The Molecular Structure of Pentafluorobenzene Sulphonyl Chloride

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The molecular geometry of pentafluorobenzene sulphonyl chloride is characterized by the following bond lengths (r_g) and bond angles from an electron diffraction study: C–F 132.6 ± 0.3 pm, C–C 139.1 ± 0.7 pm, S=O 141.5 ± 0.3 pm, S–Cl 202.7 ± 0.5 pm, C–S 179.8 ± 0.6 pm, C–S–Cl 104.8 ± 0.8°, C–S=O 108.2 ± 0.6°, O=S=O 123.6 ± 1.0°, Cl–S=O 105.3 ± 0.2°. The molecular model is asymmetric; the benzene ring is rotated by 61.8 ± 2.2° relative to the plane containing the S–Cl bond and bisecting the O=S=O angle. The benzene ring is not distorted considerably.

The CH_3/CF_3 substitution in CH_3SO_2Cl/CF_3SO_2Cl leads to a dramatic increase in the C–S bond length, viz. from 176.3 (5) [1] to 185.6 (6) pm [2]. In accordance with earlier suggestions [3], this bond lengthening was ascribed primarily to the electron withdrawing ability of the CF_3 group versus the electron releasing ability of the CH_3 group as indicated by semiempirical CNDO/2 MO calculations [4]. There is, however, practically no change in the C–S bond length as a consequence of CH_3/C_6H_5 substitution as 176.4 (9) pm was determined for r(C–S) in $C_6H_5SO_2Cl$ [5]. One of the purposes of the present study was to determine how C_6H_5/C_6F_5 substitution influences the C–S bond. It was also found to be of interest to examine the other characteristics of the sulphur bond configuration with the C_6F_5 group as ligand. Structural variations in large series of sulphur derivatives have been recently reviewed [6].

The electron diffraction experiments were carried out at the Chemistry Institute of the University of Oslo on the Balzers KD–G2 unit [7] by siv. ing. Ragnhild Seip. The nozzle temperature was about 80 °C. The data reduction and structure analysis followed the procedure described before [8]. The molecular intensities and radial distributions are shown in Figs. 1 and 2.

The structure refinement was carried out by a least-squares procedure based on the molecular

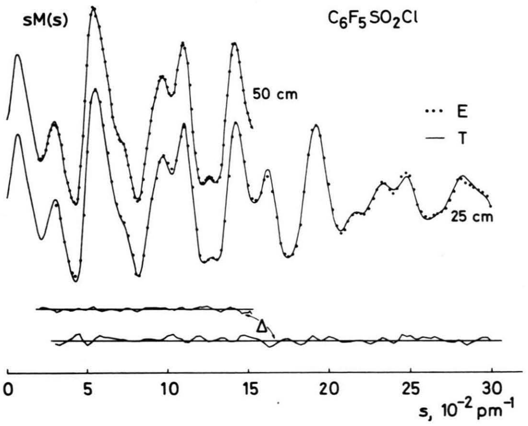

Fig. 1. Molecular intensity curves for the two camera ranges (E – experimental, T – theoretical), Δ = experimental – theoretical.

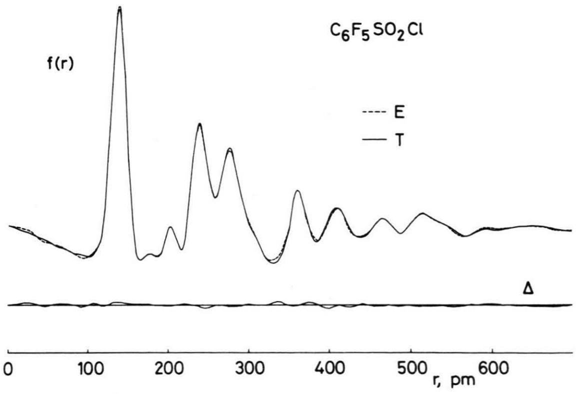

Fig. 2. Radial distribution curves (E – experimental, T – theoretical) and their difference (Δ).

