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## Molecular Geometry of 3-Bromo- $\lambda^6$ -thietane 1,1-Dioxide in the Gas Phase and Comparison with the Crystal Molecular Structure

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**Abstract.** The molecular geometry of 3-bromo- $\lambda^6$ -thietane 1,1-dioxide,  $C_3H_5BrO_2S$  ( $M_r = 185$ ), was determined in the gas phase by electron diffraction. The overall structure of the free molecule is in agreement with that determined in the crystal [Chiang (1983). *Acta Cryst.* **C39**, 737–738]. The most important differences are as follows: the ring is more puckered, the C–C bond is longer and the  $SO_2$  group is more open in the gas phase than were found in the crystal.

**Introduction.** The purpose of this study is to determine the molecular geometry of 3-bromo- $\lambda^6$ -thietane 1,1-

dioxide in the gas phase by electron diffraction, to compare it to other organosulfone structures (Hargittai, 1985a) and, in particular, to the crystal molecular structure of the same compound (Chiang, 1983).

**Experimental.** The sample was supplied by Professor D. C. Dittmer of Syracuse University. The electron diffraction patterns were recorded in Budapest with a modified EG-100A apparatus (Hargittai, Tremmel & Kolonits, 1980; Tremmel, Kolonits & Hargittai, 1977). A so-called membrane nozzle system was used (Hargittai, Hernádi, Kolonits & Schultz, 1971) with a nozzle temperature of 453 K and nozzle-to-plate distance of 50 and 19 cm. The treatment of the experimental data and the procedure of analysis followed the usual techniques of the Budapest group (see, for example, Domenicano, Schultz, Kolonits & Hargittai, 1979). The total range of

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intensity data used in the analysis was  $1.875 \leq s \leq 35.25 \text{ \AA}^{-1}$  with data steps  $\Delta s = 0.125 \text{ \AA}^{-1}$  up to  $s = 14.00 \text{ \AA}^{-1}$  and  $\Delta s = 0.25 \text{ \AA}^{-1}$  through to the upper limit of the range. The experimental radial distribution is shown in Fig. 1 together with a theoretical distribution.

The least-squares method was applied to the molecular intensities (Andersen, Seip, Strand & Stølevik, 1969) in the usual manner of our laboratory (Hargittai & Hargittai, 1973). The empirical background was corrected several times during the analysis but the structural results proved to be insensitive to changes in the background. A mixture of two models with equatorial and axial Br positions was used with identical geometries for the rest of the molecule. A mean length was determined for the five C–H bonds. The geometrical parameters of the molecule are collected in Table 1. They originate from a refinement carried out for  $r_a$  parameters but were converted into  $r_g$  bond lengths and  $r_a$  bond angles (see, for example, Kuchitsu, 1981). The estimated total errors (Hargittai & Hargittai, 1973) are also given. The ring puckering refers to the angle between the CCC and CSC planes in the ring. Generally speaking, the equatorial and axial conformations with bromine as substituent would have highly different electron scattering intensity distributions. However, the two forms are not very different in this particular case as the deviation from ring planarity is relatively small.

Spectroscopic calculations provided  $l$  and  $K$  values (see, for example, Kuchitsu, 1981), which were most useful in selecting starting  $l$  values and constraining differences between  $l$  values associated with similar distances in the refinements. Groups of distances whose contributions appear under the same maximum on the  $f(r)$  curve were formed, and the amplitudes associated with them were refined together using the above-mentioned constraints.

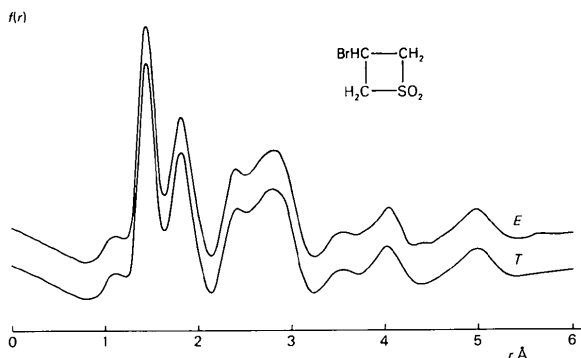


Fig. 1. Experimental (*E*) and theoretical (*T*) radial distributions for 3-bromo- $\lambda^6$ -thietane 1,1-dioxide from gas-phase electron diffraction.

Table 1. Bond lengths ( $r_g$ ) and bond angles of 3-bromo- $\lambda^6$ -thietane 1,1-dioxide from electron diffraction

The uncertainties are estimated total errors (Hargittai & Hargittai, 1973). Structural data for the crystalline molecule are cited for comparison.

