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Structure of Tris(ethylenediammonium) Bis(*cyclo*-triphosphate)

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

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'Université J. Fourier, 166X, 38042 Grenoble CEDEX, France

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Abstract. $3C_2H_{10}N_2^{2+}.2P_3O_9^{3-}$, $M_r = 660·17$, triclinic, $P\bar{1}$, $a = 15·558$ (8), $b = 10·450$ (6), $c = 7·639$ (4) Å, $\alpha = 104·14$ (5), $\beta = 102·73$ (5), $\gamma = 86·71$ (5)°, $V = 1177$ (2) Å^3, $Z = 2$, $D_x = 1·862$ Mg m^{-3}, λ(Ag $K\alpha$) = 0·5608 Å, $\mu = 0·294$ mm^{-1}, $F(000) = 684$, $T = 295$ K, final $R = 0·027$ for 7448 reflections. Rows of alternate P_3O_9 ring anions and ethylenediammonium groups, parallel to the c axis, are arranged in an almost regular hexagonal way. The channels formed by this arrangement are centred by a row of ethylenediammonium groups. Two of the four crystallographically independent ethylenediammonium groups are centrosymmetric.

Introduction. The title compound is the second example of an ethylenediammonium condensed phosphate. We have previously described the preparation and crystal structure of bis(ethylenediammonium) *cyclo*-tetraphosphate monohydrate, $[NH_3(CH_2)_2NH_3]_2P_4O_{12}.H_2O$ (Averbuch-Pouchot, Durif & Guitel, 1989).

Experimental. The title compound was prepared by a metathesis reaction based on that described by Boullé (1941) for the preparation of water-soluble inorganic *cyclo*-triphosphates. An aqueous solution of ethylenediammonium dichloride was added to a slurry of water of the sparingly soluble silver *cyclo*-triphosphate monohydrate with the stoichiometric ratio 3:2. The reaction is:

$$3[NH_3(CH_2)_2NH_3]Cl_2 + 2Ag_3P_3O_9 \rightarrow [NH_3(CH_2)_2NH_3]_3P_3O_9 + 6AgCl.$$

After mechanical stirring for ~1 h, the insoluble silver chloride was removed by filtration. The resulting solution was then kept at room temperature and, after evaporation for some weeks, stout triclinic prisms of tris(ethylenediammonium) bis(*cyclo*-triphosphate) were obtained.

Prism fragment: 0·72 × 0·56 × 0·48 mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 21 reflections ($11 < \theta < 16°$) for refining unit-cell dimensions. 10 812 reflections measured, 10 195 after averaging Friedel pairs ($3 < \theta < 27·5°$), $h + k + l$, $h_{max} = 28$, $k_{max} = 18$, $l_{max} = 12$. ω scan, scan width 1·20°, scan speed 0·03° s^{-1}, background measuring time 10 s. Two orientation and two intensity reference reflections (822 and $\bar{8}\bar{2}\bar{2}$), no significant variations. Lorentz and polarization corrections, no absorption correction.

Crystal structure solved by direct methods with *MULTAN77* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located from difference Fourier syntheses; anisotropic full-matrix least-squares refinement (on F) for non-H atoms and isotropic for H atoms. Unit weights. Final refinement with 7448 reflections ($I > 9\sigma_I$). Final $R = 0·027$ ($wR = 0·033$), $S = 0·665$. Max. $\Delta/\sigma = 0·01$. Max. peak height in final difference Fourier synthesis

