

Crystal and Molecular Structure of *cis* 11-(*p*-Iodobenzenesulfonyl)-11-azabicyclo[8.1.0]undecane

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The crystal and molecular structure of the title compound was determined by single-crystal x-ray diffraction techniques. The compound crystallizes in the orthorhombic space group $Pca2_1$, with four molecules in a unit cell of dimensions $a = 17.552 \pm .003$, $b = 8.235 \pm .0008$ and $c = 11.914 \pm .001$ Å. The structure was solved by the heavy atom method and refined by full matrix least squares to a final value of $R = 0.055$ for the 740 independently measured, statistically significant reflections. The conformation of the cyclodecane ring in the bicyclic system differs from the idealized cyclodecane ring based on conformational studies and previous x-ray determinations of simpler systems. The differences in conformation are discussed.

Introduction.

The study of 11-(*p*-iodobenzenesulfonyl)-11-azabicyclo[8.1.0]undecane (Figure 1) was undertaken as part of a more general study of aziridine-bicyclic compounds.

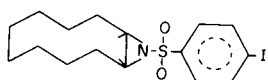


Figure 1

Based on combustion enthalpies (1,2) it has been concluded that medium-size ring systems containing either nine or ten atoms are the most highly strained. Structural studies related towards characterizing the cyclodecane ring by itself or in simply substituted compounds have already been done (3) and have led to a characterization of an "idealized" cyclodecane ring in conformity with conformational predictions (4). However, in the case of a drastic substitution, such as bicyclic fusion to an aziridine ring, pronounced changes in conformation can be expected. In addition to anticipated distortions, changes in fusion angles between the rings and a modification of the molecular parameters in the aziridine ring can also be anticipated. Consequently, the structure of the derivative named above (Figure 1) was determined and is reported herein.

Crystal Data.

A crystalline sample of the title compound was kindly furnished to us (5) by Professor Paul Fanta, Illinois Institute of Technology. A single crystal suitable for the study was obtained by recrystallizing the sample from a benzene-

hexane solution. The crystal approximated a rectangular prism with a maximum dimension of 0.2 mm.

Extinctions for the $(0k\ell)$ reflections when ℓ is odd and the $(h0\ell)$ when h is odd narrowed the space group choice to $Pca2_1$, or $Pcam$. Since it seemed unlikely that the molecule would have $2/m$ symmetry, $Pca2_1$ was originally chosen. The subsequent solution of the structure confirmed this choice. Lattice constants were determined by least squares refinement (6) of 34 reflections using $Cu-K\alpha$ radiation. Two-theta values ranging from $59^\circ - 79^\circ$ were measured under fine conditions (1° take-off angle and 0.05° receiving slit) on a G.E. XRD-5 diffractometer. The resultant constants were:

$$\begin{aligned} a &= 17.552 \pm .003 \text{ \AA} \\ b &= 8.235 \pm .0008 \text{ \AA} \\ c &= 11.914 \pm .001 \text{ \AA} \end{aligned}$$

The calculated density of $1.617 \pm .001$ g/cc³ for four molecules per unit cell was in agreement with the experimentally measured density of $1.62 \pm .02$ g/cc³ using flotation techniques.

Intensity data were taken on a G.E. XRD-490 automated diffractometer using $Mo-K\alpha$ radiation and Ross balanced filters (Zr and Y) by the stationary crystal-stationary counter method. A counting time of 15 seconds through each filter and a take-off angle of 5° were used. A set of three standards were monitored every twenty-five reflections with the crystal being manually re-aligned whenever any of the standards deviated from its original value by more than twice its standard deviation (based on counting statistics). The 2180 reflections were measured in the reflection sphere out to a 2θ of 54° , of which 740 were considered observed. Intensities were converted to

