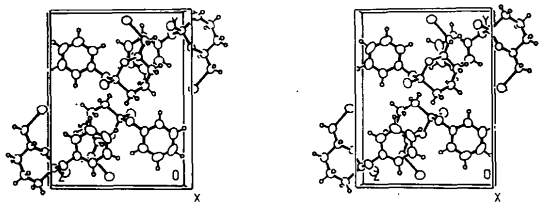

Fig. 2. A stereoview of the unit cell showing molecular packing.

around P(2) in the range 102·3 (1)–117·6 (1)°. Moreover, the endocyclic angles at C atoms in the 1,2-oxaphosphorinane ring are slightly enlarged from the tetrahedral values [range 110·2–112·4 (2)°] as is the angle I—C(7)—C(6) [112·1 (2)°]. The phenyl ring is essentially planar with maximum deviation of any atom from the least-squares plane being 0·01 Å.

The crystal structure (Fig. 2) consists of discrete molecules separated by normal van der Waals distances.

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Structure of Ethanolammonium *cyclo*-Tetraphosphate

By M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USTMG, 166 X, 38042 Grenoble CEDEX, France

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Abstract. $4C_2H_8NO^+.P_4O_{12}^{4-}$, $M_r = 564·25$, tetragonal, $I\bar{4}$, $a = 10·746$ (8), $c = 10·071$ (8) Å, $V = 1163$ (3) Å^3, $Z = 2$, $D_x = 1·611$ Mg m^{-3}, λ(Ag $K\bar{\alpha}$) = 0·5608 Å, $\mu = 0·219$ mm^{-1}, $F(000) = 592$, $T = 293$ K, final $R = 0·034$ for 1112 independent observed reflexions. The P_4O_{12} ring anions have $\bar{4}$ symmetry; they alternate with the $[OH—(CH_2)_2—NH_3]^+$ groups in planes $z \sim 0·25$ and 0·75. A three-dimensional network of strong hydrogen bonds connects the hydroxyl and the NH_3 groups to the external O atoms of the ring anion.

Introduction. The present work is part of a systematic investigation of condensed phosphates of amines, amino acids and aminoalcohols. In this practically unexplored domain we have previously described tris(methylammonium) *cyclo*-triphosphate (Averbuch-Pouchot, Durif & Guitel, 1988*a*), glycine *cyclo*-tri- and tetraphosphate (Averbuch-Pouchot, Durif & Guitel, 1988*b,c*) and calcium ethylenediammonium *cyclo*-tetraphosphate monohydrate (Averbuch-Pouchot, Durif & Guitel, 1988*d*). The title compound is the first evidence for the existence of condensed phosphates of aminoalcohols.

Experimental. The title compound has been prepared by adding slowly a stoichiometric amount of P_4O_{10} to an aqueous solution of ethanolamine kept at a temperature close to 273 K. The reaction is

$$P_4O_{10} + 2H_2O \rightarrow H_4P_4O_{12}$$

$$H_4P_4O_{12} + 4NH_2—(CH_2)_2—OH \rightarrow P_4O_{12}[NH_3—(CH_2)_2—OH]_4.$$

The resulting solution is then kept at room temperature until crystallization occurs. Many careful recrystallizations are then necessary to obtain good quality crystals. They appear as multifaceted short stout tetragonal prisms. The compound is stable at room temperature.

Density not measured. Prism fragment 0·35 × 0·35 × 0·40 mm. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: hkl, $h+k+l = 2n$. 19 reflexions ($10·2 < \theta < 13·3°$) for refining unit-cell dimensions. ω scan, 1494 reflexions measured ($3 < \theta < 30°$), h,k,l, $h_{max} = k_{max} = 16$, $l_{max} = 17$. Scan width: 1·20°, scan speed: 0·03° s^{-1}, total background measuring time: 6 s. Two intensity and orientation reference reflexions (112 and $\bar{1}\bar{1}\bar{2}$) measured every 2 h, no variation. Lorentz and polarization

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Table 1. *Final atomic coordinates for non-*H *atoms and their B_{eq} values*

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

	x	y	z	B_{eq}(Å^2)
P	0·18290 (6)	0·43900 (6)	0·24123 (6)	1·903 (8)
O(*L*)	0·1248 (2)	0·5663 (2)	0·1852 (2)	1·84 (3)
O(*E*1)	0·7811 (2)	0·6322 (2)	0·1214 (2)	3·09 (4)
O(*E*2)	0·9636 (2)	0·2258 (2)	0·1523 (2)	3·17 (4)
O	0·5402 (2)	0·1789 (3)	0·1274 (2)	3·62 (5)
C(1)	0·8022 (3)	0·9511 (3)	0·3241 (3)	3·25 (6)
C(2)	0·8013 (3)	0·9786 (3)	0·1774 (3)	2·77 (5)
N	0·3876 (2)	0·7731 (3)	0·3971 (2)	2·54 (4)

