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The Ammonium Salt of 5-Nitrobarbituric Acid, $NH_4^+.C_4H_2N_3O_5^-$

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Abstract. $M_r = 190{\cdot}12$, triclinic, $P\bar{1}$, $a = 4{\cdot}9184\,(4)$, $b = 7{\cdot}6947\,(5)$, $c = 9{\cdot}8195\,(6)$ Å, $\alpha = 104{\cdot}911\,(5)$, $\beta = 92{\cdot}666\,(6)$, $\gamma = 105{\cdot}085\,(6)°$, $V = 344{\cdot}2\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}83\,(1)$, $D_x = 1{\cdot}835\,(1)$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}164$ mm^{-1}, $F(000) = 196$, $T = 295$ K. $R = 0{\cdot}038$ for 1596 unique observed reflections. The anion is nearly planar with only small deviations from mirror symmetry related to a mirror plane perpendicular to the molecular plane. Formation of the NH_4^+ salt of 5-nitrobarbituric acid (dilituric acid) does not increase the delocalization of π-electron density to the nitro group. The crystal structure is stabilized by intermolecular hydrogen bonds involving all the H atoms.

Introduction. The structure determination of the ammonium salt of 5-nitrobarbituric acid is part of a study of structural changes associated with the steps in the series: compounds, nitro compound, anion of nitro compound. The present structure determination was thus performed to study structural changes connected with 5-nitrobarbituric acid salt formation.

Experimental. Dilituric acid prepared as described by Hartman & Sheppard (1943). Colourless crystals (prisms) of the ammonium salt were obtained by slow cooling of a solution in boiling water (1·0 g ammonium salt needs 200 ml of boiling water). D_m by flotation in CH_2BrCl/CCl_4.

Crystal: 0·1 × 0·2 × 0·3 mm, Enraf–Nonius CAD-4*F* diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from setting angles for 25 reflections with $7{\cdot}79 < \theta < 13{\cdot}52°$. 1996 unique reflections (h 0→6, k $\overline{10}$→9, l $\overline{13}$→13) with $2{\cdot}0 < \theta < 30{\cdot}0°$, 1596 with $I > 2{\cdot}5\sigma(I)$ used in refinement process together with 'less-than' reflections [$I < 2{\cdot}5\sigma(I)$] with calculated values greater than the observed (1864 contributing reflections). Mixed $\omega/2\theta$ scan technique, scan angle = 1·40° + 0·35° tan θ. Standard reflections 10$\bar{4}$, 022 and 031 used for orientation control every 100 reflections, 03$\bar{3}$ used for intensity check every 10800 s of exposure time, standard intensity variations < 2·3% of mean value. Lp correction, absorption ignored; direct methods, full-matrix least-squares refinement of anisotropic non-H atoms. Positional H parameters from $\Delta\rho$ map (remaining peak heights less than half those associated with H atoms). Refinements of H(x,y,z) with $\sin\theta/\lambda < 0{\cdot}40$ Å^{-1}, fixed isotropic H temperature factor. $\sum w(\Delta|F|)^2$ minimized, final $R = 0{\cdot}038$, $wR = 0{\cdot}074$,* weights $w = 1/\{1 + [(F_o - 6{\cdot}0)/8{\cdot}0]^2\}$ gave average $w\Delta(|F|)^2$ almost independent of $|F_o|$, $S = 2{\cdot}34$. Ratio of maximum least-squares shift to error in final refinement cycle = 0·0018. Minimum and maximum in final $\Delta\rho$ map: −0·4 and 0·4 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs from *SHELX*76 (Sheldrick, 1976) and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The positional and thermal parameters are given in Table 1.

