

References

- BAILEY, N. A., HARRISON, P. M. & MASON, R. (1968). *Chem. Commun.* **10**, 559.
- BERGIN, R. (1971). *Acta Cryst.* **B27**, 381.
- BERGIN, R. & CARLSTRÖM, D. (1968). *Acta Cryst.* **B24**, 1506.
- BERGIN, R. & CARLSTRÖM, D. (1971). *Acta Cryst.* **B27**, 2146.
- BERGIN, R. & RINGERTZ, H. (1969). In *Stereochemical Aspects of Purine Degradation*. Thesis of H. RINGERTZ. Stockholm: Balder.
- BROWN, C. J. (1966). *Acta Cryst.* **21**, 170.
- BUERGER, M. J. (1959). *Vector Space and its Application in Crystal-Structure Investigation*. New York: John Wiley.
- CARLSTRÖM, D. & BERGIN, R. (1967). *Acta Cryst.* **23**, 313.
- CRUICKSHANK, D. W. J. (1966). In *The Crystalline State*, H. LIPSON & W. COCHRAN. Vol. III, *The Determination of Crystal Structures*, p. 356. London: Bell.
- FABER, W. (1929). *Z. Kristallogr.* **70**, 497.
- FABER, W. (1930). *Z. Kristallogr.* **75**, 147.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-3794. Oak Ridge National Laboratory Oak Ridge, Tennessee.
- KLUG, H. P. (1970). *Acta Cryst.* **B26**, 1268.
- LOEWI, O. & MEYER, H. (1905). *Naunyn-Schmiedebergs Arch. exp. Path. Pharmacol.* **53**, 213.
- PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 159.
- STEWART, J. M. & HIGH, D. (1965). *X-ray 63, Program System for X-ray Crystallography for the IBM 709-7090-7094*. Depts. of Chemistry, Univ. of Washington, Seattle, and Univ. of Maryland, College Park, U.S.A.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configurations in Molecules and Ions*. Supplement. Special Publication No. 18. London: The Chemical Society.
- TSOUCARIS, G. (1961). *Acta Cryst.* **14**, 909.
- WENNEMALM, Å. (1970). Personal communication.

Acta Cryst. (1971). **B27**, 2146

The Crystal and Molecular Structure of Amphetamine Sulphate

BY ROLF BERGIN AND DIEGO CARLSTRÖM

Department of Medical Physics, Karolinska Institutet, S-104 01 Stockholm 60, Sweden

(Received 23 November 1970)

The crystals of (+)amphetamine sulphate, $(C_9H_{13}N)_2 \cdot H_2SO_4$, are monoclinic, space group $P2_1$, four formula units in a cell with $a = 10.51$, $b = 6.35$, $c = 31.34$ Å, $\beta = 95.0^\circ$. The structure was determined by iterated Fourier synthesis and was refined by least-squares methods to an R value of 0.085 with 2917 observed reflexions. The molecules have the configuration characteristic of phenethylamine derivatives, and the structure is a layer structure with $NH \cdots O$ hydrogen bonds in planes parallel to $\{001\}$. Like many other layer structures the crystals exhibited stacking faults. The disorder consisted of $\frac{1}{2}(a+b)$ displacement of layers randomly distributed throughout the crystals.

Introduction

The basic skeleton of amphetamine is a β -phenethylamine arrangement characteristic of sympathomimetic amines, e.g. the neurotransmitter noradrenaline and other biologically active catecholamines. Biochemically, (+)-amphetamine releases catecholamines from their neuronal storage sites, and it has a variety of pharmacological effects. For more than 30 years it has been known as a potent stimulatory drug for the central nervous system; on chronic administration it may lead to acute paranoid psychosis.

The conformation of molecules with neurotropic activity has recently attracted considerable interest, and the present structure determination is part of our research program on biologically-active phenethylamine derivatives.

Experimental

Reagent pure (+)-amphetamine sulphate was recrystallized by evaporation of an aqueous solution. Initially prepared crystals were extremely thin plates

on (001), measuring only a few μm in thickness. Crystals having dimensions suitable for single-crystal work were finally obtained after a month of extremely slow evaporation at room temperature. Considerable difficulty was experienced in selecting and trimming crystals of this batch. Weissenberg diagrams showed that most crystals were twins with the twin plane $\{001\}$. The single crystals encountered gave diagrams with pronounced streaks along c^* of hkl reflexions with $h+k=2n+1$. Since the crystals were easily deformable and had an eminent cleavage $\{001\}$, it was not possible to trim them mechanically. Finally, a large crystal several cm^2 in size with a thickness of 0.3 mm was selected, and by partial dissolution of the crystal a roughly spherical piece measuring $0.28 \times 0.31 \times 0.35$ mm was produced. Although this crystal also gave faint streaks of the aforementioned reflexions in Weissenberg diagrams, it was the best that could be obtained for intensity measurements.

