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Hydrogen Bond Studies. LVII.* The Crystal Structure of Picrylsulphonic Acid Tetrahydrate, $\text{H}_5\text{O}_2^+\text{C}_6\text{H}_2(\text{NO}_2)_3\text{SO}_3^-\cdot 2\text{H}_2\text{O}$

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The crystal structure of picrylsulphonic acid tetrahydrate has been determined from three-dimensional single-crystal X-ray diffraction data recorded at room temperature using a Stoe four-circle diffractometer. The crystals are triclinic, space group $P\bar{1}$, with two formula units in a cell of dimensions: $a = 8.346$ (1), $b = 11.367$ (1), $c = 8.065$ (2) Å, $\alpha = 97.77$ (2), $\beta = 109.32$ (1), $\gamma = 83.22$ (1)°. A full-matrix least-squares refinement based on F gave a final weighted R value of 0.042. The structure comprises H_5O_2^+ ions, picrylsulphonate ions and water molecules. The H_5O_2^+ ions, water molecules and sulphonate groups are hydrogen bonded together to form layers. The $\text{O}\cdots\text{O}$ distance within the H_5O_2^+ ion is 2.429 (2) Å. Other $\text{O}\cdots\text{O}$ hydrogen bond lengths are in the range 2.61 to 2.88 Å.

Introduction

This work is part of a series of systematic studies of solid hydrates of strong acids currently in progress at this Institute. The crystal structures of the hydrates of two other sulphonic acids, 2,5-dibromobenzenesulphonic acid trihydrate and 2,5-dichlorobenzenesulphonic acid trihydrate, have been reported earlier (Lundgren, 1972; Lundgren & Lundin, 1972). References to several papers describing crystal structures of hydrates of strong inorganic acids can be found in the paper by Lundgren (1972). The structure determination of picrylsulphonic acid tetrahydrate reported in the present paper is based on single-crystal X-ray diffraction data collected at room temperature.

Crystal data

2,4,6-Trinitrobenzenesulphonic acid tetrahydrate (picrylsulphonic acid tetrahydrate),

$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{SO}_3\text{H}\cdot 4\text{H}_2\text{O}$. F. W. 365.231. Triclinic, $a = 8.346$ (1),* $b = 11.367$ (1), $c = 8.065$ (2) Å, $\alpha = 97.77$ (2), $\beta = 109.32$ (1), $\gamma = 83.22$ (1)°, $V = 713.2$ Å³ at 22°C. $Z = 2$, $D_x = 1.701$ g.cm⁻³. Space group $P\bar{1}$.

Experimental

Picrylsulphonic acid is commercially available. Well-shaped parallelepipedal crystals of the tetrahydrate are easily grown from an aqueous solution of the acid by slow evaporation at room temperature. The crystals show a tendency to lose some of their water when exposed to the atmosphere for a few days. Crystals of suitable dimensions were therefore mounted and sealed in thin-walled glass capillaries.

The intensity data were recorded at room temperature using a crystal of dimensions $0.19 \times 0.23 \times 0.51$ mm. The measurements were made on a Stoe four-

* Numbers in parenthesis here and throughout this paper are the estimated standard deviations in the least significant digits.

* Part LVI: *Acta Chem. Scand.* (1972). In the press.

circle computer-controlled diffractometer with a graphite monochromator using Mo $K\alpha$ radiation (0.7107 Å) and an ω - 2θ scan technique. Different combinations of scan time and filter selection were used to obtain an approximately equal number of counts for all reflexions. A total of 3177 independent reflexions with $2\theta < 55^\circ$ were measured. 329 of these reflexions with $I < 2\sigma(I)$, where $\sigma(I)$ is based on counting statistics, were considered to be insignificantly different from the background and thus given zero weight in the refinements. Two reference reflexions measured at regular intervals showed a slight weakening in intensity during the data collection. The intensities had reached 94% of their initial values by the end of the experiment. The measured intensities were corrected for this effect.

The data were corrected for Lorentz, polarization [$p = (1 + \cos^2 2\theta_M \cos^2 2\theta)/(1 + \cos^2 2\theta_M)$ with $\theta_M = 6.1^\circ$] and absorption effects using the program *DATAPH*. This and other programs mentioned in this paper are briefly discussed by Jönsson & Liminga (1971) and Liminga (1967). The calculated linear absorption coefficient for Mo $K\alpha$ radiation is 3.1 cm^{-1} . The minimum and maximum transmission factors were 0.9333 and 0.9464.

