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The Crystal and Molecular Structure of (±)-Octopamine Hydrochloride

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The hydrochloride of octopamine [α-(aminomethyl)-p-hydroxybenzyl alcohol] crystallizes in the monoclinic space group $P2_1/c$ with $a = 10{\cdot}73\,(1)$, $b = 8{\cdot}50\,(1)$, $c = 10{\cdot}58\,(1)$ Å, $\beta = 106{\cdot}1\,(1)^\circ$, $Z = 4$. The structure was refined by least squares to R 7·6% for 416 observed counter amplitudes. Estimated standard deviations for bond lengths, bond angles and torsion angles average 0·02 Å, 1·5 and 2·0°. The ethanolamine side chain is in the extended conformation, the C—C—C—N$^+$ torsion angle being 171°. The best plane through these atoms makes an angle of 79° with the plane of the phenyl ring.

Introduction

Octopamine, α-(aminomethyl)-p-hydroxybenzyl alcohol, a biogenic amine closely related to noradrenaline was first discovered in the posterior salivary gland of the octopus (Erspamer, 1952) and was subsequently identified in urine from several mammalian species (Kakimoto & Armstrong, 1962). More recently, octopamine has been found in sympathetically innervated mammalian organs (Molinoff & Axelrod, 1969), in a number of other molluscs (Juorio & Molinoff, 1974; Saavedra, Brownstein, Carpenter & Axelrod, 1974; Roseghini & Alcala, 1976), and in the insect nervous system (Robertson, 1976; Robertson & Carlson, 1976). In anaesthetized dogs and cats it produces sympathomimetic cardiovascular effects, although it is markedly less potent than noradrenaline (Kappe & Armstrong, 1964). The physiological role of octopamine is not known with certainty, but it has been suggested (Saavedra *et al.*, 1974; Robertson & Carlson, 1976) that in invertebrate nervous systems it may act as a neurotransmitter.

We now report the crystal structure analysis of (±)-octopamine hydrochloride. It was hoped that by comparing its structure with those of the sympathomimetic catecholamines, whose structures have previously been determined (Carlström, Bergin & Falkenberg, 1973; Giesecke, 1976), a stereochemical basis for the differences in biological function might be obtained. The results of the present analysis, however, show that in the solid state, octopamine adopts a conformation which is virtually identical to that found for noradrenaline (Carlström & Bergin, 1967). Most of the related catecholamines whose structures are known also adopt similar conformations (Carlström *et al.*, 1973).

Experimental

Crystals suitable for X-ray analysis were kindly supplied by Dr R. A. Thornhill of the Department of Zoology, Birmingham University. After initial examination by photographic methods final cell dimensions and intensities were measured on a Stoe two-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The crystal, 0·5 × 0·15 × 0·05 mm, was mounted about the direction of elongation (**c**). With the diffractometer operating in the ω-scan mode, 140 counts of 1 s at intervals of 0·01° were taken for each reflexion on layers 0–2. For reflexions on the third and higher layers, the peak scan was defined by the expression $(A + B \sin \mu/\tan \theta')^\circ$ where μ is the equi-inclination angle and θ' is half the azimuth angle. The constants A and B were assigned the values 1·2 and 0·5°, respectively. Backgrounds were measured for 30 s at each end of the scan. Reflexions were scanned within the range $0{\cdot}1 < \sin\theta/\lambda < 0{\cdot}54$ and, of these, 416 $[I > 2{\cdot}5\sigma(I)]$ were considered observed and used in the structure analysis. In the conversion of intensities to structure amplitudes, the polarization factor appropriate to monochromated radiation was used. Absorption corrections were not applied.

Crystal data

$C_8H_{11}NO_2.HCl$, M_r = 189·64. Monoclinic, a = 10·73 (1), b = 8·50 (1), c = 10·58 (1) Å, β = 106·1 (1)°, U = 927·2 Å^3, Z = 4, D_c = 1·358 g cm^{-3}, $F(000)$ = 400. Systematic absences: $0k0$, k odd; $h0l$, l odd; space group $P2_1/c$. Mo $K\alpha$ radiation, λ = 0·71069 Å; μ(Mo $K\alpha$) = 3·2 cm^{-1}.

