

$[\sum(\Delta/\sigma)^2]$  values are 5.9, 1.6 and 12.0, respectively. The dihedral angle between the pyridine and phenyl rings is  $9.4 (9)^\circ$ ; between the pyridine ring and plane 3 it is  $10.7 (9)^\circ$ . Similar values were also observed in *N*-salicylidene-3-aminopyridine [2-(3-pyridylimino-methyl)phenol] (Moustakali-Mavridis, Hadjoudis & Mavridis, 1980), where the corresponding dihedral angles were  $14.8$  and  $14.2^\circ$  respectively.

The deformation of the molecule can be seen from the torsion angles  $C(1)-C(7)-N(1)-C(8) = 178.0 (8)$ ,  $C(7)-N(1)-C(8)-C(9) = 167.6 (9)$  and  $C(7)-N(1)-C(8)-N(2) = -11.4 (13)^\circ$ . The latter two values show that the pyridine ring is rotated by  $\sim 12^\circ$  about  $N(1)-C(8)$  relative to the rest of the molecule, as observed in *N*-salicylidene-3-aminopyridine. In the latter case, H(7) and the corresponding H of the C atom that substitutes N(2) are located at a distance less than the van der Waals radii. This fact was used to explain the observed deformation, since steric hindrance was supposed to exist. However, in the present compound N(2) is *cis* to H(7) and there is no possibility for  $H \cdots H$  steric hindrance. Since some authors claim that there is a relation between the photochromic properties of a compound and its planarity (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978), studies of these properties will be undertaken in this case.

Fig. 2 shows the projection of the structure onto the  $xz$  plane, revealing some of the shortest intermolecular distances. These indicate that the packing in the crystal is due only to van der Waals interactions.

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## Structure Refinement of 1,2,3-Triaminoguanidinium Chloride, $CH_5N_6^+Cl^-$

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**Abstract.**  $M_r = 140.57$ ,  $P6_3/m$ ,  $a = 7.480 (1)$ ,  $c = 6.218 (1) \text{ \AA}$ ,  $V = 301.3 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_m = 1.550$ ,  $D_x = 1.549 \text{ Mg m}^{-3}$ ,  $Cu K\alpha$ ,  $\lambda = 1.54184 \text{ \AA}$ ,  $\mu = 4.92 \text{ mm}^{-1}$ ,  $F(000) = 148$ ,  $T = 296 (1) \text{ K}$ ,  $R = 0.049$ , 280 unique

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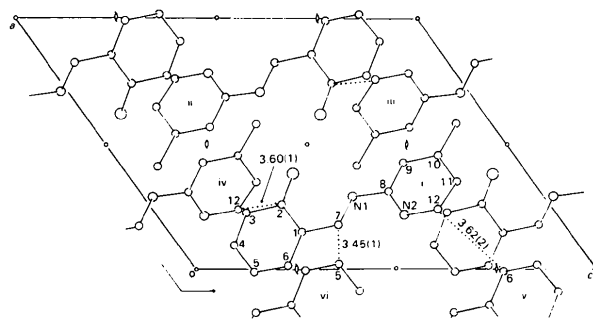


Fig. 2. Structure as viewed along the  $b$  axis. The shortest intermolecular distances ( $\text{\AA}$ ) are shown. Symmetry code: (i)  $x, y, z$ ; (ii)  $-x, -y, -z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (v)  $x, 1-y, 1-z$ ; (vi)  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ .

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reflections. The crystal structure consists of layers of ions parallel to (001) at  $\pm \frac{1}{4}c$ . Each  $Cl^-$  anion is hydrogen bonded to three triaminoguanidinium cations within each layer. Only the guanidinium H atoms form

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hydrogen bonds with the  $\text{Cl}^-$  ions. The distance  $\text{N}(1)-\text{Cl}$  is 3.158 (3) Å. The C–N and N–N bond lengths are 1.325 (2) and 1.411 (4) Å, respectively.