Unit-cell dimensions were determined in a linear automatic diffractometer. Density was measured by flotation in an xylene-chloroform mixture.

Crystal data

(+)-Amphetamine (α -methylphenethylamine or 2-amino-1-phenylpropane) sulphate: monoclinic.

(C₉H₁₃N)₂·H₂SO₄
 $a = 10.508 \pm 0.002$ Å,

$b = 6.350 \pm 0.001$,

$c = 31.336 \pm 0.005$,

$\beta = 94.99 \pm 0.06^\circ$

M.W. = 368.50, $V = 2082.96$ Å³

$D_m = 1.172 \pm 0.002$ g.cm⁻³, D_x ($Z=4$) = 1.174 g.cm⁻³,

$\mu_{\text{Mo } K\alpha} = 1.79$ cm⁻¹.

Absent reflexions: $0k0$ when k is odd. Systematic absences restrict the space group to $P2_1$ or $P2_1/m$; however the latter, being centrosymmetric, was disregarded because of the asymmetry of the amphetamine molecule. Also a statistical test of the normalized structure amplitudes showed that the space group should be acentric and $P2_1$ was also confirmed by the structure analysis. It was noted that the hkl reflexions with $h+k=\text{odd}$ were, generally, very weak, thereby approaching a c centered lattice.

The crystal selected for intensity measurements was oriented with the b axis parallel to the ω axis of the automatic diffractometer (PAILRED). Intensities of reflexions of layers $h0l$ to $h8l$ within a quarter-sphere corresponding to that delimited by Cu $K\alpha$ were collected with strictly monochromatic Mo $K\alpha$ radiation. To obtain accurate intensities, the fainter reflexions, which were in a majority, were scanned up to 7 times thereby approaching fixed-count strategy. The background was counted for two minutes on each side of every reflexion. In all, 5788 independent reflexions were recorded. A reflexion was considered observed when it had an intensity statistically significant (on a 0.1% level) from the background. This screening gave 2917 observed reflexions (50.4% of the total examined). The reason for this low percentage was partly due to a rapid fall-off of intensities at higher θ values and partly to the pseudocentred lattice. Observed reflexions were corrected for background and for Lorentz and polarization factors, but not for extinction. No absorption correction was made because of the favourable shape of the crystal and the low μ value. Structure factors were placed approximately on an absolute scale by Wilson statistics. The above calculations were performed with program system *CRYSTAL* (Bergin & Ringertz, 1969) on an IBM 360/75 computer. The *X-RAY-63* system (Stewart & High, 1965) for the IBM 7090 computer was otherwise used throughout, except for the final thermal-ellipsoid drawing which was plotted on an IBM 360/75 computer with program *ORTEP* (Johnson, 1965).

Structure determination and refinement

The structure determination was accomplished with a crystal sphere smaller than the one used for intensity measurements. It included 1110 observed reflexions.

Atomic coordinates for the two sulphur atoms were determined from a three-dimensional sharpened Patterson vector map. Two alternatives for the x coordinates, x and $x + \frac{1}{2}$ or $x + \frac{1}{4}$ and $x + \frac{3}{4}$, seemed to have the same merit. Positional parameters and an isotropic temperature factor of $B = 3.5$ Å² for these atoms were used to calculate phases. The conventional R index [$R = \sum(|F_o| - |F_c|) / \sum|F_o|$] gave 57% and 53%, respectively, for the two alternatives. The Fourier syntheses computed using these phases and the observed structure factors revealed additional maxima at correct distances for oxygen atoms of the sulphate groups. Also, the oxygen positions fitted the general orientation of the sulphate groups obtained from a sharpened shell Patterson function. The introduction of the oxygen atoms reduced the R value to 49 and 45%, respectively, and new electron-density maps showed about 12 additional maxima. The general orientation of the four amphetamine molecules with their terminal amino-nitrogen atoms pointing towards the sulphate ions now seemed clear, and from steric considerations it became evident that only the latter of the two alternatives mentioned above could be the correct one. Continued iterated Fourier refinement gave rather disgusting results: the six-membered rings did not show up very well in the electron-density maps and the R value did not decrease below 30%. Because of the pseudocentred lattice it was thought that the four dexamphetamine molecules should have about the same orientation in relation to the sulphate groups. After producing nearly 20 three-dimensional electron-density maps and several $F_o - F_c$ syntheses it became evident that only three of the four benzene rings were approximately parallel to the 010 plane, while the fourth was almost perpendicular to this plane. When this was realized refinement dropped the R value immediately to 22%.

