

Fig. 3. Projection of the crystal structure of Lys-P-1 along the *c* axis.

The planarity of the molecule can be seen from Table 3, which lists the deviations of atoms from the least-squares plane. The atoms in ring *E* do not deviate significantly from the plane even though the ring contains three saturated methylenic C atoms; only a slight puckering of the *E* ring occurs.

The crystal structure is illustrated in Fig. 3 by the *c*-axis projection. The molecules are stacked along the *c* axis with a perpendicular separation of 3.541 Å. The inclination of the normal of the molecular plane to the *c* axis is 47.21°.

One type of hydrogen bond occurs which connects the N(1)–H group of ring *B* to the N(2) atom of ring *D*, binding the molecules along the *a* glide plane. The N(1)⋯N(2) distance is 2.989 (3) Å and H(N1)⋯N(2) is 2.12 (3) Å.

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## Refinement of the Structure of Dopamine Hydrochloride

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**Abstract.** C<sub>8</sub>H<sub>12</sub>NO<sub>2</sub><sup>+</sup>.Cl<sup>-</sup>, orthorhombic, *Pbc*2<sub>1</sub>, *a* = 10.421 (2), *b* = 11.105 (2), *c* = 7.936 (2) Å, *Z* = 4, *D*<sub>m</sub> = 1.356 (2), *D*<sub>c</sub> = 1.355 (1) Mg m<sup>-3</sup>, μ(Mo *K*α) = 0.325 mm<sup>-1</sup>. The structure, which has already been solved, was refined by counter-measured data to *R* = 0.032. All H atoms were located and the average e.s.d.

of the refined parameters decreased by two thirds compared to the previous investigation.

**Introduction.** In recent years a number of dopaminergic substances have been studied by X-ray diffraction at our department. The aim of this project is to elucidate

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the stereochemical requirements for dopaminergic activity. The series started with dopamine itself (Bergin & Carlström, 1968), followed by apomorphine (Giesecke, 1973, 1977), epinine (Giesecke, 1976), and a 2-aminotetralin (Giesecke, 1980). The original dopamine study was performed by photographic techniques, and since a detailed comparison of the substances above requires accurate parameters, it was felt necessary to refine the dopamine parameters with the aid of counter-measured data.

Colourless, orthorhombic crystals of dopamine hydrochloride were readily grown from an aqueous solution. The one chosen for study was trimmed to be nearly spherical in shape with a diameter of 300  $\mu\text{m}$ . The space group was shown by Bergin & Carlström (1968) to be  $Pba2_1$ , but they chose the non-standard setting  $Pbc2_1$ , with  $b$  as the longest axis. The new crystal was therefore mounted along  $b$  on a Paired linear automatic diffractometer. All unit-cell edges were found to be slightly shorter than in the previous study, probably because of the lower temperature in the new diffractometer laboratory. A molybdenum tube and a graphite monochromator were used to obtain strictly monochromatic Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Each reflexion was scanned up to three times, and the background was measured for 1 min on each side. The layers  $h0l$  through  $h10l$  were scanned, representing an octant of the Mo sphere ( $\sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$ ). Of the 1165 accessible reflexions, the 36 with negative intensities and the 161 with intensities less than  $2\sigma(I)$  were discarded. The remaining 968 reflexions were corrected for Lorentz and polarization factors, but not for absorption, because of the low  $\mu$  value. The rest of the calculations were carried out using the *SHELX* system (Sheldrick, 1975) on an IBM 370/165 computer. This system applies the atomic scattering factors given in *International Tables for X-ray Crystallography* (1974).

Table 1. *Final positional parameters for non-hydrogen atoms*

E.s.d.'s in parentheses are in units of the last digit. Approximate  $B$  values ( $\text{\AA}^2$ ) were calculated from the last refinement.