The cell dimensions were determined from quartz-calibrated oscillation photographs taken using a Weissenberg camera and Cu $K\alpha$ radiation [$\lambda(\text{Cu } K\alpha_1) = 1.54051$, $\lambda(\text{Cu } K\alpha_2) = 1.54433 \text{ Å}$, $a_{\text{SiO}_2} = 4.9131 \text{ Å}$]. The cell parameters were fitted to the 77 measured θ values by a least-squares procedure using the program *CELSIUS*.

Structure determination and refinement

The structure was solved by direct methods. A scale factor and an overall temperature factor were obtained by the method of Wilson (1942). Normalized structure factor amplitudes $|E|$ were then calculated from the expression

$$E^2 = F^2 / \sum_{j=1}^N f_j^2,$$

where F^2 has been corrected for thermal motion, f_j is the atomic scattering factor for the j th atom in the cell and N is the number of atoms in the unit cell. In Table 1 the statistical averages and distribution of the $|E|$ values are compared with the theoretical values expected for centrosymmetric and non-centrosymmetric structures as given by Karle, Dragonette & Brenner (1965). These values suggested a centrosymmetric structure; the space group $P\bar{1}$ was therefore chosen.

The signs of 260 reflexions with $|E| \geq 1.68$ were determined using a program devised by Long (1965). This program uses Sayre's equation reiteratively to predict the signs, using in this case seven signs in the starting set. Sixteen solutions were thus derived. A three-dimensional Fourier synthesis based on the phased E values from that solution showing the best consistency

Table 1. *Statistical averages and distribution of normalized structure factors*

	Observed	Theoretical	
		Centric	Acentric
$\langle E^2 \rangle$	0.985	1.000	1.000
$\langle E \rangle$	0.796	0.798	0.886
$\langle E^2 - 1 \rangle$	0.939	0.968	0.736
$ E > 3(\%)$	0.3	0.3	0.01
$ E > 2(\%)$	3.9	5.0	1.8
$ E > 1(\%)$	31.0	32.0	37.0

and convergence (excluding the solution with positive phases only) revealed the structure. The 23 non-hydrogen atoms could all be located from the maps. An electron density calculation based on the positions obtained from the E maps showed no peaks other than those expected. It was later found that for this solution all signs except one agreed with those of the calculated structure factors after the final refinement.

The structure was then refined by a full-matrix least-squares procedure using the program *LALS*. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Each reflexion was assigned a weight w inversely proportional to the estimated variance of the observation,

$$w^{-1} = \sigma^2(F) = \sigma_c^2(F^2)/4F^2 + (0.01F)^2$$

where σ_c^2 is based on counting statistics. The scale factor, positional parameters and individual isotropic thermal parameters for the 23 non-hydrogen atoms were first refined. The refinement converged with agreement factors

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.113 \quad (0.121)$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.153.$$

The R value including zero-weight data is given in parentheses.

A few cycles of refinement with anisotropic thermal parameters included reduced the R values to 0.045 (0.053) and R_w to 0.066. The number of parameters in the anisotropic refinement was 208 compared with 93 in the isotropic refinement. A difference Fourier synthesis calculated at this stage showed well resolved peaks corresponding to eight of the hydrogen atoms. An anisotropic refinement with these hydrogen atoms included with fixed parameters gave $R = 0.035$ (0.041) and $R_w = 0.050$. The hydrogen atoms were given Debye-Waller factors of $B = 5.0 \text{ Å}^2$. A difference Fourier synthesis was then calculated in which the remaining three hydrogen atoms could readily be located. Two of these must occupy disordered sites in the space group chosen here (see below).

Two cycles of anisotropic refinement with all hydrogen atoms included with fixed parameters were then performed using the program *LINUS*. Since the strongest reflexions all showed $|F_o|$ less than $|F_c|$, an isotropic extinction parameter was also refined. In the last cycle the shifts on the parameters were all less than

0.1σ except for the extinction parameter, where the shift was 1.0σ . The final agreement factors were $R=0.030$ (0.036) and $R_w=0.042$.