TABLE I

Final Coordinates and Anisotropic Temperature Factors

Atom	Coordinates			Anisotropic Temperature Factors (a)					
	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
I	.1789	.2400	.2500	.0056	.0125	.0070	-.0001	.0005	-.0011
C ₁	.1843	.4395	.3610	.0044	.0104	.0082	-.0002	-.0001	.0010
C ₂	.2096	.4127	.4724	.0042	.0143	.0055	.0010	.0001	-.0023
C ₃	.2238	.5501	.5413	.0109	.0102	.0057	-.0005	-.0001	-.0022
C ₄	.1956	.7049	.4987	.0030	.0080	.0087	.0006	.0010	-.0004
C ₅	.1646	.7227	.3939	.0044	.0211	.0058	.0004	-.0003	.0016
C ₆	.1576	.5927	.3231	.0033	.0141	.0062	-.0010	-.0000	-.0006
S	.2084	.8746	.5895	.0049	.0117	.0065	.0003	.0006	.0004
O ₁	.2753	.8434	.6543	.0050	.0212	.0088	-.0009	.0002	-.0001
O ₂	.2063	.0180	.5247	.0074	.0100	.0069	.0005	.0005	.0008
N	.1284	.8675	.6626	.0029	.0165	.0043	-.0005	-.0000	-.0008
C ₇	.1246	.7606	.7700	.0036	.0154	.0022	-.0000	-.0001	.0025
C ₈	.0534	.6523	.7630	.0059	.0177	.0132	-.0011	-.0012	-.0037
C ₉	.0568	.5240	.8614	.0067	.0078	.0139	.0010	.0018	.0013
C ₁₀	.0708	.5781	.9826	.0080	.0247	.0092	.0025	.0011	.0048
C ₁₁	.0099	.6625	.0441	.0034	.0169	.0106	.0004	.0004	.0009
C ₁₂	.9887	.8422	.9997	.0042	.0286	.0058	-.0023	-.0006	.0011
C ₁₃	.0624	.9506	.0154	.0085	.0132	.0070	.0002	-.0008	-.0000
C ₁₄	.0592	.1016	.9330	.0092	.0128	.0044	.0017	.0003	.0014
C ₁₅	.0638	.0509	.8074	.0073	.0120	.0073	.0017	.0011	.0013
C ₁₆	.1318	.9419	.7805	.0058	.0095	.0056	.0005	.0005	.0016

(a) The Temperature Factor is of the form $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$.

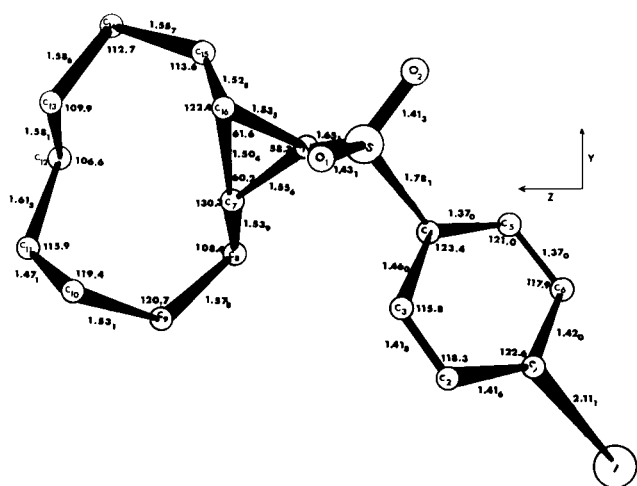


Figure II. Perspective Drawing of the Molecule with Bond Angles and Bond Distances Indicated.

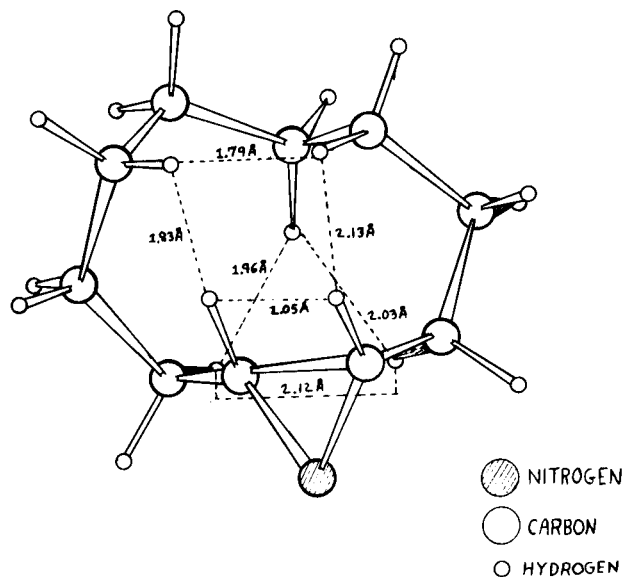


Figure III. Bicyclic System with Close Transannular Hydrogen Distances Indicated.

