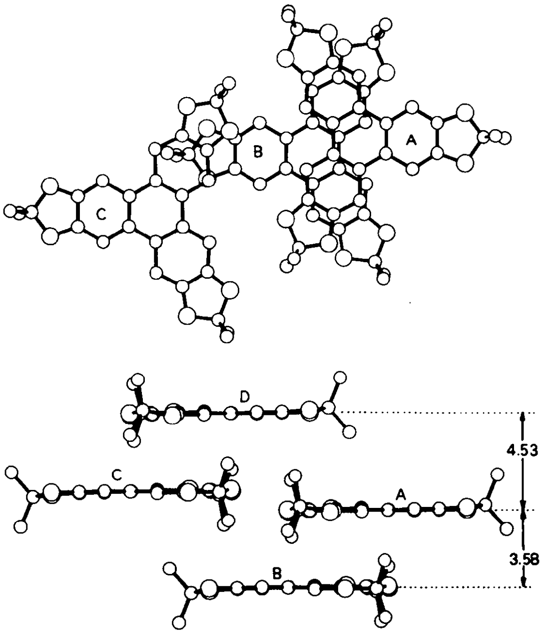

Fig. 3. The overlap. Upper: viewed perpendicular to the best plane of the center ring, lower: perpendicular to the upper view. Distances between the molecules in Å, e.s.d.'s 0·05 Å. Symmetry operations: *A* (*x*, *y*, *z*), *B* (−*x*, 2−*y*, −*z*), *C* (−*x*, 1−*y*, −*z*), *D* (*x*, 1+*y*, *z*).

and C(19) to C(27) and all O anisotropic, no attempt to locate the H atoms, 208 parameters refined, $R = 0{\cdot}076$, $wR = 0{\cdot}097$, $w = [\sigma^2(F_o) + 0{\cdot}0008F_o^2]^{-1}$, $(\Delta/\sigma)_{\max} = 0{\cdot}014$ in the final cycle, $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0{\cdot}33/-0{\cdot}24$ e Å^{-3}. Computer programs used are *SHELX*76 (Sheldrick, 1976) with atomic scattering factors, and *PLUTO* (Motherwell, 1978).

Discussion. Final positional and thermal parameters are given in Table 1, bond lengths and angles in Table 2.* The molecule with atomic labels is shown in Fig. 1. The distances from the best plane through C(1)—C(18) to C(19), C(22) and C(25) are 0·20, 0·03 and 0·18 Å, respectively. The three tetrahedra formed by two CH_3 groups and two O atoms around C(29), C(22) and C(25) are only slightly distorted. The angles between the normals to the best plane through C(1)—C(18) and the planes through the three benzene rings are 1·70, 1·85 and 1·46°, respectively. The angles between the normal to the molecular plane and **a**, **b** and **c** are 56·8, 59·8 and 67·1°, respectively. The packing is shown in Fig. 2, and the overlap in Fig. 3.

The molecules are not packed in regular segregated stacks. The overlap between two neighbouring molecules *A* and *B* in Fig. 3 does not indicate strong interaction.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51376 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Jørgensen, M., Bjørnholm, T. & Bechgaard, K. (1988). *Synthetic Metals*. In the press.

Miller, J. S., Epstein, A. J. & Reif, W. M. (1988). *Chem. Rev.* **88**, 201–220.

Motherwell, S. (1978). *PLUTO*. Program for plotting crystal and molecular structures. Univ. of Cambridge, England.

