Molecular Packing Modes. Part V.† Crystal and Molecular Structures of Fumaramic Acid

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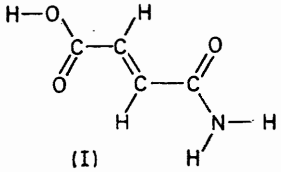
The crystal structure of the title compound has been solved from *X*-ray diffractometer data by direct methods and refined by least-squares to *R* 0·038 for 1182 independent reflections. Crystals are monoclinic, space group $P2_1$, with $Z = 2$ in a unit cell of dimensions: $a = 7{\cdot}367(1)$, $b = 9{\cdot}041(1)$, $c = 3{\cdot}742(1)$ Å, $\beta = 99{\cdot}39(1)°$. The mean σ for bond lengths not involving hydrogen is 0·002 Å.

The hydrogen-bond network is two-dimensional. The amide and carboxy-groups of molecules related by translation form cyclic hydrogen-bonded (asymmetric) pairs (OH · · · O, 2·660; NH · · · O, 2·838 Å) generating chains which are interlinked, along the 2_1 axis, by NH · · · O (2·935 Å) bonds. The conformations of the groups C⁚C·C(NH$_2$)⁚O and C⁚C·C(OH)⁚O are *syn*-planar, in contrast to the antiplanar C⁚C·C⁚O arrangements in the α- and β-forms of fumaric acid.

The bond lengths are: C=C 1·320, C(OH)–C 1·497, C(NH$_2$)–C 1·486, C(OH)=O 1·209, C(NH$_2$)=O 1·247, C–OH 1·310, and C–NH$_2$ 1·323 Å.

THE structure analysis of fumaramic acid (I) was carried out as part of a programme on the study of the packing arrangements of primary amides[1] and of carboxylic acids, as well as on the determination of the electron-density distribution in functional groups.[2] (I) seemed well suited for the latter purpose in view of its high melting point and stability to *X*-radiation. A detailed study of the electron-density distribution of fumaramic acid is presented elsewhere.[3]



(I)

EXPERIMENTAL

Crystals of fumaramic acid, grown from slowly cooled aqueous solutions, were colourless monoclinic plates showing the {100}, {10$\bar{1}$}, and {110} forms, and the (10$\bar{1}$) and (010) cleavage planes.

Lattice constants were determined by a least-squares procedure from 19 high-order ($2\theta > 122°$) reflections measured on a General Electric diffractometer (Cu-K_α).

Crystal Data.—Fumaramic acid. $C_4H_5NO_3$, $M = 115{\cdot}1$, m.p. 218—222 °C. Monoclinic, $a = 7{\cdot}367(1)$, $b = 9{\cdot}041(1)$, $c = 3{\cdot}742(1)$ Å, $\beta = 99{\cdot}39(1)°$, $U = 245{\cdot}9$ Å^3, $D_m = 1{\cdot}54$, $Z = 2$, $D_c = 1{\cdot}554$, $F(000) = 120$. Space group $P2_1$ from systematic absences $0k0$ for k odd. Mo-K_α radiation, $\lambda = 0{\cdot}70926$ Å; μ(Mo-K_α) = 0·7 cm^{-1}.

A crystal specimen of (I) [of dimensions 0, 0·11, 0, 0·42, 0·34, 0·42, and 0 mm measured normal to the faces 100, $\bar{1}$00, $\bar{1}$01, 10$\bar{1}$, 110, $\bar{1}$10 and 010] was mounted along $a^* + 10b^*$ on a Siemens paper-tape controlled diffractometer; the $I(hkl)$ and $I(\bar{h}kl)$ were recorded for $\sin\theta/\lambda \lesssim 0{\cdot}68$ with Mo-K radiation filtered with a set of balanced zirconium and yttrium metal foils.

Intensities were measured by a moving-crystal, moving-

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† Part IV, S. E. Filippakis, L. Leiserowitz, D. Rabinovich, and G. M. J. Schmidt, preceding paper.

[1] Part III, L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc.* (*A*), 1969, 2372.

[2] H. Irngartinger, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1970, 497.