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Table 1. The molecular parameters (r_a) of pentafluorobenzene sulphonyl chloride from least-squares refinement (the standard deviations are parenthesized as units in the last digit). The symbols *i* through *X* indicate vibrational amplitudes coupled with fixed differences in the refinements. Bracketted values were taken and fixed from the spectroscopic calculation. The bond lengths (r_g and bond angles with estimated total errors (see [21]) are given in the Abstract.

	r_a (pm)/ ∢ (°)	*l* (pm)	Coupling scheme for *l* values
Independent parameters			
C–F	132.4 (1)	[4.55]	
C–C	139.0 (1)	[4.64]	
S=O	141.4 (1)	[3.56]	
S–Cl	202.6 (2)	4.4 (2)	
C–S	179.7 (3)	[4.71]	
O … O	249.3 (9)	[5.67]	
∢ C–S–Cl	104.8 (4)		
∢ C–S=O	108.2 (4)		
∢ C–C–C	120.0 fixed		
τ	61.8 (13)		
Dependent parameters			
C1 … F8	235.0 (1)	6.7 (1)	i
C1 … C3	240.7 (2)	5.5	i
F8 … O15	249.1 (9)	19.5	i
C1 … O14	261.0 (7)	7.3	i
F8 … F9	271.4 (1)	11.9 (2)	ii
C1 … O14	276.0 (3)	7.6	ii
C2 … S	276.7 (3)	7.5	ii
C1 … C4	277.9 (2)	6.4	ii
F12 … O14	290.5 (18)	23.5	ii
C2 … O15	293.9 (9)	12.2 (4)	iii
S … F8	297.8 (2)	12.3	iii
C1 … Cl	303.1 (9)	7.3	iii
C6 … O14	312.8 (9)	13.1	iii
F12 … Cl	324.2 (30)	28.4	iii
C6 … Cl	347.9 (18)	16.9 (2)	iv
C1 … F9	360.6 (1)	6.7	iv
C2 … O14	373.2 (12)	10.4	iv
C6 … O15	388.2 (6)	7.7	iv
C2 … Cl	406.9 (15)	16.0 (3)	v
C3 … S	404.9 (4)	8.7	v
F8 … O14	406.6 (16)	18.8	v
C1 … F10	409.2 (1)	8.8	v
C3 … O15	432.7 (9)	12.6 (14)	vi
F12 … O15	433.2 (4)	11.8	vi
F8 … Cl	438.3 (22)	22.6	vi
C5 … O14	445.7 (8)	13.1	vi
C4 … S	457.6 (4)	6.4	vi
F8 … F10	468.6 (1)	9.8 (6)	vii
C5 … Cl	473.2 (16)	18.2	vii
C3 … O14	490.0 (11)	11.0 (6)	viii
C5 … O15	501.5 (7)	9.0	viii
F9 … O15	508.8 (9)	17.2	viii
S … F9	509.5 (3)	9.3	viii
C3 … Cl	518.2 (14)	14.8	viii
C4 … O14	519.4 (9)	11.8	viii
F11 … O14	530.3 (10)	18.2	viii
F8 … F11	540.9 (2)	10.8 (12)	ix
C4 … Cl	545.6 (12)	17.9	ix
F11 … Cl	553.2 (21)	26.2	ix
S … F10	587.5 (3)	7.8 (13)	x
F9 … O14	601.8 (14)	13.2	x
F11 … O15	620.1 (7)	9.3	x
F9 … Cl	626.9 (18)	19.2	x
F10 … O14	648.2 (9)	[12.54]	
F10 … Cl	670.9 (13)	[16.60]	
∢ O=S=O	123.6 (7)		
∢ Cl–S=O	105.3 (1)		

intensities [9]. The molecular model with atom numbering is shown in Figure 3. The overall geometry of $C_6F_5SO_2Cl$ is similar to that of benzenesulphonyl chloride [5]. The molecular parameters are presented in Table 1. A model with C_1 symmetry gave the best fit. The model with C_s symmetry in which the plane bisecting the O=S=O angle and the benzene plane are perpendicular ($\tau = 90°$), could be rejected by statistical test [10].

