The Crystal Structure of Dibromodehydrobispulegone

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The crystal structure of 'dibromodehydrobispulegone', $C_{20}H_{26}Br_2O$, has been determined from three-dimensional X-ray analysis. The crystals are orthorhombic, space group $P2_12_12_1$, and the cell dimensions are: $a = 16·88 \pm 0·01$, $b = 13·45 \pm 0·01$, $c = 8·54 \pm 0·01$ Å. There are four molecules per unit cell. The structure has been solved by the heavy-atom technique and refined by three-dimensional differential synthesis.

Introduction

The present work was undertaken to investigate particularly the stereochemistry of 'dibrmoodehydrobispu-

Fig. 1. Molecular structures proposed for dibromodehydrobispulegone.

legone', $C_{20}H_{26}Br_2O$. An extensive chemical study of this compound has already appeared in the literature (Camps, Esquefa, Ferrer, Magrans, Pasqual & Sust, 1961). Two possible structures (*a*) and (*b*) in Fig. 1) had been proposed. It was thought convenient to study this compound by X-ray techniques to establish its correct structure.

Experimental

A cristalline specimen of 'dibromodehydrobispulegone' was kindly made available to us by Dr J. Pascual Vila (Departamento de Química Orgánica, Universidad de Barcelona). Crystals were colourless needles elongated along the *b* axis. The space group was determined from zero, first and second layer Weissenberg photographs around the *b* and *c* axes. Unit-cell dimensions were determined from zero layer Weissenberg photographs. The density of the crystals was measured by the flotation method in aqueous potassium iodide.

Crystal data

Crystal system: orthorhombic.

Systematic absences: $h00$ when h is odd
$0k0$ when k is odd
$00l$ when l is odd

Space group: $P2_12_12_1$.
$a = 16·88 \pm 0·01$, $b = 13·45 \pm 0·01$, $c = 8·54 \pm 0·01$ Å. $Z = 4$, $D_m = 1·532$ g.cm⁻³, $D_x = 1·498$ g.cm⁻³.

The number of electrons per unit cell $F(000)$ is 896 and the absorption coefficient for Cu $K\alpha$ radiation is 65·179 cm⁻¹.

Intensity data were collected at room temperature from the zero to four levels around the *b* axis and the zero to third levels around the *c* axis with an equi-inclination Weissenberg camera. The multiple film technique was used. Intensities were estimated visually with a calibrated standard scale. Geometrically corrections were applied, and all the intensities were converted into structure amplitudes and placed on a common scale by a least-squares method described by Rollett & Sparks (1960), on an IBM 7070 computer. Since a sufficiently
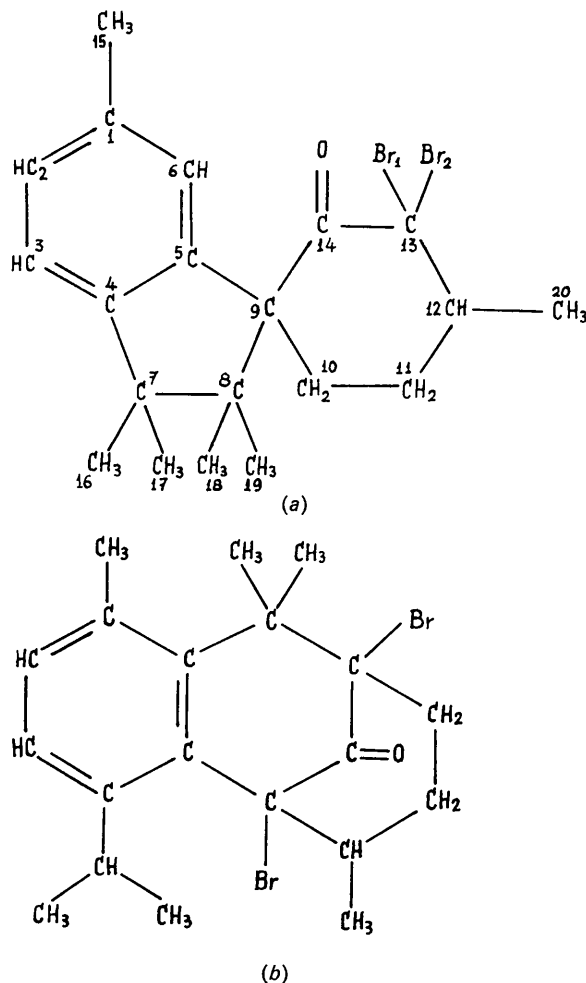
Table 1. *Observed and calculated structure factors*

H	K	L	FOBS	FCAL

Table 1 (cont.)

small crystal was used, no absorption corrections were applied.