[3] F. L. Hirshfeld, *Acta Cryst.*, 1971, *B*, **27**, 769.

counter method described previously.[2] Absorption corrections [4] were applied in the data-reduction routine; secondary extinction of the very strong reflections was appreciably reduced by their measurement on a crystal *ca.* 1/30th the volume of the large crystal.

TABLE 1

Atomic co-ordinates (fractional) and standard deviations referred to axes *a*, *b*, *c*

Atom	*x*	*y*	*z*
C(1)	0·56902(17)	−0·02266(20)	0·27871(38)
C(2)	0·38295(18)	−0·05548(23)	0·06693(38)
C(3)	0·24989(18)	0·04150(23)	0·07619(38)
C(4)	0·06132(17)	0·02422	−0·13181(35)
N	−0·04985(18)	0·13802(23)	−0·11621(42)
O(1)	0·68839(14)	−0·12938(21)	0·26913(35)
O(2)	0·60376(16)	0·09236(23)	0·44001(35)
O(3)	0·01303(12)	−0·08892(20)	−0·31304(29)
H(1)	0·7986(29)	−0·1141(29)	0·3977(29)
H(2)	0·3657(30)	−0·1506(31)	−0·0743(63)
H(3)	0·2745(30)	0·1301(30)	0·2134(59)
H(4)	−0·1647(35)	0·1309(33)	−0·2431(68)
H(5)	−0·0180(36)	0·2090(31)	0·0017(75)

TABLE 2

Observed thermal parameters u^{ij} and U and standard deviations (Å^2) referred to axes *a*, *b*, *c*

Atom	u^{11}	u^{22}	u^{33}	u^{12}	u^{23}	u^{13}
C(1)	0·0200(5)	0·0361(7)	0·0324(6)	−0·0021(5)	−0·0004(5)	−0·0021(4)
C(2)	0·0200(4)	0·0333(7)	0·0332(6)	−0·0027(4)	−0·0008(5)	−0·0032(4)
C(3)	0·0228(5)	0·0327(7)	0·0298(6)	−0·0040(5)	0·0007(5)	−0·0042(4)
C(4)	0·0194(4)	0·0253(5)	0·0289(5)	−0·0010(4)	0·0032(4)	−0·0023(4)
N	0·0280(5)	0·0267(5)	0·0500(7)	0·0022(5)	−0·0071(5)	−0·0105(5)
O(1)	0·0239(4)	0·0368(6)	0·0565(7)	0·0028(4)	−0·0101(5)	−0·0073(4)
O(2)	0·0257(4)	0·0436(6)	0·0622(7)	0·0037(4)	−0·0177(6)	−0·0129(4)
O(3)	0·0237(4)	0·0271(4)	0·0395(4)	−0·0001(3)	−0·0045(4)	−0·0062(3)

Atom	U	Atom	U	Atom	U	Atom	U	Atom	U
H(1)	0·022(6)	H(2)	0·025(6)	H(3)	0·020(5)	H(4)	0·037(7)	H(5)	0·026(6)

Within the Cu-K_α sphere of diffraction a total of 703 independent reflections were recorded, of which eight were treated as unobserved.

Structure Determination.—The structure was solved from packing considerations. The bond lengths and angles of the planar molecular model were derived from the crystal structures of α- and β-fumaric acids,[5,6] and of sorbamide.[7] The molecule was assumed to lie in the $(11\bar{1})$ plane in view of the very high value of $F(11\bar{1})$. This model was tested on the 27 lowest-order reflections in a rigid-body least-squares programme in which only the scale factor, the orientation (three Eulerian angles), and translational (x,z) parameters of the model were adjusted. In 5 cycles the discrepancy factor R was reduced to 0·13.

Next, individual atomic parameters were refined, first with isotropic thermal parameters and fixed hydrogen parameters, and finally with anisotropic parameters for all but the hydrogen atoms which were now allowed to shift. At the end of this refinement R had reached 0·03 and R' 0·004 for 703 reflections $[R' = \Sigma\omega(k^2F_o{}^2 - |F_c|^2)^2/\Sigma\omega k^4F_o{}^4]$. Next, 479 reflections calculated from this model as 'strong' in the range $0{\cdot}68 \leq \sin\theta/\lambda \leq 1{\cdot}12$ were measured and added for further refinement. Inclusion of these reflections produced an average change in bond lengths and thermal parameters of 0·003 and 0·001 Å^2 respectively. The final agreement factors were $R = 0{\cdot}038$ and $R' = 0{\cdot}005$ for 1182 reflections. The scattering factor curves used for carbon, nitrogen, and oxygen were taken from ref. 8, and for hydrogen from ref. 9.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20325 (3 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Tables 1 and 2 list the experimental positional and thermal parameters and their estimated standard deviations. Table 3 lists the short intra-molecular contacts.