The atomic parameters from the final refinement are given in Tables 2 and 3. The coordinates of the hydrogen atoms as obtained from the difference syntheses are given in Table 4. Observed and calculated structure factor amplitudes are listed in Table 5. The $|F_o|$ values are corrected for extinction using the expression (strictly valid for unpolarized X-rays only)

$$|F_{o}|_{\text{corr}} = |F_o| \left(1 + \frac{\bar{T}^2 (1 + \cos^4 2\theta) |F_c|^2 12.593 g \lambda^3}{V^2 \sin 2\theta (1 + \cos^2 2\theta)} \right)^{1/4}$$

where λ is in Å and V is the unit-cell volume in Å³ (Coppens & Hamilton, 1970). \bar{T} is the mean path length through the crystal for a particular reflexion appropriately corrected for absorption. The refined value of the isotropic extinction parameter is $g=3734(563)$. The extinction correction factors as given above were in the range 1.00 to 1.15.

Table 2. Atomic coordinates ($\times 10^5$)

	<i>x</i>	<i>y</i>	<i>z</i>
S	28141 (4)	75641 (3)	40279 (5)
O(1)	37884 (15)	73631 (10)	58095 (15)
O(2)	36961 (16)	81032 (10)	30888 (16)
O(3)	11222 (14)	81275 (9)	38027 (16)
C(1)	25135 (16)	60957 (11)	28513 (18)
C(2)	24413 (17)	51054 (12)	36710 (18)
C(3)	24479 (18)	39495 (12)	28724 (19)
C(4)	24976 (18)	37864 (12)	11781 (19)
C(5)	25382 (18)	47123 (13)	2544 (19)
C(6)	25356 (17)	58478 (12)	11222 (18)
N(1)	23623 (17)	52326 (11)	54874 (17)
N(2)	25488 (17)	25599 (12)	3030 (20)
N(3)	25301 (18)	68132 (11)	591 (17)
O(11)	12194 (16)	58972 (11)	58061 (17)
O(12)	34099 (20)	46276 (13)	65292 (17)
O(21)	27279 (18)	17445 (10)	12039 (19)
O(22)	24156 (21)	24423 (12)	-12577 (19)
O(31)	37777 (17)	68420 (11)	-3860 (18)
O(32)	12428 (17)	74727 (11)	-3513 (18)
O(W1)	2406 (14)	-338 (10)	83658 (16)
O(W2)	11007 (15)	16810 (11)	43106 (16)
O(W3)	37081 (15)	5820 (11)	59141 (16)
O(W4)	36500 (15)	-5017 (10)	85407 (18)

Table 4. Hydrogen atom coordinates ($\times 10^3$)

The coordinates are obtained from Fourier difference syntheses. Atoms marked with an asterisk occupy disordered sites.

	<i>x</i>	<i>y</i>	<i>z</i>
H(3)	242	328	346
H(5)	254	457	908
H(11)	-7	60	789
H(12)*	23	1	940
H(13)*	123	-12	871
H(21)	35	180	488
H(22)	62	121	339
H(31)	453	99	621
H(32)	375	31	682
H(33)	239	105	520
H(41)	376	-110	825
H(42)*	260	-36	851
H(43)*	460	-25	948

The atomic scattering factors used in the calculations were those for neutral S, O, N and C given by Hanson, Herman, Lea & Skillman (1964). The spherical scattering factor used for the hydrogen atoms was that proposed by Stewart, Davidson & Simpson (1965).

Most calculations were carried out on the CDC 3600

Table 3. Anisotropic thermal parameters ($\times 10^5$)

