Baldy) pour la mise à notre disposition du diffractomètre automatique, et l'Office Central de Mécanographie d'Abidjan où ont été effectués les calculs.

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Structure of Tris(methylammonium) *cyclo*-Triphosphate

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Abstract. $(CH_3NH_3)_3P_3O_9$, $M_r = 333{\cdot}11$, monoclinic, $P2_1/n$, $a = 12{\cdot}144$ (7), $b = 15{\cdot}361$ (5), $c = 7{\cdot}203$ (7) Å, $\beta = 97{\cdot}32$ (8)°, $V = 1333$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}660$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}494$ mm^{-1}, $F(000) = 696$, $T = 295$ K, final $R = 0{\cdot}024$ for 2926 unique reflexions. All the external oxygen atoms of the non-acidic phosphoric groups, P_3O_9, are involved in hydrogen bonds with the hydrogen atoms of the NH_3 groups to build a three-dimensional network.

Introduction. In the course of a systematic investigation of compounds resulting from interactions between condensed phosphoric acids ($H_4P_2O_7$, $H_3P_3O_9$, $H_4P_4O_{12}$...) and amines, diamines and amino acids we prepared the title compound, to experiment on the possibility of using, in this new field, some classical processes already extensively used for the syntheses of inorganic condensed phosphates.

Experimental. The title compound has been synthesized by using a process similar to that described by Boullé (1941) for the preparation of water-soluble *cyclo*-triphosphates. A slurry in water of the sparingly soluble silver *cyclo*-triphosphate monohydrate is slowly added to a solution of methylamine hydrogen chloride (NH_2CH_3.HCl). The reaction is:

$$Ag_3P_3O_9.H_2O + 3(NH_2CH_3.HCl) \rightarrow 3\,AgCl + (NH_3CH_3)_3P_3O_9.$$

After removing the insoluble silver chloride by filtration, the solution is kept at room temperature. Crystals of the title compound appear after some days of evaporation. They are large monoclinic prisms. The compound is stable at room temperature.

Density not measured. Prism fragment 0·37 × 0·30 × 0·32 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $0k0$, $k = 2n$; $h0l$, $h + l = 2n$. 22 reflexions ($11 < \theta < 13°$) for refining unit-cell dimensions. ω scan. 3999 reflexions measured ($3 < \theta < 30°$), $\pm h, k, l$, $h_{max} = 17$, $k_{max} = 21$, $l_{max} = 10$. Scan width: 1·20°, scan speed between 0·02 and 0·04° s^{-1}, total background measuring time: between 17 and 30 s. One orientation ($\bar{5}60$) and two intensity ($56\bar{0}$ and $\bar{1}81$) reference reflexions, no variation. Lorentz and polarization corrections. No absorption correction. Crystal structure solved by direct methods (*MULTAN*: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). Anisotropic full-matrix least-squares refinement (on F) for non-hydrogen atoms, isotropic for H atoms. Unit weights. Final refinement with 2926 reflexions ($F > 3\sigma_F$). Final $R = 0{\cdot}024$ ($wR = 0{\cdot}028$). For the complete set of unique reflexions (3733) $R = 0{\cdot}034$. Extinction not refined. Max. $\Delta/\sigma = 0{\cdot}0$. Max peak height in final difference Fourier map: 0·251 e Å^{-3}. $S = 0{\cdot}624$. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: VAX780.

Discussion. Table 1 reports the final atomic coordinates. A projection of the atomic arrangement is given in Fig. 1.*

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44323 (26 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. *Final atomic coordinates and B_{eq} or B_{iso} (for hydrogen atoms) with e.s.d.'s in parentheses*