TABLE 3

Short intramolecular contacts (Å)

(*a*) 1,3

H(4) · · · H(5)	1·48
C(1) · · · H(1)	1·87
C(1) · · · H(2)	2·16
C(2) · · · H(3)	1·98
C(3) · · · H(2)	2·06
C(4) · · · H(3)	2·10
C(4) · · · H(4)	1·91
C(4) · · · H(5)	1·87
C(3) · · · C(1)	2·42
C(4) · · · C(2)	2·47
C(3) · · · N	2·37
C(2) · · · O(1)	2·35
C(2) · · · O(2)	2·38
C(3) · · · O(3)	2·39
O(1) · · · O(2)	2·23
N · · · O(3)	2·25

(*b*) 1,4

H(2) · · · H(3)	2·89
C(1) · · · H(3)	2·56
C(3) · · · H(5)	2·47
C(4) · · · H(2)	2·72
C(2) · · · O(3)	2·88
C(3) · · · O(2)	2·78
N · · · H(3)	2·50
O(1) · · · H(2)	2·52
O(2) · · · H(1)	2·38
O(3) · · · H(4)	2·42
O(3) · · · H(5)	2·97

(*c*) 1,5

H(3) · · · H(5)	2·28
O(2) · · · H(3)	2·46
O(3) · · · H(2)	2·67

Molecular Shape.—Deviations from the best planes through the carbon chain (C·C:C·C), the carboxy-group, the amide group, and the (asymmetric) acid–amide pair, (II) are listed in Table 4. These groups, with the exception of their hydrogen atoms, are each planar, to within 0·014, 0·002, 0·006, and 0·06 Å. The molecule itself is not fully planar: the angles between the plane of the carbon chain and the planes of the amide and carboxy-groups are 4·6 and 4·3° respectively. The line

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[4] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[5] C. J. Brown, *Acta Cryst.*, 1966, **21**, 1.

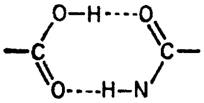
[6] A. L. Bednowitz and B. Post, *Acta Cryst.*, 1966, **21**, 566.

[7] S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1967, 297.

[8] J. Berghius, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[9] R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.

of intersection of the planes of the carbon chain and the amide group makes an angle of 16·5° with the C–C bond



(II)

axis of the amide system. The corresponding angle for the carboxy-group is 12·5°. Consequently, the deviations from molecular planarity are, in the main, due to twisting of both the amide and carboxy-groups about their respective C–C single bonds in the same sense.

Table 4

Equations of the planes in the form $Ax + By + Cz + D = 0$, where x, y, z, are the fractional atomic co-ordinates; distances (10^3 Å) of relevant atoms from the planes, are given in square brackets

Plane (I):

C(1)—(4) $-2{\cdot}9351x - 4{\cdot}2908y + 3{\cdot}1416z + 0{\cdot}6857 = 0$

[C(1) −12, C(2) 10, C(3) 14,C (4) −12, H(2) 25, H(3) −12, N −125, O(1) 66, (O2) −100, O(3) 46]

Plane (II):

C(3), C(4), N, O(3) $-3{\cdot}2548x - 3{\cdot}6927y + 3{\cdot}2191z + 0{\cdot}7195 = 0$

[C(3) −2, C(4) 6, N −2, H(4) −10, H(5) 12]

Plane (III):

C(1), C(2), O(1), O(2) $-3{\cdot}0480x - 3{\cdot}6765y + 3{\cdot}2603z + 0{\cdot}7444 = 0$

[C(1) 2, C(2) −1, O(1) −1, O(2) −1, H(1) 26]

Plane (IV):

C(1)—(4), N, O(1)—(3) * $-3{\cdot}3848x - 3{\cdot}7285y + 3{\cdot}1853z + 0{\cdot}7387 = 0$

[C(1) −16, C(2) 62, C(3) −19, C(4) 21, N 23, O(1) −52, O(2) −48, O(3) 29, H(1) −73, H(4) 34, H(5) 26]

* Hydrogen-bonded carboxylic acid–amide pair.