Determination of the structure

The structure was solved by the heavy atom technique. Approximate x and z coordinates for the bromine atoms were obtained from an (010) Patterson projection and from a Buerger's minimum function. The first Fourier synthesis, calculated with phases from these co-ordinates, gave no further information about the rest of the molecule.

The structure amplitudes for all observed reflexions were used in preparing a three-dimensional Patterson synthesis. In this synthesis the bromine atoms coordinates have been referred to the conventional origin given in *International Tables for X-ray Crystallography* (1952), namely, midway between the three non-intersec-
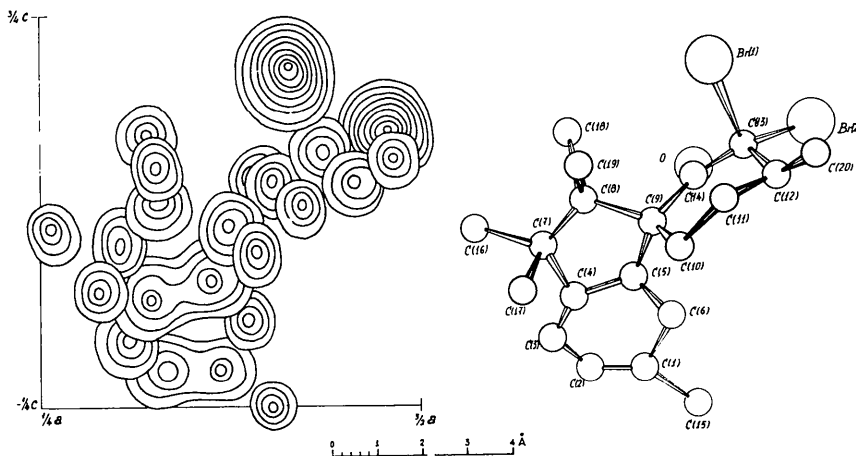
Fig. 2. A composite diagram of the last electron-density function. Contours are drawn at arbitrary intervals.

ting screw axes. The x and z coordinates of the bromine atoms were in agreement with those found from the minimum function M_2 and from the (010) Fourier projection, but no attempt was made to locate any other atoms from the Patterson synthesis. An average isotropic temperature factor $B = 3.57$ Å^{-2} was calculated from a Wilson plot. A set of structure factors, calculated from the coordinates of the bromine atoms alone, produced an R value of 0.358. The positional and isotropic thermal parameters of the bromine atoms were refined by three-dimensional differential synthesis and the corresponding phases were calculated for all reflexions in order to compute a three-dimensional Fourier synthesis. In this synthesis reflexions for which $F_c < 5.00$ and $\sin \theta > 0.70$ were omitted.

Together with the large bromine peaks, the Fourier synthesis showed a number of other peaks, all of which had to be investigated as possible locations for the lighter atoms of the structure; distances from such peaks to the bromine atoms were obtained, and it was checked whether maxima and/or areas of positive density could be located in the Patterson map, which would agree with such distances. A this stage, a model based on the structure A in Fig. 1 was built and it was considered to be the most likely since eight of the twenty light atoms of the structure could be identified in the electron density map.

Positional and isotropic thermal parameters for these atoms were refined by three-dimensional differential Fourier synthesis. Next, employing the coordinates of

