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Crystal and Molecular Structure of 6-(*p*-Iodobenzenesulfonyl)-

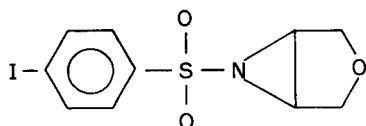
3-oxa-6-azabicyclo[3.1.0]hexane

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The crystal and molecular structure of 6-(*p*-iodobenzenesulfonyl)-3-oxa-6-azabicyclo[3.1.0]hexane has been determined by a three-dimensional single-crystal x-ray diffraction study. The compound crystallizes in the monoclinic space group C_2/c with cell dimensions, $a = 19.76$, $b = 8.17$, $c = 15.72 \pm 0.003 \text{ \AA}$ and $\beta = 109.3^\circ \pm 0.2^\circ$. The aziridine ring is fused *cis* to the oxo-cyclopentane ring with fusion angles of 112° . The bicyclic system is in the boat conformation with the *p*-iodobenzenesulfonate group at an angle of 98.0° to it. The conformation of the ring system is discussed. A final value of $R = 0.099$ was obtained for the 1107 independent reflections.

INTRODUCTION

The study of 6-(*p*-iodobenzenesulfonyl)-3-oxa-6-azabicyclo[3.1.0]hexane (I) was undertaken as part of a more general study of polycyclic compounds with at least one small ring system containing nitrogen. In this case, it was of interest to see how the fusion of the smaller ring system containing the nitrogen atom--aziridine--affects the conformation, structure and molecular parameters of the larger ring system--oxa-cyclopentane.



(I)

The structural changes observed in the aziridine ring by the fusion of larger ring systems containing no heteroatoms has been investigated extensively in this laboratory (1,2,3,4). Whether trends predicted on the basis of these previous studies also apply for a system in which the second ring is small (less than six atoms) and in which the second ring also contains a hetero-atom were among the points of particular interest. Additionally, a rather large fusion angle of $123 \pm 1^\circ$ was found in all cases in which the aziridine ring is fused *cis*- to the second ring provided, again, that the second ring contains at least six atoms (1,2,3). Geometric considerations make such large fusion angles extremely unlikely when the second ring has less than six atoms. Consequently, it was of prime interest to find the

fusion angles in this case. Lastly, the study in which an aziridine ring is fused *cis*- to a cyclohexane ring (1) indicated pronounced flattening of the cyclohexane ring. Whether this trend would continue, leading to a complete flattening of the second ring, in the case where the second ring contains only five atoms, was investigated with two model systems. In this study, the five-membered ring contained oxygen as a hetero-atom and in a study being undertaken simultaneously (5) the five-membered ring is a cyclopentane ring.

Samples of this compound were kindly furnished to us by Professor P. E. Fanta (6).

CRYSTAL DATA

The compound crystallized best from a solution of approximately equal amounts of ethyl alcohol and ethyl acetate with a small amount of benzene added. Beautiful, transparent crystals grew from such a saturated solution in about two to three days upon cooling.

Intensity data of the zero and first four levels about the [010] axis, the zero and first six levels about the [001] axis and of the additional zones ($hk\bar{h}$), ($h, h+1, l$) and ($h, k, 3k-h$) were collected using a Buerger precession camera and filtered Mo- K_α radiation. Extinctions for all reflections when ($h+k$) was odd indicated a C-centered cell and the additional extinctions when l was odd in the ($h0l$) zone indicated a c-glide. The space group choice was thus limited to either C_c or C_2/c .

