Structural Investigation of the Self-Condensation Products of *o*-Aminobenzaldehyde, Anthranilic Acid and Related Compounds. 1. The TAAB salts TAABH₂*X*₂ [*X* = Picrate (Ordered), HSO₄ (Disordered) and BF₄ (Disordered)]. Hydrogen Bonding and the Importance of Two Non-Equivalent Lone-Pair Donor Sites in the Anion for Order

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Abstract

The tetra-anhydro tetramer TAAB is one of the self-condensation products of *o*-aminobenzaldehyde. The crystal structures of three TAAB salts $C_{28}H_{22}N_4^{2+}.2X^-$ have been determined by X-ray analysis. These are (1) the picrate, $X = C_6H_2N_3O_7$, (2) the bisulfate, $X = HSO_4$, and (3) the tetrafluoroborate, $X = BF_4$, of the 4b,5,15b,16-tetrahydrodibenzo[3,4:7,8]-[1,5]diazocino[2,1-*b*:6,5-*b*]diquinazoline-11,22-diium cation. [Crystal data: (1): monoclinic, $P2/n$, $a = 22.694$ (6), $b = 9.344$ (3), $c = 9.765$ (3) Å, $\beta = 107.48$ (9)°, $V = 1907.0$ (9) Å³, $Z = 2$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.72$ cm⁻¹; (2): orthorhombic, $Pmmn$, $a = 14.100$ (3), $b = 10.789$ (3), $c = 8.876$ (2) Å, $V = 1340.7$ (5) Å³, $Z = 2$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 2.10$ cm⁻¹; (3): monoclinic, $C2/c$, $a = 19.372$ (5), $b = 8.877$ (2), $c = 17.962$ (4) Å, $\beta = 116.72$ (2)°, $V = 2759.0$ (7) Å³, $Z = 4$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.82$ cm⁻¹]. Full-matrix least-squares refinements led to R values of 5.0% for (1), 5.5% for (2) and 5.3% for (3) using 1801, 929 and 1175 unique reflections respectively [$I > 3\sigma(I)$]. The structures of the TAAB salts have been controversial. In particular, two valence-bond isomeric structures, heptacyclic and macrocyclic, have recently been proposed. The present study confirms the heptacyclic structure and the presence of a central eight-membered heterocyclic ring. It is suggested that non-equivalent lone-pair donor sites in the anion for hydrogen bonding are needed for ordered TAABH₂*X*₂ structures.

Introduction

The self-condensation of *o*-aminobenzaldehyde, OAB, (4), under acidic conditions was first investigated in the 1920s by Seidel (1926, 1927) and by Bamberger (1927). Despite extensive studies, the structures of the acid condensation products remained controversial.

The condensation of OAB (4) in the presence of metal ions (*e.g.* Ni^{II}, Cu^{II}) gives rise to metal complexes of two different types [(5), (6)]. These are based on the
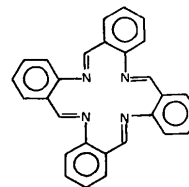

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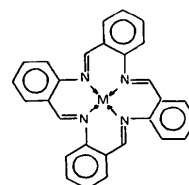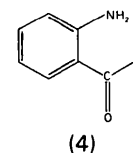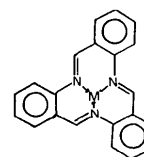
(5)   (6)

tetra-anhydro tetramer of the starting compound, where the ligand is usually designated TAAB (7), and on the tri-anhydro trimer, where the macrocycle is conventionally called TRI (8), both of which have never been isolated.
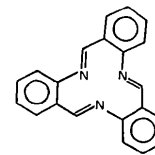
(7)   (8)

In 1977 Skuratowicz, Madden & Busch prepared a series of salts, TAABH₂*X*₂ ($X = BF_4$, ClO_4, CF_3SO_3, HSO₄) which could be described as anhydrous TAAB salts. Based on infrared spectroscopy (NH and C=N variations) the heptacyclic structure (9) was proposed for the TAABH₂ cation. Reference was made to an unpublished X-ray crystallographic study of the trifluoromethylsulfonate salt ($X = CF_3SO_3$). Disorder problems prevented the authors from reaching a definite conclusion about the bond orders within the structure.

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(9)

Table 1. *Analytical data*

Compound	Formula	Found (Calculated) (%)				
		C	H	N	S	O
(1)	$C_{40}H_{26}N_{10}O_{14}$	55·0 (55·2)	3·0 (3·0)	16·45 (16·1)		
(2)	$C_{28}H_{24}N_4O_8S_2$	55·2 (55·3)	3·85 (3·9)	9·4 (9·2)	10·8 (10·5)	
(11)	$C_{56}H_{58}N_4O_{16}S_4$	57·1 (57·4)	5·1 (4·95)	5·0 (4·8)	11·2 (10·9)	22·3 (21·8)
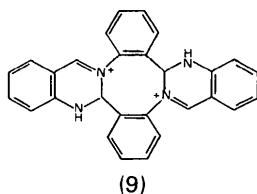
Subsequently, Goddard & Norris (1978) carried out the condensation of OAB in acetic acid in the presence of boron trifluoride diethyl etherate and obtained a red salt, $TAABH_2(BF_4)_2$, which they stated to be identical (elemental analysis, infrared, and mass spectra) to the one isolated by Skuratowicz *et al.* (1977), (9), but they preferred the valence-bond isomeric macrocyclic structure (10) without, however, giving any evidence for this point of view.

(10)

Table 2. *Additional crystal data and experimental information*

	(1)	(2)	(3)
M_r	870·70	608·64	588·17
D_m (g cm^{-3})	1·471	1·503	1·414
D_x (g cm^{-3})	1·462	1·505	1·421
Crystal size (mm)	0·41 × 0·42 × 0·23	0·35 × 0·35 × 0·48	0·31 × 0·42 × 0·35
Total unique data	5758	2141	1262
Max. Δ/σ in final least-squares cycle	0·001	0·45	0·41
Least-squares parameters	290	148	266
$(\Delta\rho)_{max}$ (e Å^{-3})	<0·3	<0·1	<0·2
Weights	$|\sigma^2(F_o)|^{-1}$	$|\sigma^2(F_o)|^{-1}$	$|\sigma^2(F_o) + 0·0003F_o^2|^{-1}$
hkl	±30, 13, 13	18, 15, 12	±24, 11, 22

In view of the variety of structures which have been proposed for apparently related compounds accurate structural data were essential and the present study on TAAB salts of type $TAABH_2X_2$ was undertaken. A preliminary report has been published (Owston, Shaw & Tasker, 1982).

Experimental

Method of preparation

20 g of crude *o*-aminobenzaldehyde was dissolved in 50 ml of acetonitrile. To the yellow solution thus obtained, 10 ml of 48% tetrafluoroboric acid was added. The solution almost immediately deposited $TAABH_2(BF_4)_2$, (3), as deep red crystals. The crystals and the solution were set aside overnight, filtered, and then washed with ethanol (Skuratowicz, Madden & Busch, 1977). The same method on a smaller scale (1 g OAB) was used to obtain crystals of $TAABH_2(HSO_4)_2$ (2), $TAABH_2$(picrate)$_2$, (1) and $TAABH_2$(*p*-tolSO$_3$)$_2$.·2*p*-tolSO$_3$H.4H$_2$O, (11), using sulfuric, picric and *p*-toluenesulfonic acids respectively. Analytical data are given in Table 1.

The crystals of (11) were not of very good quality, and were not investigated further. It is, however, worth noting that both forms (orthorhombic and monoclinic) (Lundgren & Olovsson, 1976) of *p*-tolSO$_3$H.H$_2$O contain H$_3$O$^+$ and *p*-tolSO$_3^-$ ions. It is likely that similar species are present in the above crystals, in which ample possibilities for hydrogen bonding should exist. The crystals of the other three compounds were found to be of very good quality for X-ray crystallography.

