The Crystal and Molecular Structure of
1-(p-Iodobenzenesulfonyl)-1-azaspiro[2.5]octane

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The structure of 1-(p-iodobenzenesulfonyl)-1-azaspiro[2.5]octane was determined by a single-crystal x-ray diffraction study. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions: a = 11.65$_5$, b = 11.82$_5$, c = 11.06$_8$ ± 0.002 Å. The aziridine ring is spiro-fused to the cyclohexane ring with the nitrogen atom occupying the equatorial position. The cyclohexane ring is in an undistorted chair conformation and forms a dihedral angle of 97.1° with the aziridine ring. The structure was refined to a final value of R = 0.074 for the 590 independent reflections.

Introduction.

The study of 1-(p-iodobenzenesulfonyl)-1-azaspiro-[2.5]octane (Figure 1) was undertaken as part of a more
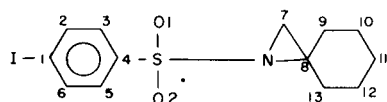

Figure 1

general study of aziridine in a variety of bonding situations. Previous studies undertaken in this laboratory (1) have characterized the trends observed when an aziridine ring is *bicyclically-fused* to a larger saturated ring (cyclopentane through cyclododecane). To our knowledge no structural information was previously available for the situation in which an aziridine ring is *spiro-fused* to a saturated ring system. Consequently, the structure determination reported herein represents the first such analysis.

Crystal Data.

A crystalline sample of the title compound was made available to us by Professor Paul Fanta of the Illinois Institute of Technology. A single crystal of sufficient quality for x-ray study was obtained by vapor-diffusion recrystallization of the sample from a solution of benzene exposed to an atmosphere saturated with hexane vapor. The crystal chosen for the study had approximate dimensions of 0.17 mm x 0.15 mm x 0.05 mm. Its shape approximated a rectangular prism.

The space group was unambiguously assigned as $P2_12_12_1$ from the extinct (h00), (0k0), (00ℓ) reflections when h, k or ℓ are odd, respectively. Cell dimensions were determined using Cu-Kα radiation. The $K\alpha_1$-$K\alpha_2$ peaks for a set of 27 reflections with the two-theta values

ranging from 57°-72° were resolved and measured under fine conditions (1° take-off angle and 0.05° receiving slit) on a G.E. XRD-5 diffractometer. These values were then refined by least-squares techniques (2) resulting in the cell dimensions (and estimated standard deviations) given below:

$$a = 11.655 \pm 0.002 \text{ Å}$$
$$b = 11.825 \pm 0.002 \text{ Å}$$
$$c = 11.068 \pm 0.002 \text{ Å}$$

The calculated density of 1.642 g/cm^3 was in agreement with the experimentally measured value of 1.62 g/cm^3 using flotation techniques.

Intensity data were collected on a G.E. XRD-490 automated diffractometer using Mo-Kα radiation and Ross balanced filters (Zr and Y) by the stationary crystal-stationary counter method. A counting time of 10 seconds for 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 two standard deviations (based on counting statistics). Two equivalent sets of data were taken; each at a different phi range of the reflection sphere, together spanning the range from 0° to 180°. In each data set, 1184 reflections were measured in the reflection sphere out to a 2θ of 45°; 590 were considered observed. Each data set was converted independently to structure factors using a program modified for the PDP-10 (3). Lorentz-polarization corrections were applied as a function of two-theta, and absorption (20% maximum) was corrected as a function of phi only. The absorption was measured at two different two-theta values and since the curves were similar, the absorption was treated as being independent of two-theta. The relatively

TABLE I

Fractional Coordinates and Anisotropic Thermal Parameters (a)
(Standard Deviations x 10^4 in parentheses)