Because of the great number of parameters involved, the refinement procedure was carried out using the block-diagonal least-squares method. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), and the structure amplitudes were given unit weight because of the counter strategy mentioned. With an overall temperature factor of 3.5 Å² a refinement of the positional coordinates decreased the R value to 17% after 2 cycles; when individual isotropic thermal parameters were introduced, R dropped further to 13%. A three-dimensional electron-density function prepared at this stage showed that some of the atoms – especially oxygen atoms of the sulphate groups – had a pronounced ellipsoidal shape indicating a high thermal anisotropy. The introduction of anisotropic thermal parameters reduced the R value to 8.8% after 10 cycles. The refinement procedure was continued with all 2917 observed structure amplitudes included. After an initial rise in the R value to 12.1%, the refinement continued to converge; the refinement procedure was stopped at $R = 8.5\%$ when the maximal shifts in the

positional coordinates were less than 0.35 estimated standard deviation and the average shift was 0.08 e.s.d. It was decided that further refinement was not justified because of the rather prohibitive computing time per cycle and because of the still large standard deviations in the varied parameters. No attempt was made to introduce the 56 hydrogen atoms, especially as only a small number of them could be recognized with certainty in the three-dimensional difference maps. A list of the final observed and calculated structure factors has been deposited in the Library of the Royal Swedish Academy of Science, 104 05 Stockholm 50, from where copies can be obtained. Positional and thermal parameters for the final structure are given in Tables 1 and 2, respectively.

Description and discussion of the structure

The cause of the rather low accuracy in the structure determination can certainly be attributed to dislocations in the crystal. These are mentioned further on. A detailed discussion of individual bond lengths would be meaningless, but there are several gross features of the structure which merit detailed comment.

Geometry of the molecules

The four amphetamine molecules in the asymmetric unit are very similar and the overall shape is the same as that found in related compounds. Like the molecules of dopamine (Bergin & Carlström, 1968), noradrenaline (Carlström & Bergin, 1967), ephedrine

(Phillips, 1954; Bergin, 1971), pseudoephedrine (Bailey, Harrison & Mason, 1968), the molecule of amphetamine is in its most extended form with the ammonium nitrogen as far as possible from the six-membered ring. Molecular geometry and the atom numbering are shown in Fig. 1. The benzene rings of the four molecules are planar within the limits of error; maximal deviation from the best planes is 0.031, 0.008, 0.012 and 0.008 Å for molecules *A*, *B*, *C* and *D*, respectively. Also, the fully extended side chain of each molecule is nearly planar with respect to the atoms C(6)–C(7)–C(8)–N, with a maximal deviation of 0.031, 0.049, 0.053, 0.091 Å for the four molecules respectively. The acute angles between the normals to the best planes through the benzene rings and the side chains are 71.5 (*A*), 76.8 (*B*), 70.2 (*C*) and 82.6° (*D*).

Bond lengths and bond angles are given in Table 3. Estimated standard deviations in the S–O distances varied between 0.007 and 0.010 Å, those of C–N were 0.011 Å and those of C–C varied between 0.011 and 0.024 Å. The e.s.d.'s in the bond angles varied between 0.40 and 0.66° for the O–S–O angles and between 0.61 and 1.45° for the C–C–C or C–C–N angles; however, the internal consistency of the distances within the aromatic rings is poor. Although mean value is 1.404 Å, it seems most unlikely that the extremes of 1.35 and 1.46 Å are as accurate as the above-mentioned error estimates imply. This is also true for the paraffinic C–C bond lengths (ranging from 1.49 to 1.57 Å) where deviations from the expected value are large. Average C–C and C–N bond distances are 1.533 and 1.527 Å, respec-

Table 1. Positional parameters and their standard deviations ($\times 10^4$)