Crystallography

The crystals of compound (1) were thick plates, of (2) were cubes and of (3) were chunky blocks. Densities were measured by the flotation method. Unit-cell parameters were determined by least-squares refinement of the setting angles for 25 reflections $|16 < 2\theta(\text{Mo } K\alpha) < 32°|$ automatically centred on a Philips PW 1100 diffractometer. Intensity data were recorded on the same instrument at 295 (2) K using Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å, graphite monochromatized) in the $\omega/2\theta$ scan mode with a θ range of 3–25°. Data for all the compounds were corrected for Lorentz and polarization effects. Additional crystal data and experimental information are given in Table 2.

Structure determination and refinement

(1) The structure was solved by direct methods using *SHELX*76 (Sheldrick, 1976). All 16 non-hydrogen atoms of the cation were located from the best E map. (The molecule has a diad axis of symmetry going through the centre of the eight-membered ring.) Successive difference Fourier and full-matrix least-squares refinement calculations led to the location of all the non-H atoms of the picrate anion. The refinement converged at $R = 0·20$ and it was not possible to refine it further. It was concluded that the molecule has the correct orientation, but the wrong position. A tangent map was calculated with $E \geq 1·3$. The origins were selected manually and several multisolutions were introduced. 25 non-H atoms out of 32 were located from the tangent map with $E \geq 1·6$. Several cycles of refinement, followed by a difference synthesis, revealed

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for compound* (1)

	x	y	z	U_{eq}
N(1)	2591 (1)	5887 (3)	400 (4)	48
N(2)	1880 (1)	4770 (4)	1421 (3)	47
C(1)	2345 (2)	4551 (4)	650 (4)	40
C(2)	2205 (2)	7037 (4)	−7 (4)	41
C(3)	2357 (2)	8209 (5)	-731 (5)	55
C(4)	1955 (3)	9345 (5)	−1087 (5)	65
C(5)	1409 (3)	9381 (5)	−690 (6)	69
C(6)	1267 (2)	8271 (5)	59 (5)	65
C(7)	1663 (2)	7073 (4)	408 (4)	43
C(8)	1566 (2)	5955 (4)	1281 (4)	39
C(9)	3222 (2)	3589 (4)	2694 (4)	40
C(10)	3691 (2)	2647 (5)	3255 (5)	53
C(11)	3777 (2)	1514 (5)	2414 (5)	61
C(12)	3389 (2)	1333 (5)	1035 (6)	59
C(13)	2912 (2)	2315 (5)	477 (4)	46
C(14)	2826 (2)	3455 (4)	1296 (4)	38
C(p1)	119 (2)	4318 (4)	3274 (4)	40
C(p2)	−281 (2)	3317 (4)	3508 (4)	44
C(p3)	−87 (2)	2474 (4)	4737 (5)	49
C(p4)	490 (2)	2641 (4)	5722 (4)	46
C(p5)	877 (2)	3683 (5)	5509 (4)	38
C(p6)	737 (2)	4609 (4)	4247 (4)	39
N(pa)	−121 (2)	5196 (4)	1994 (4)	53
N(pb)	−515 (2)	1432 (4)	5014 (5)	67
N(pc)	1455 (2)	3835 (5)	6654 (4)	51
O(1)	227 (2)	5871 (5)	1521 (4)	103
O(2)	−680 (1)	5264 (4)	1436 (3)	70
O(3)	-1029 (2)	1300 (4)	4141 (4)	91
O(4)	−335 (2)	744 (4)	6149 (4)	92
O(5)	1652 (1)	2797 (4)	7433 (3)	72
O(6)	1715 (1)	5000 (4)	6818 (3)	67
O(7)	1093 (1)	5537 (3)	4039 (3)	52
HN(1)	2967 (1)	5615 (3)	171 (4)	83 (4)
H(1)	2066 (2)	4170 (4)	−332 (4)	83 (4)
H(8)	1177 (2)	5817 (4)	1431 (4)	83 (4)

all seven remaining non-H atoms. On inspection of the earlier data it was noted that the false solution is related to the correct one by a pseudo-centre of symmetry. All the H atoms were located from a difference map; for refinement the atoms H(1), H(8) and H(N1) were set in 'riding' positions on the C or N atoms and the others were placed in calculated positions with C—H = 1·08 Å (H atoms iostropic, others anisotropic), giving a final R value of 5·0% and wR = 4·9%. The data set was good and no disorder was observed either in the cation or in the anion. The positional and equivalent isotropic thermal parameters are listed in Table 3 and bond lengths and angles are shown in Fig. 1.
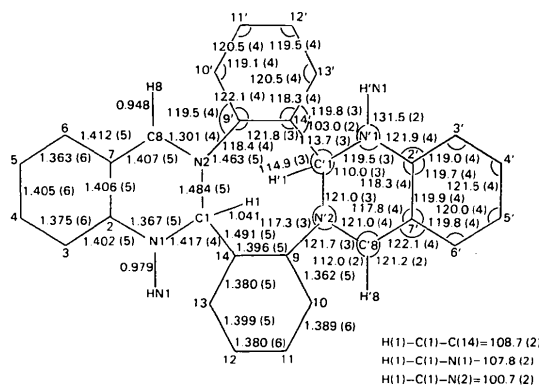
(2) Systematic absences indicated that the space group is either $Pmn2_1$ (imposing one mirror-plane symmetry on the molecule) or $Pmmn$ (imposing two mirror planes). The structure was solved using Patterson methods to locate the S atom in $Pmn2_1$. Very high correlations were observed between the coordinates of the atoms on each side of the mirror plane 2, which appears to exist (Fig. 2).

Space group $Pmmn$ with mm symmetry and statistical disorder was then examined. The asymmetric unit consists of 0·25 cations and 0·5 HSO_4 anions with the S and the two O atoms lying on the mirror plane at a special position $y = \frac{1}{4}$. Several cycles of refinement followed by difference synthesis revealed nine non-H atoms. Further cycles of refinement gave the positions of two half-oxygen atoms on the mirror plane. The refinement converged at $R = 0·09$ with all non-H atoms anisotropic. All H atoms except H(1) and H(SO_4) were located. High thermal vibrations were observed for the O atoms of the HSO_4 anion. Disorder was considered and the O atoms were resolved into two components which on refinement gave site-occupation factors of 0·5 for each of the a and b components. When all the non-H atoms were refined with anisotropic thermal parameters and all the located hydrogens included, the refinement reached $R = 0·066$. Three high-electron-density points were observed near C(1) and near the two 0·5 oxygen atoms O(2) and O(3), which were assigned as a half-hydrogen atom, H(1) near C(1), and two 0·25 H atoms, H(S2) and H(S3) near O(2) and O(3), respectively. When the statistical disorder model was considered [the N(1), N(2), C(1) and C(8) atom positions were assumed to be simultaneously occupied by 0·5 N and 0·5 C atoms], two electron-density points were observed at a distance of 1·334 and 1·510 Å from the C(1)/N(2) site. A half-hydrogen atom was assumed to be present at the distance of 1·334 Å and was included in the refinement. Finally refinement converged at $R = 0·055$ and $wR = 0·050$.

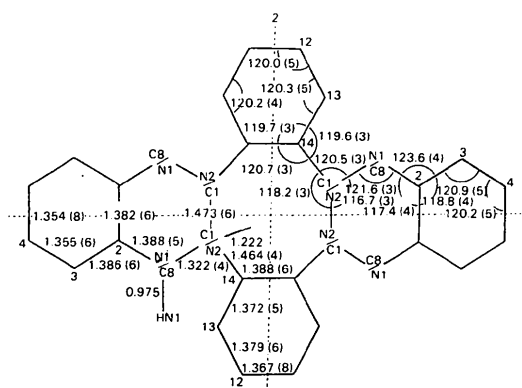The distance of 1·334 Å for the H atom at C(1)/N(2) is as expected, if we compare the

Fig. 1. Bond lengths (Å) and angles (°) for (1).

Fig. 2. Bond lengths (Å) and angles (°) for (2).

