Electron Diffraction Investigation of the Molecular Structure of Trifluoromethyl Sulphonyl Chloride

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An electron diffraction investigation yielded the following geometric parameters for trifluoromethyl sulphonyl chloride r_g(C—F) 1.326(4), r_g(S=O) 1.416(7), r_g(S—Cl) 2.016(5), r_g(S—C) 1.857(6) Å, $\sphericalangle$ O=S—C 108.3(7)°, $\sphericalangle$ C—S—Cl 98.7(4)°, $\sphericalangle$ O=S=O 122.4(10),° $\sphericalangle$ O=S—Cl 108.3(3)°, $\sphericalangle$ F—C—F 109.9(3)°. The S—C bond is in CF_3SO_2Cl by almost 0.1 Å longer than in CH_3SO_2Cl.

Recently we determined the molecular structure of trichloromethyl sulphonyl chloride [1] as an extension of our studies on simple sulphone molecules [2]. The sulphur bond configuration in CCl_3SO_2Cl is consistent with the characteristic structural variations observed in the sulphone series. There was also indication of a particularly long C—S bond, 1.87 ± 0.03 Å, as compared with that of methane sulphonyl chloride (1.763 ± 0.005 Å [3]). This result, however, suffered from very large uncertainty. Trifluoromethyl sulphonyl chloride is more suitable for an electron diffraction determination of the S—C distance. We found it also interesting to examine the influence of the CF_3 group on the sulphonyl chloride structure and to compare the barriers to internal rotation in the CF_3 and CCl_3 derivatives.

The electron diffraction patterns were taken at a nozzle temperature of about 10 °C with the Budapest EG-100 apparatus [4–6]. For references on data treatment and scattering functions, see [3]. The reduced molecular intensities and radial distributions are shown in Figs. 1 and 2.

The experimental radial distribution gave evidence for the staggered conformation, similarly to that of the trichloromethyl derivative [1]. C_s symmetry was assumed for the molecule as a whole. The CF_3 group was assumed to have C_3 symmetry with the S—C bond coinciding with the symmetry axis. The numbering of atoms is given as follows:

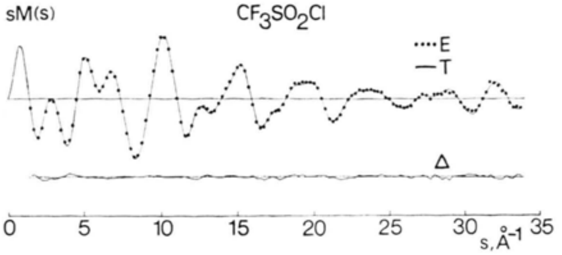


Fig. 1. Experimental (E) and theoretical (T) molecular intensities and their differences (△). The theoretical distribution was calculated from the parameters of Table 1.

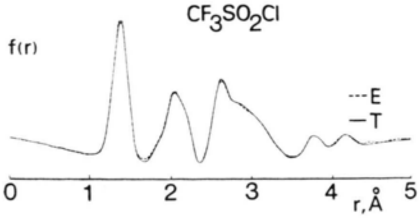
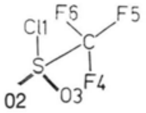


Fig. 2. Experimental (E) and theoretical (T) radial distributions.



Mean amplitudes of vibration (l values) and also perpendicular vibration corrections (K values) were calculated from an approximate force field compiled and adjusted to the frequencies given by Lindner and Weber [7]. The calculated l and K values are listed in Table 1.

Since some geometric and vibrational parameters were strongly correlated, fixed differences corresponding to the spectroscopic calculations were applied for several pairs of l values in the least-squares refinement. Of the important geometric parameters, r(S=O) showed some sensitivity to the assumption for the difference between l(S=O) and l(C—F). This was taken into account in the error estimates. For the other parameters

$$\sigma_t = [2\sigma^2 + (0.002\, r)^2]^{1/2}$$

(for distances and angles) and

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

(for the l values) were used, where σ is the standard deviation from the least-squares refinement.

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Table 1. Structural parameters of trifluoromethyl sulphonyl chloride.

	r_a (Å), ∢ (°)	σ_t	l^{ED} (Å)	σ_t	l^{SP} (Å)	K^{SP} (Å)
Independent parameters						
C—F	1.324	0.004	0.052	0.005	0.049	0.0149
S=O	1.415	0.007	0.042	0.003	0.035	0.0066
S—Cl	2.015	0.005	0.045	0.002	0.049	0.0061
S—C	1.856	0.006	0.046	0.006	0.052	0.0013
O ... O	2.480	0.014	0.066	0.018	0.066	0.0097
Cl ... F4 (*anti*)	4.153	0.012	0.080	0.009	0.070	0.0010
C—S=O	108.3	0.7				
S—C—F	109.1	0.4				
Dependent parameters						
Cl ... O	[2.802]		0.070	0.004 [a]	0.072	0.0091
Cl ... F5 (*gauche*)	[3.125]		0.173	0.030 [b]	0.175	0.0079
Cl ... C	[2.939]		0.067	[a]	0.069	0.0035
F4 ... O2	[3.089]		0.138	[b]	0.140	0.0107
F5 ... O2	[3.765]		0.069	0.034	0.070	0.0021
F6 ... O2	[2.966]		0.140	[b]	0.143	0.0096
O ... C	[2.664]		0.070	0.016 [c]	0.070	0.0042
F ... F	[2.169]		0.055	0.003	0.059	0.0240
F ... S	[2.608]		0.068	[c]	0.068	0.0072
Cl—S—C	[98.7]	[0.4]				
O=S=O	[122.4]	[1.0]				
Cl—S=O	[108.3]	[0.3]				
F—C—F	[109.9]	[0.3]				

[a, b, c] mean amplitudes refined in groups.

The long S—C bond is the only striking feature of the molecular geometry of trifluoromethyl sulphonyl chloride as compared with that of methane sulphonyl chloride [3, 8]. The difference in r(S—C) is larger than would have been expected on the basis of known structural changes by CH_3/CF_3 substitution [9].

The other geometric parameters of the sulphur bond configuration in trifluoromethyl sulphonyl chloride are consistent with the structural variations in the sulphone series [2]. The S=O bond length agrees within the error limits with the estimates from the correlation relationship between bond lengths and bond stretching frequencies [10]. The C—F bond seems to be of normal length for this compound (cf. the compilation of Yokozeki and Bauer [9]).

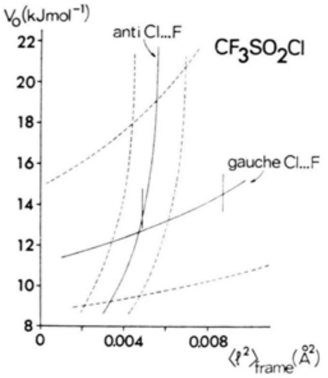

Fig. 3. Estimation of the barrier to internal rotation around the S—C bond according to Ref. [11]. The solid lines correspond to the experimental l-values and the broken lines to their error limits. The straight vertical lines indicate the calculated framework contributions.

The barrier to internal rotation in CF_3SO_2Cl was estimated to be between 2.2 and 5.0 kcal mol^{-1} (9 and 21 kJ mol^{-1}) using Karle's method [11] as shown in Figure 3. These values can be compared with the interval of 3.9 to 5.6 kcal mol^{-1} estimated for CCl_3SO_2Cl [1]. The barrier to internal rotation in CH_3SO_2Cl was reported to be at least 2 kcal mol^{-1} [8].

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