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

	x	*y*	*z*	B_{eq}/B_{iso}(Å²)
P(1)	0·27353 (3)	0·01857 (3)	0·70354 (6)	1·833 (6)
P(2)	0·15535 (3)	0·16379 (3)	0·82538 (5)	1·696 (6)
P(3)	0·36751 (3)	0·19003 (3)	0·69662 (5)	1·854 (6)
O(*L*12)	0·20199 (9)	0·06567 (7)	0·8469 (2)	2·07 (2)
O(*L*13)	0·37489 (8)	0·08567 (7)	0·7060 (2)	2·47 (2)
O(*L*23)	0·23595 (9)	0·20422 (7)	0·6868 (1)	1·91 (2)
O(*E*11)	0·2096 (1)	0·01715 (8)	0·5149 (2)	2·68 (2)
O(*E*12)	0·6843 (1)	0·06365 (8)	0·2129 (2)	2·99 (2)
O(*E*21)	0·6783 (1)	0·29493 (8)	0·5111 (2)	2·55 (2)
O(*E*22)	0·54279 (9)	0·33608 (8)	0·2245 (2)	2·67 (2)
O(*E*31)	0·9238 (1)	0·27524 (8)	0·3750 (2)	2·78 (2)
O(*E*32)	0·9011 (1)	0·27843 (9)	0·0203 (2)	2·87 (2)
N(1)	0·5764 (1)	0·35665 (9)	0·8076 (2)	2·30 (2)
C(1)	−0·0017 (2)	0·0773 (2)	0·2239 (3)	4·02 (4)
N(2)	0·9837 (1)	0·35644 (9)	0·7196 (2)	2·44 (3)
C(2)	0·9131 (2)	0·4343 (1)	0·7167 (3)	3·24 (4)
N(3)	0·8098 (1)	0·15067 (9)	0·6498 (2)	2·50 (3)
C(3)	0·7422 (2)	0·1332 (2)	0·7997 (3)	3·98 (4)
H(1N1)	0·110 (2)	0·174 (1)	0·225 (3)	3·6 (5)
H(2N1)	0·542 (2)	0·313 (2)	0·867 (3)	4·2 (5)
H(3N1)	0·120 (2)	0·118 (1)	0·390 (3)	3·4 (5)
H(1C1)	0·949 (2)	0·103 (2)	0·141 (4)	6·2 (7)
H(2C1)	0·537 (2)	0·471 (2)	0·674 (4)	6·0 (7)
H(3C1)	0·975 (2)	0·045 (2)	0·317 (4)	6·6 (7)
H(1N2)	0·466 (2)	0·173 (1)	0·119 (3)	3·7 (5)
H(2N2)	0·058 (2)	0·374 (1)	0·726 (3)	3·5 (5)
H(3N2)	0·472 (2)	0·176 (1)	0·311 (3)	3·3 (4)
H(1C2)	0·340 (2)	0·083 (2)	0·208 (3)	5·3 (6)
H(2C2)	0·432 (2)	0·031 (2)	0·112 (3)	4·4 (5)
H(3C2)	0·937 (2)	0·472 (2)	0·829 (4)	5·4 (6)
H(1N3)	0·807 (2)	0·100 (2)	0·572 (3)	4·2 (5)
H(2N3)	0·783 (2)	0·195 (2)	0·591 (3)	4·3 (5)
H(3N3)	0·875 (2)	0·160 (2)	0·687 (3)	4·8 (6)
H(1C3)	0·165 (2)	0·369 (2)	0·244 (3)	4·4 (5)
H(2C3)	0·249 (2)	0·323 (2)	0·374 (4)	6·6 (7)
H(3C3)	0·761 (2)	0·077 (2)	0·857 (4)	7·2 (8)

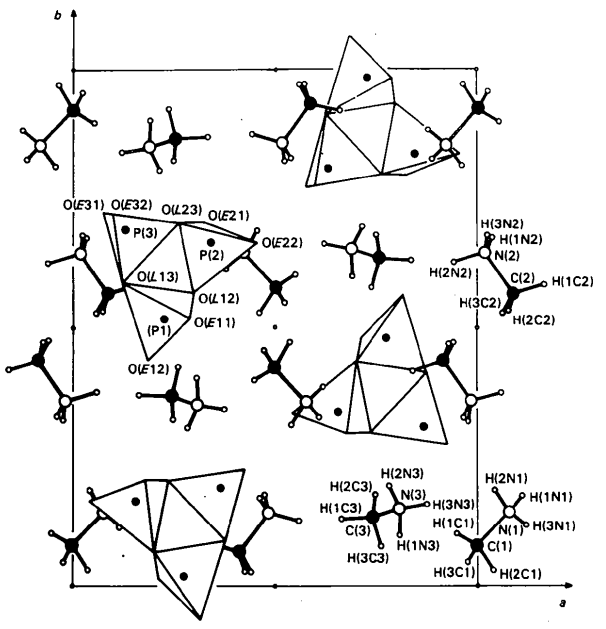

Fig. 1. Projection along the *c* axis of the atomic arrangement of $(CH_3NH_3)_3P_3O_9$.

