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Structure of Putrescinium Dinitrate*†‡

BY MARIUSZ JASKÓLSKI

Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6,
60–780 *Poznań, Poland*

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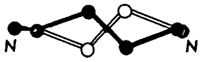
Abstract. $C_4H_{14}N_2^{2+}.2NO_3^-$, $M_r = 214{\cdot}2$, triclinic, $P\bar{1}$, $a = 8{\cdot}553$ (2), $b = 5{\cdot}507$ (1), $c = 10{\cdot}562$ (2) Å, $\alpha = 91{\cdot}08$ (2), $\beta = 92{\cdot}45$ (2), $\gamma = 102{\cdot}10$ (2)°, $V = 485{\cdot}8$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}464$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 1{\cdot}08$ mm^{-1}, $F(000) = 228$, $T = 291$ K, $R = 0{\cdot}060$ for 1229 observed reflexions. The unit cell contains two independent dications located on different inversion centers. One of them (I) has the extended all-*trans* zigzag conformation. Cation II has a partly folded *gauche*$^+$–*trans*–*gauche*$^-$ conformation and exists in the crystal in two alternative forms [73 (2)% form *A* and 27 (2)% form *B*] sharing common terminal C—NH_3^+ bonds. The two independent —NH_3^+ groups enter into similar patterns of H bonds. Each of them is bonded through relatively weak H bonds to three different NO_3^- groups. One of the N—H donors on each ammonium group forms a bifurcated H bond but only one of the nitrate ions accepts those bifurcated H bonds.

Introduction. Putrescine (1,4-butanediamine) is a linear aliphatic diamine present in all prokaryotic and eukaryotic cells. It is a biosynthetic precursor to both spermidine [$NH_2(CH_2)_3NH(CH_2)_4NH_2$] and spermine [$NH_2(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$]. It is now well recognized that these biogenic polyamines play a very important role in various biological processes, among which their stabilizing effect on secondary and tertiary structures of nucleic acids is particularly important. In normal conditions these amines exist as polycations which, by forming H bonds with nucleic-acid polyanions, influence their conformations. Being quite flexible, the polyamine cations can play a key role in the functional dynamic conformation of nucleic acids. This paper describes the crystal and molecular structure of putrescinium dinitrate. So far, the putrescinium dication (Put^{2+}) has been studied in the following salts: putrescinium di(diethylphosphate), $Put^{2+}.2[(EtO)_2PO_2^-]$ (Furberg & Solbakk, 1972), putrescinium diphosphate, $Put^{2+}.2(H_2PO_4^-)$ (Takusagawa & Koetzle, 1978; Woo, Seeman & Rich, 1979), putrescinium dichloride, $Put^{2+}.2Cl^-$ (Chandrasekhar & Pattabhi, 1980) and putrescinium hydrogen phosphate dihydrate, $Put^{2+}.HPO_4^{2-}.2H_2O$ (Jaskólski, Alejska & Wiewiórowski, 1986). Except in $Put^{2+}.HPO_4^{2-}.2H_2O$, the Put^{2+} dication was always found to be located on a crystallographic inversion center and thus exactly centrosymmetric. Even though not located on an inversion center, the Put^{2+} dication in $Put^{2+}.HPO_4^{2-}.2H_2O$ assumed a symmetric conformation with a non-crystallographic inversion center relating its chemically equivalent halves. In the two diphosphate salts [$Put^{2+}.2(EtO)_2PO_2^-$), $Put^{2+}.2H_2PO_4^-$] the Put^{2+} dication has a partly folded *gauche*$^+$–*trans*–*gauche*$^-$ (g^+tg^-) conformation while in the remaining two structures it exists in the fully extended all-*trans* zigzag conformation. The most interesting situation (from a conformational point of view) was reported for $Put^{2+}.2[(EtO)_2PO_2^-]$ where the cation is disordered and assumes two different centrosymmetric g^+tg^- forms located on a single inversion center. Those two forms share common C—N^+ termini but their central C—C bridges are different and cross at the inversion center (see sketch). Furberg & Solbakk (1972) did not attempt to determine the proportion of those two alternative forms of the dication but refined the structure assuming 0·5 occupancies for each. The above brief survey can be taken to indicate that the Put^{2+} cation is flexible and can assume different conformations and that in all situations it tends to retain its potential center of symmetry. The aim of this paper was to study the conformation and interactions of Put^{2+} in a completely new environment and to provide further data to verify the above conclusions. NO_3^- was chosen as the counter-ion since its properties are drastically different from those of the anions used so far (Cl^-, phosphates) and since it is rather uncommon as the anion in ionic organic structures.



