

Fig. 1. Perspective view of the cation.

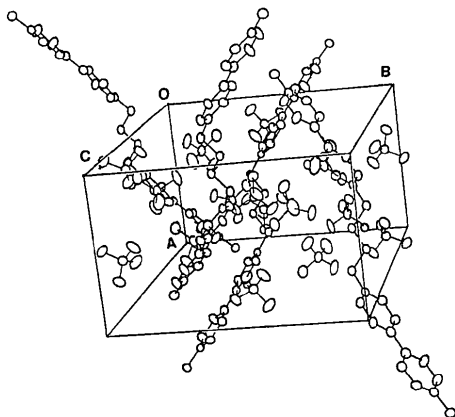


Fig. 2. Unit-cell packing diagram.

Related literature. The photoreduction behaviour and radical reaction of the title compound have been reported by Yu & Wang (1985) and Atherton, Tsukahara & Wilkins (1986). Crystal structure analysis of related compounds: *N,N'*-dimethyl-4,4'-bipyridinium tetrachlorocuprate (Russell & Wallwork, 1969); *N,N'*-dimethyl-4,4'-bipyridinium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide (Nakamura, Kai, Yasuoka & Kasai, 1981).

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Structures of 1,2-Ethanediammonium Dinitrate (1) and 1,3-Propanediammonium Dinitrate (2)

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Abstract. (1): $C_2H_{10}N_2^{2+} \cdot 2NO_3^-$, $M_r = 186.1$, triclinic, $P\bar{1}$, $a = 5.068$ (1), $b = 5.514$ (4), $c = 7.185$ (3) Å, $\alpha = 105.03$ (3), $\beta = 90.16$ (3), $\gamma = 93.58$ (4)°, $V = 193.5$ (2) Å³, $Z = 1$, $D_x = 1.597$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.15$ mm⁻¹, $F(000) = 98$, $T = 295$ K, final $R = 0.057$, $wR = 0.057$ for 379 independent observed reflections. (2): $C_3H_{12}N_2^{2+} \cdot 2NO_3^-$, $M_r = 200.2$, monoclinic, Cc , $a = 8.161$ (1), $b = 8.724$ (2), $c = 13.048$ (2) Å, $\beta = 95.86$ (1)°, $V = 924.2$ (2) Å³, $Z = 4$, $D_x = 1.439$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 0.12$ mm⁻¹, $F(000) = 424$, $T = 295$ K, final $R = 0.041$, $wR = 0.053$ for 649 independent observed reflections. In (1) there is an inversion center midway between the two C atoms, and only half of the dication and one nitrate are crystallographically unique. In both (1) and (2) the dications are in a

trans configuration and there is extensive intermolecular hydrogen bonding present, with each of the diammonium H atoms participating in moderate to weak hydrogen bonds.

Experimental. Colorless 0.12 × 0.23 × 0.34 mm (1) and 0.23 × 0.35 × 0.45 mm (2) data crystals were provided by Dr Robert McKenney of Air Force Armament Laboratory, Eglin AFB, FL. Hereafter, values for (2) where different will be given in square brackets []. Automated Siemens *R3m/V* diffractometer with incident-beam monochromator. 25 centered reflections within $18 \leq 2\theta \leq 28^\circ$ [$36 \leq 2\theta \leq 56^\circ$] used for determining lattice parameters. $(\sin\theta/\lambda)_{\max} = 0.54$ [0.55] Å⁻¹, range of hkl : $-5 \leq h \leq 2$, $-5 \leq k \leq 5$, $-7 \leq l \leq 7$ [$0 \leq h \leq 8$, $0 \leq k \leq 9$, $-13 \leq l \leq 13$].

