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Hydrogen Bond Studies. LXXXVI.* An Asymmetric Non-Centred H_5O_2^+ Ion: Neutron Diffraction Study 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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A three-dimensional single-crystal neutron diffraction study has been made of picrylsulphonic acid tetrahydrate. 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^2 gave a final R value of 0.052. The structure comprises H_5O_2^+ ions, picrylsulphonate ions and water molecules. The diaquahydrogen ion is of the asymmetric non-centred type. The hydrogen atom in the short [2.436(2) Å] practically linear hydrogen bond is situated 0.09 Å from the centre of the bond. X-ray – neutron (X–N) difference Fourier syntheses have been calculated to illustrate the asphericity of the atomic charge distribution in the H_5O_2^+ and picrylsulphonate ions.

Introduction

The diaquahydrogen ion, H_5O_2^+ , has been found in X-ray structure determinations of several hydrates of strong acids. However, no definite information as to the location of the hydrogen atoms of the H_5O_2^+ ion can be obtained from the X-ray studies. The configuration of the ion has thus been deduced from the positions of the non-hydrogen atoms. A neutron diffraction study of picrylsulphonic acid tetrahydrate was therefore undertaken to study the geometry of the diaquahydrogen ion in more detail. In this compound the hydrogen atom in the very short $\text{O} \cdots \text{O}$ bond has an asymmetric environment and is not forced by symmetry to be located in the centre of the bond. The X-ray structure determination of picrylsulphonic acid

tetrahydrate has been reported earlier by Lundgren (1972). This work is part of a series of systematic studies of solid hydrates of strong acids currently in progress at this Institute.

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. 365.23. 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 $P\bar{1}$ (Lundgren, 1972).

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

* Part LXXXV: *J. Chem. Phys.* In the press.

are listed in Table 3. The $|F_o|$ values are corrected for extinction using the expression

$$|F_o|_{\text{corr}} = |F_o| \left[1 + \frac{2\bar{T}F_c^2 g \lambda^3}{V^2 \sin^2 2\theta} \right]^{1/4}$$

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, calculated using the expression $\bar{T} = -\ln A^*/\mu$ where A^* is the transmission factor and μ is the linear absorption coefficient in cm⁻¹. The refined value of the isotropic extinction parameter is $g = 12923$ (307). The extinction correction factors as given above were in the range 1.00 to 1.60 for the reflexions used in the refinement. The reflexions 010 and 200 having very large extinction corrections (>2) were given zero weight in the refinements. An anisotropic extinction correction was also attempted but resulted in no further improvement.

Table I. Atomic coordinates

The parameter from the present neutron study is followed on the next line by the corresponding parameter from the X-ray refinement. Values are $\times 10^5$ for all atoms except H and 10^4 for H atoms.

	x	y	z
S	28135 (30)	75666 (19)	40246 (31)
	28143 (4)	75642 (3)	40278 (5)
O(1)	37899 (19)	73651 (12)	58080 (19)
	37876 (15)	73636 (10)	58093 (14)
O(2)	36960 (20)	81037 (12)	30906 (20)
	36962 (15)	81024 (10)	30897 (16)
O(3)	11240 (18)	81276 (11)	38046 (10)
	11224 (14)	81275 (9)	38029 (15)
C(1)	25127 (12)	60937 (8)	28518 (12)
	25138 (15)	60952 (11)	28497 (17)
C(2)	24427 (12)	51055 (8)	36765 (13)
	24406 (16)	51063 (11)	36696 (17)
C(3)	24492 (14)	39457 (8)	28834 (14)
	24493 (18)	39508 (12)	28701 (19)
C(4)	24974 (13)	37783 (8)	11710 (14)
	24980 (17)	37871 (11)	11785 (19)
C(5)	25371 (14)	47119 (9)	2500 (14)
	25388 (18)	47118 (12)	2576 (19)
C(6)	25352 (12)	58506 (8)	11172 (13)
	25348 (16)	58478 (12)	11227 (18)
N(1)	23619 (11)	52359 (7)	54869 (10)
	23634 (17)	52334 (10)	54886 (17)
N(2)	25489 (11)	25590 (7)	3051 (12)
	25492 (16)	25602 (11)	3023 (19)
N(3)	25321 (11)	68111 (7)	583 (10)
	25322 (17)	68129 (11)	593 (16)
O(11)	12284 (21)	58921 (14)	58090 (21)
	12200 (15)	58973 (10)	58061 (16)
O(12)	34108 (27)	46307 (17)	65279 (21)
	34110 (20)	46282 (12)	65296 (17)
O(21)	27280 (23)	17449 (12)	12001 (24)
	27281 (17)	17441 (10)	12038 (18)
O(22)	24209 (30)	24366 (15)	-12539 (25)
	24193 (21)	24425 (11)	-12541 (19)
O(31)	37720 (23)	68427 (15)	-3897 (22)
	37774 (16)	68425 (11)	-3856 (17)
O(32)	12428 (22)	74709 (14)	-3511 (23)
	12423 (16)	74729 (11)	-3514 (18)
O(W1)	2439 (22)	-324 (13)	83668 (22)
	2428 (20)	-393 (12)	83673 (18)

Table 1 (cont.)