Table 1. *Final atomic coordinates and B_{eq} values for the title compound, 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}(Å^2)
P(1)	0·36103 (2)	0·86849 (3)	0·01221 (5)	1·180 (5)
P(2)	0·37124 (2)	0·15288 (3)	0·15722 (5)	1·262 (5)
P(3)	0·20206 (2)	0·02640 (3)	0·00545 (5)	1·300 (5)
P(4)	0·12655 (2)	0·64542 (3)	0·49916 (5)	1·271 (5)
P(5)	0·29597 (2)	0·51279 (4)	0·48965 (5)	1·407 (6)
P(6)	0·13511 (2)	0·35954 (3)	0·36322 (5)	1·210 (5)
O(*L*12)	0·41096 (7)	0.0060 (1)	0·1048 (2)	2·09 (2)
O(*L*13)	0·26727 (6)	0·9171 (1)	0·9131 (1)	1·43 (2)
O(*E*11)	0·34802 (8)	0·8073 (1)	0·1606 (2)	2·03 (2)
O(*E*12)	0·40469 (8)	0·7907 (1)	0·8681 (2)	1·95 (2)
O(*E*21)	0·37281 (8)	0·2201 (1)	0·0093 (2)	2·24 (2)
O(*E*22)	0·41573 (7)	0·2146 (1)	0·3502 (2)	1·86 (2)
O(*L*23)	0·27231 (7)	0·1217 (1)	0·1625 (1)	1·50 (2)
O(*E*31)	0·15800 (8)	0·0936 (1)	0·8608 (2)	2·19 (2)
O(*E*32)	0·14800 (7)	0·9655 (1)	0·0992 (2)	2·26 (2)
O(*L*45)	0·23123 (7)	0·6347 (1)	0·5455 (2)	2·29 (2)
O(*L*64)	0·09777 (7)	0·4960 (1)	0·4720 (2)	1·78 (2)
O(*E*41)	0·09830 (8)	0·7256 (1)	0·6648 (2)	1·97 (2)
O(*E*42)	0·09660 (8)	0·6844 (1)	0·3208 (2)	2·02 (2)
O(*E*51)	0·33335 (9)	0·4620 (1)	0·6538 (2)	2·57 (2)
O(*E*52)	0·35564 (8)	0·5568 (1)	0·3905 (2)	2·79 (2)
O(*L*56)	0·22800 (7)	0·4081 (1)	0·3429 (1)	1·54 (2)
O(*E*61)	0·08125 (8)	0·3126 (1)	0·1777 (2)	2·25 (2)
O(*E*62)	0·14930 (7)	0·2725 (1)	0·4948 (2)	1·79 (2)
C(1)	0·0948 (1)	0·4865 (1)	0·9010 (2)	1·75 (2)
C(2)	0·1886 (1)	0·5338 (2)	0·9564 (2)	1·77 (2)
N(1)	0·08711 (9)	0·3431 (1)	0·8228 (2)	1·89 (2)
N(2)	0·1857 (1)	0·6784 (1)	0·0322 (2)	2·31 (2)
C(3)	0·30786 (9)	0·0337 (1)	0·5624 (2)	1·65 (2)
C(4)	0·4010 (1)	0·9824 (2)	0·5939 (2)	1·99 (3)
N(3)	0·31105 (9)	0·1791 (1)	0·6229 (2)	2·03 (2)
N(4)	0·40525 (9)	0·8376 (1)	0·5358 (2)	1·92 (2)
C(5)	0·03838 (9)	0·0021 (1)	0·4549 (2)	1·66 (2)
N(5)	−0·00858 (8)	0·9551 (1)	0·7201 (2)	1·69 (2)
C(6)	0·4671 (1)	0·5176 (2)	0·0602 (2)	2·24 (3)
N(6)	0·48825 (9)	0·4495 (1)	0·2118 (2)	1·96 (2)

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0·490 e Å^{-3}. The final R value = 0·035 for the complete set of 10 195 reflections. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* employed for all calculations. Computer used: MicroVAX II.