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
(1)				
N(1)	4601 (9)	8215 (8)	7388 (6)	37 (2)
C(1)	4920 (12)	8623 (8)	9493 (7)	39 (2)
N(2)	616 (8)	2814 (7)	6988 (5)	39 (2)
O(2a)	3001 (6)	3031 (5)	6520 (5)	41 (1)
O(2b)	-214 (7)	755 (6)	7246 (5)	54 (1)
O(2c)	-758 (8)	4568 (8)	7251 (7)	82 (2)
(2)				
N(1)	342	1002 (5)	9381	58 (1)
C(1)	1072 (9)	2436 (6)	9040 (5)	59 (1)
C(2)	-39 (9)	2987 (6)	8105 (5)	60 (1)
C(3)	649 (9)	4465 (6)	7695 (5)	66 (2)
N(2)	-333 (8)	4909 (5)	6724 (5)	54 (1)
N(3)	758 (8)	8652 (4)	7220 (4)	53 (1)
O(3a)	1212 (8)	7860 (4)	6519 (4)	63 (1)
O(3b)	1479 (8)	9903 (4)	7430 (5)	75 (1)
O(3c)	-339 (8)	8242 (6)	7736 (5)	87 (2)
N(4)	1655 (8)	-2531 (4)	10196 (4)	54 (1)
O(4a)	2618 (7)	-1480 (4)	10033 (4)	63 (1)
O(4b)	2130 (8)	-3889 (4)	10158 (5)	83 (2)
O(4c)	240 (8)	-2252 (5)	10396 (5)	80 (1)

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and hydrogen-bond parameters ($\text{\AA}, ^\circ$)

(1)				
N(1)—C(1)	1.477 (7)	C(1)—C(1a)	1.502 (8)	
N(2)—O(2a)	1.263 (5)	N(2)—O(2b)	1.245 (6)	
N(2)—O(2c)	1.203 (6)			
(2)				
N(1)—C(1)	1.474 (7)	C(1)—C(2)	1.520 (9)	
C(2)—C(3)	1.525 (8)	C(3)—N(2)	1.479 (9)	
N(3)—O(3a)	1.233 (7)	N(3)—O(3b)	1.257 (6)	
N(3)—O(3c)	1.228 (9)	N(4)—O(4a)	1.240 (7)	
N(4)—O(4b)	1.249 (6)	N(4)—O(4c)	1.234 (9)	
(1)				
N(1)—C(1)—C(1a)	111.2 (5)	O(2a)—N(2)—O(2b)	117.4 (4)	
O(2a)—N(2)—O(2c)	120.9 (4)	O(2b)—N(2)—O(2c)	121.6 (4)	
(2)				
N(1)—C(1)—C(2)	106.5 (5)	C(1)—C(2)—C(3)	109.8 (5)	
C(2)—C(3)—N(2)	109.6 (5)	C(3a)—N(3)—O(3b)	118.6 (6)	
O(3a)—N(3)—O(3c)	122.3 (5)	O(3b)—N(3)—O(3c)	119.0 (6)	
O(4a)—N(4)—O(4b)	119.3 (6)	O(4a)—N(4)—O(4c)	120.9 (5)	
O(4b)—N(4)—O(4c)	119.8 (5)			
(1)				
N—H	N...O	H...O	N—H...O	
(1)				
N(1)—H(1a)...O(2b)(1+x, 1+y, z)	0.91 (6)	2.915 (6)	2.11 (6)	147 (3)
N(1)—H(1a)...O(2a)(1-x, 1-y, 1-z)	0.91 (6)	2.993 (6)	2.41 (7)	122 (3)
N(1)—H(1b)...O(2a)(x, 1+y, z)	0.76 (6)	3.037 (6)	2.33 (7)	155 (4)
N(1)—H(1b)...O(2b)(x, 1+y, z)	0.76 (6)	2.903 (6)	2.23 (7)	148 (3)
N(1)—H(1c)...O(2a)(x, y, z)	0.95 (5)	2.828 (5)	1.91 (6)	161 (4)
(2)				
N(1)—H(1N1)...O(3b)(x, y-1, z)	0.84 (7)	2.957 (8)	2.22 (8)	148 (5)
N(1)—H(2N1)...O(4a)(x, y, z)	0.76 (6)	2.922 (8)	2.37 (7)	131 (5)
N(1)—H(3N1)...O(4b)(x-0.5, y+0.5, z)	0.86 (7)	2.907 (8)	2.06 (8)	169 (5)
N(2)—H(1N2)...O(3b)(x-0.5, y-0.5, z)	0.85 (8)	2.847 (8)	2.02 (9)	165 (5)
N(2)—H(2N2)...O(4c)(x, -y, z-1)	0.85 (7)	2.960 (8)	2.15 (8)	160 (4)
N(2)—H(3N2)...O(3a)(x, y, z)	0.81 (7)	2.891 (8)	2.10 (8)	163 (4)

