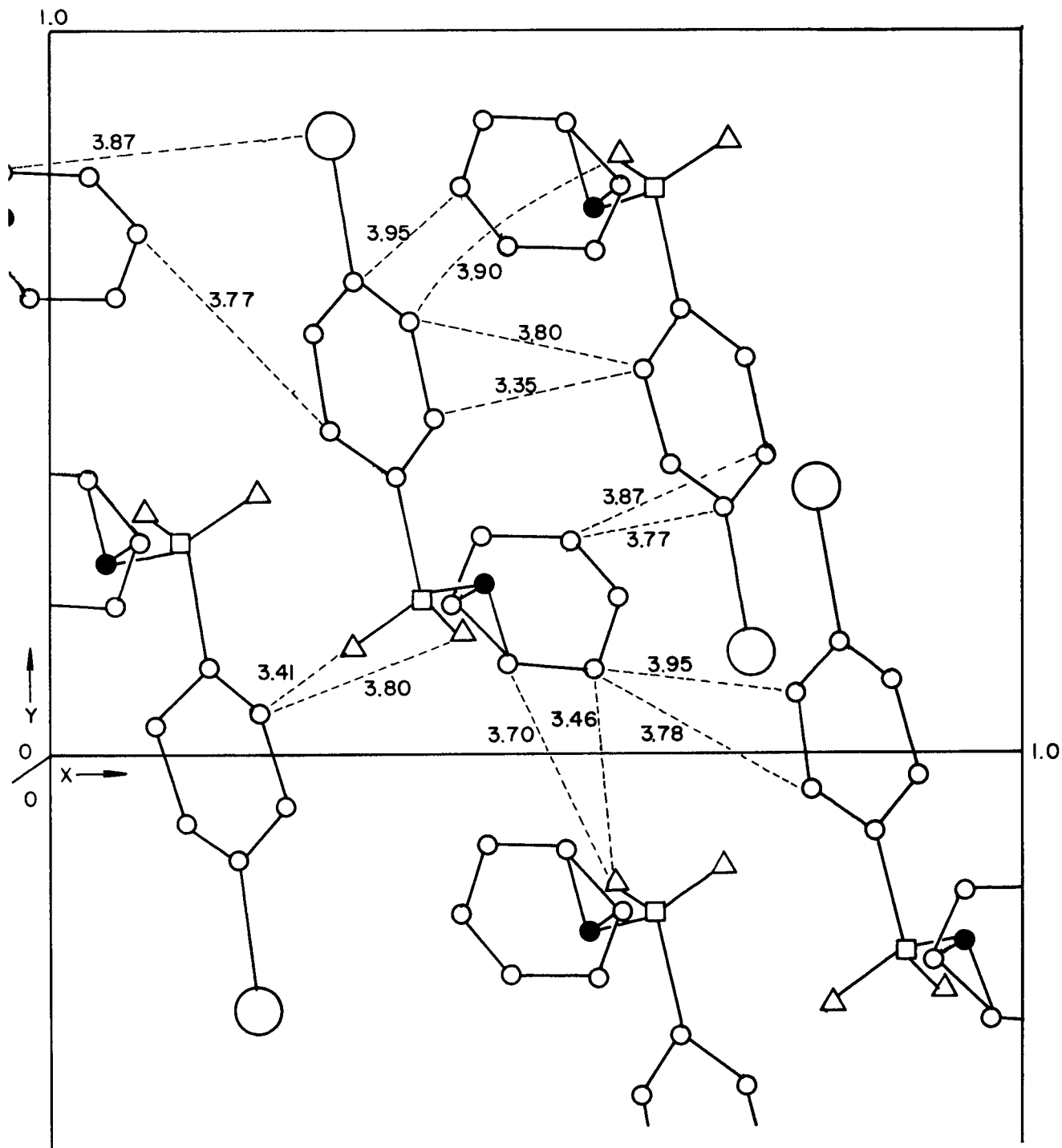
Figure V.   Contents of the unit cell with closest-intermolecular contacts indicated.

