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Crystal Packing of Amides: X-ray Structure Analysis of Optically Active Dilactylamide

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Crystals of optically active dilactylamide are hexagonal, space group $P6_522$ ($P6_122$), $a=b=8\cdot246\pm0\cdot005$, $c=22\cdot607\pm0\cdot015$ Å. The structure has been solved assuming that the molecules are held together in an infinite chain by hydrogen bonds and calculating all the possible helical conformations obeying the space-group symmetry. On the basis of packing criteria a unique solution was derived. The model was refined by least-squares methods to an R value of 0·045 for the 492 independent reflexions collected on a Siemens automatic diffractometer.

Introduction

The molecular packing modes of primary amides have been extensively reviewed by Rabinovich (1969), Leiserowitz & Rabinovich (1969) and Leiserowitz & Schmidt (1969). These authors have pointed out the role of the NH···O lone-pair geometry in the packing arrangement of primary amides and, by analysing different structures, have shown some possible modes of deformation of the ideal arrangement of the hydrogen-bond system. The purpose of this paper is to show the way in which the general criteria of the NH···O lone-pair geometry, combined with the lattice symmetry, can be usefully applied to obtain a straightforward solution of the crystal structure of an amide, the optically active dilactylamide. Preliminary data on this compound have been already reported (Martuscelli, Mazzarella, Palumbo & Pedone, 1969).

Experimental

Optically active dilactylamide, $O[CH(CH_3)CONH_2]_2$, was prepared according to the procedure described by Vièles (1935). Crystals were grown from a warm satu-rated aqueous solution by slow cooling. They are colourless prismatic, with hexagonal section, elongated along the c axis.

Crystals are hexagonal, space group $P6_522$ ($P6_122$) from systematic absences (00l absent for $l\neq6n$) and the symmetry relationship of the reciprocal lattice ($I_{hkl}=I_{khl}$). Precise lattice constants were obtained from a least-squares refinement of the setting angles of 14 high angle reflexions on a Siemens AED automatic diffractometer with Cu $K\alpha$ radiation ($\lambda=1\cdot5418$ Å). A summary of the crystal data is given in Table 1. For the intensity measurements, the θ–2θ scan technique was employed. A standard reflexion was measured at regular intervals to monitor crystal stability. Its intensity remained essentially constant throughout the run. A total of 492 independent reflexions ($\theta_{max}=65°$) with intensity values larger than $2\cdot5\sigma(I)$, was collected. Their intensities were corrected for Lorentz and polarization effects in the usual way.

Structure determination

The space-group symmetry requires a dyad axis, through the oxygen atom, to be present in the molecule.

Table 1. *Crystal data*

Formula	$C_6H_{12}O_3N_2$
M.W.	192
$a = b$	8.246 ± 0.005 Å
c	22.607 ± 0.015
γ	$120°$
V	1331.3
Space group	$P6_522$ $(P6_122)$
Z	6
d_{RX}	1.202 g cm^{-3}
d_{exp}	1.19 g cm^{-3}

Assuming the presence of one hydrogen bond NH···O =C between two screw-related molecules, the dyad axis imposes the presence of a pair of hydrogen bonds of the type shown in Fig. 1(*a*), so that an infinite chain is generated having either $S6_1$ or $S3_1$ or $S2_1$ symmetry. A trial model of the structure can be derived as follows:

(1) Assuming an ideal geometry for the pair of hydrogen bonds, the chain can be simply schematized as in Fig. 1(*b*).

(2) All the helical conformations of the chain can be specified in terms of two internal rotation angles ψ and χ with fixed values for the other internal coordinates [see Fig. 1(*b*)]. The possible helices must have the symmetry quoted above and identity period '*d*' equal to the *c* axis (22·6 Å).

Fig. 2 shows, as function of the two internal rotation angles, all the helical conformations having an identity period '*d*' equal to the *c* axis (dotted lines) and a number of monomer per turn '*K*' equal to 2, 3 and 6 respectively. The solid lines, which correspond either to $K = 2.0$ or to $d = 0.0$ Å, divide zones of left and right-handed helices.

The $S2_1$ symmetry ($K = 2.0$) has no solution because the identity period is always much shorter than the length of the *c* axis. The $S6_1$ helices were left aside because, due to the large radius, the pattern of the packing seemed highly improbable.

The crossing points of the $K = 3.0$ and $d = 22.6$ Å

lines (helices having $S3_1$ symmetry) were considered possible solutions for the structure. Solutions occur in pairs, the pairs being the non-enantiomorphous right and left-handed helices; on the choice of an S,S configuration for the molecule, solutions occurring for ψ values less than $180°$ can be discarded, owing to a short methyl–methyl intramolecular interaction. Each of the four remaining solutions (A, B, C, D, Fig. 2), can be placed in two alternative positions of the unit cell, giving rise to a total of eight models. In every case the plane of the amide group was placed parallel to the helix axis for space-group conditions.