Table 4. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$ *for compound* (2)

	x	y	z	U_{eq}
N(1)/C(8)	1550 (3)	−945 (3)	5276 (4)	52
C(1)/N(2)	1974 (2)	−1164 (4)	3972 (3)	55
C(2)	2006 (2)	−301 (3)	6422 (4)	47
C(3)	1529 (4)	254 (5)	7612 (5)	78
C(4)	2017 (3)	822 (4)	8736 (5)	69
C(12)	569 (3)	−1866 (4)	515 (5)	60
C(13)	1025 (3)	−1227 (4)	1652 (5)	58
C(14)	1480 (2)	−1857 (3)	2787 (3)	43
S	989 (1)	2500	3526 (2)	49
O(1A)	399 (13)	1529 (14)	3131 (11)	105
O(1B)	459 (10)	1374 (13)	3899 (10)	79
O(2)	1609 (4)	2177 (6)	4809 (5)	70
O(3)	1621 (4)	2078 (5)	2250 (5)	71
H(1)	2057 (35)	−103 (57)	3506 (62)	50 (19)
HN(1)	880 (28)	−1185 (33)	5352 (38)	71 (12)
H(3)	897 (32)	274 (41)	7596 (46)	90 (16)
H(4)	1677 (28)	1230 (36)	9455 (43)	81 (14)
H(12)	274 (24)	−1429 (29)	−182 (38)	56 (11)
H(13)	1051 (25)	−350 (36)	1610 (38)	69 (12)
HS(2)	2116	2172	4992	50
HS(3)	2140	2076	2184	50

The calculations were performed on a DEC10 computer using the *SHELX*76 (Sheldrick, 1976) program system. Neutral-atom scattering factors were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) for the non-H and H atoms respectively.*

Discussion of structures

As (1) is ordered whilst (2) and (3) are disordered, it is most useful to discuss the structures in this order.

(1) The X-ray results show clearly that the heterocyclic skeleton (9) proposed by Skuratowicz, Madden & Busch (1977) is correct. The whole molecule can be described as having a double-saddle shape. One pair of opposite benzene rings are folded down with respect to the central eight-membered ring, and the other pair are folded up with respect to the same reference feature (Fig. 4). Hence this gives a boat conformation to the eight-membered heterocyclic ring. There is also a fold of 22° along the N(1), C(8) line (Fig. 5). The sums of the bond angles around N(1) and C(8) are 354·0 (4) and 354·2 (5)° respectively, indicating deviation of both atoms from a trigonal-planar bonding arrangement. This is in keeping with the fold along the N(1), C(8) line.

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* Lists of anisotropic thermal parameters, structure factors, data related to least-squares-plane calculations, and other geometrical data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44468 (74 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pyramidality of this site with that of the C(1) site in the ordered picrate salt (1). The C(1)/N(2) and C(1) sites are 0·175 and 0·398 Å above the plane of the three connected atoms for (2) and (1), respectively. Hence one would expect to observe the C(1)/N(2) hydrogen distance at $0·398 - 0·175 + 1·080 = 1·303$ Å. The observed value (1·334 Å) is very near to this value. The positional and equivalent isotropic thermal parameters are listed in Table 4 and bond lengths and angles are given in Fig. 2.

(3) The structure was solved by direct methods using *SHELX*76 (Sheldrick, 1976). All 21 non-H atoms of the asymmetric unit (the molecule has a diad axis of symmetry along the line passing through the centre of the eight-membered heterocyclic ring) were located from the best E map. After several cycles of least squares, disorder was observed in the BF_4 ion, which was resolved into a and b components with site occupation factors of 0·617 and 0·383 respectively. All the H atoms were located from difference Fourier maps and, except for H(1), refined freely with common temperature factors. The refinement converged at $R = 0·065$, $wR = 0·072$.

A disordered model was assumed as in (2), with the possibility of a different ratio from 1:1. The N(1), N(2), C(1) and C(8) atom positions were assumed to be simultaneously occupied by N and C atoms and the refinement gave a ratio of 0·383 to 0·617. It was postulated that the electron densities observed near C(1) and N(2) correspond to two 0·5 hydrogen atoms, H(1) and H(N2). Further cycles of least-squares calculations, with H(1) and H(N2) refined freely, led to $R = 0·053$, $wR = 0·057$. The positional and equivalent isotropic thermal parameters for the two types of refinement are listed in Table 5 and the bond lengths and angles are given in Fig. 3 (ordered model without brackets, disordered model with brackets).

Table 5. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$ *for compound* (3)

	x	y	z	U_{eq}
Ordered model				
N(1)	435 (3)	543 (6)	3859 (3)	76
N(2)	938 (3)	−636 (7)	3035 (3)	101
C(1)	490 (3)	−721 (6)	3499 (3)	65
C(2)	965 (3)	1713 (6)	4051 (3)	57
C(3)	1050 (3)	2840 (7)	4628 (4)	78
C(4)	1555 (4)	4012 (7)	4735 (4)	79
C(5)	1954 (4)	4112 (7)	4260 (4)	80
C(6)	1869 (4)	3027 (8)	3688 (4)	81
C(7)	1385 (3)	1775 (6)	3575 (3)	58
C(8)	1243 (3)	682 (6)	2978 (3)	52
C(14)	−88 (3)	−1873 (5)	3315 (3)	55
C(13)	45 (3)	−3051 (6)	3872 (3)	69
C(12)	−522 (4)	−4115 (7)	3715 (4)	82
C(11)	−1214 (4)	−4029 (8)	3018 (4)	84
C(10)	−1346 (3)	−2895 (8)	2450 (4)	78
C(9)	−793 (3)	−1809 (6)	2591 (3)	63
B	1447 (4)	1543 (9)	1036 (5)	64
F(1A)	1805 (9)	1903 (18)	563 (8)	112
F(2A)	1895 (7)	562 (13)	1622 (7)	108
F(3A)	1243 (15)	2575 (16)	1375 (13)	202
F(4A)	797 (6)	754 (22)	521 (4)	128
F(1B)	1796 (17)	2501 (41)	776 (22)	226
F(2B)	1867 (13)	1409 (52)	1860 (13)	209
F(3B)	825 (9)	2330 (30)	886 (16)	138
F(4B)	1240 (21)	347 (31)	747 (23)	242

Table 5 (cont.)

	x	y	z	U_{eq}
H(1)	1116	-1435	4039	60
H(3)	791 (31)	2808 (67)	5002 (34)	99 (6)
H(4)	1632 (32)	4816 (69)	5152 (35)	99 (6)
H(5)	2316 (33)	4980 (69)	4315 (33)	99 (6)
H(6)	2123 (34)	2816 (68)	3355 (37)	99 (6)
H(8)	1521 (32)	698 (62)	2626 (33)	99 (6)
H(13)	583 (35)	-3308 (59)	4397 (37)	99 (6)
H(12)	-429 (32)	-4924 (71)	4139 (34)	99 (6)
H(11)	-1587 (32)	-4886 (70)	2848 (33)	99 (6)
H(10)	-1896 (35)	-2803 (61)	1897 (36)	99 (6)
HN(1)	124 (33)	622 (67)	4148 (35)	99 (6)
Disordered model				
N(1)/C(8)	437 (2)	556 (5)	3868 (2)	61
N(2)/C(1)	931 (2)	-646 (6)	3033 (3)	84
C(1)/N(2)	481 (3)	-701 (5)	3496 (3)	71
C(2)	963 (2)	1703 (5)	4051 (3)	57
C(3)	1051 (3)	2844 (6)	4630 (3)	79
C(4)	1555 (4)	4008 (6)	4735 (4)	79
C(5)	1953 (3)	4109 (6)	4261 (4)	79
C(6)	1870 (3)	3027 (6)	3690 (3)	81
C(7)	1382 (2)	1780 (5)	3576 (3)	60
C(8)/N(1)	1237 (2)	671 (5)	2978 (2)	62
C(9)	-794 (2)	-1810 (5)	2589 (3)	63
C(10)	-1347 (3)	-2898 (6)	2451 (3)	77
C(11)	-1215 (3)	-4034 (6)	3016 (3)	83
C(12)	-527 (3)	-4112 (6)	3712 (3)	81
C(13)	42 (3)	-3048 (5)	3869 (3)	68
C(14)	-90 (2)	-1871 (4)	3315 (2)	57
B	1451 (3)	1547 (8)	1037 (4)	66
F(1A)	1804 (8)	1895 (14)	561 (6)	111
F(2A)	1885 (6)	542 (11)	1612 (6)	110
F(3A)	1266 (11)	2577 (13)	1396 (9)	196
F(4A)	785 (5)	779 (17)	520 (4)	135
F(1B)	1801 (15)	2519 (33)	785 (18)	225
F(2B)	1884 (10)	1364 (38)	1855 (11)	188
F(3B)	835 (7)	2377 (21)	906 (12)	125
F(4B)	1203 (14)	354 (25)	708 (15)	219
H(1)/H(N2)	988 (41)	-1148 (73)	4019 (46)	82 (22)
H(3)	818 (25)	2714 (56)	5014 (27)	96 (5)
H(4)	1638 (26)	4831 (55)	5164 (28)	96 (5)
H(5)	2297 (26)	5008 (56)	4319 (26)	96 (5)
H(6)	2094 (28)	2895 (56)	3360 (31)	96 (5)
H(8)/H(N1)	1516 (25)	681 (49)	2618 (27)	96 (5)
H(13)	571 (29)	-3193 (47)	4365 (30)	96 (5)
H(12)	-453 (26)	-4979 (58)	4089 (28)	96 (5)
H(11)	-1592 (26)	-4845 (56)	2881 (27)	96 (5)
H(10)	-1894 (28)	-2678 (51)	1892 (29)	96 (5)
HN(1)/H(8)	169 (27)	618 (56)	4118 (29)	96 (5)
HN(2)/H(1)	1554 (36)	-1041 (66)	3680 (37)	13 (16)