Experimental. Suitable crystals from ethanol/water solution. Crystal 0·2 × 0·45 × 0·5 mm, Syntex $P2_1$

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* Systematic name: 1,4-butanediammonium dinitrate.

† Studies of Biogenic Polyamines. II. Part I: Jaskólski, Alejska & Wiewiórowski (1986).

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diffractometer, graphite monochromator, Cu *Kα* radiation. Cell parameters from least-squares treatments of setting angles of 15 reflexions ($19 \leq 2\theta \leq 30°$). θ:2θ profiles measured and analysed according to Lehmann & Larsen (1974). The intensity data were collected twice: (I) The intensities of two check reflexions remeasured every 1·5 h were constantly increasing during the 16·5 h of data collection; intensity increase: $\bar{2}10$ 12·3%, $\bar{1}0\bar{2}$ 10·3%. The crystal was then exposed for several hours to the X-ray beam. The check reflexions were remeasured over that period from time to time. Their intensities were still increasing but the rate of increase became slower near the end of irradiation. The second data set was then collected, (II). During the 18·8 h of data collection the intensity of $\bar{2}10$ increased by 4·1% and of $\bar{1}0\bar{2}$ by 3·3%. At that stage it was decided that the intensity stability achieved in (II) was sufficient for structure determination. Data set (I) was rejected and in the following only data set (II) was considered. The data were not corrected for intensity variation since there was no unique pattern of intensity changes: for some strong reflexions (*e.g.* $20\bar{1}$) an intensity decrease was detected. 1317 unique $+h\pm k\pm l$ reflexions collected with $2\theta \leq 115°$ ($0 \leq h \leq 9, -6 \leq k \leq 5, -11 \leq l \leq 11$). No absorption or extinction correction. 1233 observed reflexions with $I \geq 1{\cdot}96\sigma(I)$. Structure solved by direct methods using *SHELX76* (Sheldrick, 1976). H atoms generated geometrically. Full-matrix least-squares refinement on *F*, unit weights. Final refinement: anisotropic non-H atoms; orientation of rigid $-NH_3$ groups; methylene H atoms riding on their C atoms; isotropic temperature factors for H atoms, one value for each group of atoms attached to a common heavy atom, except for $U_{\rm iso}$ of H atoms at C(23*A*) and C(23*B*) which were fixed at 0·06 Å^2; occupancy factor for the disordered alternatives of cation (II); C—C bonds in the disordered cation (II) constrained to 1·54 Å; four strong reflexions ($11\bar{1}$, 111, $21\bar{2}$, 103) judged to suffer seriously from extinction removed from the data set; final refinement of 148 parameters using 1229 reflexions and four constraints converged at $R = 0{\cdot}060$ and $wR = 0{\cdot}063$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}18$, largest peak in final ΔF map = 0·29, largest trough = −0·26 e Å^{-3}. Computer programs: *SHELX76* and local programs (Jaskólski, 1982), molecular illustrations drawn using *ORTEP* (Johnson, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N(11)	0·2828 (4)	−0·2245 (6)	0·6122 (3)	0·038 (1)
C(12)	0·2050 (4)	−0·0130 (7)	0·5784 (4)	0·038 (1)
C(13)	0·0402 (4)	−0·1090 (7)	0·5156 (4)	0·039 (1)
N(21)	0·2501 (4)	0·0879 (7)	0·1306 (3)	0·050 (1)
C(22)	0·3146 (5)	0·1539 (8)	0·0053 (4)	0·055 (2)
C(23*A*)	0·4195 (3)	−0·0243 (9)	−0·0386 (4)	0·044 (3)
C(23*B*)	0·4918 (5)	0·1366 (2)	0·003 (2)	0·055 (6)
N(10)	0·4189 (4)	0·6124 (6)	0·3294 (3)	0·041 (1)
O(11)	0·4204 (3)	0·8394 (5)	0·3428 (3)	0·047 (1)
O(12)	0·5028 (4)	0·5348 (6)	0·2514 (3)	0·066 (1)
O(13)	0·3291 (4)	0·4629 (6)	0·3955 (3)	0·074 (2)
N(20)	−0·0026 (4)	0·5163 (7)	0·8285 (3)	0·043 (1)
O(21)	0·0450 (4)	0·7462 (6)	0·8225 (3)	0·059 (1)
O(22)	−0·1307 (3)	0·4341 (5)	0·8806 (3)	0·056 (1)
O(23)	0·0761 (4)	0·3758 (7)	0·7819 (3)	0·077 (2)

