

enthusiasm. Graphite samples were kindly furnished by M. B. Carter, Advanced Materials Laboratory, Union Carbide Corporation, Lawrenceburg, Tennessee. The study was supported by the Engineering Experiment Station of the School of Engineering, Auburn University.

#### References

BUERGER, M. J. & DOLLASE, W. A. (1964). *Science*, **145**, 264.  
BURTON, L. P. (1964). Private communication.

CARTER, M. B. (1964). Private communication.  
CULLITY, B. D. (1959). *Elements of X-ray Diffraction*, 93. *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935). Vol. II. Berlin: Bornträger.  
LEONHARDT, J. (1924). *Z. Kristallogr.* **61**, 100.  
SCHWARZMANN, M. (1900). *Neues Jb. Miner.*, **2**, 1.  
SCHWARZMANN, M. (1901). *Neues Jb. Miner.*, **1**, 9.  
SOHON, F. W. (1941). *The Stereographic Projection*.  
UBBELOHDE, A. R., YOUNG, D. A. & MOORE, A. W. (1963). *Nature, Lond.* **198**, 1192.

*Acta Cryst.* (1966). **20**, 54

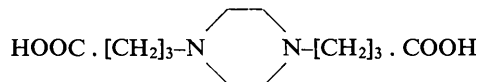
## The Crystal Structure of 1,4-Piperazine- $\gamma,\gamma'$ -dibutyric Acid

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(Received 13 May 1964 and in revised form 20 May 1965)

1,4-Piperazine- $\gamma,\gamma'$ -dibutyric acid crystallizes in the space group  $P2_1/a$  with two molecules of

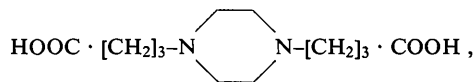


in the unit cell of dimensions  $a = 15.554 \pm 0.004$ ,  $b = 6.502 \pm 0.002$ ,  $c = 6.702 \pm 0.002$  Å;  $\beta = 91.54^\circ \pm 0.04^\circ$ .

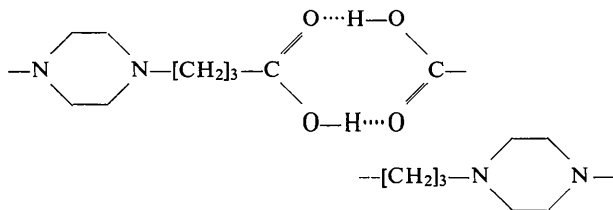
A trial structure was obtained by a sign-relation method developed for three dimensions, and this has been refined by electron-density and least-squares syntheses. The only hydrogen bonds in the structure are between hydroxyl oxygen atoms and the ring nitrogen atoms in adjacent molecules; the O—H...N distance is  $2.60 \pm 0.01$  Å.

#### Introduction

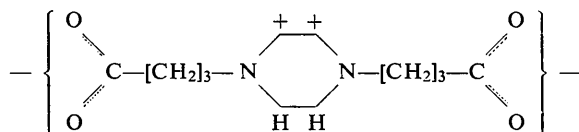
1,4-Piperazine- $\gamma,\gamma'$ -dibutyric acid,



was prepared during investigations in polymer chemistry. The infrared spectrum does not correspond with either the dimer form



or the zwitterion form



of hydrogen bonding, although the potassium salt and the hydrochloride give the expected spectra (Stace,

1962). It appeared therefore that the hydrogen bonding should be investigated by X-ray analysis. [A preliminary report of the structure has already been published (Potter, 1962)].

#### Experimental

This amino acid crystallizes from anhydrous methanol in the presence of dry ether as colourless laths which cleave very readily parallel to (100). Care was necessary during all operations to keep moisture out, as the substance has a great affinity for water. The crystals last only a few hours on exposure to air; they gradually turn white owing to uptake of water. When the crystals are coated with a clear thixotropic varnish, their crystalline 'life' is increased to a few days.