O(W2)	10958 (21)	16779 (15)	43089 (24)
	11052 (18)	16813 (12)	43126 (19)
O(W3)	37106 (20)	5771 (15)	59194 (23)
	37065 (16)	5795 (12)	59150 (18)
O(W4)	36513 (22)	-5074 (14)	85413 (25)
	36492 (18)	-5015 (12)	85404 (21)
H(3)	2404 (4)	3201 (2)	3572 (4)
	2394 (23)	3292 (17)	3460 (25)
H(5)	2612 (4)	4555 (2)	-1073 (4)
	2550 (22)	4623 (15)	-895 (26)
H(11)	-199 (4)	706 (2)	7871 (4)
	-92 (29)	545 (22)	8092 (32)
H(12)*	115 (8)	-23 (6)	9496 (9)
	152 (55)	-68 (38)	9479 (56)
H(13)*	1391 (9)	-87 (6)	8582 (8)
	1195 (72)	-241 (41)	8697 (64)
H(21)	267 (4)	1874 (3)	4939 (4)
	399 (35)	1797 (23)	4811 (37)
H(22)	565 (4)	1161 (3)	3241 (4)
	624 (31)	1222 (24)	3353 (38)
H(31)	4707 (4)	1055 (3)	6258 (4)
	4513 (29)	948 (19)	6205 (29)
H(32)	3694 (3)	185 (2)	6946 (4)
	3624 (34)	259 (24)	6906 (38)
H(33)	2492 (4)	1104 (2)	5235 (4)
	2294 (43)	1142 (27)	5135 (42)
H(41)	3797 (5)	-1336 (3)	8223 (6)
	3849 (41)	-1154 (32)	8197 (45)
H(42)*	2534 (9)	-344 (5)	8672 (8)
	2540 (67)	-354 (37)	8733 (56)
H(43)*	4565 (9)	-223 (6)	9564 (10)
	4292 (69)	-299 (52)	9510 (82)

* Hydrogen atoms occupying disordered sites.

The coherent scattering amplitudes used were $b_s = 0.280$, $b_o = 0.580$, $b_c = 0.665$, $b_N = 0.940$ and $b_H = -0.374$ (in units of 10^{-12} cm) (Bacon, 1972).

The hydrogen atom coordinates given in the X-ray work (Lundgren, 1972) were taken from difference Fourier syntheses. Inadequate computing facilities at the time of this investigation meant that these coordinates could not be varied in the least-squares calculations. The comparison made in the present paper is based on X-ray parameters obtained in a refinement where hydrogen atom coordinates and their associated isotropic thermal parameters were also allowed to vary. Only four of the hydrogen atom coordinates resulting from this refinement showed significant deviations ($3-5\sigma$) from the values obtained from the difference syntheses.

The computer programs used have been described by Lundgren (1974).

General comparison of neutron and X-ray parameters

Atomic positional and thermal vibrational parameters from the present neutron study and from the refinement of the X-ray data are given in Tables 1 and 2. Close agreement is generally found between non-hydrogen atom coordinates from the neutron and X-ray study; significant differences arise, however, for some of the atoms. The hydrogen atom coordinates show their characteristic disparity, resulting from the

asphericity of the electron distribution associated with these atoms. This will be discussed later in more detail.

Comparison of the thermal vibrational parameters reveals some differences, especially for the carbon atoms, for which the β_{11} values are all significantly *higher* than the corresponding X-ray values. The β_{11} values correspond to a direction perpendicular to the plane of the carbon ring. Those β_{22} and β_{33} values for the carbon atoms which deviate significantly from the X-ray values are all *lower* than these values.

X-N difference Fourier syntheses

A combination of X-ray and neutron diffraction data was used to study the asphericity of the electronic

charge distribution. Quantities $(F_x - F_N)$, used as coefficients in Fourier summations, were calculated from a combination of X-ray data and neutron least-squares parameters. F_x is the observed structure-factor amplitude from the X-ray study with the calculated sign and corrected for extinction effects using the isotropic extinction parameter obtained from the X-ray refinement; F_N is calculated using positional and thermal parameters found in the neutron study and the spherical free-atom X-ray scattering factors given by Hanson, Herman, Lea & Skillman (1964) (non-hydrogen atoms) and by Stewart, Davidson & Simpson (1965) (hydrogen atoms). Before calculating the difference maps an additional cycle of least-squares refinement was made on the scale factor k alone, using the neutron

Table 2. *Anisotropic thermal parameters*

The parameter from the neutron study is followed on the next line by the parameter from the X-ray refinement. The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$.