Discussion. The atoms in the anion show only small deviations from a least-squares plane defined by all the non-H atoms (except ammonium N). The deviations are within 0·03 (3) Å for endocyclic atoms and 0·05 (3) Å for exocyclic atoms. The anion does not

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and $NH_4^+\cdots O$ distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42231 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates* (× 10^4) *and equivalent isotropic thermal parameters of non*-H *atoms with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	$B_{\rm eq}$(Å^2)
O(2)	−4284 (3)	3236 (2)	5735 (1)	2·66 (8)
O(4)	−1688 (3)	4734 (2)	1752 (1)	2·64 (8)
O(6)	1190 (3)	−12 (2)	3287 (1)	2·95 (8)
O(51)	2973 (3)	874 (2)	996 (1)	2·83 (8)
O(52)	1735 (3)	3052 (2)	355 (1)	3·18 (9)
N(1)	−1578 (3)	1618 (2)	4443 (1)	2·17 (8)
N(3)	−2895 (3)	3936 (2)	3719 (1)	1·90 (7)
N(5)	1636 (3)	2057 (2)	1185 (1)	1·77 (7)
N(7)	3697 (3)	7353 (2)	1422 (1)	2·42 (9)
C(2)	−2999 (3)	2940 (2)	4686 (1)	1·75 (8)
C(4)	−1488 (3)	3720 (2)	2509 (1)	1·68 (8)
C(5)	39 (3)	2321 (2)	2333 (1)	1·63 (8)
C(6)	−4 (3)	1222 (2)	3318 (1)	1·73 (8)

Table 2. *Bond distances and some bond angles in dilituric acid and its ammonium salt; e.s.d.'s in parentheses*

Bond (Å)/Angle (°)	Dilituric acid	Ammonium salt of dilituric acid
N(1)–C(2)	1·366 (5)	1·356 (2)
C(2)–N(3)	1·361 (5)	1·358 (2)
N(3)–C(4)	1·348 (5)	1·396 (2)
C(4)–C(5)	1·408 (5)	1·445 (2)
C(5)–C(6)	1·452 (5)	1·435 (2)
C(6)–N(1)	1·382 (5)	1·393 (2)
C(4)–O(4)	1·302 (5)	1·225 (2)
C(6)–O(6)	1·223 (5)	1·234 (2)
C(5)–N(5)	1·406 (5)	1·404 (2)
N(5)–O(51)	1·222 (5)	1·236 (2)
N(5)–O(52)	1·259 (5)	1·246 (2)
C(5)–N(5)–O(51)	120·7 (3)	121·2 (2)
C(5)–N(5)–O(52)	119·4 (3)	119·2 (2)
O(51)–N(5)–O(52)	120·0 (3)	119·6 (2)

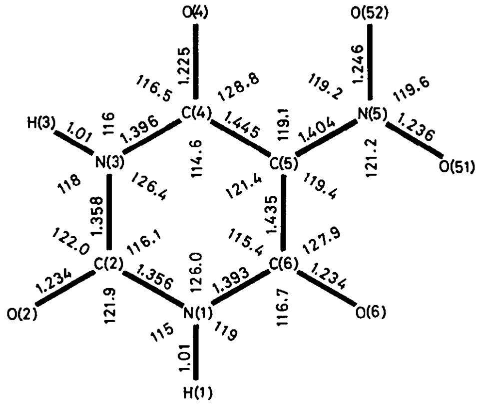
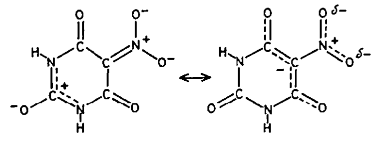


Fig. 1. Bond distances (Å), angles (°), and the atom-numbering scheme for the anion of 5-nitrobarbituric acid. The e.s.d.'s are 0·002 Å and 0·2° when no H atoms are involved, otherwise 0·04 Å and 2°.

deviate much from non-crystallographic mirror symmetry related to a mirror plane through O(2), C(2), C(5), N(5) and normal to the molecular plane. A comparison between corresponding 'mirror-related' bonds in the anion shows no significant difference in bond length between [N(1)–C(2), C(2)–N(3)] and [N(1)–C(6), N(3)–C(4)] (Fig. 1). The three pairs of corresponding bonds [C(4)–O(4), C(6)–O(6)], [C(4)–C(5), C(5)–C(6)] and [N(5)–O(51), N(5)–O(52)] have a bond-length difference of 0·010 Å which is probably significant. The difference between related angles involving non-H atoms is less than 1·0 (3)°, except for C(5)–N(5)–O(51) = 121·2 (2)° and C(5)–N(5)–O(52) = 119·2 (2)°.