Oscillation and Weissenberg photographs taken with Cu  $K\alpha$  radiation indicated the Laue symmetry  $2/m$ , with systematic absences  $h0l$  for  $h$  odd and  $0k0$  for  $k$  odd, thus uniquely determining the space group as  $P2_1/a$ . The unit cell dimensions are:

$$a = 15.554 \pm 0.004, \quad b = 6.502 \pm 0.002, \quad c = 6.702 \pm 0.002 \text{ \AA} \\ \beta = 91.54^\circ \pm 0.04^\circ.$$

$$D_m = 1.27 \text{ g.cm}^{-3}; \quad D_x = 1.24 \text{ g.cm}^{-3}; \quad Z = 2.$$

Absorption coefficient for Cu  $K\alpha$  radiation,  $9 \text{ cm}^{-1}$ .

The space group indicates that the molecule must be centrosymmetric, thus locating the centre of the ring at a crystallographic centre of symmetry.

The intensities were recorded on multiple-film equi-inclination Weissenberg photographs taken about [010] (the needle axis) with Cu  $K\alpha$  radiation. All layer lines

having inclination angles less than  $45^\circ$  were recorded ( $k$  from 0 to 5 inclusive). Measurements were made by visual comparison with a calibrated wedge prepared from a strong reflexion from one of the crystals used for the intensity photographs. No attempt was made to correct the upper-layer intensities for spot distortion, measurements being made on spots on the contracted side of the film. Lorentz-polarization corrections only were applied, and intensities placed approximately on the absolute scale by the method due to Wilson (1942). The 995 reflexions measured in this way represent 78% of the possible number. Owing to the affinity for moisture, a different crystal had to be used for each layer; crystals of approximately the same dimensions were used in each case.

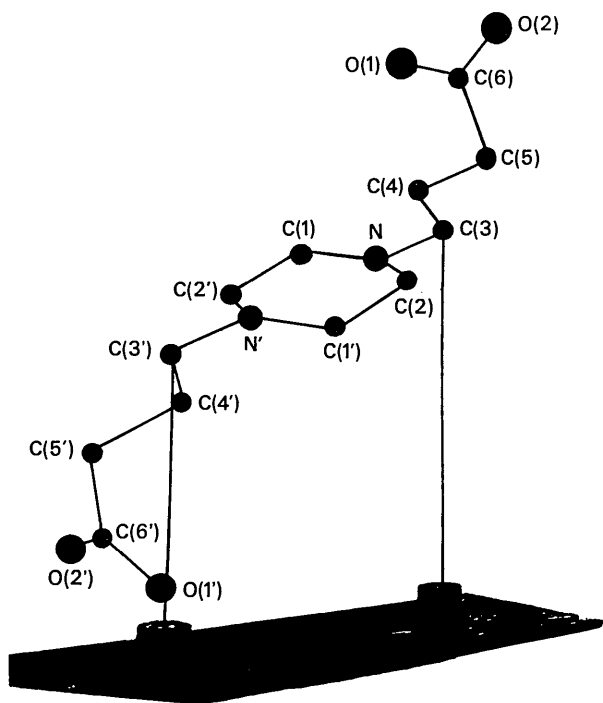


Fig. 1. Numbering of atoms adopted in the text.

### Structure determination

A trial structure was obtained by the sign-fixing method developed by Grant, Hine & Richards (1960) for three-dimensional data. Of the 995 observed intensities, 87 terms with unitary structure factors  $\geq 0.15$  were included in the search for products and an iterative process yielded 71 signs for inclusion in an electron-density synthesis. This showed the structure in detail; later work indicated that all 71 signs were correct.

Initial refinement of the trial structure was carried out by electron-density syntheses. Structure factors were calculated on the basis of coordinates obtained from the first electron-density synthesis, from which 331 signs could be confidently allocated to the observed terms. Two further cycles were completed; at this stage, signs had been allocated to 913 of the 995 observed terms.