(a) Heavy atoms. Values are $\times 10^5$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	1057 (34)	396 (14)	1053 (39)	-152 (18)	413 (29)	-96 (19)
	1096 (6)	363 (3)	1056 (7)	-128 (3)	460 (4)	-88 (3)
O(1)	1686 (25)	640 (10)	1135 (22)	-211 (12)	184 (18)	-128 (12)
	1763 (21)	646 (9)	1126 (20)	-202 (11)	203 (16)	-149 (10)
O(2)	1946 (27)	627 (10)	1748 (28)	-574 (13)	1009 (22)	-197 (13)
	1960 (22)	644 (9)	1794 (24)	-560 (12)	1028 (19)	-207 (11)
O(3)	1474 (22)	542 (9)	1791 (27)	170 (11)	820 (20)	153 (13)
	1472 (19)	536 (8)	1763 (23)	170 (10)	807 (17)	134 (10)
C(1)	943 (14)	373 (6)	846 (15)	-70 (7)	315 (11)	-7 (7)
	806 (19)	394 (9)	933 (22)	-48 (10)	322 (16)	-6 (11)
C(2)	1080 (15)	395 (6)	921 (16)	-64 (7)	387 (12)	25 (8)
	1005 (20)	442 (10)	897 (23)	-74 (11)	397 (17)	5 (11)
C(3)	1305 (16)	381 (6)	1103 (18)	-91 (8)	469 (13)	30 (8)
	1161 (23)	395 (10)	1200 (26)	-78 (12)	444 (19)	55 (12)
C(4)	1155 (16)	418 (7)	1094 (17)	-113 (8)	419 (13)	-84 (8)
	1067 (22)	394 (10)	1208 (26)	-102 (11)	398 (19)	-140 (12)
C(5)	1334 (17)	489 (7)	942 (17)	-116 (8)	440 (13)	-80 (9)
	1180 (23)	553 (11)	898 (24)	-88 (12)	415 (19)	-75 (12)
C(6)	1069 (15)	437 (6)	857 (15)	-68 (7)	367 (12)	21 (8)
	977 (20)	463 (10)	898 (23)	-85 (11)	332 (17)	70 (11)
N(1)	1580 (14)	546 (5)	1065 (13)	-79 (7)	629 (10)	58 (6)
	1612 (24)	532 (10)	1092 (23)	-144 (12)	642 (18)	21 (11)
N(2)	1443 (13)	484 (5)	1669 (17)	-161 (7)	586 (12)	-268 (7)
	1368 (23)	528 (10)	1711 (29)	-175 (12)	570 (20)	-324 (13)
N(3)	1520 (14)	549 (5)	1083 (13)	-105 (7)	487 (10)	146 (6)
	1642 (24)	536 (10)	1010 (22)	-144 (12)	499 (18)	79 (11)
O(11)	1819 (26)	782 (12)	1627 (28)	-30 (14)	1080 (22)	-74 (14)
	1821 (23)	786 (10)	1714 (25)	-52 (12)	1117 (19)	-84 (12)
O(12)	2778 (40)	1052 (16)	1160 (26)	419 (20)	773 (25)	458 (17)
	2839 (32)	1061 (13)	1207 (23)	423 (16)	759 (21)	449 (14)
O(21)	2226 (32)	412 (9)	2330 (36)	-52 (13)	733 (27)	-107 (14)
	2222 (26)	433 (9)	2416 (30)	-42 (12)	720 (22)	-68 (12)
O(22)	3405 (49)	744 (13)	1757 (33)	-433 (20)	1194 (32)	-536 (17)
	3420 (37)	819 (12)	1818 (29)	-461 (17)	1230 (26)	-574 (14)
O(31)	2145 (31)	836 (12)	1825 (30)	-229 (15)	1261 (25)	208 (15)
	2192 (25)	860 (11)	1896 (27)	-276 (13)	1288 (21)	158 (13)
O(32)	1859 (29)	762 (12)	1925 (32)	154 (15)	439 (24)	546 (16)
	1904 (24)	776 (11)	1981 (28)	198 (13)	436 (20)	525 (13)
O(W1)	1546 (29)	556 (10)	1538 (31)	-25 (13)	477 (24)	141 (13)
	1556 (25)	589 (10)	1633 (26)	15 (12)	510 (20)	192 (12)
O(W2)	1574 (26)	794 (12)	1681 (31)	-82 (14)	793 (24)	67 (16)
	1643 (23)	818 (11)	1642 (26)	-77 (13)	823 (20)	3 (13)
O(W3)	1332 (25)	803 (12)	1809 (31)	-294 (14)	670 (22)	-124 (16)
	1400 (21)	815 (11)	1827 (27)	-329 (12)	715 (19)	-119 (13)
O(W4)	1362 (26)	622 (12)	2088 (35)	-25 (13)	496 (26)	81 (15)
	1443 (22)	612 (10)	2182 (31)	-11 (12)	506 (22)	40 (14)

Table 2 (cont.)

(b) Hydrogen atoms. The anisotropic parameters are $\times 10^4$.

	β_{11}					
	B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
H(3)	267 (6)	55 (2)	190 (5)	-14 (2)	100 (4)	15 (2)
	3.5 (4)					
H(5)	256 (6)	87 (2)	136 (44)	-21 (3)	94 (4)	-12 (2)
	3.1 (3)					
H(11)	230 (6)	71 (2)	245 (6)	10 (3)	79 (5)	30 (3)
	4.6 (6)					
H(12)*	191 (10)	98 (4)	196 (15)	-9 (5)	85 (10)	7 (7)
	3.7 (9)					
H(13)*	174 (12)	105 (5)	211 (12)	-16 (6)	54 (9)	26 (6)
	4.8 (12)					
H(21)	196 (5)	101 (2)	217 (6)	11 (3)	102 (4)	0 (3)
	6.4 (7)					
H(22)	184 (5)	106 (2)	185 (5)	-3 (3)	73 (4)	13 (3)
	6.3 (6)					
H(31)	164 (4)	103 (2)	229 (6)	-39 (3)	76 (4)	0 (3)
	4.5 (5)					
H(32)	160 (4)	91 (2)	211 (6)	-26 (2)	74 (4)	0 (3)
	7.1 (7)					
H(33)	222 (6)	91 (2)	208 (5)	-45 (3)	110 (5)	-18 (3)
	9.0 (8)					
H(41)	235 (6)	69 (2)	456 (12)	12 (3)	77 (7)	10 (4)
	8.5 (9)					
H(42)*	178 (11)	96 (5)	240 (13)	-10 (6)	95 (9)	32 (6)
	5.0 (9)					
H(43)*	216 (13)	114 (6)	228 (15)	-20 (7)	33 (11)	22 (7)
	7.6 (16)					

* Hydrogen atoms occupying disordered sites.

least-squares parameters and the X-ray observations. This led to a 2.6% increase in k (defined by $kF_c = F_o$). The X-N syntheses will be discussed later.

Description and discussion of the structure

Hydrogen bonds, $H_5O_2^+$

A stereoscopic view of the hydrogen-bond system is shown in Fig. 1. Selected distances and angles are listed in Table 4 and are illustrated in Fig. 2. No significant differences in hydrogen-bond distances and angles involving the non-hydrogen atoms are observed on comparison with results from the X-ray study. The hydrogen atom disorder found in the X-ray study is confirmed in the present study. The O-H distances involving the ordered hydrogen atoms are 0.10-0.26 Å longer than the distances found in the X-ray case. The corresponding values for the disordered hydrogen atoms are 0.05-0.30 Å. The O-H directions agree to within 9(3)° for the ordered hydrogen atoms and to within 18(5)° for the disordered hydrogen atoms.

The water molecules $H_2O(W1)$ and $H_2O(W4)$ are bonded together to form chains extending in the a direction. Within a single chain the water molecules are oriented in one of two ways. Fragments of the two possible disordered chains are shown at the top and bottom of Fig. 1. The chains are interconnected *via* $H_5O_2^+$ ions, consisting of two water molecules bonded together by a very short hydrogen bond, 2.436 Å. The $H_5O_2^+ \cdots H_2O$ bonds, 2.604 and 2.685 Å (Fig. 2), are considerably longer than the bond within $H_5O_2^+$ and

this may be taken as a criterion for the characterization of the $H_5O_2^+$ complex.