Piattelli, M., Fattorusso, E., Nicolaus, R. A. & Magno, S. (1965). *Tetrahedron*, **21**, 3229–3236.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1989). C**45**, 269–273

Structure of (4*S*,5*R*)-6-Bromo-6-deoxyascorbic Acid

By Ž. Ružić-Toroš, B. Kojić-Prodić* and D. Horvatić

Rudjer Bošković Institute, P.O. Box 1016, 41001 *Zagreb, Yugoslavia*

and B. Šušković

Research Institute PLIVA, Zagreb, Yugoslavia

(*Received* 27 *June* 1988; *accepted* 22 *September* 1988)

Abstract. $C_6H_7BrO_5$, $M_r = 239{\cdot}02$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}384$ (4), $b = 8{\cdot}247$ (5), $c = 8{\cdot}188$ (4) Å, $V = 836{\cdot}25$ Å^3, $Z = 4$, $D_x = 1{\cdot}899$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 4{\cdot}77$ mm^{-1}, $F(000) = 472$, $R = 0{\cdot}040$, $wR = 0{\cdot}041$ for 828 unique reflections having $I \geq 3\sigma(I)$. The γ-lactone ring shows a conformation between twisted $^1T_2$ and envelope ^1E. Intermolecular hydrogen bonds O(3)—

---

* To whom correspondence should be addressed.

0108-2701/89/020269-05$03.00

H···O(5) 2·579 (6) Å, O(2)—H···O(1) 2·866 (6) Å and O(5)—H···O(1) 2·772 (6) Å connect molecules into helices running in the **c** direction. The C(6) parts of the side chains with bromine atoms fit into spaces between helices.

Introduction. Besides their versatile biological activity (Lewin, 1976; Counsell & Horning, 1982; Englard & Seifter, 1986) ascorbic acid and its derivatives have shown interesting properties as mediators in the process of heterogeneous catalytic hydrogenation of exocyclic double bonds. Of special interest have been the 6-deoxy-6-halogeno derivatives (halogen = F, Cl, Br and I) prepared and characterized by Kiss, Berg, Discherl, Oberhänsli & Arnold (1980); the physiological properties (antiscurvy activity) and the crystal structure of the 6-chloro-6-deoxy derivative (with nitromethane solvate) were reported. The more general, one-step preparation of 6-deoxy-6-halogenoascorbic acid (halogen = Cl, Br and I) using triphenylphosphine–carbon tetrahalide was published (Šušković, 1985). The physical data of 6-deoxy-6-halogenoascorbic acids (Šušković, 1985) agree with those recorded in the literature (Kiss *et al.*, 1980) with the exception of the optical rotation of the iodo derivative. Kiss *et al.* (1980) prepared the iodo derivative by an indirect method which might involve the inverse conformation at the C(5) atom. The discrepancy in the sign and value of optical rotation for the iodo derivative initiated the crystal structure determination of the 6-bromo-6-deoxy derivative. According to the unit cell parameters, space group symmetry, and X-ray powder diagrams, the bromo and iodo derivatives are isostructural; the 6-chloro-6-deoxy derivative crystallizes in a different structure with a molecule of solvent (Kiss *et al.*, 1980). The crystal quality and the considerably lower absorption coefficient made the bromo derivative our choice for X-ray structure analysis. The present structure determination confirms that the configuration at the C(5) atom is retained from the L-ascorbic acid.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 × 10^2)

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

	x	y	z	U_{eq}(Å^2)
Br	9789 (1)	977 (1)	3341 (1)	8·1 (1)
O(1)	7581 (4)	5647 (5)	9162 (5)	4·7 (5)
O(2)	6955 (4)	2706 (5)	11161 (6)	4·5 (4)
O(3)	8529 (4)	145 (5)	9808 (6)	4·2 (4)
O(4)	8849 (3)	4060 (4)	8110 (5)	3·5 (3)
O(5)	7930 (3)	1693 (5)	6082 (5)	3·8 (4)
C(1)	8005 (5)	4317 (7)	9145 (7)	3·5 (4)
C(2)	7784 (5)	2854 (6)	10051 (8)	3·5 (5)
C(3)	8432 (5)	1710 (7)	9493 (3)	3·2 (5)
C(4)	9169 (4)	2363 (6)	8218 (7)	2·8 (5)
C(5)	9025 (5)	1568 (6)	6566 (8)	3·2 (4)
C(6)	9782 (6)	2252 (8)	5321 (7)	4·2 (6)