The cell dimensions of this crystal were $a = 19.75_8$, $b = 8.17_1$, $c = 15.71_7 \pm 0.003 \text{ \AA}$, $\beta = 109^\circ 20' \pm 5'$. On the basis of eight molecules per unit cell, the calculated density was found to be 1.66 g. per c.c. as compared to a rough measurement of the density by flotation methods which

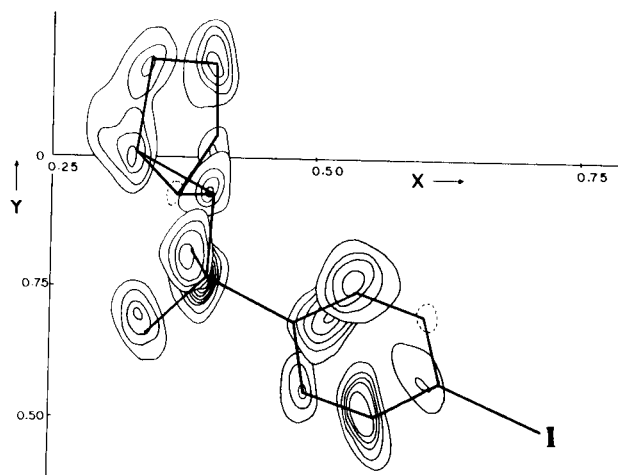


FIGURE 1

Figure 1. Composite drawing of electron density peaks in one molecule, projected down the z -axis. Contours in arbitrary units and no contours shown for the iodine atom. Difference Fourier map based on iodine parameters only. Dotted contours at less than one half the values of first solid contour.

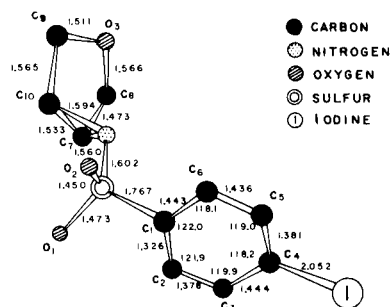


FIGURE 3

Figure 3. Three-dimensional perspective drawing of the molecule with individual bond distances indicated.

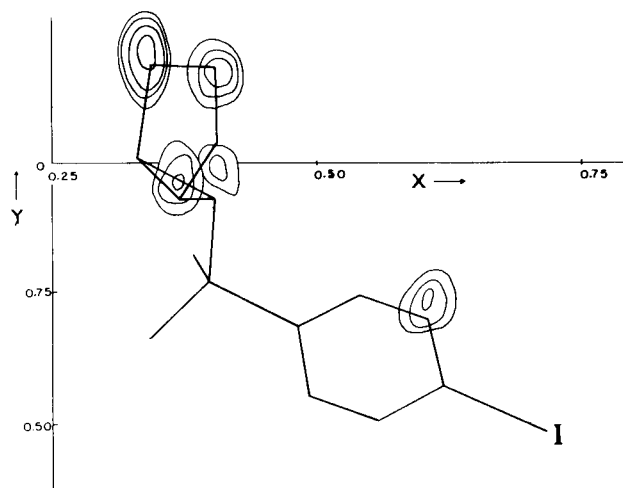


FIGURE 2

Figure 2. Difference Fourier map subtracting out all peaks except those shown. Contours drawn at $1.0 e/\text{Å}^3$. The outline of the structure based on the final Least Squares results is indicated for comparative purposes.

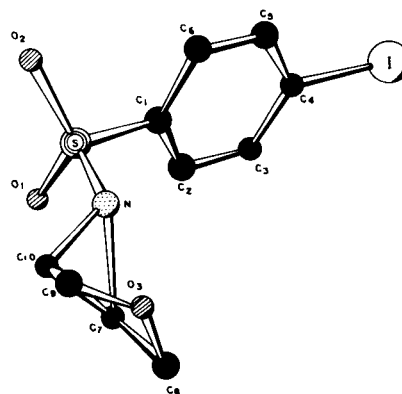


FIGURE 4

Figure 4. Perspective drawing of molecule down y -axis to indicate planarity of carbon atoms in oxacyclopentane ring.

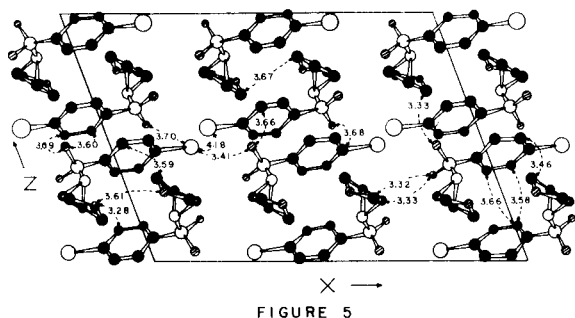


FIGURE 5

Figure 5. Contents of unit cell with closest-intermolecular contents indicated.