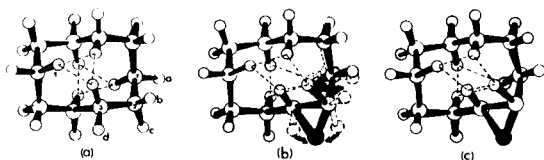


Figure IV. Sketch of Conformational Changes.

- (a) Conformation of Idealized Cyclodecane Ring.
 (b) Changes in Conformation from Idealized Model (dotted spheres) to that in Bicyclic System (solid spheres). Arrows indicate shifts necessary. Resultant close-contacts indicated.
 (c) Conformation of Final Bicyclic System.

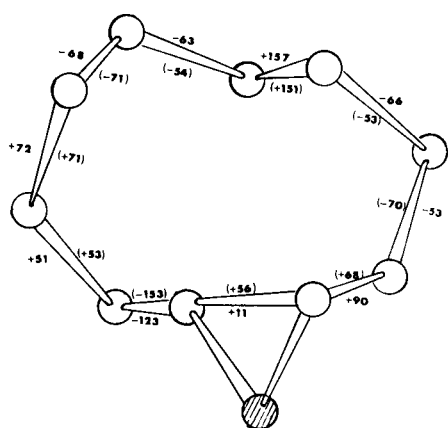


Figure V. Bicyclic System (with hydrogens removed for clarity). Torsion Angles of Idealized Cyclodecane (parentheses) Compared to Torsion Angles in Cyclodecane Moiety of Bicyclic System (no parentheses).

structure factors using a program modified for the P.D.P.-10 (7). Lorentz-polarization corrections were applied as a function of two-theta and absorption (7% maximum) was corrected as a function of phi only. Finally, a linear decay correction based on the apparent decay of the standards (approximately 15%) was applied.

Structure Determination.

The iodine coordinates were readily obtained from a three-dimensional Patterson synthesis and refined to a value of $R = 0.28$. A three dimensional Fourier map was immediately calculated based upon the magnitudes of the observed structure factors and the phases obtained from the refined iodine position. This map was calculated assuming the space-group $Pca2_1$, with the origin fixed by setting $z = 1/4$ for the iodine. This, of course, generated a

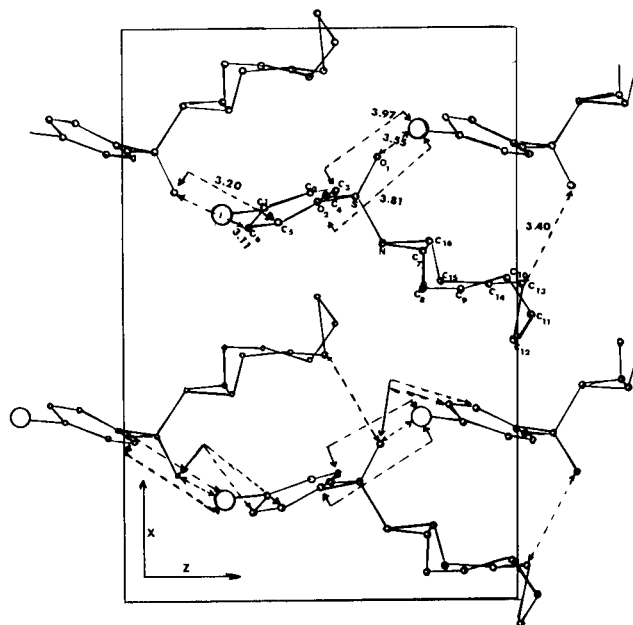


Figure VI. Packing Diagram for Unit Cell (projected down Y-axis). Closest Contacts Indicated.