Table 2. *Main interatomic bond distances* (Å) *and bond angles* (°) *for the title compound, with e.s.d.'s in parentheses*

The first P_3O_9 ring anion

$P(1)O_4$ tetrahedron

P(1)	O(*L*12)	O(*L*13)	O(*E*11)	O(*E*12)
O(*L*12)	1·600 (1)	2·481 (1)	2·511 (2)	2·508 (1)
O(*L*13)	101·33 (6)	1·607 (1)	2·514 (2)	2·495 (1)
O(*E*11)	108·91 (7)	108·74 (7)	1·485 (1)	2·543 (2)
O(*E*12)	109·48 (7)	108·23 (6)	118·73 (7)	1·470 (1)

$P(2)O_4$ tetrahedron

P(2)	O(*L*12)	O(*E*21)	O(*E*22)	O(*L*23)
O(*L*12)	1·612 (1)	2·519 (2)	2·496 (1)	2·487 (1)
O(*E*21)	109·33 (7)	1·474 (1)	2·556 (2)	2·542 (2)
O(*E*22)	107·30 (6)	119·48 (7)	1·485 (1)	2·480 (1)
O(*L*23)	101·23 (6)	111·21 (7)	106·68 (6)	1·606 (1)

$P(3)O_4$ tetrahedron

P(3)	O(*L*13)	O(*L*23)	O(*E*31)	O(*E*32)
O(*L*13)	1·620 (1)	2·484 (1)	2·482 (2)	2·537 (2)
O(*L*23)	100·52 (5)	1·6100 (9)	2·548 (1)	2·493 (2)
O(*E*31)	106·56 (7)	111·29 (6)	1·475 (1)	2·545 (2)
O(*E*32)	110·01 (7)	107·72 (6)	119·15 (7)	1·476 (1)

P(1)—P(2)	2·9073 (5)	P(1)—P(2)—P(3)	59·92 (1)
P(1)—P(3)	2·8952 (5)	P(1)—P(3)—P(2)	60·34 (1)
P(2)—P(3)	2·8896 (5)	P(2)—P(1)—P(3)	59·73 (1)

P(1)—O(*L*12)—P(2)	129·66 (7)
P(1)—O(*L*13)—P(3)	127·57 (6)
P(2)—O(*L*23)—P(3)	127·95 (7)

The second P_3O_9 ring anion

$P(4)O_4$ tetrahedron

P(4)	O(*L*45)	O(*L*64)	O(*E*41)	O(*E*42)
O(*L*45)	1·595 (1)	2·486 (2)	2·492 (2)	2·519 (2)
O(*L*64)	102·07 (6)	1·602 (1)	2·490 (1)	2·512 (2)
O(*E*41)	108·35 (7)	107·87 (7)	1·477 (1)	2·551 (2)
O(*E*42)	109·59 (8)	108·81 (6)	118·84 (7)	1·487 (1)

$P(5)O_4$ tetrahedron

P(5)	O(*L*45)	O(*E*51)	O(*E*52)	O(*L*56)
O(*L*45)	1·612 (1)	2·509 (2)	2·487 (2)	2·488 (1)
O(*E*51)	108·86 (8)	1·470 (1)	2·543 (2)	2·528 (2)
O(*E*52)	107·20 (8)	119·35 (8)	1·476 (2)	2·503 (2)
O(*L*56)	101·19 (6)	110·29 (7)	108·38 (7)	1·608 (1)

$P(6)O_4$ tetrahedron

P(6)	O(*L*64)	O(*L*56)	O(*E*61)	O(*E*62)
O(*L*64)	1·613 (1)	2·483 (2)	2·547 (2)	2·460 (2)
O(*L*56)	100·66 (6)	1·613 (1)	2·489 (2)	2·548 (2)
O(*E*61)	110·80 (6)	108·03 (7)	1·462 (1)	2·546 (2)
O(*E*62)	104·95 (6)	110·47 (6)	119·34 (7)	1·488 (1)

P(4)—P(5)	2·9183 (5)	P(4)—O(*L*45)—P(5)	130·98 (7)
P(5)—P(6)	2·9023 (5)	P(5)—O(*L*56)—P(6)	128·61 (7)
P(4)—P(6)	2·9190 (5)	P(4)—O(*L*64)—P(6)	130·51 (8)

P(4)—P(5)—P(6)	60·20 (1)
P(5)—P(6)—P(4)	60·17 (1)
P(5)—P(4)—P(6)	59·63 (1)