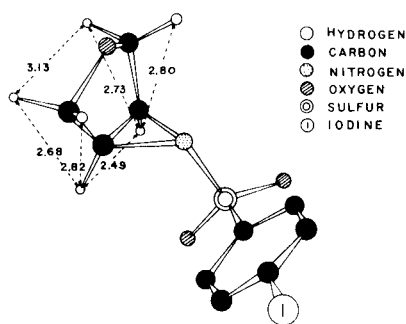


FIGURE 6

Figure 6. Perspective drawing of molecule with calculated hydrogen atom positions indicated.

yielded a value of $1.70 + .05$ g. per c.c. The space group C_2/c was chosen initially as the probable space group. The subsequent complete structure determination confirmed the choice of C_2/c as the correct space group.

Intensities were estimated visually using timed exposures of a selected "typical" reflection from this crystal. Lorentz and polarization corrections were made in the usual manner (7) and then reflections common to more than one zone were utilized in putting all intensities on the same relative scale. A total of 1107 independent reflections were observed.

STRUCTURE DETERMINATION

The iodine position was determined by trial and error methods and subsequently refined on the basis of the complete three-dimensional data. An immediate and obvious problem presented itself by the awkward position of the iodine atom. The value of its y coordinate was very close to 0 and hence the contribution of the iodine atom to the structure

factors whose indices, $h+k+l = 2n+1$ was negligible. In a practical sense, this meant that the reflections for which $h+k+l = 2n+1$ were limited in number (236 out of 1107) and generally of low intensity. Furthermore, Fourier maps of the structure, based only upon the iodine position would contain not only the correct peak for a given atom but also its approximate image reflected across $y = 0, 1/2$. Thus one had the additional problem of deciding which of the two peaks for any given atom is the correct one and which is its spurious mate.

A three-dimensional difference Fourier map was calculated using the phases derived from least-squares refinement of the iodine position ($R = 0.33$). Figure 1 shows a composite drawing of a section of this original Fourier map in which only those atoms belonging to one of these sets is shown. The final refined structure is superimposed for clarity.

Coordinates were chosen for all of the atoms in the benzene ring (except C_5), for the atoms in the SO_2 group, the nitrogen atom and atom C_{10} and a series of least squares refinements were carried out assuming an initial isotropic temperature factor $B = 4.5 \text{ \AA}^2$ for each atom. Six cycles of refinement resulted in R, r values of .23₅, .28₇, respectively (8).

A second difference Fourier map was calculated based on the phases from the last cycle of refinement and the observed structure factors. Figure 2 shows the second map which was calculated again with the final structure superimposed for illustrative purposes. All of the missing peaks showed up quite well and for the first time, the structure of the five-membered ring was clear.

Least squares refinements were then carried out using all of the atoms in the structure with each atom assigned its correct atomic scattering factor and anisotropic temperature factors. After many cycles of refinement values of $R, r = 0.12_3, 0.14_4$ were obtained.

At this point, a calculation of intermolecular distances within the unit cell revealed some extremely short intermolecular contacts. Additionally, the R value of 0.12₃ was a composite of a lower R value when $h+k+l = 2n$ and a significantly higher R value for those reflections where $h+k+l = 2n+1$. A translation of the molecule as a whole by $(0, 0, 1/4)$ resulted in reasonable intermolecular contacts and immediately corrected most of the large discrepancies between observed and calculated structure factors for which $h+k+l = 2n+1$. Finally, sufficient additional refinements with the molecule in the new position resulted in final R, r values of 0.09₉, 0.11₁. All shifts in coordinates were 0.001 \AA or less and all shifts in temperature factors 0.002 \AA^2 or less and so the refinement was terminated. A final difference Fourier map showed no regions of height greater than 1.7 $e/\text{\AA}^3$, with the final electron density sufficiently diffuse that no attempts to place the hydrogen atoms were made based on this Fourier map.