	Gas (present work)	Crystal* (Chiang, 1983)
Bond lengths (Å)		
C–H	1.109 (7)	
C–C	1.567 (6)	1.525
S–C	1.801 (4)	1.793
S=O	1.442 (3)	1.410 (mean)
Br–C	1.933 (6)	1.940
Bond angles (°)		
CCS	89.2 (5)	87.9
CSC	80.4 (4)	82.2
CCC	95.8 (7)	101.3
OSO	121.5 (5)	116.2
Puckering angle (°)		
CCC/CSC	25.0 (14)	9.0
Relative abundance		
Br (equatorial (%))	76 (10)	

\* The e.s.d.'s for bond distances are 0.01–0.02 Å, for bond angles 0.6–1.4°.

Calculations have been carried out employing as well as ignoring perpendicular correction terms. The former did not lead to improvement in the agreement between experimental and calculated data perhaps because the spectroscopic calculations were based on an assumed and rather crude force field. The structural results, including ring puckering, however, did not change appreciably under these varying refinement conditions.

**Discussion.** The overall molecular geometry in the gas phase is consistent with the crystallographic results. The electron diffraction bond lengths are markedly more accurate.

Both the C–C and S=O bonds seem to be longer in the free molecule than in the crystal. The C–C bond is rather long in the gas phase by any standard, and it is a general observation that four-membered rings tend to have long bonds – longer than, for example, the analogous three-membered and five-membered molecules (Hargittai, 1985a). Recently Luger & Buschmann (1984) noted a relatively long C–O bond in oxetane as determined by X-ray diffraction of the crystal. The bonds were longer at the lower temperature (90 K) than at a somewhat higher temperature (140 K), the differences amounting to nearly two hundredths of an Å for both C–C and C–O bonds.

The length of the S–C bond in the title molecule is not remarkable at all and the agreement is good between the gas and crystal data. The S–C bond lengths in fact have been observed to vary in a wide range (Hargittai, 1985b).

The geometry of the sulfone group itself shows some curious discrepancy in the two phases. Here it is also instructive to examine the O...O non-bonded distance.

Open-chain sulfones show a remarkable constancy for this distance (Hargittai, 1985a); its mean value is 2.484 Å with a standard deviation of 0.004 Å in a large group of substances. This result refers to free gas-phase molecules. The SO<sub>2</sub> geometries in crystalline sulfones are generally similar to those of the free molecules. The O...O distances, however, show a much greater variation in the crystalline phase (Hargittai, 1985a). The mean value of the O...O distances in some crystalline sulfones is 2.47 Å ( $\sigma = 0.02$  Å). Thermal-motion corrections have not always been employed in the sample examined, therefore one has to be cautious in making conclusions.

There are only few data for cyclic sulfones and only the ethylene episulfone (thiirane 1,1-dioxide), (CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>, O...O distance was determined accurately, viz. 2.501 (3) Å, by microwave spectroscopy (Nakano, Saito & Morino, 1970).

The present result of  $r_g(\text{O}\cdots\text{O}) = 2.516$  (10) Å seems to be more plausible than the 2.39 Å observed in the crystal structure. If the latter were correct, it could be a consequence of intermolecular interactions. However, in the above-mentioned sample of 35 crystalline molecules, none had an O...O distance shorter than 2.44 Å (Hargittai, 1985a).

The molecule is puckered both in the gas and in the crystal phase. The equilibrium structure is not necessarily different as the consequences of averaging over intramolecular motion are not the same in the two experiments.

The presence of both equatorial and axial bromine positions is indicated by the electron diffraction data. This is an interesting result that will hopefully incite spectroscopic studies of this structure. Further infor-

mation on the molecular vibrations of this compound could make a more detailed analysis of the present electron diffraction data worthwhile.

The electron diffraction patterns were recorded by Mrs Mária Kolonits and we appreciate her skillful assistance. Dr Béla Rozsonai did some work on the experimental intensity curves and instructed one of us (JB) in the use of some programs.

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## Nonsteroidal Antiinflammatory Drugs. I. Structure of 2-(2-Isopropyl-5-indanyl)-2-methylpropionic Acid

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**Abstract.** C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>,  $M_r = 246.4$ , monoclinic,  $P2_1/c$ ,  $a = 13.674$  (2),  $b = 6.686$  (2),  $c = 15.670$  (2) Å,  $\beta = 92.14$  (2)°,  $V = 1431.6$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.14$  g cm<sup>-3</sup>, graphite-monochromated Cu K $\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 5.9$  cm<sup>-1</sup>,  $F(000) = 536$ ,  $T = 298$  K, final  $R = 0.074$  for 1748 reflections. The torsion angle

of the 2-methyl-2-phenylpropionic acid moiety with respect to the benzene ring is larger than those of 2-phenylpropionic acid derivatives owing to the substituted methyl groups. Such a restriction in conformation may be related to the attenuation of the antiinflammatory activity.