Discussion. Atomic coordinates are listed in Table 1.* The centrosymmetric unit cell contains two independent cations located on different inversion centers and two nitrate anions in general positions. One of the centrosymmetric dications (I), located at $00\tfrac{1}{2}$, has the extended all-*trans* zigzag conformation. Cation II, located at $\tfrac{1}{2}00$, has a partly folded *gauche*$^+$–*trans*–*gauche*$^-$ conformation and exists in the crystal in two alternative g^+tg^- forms sharing common terminal C(22)—N(21)$^+$ bonds (Figs. 1, 2). The disordered atom is C(23) and in consequence there are two alternative C—C—C—C fragments of cation II [C(22)—C(23*A*)—C(23*A*′)—C(22′) and C(22)—C(23*B*)—C(23*B*′)—C(22′)] which cross at the $\tfrac{1}{2}00$ crystallographic inversion center. The mode of disorder of cation II is analogous to that reported for the Put^{2+} dication in putrescinium di(diethylphosphate) (Furberg & Solbakk, 1972; see *Introduction*). In contrast to the approach adopted by Furberg & Solbakk (occupancies of the two forms fixed at 0·5), the occupancies (k and $1-k$) of the two alternatives (*A* and *B*) of cation II have been subject to refinement and converged at $k = 0{\cdot}73$ (2). At the present moment it is not possible to decide the character of the disorder. It is also an intriguing question how sensitive the *A*:*B* ratio is to such factors as temperature, radiation *etc.* If the proportion *A*:*B* could easily change during the time of data collection then one could hope to find an explanation of the curious behavior of the intensities described in the *Experimental* section. Further studies of these questions are in progress.

The dimensions of the Put^{2+} dications (Table 2) are comparable with the values found in other aliphatic polyamine cations. The C—C bond distances in the disordered cation II have been constrained during the refinement to 1·540 Å. Cation I has a nearly ideal all-*trans* conformation while the conformation of both forms of cation II (*A* and *B*) is distorted by *ca* 15° from the ideal *gauche* (60°) situation. The nitrate anions have typical dimensions (Table 2) and are planar with χ^2 2·0 [N(10)] and 1·9 [N(20)]. They are roughly

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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 43998 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parallel, the angle between their best planes being 17·0 (4)°.

The two independent $-NH_3^+$ groups enter into rather similar patterns of H-bond interactions. Each of them is bonded through relatively weak H bonds to three different NO_3^- groups. One of the N—H donors on each ammonium group forms a bifurcated H bond but only one of the nitrate ions accepts these bifurcated H bonds (Fig. 2, Table 3). Owing to these bifurcated bonds, each of the $-NH_3^+$ ammonium groups is surrounded by four H-bond acceptors, in contrast to the suggestion by Woo, Seemann & Rich (1979) that such groups should tend to interact with three electron-rich atoms arranged on an equilateral triangle. One of the nitrate ions accepts as many as five H bonds (two, two and one at each O atom) while the other accepts three such bonds (one, one, one).