Table 2. *The atomic parameters*

	Fractional coordinates with e.s.d.'s in parenthesis			Anisotropic temperature coefficients* (Å²)					
	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1)	0·4988 (0·0022)	0·2271 (0·0023)	−0·1647 (0·0035)	18·61	6·33	8·52	−1·86	3·20	−4·09
C(2)	0·4156 (0·0018)	0·2323 (0·0022)	−0·1833 (0·0062)	7·38	4·56	7·32	−0·26	−0·44	0·73
C(3)	0·3705 (0·0015)	0·2957 (0·0032)	−0·0906 (0·0042)	11·58	10·42	6·38	3·08	2·00	2·39
C(4)	0·3950 (0·0016)	0·3444 (0·0023)	0·0456 (0·0048)	13·99	8·54	12·80	−1·04	0·56	0·31
C(5)	0·4773 (0·0014)	0·3334 (0·0022)	0·0695 (0·0030)	14·25	7·20	4·50	1·31	−0·14	−0·55
C(6)	0·5244 (0·0015)	0·2784 (0·0025)	0·0321 (0·0037)	8·97	6·20	8·46	−1·03	1·86	−1·40
C(7)	0·3573 (0·0017)	0·4053 (0·0020)	0·1655 (0·0040)	11·54	6·17	7·31	0·76	1·52	2·60
C(8)	0·4146 (0·0016)	0·4231 (0·0022)	0·2768 (0·0047)	10·63	5·68	8·54	−0·91	−0·31	3·68
C(9)	0·5044 (0·0021)	0·3967 (0·0023)	0·1997 (0·0059)	12·23	7·76	8·71	−2·26	4·54	0·92
C(10)	0·5425 (0·0021)	0·4925 (0·0024)	0·1139 (0·0061)	14·88	11·34	13·14	−2·70	9·30	−3·41
C(11)	0·5986 (0·0019)	0·5554 (0·0023)	0·2425 (0·0051)	7·23	8·02	9·79	−0·72	1·09	−0·63
C(12)	0·6645 (0·0025)	0·4827 (0·0030)	0·3105 (0·0078)	9·86	11·82	17·07	0·60	2·95	−3·92
C(13)	0·6257 (0·0018)	0·3889 (0·0012)	0·3962 (0·0044)	8·59	4·86	7·81	3·57	−1·00	−2·25
C(14)	0·5626 (0·0015)	0·3462 (0·0023)	0·3017 (0·0054)	6·35	5·38	8·27	−2·17	2·67	0·65
C(15)	0·5529 (0·0013)	0·1705 (0·0021)	−0·2602 (0·0023)	7·18	3·25	0·95	3·50	0·75	2·42
C(16)	0·2728 (0·0019)	0·3573 (0·0035)	0·2022 (0·0056)	10·20	14·20	9·78	1·50	0·19	−0·01
C(17)	0·3438 (0·0028)	0·5039 (0·0032)	0·0601 (0·0072)	16·93	11·55	12·37	3·86	−2·16	−1·69
C(18)	0·4084 (0·0021)	0·3418 (0·0025)	0·4243 (0·0056)	14·03	9·40	15·52	0·30	−2·20	4·07
C(19)	0·4084 (0·0016)	0·5258 (0·0021)	0·3708 (0·0071)	12·54	6·35	14·82	1·43	0·40	4·30
C(20)	0·7264 (0·0016)	0·5448 (0·0028)	0·3955 (0·0042)	8·46	8·57	14·30	−0·29	4·80	−3·15
O	0·5507 (0·0013)	0·2546 (0·0014)	0·3303 (0·0030)	11·76	5·23	7·22	1·32	0·90	−0·23
Br(1)	0·5891 (0·00022)	0·4378 (0·00031)	0·6030 (0·00048)	9·94	7·18	7·59	0·08	0·86	0·53
Br(2)	0·7139 (0·00024)	0·3919 (0·00035)	0·4330 (0·00066)	11·72	9·19	11·53	2·08	1·81	−0·78

* In the expression $f_0 \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + \ldots + B_{13}2hla^*c^*)\right]$.

these additional atoms, a new set of phases was determined, for which the agreement index R, dropped to 0·318.

A second three-dimensional Fourier synthesis was computed, and four new atomic positions were identified. Positional and isotropic thermal parameters for those new atoms were refined as before and structure factors were determined. The R value dropped to 0·308. Phase changes affected weak reflexions only. The following step was to calculate a new three-dimensional synthesis, excluding the contribution of the two bromine atoms.