TABLE I
Coordinates and Temperature Factors

Atom	X	Y	Z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₂₃	B ₁₃
I	0.2179	0.9901	0.4610	0.0017	0.0094	0.0041	0.0008	0.0006	0.0008
S	0.8906	0.2787	0.3848	0.0012	0.0106	0.0020	0.0002	0.0002	0.0008
O ₁	0.8379	0.1576	0.3326	0.0024	0.0060	0.0062	0.0010	0.0003	0
O ₂	0.8799	0.3377	0.4664	0.0019	0.0222	0.0020	0.0026	0.0017	0.0016
O ₃	0.9037	0.6863	0.2229	0.0022	0.0200	0.0070	-0.0027	-0.0002	0.0090
N	0.9005	0.4294	0.3248	0.0030	0.0049	0.0012	-0.0009	0.0012	0.0014
C ₁	0.9764	0.1903	0.4077	0.0010	0.0094	0.0027	0.0023	-0.0010	0
C ₂	0.9871	0.0648	0.3601	0.0013	0.0056	0.0036	0.0010	-0.0003	-0.0042
C ₃	0.0555	0.0045	0.3775	0.0016	0.0157	0.0056	-0.0016	0.0010	-0.0060
C ₄	0.1170	0.0787	0.4434	0.0020	0.0059	0.0039	0.0012	0.0015	0.0022
C ₅	0.1066	0.2197	0.4859	0.0012	0.0226	0.0035	0.0010	-0.0013	0.0007
C ₆	0.0347	0.2695	0.4761	0.0022	0.0098	0.0031	-0.0008	-0.0001	0.0002
C ₇	0.8699	0.4151	0.2200	0.0030	0.0133	0.0005	0.0014	0.0003	0.0002
C ₈	0.9068	0.5215	0.1735	0.0039	0.0319	0.0035	-0.0031	0.0010	-0.0072
C ₉	0.8391	0.7000	0.2537	0.0029	0.0083	0.0025	0.0003	0.0006	0.0007
C ₁₀	0.8268	0.5140	0.2673	0.0019	0.0113	0.0035	-0.0003	-0.0001	0.0002

TABLE II
Bond Distances and Bond Angles

Atoms Involved	Distances (Å)	Average Deviations	Atoms Involved	Angles (Å)	Average Deviations
C-I	2.05 ₂	---	CCI	120.7	0.8°
C-S	1.76 ₇	---	CSO	109.2	2.5
S-O	1.46 ₁	0.1	NSO	111.6	1.3
S-N	1.60 ₂	---	OSO	115.7	---
C-C (Benzene Ring)	1.38 ₃	.04	CSN	98.0	---
N-C (Aziridine Ring)	1.57 ₄	.02	CCC (Benzene Ring)	119.8	1.6
C-C (Aziridine Ring)	1.53 ₃	---	NCC (Aziridine Ring)	61.1	1.0
C-C (Oxa-cyclopentane Ring)	1.52 ₀	.04	CNC (Aziridine Ring)	58.2	---
C-O (Oxa-cyclopentane Ring)	1.53 ₈	.03	CCC (Fusion Angles)	112.0	1.7
			CCO (Oxa-cyclopentane Ring)	98.5	0.5
			COC (Oxa-cyclopentane Ring)	113.5	---

DISCUSSION

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 in coordinates estimated for the various atoms on the basis of the last cycle of least squares, were, 0.01 Å for iodine, 0.02 Å for sulfur, and less than 0.03 Å for the lighter atoms. A perspective drawing of the molecule identifying the atoms is shown in Figure 3.

If one considers the benzene ring first, the average

C-C distance (and its average deviation) is 1.38₃ ± 0.04 Å. This value is well within one average deviation of the value of the C-C distance value of 1.39₇ (9) found in benzene. The bond angles within the benzene ring average 119.8° with an average deviation of 1.6°.