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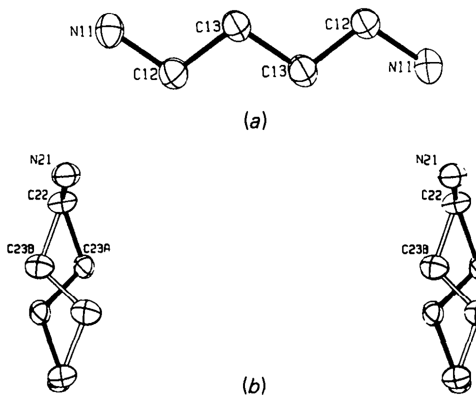

Fig. 1. Putrescinium dinitrate: (*a*) perspective view of cation I and (*b*) stereoview of cation II. H atoms are not shown.

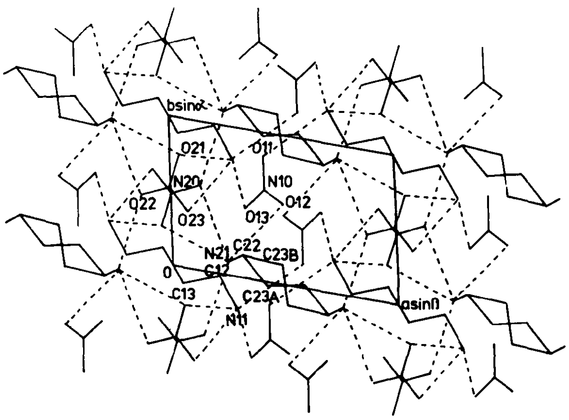

Fig. 2. Crystal packing viewed along **c**. H atoms have been omitted for clarity. Broken lines represent H bonds.

Table 2. *Bond distances* (Å), *angles* (°) *and torsion angles* (°)

N(11)—C(12)	1·499 (5)	N(21)—C(22)	1·478 (6)
C(12)—C(13)	1·516 (5)	C(22)—C(23*A*)	1·540*
C(13)—C(13^{i})	1·538 (6)	C(22)—C(23*B*)	1·540*
N(10)—O(11)	1·253 (5)	C(23*A*)—C(23*A*^{ii})	1·540*
N(10)—O(12)	1·242 (5)	C(23*B*)—C(23*B*^{ii})	1·540*
N(10)—O(13)	1·248 (5)	N(20)—O(21)	1·249 (5)
		N(20)—O(22)	1·249 (5)
		N(20)—O(23)	1·235 (5)

N(11)—C(12)—C(13)	110·6 (3)	O(11)—N(10)—O(12)	121·5 (3)
C(12)—C(13)—C(13^{i})	110·2 (3)	O(11)—N(10)—O(13)	118·5 (3)
N(21)—C(22)—C(23*A*)	111·6 (3)	O(12)—N(10)—O(13)	120·0 (3)
N(21)—C(22)—C(23*B*)	110·9 (6)	O(21)—N(20)—O(22)	118·8 (3)
C(22)—C(23*A*)—C(23*A*^{ii})	110·8 (3)	O(21)—N(20)—O(23)	119·7 (3)
C(22)—C(23*B*)—C(23*B*^{ii})	110·8 (3)	O(22)—N(20)—O(23)	121·5 (3)

N(11)—C(12)—C(13)—C(13^{i})	178·6 (3)
N(21)—C(22)—C(23*A*)—C(23*A*^{ii})	−72·5 (4)
N(21)—C(22)—C(23*B*)—C(23*B*^{ii})	74 (1)

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

* Constrained.

Table 3. *Geometry of the hydrogen bonds*

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	∠*D*—H···*A* (°)
N(11)—H(111)···O(11^{i})	1·08	1·98	2·961 (4)	149
N(11)—H(112)···O(13^{ii})	1·08	1·85	2·928 (5)	174
N(11)—H(113)···O(21^{ii})	1·08	2·25	3·060 (4)	130
N(11)—H(113)···O(23^{ii})	1·08	2·11	3·158 (5)	164
N(21)—H(211)···O(12)	1·08	2·23	3·126 (5)	139
N(21)—H(212)···O(22^{iii})	1·08	1·79	2·840 (5)	163
N(21)—H(213)···O(21^{iv})	1·08	1·86	2·916 (5)	166
N(21)—H(213)···O(22^{iv})	1·08	2·21	3·019 (5)	130

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

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