Determination of the structure

The structure was solved by direct methods (Karle & Karle, 1966) with the *SHELX* programs (Sheldrick, 1975). Phases (0 or 180°) were assigned to 240 reflexions with $E > 1 \cdot 2$ and from the E map all the atoms in the asymmetric unit (apart from H atoms) could be located. Least-squares refinement of positional and isotropic thermal parameters reduced R to 11·1%. Further refinement with first the Cl ion and then the remaining atoms allowed to vibrate anisotropically resulted in an R of 9·5%. At this stage all the H atoms, except those linked to the O atoms, were introduced in calculated positions and the anisotropic refinement of the heavier atoms continued until all shifts were $<0 \cdot 1\sigma$ and R was 7·6% for the 416 observed structure amplitudes. Attempts to locate the alcohol and phenol H atoms from a difference synthesis were not successful. Final atomic parameters are listed in Table 1.*

The weighting scheme was $w = 1/[\sigma^2(F) + 0 \cdot 0006F^2]$ where $\sigma(F)$ is the standard deviation in the observed $|F(hkl)|$ values derived from counting statistics.

Computations were carried out on the Birmingham University 1906A computer with the *SHELX* system of programs (Sheldrick, 1975), together with ancillary programs written by Dr J. J. Guy and TAH.

Table 1. *Fractional atomic coordinates* (×10^4)

	x	*y*	*z*
C(1)	−1424 (13)	1567 (19)	5442 (15)
C(2)	−636 (15)	2611 (19)	5080 (18)
C(3)	662 (13)	2727 (18)	5692 (16)
C(4)	1231 (15)	1748 (19)	6698 (21)
C(5)	472 (15)	700 (20)	7189 (19)
C(6)	−847 (14)	595 (19)	6507 (18)
C(7)	−2874 (13)	1523 (16)	4760 (16)
C(8)	−3583 (14)	2439 (16)	5589 (19)
N	−4999 (12)	2593 (15)	4782 (16)
O(1)	2561 (9)	1827 (12)	7420 (12)
O(2)	−3389 (9)	−56 (11)	4645 (11)
Cl	4113 (4)	4599 (5)	6847 (4)
H[C(2)]	−1054	3392	4269
H[C(3)]	1239	3601	5373
H[C(5)]	884	−3	8054
H[C(6)]	−1438	−271	6816
H[C(7)]	−2988	2008	3791
H^1[C(8)]	−3149	3586	5826
H^2[C(8)]	−3538	1807	6486
H^1[N]	−5537	3232	5337
H^2[N]	−5419	1433	4547
H^3[N]	−5030	3212	3887

Table 2. *Molecular dimensions*

(*a*) Bond lengths (Å)

C(1)–C(2)	1·35 (2)	C(4)–O(1)	1·42 (2)
C(2)–C(3)	1·37 (2)	C(1)–C(7)	1·52 (2)
C(3)–C(4)	1·36 (2)	C(7)–O(2)	1·44 (1)
C(4)–C(5)	1·40 (2)	C(7)–C(8)	1·52 (2)
C(5)–C(6)	1·40 (2)	C(8)–N	1·53 (2)
C(6)–C(1)	1·40 (2)		

(*b*) Bond angles (°)

C(6)–C(1)–C(2)	116·4 (14)	C(4)–C(5)–C(6)	117·2 (17)
C(7)–C(1)–C(2)	121·3 (15)	C(5)–C(6)–C(1)	122·5 (15)
C(7)–C(1)–C(6)	122·3 (15)	C(1)–C(7)–C(8)	108·8 (12)
C(1)–C(2)–C(3)	123·3 (17)	O(2)–C(7)–C(1)	112·3 (12)
C(2)–C(3)–C(4)	120·4 (16)	O(2)–C(7)–C(8)	106·4 (11)
C(3)–C(4)–C(5)	120·0 (15)	C(7)–C(8)–N	107·5 (13)
O(1)–C(4)–C(3)	124·0 (16)		
O(1)–C(4)–C(5)	115·5 (17)		

(*c*) Selected torsion angles (°). Mean standard deviation 2·0°. Sign convention as defined by Klyne & Prelog (1960)

C(2)–C(1)–C(7)–C(8)	−98
C(6)–C(1)–C(7)–C(8)	79
C(2)–C(1)–C(7)–O(2)	145
C(6)–C(1)–C(7)–O(2)	−39
C(1)–C(7)–C(8)–N	171
O(2)–C(7)–C(8)–N	−67

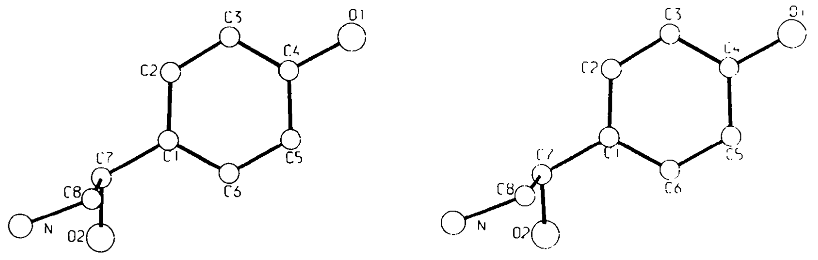

Fig. 1. Stereoscopic view of the octopamine cation.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32424 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results and discussion

Bond lengths, bond angles and torsion angles are listed in Table 2. Estimated standard deviations are *ca* 0·02 Å for lengths and 1·5 and 2·0° for bond and torsion angles. Fig. 1 shows a stereoscopic view of the cation in a direction perpendicular to the mean plane of the phenyl ring, and also indicates the numbering scheme.

