On the Molecular Geometry of 1,2-Bis(methylsulfonyl)ethane from Electron Diffraction

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The molecules of organic sulfur compounds show interesting structural variations.[1,2] The sensitivity of the S–C bond length to its environment has been noted. However, the S–C bond in the CH_3SO_2 moiety has been observed to be remarkably constant at 1.76–1.77 Å in a series of CH_3SO_2X molecules with X=F[3], Cl[4], CH_3[5], $N(CH_3)_2$[6]. Another characteristic feature of these methane sulfone structures is the remarkable constancy of some of the 1,3 non-bonded distances[1,2], *viz.* O···O at 2.48 Å and C···O at 2.61 Å.

The present electron diffraction investigation of the molecular geometry of 1,2-bis(methylsulfonyl)ethane is an extension of the above mentioned studies. This compound is not ideally suited for gas-phase electron diffraction and had been examined previously by X-ray diffraction in the crystal.[7] *Anti* orientation of the S–C–C–S and a *gauche* orientation of the C–C–S–C bond sequences were established. The nonterminal S–C bond was found to be longer than the terminal S–C bond by 0.02 Å. The published structure originated from a room-temperature X-ray study[7] while a subsequent low-temperature investigation[8] (cf. Table 1) confirmed all earlier findings. The present electron diffraction work was initiated at the suggestion of Dr. F. Mo and was aimed at comparing the gas-phase structure with the crystal-phase one. As the molecule is relatively complex, the task of the electron diffraction work was formulated in such a way as to examine the S=O bond length, the conformational properties and the nonterminal bond lengths of this molecule making use of the rather well-know geometry of the CH_3SO_2 moiety. Special attention was paid to evaluate the possible consequences of the extensive assumptions needed in this study on the parameters which were determined.

The sample of 1,2-bis(methylsulfonyl)ethane (synthesized by the late Dr. T. Brun) was a gift from Dr. F. Mo. The electron scattering experiment and data treatment followed the usual procedure of the Budapest group.[9] A stainless steel nozzle similar to the one usually employed in our high-temperature experiments[10] was used with a 205 °C nozzle temperature. Molecular intensities and radial distributions are shown in Figs. 1 and 2.

The heavy-atom skeleton of 1,2-bis(methylsulfonyl)ethane has three axes of rotation (see Fig. 3). As regards rotation about the central C–C bond an *anti* or nearly *anti* S–C–C–S orientation was established. A few degrees deviation from coplanarity according to the electron diffraction data could well be the consequence of shrinkage as a result of torsional vibrations. As regards rotation about the C–S bonds, two models were found to approximate the experimental data about equally well. In one, one of the C–C–S–C chains had *anti* orientation and the other deviated from such an orientation by some 150° nearing a *syn* orientation in fact. In the other model, the skeleton had an inversion center with the C–S–C planes being essentially perpendicular to the S–C–C–S plane. The relative orientation about the C–S bonds influenced the electron diffraction distributions relatively little. Accordingly, the choice between these two models did not influence appreciably the results for the other parameters obtained in various refinements. Similar results should be expected for their mixture. The model with the inversion center (see Fig. 3) was preferred in most calculations as it was similar to the conformation in the crystal phase. Considerably worse agreement between calculated and experimental distributions was observed for the following models of internal rotation: 1) S–C–C–S *anti* and both C–C–S–C *anti*; 2) S–C–C–S *gauche* (112°) and both C–C–S–C *anti*; 3) S–C–C–S *gauche* (98°), one C–C–S–C *anti*, the other *gauche* (105°).

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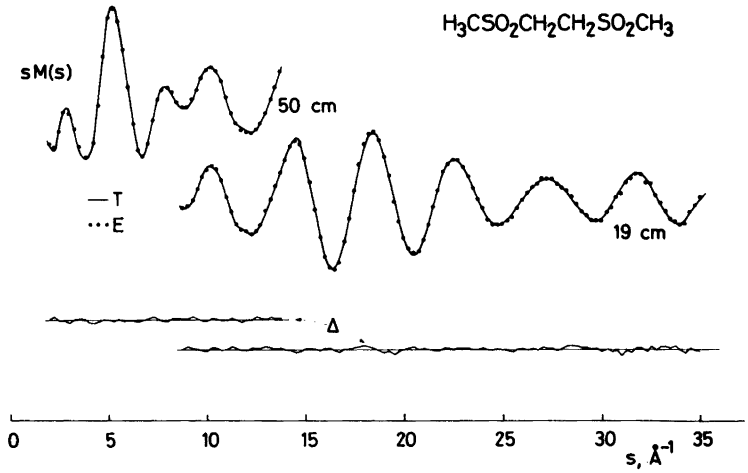

Fig. 1. Experimental (E) and theoretical (T) electron diffraction molecular intensities and difference curve (△) for 1,2-bis(methylsulfonyl)ethane.

The electron diffraction analysis was augmented by spectroscopic calculations in which accumulated experience from a large number of related compounds has been utilized.[1,11] From an approximate diagonal valence force field mean amplitudes of vibration were computed. They were used as starting values in the least-squares refinements. When amplitudes were refined in groups, differences between the individual *l* values were kept at the computed differences.