Only one of the eight models shows satisfactory intermolecular contacts. A least-squares isotropic refinement process, starting with the initial coordinates derived from the selected model ($R_{in} = 0.36$), converged in four cycles to a disagreement index $R = 0.16$ for all
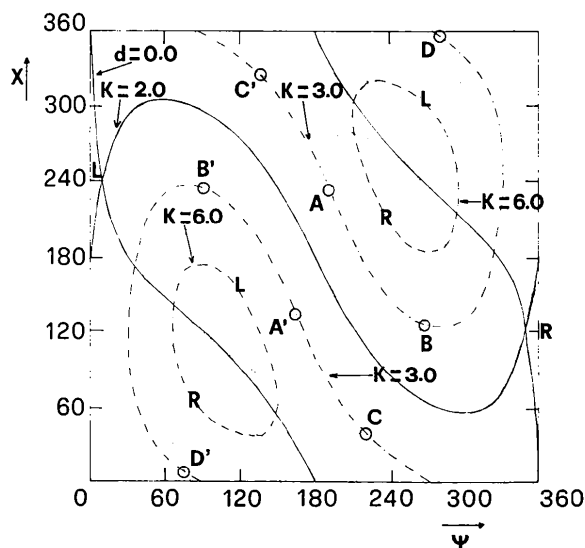

Fig. 2. Helical conformations as function of Ψ and χ. Dotted lines show helix chains with identity period equal to the *c* axis.
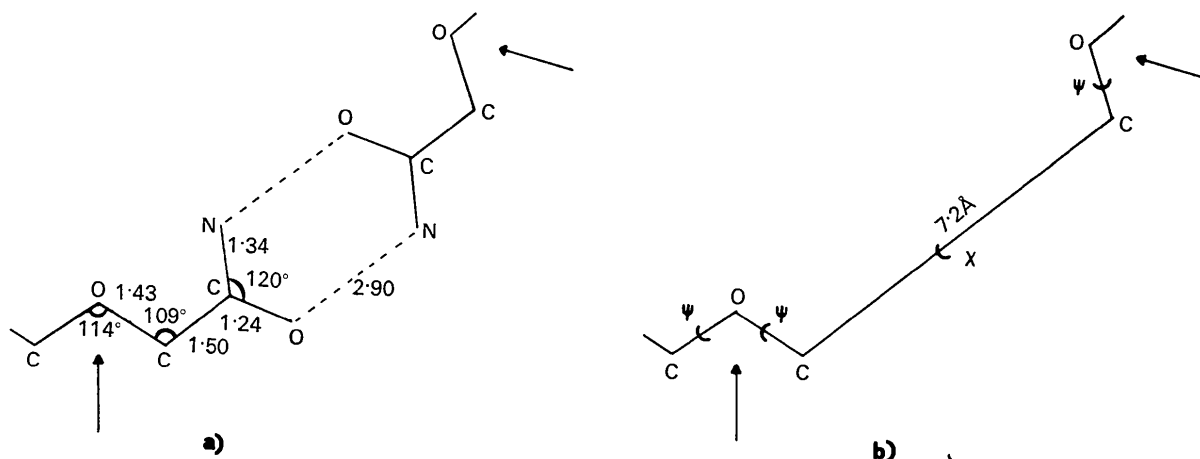

Fig. 1. Assumed hydrogen-bond scheme for optically active dilactylamide (*a*); idealized chain model (*b*).

the observed data $(R = \sum ||F_o| - |F_c||/\sum |F_o|)$. Introducing anisotropic thermal parameters for all atoms, R dropped to a value of 0·084. At this stage all the hydrogen atoms were located from a difference Fourier map and their parameters were refined in the last cycles

of the least-squares calculations with an individual isotropic temperature factor. A unitary weight factor was adopted and the refinement was continued until the calculated shift of heavy-atom coordinates was less than $\frac{1}{3}$ of the corresponding e.s.d.'s. The final conventional R value is 0·045. In Table 2 the final fractional coordinates and thermal factors are reported together with the corresponding standard deviations. A list of the structure factors is available on request from the authors.

Atomic scattering factors for C, N and O atoms were taken from Cromer & Mann (1968) and for hydrogen atoms from Moore (1963).