Table 2. *Bond angles* (°) *for non*-H *atoms*

C(4)—O(4)—C(1)	108·6 (4)
O(4)—C(1)—O(1)	118·6 (5)
C(2)—C(1)—O(1)	131·8 (6)
C(2)—C(1)—O(4)	109·6 (5)
C(1)—C(2)—O(2)	123·7 (5)
C(3)—C(2)—O(2)	128·2 (5)
C(3)—C(2)—C(1)	107·7 (5)
C(2)—C(3)—O(3)	133·3 (6)
C(4)—C(3)—O(3)	115·8 (5)
C(4)—C(3)—C(2)	110·9 (5)
C(3)—C(4)—O(4)	102·9 (4)
C(5)—C(4)—O(4)	109·3 (4)
C(5)—C(4)—C(3)	113·5 (4)
C(4)—C(5)—O(5)	109·3 (5)
C(6)—C(5)—O(5)	112·5 (5)
C(6)—C(5)—C(4)	111·8 (5)
C(5)—C(6)—Br	111·7 (4)

Experimental. Crystals suitable for X-ray structure analysis were grown from ethyl acetate saturated with water. Weissenberg photographs (Cu $K\alpha$ radiation) determined $P2_12_12_1$ uniquely for the bromo and iodo derivatives. Cell dimensions of iodo compound (from oscillation photographs) are $a = 12{\cdot}37$ (2), $b = 8{\cdot}48$ (1), $c = 8{\cdot}20$ (1) Å. Cell dimensions of bromo derivative from diffractometer measurements, 15 reflections in θ range 7·5 to 15·5°. Crystal of dimensions 0·21 × 0·24 × 0·30 mm was used; intensity data collection with Philips PW 1100 computer-controlled four-circle diffractometer, ω scan mode [scan width = 1·20° (θ), scan speed 0·04 (θs^{-1})] with graphite-monochromated Mo $K\alpha$ radiation; three standard reflections with 2% intensity variation; range of hkl 0,0,0 to 16,11,11; 1114 reflections scanned, 828 independent reflections with $I \geq 3\sigma(I)$ in the range $3 < \theta < 30°$ were recorded. The intensity data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by the Patterson method using *SHELX*86 (Sheldrick, 1985). Difference syntheses located the H atoms; refinement by full-matrix least squares minimizing $\sum w(|F_o| - k|F_c|)^2$ with final $w = [\sigma^2(F_o) + 0{\cdot}0001F_o^2]^{-1}$. The non-H atoms were refined anisotropically (Sheldrick, 1976). The H-atom coordinates and isotropic thermal parameters were refined. The residual electron density in the final map $0{\cdot}49 > \Delta\rho > -0{\cdot}50$ e Å^{-3}, max, shift/e.s.d. = 0·025. Scattering factors are those included in *SHELX*76 (Sheldrick, 1976) with applied anomalous-dispersion correction. Final atomic coordinates of the non-H atoms and equivalent isotropic thermal parameters are given in Table 1.* In the chemical synthesis L-ascorbic acid was used. This compound involves the (4*S*) configuration which can be used as an internal standard for the

---

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles involving non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51420 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Conformation analyses of* L-*ascorbic acid and its* 6-*deoxy*-6-*halogeno* (*bromo and chloro*) *derivatives with illustrations of ring puckering*

L-Ascorbic acid (Hvoslef, 1968)				Bromo derivative (This paper)		Chloro derivative (Kiss *et al.*, 1980)			
A		B				A		B	
O4*	0·0 (Å)	C1*	0·0 (Å)	O4*	0·0 (Å)	O4*	0·0 (Å)	C1*	0·0 (Å)
C3*	0·0	C2*	0·0	C3*	0·0	C1*	0·0	C2*	0·0
C4*	0·0	C3*	0·0	C4*	0·0	C2*	0·0	C3*	0·0
C1	0·004 (6)	O4	0·034 (6)	C1	0·047 (9)	C3	0·07 (2)	C4	0·01 (2)
C2	−0·022 (6)	C4	−0·075 (6)	C2	−0·009 (10)	C4	−0·05 (2)	O4	−0·06 (2)
$q = 0{\cdot}01$	$\varphi = -111{\cdot}3°$	$q = 0{\cdot}05$	$\varphi = 24{\cdot}6°$	$q = 0{\cdot}03$	$\varphi = -140{\cdot}2°$	$q = 0{\cdot}07$	$\varphi = -58°$	$q = 0{\cdot}04$	$\varphi = 173°$