The form of the temperature factor is $\exp [-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. The r.m.s. components (R_i) of thermal displacement of the atoms along the ellipsoid axes are also listed ($\times 10^3$ Å).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
S	1083 (6)	357 (3)	1039 (7)	-127 (3)	458 (5)	-88 (3)	140 (2)	168 (1)	194 (1)
O(1)	1791 (22)	656 (9)	1140 (21)	-206 (11)	209 (17)	-152 (10)	162 (5)	223 (4)	250 (2)
O(2)	1981 (23)	657 (9)	1807 (25)	-579 (12)	1043 (20)	-209 (12)	159 (5)	196 (4)	285 (3)
O(3)	1494 (20)	542 (8)	1778 (24)	167 (10)	812 (17)	134 (11)	166 (5)	207 (4)	241 (3)
C(1)	819 (19)	399 (9)	940 (24)	-53 (11)	326 (17)	-5 (11)	152 (5)	159 (4)	173 (5)
C(2)	1011 (21)	446 (10)	907 (24)	-74 (11)	401 (18)	3 (12)	153 (4)	169 (4)	181 (3)
C(3)	1155 (23)	412 (10)	1191 (27)	-75 (12)	438 (30)	39 (12)	162 (6)	180 (5)	192 (2)
C(4)	1086 (23)	400 (10)	1210 (27)	-103 (12)	397 (19)	-141 (13)	144 (8)	183 (3)	204 (5)
C(5)	1177 (24)	547 (11)	957 (25)	-86 (13)	413 (19)	-70 (13)	155 (5)	190 (3)	198 (4)
C(6)	992 (21)	467 (10)	896 (24)	-83 (11)	339 (17)	70 (12)	158 (5)	170 (6)	178 (4)
N(1)	1628 (24)	533 (10)	1102 (24)	-136 (12)	651 (19)	30 (12)	164 (3)	183 (5)	227 (2)
N(2)	1383 (24)	534 (11)	1728 (30)	-177 (12)	578 (21)	-327 (14)	154 (8)	204 (3)	254 (4)
N(3)	1662 (25)	541 (10)	1019 (23)	-151 (13)	505 (19)	76 (11)	166 (4)	184 (5)	229 (2)
O(11)	1843 (23)	798 (10)	1732 (26)	-50 (12)	1132 (20)	-80 (12)	166 (4)	232 (3)	261 (2)
O(12)	2849 (33)	1071 (14)	1228 (24)	425 (17)	755 (22)	452 (14)	168 (5)	238 (5)	329 (2)
O(21)	2253 (27)	432 (9)	2425 (31)	-42 (12)	731 (23)	-61 (13)	164 (7)	265 (2)	273 (3)
O(22)	3454 (39)	821 (12)	1844 (30)	-472 (17)	1255 (27)	-579 (15)	157 (11)	270 (4)	336 (2)
O(31)	2217 (26)	868 (12)	1922 (28)	-288 (14)	1303 (22)	149 (13)	168 (6)	237 (6)	282 (2)
O(32)	1908 (25)	782 (11)	1992 (29)	202 (13)	433 (21)	522 (14)	180 (6)	259 (4)	266 (4)
O(W1)	1538 (21)	608 (9)	1620 (23)	-22 (10)	513 (17)	159 (11)	194 (4)	217 (10)	221 (10)
O(W2)	1680 (22)	812 (11)	1641 (24)	-71 (12)	831 (18)	23 (12)	190 (4)	230 (3)	240 (3)
O(W3)	1425 (20)	827 (11)	1782 (25)	-300 (12)	685 (18)	-114 (12)	191 (4)	208 (4)	256 (3)
O(W4)	1452 (21)	608 (9)	2212 (28)	-14 (11)	523 (19)	50 (12)	194 (5)	216 (3)	259 (2)

Table 5. *Observed and calculated structure factor amplitudes*

The columns are in order $k, l, 10|F_o|, 10|F_c|$.

Reflexions marked * were given zero weight in the refinements.

k	l	$10 F_o $	$10 F_c $
1	0	100	100
2	0	100	100
3	0	100	100
4	0	100	100
5	0	100	100
6	0	100	100
7	0	100	100
8	0	100	100
9	0	100	100
10	0	100	100
11	0	100	100
12	0	100	100
13	0	100	100
14	0	100	100
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286	0	100	100
287	0	100	100
288	0	100	100
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341	0	100	100
342	0	100	100
343	0	100	100
344	0	100	100
345	0	100	100
346	0	100	100
347	0	100	

Table 5 (cont.)