Possible distorsions of the benzene ring have been extensively examined. As regards the relative distribution of the substituents and their electronegativities, $C_6F_5SO_2Cl$ could be compared to toluene assuming the electronegativity of the SO_2Cl group to be the same as, say that of chlorine [12]. Domenicano and Murray-Rust [13] have communicated empirical angular parameters for the ring distortion which were then used as starting values. Another approach was to vary the parameters characterizing the ring distortion starting from various parameter sets including that for an undistorted ring. None of these attempts have led to solutions in which both the improvement in agreement and the reasonableness of the parameters would be satisfactory. It may be stated that the distortion is probably smaller than that in toluene. Small distortions, like 1° differences in angles and 0.5 pm differences in bond lengths, however, cannot be excluded. The final results are presented from refinements in which the

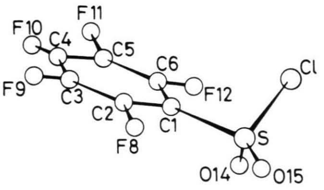

Fig. 3. The numbering of atoms.

benzene ring was assumed to be undistorted. This assumption was taken into consideration as a possible error source in the estimations of the total errors (cf. Footnote to Table 1 and Abstract).

Spectroscopic calculations by Dr. Jon Brunvoll [14] paralleled our structure analysis. They were based on an approximate force field and estimated vibrational frequencies [15, 16] as only the S=O stretching frequencies have been reported [17] for $C_6F_5SO_2Cl$. The calculated amplitudes (l) for the rotation-dependent distances (with respect to the S−C bond) considerably depended on the assumption used for the respective torsional frequency. Sets of calculated l values based on torsional frequencies of 105 and 42.4 cm^{-1} were tested in the structure refinement. The set referring to the lower torsional frequency gave considerably better agreement with the electron diffraction experimental distributions than the other. Thus this set was selected for *starting parameters* for further refinement. Many differences in the l values for similar distances were assumed throughout the analysis. The corresponding coupling scheme is indicated in Table 1. Shrinkages were estimated for several distances from calculations on C_6F_6 [18] and experience with other molecules [19]. These shrinkages, viz. C_1F_9 0.9, C_1F_{10} 1.1, F_8F_{10} 1.45, F_8F_{11} 1.81, SF_9 2.0, SF_{10} 2.5, and SC_3 1.5 pm, were assumed in the refinements. Shrinkages for rotation-dependent distances were not readily available from analogous molecules. Attempts to determine them failed in that unreasonable values were obtained. Eventually the shrinkages for rotation-dependent distances were ignored. The corresponding results are shown in Table 1. The uncertainty originating from this assumption was tested by carrying out calculations with assumed values of shrinkages for the rotation-dependent distances (viz., e.g., 3 pm). The resulting changes in the independent geometrical parameters were smaller than their standard deviations.

The most striking difference in the structure of $C_6F_5SO_2Cl$ as compared with $C_6H_5SO_2Cl$ is the lengthening of the S−C bond, the shortening of the S−Cl bond, and the opening of the C−S−Cl bond angle

	$C_6H_5SO_2Cl$ [5]	$C_6F_5SO_2Cl$ [present work]
r_g(C−S)	176.5 ± 0.9 pm	179.8 ± 0.6 pm
$\angle_\alpha$(C−S−Cl)	100.9 ± 2°	105.1 ± 0.8°
r_g(S−Cl)	204.9 ± 0.8 pm	202.7 ± 0.5 pm

The comparison of the other parameters of the sulphur bond configuration is marred by the relatively large uncertainties reported in the determination of the $C_6H_5SO_2Cl$ structure [5]. The structural changes listed above are not in disagreement with the VSEPR model if competing effects are taken into consideration [6, 20]. The considerable lengthening of the C−S bond upon C_6H_5/C_6F_5 substitution points to the greater electron withdrawing ability of the C_6F_5 group as compared with the C_6H_5 group. The effect, though considerable, is certainly smaller than that observed upon CH_3/CF_3 substitution indicating a smaller susceptibility of the phenyl group to structural changes under the impact of H/F substitution.

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[21] $r_g \approx r_a + l^2/r_a$. The estimated total errors for distances $\sigma_t = [(0.002\,r)^2 + 2\,\sigma^2 + (\Delta/2)^2]^{1/2}$, for angles $\sigma_t = [2\,\sigma^2 + (\Delta/2)^2]^{1/2}$, where σ is the standard deviation from the least-squares results (see Table 1), Δ is the difference between the parameter values obtained with a distorted and the undistorted ring. For error estimation, cf. K. Hedberg and M. Iwasaki, J. Chem. Phys. **36,** 589 (1962).