**Introduction.** In an X-ray diffraction structure determination of hexagonal triaminoguanidinium chloride (TAGCl) using limited two-dimensional data, Okaya & Pepinsky (1957) reported unit-cell dimensions of  $a = 7.528$  and  $c = 6.253$  Å, and C–N and N–N bond lengths of 1.318 (9) and 1.450 (14) Å, respectively. In a structure determination of orthorhombic triaminoguanidinium nitrate (TAGN), Bracuti (1979), utilizing three-dimensional diffraction data, reported C–N bond lengths of 1.324 (6), 1.324 (6) and 1.318 (5) Å [mean value 1.322 (6) Å], and significantly shorter N–N bond lengths of 1.415 (6), 1.407 (5) and 1.397 (5) Å [mean value 1.406 (5) Å]. In a neutron diffraction crystal structure refinement of TAGN, Choi & Prince (1979) reported longer C–N bond lengths of 1.332 (3), 1.324 (4), and 1.336 (4) Å [mean value 1.331 (4) Å], and significantly shorter N–N bond lengths of 1.411 (9), 1.401 (5), and 1.396 (4) Å [mean value 1.403 (6) Å].

In view of the disagreement in the reported N–N bond lengths and the large standard deviations in bond lengths reported by Okaya & Pepinsky, a refinement of the TAGCl crystal structure utilizing three-dimensional data was undertaken.

**Experimental.** TAGCl recrystallized from water, colorless prismatic crystal (0.15 × 0.15 × 0.20 mm) mounted on a glass fiber with its long axis approximately coaxial with the  $\varphi$  axis of the goniometer. Enraf–Nonius CAD-4 computer-controlled  $\kappa$ -axis diffractometer equipped with a graphite-crystal incident-beam monochromator. Lattice parameters obtained using 20 reflections in the range of  $18^\circ < \theta < 24^\circ$ . Intensity data (upper limit  $150^\circ 2\theta$ ) collected with the  $\omega$ - $\theta$  scan technique on 302 reflections. 19 reflections rejected as unobserved [ $F \leq 2\sigma(F)$ ;  $\sigma(F)$  from counting statistics]. Three representative reflections measured every 25 min in order to check the crystal and electronic stability of the system yielded constant intensities within experimental error. Data corrected for Lorentz and polarization effects, no correction for absorption. Scattering factors from Cromer & Liberman (1970). Non-hydrogen-atom positions for the trial structure taken from the Okaya & Pepinsky (1957) TAGCl structure; H-atom positions from the TAGN structure determination (Bracuti, 1979). Anisotropic refinement carried out with the full-matrix least-squares program *FLINUS*, a modification of *ORFLS* (Busing, Martin & Levy, 1962).  $\sum w(|F_o| - |F_c|)^2$  minimized;  $w = 1/\sigma^2(F)$ . A secondary-extinction function,  $g = 1.370 \times 10^{-5}$ , was also refined (Coppens & Hamilton, 1970) with the mean free path length,  $T$ , treated as a constant. Refinement of 19 variable parameters con-

verged with a largest parameter shift of 0.009 times its e.s.d.;  $R = 0.049$ ,  $R_w = 0.074$ ,  $S = 2.44$  (261 observations, and 19 parameters varied).

**Discussion.** The atomic coordinates and thermal parameters are presented in Table 1;\* the TAG cation and relevant bond lengths and angles are presented in Fig. 1; the crystal structure is shown in Fig. 2.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38695 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors and their standard deviations

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}$ (Å <sup>2</sup> )
C	0.0	0.0	0.25	2.89 (1)
N(1)	0.1864 (4)	0.1660 (4)	0.25	3.16 (9)
N(2)	0.2035 (5)	0.3626 (5)	0.25	3.86 (4)
H(1)	0.291 (7)	0.150 (6)	0.25	4 (1)
H(2)	0.261 (6)	0.405 (5)	0.362 (4)	4.8 (7)
Cl	0.6667	0.3333	0.25	3.51 (6)

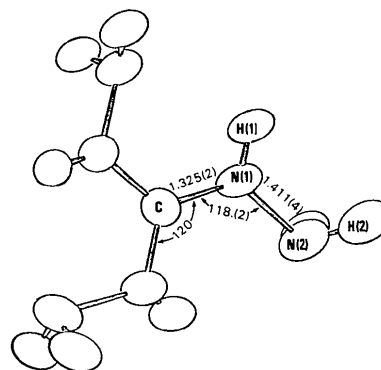


Fig. 1. Triaminoguanidinium ions with relevant bond lengths (Å) and bond angles ( $^\circ$ ).