	$x$	$y$	$z$	$B$
Cl	0.0080 (1)	0.3250 (1)	0.2500	3.7
C(1)	0.5222 (3)	0.2171 (3)	0.2019 (4)	2.7
C(2)	0.6459 (3)	0.2098 (3)	0.2651 (4)	2.8
C(3)	0.7231 (2)	0.1132 (2)	0.2220 (3)	2.3
C(4)	0.6749 (2)	0.0234 (2)	0.1164 (4)	2.3
C(5)	0.5510 (3)	0.0306 (3)	0.0555 (4)	2.5
C(6)	0.4731 (2)	0.1268 (2)	0.0987 (4)	2.3
C(7)	0.3354 (3)	0.1316 (3)	0.0394 (4)	2.8
C(8)	0.2522 (3)	0.0501 (4)	0.1425 (4)	3.5
N(1)	0.1151 (3)	0.0649 (3)	0.0991 (4)	3.5
O(1)	0.8448 (2)	0.0975 (2)	0.2820 (4)	3.3
O(2)	0.7476 (2)	-0.0731 (2)	0.0697 (4)	3.6

Table 2. *Final positional parameters for hydrogen atoms*

E.s.d.'s are in units of the last digit.  $B = 5.5 \text{ \AA}^2$ .

	$x$	$y$	$z$
H(1)	0.461 (4)	0.289 (4)	0.247 (9)
H(2)	0.673 (4)	0.264 (5)	0.332 (7)
H(5)	0.514 (5)	-0.024 (5)	-0.008 (9)
H(7A)	0.322 (5)	0.106 (5)	-0.062 (8)
H(7B)	0.305 (4)	0.219 (5)	0.061 (7)
H(8A)	0.262 (5)	0.071 (4)	0.260 (9)
H(8B)	0.284 (5)	-0.037 (5)	0.157 (7)
H(N1A)	0.098 (5)	0.074 (5)	-0.015 (8)
H(N1B)	0.078 (5)	0.004 (5)	0.163 (7)
H(N1C)	0.082 (5)	0.138 (5)	0.118 (6)
H(O1)	0.890 (4)	0.160 (5)	0.294 (7)
H(O2)	0.818 (6)	-0.075 (5)	0.136 (9)

No H atoms were found in the previous dopamine study. The present refinement procedure was therefore begun with a difference synthesis, based on Bergin & Carlström's (1968) coordinates and the new  $F_o$ 's. The initial conventional  $R$  value was found to be 0.28. Seven out of the twelve H atoms could be located from this synthesis. After three refinement cycles the remaining five H atoms were easily located from a new difference map. Three more cycles of full-matrix least-squares refinement resulted in an  $R$  of 0.033. At this point a weighting scheme of the type  $w = k/[\sigma_{(F)}^2 + gF^2]$  was introduced and the parameter  $g$  refined. This resulted in a final unweighted  $R$  of 0.032 (weighted  $R = 0.036$ ) with  $k = 1.0$  and  $g = 0.004$  for the 968 observed reflexions. In the final cycle the temperature factors of all H atoms were fixed at  $U = 0.07 \text{ \AA}^2$ . The average parameter shift expressed as a fraction of the corresponding e.s.d. was 0.4.

As was pointed out in the former dopamine study there is some extinction in the dopamine hydrochloride crystal. The *SHELX* program offers the possibility to correct for this by applying a 'physically dubious' (Sheldrick, 1975) extinction parameter  $x$ , so that each  $F_c$  is multiplied by  $(1 - xF^2/\sin \theta)$ . After this parameter had been refined in three cycles of full-matrix calculations the weighted  $R$  dropped to 0.026, but the e.s.d.'s of the atomic parameters increased about tenfold. Extinction correction was thus discarded and the structure derived by the use of the weighting scheme above was considered conclusive.

Final atomic parameters are given in Tables 1 and 2.\*

**Discussion.** Selected bond distances and angles are given in Fig. 1.† The mean standard deviations are

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34731 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The full table can be obtained from the author.

Table 3. *Hydrogen bonds*

$x', y', z'$  gives the symmetry of the acceptor atom  $Y'$ . The reference molecule is in  $x, y, z$ .