Table 5 (cont.) contains multiple columns of data, likely representing bond lengths and angles for various atoms in the structure. The data is organized into several sections, with some rows starting with atom labels like C(1), C(2), C(3), C(4), C(5), C(6), C(1), C(1)-S, C(2)-N(1), C(4)-N(2), C(6)-N(3), C(3)-H(3), and C(5)-H(5). The values are presented in a tabular format, often with units like Å or degrees.

computer in Uppsala. The anisotropic refinements using the program *LALS* were made on the UNIVAC 1108 computer in Lund and the final refinement using the program *LINUS* was performed on the IBM 360/75 computer in Stockholm.

Description of the structure

The structure is illustrated in Figs. 1 and 2. Bond distances and angles are shown in Figs. 3 and 4. The bond distances are also listed in Table 6. The interatomic distances and angles have been calculated with the program *ORFFE*. All illustrations in this paper have been prepared using the plotting program *ORTEP*.

The hydrogen bonds in the structure have been derived from interatomic distances and angles involving non-hydrogen atoms and from hydrogen positions obtained from Fourier difference syntheses.

The structure comprises $H_5O_2^+$ ions (see below), picrylsulphonate ions and water molecules. The $H_5O_2^+$ ions, water molecules and sulphonate groups are hydrogen bonded together to form layers parallel to the *ac* plane. The carbon rings point outward from these layers alternately in the positive and negative *b* direction (see Fig. 1). The angle between the plane of the carbon ring and the *bc* plane is 2° . The distances between the parallel carbon rings are 3.83 Å (rings related by a centre of symmetry at 0,0,0) and 4.04 Å

(rings related by a centre of symmetry at 0.5,0.5,0.5). The shortest distance between atoms in different hydrogen bonded layers occurs between O(3) and O(22) where the distance is 3.07 Å (the hydrogen atoms are

Table 6. Interatomic distances

(a) Covalent bonds

C(1)-C(2)	1.397 (2) Å	N(1)-O(11)	1.219 (2) Å
C(2)-C(3)	1.383 (2)	N(1)-O(12)	1.213 (2)
C(3)-C(4)	1.367 (2)	N(2)-O(21)	1.219 (2)
C(4)-C(5)	1.379 (2)	N(2)-O(22)	1.216 (2)
C(5)-C(6)	1.383 (2)	N(3)-O(31)	1.213 (2)
C(6)-C(1)	1.390 (2)	N(3)-O(32)	1.211 (2)
C(1)-S	1.806 (1)	S-O(1)	1.432 (1)
C(2)-N(1)	1.475 (2)	S-O(2)	1.446 (1)
C(4)-N(2)	1.478 (2)	S-O(3)	1.444 (1)
C(6)-N(3)	1.480 (2)		
C(3)-H(3)	0.95		
C(5)-H(5)	0.93		

(b) Hydrogen bonds

O(W1)···O(3)	2.859 (2) Å
···O(W1)	2.784 (2)
···O(W2)	2.687 (2)
···O(W4)	2.792 (2)
O(W2)···O(3)	2.736 (2)
···O(W3)	2.429 (2)
O(W3)···O(2)	2.619 (2)
···O(W4)	2.606 (2)
O(W4)···O(W4)	2.879 (3)

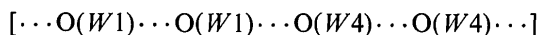
Other intermolecular O···O distances are > 3.07 Å.

not considered in the discussion of distances unless it is explicitly stated otherwise). In Fig. 2 a hydrogen-bonded layer is viewed in a direction perpendicular to the *ac* plane.

Hydrogen bonds, H_5O_2^+

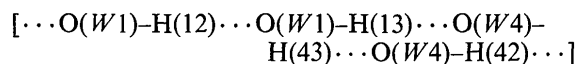
There are eleven hydrogen atoms available for hydrogen bonding in the asymmetric unit. The interatomic distances and angles suggest ten $\text{O}\cdots\text{O}$ hydrogen bonds. The shortness of the bond $\text{O}(W2)\cdots\text{O}(W3)$ (2.429 Å) and the equality of the S–O bonds in the sulphonate group indicate that the proton of the acid has been transferred to the water molecules (a hydrogen bond between water molecules is normally about 2.76 Å). The hydrogen atom positions as found from the Fourier difference syntheses are shown in Fig. 3(b).

