

Structure of Putrescinium Dihydrogendiphosphate*†

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Abstract. $C_4H_{14}N_2^+H_2P_2O_7^-$, $M_r = 266.1$, monoclinic, $C2/c$, $a = 16.569(2)$, $b = 8.4497(6)$, $c = 7.998(1)$ Å, $\beta = 96.282(9)^\circ$, $V = 1113.0(2)$ Å³, $Z = 4$, $D_m = 1.570$, $D_x = 1.587$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 3.49$ cm⁻¹, $F(000) = 560$, $T = 290$ K, $R = 0.030$ for 862 observed reflections. The putrescinium dication is located on a center of symmetry and has the extended all-*trans* conformation. The dihydrogendiphosphate anion is located on a two-fold axis with the bridge P—O—P angle $134.26(7)^\circ$ and the two PO₃ groups staggered about the P...P axis. The ions are H bonded into two-dimensional layers perpendicular to **b** with no H bonding between the layers.

Introduction. Putrescine is a linear biogenic diamine. In biological systems it exists as a diprotonated cation which interacts with nucleic acids primarily through H bonding. To date, the behavior of the putrescinium dication in crystals has been studied in the following salts: bis(diethylphosphate) (I) (Furberg & Solbakk, 1972), bisphosphate (II) (Taku-sagawa & Koetzle, 1978, 1979; Woo, Seeman & Rich, 1979), dichloride (III) (Chandrasekhar & Pat-tabhi, 1980), hydrogen phosphate dihydrate (IV) (Jaskólski, Alejska & Wiewiórowski, 1986), and dinitrate (V) (Jaskólski, 1987; Jaskólski & Olovsson, 1989). These studies revealed that the putrescinium dication has a strong preference to occupy crystallographic inversion centers; in (IV), it was found in a general position, but in a symmetric conformation with a non-crystallographic inversion center. This tendency to be highly symmetric is combined with conformational flexibility, as the putrescinium dication has been found in the extended all-*trans* conformation [(III), (IV) and molecule I in (V)] and in the partly folded *gauche*⁺-*trans*-*gauche*⁻ form [(I), (II) and molecule II in (V)]. Here, we report the X-ray structure of the putrescinium dication in its dihydrogendiphosphate salt.

Experimental. Colorless prismatic crystals from methanol/water at room temperature. D_m by flotation in a mixture of chlorobenzene and CCl₄. $0.31 \times 0.44 \times 0.55$ mm crystal for data collection. Syntex P2₁ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, unit-cell dimensions from a least-squares refinement of the setting angles of 15 reflections ($20.8 \leq 2\theta \leq 27.9^\circ$). Intensity data for 958 unique reflections collected with variable $\theta:2\theta$ scan up to $2\theta_{\max} = 50^\circ$ [$-19 \leq h \leq 19$, $0 \leq k \leq 10$, $0 \leq l \leq 9$], two check reflections (151, 731) monitored every 1.5 h, intensity fluctuations within 3%. Integrated intensities obtained according to the profile analysis method of Lehmann & Larsen (1974), data corrected for Lorentz and polarization effects but not for absorption. The position of the P atom from a Patterson map, other non-H atoms from a Fourier map and the H atoms from a $\Delta\rho$ map. The structure refined (anisotropic non-H atoms, isotropic H atoms) by a full-matrix least-squares method which minimized $\sum w(F_o - F_c)^2$ where $w = 1/[\sigma^2(F_o) + 0.00005F_o^2]$, final $R = 0.030$, $wR = 0.041$, $S = 3.12$, $\Delta/\sigma_{\max} = 0.13$ for 862 observed data [$I \geq 1.96\sigma(I)$], extinction correction according to $F_c' = F_o(1 - xF_c^2/\sin\theta)$ where x refined to $60(2) \times 10^{-7}$, maximum and minimum residues in final ΔF map 0.24 and -0.28 e Å⁻³.

Computer programs: *SHELX76* (Sheldrick, 1976) and local programs (Jaskólski, 1982) on a RIAD-32 computer. Molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final positional and thermal parameters are listed in Table 1. ‡ Bond distances and angles are given in Table 2 and the conformations of the cation and the anion are illustrated in Fig. 1. The geometry of the cation does not show any unusual features and

* Systematic name: 1,4-butanediammonium dihydrogendiphosphate.

† Studies of Biogenic Polyamines. VI. Part V: Jaskólski & Olovsson (1989).