The bond lengths C(1)(sp^3)–N(2)(sp^2), C(9')(sp^2)–N(2)(sp^2) and C(1)(sp^3)–C(14)(sp^2) are 1·484 (5), 1·463 (5) and 1·491 (5) Å respectively; these have single-bond character. Dewar (1962) gives a value of 1·485 Å for an sp^2–sp^2 carbon–carbon bond with zero π-bond order. He also quotes a value of 1·483 Å for the central bond in butadiene. The angle between the benzo ring (2) and the segment (4) of the heterocyclic ring is 89° (Fig. 5, Table 6).

The benzo ring is thus orthogonal to the segment (4), and hence no conjugation or hyperconjugation between C(1) and C(14) is possible. A value comparable in accuracy to the above (Csp^2–Csp^2) for a pure C–C single bond between sp^3- and sp^2-hybridized C atoms is not available. The value of 1·491 (5) Å between C(1) and C(14) is not significantly longer than the value quoted by Dewar for the sp^2–sp^2 single bond.

A similar geometrical relationship holds between benzo ring (1) and segment (4). The angle is 82°, again preventing any π-bonding interaction between these two segments. The bond length of 1·463 (5) Å between N(2) and C(9') can thus be taken as an sp^2–sp^2 single bond between C and N without any π-bond character.

The bond length of 1·484 (5) Å between C(1) and N(2), which is 0·021 (7) Å longer than that between N(2) and C(9'), 1·463 (5) Å, is an eminently reasonable bond length on passing from an sp^2- to an sp^3-hybridized C atom in an otherwise analogous bond.

The N(2)–C(8) bond length of 1·301 (5) Å is in the range of a C=N double bond. The bond lengths C(8)–C(7) and C(1)–N(1) are 1·407 (5) and 1·417 (4) Å respectively. These are somewhat short for single bonds. The bond length N(1)–C(2) = 1·367 (5) Å is intermediate between that of a single and of a double C–N bond. Much of the above can be rationalized by assuming a contribution from an *ortho*-quinonoid resonance form arising from back-donation of the lone pair of electrons on N(1). This back-donation is further strengthened by the hydrogen bonding of the NH group (see end of this section). Similar structural types (Elguero, Katritzky, El-Osta,
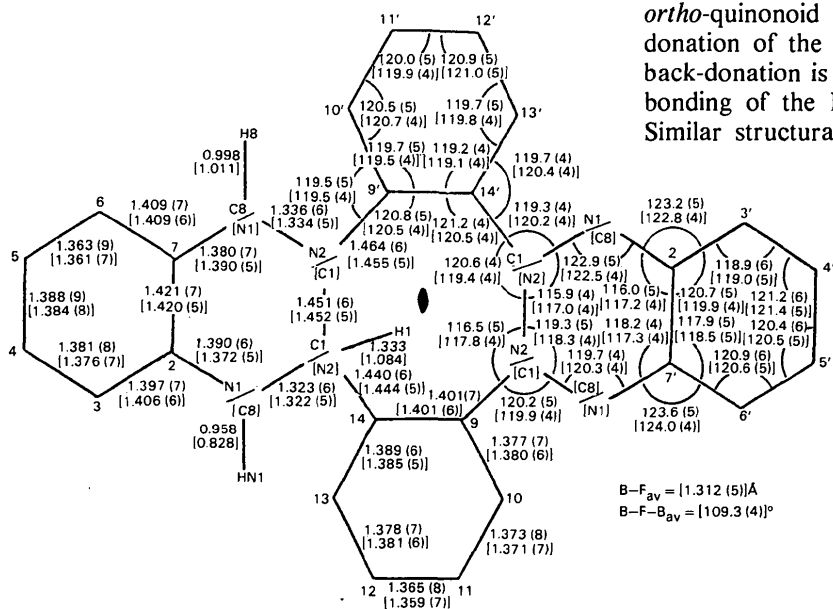
B–F$_{av}$ = [1·312 (5)]Å
B–F–B$_{av}$ = [109·3 (4)]°

Fig. 3. Bond lengths (Å) and angles (°) for (3). The complete list for the BF$_4$ ion has been deposited.

Harlow & Simonsen, 1976; Sheldrick & Trotter, 1978), where such back-donation is also possible, show similar bond lengths. Contributions from this *ortho*-quinonoid resonance form would account for the observed shortening of the N(1)—C(2) and the C(7)—C(8) bonds from values expected for single bonds. Regardless of which route this mesomeric effect takes through the benzene ring, a shortening of the bonds C(3)—C(4) and C(5)—C(6) would be expected, as observed. C(3)—C(4) and C(5)—C(6) bonds are marginally shorter than the two bonds flanking them. In the latter this shortening is just over, in the former just under, 3 e.s.d.'s.

By reasoning similar to the above, one might expect the double bond between C(8) and N(2) to be somewhat lengthened. Some C=N double bonds slightly shorter than the one observed here have been reported (Tucker, Hoekstra, Ten Cate & Vos, 1975; Ottersen, Christophersen & Treppendahl, 1975). It may well be, however, that the lengthening of a double bond caused by such a resonance contribution is rather less than the shortening of the single bonds; a given percentage change in bond character is likely to lead to greater bond-length changes in weaker rather than in stronger bonds.
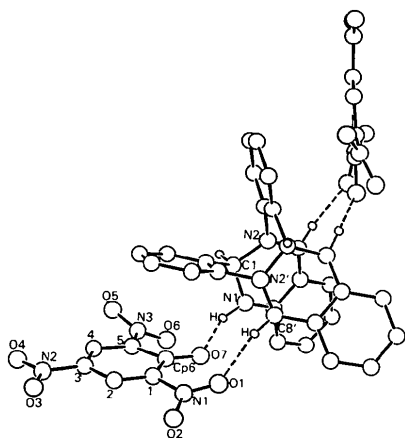

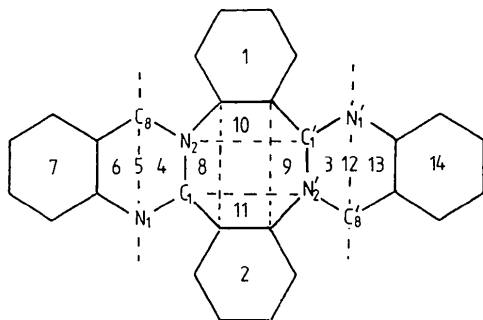Fig. 4. Molecular drawing of compound (1).