Standards 003, 11 $\bar{1}$, 200 [400, 040, 008] monitored every 60 reflections with random variation of 2.4 [2.2]% over data collection, $\theta/2\theta$ scan mode, scan width $[2\theta(K\alpha_1) - 1.0]$ to $[2\theta(K\alpha_2) + 1.0]^\circ$, ω scan rate a function of count rate ($3.0^\circ \text{ min}^{-1}$ minimum, $15.0^\circ \text{ min}^{-1}$ maximum), 576 [709] reflections meas-

ured, 487 [651] \dagger unique, $R_{int} = 3.4$ [\dagger]%, 379 [649] observed with $F_o > 3\sigma(F_o)$. Data corrected for Lorentz and polarization effects, but not for absorption. The structure solution was by direct methods, and the full-matrix least-squares refinement used programs in *SHELXTL* (Sheldrick, 1980). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(F_o) + g(F_o)^2]$, $g = 0.0003$. Secondary-extinction parameter $p = 0.025$ (8) [0.112 (9)] in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin^2\theta]^{0.25}$. There were 71 [135] parameters refined: atomic coordinates and anisotropic thermal parameters for all non-H atoms, methylene H in (2) included using riding model, C—H distance set to 0.96 \AA , H angles idealized, and $U_{iso}(H)$ set to $1.1 \times U_{eq}(C)$. All other H coordinates refined with fixed thermal parameters. $(\Delta/\sigma)_{max} = 0.2$ [0.8], ratio of observations to parameters 5.4:1 [4.8:1], $R = 0.057$, $wR = 0.057$, $S = 1.60$. $R = 0.075$ for all data [$R = 0.041$, $wR = 0.054$, $S = 1.97$, $R = 0.041$ for all data]. Final difference Fourier excursions 0.22 and -0.25 [0.31 and -0.22] $e \text{\AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). \ddagger Atom numbering for Table 1, atom coordinates, and Table 2, bond distances and angles, follows that shown in Figs. 1. and 2.

Related literature. Information on the synthesis, thermal stability and impact sensitivity of the title compounds and other polyammonium nitrate salts has

\dagger Friedel opposites not merged.

\ddagger Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54424 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

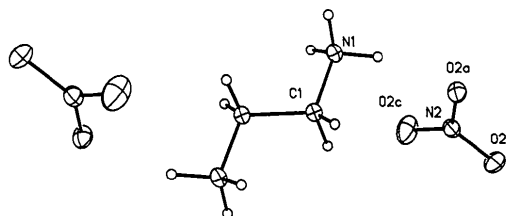


Fig. 1. A thermal ellipsoid plot of 1,2-ethanediammonium dinitrate with ellipsoids drawn at the 20% probability level.