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	.1102 (3)	.2221 (3)	.1859 (3)	.0089 (2)	.0096 (2)	.0150 (3)	.0044 (2)	.0015 (3)	-.0011 (3)
S	.6283 (8)	.5081 (8)	.2423 (9)	.0074 (8)	.0074 (8)	.0085 (9)	.0005 (8)	.0007 (9)	-.0004 (8)
O_1	.5826 (19)	.5299 (27)	.1285 (22)	.0059 (22)	.0248 (41)	.9903 (27)	.0097 (26)	-.0017 (21)	.0006 (30)
O_2	.6497 (18)	.5998 (17)	.3196 (14)	.0100 (23)	.0057 (17)	.0110 (26)	.0005 (17)	-0039 (26)	-.0040 (24)
N	.5510 (27)	.4165 (27)	.3105 (34)	.0129 (34)	.0124 (34)	.0135 (42)	.0024 (29)	.0035 (28)	.0089 (40)
C_1	.9560 (24)	.3166 (24)	.2097 (27)	.0069 (27)	.0045 (26)	.0043 (38)	-.0009 (22)	-.0009 (26)	.0000 (26)
C_2	.9233 (31)	.3449 (31)	.3193 (35)	.0123 (41)	.0117 (37)	.0055 (36)	.0001 (32)	-.0060 (41)	.0038 (39)
C_3	.8172 (32)	.4007 (30)	.3326 (33)	.0130 (40)	.0090 (34)	.0056 (38)	.0077 (33)	.0007 (38)	.0051 (35)
C_4	.7577 (24)	.4316 (25)	.2335 (22)	.0060 (27)	.0064 (28)	-.0019 (24)	.0059 (24)	.0015 (23)	.0008 (23)
C_5	.7929 (35)	.3930 (30)	.1154 (41)	.0128 (43)	.0049 (32)	.0184 (60)	.0039 (35)	.0070 (46)	-.0021 (39)
C_6	.8946 (37)	.3310 (32)	.1068 (33)	.0129 (43)	.0113 (39)	.0102 (46)	-.0015 (41)	.0098 (46)	-.0043 (37)
C_7	.4541 (29)	.3571 (29)	.2476 (47)	.0075 (34)	.0067 (32)	.0294 (81)	-.0037 (28)	.0020 (45)	-.0156 (45)
C_8	.4329 (29)	.4443 (35)	.3391 (39)	.0060 (31)	.0148 (46)	.0130 (54)	-.0022 (33)	-.0010 (37)	-.0018 (48)
C_9	.4038 (42)	.4051 (45)	.4660 (48)	.0113 (48)	.0197 (61)	.0206 (67)	.0009 (54)	.0007 (59)	.0055 (59)
C_{10}	.2673 (41)	.3956 (47)	.4910 (51)	.0124 (51)	.0179 (62)	.0258 (93)	.0073 (51)	.0032 (58)	.0000 (65)
C_{11}	.2087 (38)	.5026 (59)	.4515 (58)	.0088 (47)	.0339 (96)	.0329 (99)	.0006 (64)	-.0027 (63)	-.0283 (88)
C_{12}	.2385 (37)	.5353 (51)	.3251 (36)	.0141 (48)	.0352 (92)	.0063 (42)	.0089 (55)	.0127 (44)	-.0082 (60)
C_{13}	.3658 (25)	.5570 (37)	.3076 (37)	.0028 (27)	.0225 (55)	.0134 (47)	-.0019 (31)	.0107 (37)	-.0087 (51)

(a) Anisotropic temperature factors of the form: $\exp[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell]$

TABLE II

Calculated Hydrogen Positions

Atom (a)	X	Y	Z
$H_{1,7}$	.4373	.2760	.2654
$H_{2,7}$	.4378	.3729	.1604
$H_{1,9}$	.4372	.4601	.5249
$H_{2,9}$	.4389	.3289	.4789
$H_{1,10}$	.2538	.3836	.5793
$H_{2,10}$	.2353	.3302	.4446
$H_{1,11}$	.2321	.5651	.5071
$H_{2,11}$	.1235	.4912	.4569
$H_{1,12}$	.1956	.6059	.3039
$H_{2,12}$	.2146	.4729	.2695
$H_{1,13}$	.3914	.6193	.3626
$H_{2,13}$	.3812	.5789	.2219

(a) Second number refers to carbon atom to which the hydrogen is bonded.

low linear absorption coefficient of $\mu = 22.5$ cm^{-1} was consistent with the experimentally observed two-theta independence. The standard reflections indicated that there was no observable crystal decay. At this point an agreement factor was calculated between the two sets of data of R = 0.078. The precision of the data was considered to be sufficient to allow the data to be combined. The structure determination was then carried out with the averaged set of structure factors.

Structure Determination.

The iodine and sulfur coordinates were readily obtained from the three-dimensional Patterson map. From the Patterson vectors of these atoms and geometric considerations, reasonable coordinates for the two phenyl carbon atoms lying along the straight line determined by the iodine and sulfur were obtained. Using the coordinates of these 4 atoms in 4 cycles of least-squares refinement, the data refined to an R value of 0.26. From a combination of Fourier and difference Fourier syntheses, the rest of the structure was obtained (see Figure 2). Using the coordinates of all 18 atoms in 10 cycles of isotropic refinement, with a block diagonal approximation, the data refined to a value of R = 0.18. At this point the isotropic

temperature factors were converted to anisotropic temperature factors. After an additional 20 cycles of refinement, the R value had dropped to 0.074 with the largest shifts in both coordinate and temperature factor parameters being less than one-tenth the estimated standard deviation of any of the parameters. A final difference map was calculated and showed no peak at a height greater than about 1.0 $e^-/Å^3$, and so the structure refinement was considered to be complete.
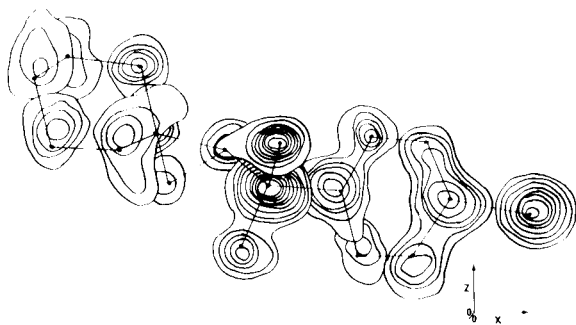