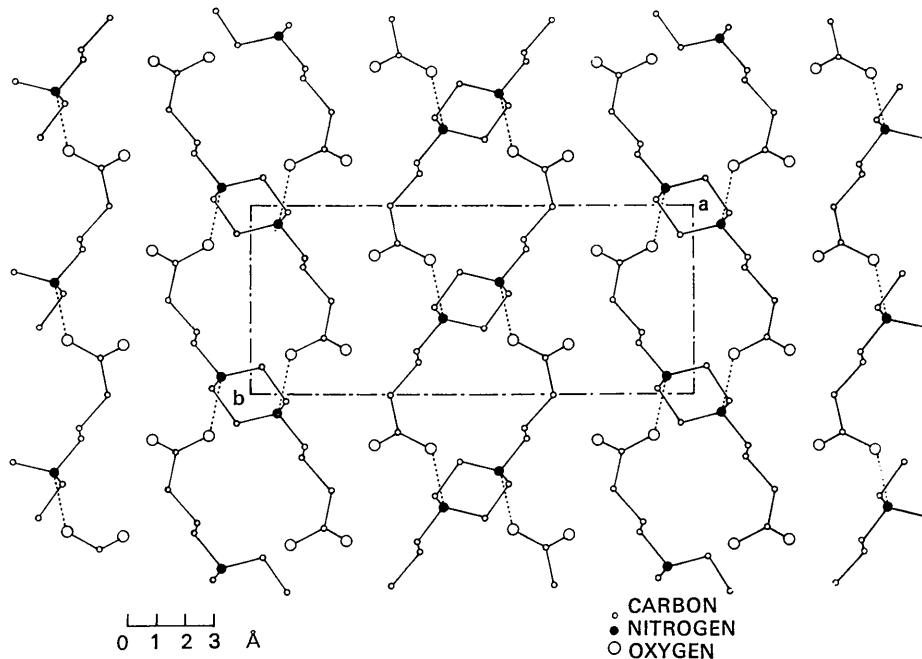


Fig. 2. Unit-cell contents. Hydrogen bonding indicated by broken lines.

The parameters were refined to the values finally adopted by three-dimensional least-squares syntheses using a program written for the Ferranti Pegasus computer (Cruickshank, 1962). Four cycles were completed before the contribution of the hydrogen atoms was considered. An  $F_o-F_c$  synthesis (where  $F_c$  does not include hydrogen contributions) revealed the hydrogen atoms as well-resolved maxima. This synthesis showed quite clearly that hydrogen bonding occurs between carboxyl oxygen atoms and the ring nitrogen atoms in adjacent molecules (Fig. 2). Hydrogen positions were also calculated from known bond distances and angles. For the hydrogen atoms bonded to carbon the normal tetrahedral arrangement was assumed with C-H distances of 1.07 Å. The calculated hydrogen atomic positions were kept fixed during the least-squares refinement. Three more cycles of least-squares were computed, layer by layer, before combining all layers together. Two further cycles yielded a final overall 'R' value of 0.147.

The final observed and calculated structure factors are listed in Table 1, and final values of the coordinates in Table 2. The final composite electron-density map is shown in Fig. 3; a comparison of the final calculated hydrogen atomic positions with those measured from the final  $F_o-F_c$  synthesis is made in Table 3. The composite difference synthesis showing the hydrogen atoms is shown in Fig. 4.

### Discussion

Bond lengths and angles calculated on the basis of the final coordinates are shown in Fig. 5, and listed together with the estimated standard deviations in Table 4. Fig. 2 shows the unit-cell contents. The short intermolecular hydrogen bonds are between hydroxyl oxygen atoms and the ring nitrogen atoms of adjacent molecules. O-H...N bonds are necessarily of infrequent occurrence (Donohue, 1952; Pimentel & McClellan, 1960), because, from energy considerations, O-H...O bonds are preferentially formed when possible. Amino-acids in general have a hydrogen bonding system involving O-H...N bonds which are rather long: for example L-glutamic acid (Hirokawa, 1955) has such bonds of length 2.86, 2.92, 2.94, 2.86 Å, DL-norleucine (Mathieson, 1953) 2.73, 2.87 Å. By comparison, the O-H...N distance in 1,4-piperazine- $\gamma,\gamma'$ -dibutyric acid is  $2.60 \pm 0.01$  Å. However, there are examples in the literature of O-H...N distances of this order of magnitude; for example cysteylglycine-sodium iodide (Dyer, 1951) and guanine hydrochloride (Broomhead, 1951) have such bonds of length 2.55 and 2.62 Å respectively.

The N-H distance in 1,4-piperazine- $\gamma,\gamma'$ -dibutyric acid is found to be 1.11 Å. This 'lengthening' of the covalent bond is a feature of very strong hydrogen bonds. (It has not been possible to locate this hydrogen atom with any precision, but it is hoped that this may be possible later by neutron diffraction.) No intermolecular distance in the structure, other than the hydrogen bonds mentioned above, is shorter than 3.27 Å.