The diaquahydrogen ion, $H_5O_2^+$, is of the asymmetric non-centred type. The hydrogen atom in the short, practically linear hydrogen bond is situated 0.09 Å from the centre of the bond. The conformation of the ion is *gauche*. The angle between the planes formed by the central O...O bonds of each end is 105.7°. The corresponding angle is 106.9° when the outer O-H bonds are considered.

The vibrational motion of the hydrogen atoms in $H_5O_2^+$, as illustrated by the thermal parameters from the least-squares refinement, shows some noticeable features. The thermal motion of H(33) relative to O(W2) and O(W3) is shown in Fig. 3. The thermal ellipsoid of the hydrogen atom represents the difference between the thermal motion of the hydrogen atom itself and the oxygen atoms to which it is bonded [O(W2) and O(W3)]. The motion is mainly in the direction of the bond. This is in complete agreement with the observation that the hydrogen atom in very short hydrogen bonds vibrates in a broad potential-energy well (Albertsson & Grenthe, 1973; Kvik, Koetzle, Thomas & Takusagawa, 1974). Several *ab initio* calculations on the $H_5O_2^+$ complex also show that the potential-energy curve for the proton in the short hydrogen bond is very flat in the region of its minimum and that rather large proton shifts (~ 0.3 Å) are possible without any significant change in energy (Kollman & Allen, 1970; Kraemer & Dierksen, 1970; Newton & Ehrenson, 1971).

Table 3. *Observed and calculated neutron structure-factor amplitudes*The columns are in order k , l , $100|F_o|$, $100|F_c|$. Reflexions marked * were given zero weight in the refinements.

k	l	$100 F_o $	$100 F_c $
1	0	100	100
1	1	100	100
1	2	100	100
1	3	100	100
1	4	100	100
1	5	100	100
1	6	100	100
1	7	100	100
1	8	100	100
1	9	100	100
1	10	100	100
1	11	100	100
1	12	100	100
1	13	100	100
1	14	100	100
1	15	100	100
1	16	100	100
1	17	100	100
1	18	100	100
1	19	100	100
1	20	100	100
1	21	100	100
1	22	100	100
1	23	100	100
1	24	100	100
1	25	100	100
1	26	100	100
1	27	100	100
1	28	100	100
1	29	100	100
1	30	100	100
1	31	100	100
1	32	100	100
1	33	100	100
1	34	100	100
1	35	100	100
1	36	100	100
1	37	100	100
1	38	100	100
1	39	100	100
1	40	100	100
1	41	100	100
1	42	100	100
1	43	100	100
1	44	100	100
1	45	100	100
1	46	100	100
1	47	100	100
1	48	100	100
1	49	100	100
1	50	100	100
1	51	100	100
1	52	100	100
1	53	100	100
1	54	100	100
1	55	100	100
1	56	100	100
1	57	100	100
1	58	100	100
1	59	100	100
1	60	100	100
1	61	100	100
1	62	100	100
1	63	100	100
1	64	100	100
1	65	100	100
1	66	100	100
1	67	100	100
1	68	100	100
1	69	100	100
1	70	100	100
1	71	100	100
1	72	100	100
1	73	100	100
1	74	100	100
1	75	100	100
1	76	100	100
1	77	100	100
1	78	100	100
1	79	100	100
1	80	100	100
1	81	100	100
1	82	100	100
1	83	100	100
1	84	100	100
1	85	100	100
1	86	100	100
1	87	100	100
1	88	100	100
1	89	100	100
1	90	100	100
1	91	100	100
1	92	100	100
1	93	100	100
1	94	100	100
1	95	100	100
1	96	100	100
1	97	100	100
1	98	100	100
1	99	100	100
1	100	100	100
2	0	100	100
2	1	100	100
2	2	100	100
2	3	100	100
2	4	100	100
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2	92	100	100
2	93	100	100
2	94	100	100
2	95	100	100
2	96	100	100
2	97	100	100
2	98	100	100
2	99	100	100
2	100	100	100

Table 3 (cont.)

Table 3 (cont.) contains multiple columns of data, likely representing bond lengths and angles for various atoms in a crystal structure. The data is organized into several vertical columns, with some columns containing labels like O(1), O(2), O(3), O(4), H(1), H(2), H(3), H(4), H(11), H(12), H(13), H(21), H(22), H(31), H(32), H(41), H(42), H(43) and their corresponding coordinates or distances. The data is presented in a dense, tabular format typical of scientific publications.

Table 4. Distances (Å) and angles (°) within the hydrogen-bond system

(a) Hydrogen bonds O—H...O

	O—H	H...O	O...O	O...O X-rays	∠O—H...O
O(W3)—H(33)...O(W2)	1.128 (4)	1.310 (4)	2.436 (2)	2.427 (2)	175.0 (3)
O(W2)—H(21)...O(3)	0.976 (4)	1.776 (3)	2.734 (2)	2.738 (2)	166.3 (3)
O(W2)—H(22)...O(W1)	0.977 (4)	1.720 (4)	2.685 (2)	2.686 (2)	168.7 (3)
O(W3)—H(31)...O(2)	0.988 (3)	1.634 (3)	2.621 (2)	2.623 (2)	176.3 (3)
O(W3)—H(32)...O(W4)	0.996 (4)	1.609 (4)	2.604 (3)	2.604 (2)	177.2 (3)
O(W1)—H(11)...O(3)	0.960 (3)	1.932 (3)	2.860 (2)	2.865 (2)	161.9 (3)
O(W1)—H(12)...O(W1)	0.951 (7)	1.836 (7)	2.786 (4)	2.782 (3)	177.1 (6)
O(W1)—H(13)...O(W4)	0.911 (8)	1.900 (8)	2.791 (3)	2.790 (2)	165.4 (6)
O(W4)—H(42)...O(W1)	0.967 (7)	1.842 (7)	2.791 (3)	2.790 (2)	166.8 (6)
O(W4)—H(43)...O(W4)	0.967 (7)	1.920 (7)	2.883 (4)	2.880 (3)	173.3 (6)