TABLE I

Coordinates and Temperature Factors

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
I	0.8554	0.2908	0.6161	0.0089	0.0039	0.0237	0.0003	0.0033	-0.0023
S	0.2293	0.3851	0.5616	0.0057	0.0051	0.0130	0.0001	0.0010	-0.0029
O_1	0.1541	0.3108	0.5845	0.0087	0.0069	0.0269	-0.0016	0.0047	-0.0048
O_2	0.1871	0.4282	0.4195	0.0145	0.0100	0.0040	0.0064	-0.0001	-0.0004
N	0.2457	0.4509	0.7180	0.0093	0.0040	0.0162	-0.0019	0.0017	-0.0020
C_1	0.1224	0.4740	0.7794	0.0061	0.0045	0.0160	0.0000	0.0037	-0.0057
C_2	0.2126	0.4155	0.8777	0.0116	0.0033	0.0072	0.0031	0.0005	0.0023
C_3	0.3067	0.4410	0.0264	0.0218	0.0028	0.0163	0.0016	0.0073	-0.0075
C_4	0.3047	0.5310	0.0668	0.0225	0.0036	0.0135	0.0040	0.0001	-0.0009
C_5	0.2263	0.5904	0.9532	0.0254	0.0053	0.0450	-0.0048	0.0046	-0.0065
C_6	0.1205	0.5624	0.8230	0.0107	0.0010	0.0095	-0.0002	0.0003	-0.0033
C_7	0.4716	0.3994	0.4774	0.0102	0.0028	0.0094	0.0018	-0.0009	0.0041
C_8	0.6025	0.3749	0.4736	0.0099	0.0040	0.0136	-0.0001	0.0015	0.0011
C_9	0.6581	0.3141	0.5889	0.0042	0.0035	0.0090	0.0017	0.0014	-0.0036
C_{10}	0.5763	0.2703	0.6981	0.0080	0.0058	0.0254	-0.0044	-0.0013	-0.0004
C_{11}	0.4443	0.2900	0.6744	0.0048	0.0031	0.0236	-0.0007	0.0029	-0.0004
C_{12}	0.3907	0.3562	0.5781	0.0020	0.0033	0.0122	-0.0004	-0.0007	-0.0010

TABLE II

Bond Distances and Bond Angles

Atoms Involved	Distances (Å)	Average Deviations	Atoms Involved	Angles (°)	Average Deviations
C-I	2.05	----	CCI	$\overline{119.3}$	$^{\pm}0.3$
C-S	1.72	----	CSO	$\overline{109.4}$	$^{\pm}2.4$
S-O	$\overline{1.43}$	$^{\pm}.05$	NSO	$\overline{111.4}$	$^{\pm}3.6$
S-N	1.66	----	OSO	115.7	----
N-C	$\overline{1.51}$	$^{\pm}.02$	CSN	98.3	----
C-C (Benzene Ring)	$\overline{1.43}$	$^{\pm}.04$	CNC (Aziridine Ring)	58.5	----
C-C (Aziridine Ring)	1.48	----	NCC (Aziridine Ring)	$\overline{60.7}$	$^{\pm}1°$
C-C (Cyclohexane Ring)	$\overline{1.49}$	$^{\pm}.02$	CCC (Benzene Ring)	$\overline{119.8}$	$^{\pm}2.2$
			CCC (Cyclohexane Ring, excluding fusion angles)	$\overline{118.4}$	$^{\pm}2.8$
			CCC (Fusion Angles)	$\overline{122.1}$	$^{\pm}0.2$

2.2, 2.0 and 1.6 on this same scale and were tentatively assigned to atoms C_4, C_5, and C_{10}. In addition to these peaks, there were alternating negative and positive regions originating from the iodine atom position and declining very rapidly, which were evidently iodine ripples. Lastly, there was one additional peak of height 3.1 which was not within a reasonable distance of any of the other peaks. Initially, this was assumed to be a false peak.