The water molecules $\text{H}_2\text{O}(W1)$ and $\text{H}_2\text{O}(W4)$ are bonded together to form chains



extending in the *a* direction (see Fig. 2). According to the

space group chosen here, a centre of symmetry must occur at the centre of the $\text{O}(W1)\cdots\text{O}(W1)$ and the $\text{O}(W4)\cdots\text{O}(W4)$ bonds. In view of the lengths of these bonds (2.78 and 2.88 Å) the hydrogen atoms $\text{H}(12)$ and $\text{H}(43)$ must therefore be disordered. As a consequence of this the hydrogen atom in the $\text{O}(W1)\cdots\text{O}(W4)$ bond must occupy one of the two positions $\text{H}(13)$ and $\text{H}(42)$. The double peaks for $\text{H}(12)$ and $\text{H}(43)$ in the difference maps are a direct result of the choice of space group. However, the peaks representing the hydrogen atom in the $\text{O}(W1)\cdots\text{O}(W4)$ bond do not follow as a result of symmetry and may therefore be interpreted as a real disorder effect. In a single chain the hydrogen atoms must be ordered, however. The chains run either in the positive *a* direction,



or in the negative *a* direction,

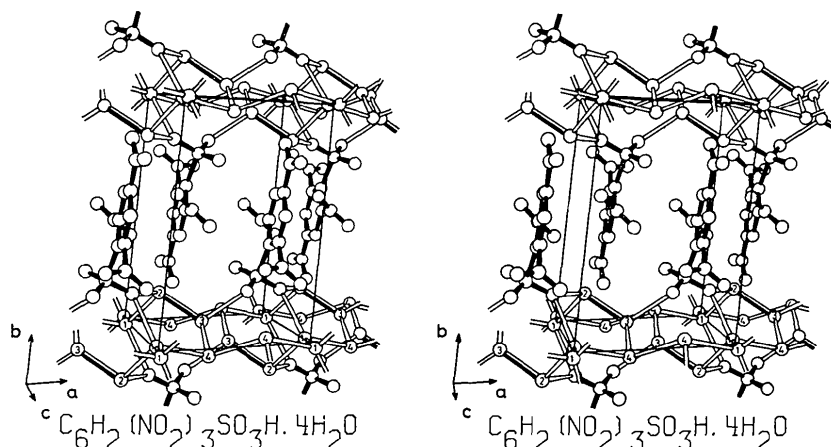
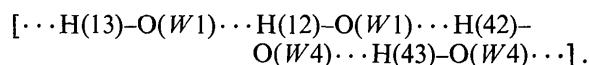


Fig. 1. Stereoscopic drawing of the crystal structure of $\text{H}_5\text{O}_2^+\text{C}_6\text{H}_2(\text{NO}_2)_3\text{SO}_3^- \cdot 2\text{H}_2\text{O}$. The structure is viewed along the *c* axis. Covalent bonds are filled. Hydrogen bonds within H_5O_2^+ are half-filled and other hydrogen bonds are open. The water oxygen atoms are denoted by 1, 2, 3 and 4.