The ethylenediammonium groups

C(1)—C(2)	1·507 (2)	N(1)—C(1)—C(2)	113·0 (1)
C(1)—N(1)	1·473 (2)	N(2)—C(2)—C(1)	106·7 (1)
C(2)—N(2)	1·483 (2)		
C(3)—C(4)	1·507 (2)	N(3)—C(3)—C(4)	107·9 (1)
N(3)—C(3)	1·477 (2)	N(4)—C(4)—C(3)	112·3 (1)
N(4)—C(4)	1·471 (2)		
C(5)—C(5)	1·514 (2)	C(5)—C(5)—N(5)	110·5 (1)
C(5)—N(5)	1·483 (2)		
C(6)—C(6)	1·496 (2)	C(6)—C(6)—N(6)	110·4 (1)
C(6)—N(6)	1·471 (2)		

Table 2 (*cont.*)

The hydrogen-bond network

N—H···O	N—H	H···O	N—O	N—H···O
N(1)—H(N11)···O(*E*62)	0·81 (2)	2·00 (2)	2·801 (2)	170 (2)
N(1)—H(N12)···O(*E*42)	0·95 (3)	1·93 (3)	2·836 (2)	159 (3)
···O(*E*31)		2·23 (2)	2·828 (2)	130 (2)
N(1)—H(N13)	0·92 (3)			
···O(*E*61)		2·23 (3)	2·828 (2)	130 (2)
N(2)—H(N21)···O(*E*42)	0·86 (2)	2·01 (3)	2·840 (2)	163 (2)
N(2)—H(N22)···O(*E*41)	0·89 (2)	2·17 (2)	2·982 (2)	152 (2)
N(2)—H(N23)···O(*E*11)	0·87 (3)	1·94 (3)	2·798 (2)	173 (2)
N(3)—H(N23)···O(*E*31)	0·83 (2)	2·01 (2)	2·829 (2)	171 (2)
N(3)—H(N32)···O(*E*62)	0·84 (3)	1·88 (3)	2·714 (2)	171 (2)
N(3)—H(N33)···O(*E*22)	0·86 (3)	2·23 (3)	3·014 (2)	152 (2)
N(4)—H(N41)···O(*E*11)	0·82 (2)	1·99 (2)	2·752 (2)	160 (2)
N(4)—H(N42)···O(*E*12)	0·84 (3)	2·06 (3)	2·701 (2)	133 (2)
N(4)—H(N43)···O(*E*22)	0·83 (2)	1·98 (2)	2·798 (2)	168 (2)
N(5)—H(N51)···O(*E*31)	0·85 (2)	2·10 (2)	2·904 (2)	158 (2)
N(5)—H(N52)···O(*E*32)	0·93 (3)	1·92 (3)	2·806 (2)	159 (2)
N(5)—N(H53)···O(*E*41)	0·94 (3)	1·94 (3)	2·839 (2)	159 (3)
N(6)—H(N61)···O(*E*52)	0·92 (3)	1·88 (3)	2·761 (2)	159 (3)
N(6)—H(N62)···O(*E*51)	0·88 (3)	2·01 (3)	2·866 (2)	166 (3)
N(6)—H(N63)···O(*E*21)	0·94 (3)	2·19 (3)	2·972 (2)	140 (3)

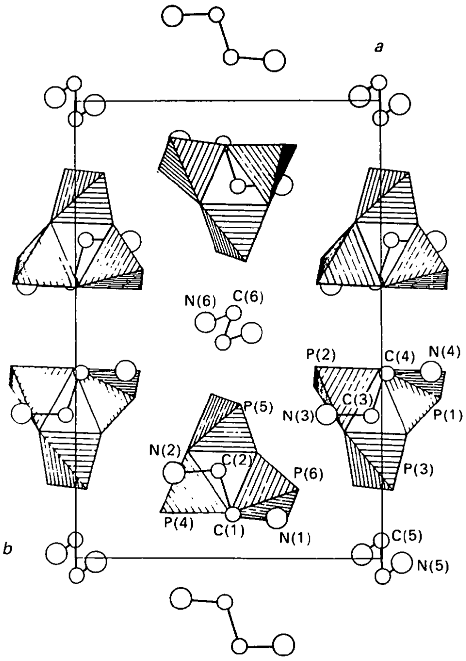

Fig. 1. Projection of the atomic arrangement of $[NH_3(CH_2)_2NH_3]_3(P_3O_9)_2$ along the c axis. The PO_4 tetrahedra of the P_3O_9 groups are simply denoted by the names of their central P atoms.