Fig. 5. Planes in the TAABH$_2$ cation. For complete numbering scheme see Fig. 1. The atoms forming each plane are lying in that plane (except planes 5 and 12).

Table 6. *Angles* (°) *between the planes in the TAAB salts*

Planes	BF$_4$	HSO$_4$	Picrate
1–2	68	65	68
3–4	27	23	16
6–13	72	69	60
4–8, 3–9	22	24	27
7–14	61	61	52
8–9	71	71	70
10–11	68	67	63
1–10	3	1	3
2–11	3	1	3
4–6	22	23	22
1–4	80	84	82
2–4	95	96	89

As the C=N length in (1) is little affected by the above-mentioned resonance, it is not surprising that the geometry around nitrogen is planar. The sum of the bond angles is 360·0 (5)°, and this atom is only 0·012 (5) Å above the plane through its three bonding partners. The sum of the bond angles around C(1), however, is 338·6 (5)° and this atom is 0·398 (5) Å above the plane of its three bonding partners.

The bond lengths and angles in the picrate ion are close to those found in other structures (Table 7). In particular the bonds C(*p*1)—C(*p*6) 1·464 (5) Å and C(*p*5)—C(*p*6) 1·461 (5) Å are longer than the other C—C bonds in the aromatic ring, with a bond angle C(*p*1)—C(*p*6)—C(*p*5) = 111·1 (3) rather than the normal 120°. Similar values are found in other picrates, and serve to distinguish the picrate ion from the picric acid molecule, where these bond lengths are near 1·400 Å and the angle 115°. Similarly, the C—O bond [1·243 (4) Å] is much shorter than in picric acid [1·327 (3) Å]. These suggest an important contribution in the ion from the canonical form (Fig. 6).

The TAABH$_2^{2+}$ ion is linked to each of its two associated picrate ions by a relatively strong hydrogen bond O(7)···H(N1)—N(1) with O···N = 2·89, O···H = 2·04 Å and ∠ O···H—N = 144° (Figs. 4 and 7). There is also a close interionic contact involving C(8) of the TAABH$_2^{2+}$ ion and one nitro group of the picrate, with O(1)···C(8′) = 3·12, O···H = 2·18 Å and ∠ O···H—C = 169°. This appears to be the shortest C—H···O hydrogen bond so far reported (Jeffrey & Maluszynska, 1982; Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Rogers, Kurihara & Richards, 1987). There is no evidence of any significant interaction between each [TAABH$_2$](picrate)$_2$ unit and its neighbours.

(2) This compound was totally insoluble in every solvent investigated (*e.g.* CHCl$_3$, CH$_3$CN, Et$_2$O, PhH). From this total insolubility (the crystals have a deep red colour, which allows the detection of even small amounts in solution), the presence of a macromolecular structure linked through intermolecular hydrogen bonding was suspected. The structure of the salt is

Table 7. *Bond lengths* (Å) *and angles* (°) *in the picrate ions and picric acid*

Compound	|C(p1)–C(p6) C(p5)–C(p6)|ₐᵥ	|C(p4)–C(p5) C(p2)–C(p1)|ₐᵥ	|C(p4)–C(p3) C(p2)–C(p3)|ₐᵥ	|C(p)–N|ₐᵥ	(N–O)ₐᵥ	C(p6)–O(7)
TAABH₂(picrate)₂	1·463 (4)	1·368 (4)	1·387 (4)	1·456 (3)	1·225 (2)	1·243 (4)
(i)	1·440 (6)	1·395 (6)	1·380 (6)	1·451 (5)	1·212 (4)	1·240 (9)
(ii)	1·464 (5)	1·365 (5)	1·390 (5)	1·454 (5)	1·223 (3)	1·234 (5)
(iiia)	1·452 (3)	1·372 (4)	1·382 (3)	1·446 (5)	1·229 (2)	1·243 (7)
(iv)	1·454 (2)	1·370 (2)	1·383 (2)	1·452 (2)	1·229 (1)	1·240 (4)
(iiib)	1·450 (3)	1·372 (4)	1·368 (3)	1·459 (3)	1·218 (2)	1·239 (6)
(v)	1·448 (5)	1·358 (6)	1·382 (6)	1·450 (4)	1·218 (3)	1·249 (7)
(via)	1·449 (3)	1·371 (3)	1·384 (3)	1·450 (3)	1·222 (2)	1·237 (4)
(vib)	1·403 (3)	1·378 (4)	1·370 (4)	1·473 (3)	1·217 (2)	1·321 (4)
(vii)	1·404 (3)	1·374 (3)	1·383 (3)	1·464 (3)	1·219 (2)	1·327 (3)

	C(p1)–C(p6)–C(p5)	|C(p4)–C(p5)–C(p6) C(p2)–C(p1)–C(p6)|ₐᵥ	|C(p3)–C(p4)–C(p5) C(p3)–C(p2)–C(p1)|ₐᵥ	C(p4)–C(p3)–C(p2)
TAABH₂(picrate)₂	111·1 (3)	124·6 (3)	119·0 (3)	121·6 (4)
(i)	113·3 (6)	123·9 (4)	117·5 (4)	123·6 (6)
(ii)	110·4 (4)	125·1 (3)	118·9 (4)	121·3 (4)
(iiia)	111·1 (5)	124·9 (3)	118·5 (3)	122·0 (5)
(iiib)	111·1	124·6	119·3	120·8
(iv)	111·5 (4)	124·2 (2)	119·1 (2)	121·9 (3)
(v)	111·6 (5)	124·4 (3)	119·3 (3)	120·9 (5)
(via)	111·2 (2)	124·7 (2)	118·9 (2)	121·3 (3)
(vib)	115·6 (3)	122·8 (2)	118·1 (2)	122·5 (3)
(vii)	115·3 (3)	123·3 (2)	118·0 (2)	122·0 (3)

(i) The ternary charge-transfer salt pyridinium 1-(naphthylamine)picrate (Bernstein, Regev & Herbstein, 1980); (ii) succinylcholine picrate (Jensen. 1975a): (iiia) potassium picrate, (iiib) ammonium picrate (Maartmann-Moe, 1969); (iv) serotonin picrate monohydrate (Thewalt & Bugg. 1972): (v) 2,2-di-(o-carboxymethoxyphenoxy)diethyl ether potassium picrate (Hughes, Mortimer & Truter, 1978); (via) 1:1 complex carbamoylcholine picrate–picric acid, (vib) picric acid (Jensen, 1975b); (vii) picric acid in anthracene–picric acid complex (Herbstein & Kaftory, 1976).
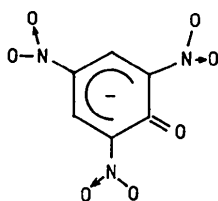

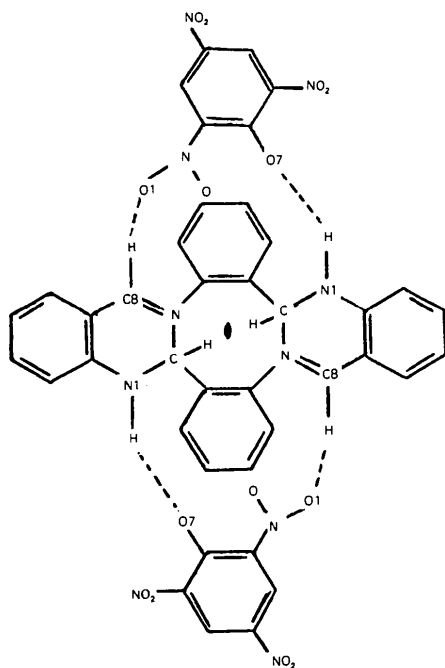Fig. 6. Canonical form of the picrate ion.

Fig. 7. Hydrogen bonding in compound (1).

shown in Fig. 8. The structure and conformation of the organic ion are virtually the same as in the picrate salt, but cannot be analysed in such detail. This is because the molecular symmetry in the bisulfate salt is *mm*, and the refinement shows 'atoms' which are at the average positions of the ions in the two orientations.