‡ 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 52999 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
P	0.45190 (3)	0.28106 (7)	-0.10432 (7)	0.0193 (2)
O(1)	0.5	0.2071 (2)	-0.25	0.0303 (6)
O(2)	0.51055 (9)	0.3072 (2)	0.0486 (2)	0.0290 (6)
O(3)	0.38506 (9)	0.1667 (2)	-0.0850 (2)	0.0279 (5)
O(4)	0.4167 (1)	0.4418 (2)	-0.1755 (2)	0.0287 (6)
N	0.3731 (1)	0.1271 (2)	0.2592 (2)	0.0229 (6)
C(1)	0.2964 (1)	0.2080 (3)	0.2937 (3)	0.0294 (6)
C(2)	0.2864 (2)	0.2025 (3)	0.4791 (3)	0.0331 (8)

Table 2. Bond distances (\AA) and angles ($^\circ$)

N—C(1)	1.496 (3)	P—O(2)	1.493 (2)
C(1)—C(2)	1.511 (3)	P—O(3)	1.490 (2)
C(2)—C(2')	1.515 (5)	P—O(4)	1.561 (2)
P—O(1)	1.608 (1)		
N—C(1)—C(2)	110.7 (2)	O(2)—P—O(3)	115.83 (9)
C(1)—C(2)—C(2')	112.0 (2)	O(2)—P—O(4)	110.70 (9)
O(1)—P—O(2)	108.74 (7)	O(3)—P—O(4)	110.48 (9)
O(1)—P—O(3)	104.81 (8)	P—O(1)—P ⁱⁱ	134.3 (1)
O(1)—P—O(4)	105.60 (9)		

Symmetry codes: (i) 0.5 - x, 0.5 - y, 1 - z; (ii) 1 - x, y, -0.5 - z.

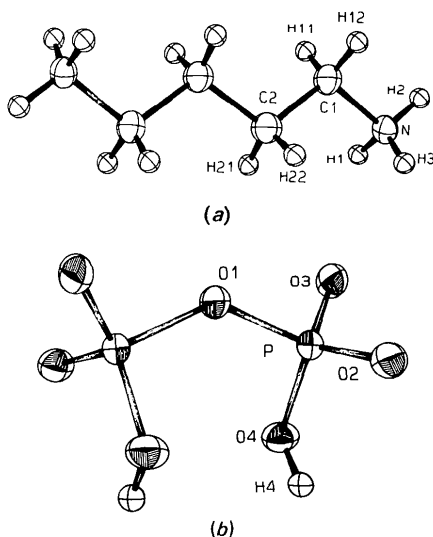


Fig. 1. Thermal-ellipsoid perspective view of the 1,4-butanediammonium cation (a) and the dihydrogendiphosphate anion (b).

agrees with that reported in a careful study of putrescine bisphosphate (Takusagawa & Koetzle, 1979). The 1,4-butanediammonium dication is located on a center of symmetry in the fully extended all-*trans* conformation [the torsion angle N—C(1)—C(2)—C(2') is 174.3 (2) $^\circ$].

The dihydrogendiphosphate anion has exact C_2 symmetry with the bridge O atom located on a twofold axis. The sum of the P—O distances in the PO_4 unit equals 6.152 (4) \AA and is close to the value of 6.184 \AA given by Matheja & Degens (1971). The PO_3 groups of the diphosphate anion take on a

Table 3. Geometry of the H bonds

D—H...A	D—H (\AA)	H...A (\AA)	D...A (\AA)	\angle D—H...A ($^\circ$)
N—H(1)...O(2)	0.95 (3)	1.85 (3)	2.783 (3)	171 (2)
N—H(2)...O(3)	0.95 (3)	1.86 (3)	2.802 (3)	172 (2)
N—H(3)...O(3 ⁱⁱ)	0.89 (3)	1.89 (3)	2.775 (3)	174 (2)
O(4)—H(4)...O(2 ⁱⁱⁱ)	0.87 (3)	1.72 (3)	2.591 (2)	173 (2)

Symmetry codes: (i) 1 - x, y, 0.5 - z; (ii) x, -y, 0.5 + z; (iii) 1 - x, 1 - y, -z.

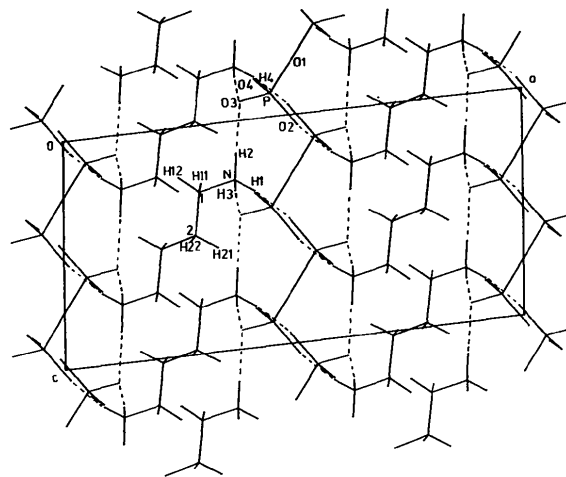


Fig. 2. Crystal packing viewed along **b**. Hydrogen bonds are indicated by broken lines.