Discussion. The final atomic coordinates are reported in Table 1.* The atomic arrangement is built by two crystallographically independent P_3O_9 ring anions

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[*] Lists of structure factors, anisotropic thermal parameters, distances and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51841 (67 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and four ethylenediammonium groups, which are also independent. Of these four organic groups two are centrosymmetric.

As shown in Fig. 1, a projection along the *c* axis, the structure can be easily described as a set of rows parallel to the *c* axis. The first kind of row consists of alternating P_3O_9 and ethylenediammonium groups. These rows are arranged in an almost regular hexagonal way to give large hexagonal channels, which are centered by rows of ethylenediammonium groups. Main interatomic distances and bond angles in the P_3O_9 ring anions and the organic groups are reported in Table 2.

The three-dimensional network of hydrogen bonds, connecting the H atoms of the NH_3 radicals to the external O atoms of the phosphoric ring anions, is also detailed in Table 2.

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A New Indole Alkaloid from *Aristotelia chilensis*

BY WILLIAM H. WATSON* AND ANTE NAGL†

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, *USA*

MARIO SILVA AND CARLOS CESPEDES

Departamento de Bontánica, Laboratorio de Productos Naturales, Universidad de Concepcion, Concepcion, Chile

AND J. JAKUPOVIC

*Institute of Organic Chemistry, Technical University of Berlin, D-*1000 *Berlin* 12, *Federal Republic of Germany*

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Abstract. 4,4-Dimethyl-8-methylene-3-azabicyclo[3.3.1]non-2-en-2-yl 3-indolyl ketone (1), $C_{20}H_{22}N_2O$, $M_r = 306{\cdot}41$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}480$ (1), $b = 12{\cdot}844$ (2), $c = 19{\cdot}960$ (3) Å, $V = 1661{\cdot}3$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}225$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}71$ cm^{-1}, $F(000) = 656$, $T = 293$ K, $R = 0{\cdot}0498$ for 923 reflections. The indole portion of the molecule is planar (0·018 Å r.m.s.d.). The heterocyclic six-membered ring exhibits a 1,2-diplanar conformation while the cyclohexane ring is in a chair conformation. The carbonyl group is almost coplanar with the indole system but the planar portion of the heterocyclic six-membered ring is twisted out of the indole plane by 47·4 (7)°.

Introduction. Members of the genus *Aristotelia* (Eleocarpaceae) are of interest because of the taxonomic problems they present (Allan, 1961) and because they produce a number of unique and interesting alkaloids. *Aristotelia peduncularis* Hook, collected in Tasmania, yielded peduncularine (2) plus three unidentified components (Bick, Bremner, Preston & Calder, 1971). *Aristotelia serrata* from New Zealand contains peduncularine (2), aristoteline (3) and several unidentified components (Anderson, Robertson, Avey, Donovan, Bick, Bremner, Finney, Preston, Gallagher & Russell, 1975). *Aristotelia chilensis,* collected in Chile, has yielded aristoteline (3), aristotelinine (4) (Gopalakrishna, Watson, Silva & Bittner, 1978), aristotelone (5) (Bhakuni, Silva, Matlin & Sammes, 1976), and aristone (6) (Bittner, Silva, Gopalakrishna, Watson, Zabel, Matlin & Sammes, 1978). Compound (6) was postulated to arise *via* rearrangement of a derivative of (4) (Zabel, Watson, Bittner & Silva, 1980). A reinvestigation of *A. chilensis* yielded two new isomeric indole alkaloids of unknown structure which differ only in the posi-

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* Author to whom correspondence should be addressed.

† On leave from the Faculty of Technology, University of Zagreb, Zagreb, Yugoslavia.

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