The dihedral angle between the planes of the carboxy- and amide groups is 1·85°, which is in fact the angle between these systems in the hydrogen-bonded asymmetric pair (II).

The *syn*-planar conformations of both $C{:}C{\cdot}C(NH_2){:}O$ and $C{:}C{\cdot}C(OH){:}O$ are consistent with the conformational pattern of carboxylic acids,[10] but in contradistinction to the *anti*-planar conformation of $C{:}C{\cdot}C{:}O$ in both the α- and β-forms of fumaric acid.

Rigid-body Motion.—The rigid-body motion analysis was carried out by the method of Schomaker and Trueblood.[11] The rigid-body tensors **L**, **S**, **T** (Table 5) were expressed, for ease of interpretation, in terms of the molecular inertial-axial system ($\boldsymbol{M}_i$) defined in Table 5.

There is fairly good agreement between the observed and calculated vibrations u^{ij}. However, the root-mean-square discrepancy Δu^{ij} of 0·0019 Å² is significantly higher than the averaged estimated standard deviation (0·0005 Å²) of the observed u^{ij} (Table 2)

Table 5

The components of the tensors and the unit vectors along their principal axes are referred to the axial system of inertia ($\boldsymbol{M}_i$) defined below. The calculation is referred to the origin which symmetrises **S** and reduces the trace of **T**. The co-ordinates of this origin in the inertial system with its origin at the centre of mass, are: $m_1 = -7{\cdot}458$, $m_2 = 0{\cdot}394$, $m_3 = -0{\cdot}129$ Å

Covariant components of the $\boldsymbol{M}_i$ set

	x_1	x_2	x_3
$\boldsymbol{M}_1$	6·7032	−1·0716	0·9117
$\boldsymbol{M}_2$	0·4911	−8·1780	−1·5992
$\boldsymbol{M}_3$	3·0154	3·7141	−3·2581

Tensor elements $\times 10^5$

Tensor	11	22	33
L/radian²	2605(132)	64(17)	−23(17)
T/Å²	1986(68)	909(900)	3306(941)
S/radian × Å	−99(55)	128(150)	−30(159)

Tensor	12	23	13
L/radian²	−94(10)	−6(20)	47(11)
T/Å²	135(202)	1237(1026)	701(251)
S/radian × Å	73(33)	245(128)	25(26)

	Root-mean-square amplitudes	Principal axes		
		m_1	m_2	m_3
L/deg.	9·26	0·9992	−0·0371	0·0177
	1·41	0·0380	0·9979	−0·0533
	(−0·88)	−0·0157	0·0539	0·9984
T/Å	0·202	0·3193	0·3577	0·8775
	0·133	0·9423	−0·2180	−0·2540
	0·061	0·1005	0·9080	−0·4067

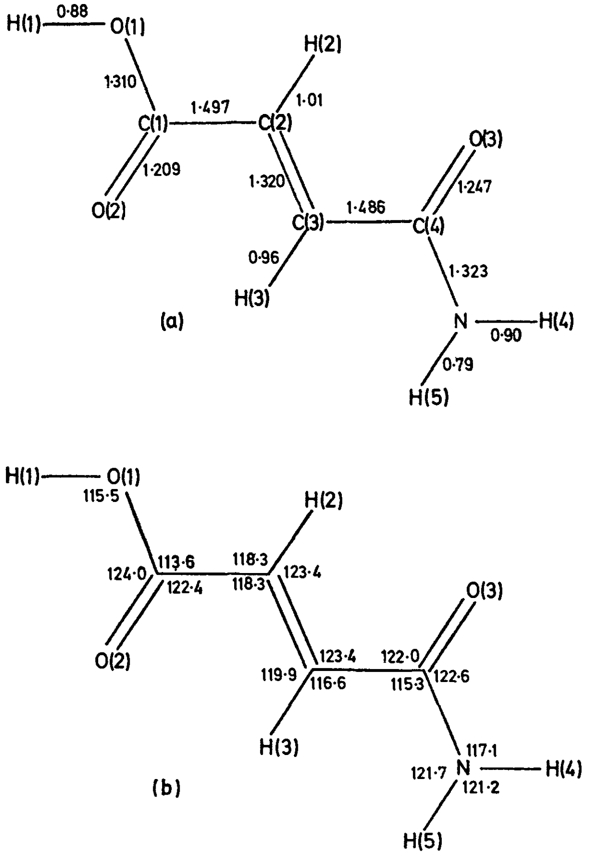


Figure 1 (a) Bond lengths (Å), and (b) bond angles (°)

