Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond geometry* (Å, °)

O(1)—C(9)	1.276 (1)	C(2)—C(3)	1.369 (3)
O(2)—C(9)	1.248 (1)	C(3)—C(4)	1.399 (2)
O(3)—N(1)	1.225 (1)	C(4)—C(5)	1.387 (2)
O(4)—N(1)	1.212 (1)	C(4)—C(7)	1.465 (1)
N(1)—C(1)	1.467 (1)	C(5)—C(6)	1.381 (2)
C(1)—C(2)	1.375 (2)	C(7)—C(8)	1.321 (2)
C(1)—C(6)	1.374 (1)	C(8)—C(9)	1.457 (2)
O(1)—C(9)—O(2)	122.8 (1)	C(1)—C(6)—C(5)	118.5 (1)
O(1)—C(9)—C(8)	116.0 (1)	C(2)—C(3)—C(4)	120.9 (2)
O(2)—C(9)—C(8)	121.2 (1)	C(2)—C(1)—C(6)	122.2 (1)
O(3)—N(1)—O(4)	124.0 (1)	C(3)—C(4)—C(5)	118.6 (1)
O(3)—N(1)—C(1)	117.6 (1)	C(3)—C(4)—C(7)	121.9 (1)
O(4)—N(1)—C(1)	118.4 (1)	C(4)—C(5)—C(6)	121.0 (2)
N(1)—C(1)—C(2)	118.6 (1)	C(4)—C(7)—C(8)	126.1 (1)
N(1)—C(1)—C(6)	119.2 (1)	C(5)—C(4)—C(7)	119.5 (1)
C(1)—C(2)—C(3)	118.8 (2)	C(7)—C(8)—C(9)	123.6 (2)

D	A	$D\cdots A$	$\mathrm{H}\cdots A$	D—H$\cdots A$
O(1)	O(2$^{\mathrm{i}}$)	2.641 (1)	1.62 (3)	174 (3)

Symmetry code: (i) $1 - x, 3 - y, -z$.

D_m was measured by flotation in aqueous KI. The scan width was $(1.2+0.15\tan\theta)^\circ$ in ω with a scan rate of 4° min^{-1} in ω and background counts for 4 s on each side of every scan. Refinement was by block-diagonal least-squares methods. Data collection and cell refinement: Rigaku AFC-5 software. Data reduction: *NTDATAIN* (Tanaka, 1979). Program used to solve structure: *RSSFR*-5 (Sakurai, 1967). Program used to refine structure: *HBLS*-V (Ashida, 1973). Software used to prepare material for publication: *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979), *ORTEP*II (Johnson, 1971). Computations were carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55748 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1006]

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2-Amino-5-nitropyridinium Monohydrogenphosphite

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Abstract

The crystal structure of this new 2-amino-5-nitropyridinium salt consists of centrosymmetric double layers built up with $C_5H_6N_3O_2^+$ cations and $H_2PO_3^-$ phosphite anions. The main feature of this stacking is the presence of centrosymmetric $(H_4P_2O_6)^{2-}$ clusters holding both layers together through relatively strong hydrogen bonds. Weaker hydrogen bonds maintain the cohesion of the organic–inorganic arrangement within a layer. Direct bonding exists neither between the organic entities, nor between the double layers. The dimension charge compromise of the anionic group is not favourable for inducing a polar packing of cations which would be necessary to originate nonlinear optical properties.

Comment

The design of organic–inorganic polar crystals for quadratic nonlinear optical applications is today oriented and supported by two main observations: (i) the organic molecules containing π-electron systems asymmetrized by electron donor–acceptor groups are highly polarizable entities in which problems of transparency and crystal growth may arise from their molecular crystal packing; (ii) the ionic inorganic host-matrices are able to increase the cohesion of packing, to shift the transparency of organic entities towards blue wavelengths and to originate the acentricity of packing. This approach has been applied to the 2-amino-5-nitropyridinium cation encapsulated in various anionic inorganic subnetworks (Masse, Bagieu-Beucher, Pécaut, Levy & Zyss, 1992).