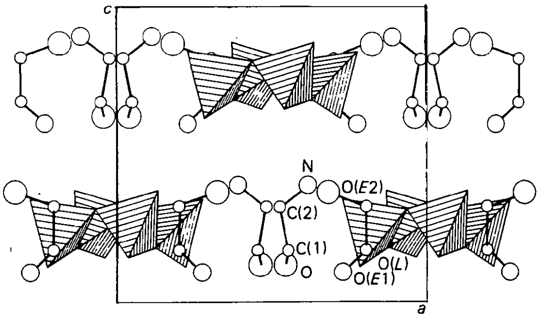

Fig. 1. Projection along the *b* axis of the atomic arrangement of ethanolammonium *cyclo*-tetraphosphate.

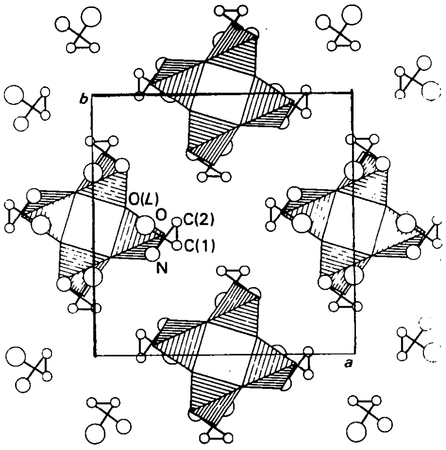

Fig. 2. Projection along the *c* axis of the atomic arrangement of ethanolammonium *cyclo*-tetraphosphate.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in ethanolammonium cyclo-tetraphosphate*

The PO_4 tetrahedron

P–O(*L*)	1·606 (2)	O(*L*)–P–O(*L*)	102·8 (1)
P–O(*L*)	1·609 (2)	O(*L*)–P–O(*E*2)	104·8 (1)
P–O(*E*1)	1·480 (2)	O(*L*)–P–O(*E*2)	111·2 (1)
P–O(*E*2)	1·477 (2)	O(*L*)–P–O(*E*1)	111·0 (1)
		O(*L*)–P–O(*E*2)	105·0 (1)
P–P	2·9353 (9)		
		O(*E*1)–P–O(*E*2)	120·7 (1)
O(*L*)–O(*L*)	2·513 (3)		
O(*L*)–O(*E*1)	2·547 (3)	P–O(*L*)–P	131·9 (1)
O(*L*)–O(*E*1)	2·446 (3)		
O(*L*)–O(*E*2)	2·450 (3)	P–P–P	89·79 (3)
O(*L*)–O(*E*2)	2·544 (3)		
O(*E*1)–O(*E*2)	2·570 (3)		

The ethanolammonium group

O–C(1)	1·415 (5)	O–C(1)–C(2)	108·7 (3)
C(1)–C(2)	1·506 (5)	C(1)–C(2)–N	111·9 (3)
C(2)–N	1·470 (4)		

The hydrogen bonds

N(O)–H···O	N(O)–H	H···O	N(O)–H···O	N(O)···O
O–H···O(*E*1)	0·79 (5)	1·97 (5)	162 (5)	2·728 (3)
N–H(1)···O(*E*1)	0·89 (4)	1·96 (4)	161 (4)	2·812 (3)
N–H(2)···O(*E*2)	1·06 (5)	1·76 (5)	152 (4)	2·745 (3)
N–H(3)···O	0·95 (5)	2·06 (5)	159 (5)	2·968 (4)

corrections. No absorption correction. Crystal structure solved by direct methods (*MULTAN77*: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Unit weights. Final refinement with 1112 reflexions ($F > 2\sigma_F$). Final $R = 0·034$ ($wR = 0·037$). For the complete set of 1494 unique reflexions $R = 0·046$. Extinction not refined. Max. $\Delta/\sigma = 0·14$ [B_{iso} of H(3)]. Max. peak height in final difference Fourier map: 0·149 e Å^{-3}. $S = 0·439$. 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: Microvax II.