Discussion

Bond distances, bond angles and the most relevant dihedral angles of the molecule are reported in Table 3. These values are in agreement with data reported in the literature (Denne & Small, 1971) for similar compounds. Fig. 3 shows the molecular packing projected on the ac plane. In agreement with the starting model, the molecules are held by double bridge hydrogen bonds between facing amide groups; in addition the helices are connected by hydrogen bonds involving the second hydrogen of the nitrogen atom. The hydrogen bonding scheme is best shown in Fig. 4 where the most relevant parameters are indicated. One short intramolecular distance between $O(1) \cdots N$ ($= 2·58$ Å) cannot be attributed to the presence of a bifurcated hydrogen bond, owing to the unfavourable geometry of the acceptor atom; moreover the distance $O(1) \cdots H(2)$ ($= 2·33$ Å) even though it is less than the usually quoted sum of van der Waals radii (2·60 Å), is above the 'outer limit' $H \cdots O$ distance of 2·20 Å accepted for a nonhydrogen bonding situation (Ramachandran, Ramakrishnan & Sasisekharan, 1963). The amide group
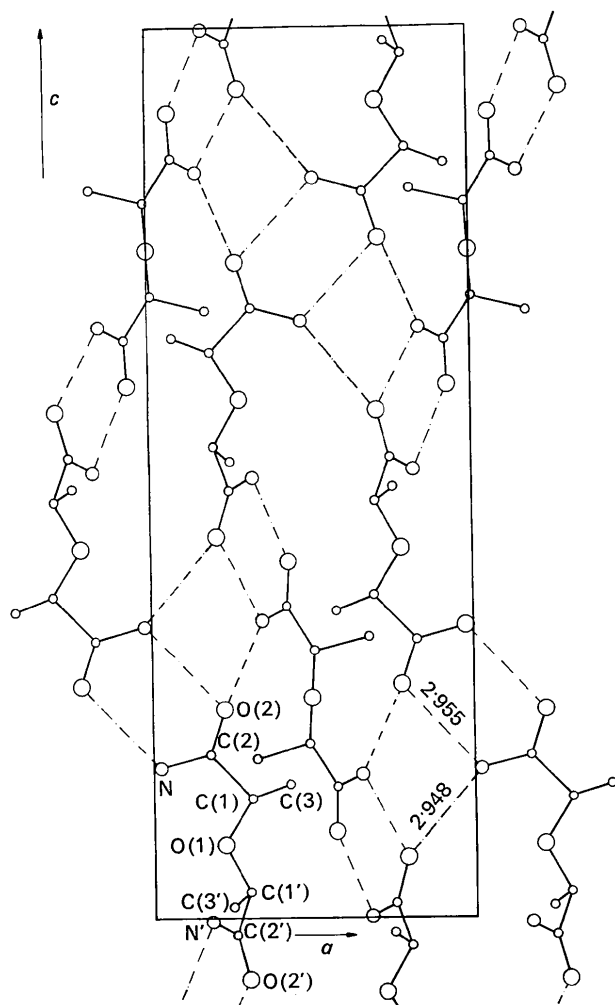

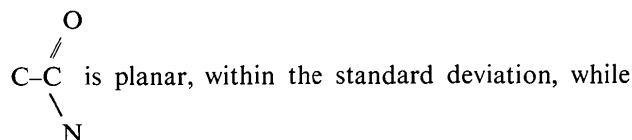Fig. 3. Molecular packing projected on the ac plane.

$$
\begin{matrix} & O \\ & \parallel \\ C\!-\!C & \text{is planar, within the standard deviation, while} \\ & \backslash \\ & N \end{matrix}
$$

Table 2. *Atomic coordinates* ($\times 10^4$) *and thermal vibration parameters* ($\times 10^2$)

The thermal vibration parameters are defined by the expression

$$[-\tfrac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)].$$

	x	y	z	B/B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	4787 (2)	5213 (2)	833	470 (11)	470 (11)	189 (8)	356 (12)	49 (8)	49 (8)
C(1)	5404 (4)	4763 (4)	1365 (1)	392 (13)	396 (14)	211 (9)	260 (11)	13 (9)	51 (10)
C(2)	4007 (4)	4463 (4)	1848 (1)	379 (13)	305 (12)	217 (8)	204 (11)	− 3 (9)	12 (9)
C(3)	7362 (5)	6271 (5)	1528 (1)	384 (15)	656 (21)	410 (13)	220 (15)	− 8 (12)	−42 (14)
N	2451 (3)	4421 (4)	1692 (1)	330 (11)	537 (13)	217 (7)	227 (11)	− 1 (8)	24 (10)
O(2)	4372 (3)	4264 (3)	2366 (1)	522 (11)	671 (12)	201 (6)	413 (10)	9 (7)	79 (8)
H(1)	5335 (39)	3544 (39)	1303 (11)	90 (62)					
H(2)	2130 (52)	4652 (49)	1281 (13)	312 (82)					
H(3)	1341 (56)	4051 (60)	1971 (17)	537 (111)					
H(4)	7528 (53)	7429 (54)	1632 (16)	489 (102)					
H(5)	7811 (50)	5993 (51)	1911 (15)	346 (84)					
H(6)	8287 (55)	6189 (57)	1132 (16)	452 (102)					