TABLE II

Calculated Hydrogen Atom Coordinates

		x	y	z
Atom C ₈	H ₁	.0029	.7281	.7722
	H ₂	.0533	.5897	.6823
Atom C ₉	H ₁	.0021	.4614	.8626
	H ₂	.1030	.4402	.8418
Atom C ₁₀	H ₁	.0836	.4699	.0318
	H ₂	.1190	.6616	.9820
Atom C ₁₁	H ₁	.0298	.6694	.1306
	H ₂	.9602	.5838	.0372
Atom C ₁₂	H ₁	.9423	.8927	.0495
	H ₂	.9736	.8379	.9110
Atom C ₁₃	H ₁	.0644	.9944	.1017
	H ₂	.1125	.8779	.9957
Atom C ₁₄	H ₁	.1075	.1808	.9508
	H ₂	.0054	.1652	.9457
Atom C ₁₅	H ₁	.0122	.9840	.7860
	H ₂	.0690	.1604	.7566
Atom C ₇	H ₁	.1552	.7162	.8434
Atom C ₁₆	H ₁	.1732	.9618	.8472

mirror plane across $z = 1/4$. To test whether this mirror plane was real or not, one of the unique sets of coordinates for the sulfur, two oxygens and the benzene ring were chosen and a new Fourier map phased by these atoms (and the iodine) was generated. From the resultant three dimensional Fourier map, the rest of the atoms in the molecule appeared, having relative heights ranging in size from $2.5 \text{ e}/\text{\AA}^3$. The lack of "ghosting" of these peaks across the earlier observed "mirror" plane confirmed our choice of $Pca2_1$, as the correct space group. Full matrix isotropic refinement using all of the atoms with their appropriate scattering factors (8) resulted in a value of $R = 0.12$ with the isotropic temperature factors ranging from $2.6 \text{ e}/\text{\AA}^2$. Because of the pronounced anisotropy evident in this map, further refinement was carried out with all of the atoms anisotropic. The data ultimately refined to a value of $R = 0.05_5$ with the largest shift in either coordinate or temperature factor parameters being less than one-tenth the estimated standard deviation of that parameter. A final difference map was calculated and showed no peaks at a height greater than one electron per cubic angstrom, and so the structure refinement was considered completed.

Discussion and Results.

Standard deviations for the positional parameters of the various atoms (based upon the last cycle of least squares) were estimated at less than 0.002 \AA for the iodine, $.005 \text{ \AA}$ for the sulfur and less than 0.02 \AA for the lighter atoms. E.S.D. for the bond angles were 2.0° or less. The E.S.D. values for carbons 10, 12, 13 are, in all likelihood, grossly underestimated since these atoms (with fractional cell coordinates very close to $x, z = 0$ and with fixed coordinate for the iodine of $z = 1/4$) are in positions in which only a small number of structure factors contribute to their refinement. Table I lists the final coordinates and anisotropic temperature factors. Figure II is a perspective drawing of the molecule with the individual bond angles and bond distances indicated on the drawing.

A comparison of the known features of the molecule to similar values in the literature further corroborate our estimates of the errors involved. Thus, the I-C₁ distance of 2.11 \AA is comparable to the 2.08 \AA distance in iodo-benzene (9). Within the benzene ring the average C-C distance (and its average deviation) of $1.40_9 \pm .02_6 \text{ \AA}$ and the average internal CCC angle of $119.9 \pm 2.5^\circ$ agree with the accepted literature values (10). The sulfur atom maintains an essentially tetrahedral environment with a S-C₄ distance of 1.78 \AA , a S-N distance of 1.65 \AA and a S-O average distance of $1.42_2 \pm .01_1 \text{ \AA}$. The major distortion from a tetrahedral environment, the C₄SN angle of 100.7° , is in agreement with results in previous studies. For example, in two other similar derivatives (11,12) the angle

between the pipsylate ring system on one side of the sulfur and the bicyclic system on the other side led to values for this angle of 98.5° and 98.0° , respectively.