SO ₄ group <i>A</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	SO ₄ group <i>B</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S	3288 (2)	1000	2539 (1)	S	8327 (2)	6011 (5)	2472 (1)
O(1)	3466 (7)	3252 (10)	2429 (2)	O(1)	8413 (8)	8243 (11)	2418 (3)
O(2)	2539 (9)	8 (13)	2181 (3)	O(2)	7678 (9)	5054 (14)	2091 (3)
O(3)	4575 (6)	40 (12)	2620 (2)	O(3)	9627 (6)	5156 (12)	2564 (2)
O(4)	2652 (7)	753 (21)	2925 (3)	O(4)	7642 (7)	5401 (21)	2828 (3)
Molecule <i>A</i>				Molecule <i>C</i>			
N	1628 (6)	6051 (13)	2085 (2)	N	16 (6)	1101 (14)	2894 (2)
C(1)	9085 (13)	2713 (25)	936 (4)	C(1)	309 (11)	7915 (22)	4307 (4)
C(2)	8813 (16)	1968 (32)	497 (5)	C(2)	9831 (13)	7262 (26)	4692 (4)
C(3)	9806 (16)	1510 (29)	263 (5)	C(3)	8546 (12)	6932 (24)	4707 (4)
C(4)	1063 (16)	1723 (27)	412 (5)	C(4)	7751 (13)	7150 (33)	4351 (4)
C(5)	1380 (14)	2324 (25)	856 (4)	C(5)	8221 (11)	7830 (31)	3952 (4)
C(6)	372 (10)	2809 (17)	1111 (3)	C(6)	9527 (9)	8175 (15)	3941 (3)
C(7)	669 (10)	3442 (16)	1568 (3)	C(7)	31 (10)	8711 (16)	3510 (3)
C(8)	1274 (9)	5678 (15)	1604 (3)	C(8)	9604 (8)	922 (17)	3346 (3)
C(9)	393 (12)	7448 (18)	1433 (4)	C(9)	234 (15)	2714 (21)	3608 (4)
Molecule <i>B</i>				Molecule <i>D</i>			
N	6546 (6)	1111 (14)	2114 (2)	N	5112 (6)	5946 (14)	2876 (2)
C(1)	4038 (13)	7915 (23)	946 (4)	C(1)	3382 (10)	5147 (20)	4234 (4)
C(2)	3775 (16)	7219 (29)	512 (5)	C(2)	3418 (11)	5705 (26)	4677 (4)
C(3)	4796 (15)	6582 (25)	283 (4)	C(3)	3712 (12)	7806 (24)	4811 (4)
C(4)	6042 (16)	6572 (26)	461 (4)	C(4)	3968 (11)	9310 (24)	4506 (4)
C(5)	6315 (14)	7251 (24)	906 (4)	C(5)	3951 (10)	8783 (19)	4076 (4)
C(6)	5301 (10)	7938 (16)	1137 (3)	C(6)	3668 (8)	6709 (17)	3943 (3)
C(7)	5552 (10)	8541 (14)	1595 (3)	C(7)	3672 (8)	6208 (19)	3461 (3)
C(8)	6162 (8)	743 (15)	1637 (3)	C(8)	5070 (7)	5879 (18)	3358 (3)
C(9)	5244 (12)	2484 (18)	1476 (4)	C(9)	5645 (10)	3710 (20)	3523 (4)

tively. The latter seems to be too long even when considering that C-N⁺ is normally longer than the standard C-N bond.

The mean S-O bond length (1.458 Å) in the two sulphate groups agrees well with the standard bond

length, and the angles are all fairly close to the tetrahedral value; but even here individual variations are much greater than the error estimates imply. The low error estimates are partly due to the use of a block-diagonal least-squares refinement procedure and partly

Table 2. *Thermal parameters and their standard deviations* ($\times 10^4$)

β_{ij} are the coefficients in the expression:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