X	H	Y'	$x'$	$y'$	$z'$	$X \cdots Y'$	$H \cdots Y'$	$X-H \cdots Y'$
N(1)	H(N1A)	Cl	$x$	$\frac{1}{2} - y$	$z - \frac{1}{2}$	3.227 (3) Å	2.37 (6) Å	154 (4)°
N(1)	H(N1B)	Cl	$-x$	$y - \frac{1}{2}$	$z$	3.190 (3)	2.28 (5)	164 (3)
N(1)	H(N1C)	Cl	$x$	$y$	$z$	3.320 (3)	2.45 (5)	164 (3)
O(1)	H(O1)	Cl	$1 + x$	$y$	$z$	3.057 (2)	2.24 (5)	164 (3)
O(2)	H(O2)	Cl	$1 - x$	$y - \frac{1}{2}$	$z$	3.133 (2)	2.31 (6)	151 (4)

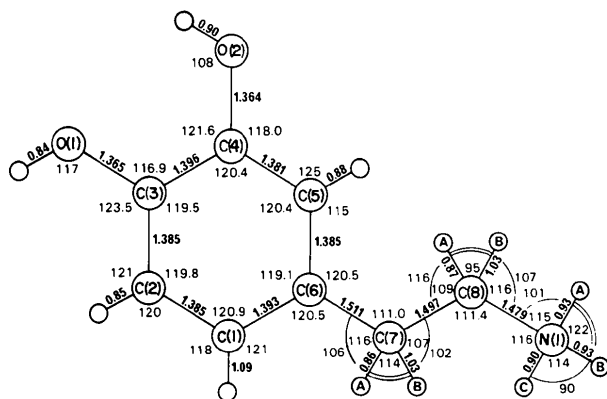


Fig. 1. Schematic drawing of the dopamine molecule with bond distances (Å) and angles (°).

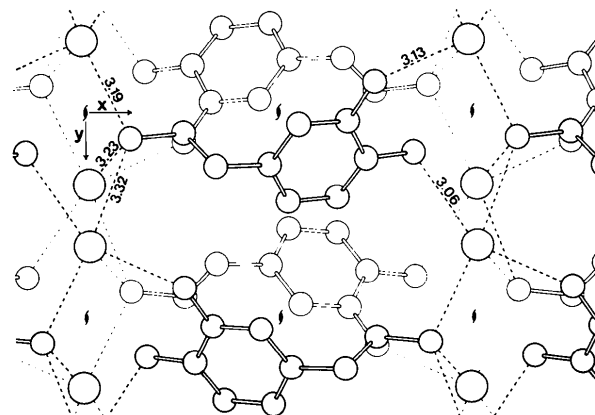


Fig. 2. Dopamine hydrochloride: projection of the structure along the  $c$  axis showing intermolecular hydrogen bonds (Å).

0.004 Å for bonds connecting non-hydrogen atoms, 0.2° for angles between these bonds, 0.05 Å for bonds to H atoms and 3° for angles involving H atoms. Values for bond distances and angles compare well with Bergin & Carlström's (1968) results. The largest discrepancies are found in the two parallel bonds C(1)–C(2) and C(4)–C(5), which in the present study are 0.03 and 0.05 Å shorter respectively, and in the C(8)–N(1) bond, which is 0.03 Å shorter here. No value deviates notably from standard figures for bonds and angles, even though the positions of the H atoms in the chain seem somewhat inaccurate. It is interesting to note that the C(2)–C(3)–O(1) angle is slightly greater than 120°, for this is also the case in all the catecholamines studied earlier in this department (Bergin, 1971; Carlström, 1973; Giesecke, 1976) and in apomorphine (Giesecke, 1973).

The aromatic ring is not entirely planar, since the atoms of the ring deviate by as much as 0.009 Å from the best plane through the ring, while the e.s.d.'s of the atom positions perpendicular to the ring are around 0.003 Å. The atoms of the chain are planar within 0.04 Å. The distance of the N atom from the centre of the ring, a parameter that may be of pharmacological importance, was previously reported as 5.12 Å, but is now found to be somewhat shorter: 5.096 (3) Å.

The torsion angles  $\tau_1$ , C(1)–C(6)–C(7)–C(8), and  $\tau_2$ , C(6)–C(7)–C(8)–N(1), are  $-100.4$  (3) and  $173.2$  (2)° respectively, which means that the chain is

almost fully extended, forming a plane that is nearly orthogonal to the plane of the ring. Quantum-chemical calculations and NMR studies by Bustard & Egan (1971) have shown that in aqueous solution at room temperature the *trans* conformation ( $\tau_2 = 180^\circ$ ) is of lowest energy, but that appreciable amounts of the *gauche* conformation ( $\tau_2 = \pm 60^\circ$ ) are also present.

