The Molecular Geometry of Trichloromethyl Sulphonyl Chloride as Studied by Electron Diffraction.
Estimation of the Barrier to Internal Rotation

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The molecular geometry of trichloromethyl sulphonyl chloride has been determined by electron diffraction. The sulphur bond configuration [r_g(S—O) 1.421 ± 0.003 Å, r_g(S—Cl) 2.021 ± 0.005 Å, r_g(S—C) 1.87 ± 0.03 Å, $\angle$O=S—C 108.3 ± 0.7°, $\angle$C—S—Cl 97.9 ± 0.8°, $\angle$O=S=O 121.5 ± 0.9° and $\angle$O=S—Cl 109.2 ± 0.6°] is consistent with the characteristic structural variations observed in the sulphone series. The barrier to internal rotation around the S—C bond was estimated to be between 3.5 and 6 kcal mol^{-1} by means of various procedures and assumptions.

The present investigation is an extension of our studies on the molecular structure of simple sulphone molecules. Previous work has been summarized recently [1]. In the light of the structural data for a relatively large series of sulphone molecules, some of the earlier reported geometrical parameters of trichloromethyl sulphonyl chloride by Alekseev [2], seemed to be erroneous. In particular the S=O bond length (1.45 ± 0.01 Å)^2 seemed to be too large, while the O=S=O bond angle (111 ± 2°)^2 seemed to be too small. Our considerations based on the geometrical variations were supported by the empirical relationships [3] between geometrical and vibrational parameters which predicted [1] 1.422 Å for r(S=O) and 121.6° for $\angle$O=S=O.

The electron diffraction patterns were taken at 70 °C nozzle temperature with the Oslo Balzers KD-G2 apparatus. For references on the apparatus, other experimental conditions, data reduction, and scattering factors, see Ref. [4]. The reduced molecular intensities and radial distributions are shown in Figures 1 and 2.

The experimental radial distribution gave evidence for the staggered conformation. The molecule as a whole was assumed to possess C_s symmetry in most of the calculations. The CCl_3 group was assumed to have C_3 symmetry with the S—C bond as symmetry axis. The numbering of atoms is given in Figure 3.

The results from the least-squares refinement based on the molecular intensities are summarized in Table 1.

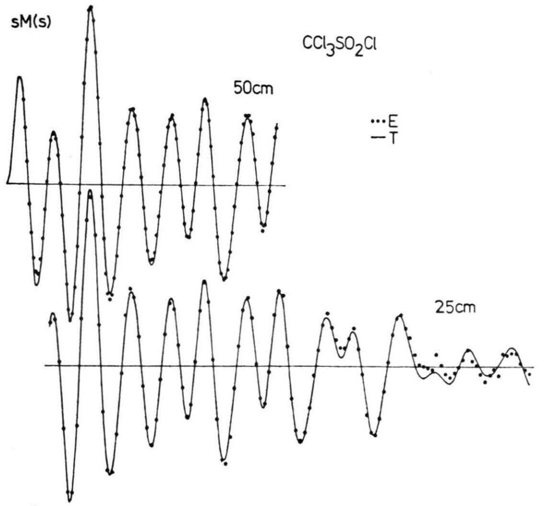

Fig. 1. Experimental (E) and theoretical (T) molecular intensities and the difference curves (Δ). The theoretical distributions were calculated from the parameters of Table 1.

Mean amplitudes of vibration (l values) were computed from an approximate force field adjusted to fit experimental frequencies given by Nagel [5]. These l values are listed in Table 1. Since the gauche-

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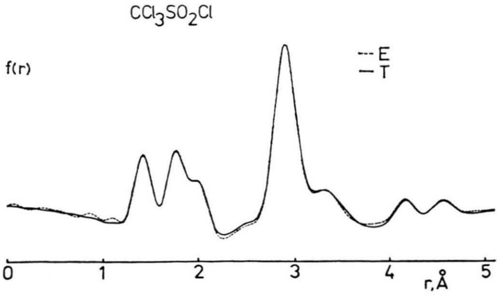

Fig. 2. Experimental (E) and theoretical (T) radial distributions.

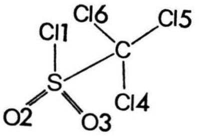

Fig. 3. The numbering of atoms.

Table 1. Structural parameters of trichloromethyl sulphonyl chloride.

Independent parameters	r_a (Å), $<$ (°)	σ_t	l(ED)	σ_t	l(SP)
C—Cl	1.757	0.010	0.037 *	0.014	0.057
S=O	1.420	0.003	0.039	0.004	0.035
S—Cl	2.020	0.005	0.051	0.008	0.049
S—C	1.865	0.030	0.039 *	0.056	0.058
O ... O	2.478	0.015	0.065	0.023	0.056
S—C—Cl	108.8	1.2			
O=S—C	108.3	0.7			
C—S—Cl	97.9	0.8			
Dependent parameters					
Cl1 ... O2	[2.825]				0.071
Cl1 ... Cl4	[4.556]		0.082	0.014	0.079
Cl1 ... Cl5	[3.283]		0.190 **	0.011	0.104
Cl1 ... C	[2.931]				0.075
Cl4 ... O2	[3.330]		0.199 **		0.113
Cl5 ... O2	[4.161]		0.063	0.010	0.078
Cl6 ... O2	[3.191]		0.208 **		0.122
O2 ... C	[2.675]				0.079
Cl4 ... Cl5	[2.880]				0.069
Cl4 ... S	[2.946]				0.077
O=S=O	[121.5]	[0.9]			
O=S—Cl	[109.2]	[0.6]			

type distances were found to have much larger l-values than computed spectroscopically, a new computation was made with the torsional frequency put arbitrarily equal to 50 cm^{-1} instead of the suggested [5] 140 cm^{-1}. This resulted in the values 0.179, 0.151, and 0.150 Å for the Cl1...Cl5, O2...Cl4, and O2...Cl6 interactions, respectively. The other l values changed very little. The l values and K values (perpendicular vibrational correction terms) calculated in the latter scheme were used for conversion when refinements by means of the r_α structure were performed.