Differences between corresponding bonds in dilituric acid (Bolton, 1963) and its ammonium salt are quoted in Table 2; as expected, release of a proton from O(4) has the greatest effect on the nearest bonds, C(4)–O(4), N(3)–C(4) and C(4)–C(5). Apparently, a redistribution of π-electron density occurs so that the geometry of the anion approaches mirror symmetry.



Unexpectedly, salt formation does not change the bond C(5)–N(5) (Table 2). The sum of the N–O distances is also unchanged. N(5)–O(51) + N(5)–O(52) has the values 2·482 (3) and 2·481 (7) Å for the ammonium salt and dilituric acid respectively. Thus,

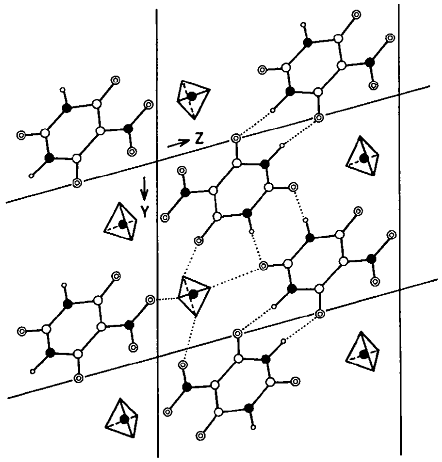


Fig. 2. Projection of the crystal structure down the x axis. Black circles: N atoms, double circles: O atoms. Ammonium ions are symbolized by tetrahedra. The dotted lines represent the hydrogen-bonding system. Some of the symmetry-related hydrogen bonds are omitted for clarity. Only the four shortest $NH_4^+\cdots O$ hydrogen bonds are drawn.

there is no change in π-electron delocalization to the nitro group by salt formation. This is a difference from the related compounds nitromalonamide (Simonsen & Thorup, 1979) and its ammonium salt (Simonsen, 1981) where the C—NO_2 distances are 1·397 (4) and 1·327 (4) Å respectively.

The anions are connected in infinite chains by pairs of N—H···O hydrogen bonds grouped around centres of symmetry (Fig. 2). These hydrogen bonds may contribute to the low solubility of the title compound (0·072 g in 100 ml H_2O, 296 K). The N···O distances involved range from 2·825 (2) to 2·831 (2) Å. The distances from the ammonium N atom to the surrounding O atoms range from 2·935 (2) to 3·068 (2) Å.

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2,4-Bis(dimethylamino)-6-phenyl-1,3,5-thiadiazinium Tetraphenylborate, $C_{13}H_{17}N_4S^+.C_{24}H_{20}B^-$

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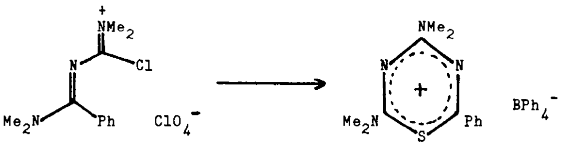
Abstract. $M_r = 580·6$, monoclinic, $P2_1/a$, $a = 26·076$ (13), $b = 9·517$ (5), $c = 13·046$ (7) Å, $\beta = 102·11$ (2)°, $V = 3165·5$ (29) Å^3, $Z = 4$, $D_x = 1·218$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 1·125$ mm^{-1}, $F(000) = 1232$, $T = 293$ (1) K, final $R = 0·057$ for 3899 significant reflections. In the almost planar 1,3,5-thiadiazinium moiety the endocyclic bond lengths indicate delocalization of electron density over the atomic centres, C(2), N(3), C(4), together with the exocyclic N atoms of the dimethylamino substituents [average C—N distance = 1·321 (9) Å], and a double bond of length 1·281 (4) Å between N(5) and C(6). The geometry of the tetraphenylborate anion is normal and there are no non-bonded contacts less than the sum of the respective van der Waals radii.

Introduction. We recently reported that 1-chloro-1,3-bis(dimethylamino)-3-phenyl-2-azapropenylium perchlorate (I) reacted with potassium thiocyanate, followed by sodium tetraphenylborate, to yield the rearranged 1,3,5-thiadiazinium salt (II), whose structure was confirmed by X-ray analysis (Boyd, Lindley & Nicolaou, 1984). Since, to our knowledge this is the first determination of the structure of a 1,3,5-thiadiazinium salt, we present in this paper details of our work.



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