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Neutron Diffraction Study of Oxonium Trifluoromethanesulphonate*

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Abstract. $H_3O^+CF_3SO_3^-$, monoclinic, $P2_1/c$, $Z = 4$, $a = 5{\cdot}9634\,(3)$, $b = 9{\cdot}975\,(3)$, $c = 9{\cdot}708\,(1)$ Å, $\beta = 98{\cdot}661\,(7)°$ [Spencer & Lundgren (1973). *Acta Cryst.* B**29**, 1923–1928]. Neutron wavelength 1·210 Å, μ(measured) = 0·57 cm^{-1}, m.p. 34 °C. Intensity data were recorded at 21 °C. Refinement with 801 observed data gave $R(F^2) = 0{\cdot}090$, $R_w(F^2) = 0{\cdot}078$. The oxonium ion, which is in an asymmetric environment, displays a moderate distortion from C_{3v} symmetry. The O—H distances are 0·986, 0·997 and 0·998 (5) Å; the H—O—H angles are 110·9, 111·7 and 116·0 (4)°. The H_3O^+ ion is hydrogen bonded to three different $CF_3SO_3^-$ ions by bonds of length 2·522 (3), 2·579 (4) and 2·673 (3) Å.

Introduction. The present investigation was undertaken to study the geometry of the oxonium ion, H_3O^+, in an environment known from an earlier X-ray study (Spencer & Lundgren, 1973) to be asymmetric. A neutron diffraction study of oxonium *p*-toluenesulphonate was reported by Lundgren & Williams (1973), where the environment of the H_3O^+ ion has a virtual threefold symmetry, *i.e.* the $H_3O^+\cdots O$ bonds are all the same length, 2·52–2·54 Å, and the $O\cdots H_3O^+\cdots O$ angles are very similar, 103·8–114·9°. Neutron diffraction studies of structures where the oxonium ion is hydrogen bonded to water molecules to form $H_5O_2^+$ or $H_7O_3^+$ complexes have been reported for picrylsulphonic acid tetrahydrate (Lundgren & Tellgren, 1974), and hydrogen bromide dihydrate and *o*-sulphobenzoic acid trihydrate (Attig & Williams, 1976*a*,*b*).

A crystal of $H_3O^+CF_3SO_3^-$ with volume 48·5 mm^3 was grown by a zone-melting technique in a quartz tube of diameter 4·1 mm. The intensities of 1588 independent reflexions were recorded at 21 °C using an ω–2θ step-scan technique on a Hilger & Watts computer-controlled four-circle diffractometer at the Swedish Atomic Energy R2 Reactor at Studsvik. Three test reflexions were monitored regularly throughout the data collection. The intensities of the test reflexions decreased linearly to about 91% of their initial values. An appropriate correction was applied to all intensities. The data were corrected for Lorentz and absorption effects. The absorption correction was made using the Gaussian quadrature method with a 4 × 4 × 4 grid. The crystal shape was here approximated by 18 rational boundary planes. The transmission factors were in the range 0·823–0·840. Standard deviations of the intensities were estimated from Poisson counting statistics, the scatter observed in the test reflexions, and the uncertainty in the scaling function (McCandlish, Stout & Andrews, 1975).

Table 1. *Atomic coordinates* ($\times 10^4$)

	x	*y*	*z*
S	−2971 (7)	2341 (4)	4773 (4)
O(1)	−3977 (4)	3602 (2)	5042 (2)
O(2)	−3459 (4)	1943 (2)	3336 (2)
O(3)	−3208 (4)	1291 (2)	5754 (2)
C	78 (4)	2688 (2)	5027 (2)
F(1)	496 (5)	3638 (3)	4173 (3)
F(2)	796 (5)	3093 (4)	6295 (3)
F(3)	1190 (6)	1621 (4)	4753 (4)
O(*w*)	4358 (5)	4595 (3)	2540 (3)
H(1)	4925 (8)	4412 (4)	3529 (4)
H(2)	4053 (7)	5554 (4)	2289 (4)
H(3)	5347 (8)	4164 (4)	1924 (4)

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* Hydrogen Bond Studies. CXXXIV. Part CXXXIII: Thomas (1978).