The bond distances C—Cl and S—C and their l values were found to be strongly correlated. Assuming the spectroscopic l values, r_a(C—Cl) $= 1.764$ and r_a(S—C) $= 1.840$ Å were obtained. When the two l values were refined, with an assumed difference between them, the distances listed in Table 1 were obtained. The latter approach gave better agreement between the theoretical and experimental distributions, although the refined l values are relatively small. The differences in the two sets of results were taken into consideration in the error estimates. The total errors in Table 1 were calculated in the following way:

$$\sigma_t = [3\,\sigma^2 + (0.001\,r)^2 + \Delta^2]^{1/2}$$

for distances and angles, and

$$\sigma_t = [3\,\sigma^2 + (0.02\,l)^2]^{1/2}$$

for l values. Here σ is the standard deviation from the least-squares refinement and Δ is the difference between the parameters obtained by applying the spectroscopically calculated l(C—Cl) and l(S—C) values and by refining them.

Refinements have also been carried out through r_α distances. This scheme did not result in significantly different results from those listed in Table 1.

Attempts were made to estimate the barrier to internal rotation, V_0, assuming the hindering potential to have the form $V = (1/2)\,V_0(1 - \cos 3\varphi)$. Since the projections of the S=O bonds and S—Cl on a plane perpendicular to the S—C bond do not make exactly 120° angles, this assumption may be rather crude.

Employing Karle's method [6] (cf. Fig. 4), V_0 was obtained to be between 3.9 and 5.6 kcal mol^{-1} considering the error limits of l(Cl1...Cl4) and l(Cl1...Cl5).

From the spectroscopically calculated framework l value [7] (0.088 Å) for the Cl1...Cl5 distance and the respective measured l(Cl1...Cl5) value, V_0 is estimated to be between 4.3 and 5.4 kcal mol^{-1}.

Another approach was to assume the spectroscopically calculated l values (cf. Table 1) for the gauche-type distances and determine the torsional angle characterizing the rotation of the CCl_3 group

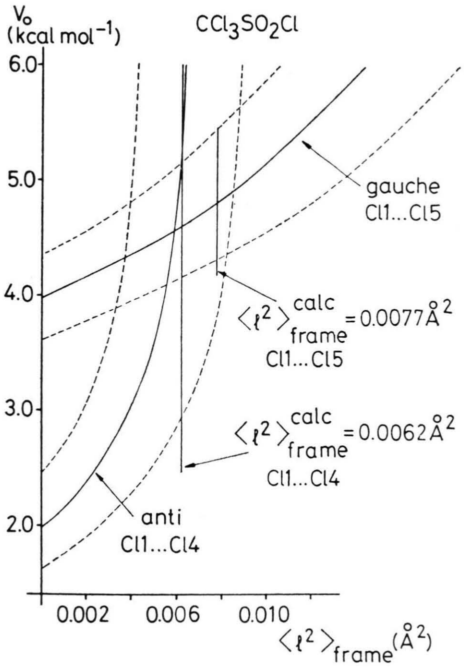

Fig. 4. Graphical solution of the equations determining the potential barrier according to Karle's method [6] implying that the framework contributions from the *anti* and *gauche* interactions are assumed to be the same. The continuous lines correspond to the experimental *l*-values and the broken lines to their error limits. The straight vertical lines correspond to the calculated framework contributions showing that the above assumption is relatively good but also that this assumption results in a little underestimating the *gauche* framework contribution.

relative to the SO_2Cl group around the S—C bond. This scheme yielded a torsional angle of 9.6°. This angle was then used following Vilkov's method [8] (cf. Fig. 5) to estimate $V_0 = 4.2$ kcal mol^{-1} finding $\langle|\varphi|\rangle$ by integration, and $V_0 = 3.5$ kcal mol^{-1} finding $\langle|\varphi|\rangle$ by an approximate formula. Since the torsional angle determined depends on the l values employed, it is difficult to give error estimate for these values.

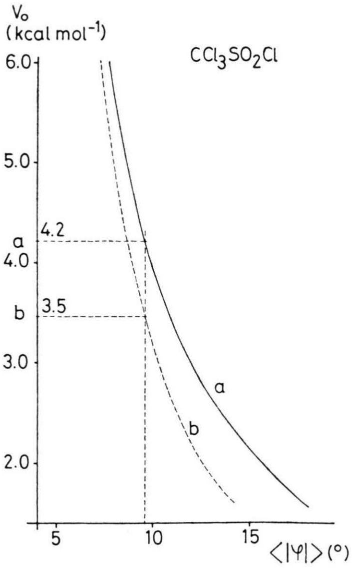

Fig. 5. Estimation of the potential barrier on the basis of the torsional angle, $\langle|\varphi|\rangle$, from the electron diffraction data, according to Vilkov's method [8]. a) numerical integration, b) by approximate formula.

The molecular geometry of trichloromethyl sulphonyl chloride as determined in this study is consistent with the structural variations observed in the series of sulphone molecules studied to date [1]. It also demonstrates the usefulness of the empirical relationships between the geometrical and vibrational parameters of the SO_2 group [3].

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