The crystal packing is shown in Fig. 2, which is that of Bergin & Carlström (1968), with new figures inserted. The five hydrogen bonds are listed in Table 3. The only conspicuous difference from the previous study is the N(1)–H(N1C)···Cl bond, which is 0.03 Å shorter here. All donor–hydrogen–acceptor angles are within 30° of a straight line. As was assumed before there is no evidence of an intramolecular O(1)···O(2) hydrogen bond. There are no short contacts in the crystal except for the five hydrogen bonds.

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## 9-Methylsulphonyl-1,7-dicarba-closo-dodecaborane(12)

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**Abstract.**  $C_3H_{14}B_{10}O_2S$ ,  $M_r = 222.41$ , orthorhombic,  $Pnma$ ,  $a = 13.440$  (2),  $b = 8.539$  (2),  $c = 10.525$  (3) Å,  $V = 1207.9$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.223$ ,  $D_m = 1.220$  Mg m<sup>-3</sup> (by flotation),  $\mu(\text{Mo } K\alpha) = 0.21$  mm<sup>-1</sup>. The structure was refined to  $R = 0.059$  for 1105 counter reflections. The methylsulphonyl group is attached to a B atom of an icosahedral cage containing two C and ten B atoms at its vertices. The molecule exhibits  $m$  crystallographic symmetry.

**Introduction.** The present study reports on the X-ray investigation of 9-CH<sub>3</sub>SO<sub>2</sub>-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> previously prepared at the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences in Řež near Prague (Plešek, Janoušek & Heřmánek, 1978). This work deals with the first example of a structure with a methylsulphonyl group attached to a B atom of a borane skeleton.

The colourless crystals are air-stable and do not decompose in X-rays. Preliminary lattice constants and space group ( $Pnma$  or  $Pn2_1a$ ) were obtained from photographs (Cu  $K\alpha$  radiation). Refined cell parameters were obtained from the orientation matrix calculated by least squares (Shoemaker, 1970) from 40 reflections centred on the diffractometer. A crystal 0.5 × 0.45 × 0.4 mm was used for intensity measurements on a Hilger & Watts four-circle diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The  $\omega$ - $2\theta$  scan technique was used with a constant scan speed of 2°

min<sup>-1</sup> over a range of 2° to measure 1708 independent reflections with  $2\theta \leq 58^\circ$ . 603 of these were classified as unobserved on the criterion  $I < 2\sigma_1(I)$ , where  $I = TC - B_1 - B_2$  and  $\sigma_1(I) = (TC + B_1 + B_2)^{1/2}$  ( $TC$  = total count,  $B_1$  and  $B_2$  = backgrounds measured at the scan limits for half the scan time). No unobserved reflections were used in the refinement. The intensity of

Table 1. Fractional atomic coordinates

E.s.d.'s (in parentheses) refer to the last decimal place.

	x	y	z
S	0.44017 (7)	0.75	0.61244 (9)
O(1)	0.4527 (1)	0.8948 (2)	0.6826 (2)
C	0.5284 (3)	0.75	0.4895 (4)
C(1)	0.1632 (2)	0.9043 (4)	0.4122 (3)
B(2)	0.0842 (4)	0.75	0.4189 (5)
B(3)	0.1897 (4)	0.75	0.3184 (5)
B(4)	0.2857 (2)	0.8534 (4)	0.3970 (3)
B(5)	0.2380 (2)	0.9171 (4)	0.5442 (3)
B(6)	0.1164 (2)	0.8477 (5)	0.5571 (3)
B(9)	0.3134 (3)	0.75	0.5377 (4)
B(10)	0.2089 (4)	0.75	0.6367 (5)
H(1C)	0.591 (3)	0.75	0.531 (4)
H(2C)	0.518 (2)	0.833 (3)	0.441 (2)
H(C1)	0.133 (3)	0.008 (4)	0.370 (3)
H(B2)	0.012 (3)	0.75	0.374 (4)
H(B3)	0.178 (3)	0.75	0.218 (4)
H(B4)	0.338 (2)	0.926 (3)	0.340 (2)
H(B5)	0.257 (2)	0.026 (3)	0.584 (2)
H(B6)	0.074 (2)	0.903 (4)	0.593 (3)
H(B10)	0.214 (3)	0.75	0.734 (4)