From all unknown peaks furnished by this synthesis, six other light atoms were identified on the basis of peak heights, shapes and persistence in former syntheses. With the coordinates of the twenty atoms found so far, a structural model was built, with the result that neither of the two proposed structures (A and B in Fig. 1) could be recognized in it. It was necessary to reconsider the significance and reliability of every atomic position, and of every prominent peak which had appeared in former syntheses, the result being that if three of the

light atoms previously found were eliminated as unreliable, then the benzene ring, the pentagonal ring and three carbon atoms of the methyl groups would show up. Also two carbon atoms, C(13) and C(14), of the cyclohexane ring and an extra peak near C(14) were consistent with configuration A of Fig. 1. Phases were recalculated with the coordinates of the two bromine bromine atoms and of fifteen light atoms (all taken as carbon atoms). A fourth synthesis was computed, and the remaining six light atoms were found.

At this stage all the data obtained were found to be in agreement with configuration (a) of Fig. 1. Thus the doubt about whether the atomic position near the C(14) atom would correspond to the oxygen atom no longer existed. There is enough chemical evidence to support this fact (Camps *et al.*, 1961). Also, the distance between these two atoms is shorter than a C–C bond, or even a C=C bond. Therefore the position of the oxygen atom was identified. Further confirmation was obtained through a fifth three-dimensional synthesis in which this atom was made to contribute as an oxygen atom. The corresponding peak in the new electron density map was now stronger than the other carbon peaks. Fig. 2 shows the electron density map along to the b axis. The subsequent agreement index was $R=0·191$.

Refinement

The structure was refined by successive cycles of the full three-dimensional data. First a set of three cycles of differential synthesis with isotropic thermal parameters was computed, the R value achieved being 0·178. Through this refinement a large anisotropic thermal vibration on the a axis could be observed, thus the refinement was continued with anisotropic thermal parameters for each atom, in the form:

$$f_0 \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + \cdots + B_{13}\,2hla^*\,c^*)\right].$$

After three cycles the agreement index dropped to $R=0·161$.

Final structure factors are given in Table 1. Table 2 gives anisotropic thermal parameters and final coordinates with standard deviations. Bond angles and bond lengths are shown in Tables 3 and 4.
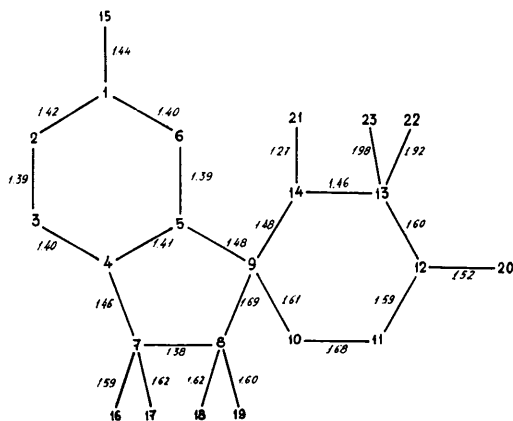
Fig. 3. Bond lengths in dibromodehydrobispulegone.
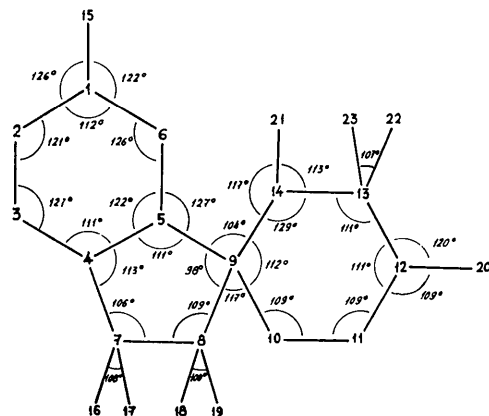
Fig. 4. Bond angles in dibromodehydrobispulegone.

A C 25B – 10*

Table 3. *Bond lengths*

C(1)–C(2)	1·42 Å	C(8)—C(18)	1·67 Å
C(3)–C(4)	1·40	C(9)—C(10)	1·62
C(2)–C(3)	1·39	C(8)—C(19)	1·60
C(4)–C(5)	1·41	C(10)–C(11)	1·68
C(5)–C(6)	1·39	C(11)–C(12)	1·59
C(6)–C(1)	1·40	C(12)–C(13)	1·60
C(5)–C(9)	1·48	C(14)–C(9)	1·48
C(9)–C(8)	1·69	C(12)–C(20)	1·52
C(8)–C(7)	1·38	C(14)–O	1·27
C(7)–C(4)	1·46	C(13)–Br(1)	1·98
C(1)–C(15)	1·44	C(13)–C(14)	1·46
C(7)–C(16)	1·60	C(13)–Br(2)	1·92
C(7)–C(17)	1·62		