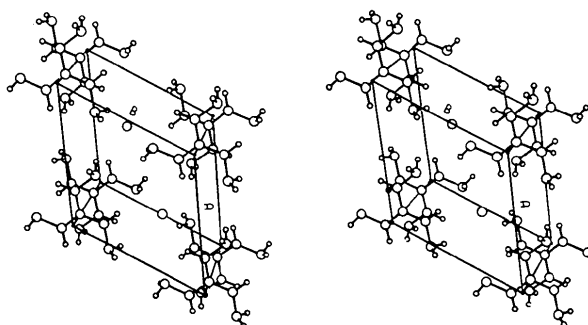


Fig. 2. Stereoscopic pair showing the TAGCl structure as viewed down the  $c$  axis.

With the exception of the six amino H atoms, all atoms in this structure lie in two parallel mirror planes at  $\pm \frac{1}{4}c$ . The planar TAG cations are stacked directly over one another in adjacent layers 3.109 (1) Å apart; the Cl<sup>-</sup> anions are stacked in alternate layers 6.218 (1) Å apart. The closest interionic contacts between layers occur among the amino groups of the TAG cations and the Cl<sup>-</sup> ions. The distance between the amino N atom and a Cl<sup>-</sup> ion N(2)—Cl is 3.684 (2) Å. Although this interatomic distance is shorter than the 3.692 Å reported by Okaya & Pepinsky (1957), it is still larger than would be observed if hydrogen bonding were involved. In view of this, only van der Waals and Coulombic forces operate between adjacent layers of ions.

Within any layer, each Cl<sup>-</sup> ion is surrounded by three TAG cations and is hydrogen bonded to three nearest-neighbor guanidinium N atoms with N(1)—Cl 3.158 (3) Å. Each Cl<sup>-</sup> also has three nearest-neighbor amino groups with N atoms [N(2)—Cl] at a distance of 3.579 (3) Å as compared to 3.596 Å reported by Okaya & Pepinsky (1957).

The TAG cation (Fig. 1) displays  $C_{3h}$  symmetry with a C—N(1) bond length of 1.325 (2) Å and an

N(1)—N(2) bond length of 1.411 (4) Å which agree with the mean bond lengths of 1.322 (6) and 1.406 (5) Å observed in TAGN for C—N(1) and N(1)—N(2), respectively.

The X-ray diffraction data presented in this paper were obtained by the Molecular Structure Corp., College Station, Texas, under Contract DAAG29-76-D-0100.

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## Structure of the Ammonium Salt of *cis*-4-Methyl-2-oxido-1,3,2-dioxaphosphorinane 2-Sulphide, NH<sub>4</sub><sup>+</sup>.C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>PS<sup>-</sup>

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**Abstract.**  $M_r = 185.2$ , orthorhombic, *Pccn*,  $a = 18.154$  (6),  $b = 13.973$  (6),  $c = 7.047$  (1) Å,  $U = 1787.6$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.38$  Mg m<sup>-3</sup>, *Mo Kα*,  $\lambda = 0.71069$  Å,  $\mu = 0.439$  cm<sup>-1</sup>,  $F(000) = 784$ ,  $T = 295$  K,  $R = 0.054$ ,  $R_w = 0.051$ , for 906 observed reflections. The structure comprises discrete C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>PS<sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions bonded by N—H...O hydrogen bonds into dimers around the twofold axis.

**Introduction.** The title compound was synthesized by Mikołajczyk & Łuczak (1972) during their systematic studies of geometric isomerism in cyclic five- and six-membered phosphorus monothioacid derivatives, occurring when the molecule contains at least one

asymmetric centre at a ring carbon atom. The chemical background of this class of compounds has been described elsewhere (Bartczak, 1983). The present investigation was undertaken, as part of our systematic studies on the conformation and crystal chemistry of the 1,3,2-dioxaphosphorinane ring, to determine the localization of the negative charge in the molecule, *i.e.* whether the NH<sub>4</sub><sup>+</sup> ion is linked to the sulphur or to the oxygen atom.

**Experimental.** Sample kindly supplied by Professor M. Mikołajczyk of the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź. Good colourless crystals grown from *n*-propanol–*n*-hexane 1:1 mixture by slow evaporation; preliminary Weissenberg and oscillation photographs

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