The results of a representative refinement are compiled in Table 1. The geometrical constraints include the S–C terminal bond length and the O···O and C···O 1,3 nonbonded distances. The standard deviations for the assumed distances were obtained in a refinement employing essentially zero "fudge factors". Although the assumed parameters appear to be characteristic for CH_3SO_2 moieties, these assumptions represent severe constraints for our analysis. Although the molecule is rather large and complex it should not necessarily be such an unsuitable object for electron diffraction. However, the simplicity of the radial distribution in Fig. 2 indicates how poor it is in structural information indeed.

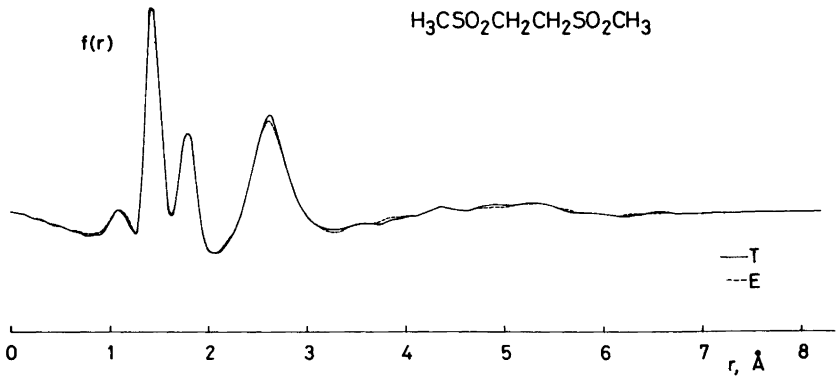

Fig. 2. Experimental (E) and theoretical (T) radial distributions for 1,2-bis(methylsulfonyl)ethane.

Table 1. Molecular parameters of 1,2-bis(methylsulfonyl)ethane from electron diffraction least-squares refinement; r_g internuclear distances (in Å), bond angles (in degrees), and mean amplitudes of vibration (in Å) with estimated total errors.

r(C–H)	1.110±0.005	l(C–H)	0.075±0.004
r(S=O)	1.443±0.003	l(S=O)	0.039±0.001[a]
r(C–C)	1.561±0.012	l(C–C)	0.057[a]
r(S–C)$_t$	1.772±0.025	l(S–C)$_t$	0.054±0.008[a]
r(S–C)$_n$	1.808±0.025	l(S–C)$_n$	0.054[a]
r(O···O)	2.488±0.019	l(O···O)	0.099±0.010
r(O···C)$_t$	2.614±0.023	l(O···C)$_t$	0.108 (assumed)
C–C–S	106.4±2.1		
C–S–C	100.4±2.0		
O=S–C$_t$	108.3		
O=S–C$_n$	109.6		
O=S=O	119.0		
S–C–H	109.5 (assumed)		
H–C–H	109.5 (assumed)		

The subscripts t and n refer to terminal and nonterminal carbon atoms; [a] indicate refinements of amplitudes with constrained differences.

The only truly well determined parameter is the S=O bond length, r_g=1.443±0.003 Å. The low-temperature x-ray data[8] gave r(S=O) 1.446 Å as mean value showing excellent agreement. It appears that the C–C bond is longer in gas, r_g 1.561±0.012 Å, than in crystal, r(C–C) 1.522 Å; unfortunately the gas parameter is very uncertain. Assuming the terminal S–C to be the same as in other molecules, the nonterminal S–C bond shows a lengthening but the uncertainties are too large to warrant any meaningful discussion. The crystal data establish this difference with same sign much more reliably. Similar differences have been observed in several substances.[12] There seems to be some characteristic difference between the *absolute* values of the S–C bond lengths in gas and crystal. Although the terminal/nonterminal difference in gas itself is not reliably determined, the mean S–C bond length is, 1.789 Å, and it is certainly larger than the mean of the two bond lengths reported from X-ray diffraction (1.758 Å and 1.781 Å).[8]

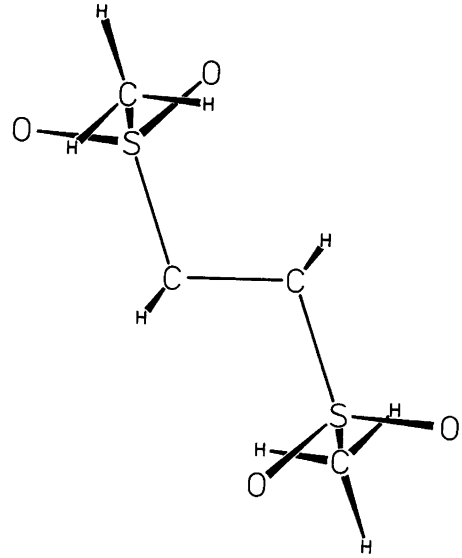

Fig. 3. Molecular model of 1,2-bis(methylsulfonyl)ethane.

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