q and φ are parameters of the ring-puckering analysis (Cremer & Pople, 1975) for the atom sequence O4, C1, C2 and C4.

* Atoms defining the least-squares plane.

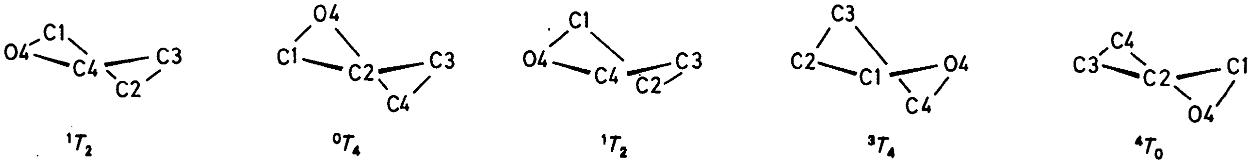

Table 4. *Selected torsion angles* (°) *of* L-*ascorbic acid and its* 6-*deoxy*-6-*halogeno* (*bromo and chloro*) *derivatives with Newman projections along the* C(5)–C(6) *bond*

	L-Ascorbic acid (Hvoslef, 1968)		Bromo derivative (This paper)	Chloro derivative (Kiss *et al.*, 1980)	
	A	B		A	B
O4–C1–C2–C3	−1·4 (5)	1·2 (5)	−4·0 (7)	−3 (2)	−2 (2)
C1–C2–C3–C4	1·8 (5)	2·4 (5)	2·6 (7)	7 (2)	0 (2)
C2–C3–C4–O4	−0·8 (5)	−4·8 (5)	−0·4 (6)	−8 (2)	3 (2)
C3–C4–O4–C1	−0·1 (4)	5·4 (5)	−2·1 (5)	6 (2)	−4 (2)
C4–O4–C1–C2	0·9 (5)	−4·3 (5)	3·7 (6)	−2 (2)	4 (2)
C2–C3–C4–C5	−121·7 (4)	−125·2 (4)	−118·2 (6)	−127 (2)	−118 (2)
C3–C4–C5–C6	−174·2 (3)	172·2 (3)	−179·8 (5)	−178 (1)	173 (1)
C3–C4–C5–O5	66·6 (4)	50·7 (4)	54·9 (6)	61 (2)	54 (2)
O5–C5–C6–O6	−171·2 (3)	−171·4 (3)			
O5–C5–C6–Br			−67·3 (5)		
O5–C5–C6–C1				−61 (2)	−131 (1)