As the space group shows that the ring is disposed about a crystallographic centre of symmetry, it must therefore be chair-shaped. This is confirmed by the structure determination. The fact that the C(6)-O(2) bond is much shorter than the C(6)-O(1) bond supports the conclusion that the hydrogen atom is attached to O(1) and not to O(2).

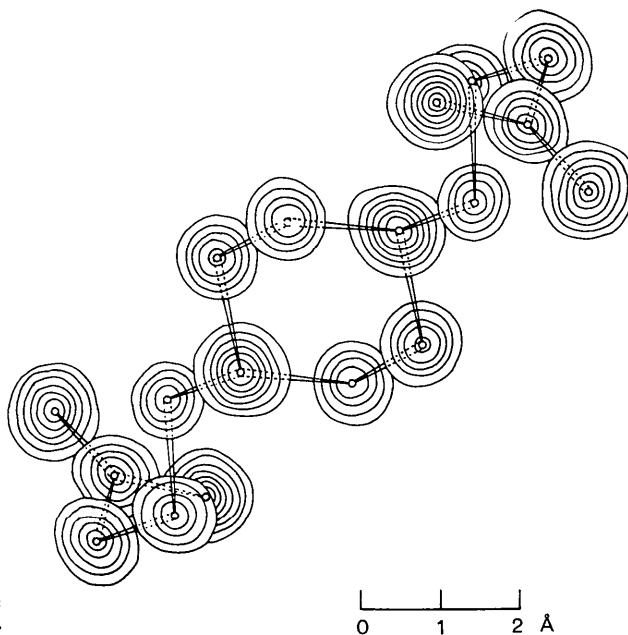


Fig. 3. Final composite electron-density synthesis. Contours at  $1 e.\text{Å}^{-3}$  starting at  $2 e.\text{Å}^{-3}$ .

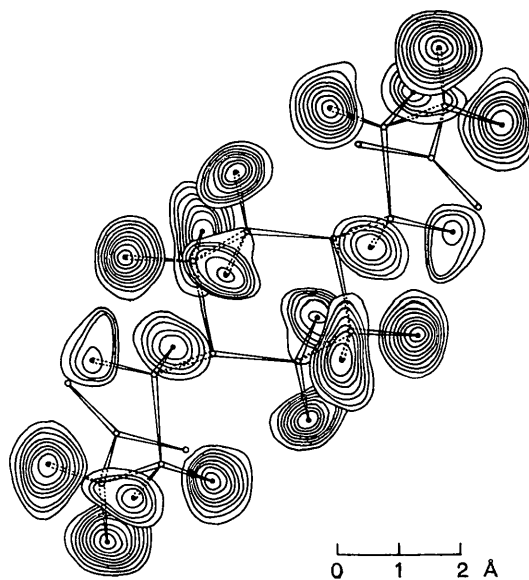


Fig. 4. Composite difference synthesis showing the hydrogen atoms. Contours at  $0.05 e.\text{Å}^{-3}$  beginning at  $0.1 e.\text{Å}^{-3}$ .

Table 1. Observed and calculated structure factors

h	F <sub>c</sub>	F <sub>o</sub>	h	F <sub>c</sub>	F <sub>o</sub>	h	F <sub>c</sub>	F <sub>o</sub>	h	F <sub>c</sub>	F <sub>o</sub>	h	F <sub>c</sub>	F <sub>o</sub>	h	F <sub>c</sub>	F <sub>o</sub>	h	F <sub>c</sub>	F <sub>o</sub>	h	F <sub>c</sub>	F <sub>o</sub>																																																																																																																																																																																													
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Table 4(a). Bond lengths and other interatomic distances with their standard deviations

N(0) is the nitrogen atom in an adjacent molecule bonded to O(1) by H(0).

