Electron Diffraction Investigation of the Molecular Structure of Trifluoromethanesulphonic acid (triflic acid)

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Z. Naturforsch. **36a**, 917–918 (1981);
received May 16, 1981

The molecular geometry of triflic acid is characterized by the following bond lengths (r_g) and bond angles from an electron diffraction study: S—C 183.3 ± 0.5, F—C 133.2 ± 0.2, S=O 141.8 ± 0.2, S—O 155.8 ± 0.3 pm, S—C—F 110.3 ± 0.3, F—C—F 108.6 ± 0.3, C—S=O 105.4 ± 1.1, C—S—O 102.3 ± 2.3, O—S=O 109.9 ± 0.7, and O=S=O 122.0 ± 1.3°. The heavy-atom-skeleton is staggered with respect to the rotation about the S—C bond with an estimated barrier of rotation of 15 kJ mol^{-1}.

The molecular structure of triflic acid has been investigated by electron diffraction as a continuation of our studies on the sulphone series [1–3]. The electron diffraction patterns were taken at a nozzle temperature of about 80 °C with the Oslo KD-G2 apparatus (for further details and references, cf. [4]). The reduced molecular intensities and radial distributions are shown in Figs. 1 and 2.

The rotation-dependent part of the radial distribution confirmed the expectation for a staggered form with respect to rotation around the C—S bond. Refinement of the rotation angle F—C—S—O showed some slight torsion similarly to CCl_3SO_2Cl [3]. On the other hand, the position of the O—H bond relative to the S—O bond could not be determined. The C—S and O—H bonds were assumed to be in anti position, and the O—H bond length and S—O—H bond angle were fixed at 96 pm and 115° in the final calculations. The CF_3 group had threefold symmetry, the C—S bond coincided with the symmetry axis, and the C—S—O plane bisected the O=S=O bond angle in our model. The results of the least-squares refinement are given in Table 1. Mean amplitudes of vibration have been coupled in groups as shown in Table 1.

The bond lengths (r_g) and bond angles characterising the triflic acid molecule together with the estimated total errors [5] are collected in the Abstract.

The sulphur bond configuration and the geometry of the CF_3 group are normal and consistent with earlier observations for analogous molecules. The C—S bond is rather long and is closer to that in CF_3SO_2Cl, 185.7 ± 0.6 pm [2] than to that in CH_3SO_2Cl, 176.3 ± 0.5 pm [6]. The lengthening of C—S bonds may be related to the electron-withdrawing ability of the CF_3 group [7].

Table 1. Results from the least-squares refinement of the structural parameters of triflic acid (the standard deviations are parenthesized as units in the last digit). The bond lengths (r_g) and bond angles with estimated total errors (see [5]) are given in the Abstract.

	r_a (pm)/∢ (°)	l (pm)	Key to the coupling scheme for the l-values
Independent parameters			
S—C	183.2 (3)	4.9 (4)	i
F—C	133.0 (1)	4.9 (2)	ii
S=O	141.7 (1)	3.9	ii
S—O	155.7 (2)	4.5	ii
=O … O=	248.0 (11)	6.4 (2)	iii
S—C—F	110.3 (2)		
C—S=O	105.3 (8)		
C—S—O	102.3 (16)		
F—C—S—O	10.5 (13)		
Dependent parameters			
S … F	261.1 (2)	7.3	iii
=O … C	259.6 (14)	9.5	iii
—O … C	264.4 (30)	9.5	iii
=O … F	373.4 (10)	6.8 (9)	iv
=O … F	284.8 (16)	14.2 (10)	v
=O … F	292.8 (20)	13.8	v
=O … F	311.5 (22)	13.8	v
=O … F	302.2 (20)	13.8	v
=O … F	371.9 (9)	6.8	iv
—O … F	308.1 (34)	16.2	v
—O … F	380.6 (23)	7.8	iv
—O … F	288.0 (39)	16.2	v
=O … O—	243.6 (7)	7.8	iii
F … F	216.0 (1)	5.9 (2)	vi
O—S=O	109.9 (5)		
F—C—F	108.6 (2)		
O=S=O	122.0 (9)		

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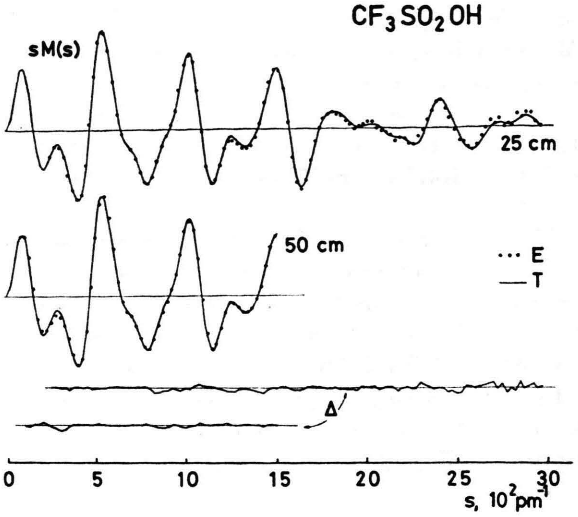

Fig. 1. Experimental (E) and theoretical (T) molecular intensities and the difference curves (Δ). The theoretical distributions were calculated from the parameters of Table 1.

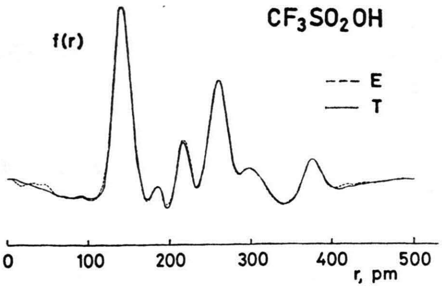

Fig. 2. Experimental (E) and theoretical (T) radial distributions.

The S=O bond length is consistent with the empirical relationships established for XSO_2Y sulphones [8] between $r(S=O)$ and the group electronegativities χ_X and χ_Y as well as between $r(S=O)$ and the bond stretching frequencies (for frequency data, see [9, 10]).

The F ... F distance of the CF_3 group ($r_g = 216.1 \pm 0.3$ pm) is the same as the one observed to be strikingly constant in a large series of trifluoromethyl derivatives [11]. The O ... O distances are considerably larger than twice the postulated nonbond radius of oxygen (viz. 113 pm [12]). It has been suggested that the O ... O distances in various OSO moieties are determined by a fine balance of non-bonded interactions and electron pair repulsions [13, 14].

The slight deviation from C_s symmetry of the CF_3SO_2O-skeleton as determined from electron diffraction may be a consequence of the torsional motion around the C–S bond. Accordingly, the average angle of the deviation, 10.5°, would suggest a barrier to internal rotation of about 15 kJ mol^{-1} (cf. [15]). Similar barriers to rotation have been estimated for CCl_3SO_2Cl [3] and CF_3SO_2Cl [2].

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[5] Here $r_g \approx r_a + l^2/r_a$. The estimated total errors for distances $\sigma_t = [(0.001\, r)^2 + 2\,\sigma^2]^{1/2}$, for angles $\sigma_t = \sqrt{2}\,\sigma$, where σ is the standard deviation from the least-squares results (see Table 1). For error estimation, cf. K. Hedberg and M. Iwasaki, J. Chem. Phys. **36**, 589 (1962).

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