Table 4. *Bond angles*

C(1)–C(2)–C(3)	120°	C(10)–C(11)–C(12)	109°
C(2)–C(3)–C(4)	126	C(11)–C(12)–C(13)	111
C(3)–C(4)–C(5)	111	C(12)–C(13)–C(14)	111
C(4)–C(5)–C(6)	121	C(11)–C(12)–C(20)	109
C(5)–C(6)–C(1)	126	C(13)–C(12)–C(20)	120
C(6)–C(1)–C(2)	112	C(13)–C(14)–C(21)	113
C(5)–C(4)–C(7)	113	C(23)–C(13)–C(22)	107
C(4)–C(7)–C(8)	106	C(14)–C(9)—C(10)	102
C(7)–C(8)–C(9)	109	C(16)–C(7)—C(17)	108
C(8)–C(9)–C(5)	98	C(18)–C(8)—C(19)	100
C(9)–C(5)–C(4)	111	C(21)–C(14)–C(9)	109
C(6)–C(1)–C(15)	122	C(21)–C(14)–C(9)	117
C(2)–C(1)–C(15)	126	C(13)–C(14)–C(9)	129

The mean standard deviation in bond lengths is 0·04 Å and the mean standard deviation in bond angles is 2·96°. Intermolecular distances less than 4·0 Å are listed in Table 5.

The molecular structure

The equations for the best least-squares planes calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) are:

for the benzene ring.
$$0.2004X + 0.9773Y - 0.0686Z - 5.6090 = 0 ;$$
for the pentagonal ring:
$$0.1342X + 0.9890Y - 0.0628Z - 5.2281 = 0 ;$$
for the cyclohexane ring:
$$0.8070X - 0.5826Y - 0.0959Z - 2.3292 = 0 .$$

The deviations of the atoms from these planes (Table 6) shows that the benzene ring is planar, that the penta-

gonal ring is non planar – it has an envelope conformation – and that the cyclohexane ring is also non planar – it has a flattened chair conformation.

Table 5. *Intermolecular distances less than* 4 Å

The following roman numbers give the symmetry relationship of the atoms concerned.

I	(X,	Y,	Z)
II	(1 − X,	−½ + Y,	½ + Z)
III	(½ + X,	½ − Y,	−Z)
IV	(−½ + X,	½ − Y,	1 − Z)
VI	(1 − X,	½ + Y,	½ + Z)

Atom i		Atom j		d_{ij}
C(6)	I	C(19)	II	3·83 Å
C(15)	I	C(16)	III	3·76
C(15)	I	C(19)	II	3·91
C(16)	I	Br(2)	IV	3·91
C(17)	I	C(15)	V	3·83
C(17)	I	O	VI	3·92
C(19)	I	O	VI	3·60
O	I	C(10)	II	3·88
O	I	C(11)	II	3·73

The benzene ring and the pentagonal ring are nearly coplanar, the equation of the mean plane being

$$0.1698X + 0.9831Y - 0.0671Z - 5.3965 = 0 .$$

This plane makes an angle of 114° 19′ with the plane of the cyclohexane ring.

Bond lengths and bond angles are shown in Figs. 3 and 4. The mean C–C distance in the aromatic ring is 1·40 Å, and the mean bond angle is 119·8°, both values
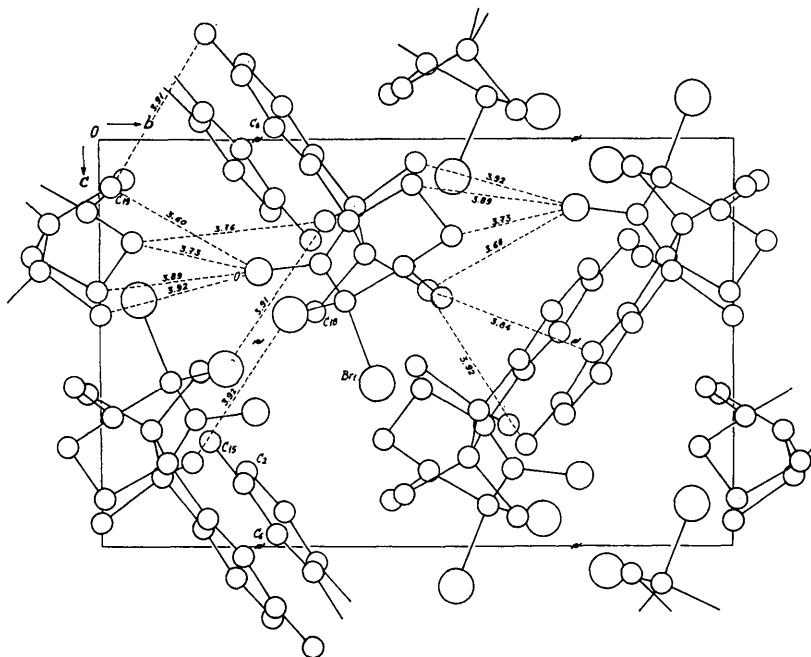
Fig. 5. Packing diagram projected down [100].