As the insolubility suggested, a macromolecular structure (infinite chains) due to intermolecular hydrogen bonding was observed (Figs. 8 and 9). Very close intermolecular distances were found between the pairs of HSO₄ ions (cyclic dimers) and between the HSO₄⁻ counter ion and the organic cation, forming three different types of hydrogen bonds.

The bond lengths found are all within ±0·02 Å of the average values calculated from the pairs of lengths in the picrate salt [the two exceptions, C(4)–C(4') and C(1)–N(1), are 0·04 and 0·05 Å respectively shorter than calculated, but the latter has a rather high e.s.d. (0·008 Å)]. Similarly, the bond angles are all within 2° of those calculated from the picrate salt [except C/N–N/C–C(14) which is 2·8° larger]. Neither the vibrational parameters nor their anisotropy are significantly greater than in the picrate. The evidence all indicates that this ion has the same structure in the two salts.

Whilst the crystallographic literature contains numerous examples of inorganic and organic chloride salts, data on corresponding HSO₄ salts are rather scarce. Examples of HSO₄ salts, mainly with inorganic cations, are given in Table 8. The O···O distances for (2), as can be seen from Table 8, are amongst the shortest so far reported for the H₂SO₄/HSO₄/SO₄ system (Ferraris & Ivaldi, 1984). Especially in cyclic
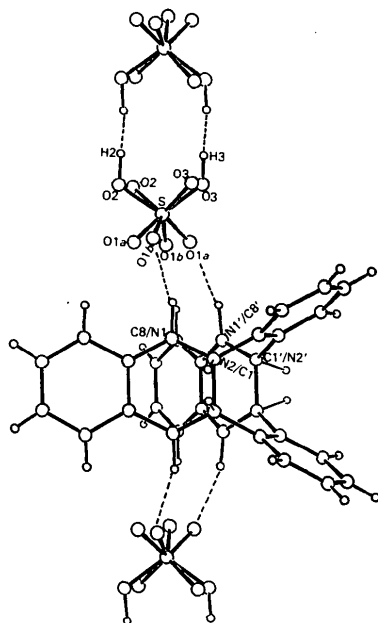
Fig. 8. Molecular drawing of compound (2) [for clarity symmetry-related hydrogen atoms of H(2) and H(3) have been omitted].
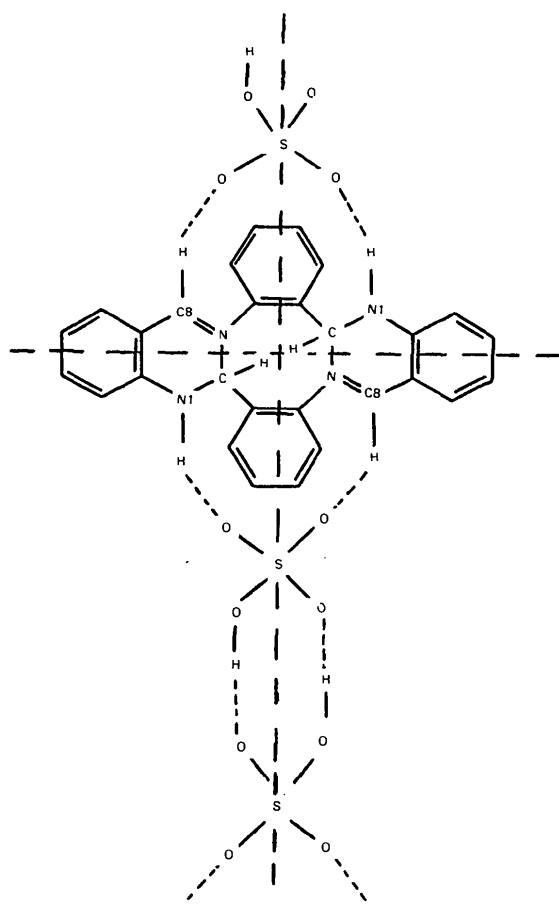

Fig. 9. Hydrogen bonding in compound (2).

dimers, *e.g.* K (Loopstra & MacGillavry, 1958; Cruickshank, 1964; Cotton, Frenz & Hunter, 1975) or β-Na (Sonneveld & Visser, 1978), the O···O distances are considerably longer, and hence the hydrogen bonds substantially weaker. Only one O···O distance shorter than the present one, namely in the acyclic dimer $Na_3H(SO_4)_2$ (Catti, Ferraris & Ivaldi, 1979), has been reported in this system.

In three of these bisulfate derivatives, N—H···O hydrogen bonding from the cation to the anion was observed (see Table 9). It can be seen that the N—H···O hydrogen bonds of the present structure belong amongst the shorter ones in the tabulated examples. The C—H···O hydrogen bonds are discussed in the final section. Hence, one can conclude that the hydrogen bonds in $TAABH_2(HSO_4)_2$ are strong, indeed stronger than most such bonds in comparable structural types.

(3) This compound was the first of this set of three to be investigated, but required the knowledge of the picrate and the bisulfate structures for a satisfactory interpretation of its data. The structure and conformation of the organic ion are almost the same as in the picrate salt with a crystallographic twofold symmetry (Fig. 3), but cannot be analysed in such detail, because of the high e.s.d.'s. The structure of the salt is shown in Fig. 10.

The bond lengths found (for both models, ordered and disordered) are all within ±0·02 Å of the average values calculated from the pairs of lengths in the picrate salt (Fig. 1). The three exceptions C(1)/[N(2)]—N(1)/[C(8)], C(1)/[N(2)]—N(2)/[C(1)] and C(1)/[N(2)]—C(14) are 0·03—0·04 Å shorter than calculated. Similarly, the bond angles are all within 3° of the ones calculated from the picrate for the disordered model, but are higher for the ordered model.

The fluorine atoms F(4a) and F(2b) point towards the N(1)/C(8) and C(8)/N(1) atom sites respectively. The distances F(4a)···N(1)/C(8) and F(2b)···C(8)/N(1) are 3·032 and 2·880 Å respectively (Figs. 10 and 11).

X-ray crystallographic investigations of N—H···F hydrogen bonds are not very numerous, but they are, on the whole, fairly accurate structure determinations. Details are given in Table 10.

A comparison of the effects of hydrogen bonding

In all three structures, unusually strong cation—anion hydrogen bonding is observed. In each, two atoms with lone pairs of electrons (O,F) approach in an acceptable geometry to the NH and to the CH groups of the cation, forming a doubly hydrogen-bridged chelated structure at each half of the cation.

CH hydrogen bonds to oxygen have been suggested for about 20 years (Sutor, 1962, 1963), although they have by no means been universally accepted. The

Table 8. *Hydrogen bonding in bisulfates*

Present structure		Type	S—OH (Å)	S—O (Å)	O—H⋯O (Å)	H⋯O (Å)	∠O—H⋯O(°)
		Cyclic dimers*	1·491 (4)av	1·420 (10)av	2·496	1·793	161·9
					2·460	1·735	173·5
H₂SO₄	(i)	Infinite two-dimensional layers	1·535	1·426	2·63		
α-NaHSO₄	(ii)	(a) Chains	1·582 (6)	1·442 (3)	2·690 (8)		
		(b) Dimers*	1·486 (6)	1·435 (6)	2·692 (8)		
			1·493 (6)	1·452 (6)	2·497 (11)		
β-NaHSO₄	(iii)	Cyclic dimers	1·58 (2)	1·46 (2)	2·67 (3)		
KHSO₄	(iv)	(a) Polymeric chain	1·564 (4)	1·448 (2)	2·630 (5)	1·907	173 (5)
		(b) Cyclic dimers	1·561 (3)	1·444 (2)	2·583 (5)	1·894	158 (7)
RbHSO₄	(v)	Two chains (a)	1·54 (2)	1·44 (1)	2·53	1·54	174
		(b)	1·58 (1)	1·43 (1)	2·62	1·59	169
NH₄HSO₄	(vi)	Two chains (a)	1·546 (3)	1·430 (1)	2·514	1·790	160
		(b)	1·557 (2)	1·440 (1)	2·598	1·920	172
NaHSO₄H₂O	(vii)	Zigzag chains	1·599	1·450	2·65		
(H₃O)HSO₄	(viii)	Zigzag chains†	1·560 (4)	1·448 (2)	2·657		
(CH₃COH₂)HSO₄	(ix)	Infinite chains‡	1·546 (4)	1·443 (2)	2·567		
[Co(NH₃)₁₀O₂]·(HSO₄)₃(SO₄)	(x)	Acyclic dimers	1·554	1·451			
Na₃(HSO₄)SO₄	(xi)	Acyclic dimers	1·527	1·474	2·434	1·40	177
(NH₄)₃(HSO₄)SO₄	(xii)	Acyclic dimers	1·518	1·450	2·540		180

