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Redetermination of the Structure of Putrescine Dihydrochloride

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Abstract. $C_4H_{14}N_2^{2+}.2Cl^-$, $M_r = 161·1$, monoclinic, $P2_1/c$, $a = 4·589$ (2), $b = 8·349$ (3), $c = 10·729$ (4) Å, $\beta = 92·54$ (2)°, $V = 410·7$ Å^3, $Z = 2$, $D_m = 1·31$ (1), $D_c = 1·305$ Mg m^{-3}, μ(Cu $K\alpha$) = 6·44 mm^{-1}; $R = 0·064$. The amino groups are protonated and N–H···Cl hydrogen bonds are observed.

Introduction. Putrescine, derived from the decarboxylation of ornithine, is one of the most active of a series of polyamines that are essential growth factors for a number of micro-organisms. The structure of its dihydrochloride (PDH) has been investigated by Ashida & Hirokawa (1963*b*) with 190 visually estimated intensities. They have not corrected for absorption, have quoted no e.s.d.'s except in the cell parameters and have refined isotropically only the zonal reflections *h*0*l* and *hk*0. In view of the marked biological importance of putrescine, we have redetermined the structure of PDH as part of a continuing programme in our laboratory on the structure and conformation of polyamines.

681 independent non-zero intensities were collected by counter methods with a θ–2θ scan and Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å). The data were corrected for Lorentz and polarization effects, and for absorption (North, Phillips & Mathews, 1966).

The position of Cl was determined from a Patterson map ($R = 0·403$) and a Cl-phased difference synthesis revealed the other non-hydrogen atoms ($R = 0·187$). Refinement by block-diagonal least-squares techniques (Shiono, 1968) with unit weights for all reflections reduced R to 0·088. The H atoms were then located from a difference map and assigned the isotropic temperature factors of the atoms to which they are attached. Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961) with anisotropic thermal parameters for the non-hydrogen atoms and Hughes's (1941) weighting ($1/\sqrt{w} = 1$ for $F_o < 28$, and $F_o/28$ otherwise) led to a final R of 0·064.

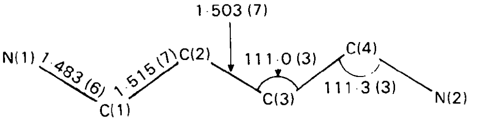

Fig. 1. Bond lengths (Å) and angles (°) in the putrescinium ion.

Table 1. *Fractional positional* (×10^4 *for non-hydrogen atoms*, ×10^3 *for hydrogen atoms*) *and isotropic thermal parameters, with e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B (Å^2)
Cl(1)	3748 (3)	995 (1)	1586 (1)	2·49 (5)*
N(1)	1164 (9)	3290 (5)	3736 (3)	2·49 (16)*
C(1)	−761 (10)	2053 (6)	4254 (4)	2·29 (20)*
C(2)	978 (10)	619 (6)	4729 (4)	2·33 (18)*
H1(N1)	10	409	352	2·47
H2(N1)	227	293	308	2·47
H3(N1)	212	350	429	2·47
H1(C1)	−171	188	375	2·24
H2(C1)	−183	251	485	2·24
H1(C2)	198	19	406	2·23
H2(C2)	221	83	536	2·23

* $B_{eq} = \frac{4}{3}\sum_i\sum_j(\mathbf{a}_i.\mathbf{a}_j)\beta_{ij}$, with $\sigma(B_{eq}) = \frac{4}{3}\sum_i\sum_j(\mathbf{a}_i.\mathbf{a}_j)\sigma(\beta_{ij})$.

The H-atom parameters were not refined. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and an anomalous-dispersion correction was applied for Cl (Cromer & Liberman, 1970). A final difference map showed no extraneous peaks.

The final atomic positions and thermal parameters are given in Table 1,† bond lengths and angles in Fig. 1.

Discussion. The gross features of the structure are in accord with those reported by Ashida & Hirokawa (1963*b*). A comparison of the bond lengths and angles with those in some relevant studies is presented in Table 2. The two N atoms are displaced from the plane of the four C atoms by only ±0·022 (4) Å, so that the entire charged molecule of putrescine is zigzag planar making angles of 25·8, 83·9 and 64·5° with the *ab*, *bc* and *ca* planes respectively. The amino groups are protonated and the three H atoms are staggered when viewed along the C–N bond.