Discussion. The final atomic parameters are reported in Table 1.[*]

The P_4O_{12} *ring anion*

The *cyclo*-tetraphosphate anion is, as usual, made up of a ring of four PO_4 tetrahedra sharing corners. Here the ring having point-group symmetry $\bar{4}$ is built up by only one crystallographically independent PO_4. Interatomic distances and bond angles in the ring are given in Table 2. These values are consistent with those already found in other inorganic condensed phosphates, P–O(bonding) [P–O(*L*)] distances being much longer (1·606–1·609 Å) than the P–O(external) bonds (1·477–1·480 Å).

The ethanolammonium group

The main geometrical features of this group are reported in Table 2; if compared with the only other previously described ethanolammonium phosphate $[NH_3-(CH_2)_2-OH]^+.HPO_4^{2-}$ (Isabev, Ibragimov,

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44934 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Talipov, Saibova & Aripov, 1981), significant differences are observed mainly for the C—O and C—N distances; these authors report C—O distances of 1·427 and 1·430 Å and C—N distances of 1·496 and 1·506 Å for the two independent groups while 1·415 and 1·470 Å are observed in the title compound.

As shown in Fig. 1, a projection along the *b* axis, the structure can be described as a succession of layers perpendicular to the *c* axis. These layers contain both the P_4O_{12} ring anions and the organic groups and are separated by a distance of *c*/2.

A three-dimensional network of hydrogen bonds, whose geometrical details are reported in Table 2, connects the layers and the organic groups and P_4O_{12} anions within each layer.

As normally observed the bonding O atoms [O(*L*)] do not take part in the hydrogen-bond network.

Fig. 2 shows a projection along the *c* axis.

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Structure of $C_{22}H_{36}N_{10}O_2S_2$

By Fusao Takusagawa

Department of Chemistry, University of Kansas, Lawrence, KS 66045, *USA*

and Dennis E. Jackman

Agricultural Chemicals Division, Mobay Chemical Corporation, Hawthorn Road, Kansas City, MO 64120, *USA*

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Abstract. Methyl 3,3-dimethyl-2-oxobutyrate, 2-(*Z*,*Z*)-azine with 2-[(1*E*,3*Z*)-3-*tert*-butyl-5-[(*Z*)-2-*tert*-butyl-4-methyl-Δ^2-1,3,4-thiadiazolin-5-ylidene]-1-formazano]-4-methyl-Δ^2-1,3,4-thiadiazolin-5-one, $M_r = 536{\cdot}71$, monoclinic, $P2_1/c$, $a = 17{\cdot}931\ (3)$, $b = 13{\cdot}311\ (3)$, $c = 26{\cdot}076\ (5)$ Å, $\beta = 102{\cdot}40\ (3)°$, $V = 6078\ (2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}173$ g cm^{-3}, $F(000) = 2288$, room temperature [298 (2) K], $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 18{\cdot}2824$ cm^{-1}, 643 parameters refined, final $R = 0{\cdot}094$ for all 6259 reflections. The structure of an undesirable blue compound formed during the manufacturing process of the herbicide metribuzin has been identified.

Introduction. The manufacture of the herbicide metribuzin (1) is periodically complicated by the formation of an undesirable blue compound of unknown structure. Because the occurrence of the blue dye could not be predicted or controlled, we initiated a program to determine its structure and how it is formed. Our study showed that the dye is formed by the oxidation of the reaction product of two impurities formed during the synthesis of (1) (Jackman, 1987), and this finding provided a semi-empirical synthesis for the dye. Since routine spectroscopic techniques (^{1}H and ^{13}C NMR, IR, UV, MS) did not unambiguously establish the structure, we have carried out an X-ray analysis of the trimethylated derivative and established its structure.

Experimental. Many attempts to obtain X-ray quality crystals of the dye and its metal salts were unsuccessful. We then tried various derivatives and finally succeeded with the trimethylated compound. A black plate, 0·4 × 0·2 × 0·1 mm, obtained by recrystallization from 2-propanol, was mounted on a glass fiber oriented approximately along $[2\bar{1}\bar{1}]$. Cell constants were determined by using 15 centered reflections widely scattered throughout reciprocal space ($35 > 2\theta > 25°$). Preliminary counter data indicated a monoclinic system with systematic absences, $k = 2n + 1$ in $0k0$ and $l = 2n + 1$ in $h0l$, uniquely determining the space group as $P2_1/c$. Four octants ($h = 0\rightarrow17$, $k = -13\rightarrow13$, $l = -25\rightarrow25$) of data out to $2\theta = 100°$ were collected using a Syntex $P2_1$ diffractometer (Cu $K\alpha$, graphite monochromator) with θ–2θ scan mode (scan angle:

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