The attempt using $(H_2PO_4^-)_n$, $(H_2AsO_4^-)_n$ polymeric anions has been successful with the crystalliza-

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tion of 2-amino-5-nitropyridinium dihydrogenmonophosphate (2A5NPDP) and 2-amino-5-nitropyridinium dihydrogenmonoarsenate (2A5NPAs) (Masse & Zyss, 1991). All the associations of 2-amino-5-nitropyridinium cations with various inorganic anions aim at evidencing a possible shielding effect of the inorganic entities which would induce at request an acentric packing of optically nonlinear cations. The title compound has been prepared in order to study this eventual interaction with the phosphite anion. Table 1 reports the final atomic coordinates.

The structure can be described as mixed layers built up with 2A5NP$^+$ organic cations, and $H_2PO_3^-$ phosphite anions, spreading parallel to the *bc* plane and separated by about 3.45 Å. Fig. 1 shows a view of the organic cations packing (phosphite anions have been removed for clarity). Two adjacent layers related by the centre of symmetry (4*d*) are bridged *via* short hydrogen bonds joining two $H_2PO_3^-$ anions. This special arrangement forms a centrosymmetric stacking of 2A5NP$^+$ cations and $(H_4P_2O_6)^{2-}$ groups. There are two such double layers related by the centre of symmetry (4*a*) in the unit cell.

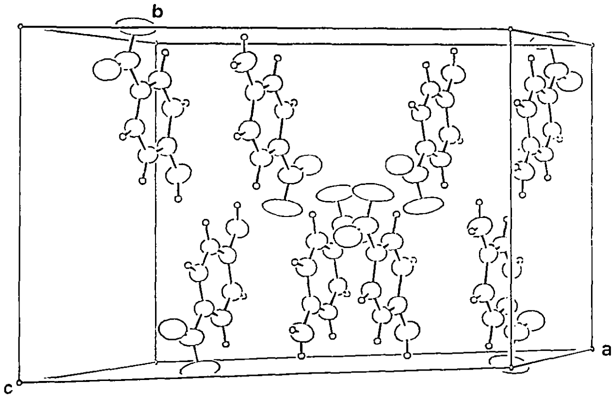

Fig. 1. The centrosymmetric arrangement of the 2-amino-5-nitropyridinium cations.

The monohydrogenphosphite anion consists of a P atom surrounded by two O atoms, O(12) and O(13), one H atom H(1) and one OH group O(11)—H(2), in a tetrahedral configuration described in Table 2. In this structure, O(11) acts only as an H-atom donor; O(12) and O(13) act as H-atom acceptors. These different roles can explain the significant differences between the P—O distances in the $(HPO_3H)^-$ tetrahedron. Indeed the P—O (H-atom acceptor) bonds are substantially shorter [1.490 (2) Å] than the P—OH (H-atom donor) bonds [1.547 (1) Å]. Otherwise all the distances and angles, P—O, P—H, O—P—O, O—P—H and P—O—H, are in accordance with the recent literature data relative to the monohydrogenphosphite domain (Loub, 1991). The outstanding feature of this structure is the linkage of each $H_2PO_3^-$ tetrahedron to an equivalent one by inversion symmetry (site 4*d*) through two relatively strong hydrogen bonds between O(11) and O(13) atoms. This type of aggregation can be considered as a cluster of formula $(H_4P_2O_6)^{2-}$ according to the short distances O(11)···O(13) of 2.563 (2) Å between the $H_2PO_3^-$ units comparable to the O—O distances in the tetrahedral unit. The internal distance P—P is 4.1599 (7) Å. The presence of such a centrosymmetric 'dimer' (with P—P = 4.212 Å and O···O = 2.560 Å) has been noticed by Altenburg & Mootz (1971) in the crystal structure of $KH_2PO_3.HF$. 2A5NP$^+$.$H_2PO_3^-$ is the second example in the monohydrogenphosphite domain studied so far. It is interesting to note that $H_2PO_3^-$ may also aggregate several $H_2PO_3^-$ units and form larger anionic groups as $(H_6P_3O_9)^{3-}$ in $La(H_2PO_3)_3.H_2O$ (Tijani, Durand & Cot, 1988), $(H_8P_4O_{12})^{4-}$ in $Ca(H_2PO_3)_2.H_2O$ (Larbot, Durand & Cot, 1984) and most frequently infinite chains $(H_2PO_3^-)_n$ as in KH_2PO_3 (Kratochvíl, Podlahová & Hašek, 1983).