A projection of the crystal structure down **a** is shown in Fig. 2 and the short N···Cl approaches are in Table 3. Donohue (1952) has indicated that in crystals containing N^+H_3 groups and Cl^- ions, the occurrence

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* Contribution No. 519.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35404 (4 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 2. *Bond lengths* (Å) *and angles* (°) *in PDH and some other relevant compounds with e.s.d.'s in parentheses*

	Average bond lengths		Average bond angles		
	C–N	C–C	∠N–C–C	∠C–C–C	Reference
(1) (–)-Lysine monohydrochloride dihydrate	1·482 (4)	1·524 (3)	110·8 (2)	111·7 (2)	Wright & Marsh (1962)
(2) Putrescine diphosphate (X-ray study)	1·4915 (9)	1·5265 (7)	111·79 (3)	113·95 (4)	Takusagawa & Koetzle (1979)
(3) Putrescine diphosphate (neutron study)	1·4921 (10)	1·5266 (11)	111·75 (5)	113·87 (5)	Takusagawa & Koetzle (1978)
(4) Spermidine phosphate trihydrate	1·488 (15)	1·523 (17)	110·6 (7)	109·1 (7)	Huse & Iitaka (1969)
(5) Spermine phosphate hexahydrate	1·498 (10)	1·526 (13)	112·0 (6)	108·9 (7)	Huse & Iitaka (1969)
(6)* Spermine tetrahydrochloride	1·496 (9)	1·522 (10)	111·9 (5)	109·9 (5)	Giglio *et al.* (1966*a*)
(7) Spermidine trihydrochloride	1·480 (12)	1·512 (13)	111·4 (9)	111·9 (9)	Giglio *et al.* (1966*b*)
(8) Hexamethylenediammonium adipate	1·50 (5)	1·54 (5)	110 (5)	110 (5)	Hirokawa, Ohashi & Nitta (1954)
(9) Hexamethylenediamine dihydrochloride	1·52	1·51	112	112	Binnie & Robertson (1949)
(10) Ethylenediammonium bromide	1·46 (1)	1·53 (2)	112·7 (9)	–	Søtofte (1976)
(11) Ethylenediammonium chloride	1·49	1·53	109·8	–	Ashida & Hirokawa (1963*a*)
(12) Putrescine dihydrochloride	1·50	1·51	110·0	110·0	Ashida & Hirokawa (1963*b*)
(13) Putrescine dihydrochloride	1·483 (6)	1·509 (7)	111·3 (3)	111·0 (3)	Present study

* Spermine in this structure has a *t–t–t–g–t–t–t–g–t–t–t* conformation, while all the others form normal extended chains.

of four short N$\cdots$Cl distances is a common feature; three may be ascribed to hydrogen-bond formation, and the fourth, a short contact directed approximately along the extension of the C–N bond, to packing requirements due to the size of the Cl^- ions. In PDH three of the C–N$\cdots$Cl angles (Table 3) are close to the tetrahedral value to allow normal hydrogen-bond formation while the C–N$\cdots$Cl(1)(*d*) angle of 163·4 (4)° is too high to merit similar consideration. The N(1)–H1(N1)$\cdots$Cl(1)(*d*) angle of 84·7° also seems too low for N(1)$\cdots$Cl(1)(*d*) to be considered a bifurcated hydrogen bond.

The molecule forms an infinite layered structure perpendicular to **a**. The putrescinium ions are held in sheets by van der Waals forces; the Cl atoms form rows between the sheets and are joined to the protonated amino groups through hydrogen bonds.

The hydrogen-bonding scheme is different from that in spermine tetrahydrochloride (Giglio, Liquori, Puliti & Ripamonti, 1966*a*) where the four short N$\cdots$Cl distances can be considered in pairs, two being normal hydrogen bonds and the other two possibly bifurcated hydrogen bonds. Further, the arrangement of Cl^- ions surrounding each N in PDH is remarkably similar to

Table 3. *Short* N$\cdots$Cl *approaches, with e.s.d.'s in parentheses*

Symmetry code

(*a*) x, y, z

(*b*) $-x, \frac{1}{2}+y, \frac{1}{2}-z$

(*c*) $x, \frac{1}{2}-y, \frac{1}{2}+z$

(*d*) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$

A	H	*B*	*A*$\cdots$*B* (Å)	H$\cdots$*B* (Å)	∠C(1)–*A*$\cdots$*B* (°)	∠*A*–H$\cdots$*B* (°)
N(1)	H2(N1)	Cl(1)(*a*)	3·262 (4)	2·400	95·6 (3)	154·0
N(1)	H1(N1)	Cl(1)(*b*)	3·199 (4)	2·374	95·9 (3)	161·8
N(1)	H3(N1)	Cl(1)(*c*)	3·285 (4)	2·576	88·5 (3)	159·9
N(1)	H1(N1)	Cl(1)(*d*)	3·278 (4)	3·244	163·4 (4)	84·7