(i) Pascard-Billy (1965); (ii) Sonneveld & Visser (1979); (iii) Sonneveld & Visser (1978); (iv) Loopstra & MacGillavry (1958): Cruickshank (1964); Cotton, Frenz & Hunter (1975); (v) Ashmore & Petch (1975); (vi) Nelmes (1971); (vii) Pringle & Broadbent (1965); Grimvall (1971); (viii) Taesler & Olovsson (1968); (ix) Jönsen & Olovsson (1968); (x) Schaefer & Marsh (1966); Schaefer, Ealick & Marsh (1981); (xi) Catti, Ferraris & Ivaldi (1979); (xii) Suzuki & Makita (1978).

* Hydrogen is disordered.
† Infinite zigzag chains linked by hydrogen bonds from H₃O⁺ ions to form infinite double layers.
‡ Infinite chains are connected to each other by hydrogen bonds through (CH₃COH₂)⁺ ions to form double layers.

Table 9. N—H⋯O *hydrogen bonds from the cation to the anion*

Present structure		N—H⋯O (Å)	H⋯O (Å)	∠N—H⋯O (°)
		2·943	2·000	162·1
NH₄HSO₄	(i)	3·04-3·13		
(NH₄)₃H(SO₄)₂	(ii)	2·86-3·12	2·13-2·51	116-162
Co(NH₃) complex	(iii)	2·80-3·18	1·95-2·64	92-168

(i) Nelmes (1971); (ii) Suzuki & Makita (1978); (iii) Schaefer & Marsh (1966); Schaefer, Ealick & Marsh (1981).

careful analysis of neutron diffraction data by Taylor & Kennard (1982), and by Jeffrey & Maluszynska (1982), now places their existence beyond reasonable doubt. Recently evidence for C—H⋯N (Harlow, Li & Sammes, 1984) and C—H⋯C (Ahlberg & Davidson, 1987) has also been presented.
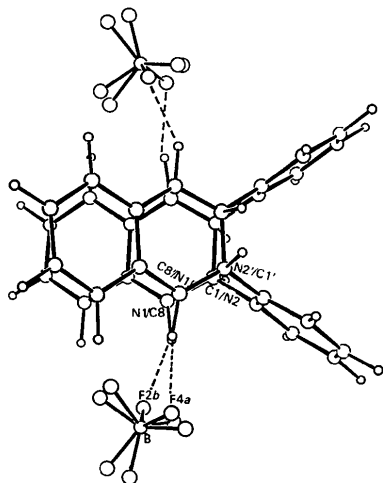
Hydrogen bonds of five types are observed either with certainty, or at least with a high degree of probability, in the three TAAB salts. These types are given in Table 11 together with their dimensions.

In the ordered picrate structure (1) the assignments of N—H⋯O and C—H⋯O contacts (2·888 and 3·119 Å respectively) are unambiguous. The phenolic oxygen atom of the picrate ion forms a strong hydrogen bond to the NH group of N(1), and another, somewhat weaker, hydrogen bond from a nitro-group oxygen, O(1), to the CH group, C(8). The structural situation,
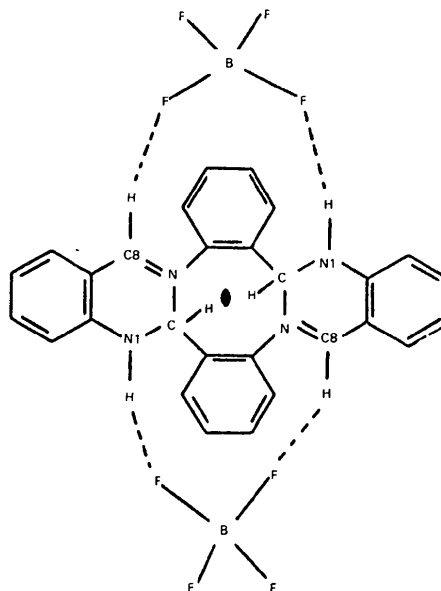

Fig. 10. Molecular drawing of compound (3).

Fig. 11. Hydrogen bonding in compound (3).

Table 10. *Examples of* N—H···F *hydrogen bonds*

Present structure		N—H···F (Å)	H···F (Å)	∠N—H···F (°)
NH_4F	(i)	2·880	1·907	160·4
NH_4HF_2	(ii)	2·707–2·709		
NH_4BF_4	(iii)	2·797–3·106		
$H_3N—BF_3$	(iv)	2·930–3·446	2·16–2·50	122·4–171·6
$(NH_4)_2SiF_6$ (cubic)	(v)	2·98–3·15		
$(NH_4)_2BeF_4$	(vi)	2·996	2·075	155
$(NH_4)_3VF_4O$	(vii)	2·785–3·094	1·93–2·51	122–171
$(NH_4)_2Ni(BeF_4)_2.6H_2O$	(viii)	2·825–3·196		
$N_2H_6F_2$	(ix)	2·777–3·022		
$N_2H_6SiF_6$	(x)	2·62		
$N_2H_6TiF_6$	(xi)	2·714–2·945	1·881–2·299	122·2–169·3
$N_2H_6ZrF_6$	(xii)	2·612–3·070		
$(N_2H_6)_2F_2(TiF_6)$	(xiii)	2·62–2·85		
		2·568–2·765		

(i) Morosin (1970); (ii) McDonald (1960); (iii) Caron & Ragle (1971); (iv) Hoard, Geller & Cashin (1951); (v) Schlemper, Hamilton & Rush (1966); (vi) Garg & Srivastava (1979); (vii) Bukovec & Golic (1980); (viii) Montgomery (1980); (ix) Kronberg & Harker (1942); (x) Frlec, Gantar, Golic & Leban (1980); (xi) Kojić-Prodić, Matkovic & Scavnicar (1971); (xii) Kojić-Prodić, Scavnicar & Matkovic (1971); (xiii) Golic, Kaucic & Kojić-Prodić (1980).

Table 11. *Hydrogen bonds in TAAB salts*

Type of H bond	Anion of TAAB salt	X—H···Y (Å)	H···Y (Å)	∠X—H···Y (°)
O—H···O	HSO_4	2·460	1·735	173·5
		2·496	1·793	161·9
N—H···O	Picrate	2·888	2·039	143·8
	HSO_4	2·943	2·000	162·1
N—H···F	BF_4	2·880	1·907	160·4
C—H···O	Picrate	3·119	2·183	168·9
	HSO_4	3·137	2·272	151·9
C—H···F	BF_4	3·032	2·222	166·0

with a doubly-bonded nitrogen atom carrying a positive charge next to the CH group in question, makes this, according to Taylor & Kennard's (1982) analysis, a particularly favourable situation. This is borne out by the fact that the CH hydrogen bond reported here (3·119 Å) is the shortest on record and the C—H···O bond angle (168·9°) is the largest.

In the HSO_4 salt (2), disorder is observed in the cation as well as in the anion, and we effectively see the average of the CH/NH sites. Two distinct contacts for C/N—H···O in the HSO_4 salt (2·943 and 3·137 Å) were observed, and their assignment by analogy to that of the picrate is quite simple as the values are close in these two salts. The distances and the geometries of the approach of the HSO_4 oxygen atoms indicate strong bonding (Fig. 9).