The I-C distance of 2.05 Å is in good agreement with a variety of studies where this distance has been cited--2.05 Å (1); 2.08 Å in iodobenzene (10); 2.05 Å in *p*-diiodobenzene (11); and 2.05 Å in 1,3,5-triiodobenzene (11). The value of 1.60₂ Å for the

S-N distance is shorter than the 1.69 Å predicted using the Shomaker-Stevenson formula or the 1.66 Å found in the analogous compound (1) containing a cyclohexane ring instead of the oxa-cyclopentane. The other distances about the sulfur parallel those found in dibzenzenesulfonyl selenide (12) namely, the S-O distances of $1.46_1 \pm 0.1$ Å (versus 1.43 Å) and the S-N distance of 1.76_7 Å (versus 1.77 Å). The OSN angles average out to $111.6 \pm 1.3^\circ$ and the OSC angles to $109.2 \pm 2.2^\circ$, making the environment about the sulfur essentially tetrahedral. Of interest here is the fact that the two ring systems (the bicyclic system on one side of the sulfur atom and the pipsylate system on the other side) are very nearly perpendicular to each other with a NSC angle of 98.0° . Within the E.S.D. this is the same as the angle of 98.3° found in the analogous system (1).

The bicyclic system in which an aziridine ring is fused to an oxa-cyclopentane ring has the most interesting (and not always anticipated) results. In the aziridine ring, the C-N distance of $1.57_4 \pm 0.02$ Å is appreciably larger than that found in either the free aziridine ring (1.48₈ Å) (13) or in other bicyclic ring systems containing an aziridine ring (1-4) -- (values range from 1.52 - 1.54 Å). The C-C distance of 1.53_3 Å in the aziridine ring again parallels the values found in these other systems.

Of particular interest to us, was the fusion angle between the two ring systems. In previous studies where an aziridine ring has been fused *cis*- to a second ring (1-3) this fusion angle has been $123 \pm 1.0^\circ$ whereas it was 127° in the only *trans*-fused compound reported (4). However, in all of those cases the second ring has contained at least six atoms. On both geometric and chemical grounds one would expect this angle to be much smaller in a five-membered ring, particularly one containing an oxygen hetero-atom in it, since the OCO angle in this ring would, itself, be large (111° in tetrahydrofuran (14)). Hence the value of $111.9 \pm 1.7^\circ$ found in this study represents the first such values in the literature. With these values for the fusion angle and the value of 113.5° for the COC angle in this ring, it is not surprising that the middle angles (CCO) average to $98.5 \pm 0.5^\circ$.

If one looks at the bicyclic system as a six-membered ring containing a nitrogen in the one position and an oxygen in the four position, one would anticipate that the system would be in the chair conformation. However, this six-membered ring sits in the boat conformation with a O...N distance of 2.65 Å. Figure 4 shows very nicely the planarity of the four carbons in the system and the boat conformation of the ring. Figure 5 shows the packing within the unit cell with all contact

distances less than 3.75 Å indicated and the closest iodine-iodine contact distance (4.18 Å) also indicated.

In order to test whether the conformation of the ring system would lead to any close contacts of the hydrogen atoms in the five-membered ring, positions were calculated for these hydrogen atoms assuming C-H = 1.10 Å, and angles HCH and CCH as close 109° as possible. Figure 6 shows the molecule with these hydrogens included. The closest transannular contacts observed were 2.49 Å, indicating that no significantly short transannular hydrogen distances were incurred by the boat conformation of the bicyclic system.

Acknowledgment.

The authors wish to express their gratitude to: The National Institutes of Health (GM-08348-05 and 06) for financial assistance in support of this and subsequent studies; Professor P. E. Fanta, Department of Chemistry, Illinois Institute of Technology, The Computer Center at L. S. U. B. R. (and especially Mr. Thomas Lang); and to the Computer Center at L. S. U. N. O. (N.S.F. No. GP-2964).

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$$r = \left[\frac{\sum W(F_0 - kF_0)^2}{\sum WF_0^2} \right]^{\frac{1}{2}}$$

Unit weighting factors were used in refining this structure.

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Received July 5, 1966

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