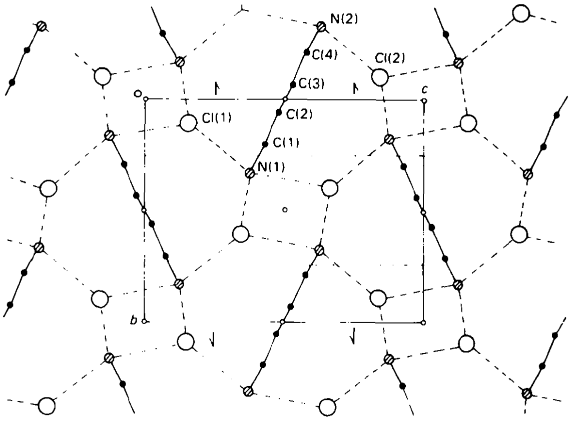

Fig. 2. Projection of the structure down **a**. Hydrogen bonds are indicated by broken lines.

Table 4. *Inter-chlorine distances* (Å) *with e.s.d.'s in parentheses*

Symmetry code

(*a*) x, y, z

(*b*) $-x, \frac{1}{2}+y, \frac{1}{2}-z$

(*c*) $x, \frac{1}{2}-y, \frac{1}{2}+z$

(*d*) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$

(*e*) $-x, -y, 1-z$

(*f*) $x, -\frac{1}{2}-y, \frac{1}{2}+z$

(*g*) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$

(*h*) $-1+x, -\frac{1}{2}-y, \frac{1}{2}+z$

Cl(*a*)–Cl(*b*)	5·806 (2)	Cl(*b*)–Cl(*f*)	11·072 (4)
Cl(*a*)–Cl(*c*)	5·924 (2)	Cl(*b*)–Cl(*g*)	8·349 (3)
Cl(*a*)–Cl(*d*)	4·732 (2)	Cl(*b*)–Cl(*h*)	10·652 (4)
Cl(*a*)–Cl(*e*)	8·396 (3)	Cl(*c*)–Cl(*d*)	4·001 (2)
Cl(*a*)–Cl(*f*)	7·927 (2)	Cl(*c*)–Cl(*g*)	8·192 (3)
Cl(*a*)–Cl(*h*)	9·278 (3)	Cl(*c*)–Cl(*h*)	9·527 (3)
Cl(*b*)–Cl(*c*)	5·014 (2)	Cl(*d*)–Cl(*h*)	12·102 (4)
Cl(*b*)–Cl(*d*)	4·589 (3)		

that of the N atoms surrounding each Cl^- ion in spermidine trihydrochloride (Giglio, Liquori, Puliti & Ripamonti, 1966*b*).

Woo, Seeman & Rich (1979) find a *gauche–trans* conformation for putrescine in the diphosphate. They point out that while in such a conformation the putrescine molecule can fit across the major groove of both A-RNA and ApU-RNA but cannot bridge the DNA helix, in the all-*trans* conformation it can bridge the DNA double helix as well as RNA helices, forming two hydrogen bonds in each case. Indeed, we do find an all-*trans* conformation for putrescine in PDH. In this context, the distances between the eight Cl^- ions surrounding each putrescine molecule may be of interest and these are listed in Table 4.

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Bis(4-nitrophenyl) Ketone

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Abstract. $C_{13}H_8N_2O_5$, triclinic, $P\bar{1}$, $a = 7{\cdot}323$ (2), $b = 12{\cdot}634$ (4), $c = 13{\cdot}301$ (3) Å, $\alpha = 89{\cdot}37$ (2), $\beta = 86{\cdot}75$ (2), $\gamma = 87{\cdot}09$ (3)°, $Z = 4$, $d_c = 1{\cdot}463$, $d_m = 1{\cdot}46$ Mg m^{-3}. $R = 0{\cdot}037$ for 1385 observations measured by diffractometer. The two independent molecules of the asymmetric unit exist in approximate C_2 conformations, with the aromatic rings tipped an average of 28° out of the plane of the ketone unit. The nitro substituents are essentially coplanar with the aromatic rings. The formula given above has been definitively determined by crystallographic tests as well as other physical and spectral techniques.

Introduction. The recent discovery of a facile means of decarbonylation (Newkome & Taylor, 1979) led us to attempt the synthesis of cyclobuta[1,2-*b*:4,3-*b*′]dipyridine (I) from 1,8-diazafluorenone (II) by treatment with sodium hydride in xylene.

(II) (I)

Rather than the anticipated compound, chemical decarbonylation produced predominantly an uncharacterized black material. Also isolated from the reaction mixture was a minute quantity of pale-yellow needles

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