In the BF_4 salt (3), as in (2), disorder is observed in the anion, and is assumed in the cation. The F atoms approach within a reasonable distance and geometry to the disordered NH/CH sites (Fig. 11). Two distinct contacts for C/N—H···F (2·880 and 3·032 Å) were observed. As N—H···O bonds are generally stronger, and therefore shorter, than otherwise similar C—H···O bonds, it seems likely that a similar relationship applies also to N—H···F and C—H···F bonds, and the assignments of the longer and the shorter distances for the BF_4 salt were made on this assumption. The two experimentally observed values are, however, close to each other. The shorter one (2·880 Å) comes close to

reported N—H···F hydrogen-bond values (Table 10). Whilst a number of N—H···F hydrogen bonds have previously been observed, the present structure may well represent the first example of a C—H···F hydrogen bond. The geometry is eminently reasonable, and as the C—H···O hydrogen bond in the picrate salt is the shortest one (3·119 Å) reported by X-ray crystallography with a large C—H···O angle of 168·9°, and hydrogen bonding is also strong in the bisulfate salt (Fig. 6), the structural situation seems very suitable for a chelated pair of hydrogen bonds in these salts. The argument is strengthened by recent observations of C—H···Cl hydrogen bonds (Jeffrey & Maluszynska, 1982; Taylor & Kennard, 1982). Most, but not all, of these are to Cl^- ions. In the BF_4 ion each F atom would have only a quarter negative charge. As fluorine is, however, much more prone to hydrogen bonding than chlorine, and as the BF_4 ion has been observed to hydrogen bond in NH_4BF_4 (Caron & Ragle, 1971), the postulate of a C—H···F hydrogen bond in the BF_4 salt seems plausible.

All three counter ions have a unit negative charge. In the picrate this will be largely localized on the phenolic oxygen atom, whilst in the HSO_4 and BF_4 ions it will be distributed over three or four equivalent sites respectively, and thus the net charge density will be lower than that on the phenolic oxygen atom on the picrate ion. As NH hydrogen bonds are much stronger than CH hydrogen bonds, it may well be that some change in bond length associated with the mean of the C(8)—N(2) and N(1)—C(1) bond lengths is related to the strength of the hydrogen bond of the NH group. According to the arguments developed above, the hydrogen bond from the phenolic O atom should be the strongest. The greater the strength of this bond the greater the possibility of mesomeric release of electrons, which will ultimately affect the C(8)—N(2) bond length. It will be shown in a later paper which deals with the condensation products of anthranilic acid that an N bonded to H is more effective in such a mesomeric effect than one which is only bonded to C atoms.

We have argued that the electron release will tend to reduce the double-bond character of this bond and hence increase its length. If, as we suggest, the HSO_4 and BF_4 ions form weaker hydrogen bonds to the NH group, the mesomeric effect will be reduced, the C(8)—N(2) bond will have more double-bond character and therefore will be shortened. As both structures are disordered the overall effect will be a shortening of the average C(8)—N(2) and N(1)—C(1) bonds. The average bond lengths and angles for the three structures are shown in Fig. 12.

On comparison of bond lengths, the same trends are apparent in all three structures. Only one significant difference in bond length is observed: the C(8)—N(2) and C(1)—N(1) mean bond length in the HSO_4 salt is significantly shorter than the corresponding mean bond

length in the picrate, suggesting, as argued above, a somewhat greater double-bond character for the C(8)—N(2) bond. Although statistically not significant, a trend, similar to that observed in the HSO₄ salt, can be seen in the BF₄ salt.

The bond angles around the bridgehead C/N sites are significantly larger for the HSO₄ and BF₄ salts than in the picrate salt. The mean sums of the bond angles per C/N bridgehead site are 355·4 (5), 356·2 (5) and 349·3 (4)° respectively for the HSO₄, BF₄ and picrate salts. As the N atom is planar in the picrate, the above data suggest a somewhat more flattened C atom in the HSO₄ and BF₄ salts than in the picrate.

The TAABH₂ cation lacks mirror symmetry. Both enantiomers are present in the crystal. In the picrate salt these occur in an ordered array as the phenolic O atom shows a preference to hydrogen bond to the N—H site. Therefore the nitro-group O atom has to bond at the C—H site. In the HSO₄ and BF₄ salts both electron-donor sites are equivalent, and therefore hydrogen bonding does not favour the ordered over the disordered cation arrangement. Bilirubin (Bonnett, Davies,

Hursthouse & Sheldrick, 1978), a neutral hydrogen-bonded molecule, also gives rise to a disordered structure owing to the two enantiomers' occupation of each other's sites.

The picrate ion is the only one where the atoms with the lone pairs involved in the hydrogen bonding are not equivalent. This structure is ordered. In the other two salts, the HSO₄ and BF₄, the two lone-pair donor sites are equivalent and these structures are disordered. Equivalence of lone-pair donor sites applies also for $X = CF_3SO_3$ and, here too, disorder was observed (Skuratowicz, Madden & Busch, 1977).

Fig. 12. Comparison of the averaged bond lengths (Å) and angles (°) in the three TAAB salts.

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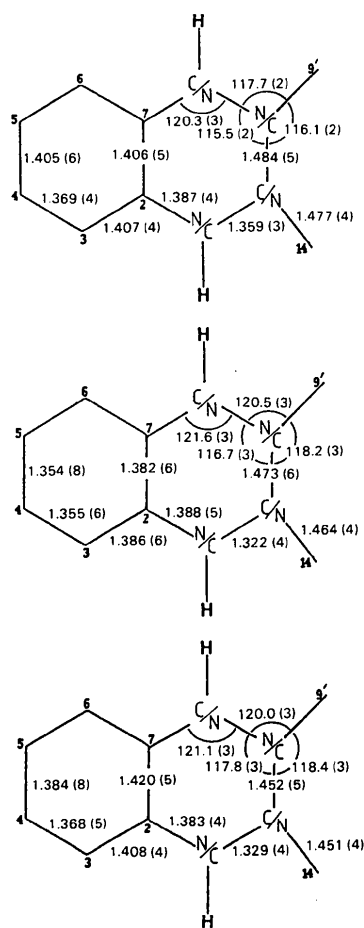JENSEN, B. (1975b). *Acta Chem. Scand. Ser. B*, **29**, 891–903.

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Experimental Electron Density Distribution of (1R*,2S*,3R*,4R*)-3,4-Epoxy-1,2,3,4-tetrahydro-1,2-naphthalenediol

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Abstract

Careful X-ray diffraction measurements at 100 K have been used to map the electron density distribution in a single crystal of *trans*-3,4-epoxy-1,2,3,4-tetrahydro-1,2-naphthalenediol, a small-molecule model for the ultimate carcinogenic metabolites of some polycyclic aromatic hydrocarbons. A least-squares-refinement procedure has been used in which additional multipole parameters are added to describe the distortions of the atomic electron distributions as a result of covalent bonding. The refinement also yields improved estimates of the X-ray phases, which have been used to plot maps of the electron distribution. In the epoxide ring, one C atom is found to be more positive than the other, suggesting that it would be the preferred site of attack by nucleophiles such as DNA bases, in agreement with other experimental evidence. Covalent-bond peaks lie outside the lines joining the atom centers of the epoxide ring, and lone-pair density on the epoxide O atom corresponds to largely unhybridized s and p orbitals. Crystal data: $C_{10}H_{10}O_3$, $M_r = 178.0$, space group $Pna2_1$, $a = 7.979$ (2), $b = 8.634$ (3), $c = 23.560$ (5) Å, $V = 1623.1$ (8) Å^3, $Z = 8$, $D_x = 1.46$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.70930$ Å, $\mu = 1.16$ cm^{-1}, $F(000) = 752$, $T = 105$ K, $R = 0.058$ for 2575 observed reflections for the multipole refinement.

Introduction

Many polycyclic aromatic hydrocarbons, such as benzo[*a*]pyrene, are known to be common environmental pollutants and potent chemical carcinogens. Several