In the 2A5NP$^+$ cation, the pyridine ring atoms are almost coplanar, but the exocyclic atoms of the amino and nitro group are significantly displaced from the mean plane (Table 3). The twist angle of the nitro group out of the pyridine ring is 7 (1)°. As observed in other structures of 2A5NP$^+$ salts the C—NH_2 distance [1.308 (3) Å] is shortened with respect to the *p*-nitroaniline one (Colapietro, Domenicano, Marciante & Portalone, 1982) [1.355 (2) Å], whereas the C—NO_2 distance [1.443 (3) Å] is lengthened [1.434 (2) Å]. The shortening of all the conjugated bonds except C—NO_2 observed in the pyridine ring is due to the proton capture and indicates that the NH$^+$ behaves as an electron-acceptor group in addition to the NO_2 end group. The NO_2 and NH$^+$ electron-withdrawing groups award a bidimensional character to the charge transfer which is consequently reflected in quadratic microscopic tensorial susceptibilities. An acentric packing of such organic cations can induce efficient macroscopic quadratic nonlinear optical susceptibilities.

Within a layer, each 2A5NP$^+$ cation is involved in three hydrogen bonds from the N atoms to the O atoms of two $H_2PO_3^-$ anions: N(1)—H(7)···O(13) and N(3)—H(3)···O(12) approximately parallel to **b** and N(1)—H(8)···O(12) approximately parallel to **c**. Within a double layer, the $(H_4P_2O_6)^{2-}$ clusters maintain the cohesion of the organic stacking by their two hydrogen bonds O(11)—H(2)···O(13) parallel to **a** (Table 3). Fig. 2 gives a detailed view of this hydrogen-bond scheme. Furthermore, there is no direct bonding between the organic entities and between the double layers. The shortest distances between non-H atoms of two cationic rings are: C(1)···C(1) = 3.404, N(1)···N(3) = 3.451 and O(22)···O(22) = 3.476 Å.

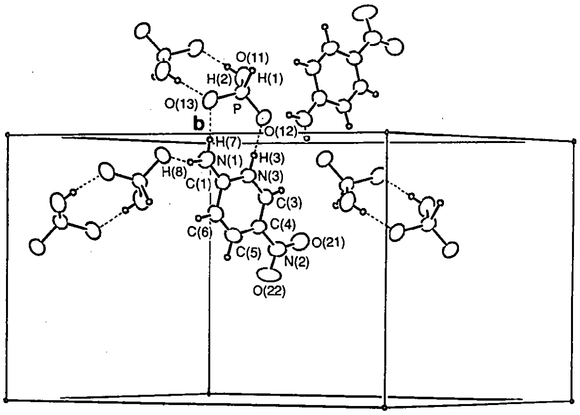

Fig. 2. A detailed view of the $(H_4P_2O_6)^{2-}$ clusters and the $2A5NP^+$ cations with their labelling scheme and the hydrogen bonds indicated by dotted lines.

By the examination of this structural arrangement (Fig. 1), it is evident that the organic cations are disposed with an antiparallel ordering within a layer and between layers. The charge and the volume (150 Å^3) of the $(H_4P_2O_6)^{2-}$ groups are similar to those of a $CuCl_4^{2-}$ anion. As in bis(2-amino-5-nitropyridinium) tetrachlorocuprate (Bagieu-Beucher, Masse & Tran Qui, 1991) the dimension charge compromise of the anionic group is not favourable for preventing the dipole–dipole interactions between two $2A5NP^+$ cations and for inducing a polar packing. As has been shown in 2A5NPDP (Masse & Zyss, 1991) with the $(H_2PO_4^-)_n$ polyanion, a layered arrangement of the anions *via* hydrogen bonds is much more favourable to such a packing.