SO ₄ group A	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	65 (2)	123 (4)	14 (0)	-16 (4)	-1 (1)	6 (1)
O(1)	127 (8)	99 (16)	19 (1)	-11 (10)	-11 (2)	6 (3)
O(2)	230 (14)	182 (23)	28 (2)	-66 (16)	-26 (4)	2 (5)
O(3)	64 (6)	255 (21)	18 (1)	58 (11)	7 (2)	9 (4)
O(4)	107 (8)	786 (55)	25 (1)	123 (22)	26 (3)	47 (9)
SO ₄ group B						
S	56 (2)	155 (5)	13 (0)	3 (4)	-1 (1)	7 (2)
O(1)	194 (11)	81 (17)	25 (1)	12 (12)	-26 (3)	-6 (4)
O(2)	224 (14)	224 (24)	23 (1)	-39 (16)	-26 (4)	-4 (5)
O(3)	77 (7)	253 (21)	16 (1)	43 (10)	5 (2)	14 (4)
O(4)	97 (8)	806 (57)	27 (2)	100 (20)	22 (3)	48 (8)
Molecule A						
N	87 (7)	128 (17)	12 (1)	0 (14)	3 (2)	3 (5)
C(1)	191 (19)	415 (53)	17 (2)	-93 (28)	-8 (5)	16 (9)
C(2)	274 (26)	554 (73)	22 (2)	-82 (39)	-23 (6)	16 (12)
C(3)	297 (27)	473 (67)	19 (2)	-16 (36)	-8 (6)	-10 (10)
C(4)	297 (27)	426 (60)	21 (2)	127 (35)	15 (6)	-11 (10)
C(5)	254 (22)	405 (53)	15 (2)	128 (31)	15 (5)	-6 (8)
C(6)	148 (14)	168 (25)	11 (1)	-1 (17)	-4 (3)	5 (5)
C(7)	142 (13)	168 (26)	9 (1)	-20 (16)	-1 (3)	0 (5)
C(8)	106 (10)	178 (28)	11 (1)	2 (15)	1 (3)	9 (5)
C(9)	206 (18)	168 (29)	15 (2)	11 (20)	-13 (4)	12 (6)
Molecule B						
N	82 (7)	154 (19)	12 (1)	-3 (14)	1 (2)	-3 (5)
C(1)	196 (18)	347 (43)	14 (2)	-51 (26)	-13 (4)	15 (8)
C(2)	297 (27)	419 (57)	20 (2)	-35 (36)	-26 (6)	2 (10)
C(3)	297 (25)	369 (54)	16 (2)	100 (31)	-12 (6)	-2 (8)
C(4)	297 (26)	386 (55)	20 (2)	103 (32)	20 (6)	-13 (9)
C(5)	234 (22)	339 (47)	18 (2)	72 (29)	11 (5)	-5 (9)
C(6)	152 (14)	146 (24)	12 (1)	-18 (17)	2 (4)	-2 (5)
C(7)	134 (13)	119 (22)	10 (1)	-18 (15)	-5 (3)	-5 (4)
C(8)	99 (10)	141 (24)	12 (1)	-39 (15)	0 (3)	0 (5)
C(9)	210 (19)	171 (29)	15 (2)	2 (20)	-18 (4)	13 (6)
Molecule C						
N	71 (7)	187 (20)	11 (1)	-14 (14)	-1 (2)	6 (5)
C(1)	136 (14)	337 (40)	14 (2)	-8 (22)	3 (4)	10 (7)
C(2)	190 (19)	432 (53)	16 (2)	-3 (29)	13 (5)	12 (9)
C(3)	194 (18)	394 (46)	13 (2)	-2 (26)	15 (4)	13 (8)
C(4)	180 (19)	741 (83)	18 (2)	-90 (36)	16 (5)	18 (12)
C(5)	118 (14)	806 (85)	17 (2)	-143 (31)	-1 (4)	43 (11)
C(6)	112 (11)	154 (25)	11 (1)	-21 (15)	3 (3)	-3 (5)
C(7)	119 (12)	162 (25)	14 (2)	-12 (16)	8 (3)	8 (5)
C(8)	93 (9)	152 (21)	13 (1)	34 (18)	1 (3)	2 (6)
C(9)	297 (24)	225 (35)	15 (2)	-69 (26)	4 (5)	-24 (7)
Molecule D						
N	75 (7)	184 (19)	12 (1)	-9 (15)	4 (2)	6 (5)
C(1)	107 (12)	306 (35)	15 (2)	4 (18)	4 (4)	22 (7)
C(2)	143 (14)	474 (56)	13 (1)	57 (28)	3 (4)	12 (9)
C(3)	172 (17)	402 (50)	17 (2)	81 (27)	-7 (5)	-15 (9)
C(4)	112 (14)	453 (54)	21 (2)	78 (23)	-6 (4)	-25 (9)
C(5)	119 (13)	235 (31)	16 (2)	23 (18)	2 (4)	-5 (6)
C(6)	63 (9)	243 (30)	15 (1)	28 (14)	0 (3)	6 (6)
C(7)	65 (8)	284 (31)	10 (1)	-10 (18)	-1 (2)	-1 (6)
C(8)	55 (7)	197 (24)	13 (1)	24 (16)	-1 (2)	5 (6)
C(9)	99 (12)	302 (36)	17 (2)	66 (19)	7 (4)	19 (7)

due to systematic errors in the primary data being collected from a slightly disordered crystal.

Hydrogen bonds and packing of the molecules

Although the positions of the hydrogen atoms were not determined, no doubt the close contacts between

the four nitrogen atoms and the oxygen atoms of the sulphate ions represent hydrogen bonds. These bonds (Fig. 1) form nearly tetrahedral angles with one another and with the C(8)-N bond, around each nitrogen atom. The 12 N...O distances range from 2.70 to 2.81 Å (average 2.76 Å). As evident in Fig. 1

Table 3. Bond lengths and angles

	<i>A</i>	<i>B</i>		<i>A</i>	<i>B</i>
S-O(1)	1.49 Å	1.43 Å	O(1)-S-O(2)	108°	110°
S-O(2)	1.46	1.45	O(1)-S-O(3)	108	109
S-O(3)	1.49	1.48	O(1)-S-O(4)	112	114
S-O(4)	1.44	1.43	O(2)-S-O(3)	112	111
			O(2)-S-O(4)	110	107
			O(3)-S-O(4)	107	105

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	
C(1)-C(2)	1.45 Å	1.43 Å	1.41 Å	1.43 Å	C(2)-C(1)-C(6)	119°	120°	122°	119°
C(2)-C(3)	1.36	1.40	1.37	1.43	C(1)-C(2)-C(3)	119	119	119	120
C(3)-C(4)	1.37	1.38	1.35	1.39	C(2)-C(3)-C(4)	124	122	120	120
C(4)-C(5)	1.45	1.46	1.45	1.40	C(3)-C(4)-C(5)	119	120	121	121
C(5)-C(6)	1.41	1.41	1.39	1.40	C(4)-C(5)-C(6)	119	118	118	120
C(6)-C(1)	1.42	1.41	1.36	1.40	C(1)-C(6)-C(5)	121	121	119	121
C(6)-C(7)	1.49	1.49	1.54	1.54	C(1)-C(6)-C(7)	119	120	122	121
C(7)-C(8)	1.56	1.54	1.55	1.54	C(5)-C(6)-C(7)	120	119	118	118
C(8)-C(9)	1.53	1.52	1.52	1.57	C(6)-C(7)-C(8)	112	111	113	108
C(8)-N	1.54	1.53	1.52	1.51	C(7)-C(8)-C(9)	114	113	113	113
					C(7)-C(8)-N	106	107	106	109
					C(9)-C(8)-N	109	109	108	108