	Length	e.s.d.
O(1)-C(6)	1.31 Å	0.01 Å
O(2)-C(6)	1.21	0.01
C(6)-C(5)	1.54	0.01
C(5)-C(4)	1.53	0.01
C(4)-C(3)	1.50	0.01
C(3)-N	1.51	0.01
N-C(2)	1.49	0.01
C(2)-C(1')	1.51	0.01
N-C(1)	1.47	0.01
C(1)-C(2')	1.51	0.01
O(1)-N(0)	2.60	0.01
O(1)-H(0)	1.52	
H(0)-N(0)	1.11	

Table 4(b). Bond angles with their standard deviations

Angle	Value	e.s.d.
O(1)-C(6)-O(2)	125°	1°
O(2)-C(6)-C(5)	122	1
O(1)-C(6)-C(5)	113	1
C(6)-C(5)-C(4)	113	1
C(5)-C(4)-C(3)	110	1
C(4)-C(3)-N	112	1

Table 4(b) (cont.)

Angle	Value	e.s.d.
C(2)-N-C(1)	110	1
C(3)-N-C(1)	114	1
N-C(2)-C(1')	110	1
N-C(1)-C(2')	111	1
C(6)-O(1)-N(0)	111	1
C(6)-O(1)-H(0)	105	
O(1)-H(0)-N(0)	163	
C(3)-N-C(2)	107	1

## References

- BROOMHEAD, J. M. (1951). *Acta Cryst.* **4**, 92.  
 CRUICKSHANK, D. W. J. (1962). I.U.Cr. *World List of Crystallographic Computer Programs*. First Ed. p. 21.  
 DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.  
 DYER, H. B. (1951). *Acta Cryst.* **4**, 42.  
 GRANT, D. F., HINE, R. & RICHARDS, J. P. G. (1960). *Acta Cryst.* **13**, 996.  
 HIROKAWA, S. (1955). *Acta Cryst.* **8**, 637.  
 MATHIESON, A. McL. (1953). *Acta Cryst.* **6**, 399.  
 PIMENTEL, G. C. & McCLELLAN, A. L. (1960). *The Hydrogen Bond*. London: Freeman.  
 POTTER, R. (1962). *Nature, Lond.* **193**, 673.  
 STACE, B. C. (1962). Private communication.  
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

*Acta Cryst.* (1966). **20**, 59

## The Crystal Structure of a Sodium Molybdenum Bronze

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(Received 11 December 1964 and in revised form 20 May 1965)

The sodium molybdenum bronze of reported composition  $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$  has a monoclinic structure with space group  $C2/m$ ,  $C2$  or  $Cm$ , and cell dimensions  $a = 9.57$ ,  $b = 5.50$ ,  $c = 12.95$  Å,  $\beta = 90^\circ$ ; and two formula units per unit cell. Crystals are always repeatedly twinned about the normals to (310) and (3 $\bar{1}$ 0), and the composite reciprocal lattice has trigonal symmetry  $P\bar{3}m1$ . The corresponding 'average structure', representing a disordered superposition of various domain arrangements, was solved by three-dimensional Patterson methods, and refined by differential Fourier techniques. It is a trigonally distorted perovskite structure, in which the sodium ions are ordered in one sixth of the voids left between the  $\text{MoO}_6$  octahedra; and it requires either a ratio  $\text{Mo}:\text{O} = 0:18$  or randomness in the distribution of 17 oxygen atoms over 18 sites. The further distortion of the true structure to monoclinic, though not fully soluble, is consistent with the ordered distribution of 34 oxygen atoms in the unit cell. The detailed environments of the atoms are discussed.

### Introduction

A recent report by Wold, Kunmann, Arnott & Ferretti (1964) describes what is probably the first synthesis of alkali-metal molybdenum bronzes. The success of this preparation is dependent upon both the reduction temperature and the molar ratio of alkali-metal molybdate to molybdic anhydride. The reduction was carried out at a platinum cathode in a melt of the above components.

The structures of the potassium molybdenum bronzes have been described (Graham, Stephenson, Wads-

ley & Wold, 1965). The present work concerns a sodium molybdenum bronze reported by Wold *et al.* to be within the composition range  $\text{Na}_{0.93}\text{Mo}_{5.9}\text{O}_{17}$  to  $\text{Na}_{0.87}\text{Mo}_{5.95}\text{O}_{17}$  and thus to approach the composition  $\text{NaMo}_6\text{O}_{17}$ ; a three-dimensional structure analysis has been made.

### Determination of the unit cell and twin relationships

Crystals of the sodium molybdenum bronze, which were apparently single, invariably gave Weissenberg photographs indicating twinning, as shown by the fact