The positions of the H atoms were obtained from a difference Fourier synthesis based on non-hydrogen parameters from the X-ray study. A subsequent least-squares refinement minimizing the function $\sum w(F_o^2 - F_c^2)^2$, where $w^{-1} = \sigma^2(F_o^2)$, included 110 parameters: one scale factor, an isotropic extinction parameter, positional and thermal parameters for the twelve independent atoms. A refinement including 801 reflexions with $F_o^2 > 2\sigma(F_o^2)$ gave the discrepancy indices $R(F^2) = \sum |F_o^2 - F_c^2|/\sum F_o^2$ = 0·090 and $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ = 0·078. The standard deviation of an observation of unit weight was s = 1·57. The inclusion of all reflexions in the refinement gave the values R = 0·148, R_w = 0·093 and s = 1·28. The parameter shifts were all less than 1σ, however. Three strong low-angle reflexions with the largest extinction corrections were given zero weight in the refinement. A δR plot of the data is shown in Fig. 1 (Abrahams & Keve, 1971). The refined value of the isotropic extinction parameter g was 1·9 (5) × 10^3 (Coppens & Hamilton, 1970). The coherent scattering amplitudes used were those given by Bacon (1972). Final positional parameters are given in Table 1.* The programs used for all calculations on IBM 370/155 and IBM 1800 computers have been described by Lundgren (1976).

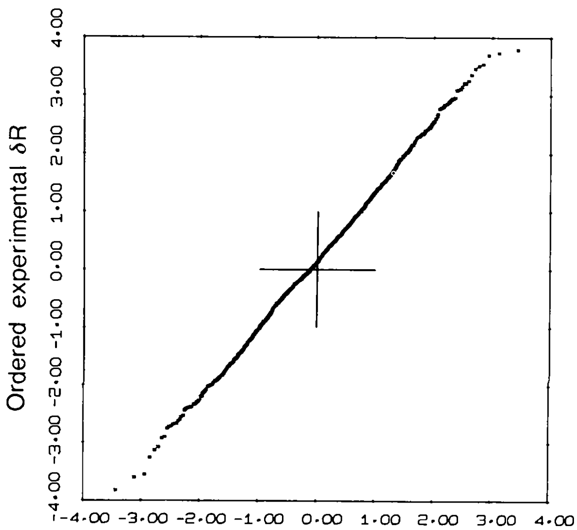

Fig. 1. A δR plot of the data after the last cycle of refinement. The slope of the least-squares line through the points is 1·19, and the y intercept is 0·16. The points for ten reflexions are outside the plot range.

Discussion. Significant differences between atomic positions from the present study and those from the room-temperature X-ray study were found only for the oxonium ion. These lead to differences of up to 5σ for distances and angles involving O(w), *i.e.* 0·02 Å and 0·9°, respectively. Hydrogen-bond distances and angles and the geometry of the H_3O^+ ions are shown in Fig. 2. Interatomic distances and angles in the $CF_3SO_3^-$ ion are listed in Table 2. The geometry of the anion and the molecular packing were discussed by Spencer & Lundgren (1973) and Lundgren (1978) and will not be considered here.

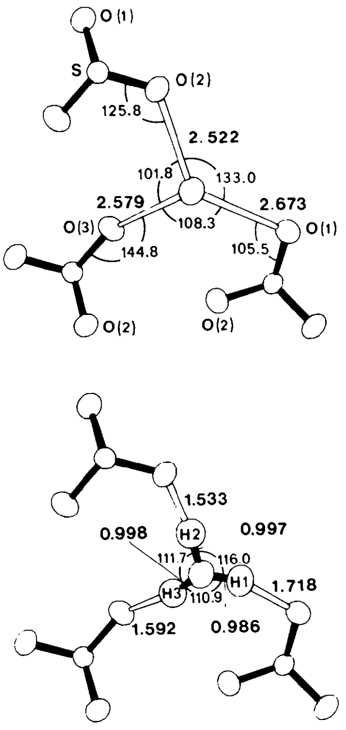

Fig. 2. Geometry of H_3O^+ and its environment in oxonium trifluoromethanesulphonate. E.s.d.'s of angles involving H atoms are 0·4°, and of O–H and H···O distances 0·005 Å. E.s.d.'s of distances and angles involving non-hydrogen atoms are 0·003 Å and 0·1–0·2°, respectively. Thermal ellipsoids are scaled to enclose 50% probability.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the* $CF_3SO_3^-$ *ion*