Figure 2 - Fourier projection based on the phases resulting from the positions of: iodine, sulfur, C_1, C_4. Contours drawn at 1.0 e/Å for light atoms.

Results and Discussion.

Standard deviation for the various atoms were calculated at 0.01 Å for the iodine, 0.02 Å for the sulfur and averaged 0.04_5 Å for the lighter atoms. Table I lists the final coordinates and anisotropic temperature factors. These values are substantially higher than would be anticipated for a structure refined to a value of R = 0.07_4. Our troubles, as is often the case under these circumstances, can be traced largely to crystal quality. The difficulty in obtaining a crystal of suitable quality and size which in turn scatters sufficiently well, was, in itself, a problem which occupied us for almost one year. Our efforts were only partially successful as is reflected in our measured data which is carried out to $2\theta = 45°$ and accounts for our ultimately obtaining only 590 out of 1184 reflections (< 50%) which were statistically significant.
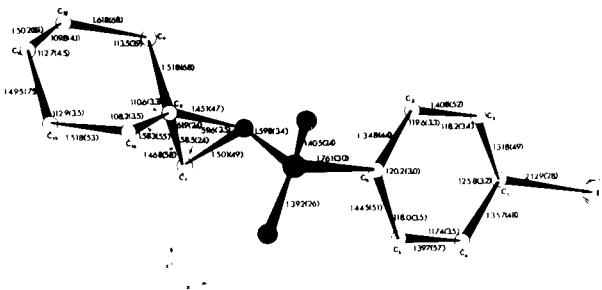

Figure 3 - Perspective drawing of molecule with distances and angles given (ESD in last Figures given in parentheses).

Figure 3 shows a perspective drawing of the molecule with the bond distances and bond angles indicated. If one focuses first on the known aspects of the structure, the p-iodobenzylsulfonyl moiety, one can gauge the reliability of the data. The S–O distances (1.39_3 and 1.40_4 Å) average to 1.40 Å which is well within the range 1.37_1 - 1.47_3 quoted (4,5,6) in other similar derivatives. Similarly, the S–C distance of 1.76_6 Å lies in the range 1.73 - 178 Å quoted for this distance in these other compounds. The angles about the sulfur atom ($\angle OSO = 118.4°$, $\angle CSO = 108.8° \pm 2.6°$, $\angle OSN = 109.7°$, and $\angle CSN = 99.5°$) are those to be anticipated and correlate quite well with the same literature values.

The phenyl ring at first glance appears more distorted than is usually anticipated with $\overline{CC} = 1.38 \pm 0.036$ Å and $\angle CCC = 119.9 \pm 2.1°$. The major distortion involves atom C1 bonded to the iodine. The very pronounced anisotropy of the iodine makes this peak both difficult to resolve in either a Fourier or difference Fourier map and also makes its least-squares refinement somewhat ambiguous. One can place it in its most likely location on the straight line connecting the iodine, C4 and the sulfur and at a reasonable I–C distance (2.03 Å) and continue refinement with its coordinates fixed at this position. If this is done, the R-value is unaffected, but the remaining phenyl atoms shift slightly resulting in the phenyl ring with C–C = $1.39_9 \pm 0.027$ Å and CCC = 118.7 ± 1°. Thus, although none of the actual distances or angles are seriously affected, the standard deviations are improved.

The bicyclic moiety is, of course, the primary interest in this study. The aziridine ring itself has C–N distances averaging 1.47_6 Å and a C–C distance of 1.46_8 Å. These values agree with those found in a microwave study of aziridine itself (7) where these values are 1.48_0 and 1.48_8 Å, respectively. The internal angles in the aziridine average to 60.1 ± 0.7° which again is the expected value.

The cyclohexane ring has distances averaging to 1.53_9 ± 0.04 Å and internal angles averaging to 111.3 ± 1.6°. These average distances and angles are in agreement with those cited in the literature (8). Only one of these distances (C9-C10 = 1.61_6 Å) deviates by two standard deviations from the average, and based on our other difficulties, it is not felt that this difference should be assigned any chemical significance. The nitrogen is equatorial to the six-membered ring, as predicted from the chemistry of this compound (9). This is shown in Figure 4.