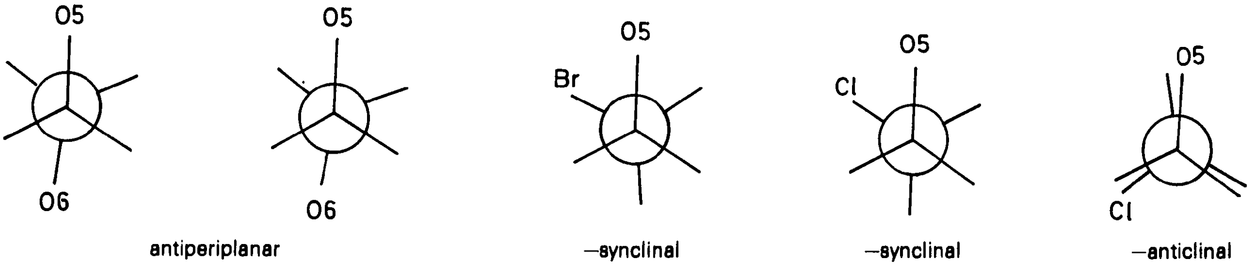

Table 5. *Hydrogen-bond geometry*

D–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*–H···*A* (Å)	*D*–H···*A* (°)	Symmetry operation on *A*
O(2)–H···O(1)	0·90 (8)	2·05 (8)	2·866 (6)	151 (7)	$-x+\frac{1}{2}+1, -y+1, z+\frac{1}{2}$
O(3)–H···O(5)	0·84 (5)	1·81 (7)	2·579 (6)	152 (7)	$-x+\frac{1}{2}+1, -y, z+\frac{1}{2}$
O(5)–H···O(1)	0·84 (5)	1·95 (6)	2·772 (6)	164 (5)	$-x+\frac{1}{2}+1, -y+1, z+\frac{1}{2}-1$

determination of the absolute configuration at C(5); thus the absolute configuration is (4*S*,5*R*). The (4*S*,5*R*) model gives the final $R = 0{\cdot}040$ whereas (4*R*,5*S*) gives $R = 0{\cdot}061$.

Discussion. The structural formula with atomic numbering and bond lengths is shown in Fig. 1; bond angles are listed in Table 2. Conformation analysis of the γ-lactone ring in L-ascorbic acid and its 6-deoxy-

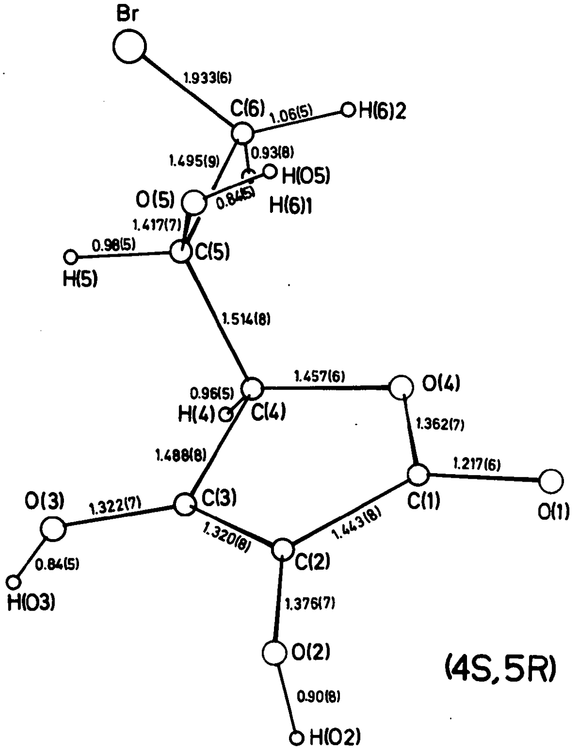

Fig. 1. Structural formula with the atom numbering and interatomic distances (Å).

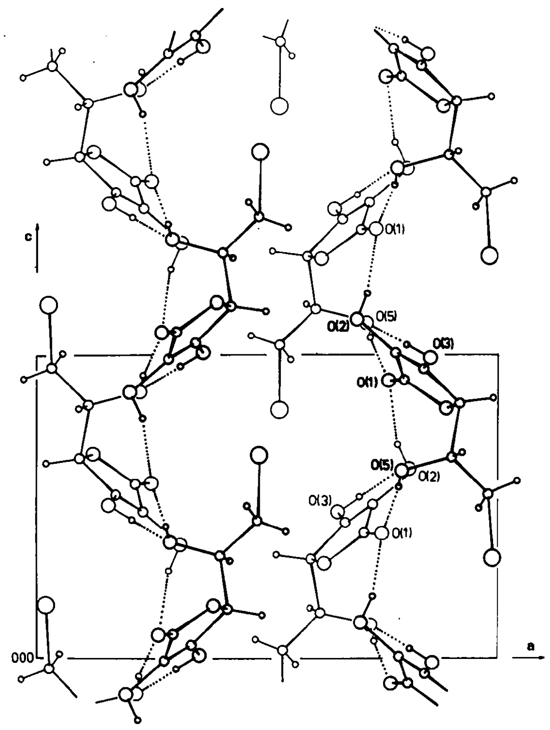

Fig. 2. View of the crystal structure along **b** with helices in the **c** direction.