S–O(1)	1·435 (4)	C–F(1)	1·308 (4)
S–O(2)	1·437 (4)	C–F(2)	1·305 (4)
S–O(3)	1·437 (4)	C–F(3)	1·302 (4)
S–C	1·830 (5)		
O(1)–S–O(2)	112·9 (3)	F(1)–C–F(2)	107·8 (3)
O(1)–S–O(3)	115·6 (3)	F(1)–C–F(3)	108·1 (3)
O(2)–S–O(3)	114·6 (3)	F(2)–C–F(3)	109·9 (3)
O(1)–S–C	104·1 (2)	F(1)–C–S	109·4 (2)
O(2)–S–C	103·6 (2)	F(2)–C–S	111·3 (2)
O(3)–S–C	104·1 (2)	F(3)–C–S	110·1 (2)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33651 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ideally, the symmetry of the oxonium ion is C_{3v}. In some cases the site symmetry of H_3O^+ in a crystal is C_{3v}, *e.g.* $H_3O^+Br^-$ (Lundgren, 1970). In other cases, the environment of H_3O^+ has a virtual threefold symmetry where the hydrogen-bond acceptors are situated at the corners of a slightly distorted equilateral triangle, *e.g.* oxonium *p*-toluenesulphonate (Lundgren & Williams, 1973). No noticeable deviation from C_{3v} symmetry for H_3O^+ could be found in this latter case. The O—H distances were 1·008–1·013 (8) Å and the H—O—H angles 109·2–111·2 (5)°.

In the present structure the hydrogen-bond acceptors are arranged asymmetrically around H_3O^+. The O(*w*)···O bonds are not equal (2·522, 2·579 and 2·673 Å) and the O···O(*w*)···O angles are also very different (101·8, 108·3 and 133·0°). Nevertheless, the geometry of the oxonium ion is reasonably regular. The incorporation of the oxonium ion in the structure results in a moderate distortion of the ion from its ideal C_{3v} symmetry and in the formation of bent O—H···O hydrogen bonds. The O—H bonds are very similar: 0·986, 0·997 and 0·998 (5) Å, and the H—O—H angles are 110·9, 111·7 and 116·0 (4)°. The O—H···O angles subtended at H(1), H(2) and H(3) assume the values 162·0, 170·7 and 169·2 (4)°, respectively. It should be noted that the longest (and weakest) hydrogen bond, 2·673 Å, is also the most bent. Although the O—H bond distances are not significantly different, it is seen that the shortest O—H bond, 0·986 Å, is associated with the longest O(*w*)···O bond, in agreement with the well known relation between O—H and O···O distances (*e.g.* Olovsson & Jönsson, 1976).

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2*a*-Phenoxy-*trans*-1-oxadecalin

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Abstract. $C_{15}H_{20}O_2$, M_r = 232·23, triclinic, $P\bar{1}$, a = 11·358 (4), b = 10·429 (4), c = 5·455 (2) Å, α = 102·26 (2), β = 92·16 (3), γ = 92·85 (2)°, U = 629·9 Å^3, Z = 2, D_x = 1·225 g cm^{-3}, μ(Cu $K\alpha$) = 5·5 cm^{-1}. The structure was refined to R = 0·047 for 1719 unique reflexions. The intra-annular C—O bond lengths are significantly different (1·405 and 1·448 Å).

Introduction. As part of a systematic examination of the effects of ground-state structure on the reactivity of acetals (Jones, Kennard, Kirby & Osborne, 1978; Jones, Kennard, Kirby, Osborne & Malik, 1978) we have prepared axial and equatorial anomers of several 2-aryloxy-*trans*-1-oxadecalins (Chandrasekhar & Kirby, 1978). The factors responsible for the anomeric effect may also control reactivity in such systems; thus the detailed structure of the acetal group is relevant to the question of stereo-electronic control. This paper

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