Experimental

Crystal data

$C_5H_6N_3O_2^+.H_2O_3P^-$
M_r = 221.11
Monoclinic
$C2/c$
a = 16.861 (7) Å
b = 11.539 (3) Å
c = 11.146 (5) Å
β = 125.08 (3)°
V = 1775 (3) Å^3
Z = 8

D_x = 1.655 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 8–15°
μ = 0.321 mm^{-1}
T = 293 K
Prism
0.96 × 0.52 × 0.40 mm
Yellow

Data collection

Nicolet XRD diffractometer
ω scans
Absorption correction: none
5685 measured reflections
2890 independent reflections
2604 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.022

θ_{max} = 30°
$h = -24 \rightarrow 24$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 500 reflections
intensity variation: 5%

Refinement

Refinement on F
Final R = 0.040
wR = 0.042
S = 0.489
2085 reflections
159 parameters
H-atom parameters refined
w = 1

$(\Delta/\sigma)_{max}$ = 0.05
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

B_{iso} for H atoms; $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	B_{iso}/B_{eq}
P	0.37234 (3)	0.17623 (4)	0.52856 (4)	3.154 (8)
O(11)	0.29727 (8)	0.2424 (1)	0.3862 (1)	4.54 (3)
O(12)	0.41052 (8)	0.0793 (1)	0.4870 (1)	4.01 (3)
O(13)	0.33234 (8)	0.1424 (1)	0.6129 (1)	4.08 (3)
H(1)	0.439 (1)	0.253 (2)	0.602 (2)	2.1 (5)
H(2)	0.260 (2)	0.281 (2)	0.393 (2)	3.2 (6)
C(1)	0.3771 (1)	0.8299 (2)	0.6306 (2)	3.14 (3)
C(3)	0.3917 (1)	0.7774 (2)	0.4397 (2)	3.12 (3)
C(4)	0.3858 (1)	0.6638 (2)	0.4638 (2)	3.47 (4)
C(5)	0.3763 (1)	0.6294 (2)	0.5752 (2)	3.97 (4)
C(6)	0.3722 (1)	0.7111 (2)	0.6576 (2)	3.69 (4)
N(1)	0.3727 (1)	0.9139 (2)	0.7053 (1)	4.18 (4)
N(2)	0.3896 (1)	0.5786 (2)	0.3725 (2)	4.87 (4)
N(3)	0.38717 (9)	0.8573 (1)	0.5223 (1)	3.01 (3)
O(21)	0.4068 (1)	0.6092 (2)	0.2867 (1)	5.72 (4)
O(22)	0.3753 (2)	0.4787 (2)	0.3884 (2)	9.83 (6)

Table 2. *Main interatomic distances* (Å) *and angles* (°)

The H_2PO_3 tetrahedron

P	O(11)	O(12)	O(13)	H(1)
O(11)	1.547 (1)	107.27 (8)	112.09 (8)	102.1 (9)
O(12)	2.447 (2)	1.491 (2)	115.58 (9)	110 (1)
O(13)	2.519 (2)	2.522 (2)	1.490 (2)	109 (1)
H(1)	2.21 (2)	2.28 (2)	2.27 (3)	1.29 (2)

P—P	4.1599 (7)	P—O(11)—H(2)	113 (2)

The 2-amino-5-nitropyridinium cation

N(1)—C(1)	1.308 (3)	N(1)—C(1)—N(3)	118.5 (2)
N(3)—C(1)	1.349 (3)	N(1)—C(1)—C(6)	123.4 (2)
N(3)—C(3)	1.336 (3)	C(6)—C(1)—N(3)	118.0 (2)
C(3)—C(4)	1.352 (3)	C(1)—N(3)—C(3)	122.8 (2)
C(4)—C(5)	1.398 (3)	N(3)—C(3)—C(4)	119.5 (2)
C(5)—C(6)	1.346 (3)	C(3)—C(4)—C(5)	120.7 (2)
C(6)—C(1)	1.415 (3)	C(4)—C(5)—C(6)	119.0 (2)
C(4)—N(2)	1.443 (3)	C(5)—C(6)—C(1)	120.1 (2)
N(2)—O(21)	1.200 (3)	C(5)—C(4)—N(2)	120.5 (2)
N(2)—O(22)	1.212 (3)	C(3)—C(4)—N(2)	118.8 (2)
		C(4)—N(2)—O(21)	119.4 (2)
		C(4)—N(2)—O(22)	116.8 (2)
		O(21)—N(2)—O(22)	123.8 (2)