in good agreement with the accepted means for the benzene ring (1·395 Å and 120°). The mean value for the sp^3–sp^3 hybridization bond is 1·562 Å (against the accepted value of 1·54 Å for such bonds). Bond angles average 107·3° for the pentagonal ring, and 113·3° for the cyclohexane ring. The C=O and C–Br distances are usual.

The average values for non-aromatic C–C distances and angles are normal. Individual values, however, range from 1·38 Å to 1·69 Å, *i.e.* there are significant deviations from the single-bond value of 1·54 Å. Bond angles also deviate from the tetrahedral value of 109°28'.

From such deviations one may conclude that the molecule is under considerable stress. It should be pointed out that the larger deviations correspond to bonds or angles involving carbon atoms with maximum substitution. This condition usually implies important deviations from the theoretical means (Hall & Maslen, 1965).

However, the significance of the present deviations may be questioned if one considers the complexity of the molecule, the presence of heavy atoms, and also that the structure is non-centrosymmetric. Under such unfavourable conditions the present crystal structure analysis can provide a reliable method for solving particular configuration problems, but its results may be insufficiently accurate for a detailed discussion in terms of the theory of valence.

The crystal structure

Figs. 5 and 6 show projections of the structure along the *a* and *b* axes. Intermolecular distances less than 4·0 Å are also shown in these Figures. Molecular packing is determined by van der Waals forces, mainly between molecules related through screw axes. No additional features are obvious. Pronounced anisotropic thermal vibrations of the atoms along the *a* axis indicate the

Table 6. *Displacements* (Å) *of the atoms from the various planes*

(i)   Plane through benzene ring
(ii) Plane through pentagonal ring
(iii) Plane through ciclohexane ring

	(i)		(ii)		(iii)
C(1)	0·031	C(4)	0·002	C(9)	−0·209
C(2)	−0·072	C(5)	−0·085	C(10)	0·265
C(3)	0·063	C(7)	0·082	C(11)	−0·521
C(4)	−0·031	C(8)	−0·114	C(12)	0·387
C(5)	−0·020	C(9)	0·116	C(13)	−0·111
C(6)	0·012	C(16)	−1·052	C(14)	0·142
C(15)	−0·062	C(17)	1·907	C(20)	0·119
		C(18)	−2·145	O	0·425
		C(19)	0·596	Br(1)	−2·644
				Br(2)	1·493

Fig. 6. Packing diagram projected down [010].

absence of marked intermolecular binding in that direction.