6-halogeno (chloro and bromo) derivatives is given in Table 3; for comparison their selected torsion angles are listed in Table 4. Molecular packing is shown in Fig. 2 and Table 5. Complete analysis of bond distances and angles of ascorbates published up to 1982 is given by Hvoslef (1982); no significant differences of chemically analogous bonds can be seen in the present structure (Fig. 1). In the title compound the atoms of the lactone group [O(4), C(4), C(1), O(1) and C(2)] show a mean deviation of 0·02 (3) Å from the least-squares plane.

The mode of ring puckering has been defined by the parameters of Cremer & Pople's (1975) analysis (Table 3). According to the values of the q and φ parameters, L-ascorbic acid (Hvoslef, 1968) and its 6-deoxy-6-halogeno derivatives (chloro and bromo) have a twisted conformation. A more plausible conformation, between twisted and envelope (Table 3), is indicated by the deviations from the least-squares planes of molecule A of L-ascorbic acid (one of two independent molecules), its bromo derivative and its chloro derivative (molecule B of two independent units). Selected torsion angles describing the ring and side-chain conformation of L-ascorbic acid (Hvoslef, 1968), and its bromo and chloro derivatives (Kiss *et al.* 1980), are listed in Table 4; Newman projections along the C(5)—C(6) bond illustrate the conformation of the side chain. Compounds compared in Table 4 are of the L-series derivatives and the configuration at C(4) is (*S*). During the halogenation at C(6), the C(5) configuration has not been changed; the values of the torsion angle along C(3)—C(4)—C(5)—O(5) are in the range from +54 (2) to +66·6 (4)°. The conformation along the C(5)—C(6) bond in both molecules of L-ascorbic acid is antiperiplanar (Klyne & Prelog, 1960). The bromo derivative and one molecule of the chloro derivative exhibit (−)-synclinal arrangement along the C(5)—C(6) bond. Molecule B of the chloro derivative shows (−)-anticlinal conformation.

The molecular packing (Fig. 2) is dominated by intermolecular hydrogen bonds (Table 5). All hydroxyl groups act as proton donors but the O(5) group has a double function. O(1) of the lactone group is an acceptor of hydrogen bonds from both the O(2) and the O(5) hydroxyl groups. Hydrogen bonds connect molecules into helices running along **c**. Canals between the helices are occupied by the Br atoms from the C(6) parts of the side chains.

Support of this research by the Self-Management Council for Scientific Research of SR Croatia is gratefully acknowledged.

References

Counsell, J. N. & Horning, D. H. (1982). Editors. *Vitamin C, Ascorbic Acid.* London: Applied Science Publishers.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1367.

ENGLARD, S. & SEIFTER, S. (1986). *Annu. Rev. Nutr.* **6**, 356–406.
HVOSLEF, J. (1968). *Acta Cryst.* B**24**, 23–35; 1431–1440.
HVOSLEF, J. (1982). *Ascorbic Acid: Chemistry, Metabolism and Uses*. In *Advances in Chemistry*, Ser. 200. Washington, DC: American Chemical Society.
KISS, J., BERG, K. P., DISCHERL, A., OBERHÄNSLI, E. & ARNOLD, W. (1980). *Helv. Chim. Acta*, **63**, 1728–1739.
KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–568.
LEWIN, S. (1976). *Vitamin C, Its Molecular Biology and Medical Potentials*. London: Academic Press.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1985). In *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD. Oxford Univ. Press.
ŠUŠKOVIĆ, B. (1985). *Croat. Chem. Acta*, **58**(2), 231–237.