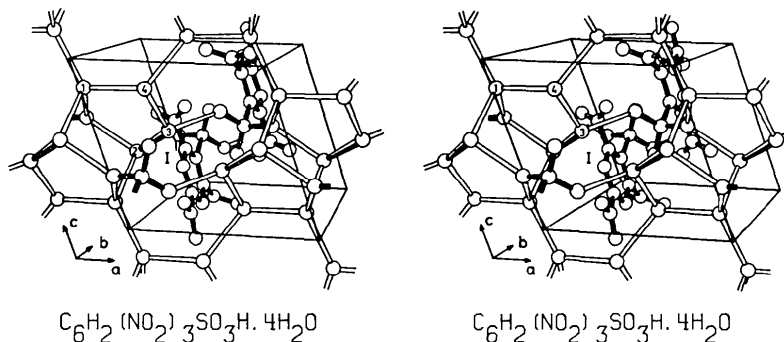
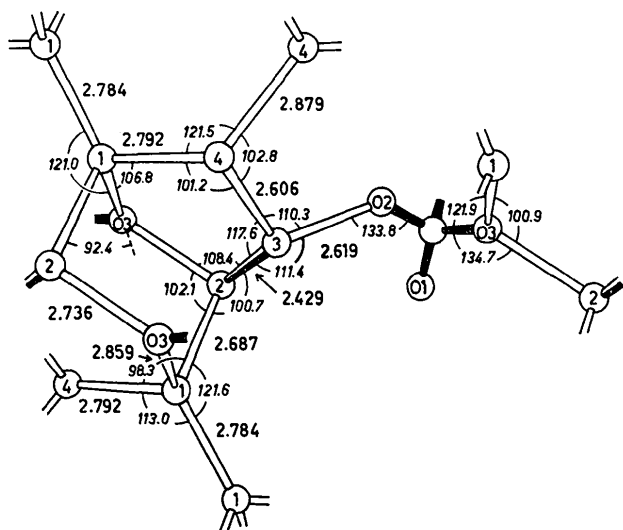
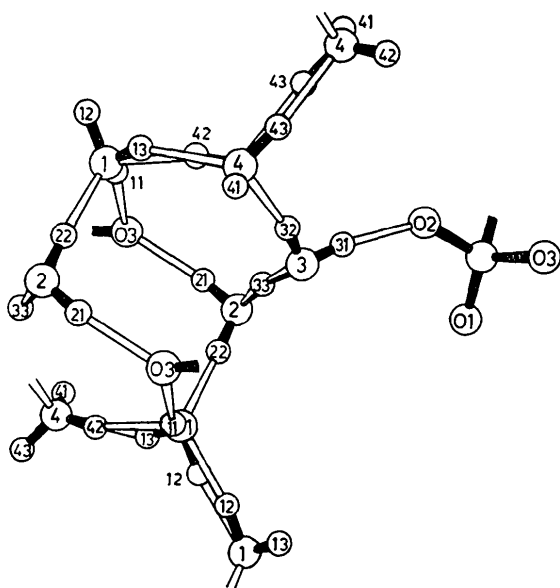


Fig. 2. Stereoscopic drawing showing the structure viewed normal to the *ac* plane. The water oxygen atoms denoted by 1, 2, 3 and 4 and the picrylsulphonate ion denoted by *I* constitute the asymmetric unit whose coordinates are given in Table 2. The remainder of the notation is as in Fig. 1.

The hydrogen bonding coordination for O(W1) is approximately tetrahedral and for O(W4) pyramidal. Only one hydrogen atom of H₂O(W4) forms a hydrogen bond; the other hydrogen atom, H(41), is not bonded to a second atom. The nearest neighbour of O(W4) apart from those shown in the Figures is a sulphate oxygen, O(1), 3.07 Å away, approximately in the O(W4)–H(41) direction.



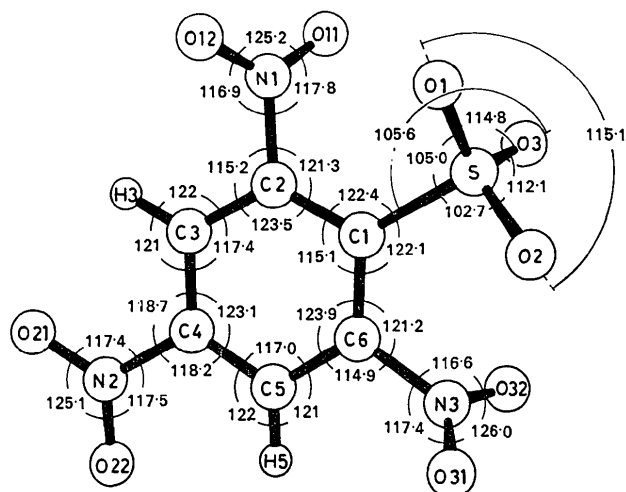
(a)



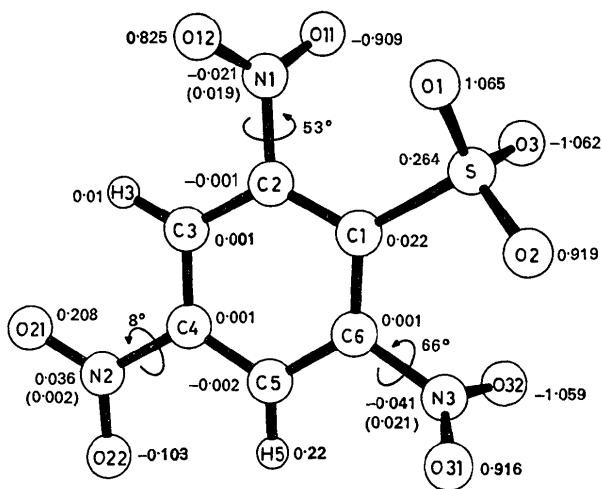
(b)