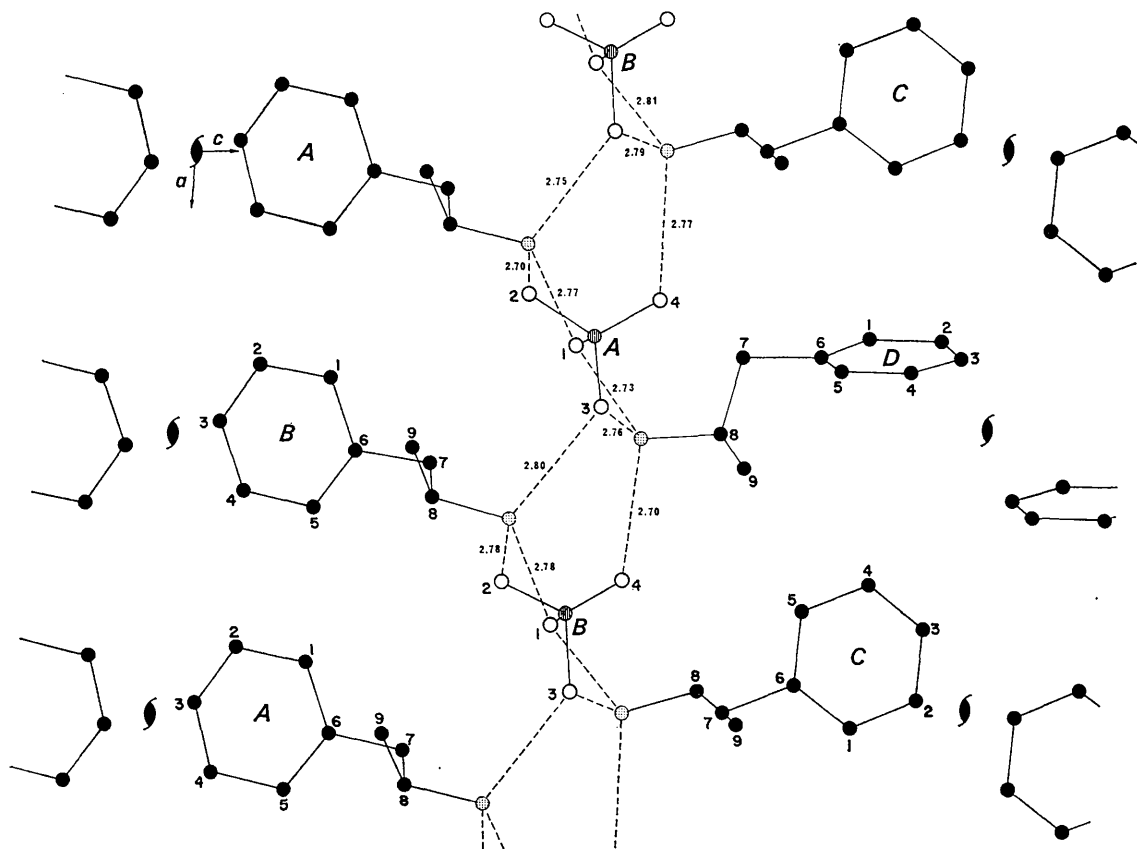


Fig. 1. Amphetamine sulphate: projection of the structure along the *b* axis. The four amphetamine molecules (*A-D*) and two sulphate groups (*A, B*) of the asymmetric unit are held together by a planar network of NH...O hydrogen bonds running essentially parallel to (001). Only carbon atoms (black) and oxygen atoms (white) are numbered here. Note the tetrahedral arrangement of the hydrogen bonds around each nitrogen atom (dotted).

and Table 4 each sulphate ion accepts six hydrogen bonds, resulting in an almost planar and very regular network parallel to (001). Thus, the structure is held firmly together in planes around $\frac{1}{4}c$ and $\frac{3}{4}c$. Halfway between these hydrogen bonded layers there are planes, likewise parallel to (001), but they are hydrophobic and the structure is here held together solely by a few van der Waals contacts. This explains the pronounced cleavage parallel to {001}. While the charged amino ends of the molecules are held in position by the hydrogen-bonding system, the opposite phenyl rings are rather free especially as the packing here is loose; the distance between the planes of the six-membered rings in the *A*, *B* and *C* molecules is 6.1 Å and the closest C...C distance in adjacent rings is 4.0 Å. This situation is reflected in the thermal parameters (Table 2) and is shown in Fig. 2 which gives the thermal ellipsoids of the atoms scaled to 50% probability. Increasing thermal movement and anisotropy with increasing distance from the terminal nitrogen is evident. Also, there is a marked anisotropy of the thermal parameters in the oxygen atoms of the sulphate groups.