Naturally occurring octopamine is optically active. The crystal used in the present analysis was, however, formed from a racemic sample and contains both enantiomers. Fig. 1 and the listed atomic coordinates refer to the enantiomer with the (*R*)-configuration at the chiral centre, C(7). This corresponds to the configuration of naturally occurring (−)-noradrenaline (Pratesi, La Manna, Campiglio & Ghislandi, 1959), natural (−)-octopamine having the same absolute configuration (Erspamer, 1952; Kappe & Armstrong, 1964).

Bond lengths and angles are normal. The phenyl ring is planar to within ±0·03 Å (Table 3) and O(1) and C(7) lie close to the plane of the ring. The ethylamine chain is in the extended conformation; C(1), C(7), C(8) and N are coplanar to within ±0·06 Å. The angle between this plane and the plane of the phenyl ring is 79°.

In terms of rotations about single bonds the conformation of the octopamine cation can be described by C(1)—C(7)—C(8)—N and C(2)—C(1)—C(7)—C(8), defining, respectively, the conformation of the side chain and the orientation of the side chain relative to the aromatic ring. Related to the latter is the torsion angle C(2)—C(1)—C(7)—O(2) which describes the position of the alcohol O atom relative to the aromatic ring. In the present structure, these torsion angles are 171, −98 and 145°. In (−)-noradrenaline hydrochloride (Carlström & Bergin, 1967) the corresponding values are 176, −97 and 147° (Carlström *et al.*, 1973). The conformations of the octopamine and noradrenaline cations are, therefore, virtually identical in the solid state. Phenethylamine (Tsoucaris, 1961), epinine (Giesecke, 1976) and most of the related sympathomimetic amines reviewed by Carlström *et al.* (1973) also adopt similar conformations. The O(2)—C(7)—C(8)—N torsion angle is −67°, a common conformation for O—C—C—N$^+$ groupings.

Table 3. *Mean-plane calculations*

Deviations (Å) of atoms from least-squares planes. In the equations of the planes *x*, *y*, and *z* are fractional coordinates relative to the cell axes.

Plane (i)

C(1)–(6) $4\cdot016x - 5\cdot807y - 7\cdot472z = -5\cdot558$

C(1)	−0·01,	C(2)	0·01,	C(3)	0·01,	C(4)	−0·03,
C(5)	0·03,	C(6)	−0·01,	O(1)	0·02,	C(7)	0·04,
O(2)	−0·76,	C(8)	1·47,	N	1·53		

Plane (ii) C(1), C(7), C(8), N

$3\cdot059x + 7\cdot229y - 5\cdot330z = -2\cdot258$

C(1)	−0·06,	C(7)	0·06,	C(8)	0·05,	N	−0·05

Dihedral angle: plane (i)–plane (ii) 79°

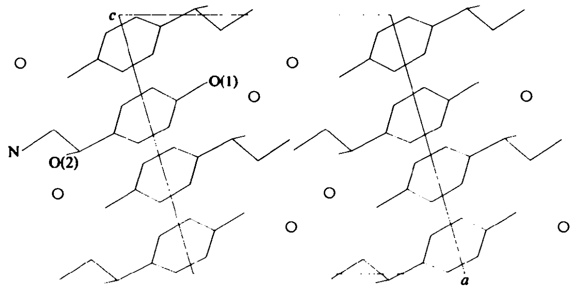

Fig. 2. The crystal structure projected along y. Circles denote chloride ions.

Table 4. *The shorter intermolecular contact distances, excluding hydrogen atoms* (Å)

N···O(2$^{\mathrm{i}}$)	2·93	O(2)···C(4$^{\mathrm{ii}}$)	3·36
O(2)···O(1$^{\mathrm{ii}}$)	2·99	O(2)···Cl$^{\mathrm{vi}}$	3·42
O(1)···Cl	3·04	N···Cl$^{\mathrm{vi}}$	3·52
O(1)···N$^{\mathrm{iii}}$	3·12	C(8)···Cl$^{\mathrm{v}}$	3·54
N···Cl$^{\mathrm{iv}}$	3·12	C(8)···Cl$^{\mathrm{iv}}$	3·62
N···Cl$^{\mathrm{v}}$	3·24	C(4)···C(1$^{\mathrm{ii}}$)	3·66