The main interatomic distances and bond angles in the cyclic P_3O_9 group are reported in Table 2. They are not significantly different from what is commonly observed in inorganic *cyclo*-triphosphates. It is to be noticed that, unlike all other compounds produced by interaction between amines and monophosphoric acid, the phosphoric group is here a non-acidic one.

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

P(1)O_4 tetrahedron

P(1)	O(*L*12)	O(*L*13)	O(*E*11)	O(*E*12)
O(*L*12)	1·604 (1)	2·465 (2)	2·518 (2)	2·488 (2)
O(*L*13)	100·41 (8)	1·604 (1)	2·515 (2)	2·495 (2)
O(*E*11)	109·57 (9)	109·41 (9)	1·477 (2)	2·530 (2)
O(*E*12)	108·32 (9)	108·78 (8)	118·8 (1)	1·463 (2)

P(2)O_4 tetrahedron

P(2)	O(*L*12)	O(*L*23)	O(*E*21)	O(*E*22)
O(*L*12)	1·611 (1)	2·480 (2)	2·481 (2)	2·522 (2)
O(*L*23)	100·75 (7)	1·609 (1)	2·522 (2)	2·474 (2)
O(*E*21)	106·95 (9)	109·70 (8)	1·474 (1)	2·550 (2)
O(*E*22)	110·10 (9)	107·16 (9)	120·42 (9)	1·464 (1)

P(3)O_4 tetrahedron

P(3)	O(*L*13)	O(*L*23)	O(*E*31)	O(*E*32)
O(*L*13)	1·607 (1)	2·475 (2)	2·493 (2)	2·521 (2)
O(*L*23)	100·79 (7)	1·605 (1)	2·521 (2)	2·479 (2)
O(*E*31)	107·87 (9)	109·71 (9)	1·476 (2)	2·535 (2)
O(*E*32)	110·27 (9)	107·61 (9)	119·06 (10)	1·465 (1)

P(1)–P(2)	2·8509 (7)	P(1)–P(2)–P(3)	60·23 (2)
P(1)–P(3)	2·8735 (7)	P(2)–P(3)–P(1)	59·46 (2)
P(2)–P(3)	2·8757 (7)	P(2)–P(1)–P(3)	60·31 (2)

P(1)–O(*L*12)–P(2)	124·95 (9)
P(1)–O(*L*13)–P(3)	127·03 (9)
P(2)–O(*L*23)–P(3)	126·94 (9)

NH_3CH_3 groups

C(1)–N(1)	1·465 (3)
C(2)–N(2)	1·470 (3)
C(3)–N(3)	1·462 (3)

Hydrogen bonds

	N–H	H···O	N–O	N–H···O
N(1)–H(1N1)···O(*E*21)	0·90 (3)	1·90 (3)	2·769 (2)	162 (3)
N(1)–H(2N1)···O(*E*31)	0·92 (3)	1·98 (3)	2·829 (2)	152 (3)
N(1)–H(3N1)···O(*E*11)	0·84 (3)	1·90 (3)	2·827 (3)	157 (3)
N(2)–H(1N2)···O(*E*31)	0·86 (3)	1·94 (3)	2·791 (3)	172 (3)
N(2)–H(2N2)···O(*E*12)	0·94 (3)	1·82 (3)	2·733 (2)	163 (3)
N(2)–H(3N2)···O(*E*32)	0·85 (3)	1·96 (3)	2·773 (2)	159 (3)
N(3)–H(1N3)···O(*E*11)	0·96 (3)	1·90 (3)	2·835 (3)	163 (3)
N(3)–H(2N3)···O(*E*21)	0·84 (3)	2·03 (3)	2·838 (3)	160 (3)
N(3)–H(3N3)···O(*E*22)	0·82 (4)	2·02 (4)	2·819 (2)	166 (3)

All the external O atoms of the ring anion are involved in hydrogen bonds connecting them to the H atoms of the ammonium groups. Details of these bonds are reported in Table 2.

The three crystallographically independent $CH_3NH_3^+$ groups have no special features. They alternate with the P_3O_9 rings to build a three-dimensional network through the hydrogen bonds.

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