Table 3. *Hydrogen-bond geometry* (Å, °), *least-squares plane referenced to the crystallographic axes and shifts of atoms from the plane* (Å)

Hydrogen bonds

	O/N—H	H···O	O/N···O	O/N—H···O
O(11)—H(2)···O(13)	0.80 (3)	1.77 (3)	2.563 (2)	173 (2)
N(1)—H(7)···O(13)	0.89 (3)	1.89 (3)	2.769 (2)	171 (3)
N(1)—H(8)···O(12)	0.84 (3)	2.03 (3)	2.823 (2)	157 (2)
N(3)—H(3)···O(12)	0.90 (3)	1.75 (3)	2.655 (2)	177 (2)

Equation of the pyridine ring plane

$-12.831\,(9)\,x + 0.369\,(9)\,y - 1.0\,(1)\,z = -5.190\,(7)$

Deviations of atoms used for defining the plane

C(1)	0.005 (2)	C(5)	−0.001 (2)
C(3)	−0.004 (2)	C(6)	−0.004 (2)
C(4)	0.005 (2)	N(3)	−0.002 (2)

Deviations of atoms excluded from the plane calculation

N(1)	0.016 (2)	N(2)	0.019 (2)
H(7)	0.17 (3)	O(21)	−0.101 (2)
H(8)	−0.04 (2)	O(22)	0.149 (3)

Crystals of the title compound were prepared by dissolving 2-amino-5-nitropyridine (0.01 *M* $C_5H_5N_3O_2$) in an aqueous solution of phosphorous acid (0.01 *M* H_3PO_3) at 320 K. Slow evaporation at room temperature yields large prismatic crystals. The chemical formula has been established on the basis of the structural determination. The crystal structure was solved by direct methods using *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). H atoms were located by difference Fourier syntheses. Refinements were run using anisotropic full-matrix least squares for non-H atoms, isotropic for H atoms. The Enraf-Nonius (1977) *SDP* program operating on a MicroVAX II computer was used for all calculations. Molecular graphics were prepared using *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55758 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1015]

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A Twist-Boat 1,3,5-Triaryl-1,3,5-triazacyclohexane: X-ray Analysis of the Inclusion Compound Formed Between 1,3,5-Tris(*p*-nitrophenyl)-1,3,5-triazacyclohexane and Pyridine

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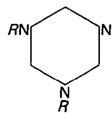
Abstract

The triazacyclohexane ring adopts a twist-boat conformation with torsion angles −25.3 (2), −41.3 (2), 70.3 (2), −27.7 (2), −35.8 (2) and 66.0 (2)°. The N—C(aryl) bonds from the ring have lengths of 1.356 (3), 1.382 (3) and 1.400 (3) Å and are inclined at 3.3 (2), 21.2 (2) and 29.5 (3)° to the CH_2—N—CH_2 planes. The N—C bond lengths in the triazacyclohexane ring are 1.442 (3)–1.474 (3) Å. The pyridine molecules are accommodated in an ordered manner in channels aligned along the screw axes parallel to **b**.

Comment

X-ray investigations of 1,3,5-trialkyl and 1,3,5-triaryl derivatives of 1,3,5-triazacyclohexane (1) have consistantly found the expected chair conformation with pyramidal arrangement of bonds at N atoms (Giumanini, Verardo, Randaccio, Bresciani-Pahor & Traldi, 1985; Zangrando, Poggi, Giumanini & Verardo, 1987; Giumanini, Verardo, Zangrando & Lassiani, 1987; Sim, 1987; Bouchemma, McCabe & Sim, 1988, 1989, 1990). We now report a study which has enabled us to isolate and examine the alternative twist-boat conformation.



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