staggered conformation about the P—P axis. A similar conformation of the diphosphate anion has been found in $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ (Collin & Willis, 1971). The central P—O—P bridge angle is 134.3 (1) $^\circ$, very similar to the value of 136.1 (1) $^\circ$ found in sodium dihydrogendiphosphate hexahydrate (Collin & Willis, 1971).

The $-\text{NH}_3^+$ group of the cation uses its N—H donors to form three nearly identical medium strong H bonds with three different anions (Table 3). Only the 'unsubstituted' O atoms of the dihydrogendiphosphate anion act as H-bond acceptors: O(3) accepts two H bonds from two different putrescine cations while O(2) accepts one H bond from the cation and one from the O(4)H donor in the anion across the inversion center. Taking into account the different properties of the NH and OH donors in Table 3, the two acceptor centers on the $\text{H}_2\text{P}_2\text{O}_7^{2-}$ group can be characterized as being involved in very similar H-bond interactions. Through H bonds, the anions and cations are arranged into two-dimensional layers perpendicular to **b** (Fig. 2). There are no H bonds to link those layers along **b**. Within each layer, the two H bonds accepted by O(3) are arranged into infinite chains parallel to **c** (Fig. 2).

In the crystal packing, alternating layers of anions and cations parallel to **bc** can be recognized (Fig. 2).

The anion layers are located at $x = 0, 1/2, 1, \dots$, while the cation layers are at $x = 1/4, 3/4, 5/4, \dots$. All N—H...O hydrogen bonds are between adjacent layers while the O—H...O bond operates within the anionic layer linking two dihydrogendiphosphate groups across an inversion center into a dimer.

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Structure du Chlorure d'[(Ethoxy-2 phénoxy)méthyl]-2 Morpholinium: Chlorhydrate de Viloxazine

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Abstract. $C_{13}H_{20}NO_3^+ \cdot Cl^-$, $M_r = 272.5$, monoclinic, $P2_1/c$, $a = 10.102$ (3), $b = 5.551$ (2), $c = 23.918$ (7) Å, $\beta = 95.11$ (2)°, $V = 1336$ Å³, $Z = 4$, $D_x = 1.36$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 25.47$ cm⁻¹, $F(000) = 584$, room temperature, $R = 0.045$ for 1445 observed reflections. The title compound is an antidepressant. The 2-[(2-ethoxyphenoxy)methyl] group is planar and subtends an angle of 33 (1)° with the mean plane of the morpholine ring defined by the four C atoms.

Introduction. Des études sont actuellement menées au laboratoire sur des séries d'amino-2 Δ -2-oxazolines-1,3 diversement substituées (Jarry, Bosc, Ouhabi & Carpy, 1990; Bosc, Forfar, Jarry, Ouhabi, Léger & Carpy, 1990). Ces molécules subissent des tests en psychopharmacologie. La [(phényl-1 pipérazinyl-4) méthyl-5]amino-2 Δ -2-oxazoline-1,3 ou COR 3224*

s'est révélée être la molécule la plus active; elle possède un profil antidépresseur proche de celui de la viloxazine. Nous nous sommes alors tout naturellement intéressés à cette dernière dans le but de rechercher d'éventuelles analogies structurales ou électroniques avec la série du COR 3224. La structure cristalline de la viloxazine est rapportée dans ce travail.

Partie expérimentale. Cristaux incolores obtenus à partir d'un mélange d'alcools (PrOH + MeOH), dimensions 0,35 × 0,15 × 0,15 mm. Densité non mesurée. Paramètres de la maille et intensités obtenus à l'aide d'un diffractomètre automatique Enraf-Nonius CAD-4, monochromateur graphite, radiation Cu $K\alpha$, mode de balayage ω/θ ($0 < \theta < 65^\circ$). Paramètres cristallins affinés par moindres carrés à partir des valeurs de θ de 25 réflexions de l'espace. Aucune dérive d'intensité notée pendant la mesure; deux réflexions standards mesurées toutes les 90 min. 2156 réflexions indépendantes mesurées; $h, k, \pm l$; h de 0 à 11, k de 0 à 6, l de -28 à +28. 1445

* Le COR 3224 est développé par les Laboratoires SARGET, 33700 Mérignac, France. Il se trouve actuellement en phase 2 de l'étude clinique.