Within the aziridine ring, the CN distances of $1.54_5 \pm .01_1 \text{ \AA}$ and the CC distance of 1.50_4 \AA follow the trend previously observed in such bicyclic systems (11-16). Namely, there is a lengthening of both bond types from the values found in the free aziridine molecule (C-C = 1.48_0 \AA and C-N = 1.48_8 \AA) (17) as one increases the size of the second ring from a five membered to a twelve membered ring. The internal angles average to $60.0 \pm 1.2^\circ$ as would be expected.

In previous aziridinium-bicyclic derivatives, a trend had been observed in the fusion angles between the aziridine and the larger ring. In all such studies where the fusion was *cis* and the larger ring contained between six and twelve carbon atoms (11,12,13,14,15) the fusion angle was $123 \pm 1.5^\circ$. In the only *trans* fused case studied (to a cyclododecane ring) the fusion angles were $126.6 \pm 2^\circ$ (12). In the present study, the fusion angles (122.4° and 130.3°) are significantly different from each other and cover the entire range in question. The variation from our previous results in this series of compounds can be attributed to two sources. First, the fusion does not occur across the symmetry element of the medium-sized ring as in all previous cases. Second, the pattern of transannular interactions postulated below, differs from that found in cyclododecane.

Excluding the fusion angles and the bond common to both rings, the distances in the cyclododecane ring average to $1.55 \pm .02_4 \text{ \AA}$ and the angles average to $113.4 \pm 4.0^\circ$. It is interesting to note that a strain minimization calculation most recently proposed for these rings presumes a zero-strain bond angle of 112.7° (18).

X-Ray investigations of five crystalline derivatives of cyclododecane (19-23) have confirmed that the conformation of the unsubstituted (idealized) cyclododecane ring possesses $2/m$ (C_{2h}) symmetry. Torsional angles are essentially preserved with the existing strain energy arising primarily as Baeyer strain (angle widening) and transannular (hydrogen) interactions. However, none of the structures studied subjects the cyclododecane ring to the distortions which could be anticipated when an aziridine ring is *cis* fused as in this compound. Thus, to investigate this anticipated distortion, hydrogen positions were calculated for our compound (assuming C-H = 1.09 \AA , $\angle\text{HCH} = 111^\circ$ and the four $\angle\text{CCH}$ angles are all essentially equal and close to tetrahedral). Figure III shows the resultant model and indicates the calculated close transannular interactions. Table II gives the coordinates of the calculated hydrogen atoms.

In an attempt to rationalize the changes from the idealized cyclododecane ring to our structure, a ball and stick

model of the idealized cyclodecane ring was distorted to accommodate a *cis*-fused aziridine. Figure IVA shows the idealized cyclodecane model with the close transannular hydrogen contacts indicated. Since the ring is symmetric, one need consider only carbon atoms 1,2,3. For these atoms, positions a-d are the only ones suitable for substitution. Sites ac or bd utilized in pairs would lead to a *trans* fusion and can thus be excluded. Site ab would lead to a *cis* fusion but would lead to major changes in torsional angles and so is less likely than the remaining alternative—namely cd. Figure IVB indicates the changes resulting in the ball and stick model as positions c and d are brought into coincidence to form the three-membered ring. Finally, Figure IVC indicates the resultant ball and stick model which conforms closely to our result both in conformation and in the pattern of transannular hydrogen contacts.

Figure V again shows our bicyclic system, stripped of its hydrogens for clarity, but with the torsion angles of the idealized cyclodecane ring compared to those found in our ring system. The agreement in magnitude and sign of symmetry related torsion angles across the two-fold axis in the idealized ring and the agreement in magnitude but with opposite sign of symmetry related torsion angles across the mirror plane is obvious for the idealized ring. What is surprising is that the cyclodecane ring in the bicyclic system studied herein also maintains a very close semblance of these same relationships (except at the fusion point) even though the C_{2h} symmetry is destroyed. If the cyclodecane ring system can thus maintain its conformational aspects after such a potentially drastic change (the *cis*-aziridine bicyclic fusion) it seems only reasonable to assume that the conformation found in the solid state would retain its major features even in solution.

Figure VI shows the packing within the unit cell. No extremely short intermolecular contacts exist although the oxygen atom (O_1) does have three contacts (to I, C_5 , C_5) slightly less than the anticipated Van der Waal contact distances.

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