A particular point of interest is centered around the question of whether the six-membered ring in this compound is distorted. In a previous study (10) in which an aziridine ring is bicyclically cis fused to a cyclohexane ring, the cyclohexane ring was badly distorted. It was appreciably flattened; the internal angles were opened up far beyond the values normally expected; and a discreet
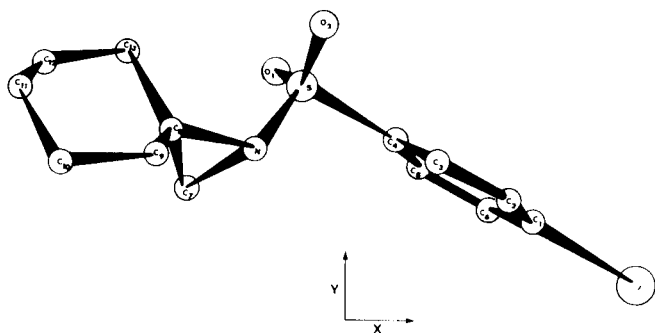
Figure 4 - Perspective drawing of molecule showing the nitrogen in the equatorial position.
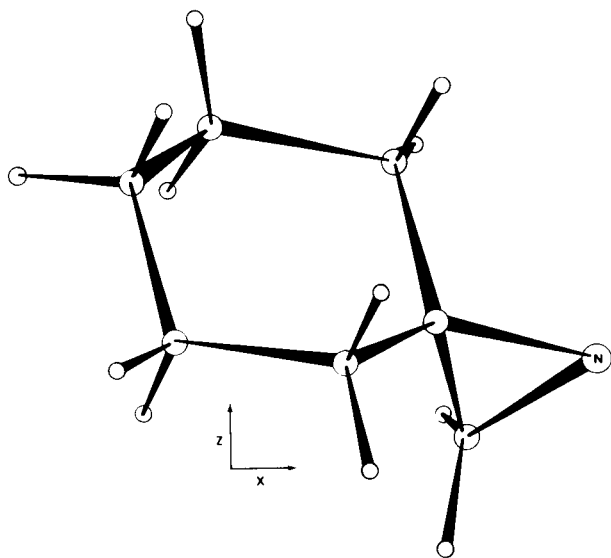

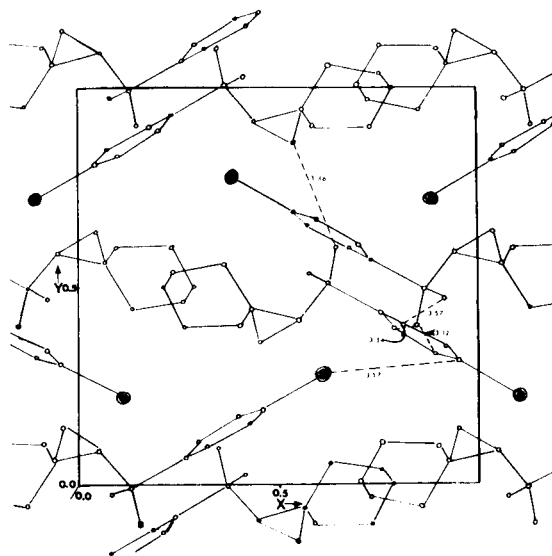Figure 5 - Perspective drawing of the spiro-fused moiety (including the calculated hydrogen atoms).

Figure 6 - Contents of the unit cell. All close contact: between molecules involving iodine which are less than 4.0 Å and all other close contacts less than 3.5 Å are indicated.

The only contact between iodine and the lighter atoms (I-Cl) less than 4.0 Å is 3.58 Å. The three closest contacts (less than 3.50 Å) between the lighter atoms consist of three distances to O_2 of 3.32, 3.34 and 3.36 Å, involving C_6, C_5, and C_7, respectively. None of these distances are close enough to merit additional comment. The packing within the unit cell is illustrated in Figure 6.

Acknowledgment.

shortening in the bond lengths was observed. By contrast, none of these effects were present in this compound. Rather, the torsion angles range from ± (50-60°) and the dihedral angles about the center bonds are 131° and 129.6° showing that the cyclohexane ring is essentially undistorted. Further, the angle between the plane of the aziridine ring and the plane of the three adjacent atoms in the cyclohexane ring has a value of 97.1°. Finally, evidence of this lack of appreciable distortion is supported by the calculated hydrogen positions in the cyclohexane ring. These calculated positions (based on geometric considerations and an assumed C–H distance of 1.00 Å) are listed in Table II. Based on these positions no transannular contacts (less than 2.30 Å) are noted in the cyclohexane ring. Figure 5 illustrates the spiro-fused moiety with the calculated hydrogen positions.

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