Acta Cryst. (1989). C**45**, 273–275

Structure of 3,3-Diphenyl-*N*-(1-phenylethyl)propylamine (Fendiline) Hydrochloride

BY A. CARPY AND A. LEMRABETT

Laboratoire de Chimie Analytique, URA 50 *CNRS, Faculté de Pharmacie,* 3 *Place de la Victoire,*
33076 *Bordeaux CEDEX, France*

(*Received* 16 *March* 1988; *accepted* 20 *September* 1988)

Abstract. $C_{23}H_{26}N^+.Cl^-$, $M_r = 351{\cdot}92$, monoclinic, $P2_1/n$, $a = 11{\cdot}762\ (2)$, $b = 11{\cdot}009\ (3)$, $c = 15{\cdot}661\ (1)$ Å, $\beta = 93{\cdot}34\ (2)^\circ$, $V = 2024$ Å^3, $Z = 4$, $D_x = 1{\cdot}15$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 16{\cdot}77$ cm^{-1}, $F(000) = 752$, room temperature, $R = 0{\cdot}044$ for 1301 observed reflections. The dihedral angle between the two rings of the diphenyl group is 79 (1)°. The aliphatic chain is nearly maximally extended. The molecules are held together by N—H···Cl hydrogen bonds.

Introduction. First prepared some 25 years ago (Harsanyi, Korbonits & Kiss, 1964), fendiline is used in therapeutics in the treatment of ischemic cardiopathy. According to the World Health Organization, it belongs to calcium antagonists type V (prenylamine-like) (Vanhoutte & Paoletti, 1987). We here report the structure of the racemic mixture of fendiline hydrochloride.

Experimental. White crystal (from methanol), dimensions 0·15 × 0·12 × 0·10 mm. Density not determined. Unit-cell parameters and intensity data obtained on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ in ω/θ scan mode ($0 < \theta < 65^\circ$). Cell dimensions refined by least-squares fitting of θ values of 25 reflections. No appreciable drop in intensity of two standard reflections ($0\bar{2}\bar{2}$ and $00\bar{4}$) checked every 5400 s. 3442 independent reflections collected in $\pm h, k, l$ range −13, 0, 0 to 13, 12, 18; 1301 with $I \geq 3\sigma(I)$ used in subsequent calculations. Intensities corrected for Lorentz and polarization effects but not for absorption. Scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965). The Wilson statistical test showed a centrosymmetric intensity distribution. Structure solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and standard Fourier techniques. H atoms located by ΔF synthesis. Block-diagonal-matrix least-squares refinement on F of observed reflections, $w = 1$ if $|F_o| < P$, $P = [F_o^2(\mathrm{max.})/10]^{1/2}$, $w = (P/F_o)^2$ if $|F_o| > P$; anisotropic thermal parameters for all non-H atoms and isotropic ones for H. Final $R = 0{\cdot}044$, $wR = 0{\cdot}054$, $S = 0{\cdot}9497$ (1301 reflections, 330 parameters). In final cycle mean and max. Δ/σ 0·1 and 0·5. Residual electron density within $\pm 0{\cdot}3$ e Å^{-3}. Calculations carried out on a Mini 6-92 CII-Honeywell–Bull computer (programs *CRISTA, CRISAF, CRISEC, UTIL*, Laboratory of Crystallography, University of Bordeaux I, Talence).*

Discussion. The atomic parameters are given in Table 1 with the numbering scheme shown in Fig. 1. Bond distances and angles, close to expected values, are listed in Table 2. A view of the crystal structure is shown in Fig. 2.

The dihedral angle between the two rings of the diphenyl group is 79 (1)°. The phenyl ring C(2)–C(7) is oriented at 65 (1) and 56 (1)° towards the phenyl rings C(12)–C(17) and C(18)–C(23) respectively. The aliphatic chain C(11)–C(10)–C(9)–N(1)–C(8)–C(24) is nearly maximally extended, the torsion angles C(11)–C(10)–C(9)–N(1), C(10)–C(9)–N(1)–C(8)

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51391 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/89/020273-03$03.00