Two sets of least-squares refinements were run.

Both sets started out with all atoms being assigned isotropic temperature factors with an initial value of B = 4.0 $\overset{\circ}{A}^2$ for all atoms included. Three cycles were run on each set with all of the atoms assigned their correct scattering factor curves (6).

The first set of refinements excluded the three doubtful carbon atoms and resulted in r, R values of .170, .156, respectively, with all coordinate shifts after the third cycle being less than 0.08 Å.

All temperature factors were less than 6.0 e/Å^3 and shifts in the temperature factors less than 0.2 e/Å^3.

The second set of refinements included all of the atoms in the structure and resulted in r, R values of $.162$, $.143$, respectively. The coordinate shifts for the last three atoms were less than 0.08 Å. However, the temperature factors ran as high as 7.8 e/Å^3 and were still increasing. In addition, the C_9-C_{10} distance in the benzene ring had increased to 1.53 Å.

It was thus decided to calculate a difference Fourier map in which these three doubtful atoms were excluded. This difference Fourier map (Figure II) revealed three interesting features. First, the iodine atom has a pronounced anisotropy, apparently due to vibrations perpendicular to the plane of the benzene ring. In addition, small positive and negative regions about each of the other atoms indicated that future refinements should proceed with all atoms refined anisotropically. Secondly, peaks of height 4.8 and 3.6 e/Å^3 showed up for atoms C_4 and C_5, respectively. However, these peaks were shifted as much as 0.20 Å from the positions originally chosen for them. It was further apparent that the least-squares refinements were shifting these atoms further from the location of these peaks, accounting for the abnormally short distance of 1.33 Å for the C_4-C_5 atoms previously obtained. The false peak obtained in the first Fourier map calculation again showed up, but now with the peak height diminished to 2.0 e/Å^3. Thirdly, the peak for atom C_{10} now showed up prominently with peak height of 5.2 e/Å^3 but still led to a large C_9-C_{10} distance (1.51 Å).

Using coordinates as indicated by this last difference Fourier map for these three atoms, further refinements were done. Initially, one cycle of differential synthesis was run. The coordinates resulting from this were used in subsequent anisotropic least-squares refinements. Because of limitations in our least-squares program (using this program, only 100 parameters can be varied simultaneously on the I.B.M. 7040) the least-squares cycles were run in pairs. One cycle would be run varying all of the parameters for iodine, sulfur, the two oxygens and the carbon atoms in the benzene ring while holding the parameters for the nitrogen atom and the carbon atoms in the cyclohexane fixed.

In the next cycle, the iodine, the two oxygen, the nitrogen, and the carbon atoms in the cyclohexane ring were allowed to vary while the parameters for the atoms in the benzene ring and the sulfur atom were held fixed. After many such pairs of least-squares refinements, the coordinate shifts became very small, although the anisotropic temperature factors had not yet completely settled down. It is probable that additional cycles would have lowered the present value of R($.115$) slightly, but the shifts in coordinates had become much less than our standard deviations and so the refinements were concluded. The final r, R values were $.136$, $.115$.

RESULTS

Table I lists the coordinates and anisotropic temperature factors for all of the atoms. Table II lists the resulting bond distances and bond angles. Standard deviations, estimated on the basis of the last pair of least-squares cycles, were 0.02 for iodine, 0.03 for sulfur, and less than 0.04_5Å for all other atoms. The final shifts in coordinates were about one third the estimated standard deviations. The estimated standard deviation was less than $2.5°$ for all of the angles. A perspective drawing of the molecules is given in Figure III.

If one considers the benzene ring first, the average C - C bond distance (and its average deviation) is $1.43 \pm .04$ Å, if one includes all of the distances and $1.41_7 \pm .01_8$, if one excludes the C_9-C_{10} distance. Both of these average values are within one E.S.D. of the accepted C - C bond distance of 1.397 Å (7). The only distance more than one E.S.D. from the average value is that of C_9-C_{10}. The CCC bond angles within the benzene ring average to $120 \pm 2°$ although they vary by as much as $3.7°$ from this average.