Fig. 3. (a) Distances and angles involving hydrogen bonds. E.s.d.'s of the angles are 0.1°. (b) The hydrogen atoms as obtained from Fourier difference syntheses. The hydrogen atoms are numbered as in Table 4. For other notation see Fig. 1. The orientation is as in Fig. 2.

The two remaining water oxygen atoms, O(W2) and O(W3), have a pyramidal bonding coordination. They are bonded together by a very short hydrogen bond, 2.429 Å. The conditions for a single potential minimum, whether symmetric or asymmetric, may therefore be fulfilled. In the difference maps the hydrogen



(a)



(b)

Fig. 4. (a) Angles in the picrylsulphonate ion. E.s.d.'s of the angles not involving hydrogen atoms are 0.1 to 0.2°. (b) Deviations of the atoms from the least-squares plane defined by the five carbon atoms C(2), C(3), C(4), C(5) and C(6) of the picrylsulphonate ion (Å). The distances of the nitrogen atoms to the planes through C(2), O(11), O(12); C(4), O(21), O(22) and C(6), O(31), O(32) are given in parentheses. E.s.d.'s of the distances are 0.001 to 0.002 Å. The angles of rotation of the nitro groups from the least-squares plane are also given. The picrylsulphonate ion shown here is the one denoted by *l* in Fig. 2 viewed along the *a* axis.

atom in this bond was found very near the centre of the bond, about 0.06 Å from the midpoint in the direction of O(W3). The hydrogen atom can thus be considered shared by O(W2) and O(W3) to approximately the same degree. The best formulation of the aggregate $[\text{H}_2\text{O}(W2)\cdots\text{H}\cdots\text{O}(W3)\text{H}_2]^+$ is thus H_5O_2^+ . The positive charge on the ion will presumably be displaced towards the O(W3) end where the hydrogen bonds are shorter. The conformation of the ion is *gauche*. The H_5O_2^+ ion is hydrogen bonded to two sulphonate oxygen atoms, O(2) and O(3), and to two water molecules, O(W1) and O(W4), in adjacent water chains.

The O(W)–H distances as obtained from the difference syntheses are in the range 0.70 to 0.94 Å. O(W2)···H(33) and O(W3)···H(33) distances are 1.28 and 1.16 Å respectively.

The picrylsulphonate ion

Bond distances and angles in the picrylsulphonate ion are given in Table 6 and Fig. 4(a).

The occurrence of a sulphonate group and two nitro groups on adjacent carbon atoms causes a distortion of the carbon ring which is reflected in the distances and angles [see Fig. 4(a)]. Carbon atom C(1) which carries the sulphonate group is displaced slightly out of the plane of the other five carbon atoms. The least-squares plane defined by these five carbon atoms was calculated using a method described by Blow (1960). The deviations of the atoms of the ion from this plane are shown in Fig. 4(b). The C(1)–S bond makes a small angle with the plane of the carbon ring and the C(2)–N(1) and C(6)–N(3) bonds point slightly out of the plane in the opposite direction. The nitro groups are all rotated out of the plane of the ring. The angles between the ring and the planes through C(2), O(11), O(12); C(4), O(21), O(22) and C(6), O(31), O(32) are 53, 8 and 66°

respectively. The nitro group at C(4) is planar; the other two nitro groups show a small but significant deviation from planarity (see Fig. 6). N(1) and O(1) are both on the same side of the plane through C(2), O(11) and O(12). Similarly, N(3) and O(2) are both on the same side of the plane through C(6), O(31) and O(32).

I would like to thank Professor I. Olovsson for the facilities he has placed at my disposal and for valuable discussions. I am also indebted to H. Karlsson for technical assistance and to Dr J. Albertsson for kind assistance with the calculations on the UNIVAC 1108 computer in Lund. This work was supported by grants from the Swedish Natural Science Research Council and the Wallenberg Foundation, which are gratefully acknowledged.

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