Symmetry code

(i)	$-x-1, -y, -z+1$	(iv)	$x-1, y, z$
(ii)	$-x, -y, -z+1$	(v)	$-x, -y+1, -z+1$
(iii)	$x+1, -y+\frac{1}{2}, z+\frac{1}{2}$	(vi)	$x-1, -y+\frac{1}{2}, z-\frac{1}{2}$

The crystal packing is illustrated in Fig. 2 and the shorter intermolecular contact distances are in Table 4. The short contacts N···O(2$^{\mathrm{i}}$), 2·93; N···Cl$^{\mathrm{iv}}$, 3·12; N···Cl$^{\mathrm{v}}$, 3·24 Å probably involve hydrogen bonding. Assuming idealized positions for the onium H atoms, the pertinent distances are H^2[N]···O(2$^{\mathrm{i}}$), 2·08; H^1[N]···Cl$^{\mathrm{iv}}$, 2·09; H^3[N]···Cl$^{\mathrm{v}}$, 2·34 Å consistent with hydrogen bonding. The O(1)···Cl contact of 3·04 Å presumably also involves hydrogen bonding. The alcohol H atom, however, does not appear to take part in any strong interaction.

We thank Dr R. A. Thornhill for suggesting this problem, Professors J. C. Tatlow and J. C. Robb for their interest, the staff of the University Computer Centre for their assistance, and the University of Birmingham for funds to purchase the diffractometer.

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The Crystal and Molecular Structure of μ-(η^5:η^5-Fulvalene)-μ-hydrido-μ-hydroxyl-bis(η^5-cyclopentadienylmolybdenum) Hexafluorophosphate Hemihydrate

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The title complex crystallizes in the monoclinic space group $P2_1$ with $a = 10{\cdot}248\,(6)$, $b = 12{\cdot}814\,(7)$, $c = 9{\cdot}995\,(5)$ Å, $\beta = 107{\cdot}35\,(2)°$, $Z = 2$. The structure was determined from four-circle diffractometer data and refined by least-squares calculations to $R = 0{\cdot}073$ for 2004 reflexions. The cation consists of two Mo(η^5-C_5H_5) moieties which are bridged by the H atom, the hydroxyl ligand, and the pentafulvalene ligand, which is η^5-bonded to both Mo atoms.

Introduction

The working up of the reaction products from the treatment of the tetramer [Mo(η^5-C_5H_5)$_2$HLi]$_4$ (Francis, Green, Luong-thi & Moser, 1976) with nitrous oxide yields three compounds whose mass spectra and analytical data are identical and correspond to the stoichiometry $[C_{10}H_{10}Mo]_2$. Prolonged treatment of each of these compounds with aqueous HPF_6 gives the same compound, a brown crystalline solid of stoichiometry $C_{20}H_{21}F_{12}Mo_2O_{1\cdot5}P_2$ whose crystal structure we report. This work has been the subject of a preliminary publication (Green, Cooper, Couldwell & Prout, 1977).

Experimental

Brown needles of [Mo_2(η^5-C_5H_5)$_2$(μ-η^5-C_5H_4-η^5-C_5H_4)(μ-H)(μ-OH)]$2PF_6.\frac{1}{2}H_2O$, were kindly supplied by Dr N. J. Cooper and Dr M. L. H. Green. The compound is sensitive to air and moisture and was mounted under dry nitrogen in a glass capillary. It was not possible to measure its density.

After survey photography the selected crystal (0·13 × 1·5 × 0·06 mm) was set up on a Hilger & Watts PDP8-controlled four-circle diffractometer and cell dimensions and orientation matrix were obtained by least squares from the setting angles of 20 reflexions.

The intensity of each independent reflexion with $\sin\theta/\lambda < 0{\cdot}66$ was measured with an $\omega/2\theta$ scan and the ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 50 steps of 0·02°. Mo $K\alpha$ radiation from a graphite monochromator was used. Reflexions with $I < 3\sigma$, where σ is the standard deviation based on simple counting statistics, and whose apparent centre was more than 0·14° from the predicted position were excluded from subsequent calculations. Lorentz and polarization corrections were applied together with an empirical absorption correction (North, Phillips & Mathews, 1968) to yield a set of 2006 independent structure amplitudes.

Crystal data

$C_{20}H_{21}F_{12}Mo_2O_{1\cdot5}P_2$, $M_r = 767{\cdot}2$. Monoclinic, $a = 10{\cdot}248\,(6)$, $b = 12{\cdot}814\,(7)$, $c = 9{\cdot}995\,(5)$ Å, $\beta =$