(b) Water molecules

H1	O	H2	H1—O	O—H2	H1—H2	∠H1—O—H2
H(11)	O(W1)	H(12)	0.960 (3)	0.951 (7)	1.578 (7)	111.4 (5)
H(11)	O(W1)	H(13)		0.911 (8)	1.502 (8)	106.8 (5)
H(21)	O(W2)	H(22)	0.976 (4)	0.977 (4)	1.572 (4)	107.2 (3)
H(21)	O(W2)	H(33)		1.310 (4)	1.911 (4)	112.6 (3)
H(22)	O(W2)	H(33)			1.863 (4)	108.1 (3)
H(31)	O(W3)	H(32)	0.988 (3)	0.996 (4)	1.629 (4)	110.4 (3)
H(31)	O(W3)	H(33)		1.128 (4)	1.755 (4)	111.9 (3)
H(32)	O(W3)	H(33)			1.797 (4)	115.4 (3)
H(41)	O(W4)	H(42)	0.947 (4)	0.967 (7)	1.542 (7)	107.4 (4)
H(41)	O(W4)	H(43)		0.967 (7)	1.595 (8)	112.9 (5)

The motions of the outer hydrogen atoms of the H_5O_2^+ complex are different from that of the hydrogen atom in the central hydrogen bond. The difference thermal ellipsoids, as illustrated for H(31) in Fig. 3,

are oriented so that their shortest axis is approximately in the bond direction. The thermal ellipsoid of the hydrogen atom represents the difference between the

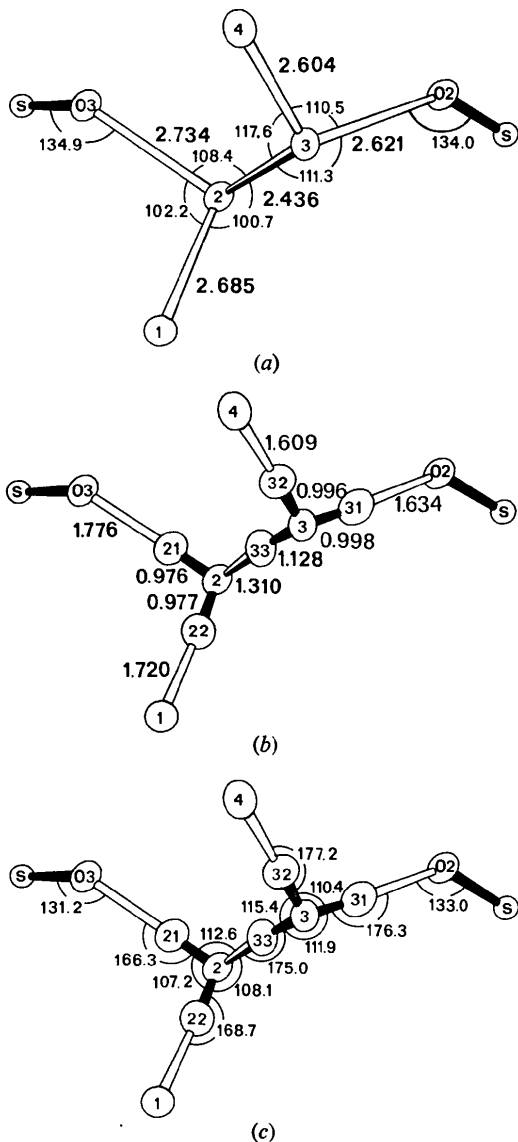


Fig. 2. Bond distances and angles in and around the H_5O_2^+ ion. (a) Distances and angles involving non-hydrogen atoms. (b) Distances involving hydrogen atoms. (c) Angles involving hydrogen atoms.

Table 6. *R.m.s. components of thermal displacement of the atoms along the ellipsoid axes* ($\times 10^3$ Å)

	R_1	R_2	R_3
S	145 (3)	171 (3)	194 (3)
O(1)	162 (2)	219 (2)	244 (2)
O(2)	154 (2)	194 (2)	291 (2)
O(3)	166 (2)	205 (2)	242 (2)
C(1)	147 (1)	163 (1)	172 (1)
C(2)	155 (1)	163 (1)	184 (1)
C(3)	155 (1)	174 (1)	202 (1)
C(4)	151 (1)	183 (1)	196 (1)
C(5)	150 (1)	187 (1)	205 (1)
C(6)	153 (1)	169 (1)	183 (1)
N(1)	161 (1)	187 (1)	223 (1)
N(2)	152 (1)	208 (1)	244 (1)
N(3)	165 (1)	191 (1)	218 (1)
O(11)	163 (2)	232 (2)	255 (2)
O(12)	161 (2)	234 (2)	325 (2)
O(21)	158 (2)	263 (2)	269 (2)
O(22)	152 (2)	263 (2)	331 (2)
O(31)	161 (2)	235 (2)	275 (2)
O(32)	175 (2)	253 (2)	263 (2)
O(W1)	187 (2)	212 (2)	222 (2)
O(W2)	192 (2)	225 (2)	236 (2)
O(W3)	185 (2)	207 (2)	255 (2)
O(W4)	196 (2)	209 (2)	250 (2)
H(3)	183 (3)	222 (3)	289 (3)
H(5)	176 (3)	242 (3)	284 (3)
H(11)	205 (3)	265 (3)	275 (3)
H(12)	219 (7)	250 (6)	255 (7)
H(13)	231 (7)	241 (7)	265 (7)
H(21)	203 (3)	264 (3)	272 (3)
H(22)	221 (3)	242 (3)	263 (3)
H(31)	202 (3)	249 (3)	276 (3)
H(32)	209 (3)	233 (3)	260 (3)
H(33)	213 (3)	216 (3)	294 (4)
H(41)	204 (4)	278 (4)	377 (5)
H(42)	210 (7)	244 (6)	272 (7)
H(43)	241 (8)	267 (8)	290 (8)

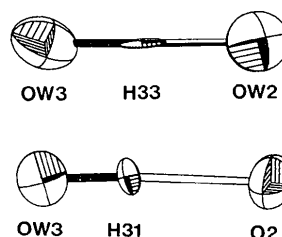


Fig. 3. Difference thermal ellipsoids of the hydrogen atoms H(33) and H(31) in the H_5O_2^+ ion. The thermal ellipsoids are scaled to enclose 50% probability.