The C - I distance of 2.05 Å is in good agreement with the C - I distances found for iodobenzene (8), *p*-diiodobenzene (9), and $1,3,5$-triiodobenzene (9). The C - S distance of 1.72 Å and the S - O distances of 1.42 are within one estimated standard deviation of the values found for dibenzenesulphonyl selendide (10), which has a C - S distance of $1.77 \pm .03$ Å and S - O distances of $1.43 \pm .02$ Å.

The S - N distance of 1.66 Å is less than the 1.73 Å which would be predicted from Pauling's covalent radii, but is in better agreement with the value of 1.69 Å obtained using the Schomaker-Stevenson formula. The spatial geometry about the sulfur atom is of interest. The angles between OSC average to $109 \pm 2°$ and the angles between OSN average to $111 \pm 3°$, but the CSN angle is $98.3°$, indicating that the pipsylate system is almost perpendicular to the bicyclic ring system containing the aziridine ring.

This bicyclic system containing the aziridine ring fused to a cyclohexane ring leads to the most unexpected results. The C - N distance of $1.51 \pm .02$ Å is discreetly (although not significant statistically) longer than that found in the free aziridine molecule--1.488 Å (11). Although not conclusive, this is similar to previous results (1,2,12) in which an aziridine was fused to another ring.

Of more interest, is the fusion angles between the aziridine and the cyclohexane ring. The average value of $122 \pm 2°$ obtained in this study is in quite good agreement with the values obtained in previous studies (2,12) of the *cis* fusion of an aziridine ring to another alicyclic ring ($122.7 \pm 2°$ and $123.2 \pm 2°$, respectively), and significantly different from the $126.6 \pm 2°$ obtained (3) in the only structural study in which an aziridine ring is fused *trans*. These angles are all larger than the fusion angles found

in 1:2 epoxycyclohexane (13) which has fusion angles of 118.5°.

It is in the cyclohexane ring itself in which the most unusual features occur. There is a pronounced flattening of the cyclohexane ring, although it is still in the chair conformation. In order to adjust to this widening at the fusion angle, there is a subsequent widening at the back end of the ring, resulting in angles of 121° and 121.5°. The center angles also pair up at 116° and 115°. This flattening out of the ring system to accommodate the fusion of the aziridine ring is accompanied by a significant shortening of the bond distances in the cyclohexane ring, resulting in an average value of 1.49 Å for the C - C bond distances. The resultant structure is much more analogous to the cyclohexane structure (14) than to the cyclohexane structure (15). `Figure IV illustrates the molecular parameters and conformations of these three systems. The results lend credence to the theoretical conclusions (16) that a three-membered ring has multiple bond character and, at least in this compound, the aziridine ring has an effect on the cyclohexane ring similar to the double bond in the cyclohexane structure.

Figure V, illustrating all intermolecular contacts under 4.0 Å, shows that *only three* close contacts (less than 3.7 Å) between molecules are observed. It is not too surprising that the atoms involved in these three close contacts are also those which display "abnormal" bond distances. In the benzene ring, atoms C_7 and C_{10} have close-contacts of 3.41 and 3.35 Å, respectively, with atoms in other molecules. It is these atoms which also are involved in bonds of length 1.51 and 1.46 Å, respectively, within the benzene ring. Within the cyclohexane ring, atom C_6 has a close intermolecular contact distance of 3.46 Å and also is involved in the shortest C - C bond (1.47 Å) within the ring.

The folding-over of one end of the molecule above the other is apparently the most compact packing scheme in the solid. Even with this folding-over, the closest approach of the two rings within the molecule is 3.87 Å between C_7 in the benzene ring and C_3 in the cyclohexane ring.

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Unit weighting factors were used in refining this structure.
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