As already mentioned, the Weissenberg diagrams showed that the crystal analysed was slightly disordered. A dislocation $\frac{1}{2}(\mathbf{a} + \mathbf{b})$ in the cleavage plane {001} should cause the observed streaks along \mathbf{c}^* of the *hkl* reflexions with $h + k = 2n + 1$. Such a slip

Table 4. *Hydrogen bond distances*

Subscripts *A–D* refer to the identification code of the molecules and sulfate groups in Fig. 1.

$N_A \cdots O(1)_A$	$(x+1, y, z)$	2.77 Å
$N_A \cdots O(2)_A$	$(x+1, y+1, z)$	2.70
$N_A \cdots O(3)_B$	(x, y, z)	2.75
$N_B \cdots O(1)_B$	(x, y, z)	2.78
$N_B \cdots O(2)_B$	$(x, y+1, z)$	2.78
$N_B \cdots O(3)_A$	$(x, y+1, z)$	2.80
$N_C \cdots O(1)_B$	(x, y, z)	2.81
$N_C \cdots O(3)_B$	$(x, y+1, z)$	2.79
$N_C \cdots O(4)_A$	$(x+1, y+1, z)$	2.77
$N_D \cdots O(1)_A$	(x, y, z)	2.74
$N_D \cdots O(3)_A$	$(x, y+1, z)$	2.76
$N_D \cdots O(4)_B$	(x, y, z)	2.70

could occur along the hydrophobic planes where the binding forces in the layered structure are weakest. But the plane through $z/c=0$ and that through $z/c=0.5$ (with the origin, here, chosen) are not equivalent. A dislocation $\frac{1}{2}(\mathbf{a} + \mathbf{b})$ in the latter plane is not possible because of steric hinderance. In the former plane a displacement leaves the relationship between the sulphate groups, as well as the *A* and *B* molecules of one layer and the next, unchanged while there is a drastic change with respect to the *C* and *D* molecules. The effect of such faults is to destroy the regularity of the crystal in the [001] direction. It is assumed that the dislocations of the layers are randomly distributed,

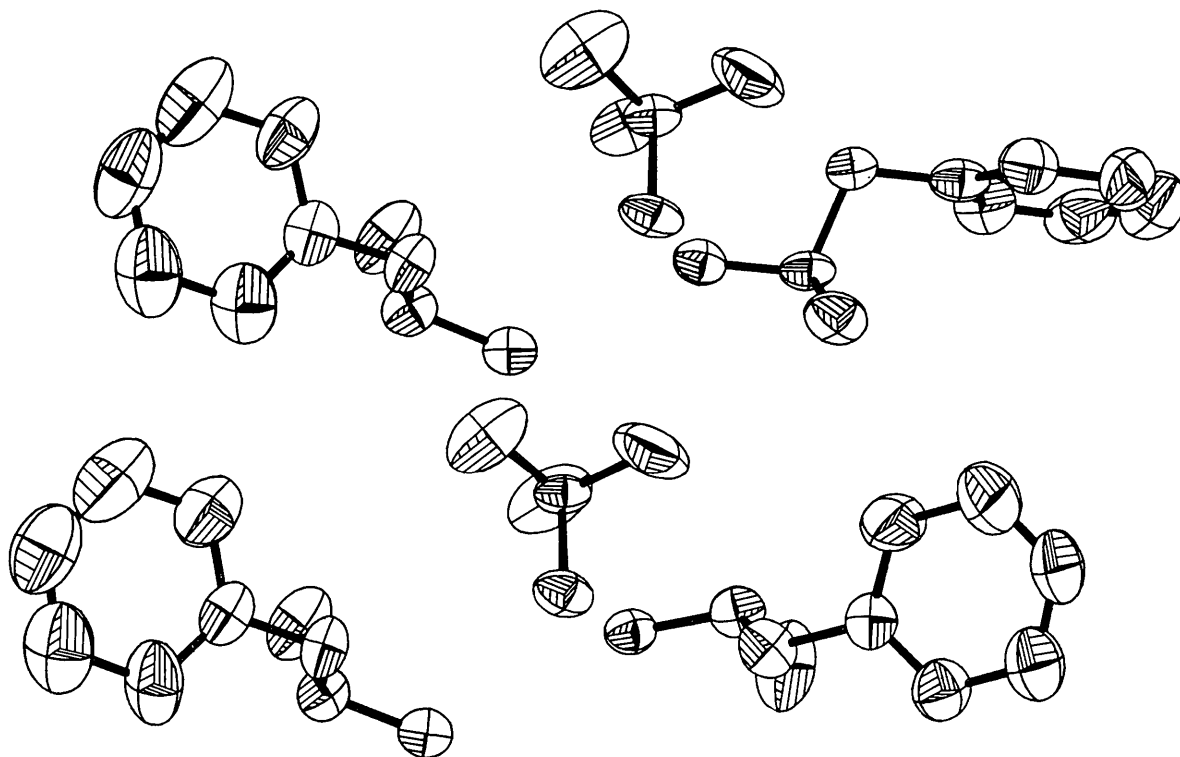


Fig. 2. Configuration of the four amphetamine molecules in the asymmetric unit. Thermal ellipsoids are scaled to 50% probability. Projection is along the *b* axis.

but no attempts were made to estimate the extent of disorder in the crystal.