Table 5. *Difference thermal motion of the hydrogen atoms in H_5O_2^+*

Root-mean-square displacements (Å) along the principal axes and the angles ($^\circ$) these make with the $\text{O}\cdots\text{O}$ bond [H(33)] and O-H bonds (other hydrogen atoms).

	R_1	R_2	R_3	Angles		
H(21)	0.027 (39)	0.124 (7)	0.161 (8)	32 (4)	99 (6)	60 (4)
H(22)	0.049 (16)	0.107 (12)	0.136 (8)	47 (6)	64 (12)	54 (10)
H(31)	0.079 (17)	0.104 (7)	0.140 (7)	25 (16)	68 (17)	79 (7)
H(32)	0.050 (19)	0.096 (12)	0.109 (7)	34 (12)	63 (16)	72 (18)
H(33)	0.031 (26)	0.071 (21)	0.172 (5)	93 (3)	94 (4)	5 (3)

thermal motion of the hydrogen atom itself and the oxygen atom to which it is covalently bonded. Root-mean-square displacements for the difference thermal ellipsoids along their principal axes and the angles these make with the hydrogen bond are listed in Table 5. The r.m.s. components of all atoms are listed in Table 6.

The X-N difference map in the plane defined by atoms O(W2), O(W3) and H(32) of the H_3O_2^+ ion is shown in Fig. 4. The hydrogen bonds $\text{O}(W3)\cdots\text{O}(W2)$ and $\text{O}(W3)\cdots\text{O}(W4)$ are thus both in the plane of the paper. The water molecule $\text{H}_2\text{O}(W4)$ is bonded to the H_3O_2^+ complex by a bond which is 0.17 Å longer than the $\text{O}(W3)\cdots\text{O}(W2)$ bond. In spite of the large difference in $\text{O}\cdots\text{O}$ bond lengths, the electron distribution is very much the same in the two bonds. The $\text{H}_2\text{O}(W2)$ -end of the H_3O_2^+ ion can thus be regarded as a water molecule very strongly bonded to an oxonium ion. In the present case the *internal* structure of the diaquahydrogen ion may best be described as $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$.

Low electron density is observed in the O-H bonds in the oxonium ion, but electrons are seen to migrate to regions above and below the flat pyramidal ion as shown in Fig. 5(a) and (b). The electron density around the $\text{H}_2\text{O}(W2)$ molecule is shown in Fig. 5(b). Here again low density is found in the O-H bonds. Concentrations of electron density are found in the O-H bonds of some of the remaining water molecules. How-

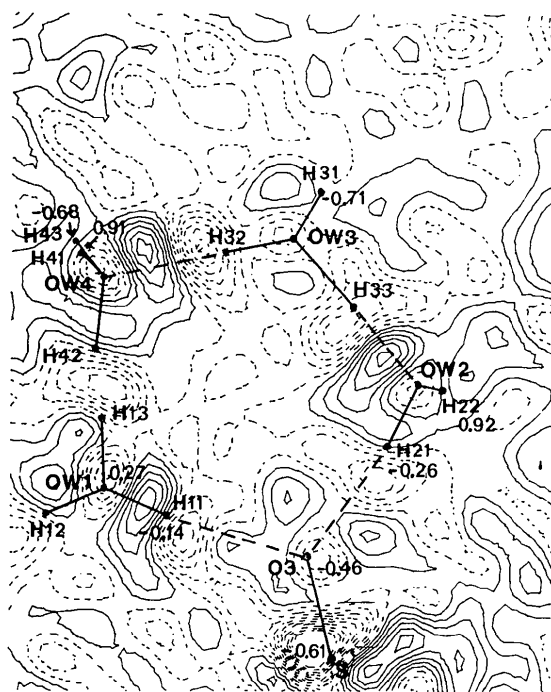


Fig. 4. X-N difference map in the plane defined by O(W2), O(W3) and H(32). The distance (Å) to this plane is given for those atoms which deviate by more than 0.10 Å from the plane. Contour intervals are at $0.06 \text{ e} \text{ \AA}^{-3}$; zero and negative contours are dashed.