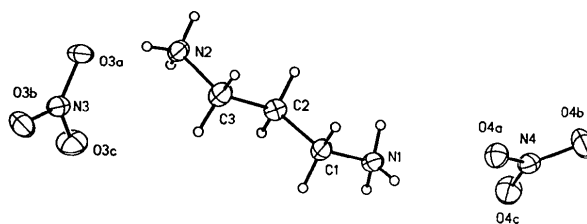


Fig. 2. A thermal ellipsoid plot of 1,3-propanediammonium dinitrate with ellipsoids drawn at the 20% probability level.

been reported (McKenney, Struck, Hildreth & Fryling, 1987). The structure of the next compound in this series, 1,4-butanediammonium dinitrate has also been reported (Jaskólski & Olovsson, 1989).

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Monoclinic Triphenylphosphine Oxide Hemihydrate

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Abstract. $C_{18}H_{15}OP \cdot \frac{1}{2}H_2O$, $M_r = 287.30$, monoclinic, $C2/c$, $a = 19.423$ (5), $b = 8.478$ (5), $c = 18.327$ (5) Å, $\beta = 90.67$ (2)°, $V = 3017.7$ (9) Å³, $Z = 8$, $D_x = 1.265$ g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 15.746$ cm⁻¹, $F(000) = 1208$, $T = 223$ K, $R = 0.050$ for 1734 reflections with $I > 3\sigma(I)$. The water O atoms sit on a crystallographic twofold axis and are linked by hydrogen bonds to two of the oxide molecules with O...O \cdots O \cdots O distances of 2.910 (3) Å and an O...H—O angle of 172.5 (4)°. The torsion angles between the plane of a phenyl ring and the plane generated by the atoms O, P and the *ipso* C atom in the corresponding ring are 66.21, 27.69 and 11.61° for rings C1—C6, C7—C12 and C13—C18, respectively.

Experimental. A crystal of the title compound was obtained from an attempted co-crystallization with an *N,N'*-unsymmetrically disubstituted urea. The crystal measured 0.70 × 0.20 × 0.08 mm and was mounted on a glass fiber using an epoxy resin. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters and their e.s.d.'s were derived from the setting angles of 25 reflections ($30 < 2\theta < 35^\circ$). The space group was unambiguously determined from the systematic absences ($hkl: h + k = 2n; h0l: h, l = 2n$). 3014 reflections ($2 < 2\theta < 135^\circ$; $0 < h < 23$, $0 < k < 10$, $-21 < l < 21$) were collected using variable speed ω - 2θ scans. Three reflections ($\bar{8}47, 9\bar{3}7, 6, \bar{2}, \bar{1}1$) showed only random variation in intensities over 42.5 h of exposure time. Data were

corrected for Lorentz and polarization effects. Symmetry equivalent data were averaged, $R_{int} = 0.044$. The structure was solved *via* direct methods using the program *SHELXS86* (Sheldrick, 1985). The refinement was carried out using full-matrix least squares on F employing 1734 reflections with $I > 3\sigma(I)$. Unless otherwise noted, all programs were from a locally modified version of the *SDP* (Frenz, 1979) software. H atoms were found in a difference Fourier map and were refined with fixed thermal parameters equal to 1.3 times their non-H-atom counterparts. An empirical absorption correction was applied using *DIFABS* (Walker & Stuart, 1983) with a θ dependent correction. The min. correction was 0.672 and the max. correction was 1.452. The average correction was 1.009. No extinction correction was applied. Convergence with anisotropic thermal parameters for the non-H atoms and fixed isotropic thermal parameters for the H atoms was achieved at $R = 0.050$, $wR = 0.065$, $w = 1/\sigma^2(F)$ with $\sigma^2(F)$ given by the expression $[\sigma^2(I_c) + (0.05F)^2]$, 1734 reflections, 234 variables, $S = 1.574$, $(\Delta/\sigma)_{max} = 0.03$. A final difference Fourier map showed no features outside the range ± 0.25 e Å⁻³. Values of the neutral-atom scattering factors were taken from Cromer (1974). Atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table.† Bond lengths and angles are given in Table 2. Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the molecule.

† Lists of structure factors, anisotropic thermal parameters, least-squares planes, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54130 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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