It is a pleasure to thank Ingrid Hacksell for making the drawings. The work has been supported by the Swedish Medical Research Council (Project No B71-13X-144-07B) and the Swedish Delegation for Applied Medical Defence Research (Project No 278).

References

- BAILEY, N. A., HARRISON, P. M. & MASON, R. (1968). *Chem. Commun.* **10**, 559.
 BERGIN, R. (1971). *Acta Cryst.* **B27**, 381.
 BERGIN, R. & CARLSTRÖM, D. (1968). *Acta Cryst.* **B24**, 1506.

- BERGIN, R. & RINGERTZ, H. (1969). In *Stereochemical Aspects of Purine Degradation*. Thesis of H. RINGERTZ. Stockholm: Balder.
 CARLSTRÖM, D. & BERGIN, R. (1967). *Acta Cryst.* **23**, 313. *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 159.
 STEWART, J. M. & HIGH, D. (1965). *X RAY 63, Program System for X-ray Crystallography for the IBM 709-7090-7094*. Depts. of Chemistry, Univ. of Washington, Seattle, and Univ. of Maryland, College Park, U.S.A.

Acta Cryst. (1971). **B27**, 2152

The Crystal Structure of L- α,γ -Diaminobutyric Acid Monohydrochloride

BY HIROSHI HINAZUMI AND TOSHIO MITSUI*

Department of Physics, Faculty of Science, Hokkaido University, Sapporo, Japan

(Received 22 March 1971)

The crystal structure of L- α,γ -diaminobutyric acid monohydrochloride, $\text{NH}_3^+(\text{CH}_2)_2\text{CHNH}_3^+\text{COO}^- \cdot \text{Cl}^-$, has been determined using three-dimensional intensity data obtained with Mo $K\alpha$ radiation. The crystal is monoclinic with the space group $P2_1$. There are two formula units in a cell of dimensions $a = 8.355$, $b = 8.267$, $c = 5.316$ Å, $\beta = 109.37^\circ$. The structure was solved by the heavy atom method and refined by the method of block-diagonal least squares. The final R value was 0.057 for 1858 observed reflexions of non-zero intensity. The L- α,γ -diaminobutyric acid molecule exists as a zwitterion, each nitrogen atom having an extra proton and forming a three-dimensional network of the hydrogen bonds. All the bond lengths and angles in the molecule are as a whole similar to those found in lysine and ornithine. The two C-NH $_3^+$ distances are equal within experimental errors, the average value being 1.495 Å. The side chain with γ nitrogen atom is of an extended, nearly planar configuration, and the average C-C distance is 1.530 Å.

Introduction

L- α,γ -Diaminobutyric acid, $\text{NH}_2(\text{CH}_2)_2\text{CHNH}_2\text{COOH}$, is a synthetic amino acid. In connexion with the molecular structure of lysine (Wright & Marsh, 1962) and that of ornithine (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967), it seems worth while to determine the molecular structure of this compound.

In the present study, the crystal structure of L- α,γ -diaminobutyric acid monohydrochloride is determined by X-ray diffraction, and the bond lengths obtained are compared with those of lysine and ornithine.

Experimental

L- α,γ -Diaminobutyric acid monohydrochloride, synthesized at the Department of Polymer Science of Hokkaido University, was supplied to us. The single crystals,

grown from aqueous solutions at about 5°C, were colourless plates elongated along the b axis. The space group was determined from Weissenberg and precession photographs. Systematic absence of reflexions for $0k0$ with k odd suggested that the space group is either $P2_1$ or $P2_1/m$, and the former was adopted since the compound is optically active. The unit-cell parameters were obtained from a least-squares procedure by minimizing the quantity $\sum w(\sin^2 \theta_{\text{obs}} - \sin^2 \theta_{\text{calc}})^2$. Values of 2θ for 25 reflexions, measured on a diffractometer, were used and the weight assigned was proportional to $1/\sin^2 2\theta$. The confidence limits are subjectively set to be three times the estimated standard deviations obtained from the least-squares calculation.

Crystal data

L- α,γ -Diaminobutyric acid monohydrochloride

Formula: $\text{C}_4\text{H}_{10}\text{N}_2\text{O}_2 \cdot \text{HCl}$

M.W. 154.6

Monoclinic

$a = 8.355 \pm 0.004$, $b = 8.267 \pm 0.004$, $c = 5.316 \pm 0.003$ Å
 $\beta = 109.37 \pm 0.06^\circ$; $U = 346.4$ Å 3

* Present address: Department of Biophysical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.