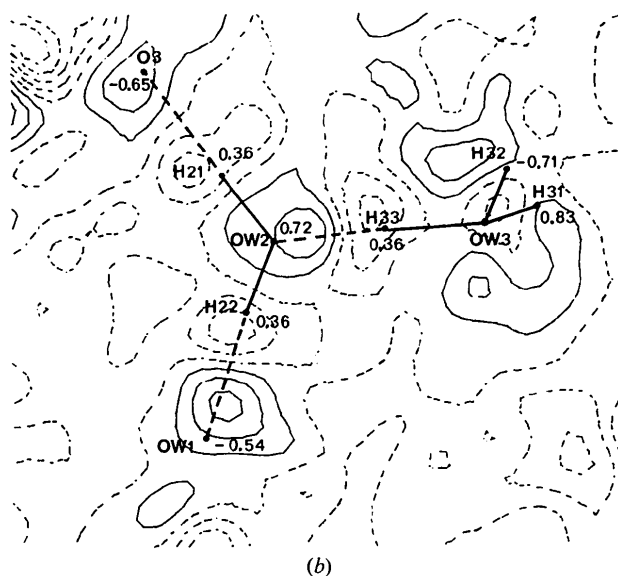
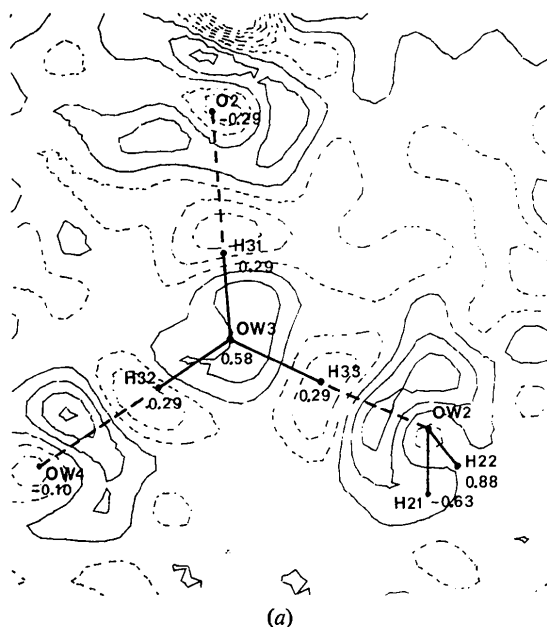


Fig. 5. X-N difference maps in planes parallel to the planes defined by (a) the hydrogen atoms H(31), H(32), H(33) and (b) the hydrogen atoms H(21), H(22), H(33). The distance (Å) to the plane is given for those atoms which deviate by more than 0.10 Å from the plane. Contour intervals are at $0.06 \text{ e} \text{ \AA}^{-3}$; zero and negative contours are dashed.

ever, it is difficult to ascertain to what extent the disorder of the hydrogen atoms of these water molecules will affect the appearance of the X-N maps. It should also be pointed out that scattering factors for the non-ionized forms of the atoms were used in the X-ray study. This means that an incorrect number of electrons was assigned to H_3O^+ (11 instead of 10) and to $-\text{SO}_3^-$ (40 instead of 41). The positive and negative charges are in these cases delocalized over several atoms so that neutral atom scattering factors would

appear to be a satisfactory approximation to the effective electron distribution.

The picrylsulphonate ion

Distances and angles within the picrylsulphonate ion are given in Table 7. The geometry of the ion agrees very well with the results from the X-ray study as far as the non-hydrogen atoms are concerned. Significant differences of 0.015 (3), 0.010 (3) and 0.012 (2) Å are observed for the C(3)–C(4), N(1)–O(11) and C(4)–N(2) distances, respectively. The C–H bond lengths are about 0.15 Å longer than the corresponding values obtained from the X-ray study. However, the C–H directions agree better [$H(X)-C-H(N)=1-4^\circ$]. In the least-squares procedure the deviation from a spherical electron distribution is thus compensated by a hydrogen atom shift towards the carbon atom to which it is covalently bonded. The asphericity of the electron density around these covalently bonded hydrogen atoms is illustrated in Fig. 6. The X–N difference map also shows the characteristic electron-density peaks in the C–C bonds in the carbon ring. No significant elongation of the peaks perpendicular to the ring plane was observed. An approximate integration of the electron densities in the C–C bonds gives values in the range 0.11 to 0.16 e. The exocyclic C–N bonds show lower electron densities than the C–C bonds. Furthermore, each of the NO₂ groups is characterized by negative regions on either side of the plane of the group.

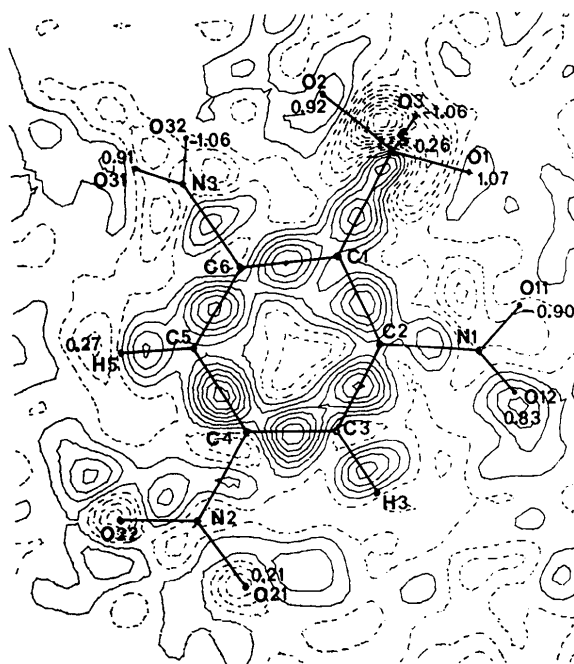


Fig. 6. X–N difference map in the plane of the carbon ring of the picrylsulphonate ion. The distance (Å) to this plane is given for those atoms which deviate by more than 0.10 Å from the plane. Contour intervals are at 0.06 e Å⁻³; zero and negative contours are dashed.

Table 7. Distances and angles in the picrylsulphonate ion

(a) Distances (Å)

		X-ray			X-ray
C(1)–C(2)	1.397 (1)	1.396 (2)	C(5)–H(5)	1.079 (3)	0.924 (19)
C(2)–C(3)	1.386 (1)	1.383 (2)	N(1)–O(11)	1.209 (2)	1.219 (2)
C(3)–C(4)	1.382 (2)	1.365 (2)	N(1)–O(12)	1.213 (2)	1.213 (2)
C(4)–C(5)	1.384 (1)	1.376 (2)	N(2)–O(21)	1.215 (2)	1.220 (2)
C(5)–C(6)	1.386 (1)	1.382 (2)	N(2)–O(22)	1.216 (2)	1.214 (2)
C(6)–C(1)	1.395 (1)	1.389 (2)	N(3)–O(31)	1.209 (2)	1.212 (2)
C(1)–S	1.810 (2)	1.807 (1)	N(3)–O(32)	1.213 (2)	1.213 (2)
C(2)–N(1)	1.471 (1)	1.477 (2)	S—O(1)	1.433 (3)	1.431 (1)
C(4)–N(2)	1.468 (1)	1.478 (2)	S—O(2)	1.442 (3)	1.445 (1)
C(6)–N(3)	1.473 (1)	1.480 (2)	S—O(3)	1.442 (3)	1.444 (1)
C(3)–H(3)	1.084 (3)	0.954 (19)			