Table 3. *Bond lengths, bond angles and dihedral angles*

(a) Bond lengths

O(1)–C(1)	1·425 (3) Å	C(1)–C(2)	1·515 (4) Å	C(1)–C(3)	1·510 (4) Å
C(2)–O(2)	1·240 (3)	C(2)–N	1·314 (5)	C(1)–H(1)	0·99 (3)
N——H(2)	1·01 (3)	N——H(3)	1·02 (4)	C(3)–H(4)	0·93 (5)
C(3)–H(5)	1·01 (4)	C(3)–H(6)	1·20 (4)		

(b) Bond angles

C(1')–O(1)–C(1)	115·3 (2)°	O(1)–C(1)–C(3)	111·4 (2)°
O(1)–C(1)–C(2)	108·0 (3)	C(2)–C(1)–C(3)	111·8 (2)
C(1)–C(2)–O(2)	119·2 (3)	C(1)–C(2)–N	117·6 (2)
N——C(2)–O(2)	123·2 (3)	O(1)–C(1)–H(1)	107
C(3)–C(1)–H(1)	111	C(2)–C(1)–H(1)	106
C(2)–N——H(2)	126	C(2)–N——H(3)	124
H(2)–N——H(3)	110	C(1)–C(3)–H(4)	117
C(1)–C(3)–H(5)	113	C(1)–C(3)–H(6)	103
H(4)–C(3)–H(5)	98	H(4)–C(3)–H(6)	119
H(5)–C(3)–H(6)	108		

(c) Dihedral angles

IUPAC convention

C(1')–O(1)–C(1)–C(2)	212°	C(1')–O(1)–C(1)–C(3)	89°
O(1)–C(1)–C(2)–N	8	O(1)–C(1)–C(2)–O(2)	188
C(3)–C(1)–C(2)–O(2)	− 49		

the two facing amide groups in the system:

```
      O——N
     /     \
  -C-C      C-C-
     \     /
      N——O
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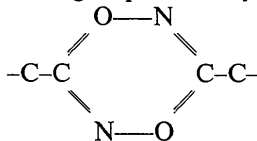
make a definite kink of about 17°.

Conclusion

We would like to point out that the type of approach used for the solution of the crystal structure of optically active dilactylamide, can also be applied to other cases where the geometry of the hydrogen bond can be safely postulated. In this context it may be worth while to quote the case of dimethylmalonic acid [$a = 12\cdot642$ (5) $c = 16\cdot237$ (5), space group $I4_1/acd$, $Z = 16$; Haas & Brenner, 1966]. The structure was solved by direct methods after, according to the authors, a previous attempt by conventional methods had failed. It can be verified that the application of a procedure such as that reported in the present paper, also leads to a straightforward solution of the structure.

Fig. 4. Hydrogen-bond scheme. The most relevant parameters are reported.

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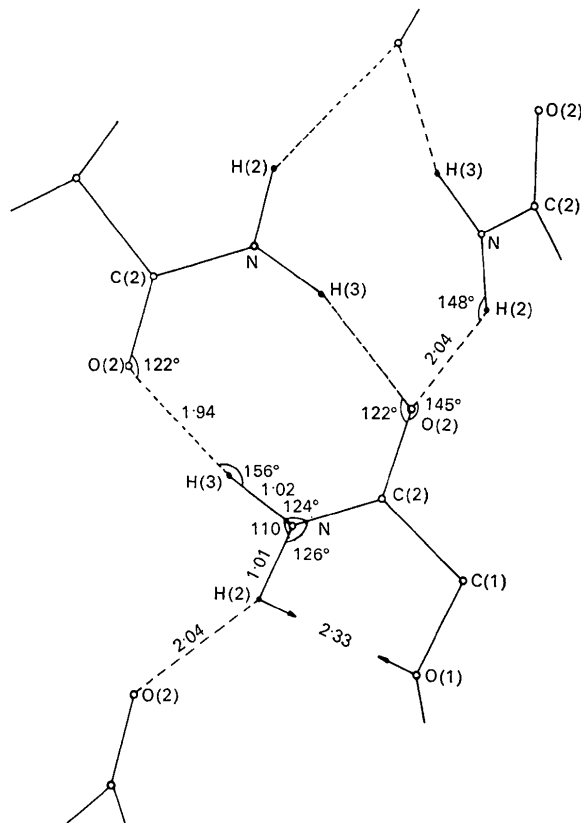MARTUSCELLI, E., MAZZARELLA, L., PALUMBO, R. & PEDONE, C. (1969). *Ric. Sci.* 39, 573–576.

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