The numerical calculations were carried out on an IBM 7070 computer (Centro de Cálculo Electrónico del C.S.I.C. Spain) with the use of programs of the Crystallography Laborato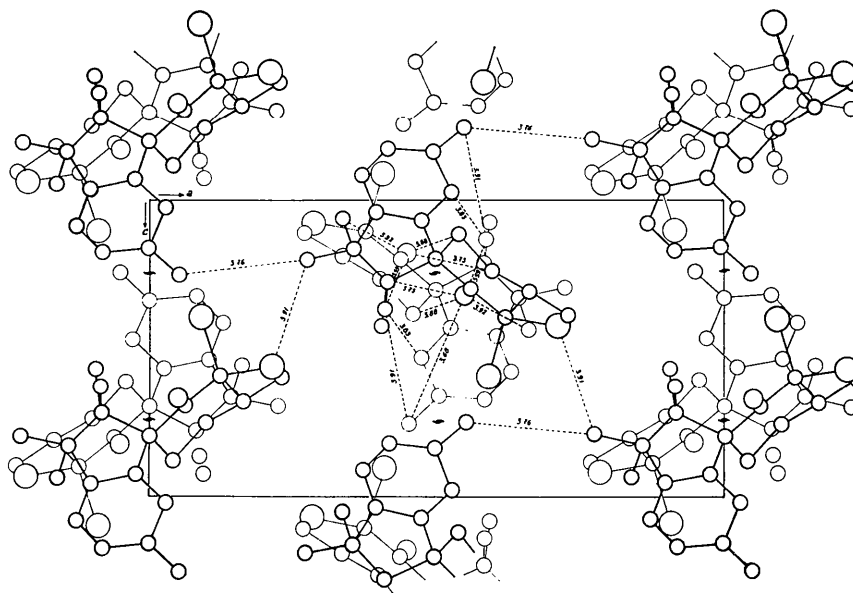ry of Pittsburg University. We wish to express our thanks to Professor G. A. Jeffrey for allowing us to use these programs. Part of this work forms part of the Ph.D. thesis of one of us (A.P.).

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The Crystal Structure of DL-Acetylleucine N-Methylamide, C9H18O2N2

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The crystal structure of DL-acetylleucine N-methylamide (ALNMA) has been determined by the symbolic addition procedure. The crystals are monoclinic, space group $P2_1/a$ with four molecules in a cell with the dimensions; $a = 8.46$, $b = 17.33$, $c = 8.24$ Å, and $\beta = 113.5°$. Full-matrix least-squares refinement with anisotropic temperature factors yielded the final R value of 0.15. The main chain of the molecule containing two *trans* planar peptide groups takes a nearly extended conformation, but the chain is puckered at the α-carbon atom as in the pleated-sheet β-structure of protein, the dihedral angle between the two peptide planes being 108.4° and the torsion angles, φ and ψ (defined by Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga, *J. Mol. Biol.* (1966, **15**, 339), are 86.2° and −41.4° respectively, for the L-molecules. Within the crystal, two kinds of chains of molecules, each consisting of D- and L-molecules, are joined together alternately through N–H···O hydrogen bonds in the **b** direction to form a sheet structure. The leucyl side chains are nearly perpendicular to the sheet and form a hydrophobic region between adjacent sheets.

Introduction

In the course of a study on near-infrared spectra of compounds containing two peptide groups, Mizushima, Shimanouchi, Tsuboi, Kuratani, Sugita, Mataga & Souda (1953) suggested that the molecules of acetylleucine N-methylamide (ALNMA) in the crystalline state take an extended form and are associated through double hydrogen bonds (Fig. 1). Since this substance can be taken as a simple model compound of the polypeptides, it may be of interest to confirm this suggestion and to determine the accurate molecular conformation. An X-ray analysis of the crystal structure of DL-ALNMA has, therefore, been carried out.

Experimental

The crystals of ALNMA were grown from ethyl acetate solution. They were colourless plates elongated along the *b* axis with easy cleavage on (001). The lattice dimensions were measured on precession photographs taken with Cu *Kα* radiation.

Three-dimensional intensity data were collected from equi-inclination Weissenberg photographs, taken with

Crystal data

DL-Acetylleucine N-methylamide, C9H18O2N2

Crystal system	Monoclinic
a	8.46 ± 0.01 Å
b	17.33 ± 0.02
c	8.24 ± 0.01
β	$113.5 \pm 0.2°$
U	1101.8 Å^3
$U/$mole	275.5 Å^3
Systematic absences	$h0l$ when $h = 2n$
	$0k0$ when $k = 2n$
Space group	$P2_1/a$
Z	4

Cu *Kα* radiation on multiple-film packs. Intensities were measured visually with a calibrated intensity scale and corrected for Lorentz, polarization and spot-shape (Phillips, 1954) factors. Because of the low linear absorption coefficient [μ(Cu *Kα*) = 7.46 cm^{-1}] and the small cross-sections of the crystals, no absorption correction was applied. These intensity data were scaled by correlating various layers and the mean temperature factor was calculated by Wilson's (1942) method.