(b) Angles (°)

		X-ray			X-ray
S—C(1)–C(2)	122.4 (1)	122.3 (1)	C(1)–S—C(5)	123.5 (1)	123.8 (1)
S—C(1)–C(6)	121.6 (1)	122.1 (1)	C(1)–S—O(1)	104.9 (1)	105.0 (1)
C(2)–C(1)–C(6)	115.6 (1)	115.2 (1)	C(1)–S—O(2)	102.9 (1)	102.7 (1)
N(1)–C(2)–C(3)	115.1 (1)	115.2 (1)	C(1)–S—O(3)	105.6 (1)	105.6 (1)
N(1)–C(2)–C(1)	121.3 (1)	121.4 (1)	O(1)–S—O(2)	115.0 (2)	115.1 (1)
C(3)–C(2)–C(1)	123.6 (1)	123.4 (1)	O(1)–S—O(3)	114.6 (2)	114.7 (1)
H(3)–C(3)–C(4)	121.4 (2)	121 (1)	O(2)–S—O(3)	112.3 (2)	112.1 (1)
H(3)–C(3)–C(2)	121.4 (2)	122 (1)	C(2)–N(1)–O(11)	118.2 (1)	117.8 (1)
C(4)–C(3)–C(2)	117.2 (1)	117.5 (1)	C(2)–N(1)–O(12)	116.7 (1)	116.9 (1)
N(2)–C(4)–C(5)	118.6 (1)	118.2 (1)	O(11)–N(1)–O(12)	125.0 (1)	125.3 (1)
N(2)–C(4)–C(3)	118.7 (1)	118.8 (1)	C(4)–N(2)–O(21)	117.7 (1)	117.4 (1)
C(5)–C(4)–C(3)	122.7 (1)	123.0 (1)	C(4)–N(2)–O(22)	117.6 (1)	117.5 (1)
H(5)–C(5)–C(6)	121.4 (2)	118 (1)	O(21)–N(2)–O(22)	124.7 (1)	125.1 (1)
H(5)–C(5)–C(4)	121.2 (2)	124 (1)	C(6)–N(3)–O(31)	117.7 (1)	117.5 (1)
C(6)–C(5)–C(4)	117.3 (1)	117.1 (1)	C(6)–N(3)–O(32)	116.4 (1)	116.5 (1)
N(3)–C(6)–C(1)	121.5 (1)	121.2 (1)	O(31)–N(3)–O(32)	125.8 (1)	125.9 (1)
N(3)–C(6)–C(5)	115.0 (1)	115.0 (1)			

In the sulphonate group electron densities are found in all S–O bonds and negative regions occur between the bonds. Negative regions are also observed at all oxygen sites, in agreement with earlier studies (*cf.* Almlöf, Kvik & Thomas, 1973). Electron densities corresponding to the lone pairs are observed around all oxygen atoms, but the densities are in most cases smeared so that no lone-pair directions can be deduced from the maps.

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Conformation of Non-Aromatic Ring Compounds. LXXXVI. The Crystal and Molecular Structure of 4-Phenyl-2,4,6-triazatricyclo[5,2,2,0^{2,6}]undecane-3,5-dione at -170°C

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The camphane-like compound 4-phenyl-2,4,6-triazatricyclo[5,2,2,0^{2,6}]undecane-3,5-dione crystallizes in the monoclinic system with $a = 5.8399$ (6), $b = 15.6402$ (16), $c = 6.7462$ (7) Å, $\beta = 100.74$ (5) $^{\circ}$ at -170°C , space group $P2_1$ and $Z = 2$. 1756 significant reflexions were collected on a three-circle diffractometer at -170°C with Mo $K\alpha$ radiation. The structure was solved by direct methods. Block-diagonal refinement including all atoms reduced the R index to 3.54%. The bicyclo[2,2,2]octane ring is slightly distorted. In this ring system the hybridization of the two vicinal atoms N(2) and N(6) is pyramidal, while that of the third nitrogen atom, N(4), is planar. The 1,2,4-triazacyclopentane-2,4-dione ring is slightly puckered: its largest torsion angle is -8.5° and its conformation an envelope with N(4) as flap. The phenyl ring has an asymmetric orientation with respect to the five-membered ring.

Introduction

This study is a continuation of earlier investigations (Altona & Sundaralingam, 1970; Altona & Sundaralingam, 1972; Offereins, Altona & Romers, 1973) into the twist of norbornane- and camphane-like structures containing nitrogen atoms in pyramidal hybridization. The title compound (hereinafter PTT) contains a bicyclo[2,2,2]octane nucleus in which two vicinal secondary carbon atoms are substituted by nitrogen atoms. Its chemical structure and the numbering of atoms are indicated in Fig. 1.

Evidence of a twisting motion about the threefold symmetry axis of bicyclo[2,2,2]octane has been reported by Ermer & Dunitz (1969) for the solid-state structure of bicyclo[2,2,2]octane-1,4-dicarboxylic acid (BOD) and by Yokozeki, Kuchitsu & Morino (1970) for the gas-phase structure of bicyclo[2,2,2]octane. This motion does not lead to a deviation from D_{3h} symmetry for the average structures observed; however, the lower D_3 symmetry has been reported by Cameron, Ferguson & Morris (1968) for the solid-state molecular structure of 1-*p*-bromobenzenesulphonyloxymethylbicyclo[2,2,2]octane (BBO). Apart from the two aza atoms,