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[10] L. Leiserowitz and G. M. J. Schmidt, *Acta Cryst.*, 1965, **18**, 1058.

[11] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, *B*, **24**, 63.

suggesting that molecular motion cannot be regarded as that of an ideally rigid body.

The principal axes of libration are nearly parallel to the molecular inertial axes $\boldsymbol{M}_1$, $\boldsymbol{M}_2$, and $\boldsymbol{M}_3$ (Table 5). The angular deviations between the libration and inertial axes are 2·4, 3·8, and 3·2°. Libration (9·26°) takes place primarily about the axis of the minimum moment of inertia ($\boldsymbol{M}_1$). The libratory motion which takes place about the normal to the molecular plane ($\boldsymbol{M}_3$), is calculated negative (−0·88°); it is thus physically meaningless. This value corresponds to the negative L_{33} diagonal tensor element with an estimated standard deviation of the same order of magnitude, and consequently is not significant.

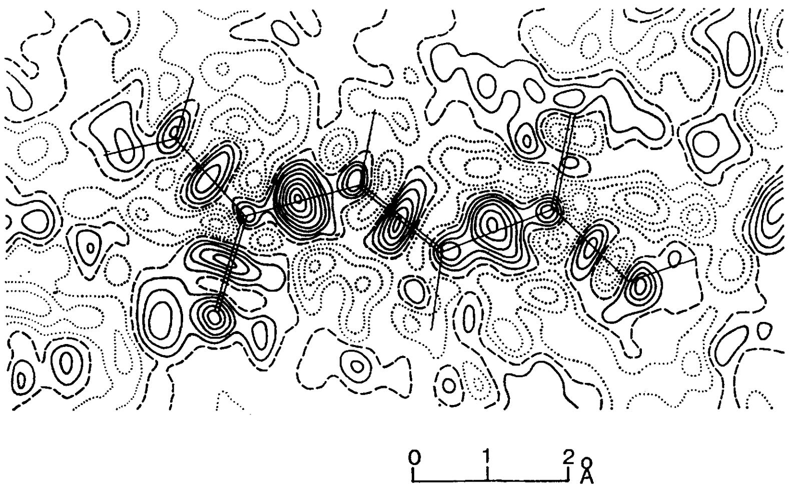

FIGURE 2 Electron density difference section through the molecular plane. Full, dashed, and dotted contour lines correspond to positive, zero, and negative contours, at intervals of 0·04 eÅ^{-3}

Molecular vibration is not isotropic; maximum vibration occurs mainly along the $\boldsymbol{M}_1$ and $\boldsymbol{M}_3$ directions.

Bond Lengths and Bond Angles.—The experimental bond lengths and angles are shown in Figure 1 which also shows the numbering system used. The bond lengths corrected for libration are given in Table 6. However, in view of the uncertainty of these corrections, the discussion of the structure is based on the uncorrected values.

TABLE 6

Bond lengths (Å) corrected for libration

C(1)–O(2)	1·223	C(3)–C(4)	1·486
C(1)–O(1)	1·322	C(4)–O(3)	1·260
C(1)–C(2)	1·498	C(4)–N	1·336
C(2)–C(3)	1·331		

The averaged σ for non-hydrogen bond lengths and angles are 0·002 Å and 0·1°. The corresponding values for bond lengths and angles involving hydrogen atoms are 0·02 Å and 1·7° respectively.

The bond lengths of fumaramic acid agree satisfactorily with those of α- and β-fumaric acids (Table 7). There is a significant difference between the C=O bond lengths of the carboxy- (1·209 Å) and the amide (1·247 Å) group in fumaramic acid. The comparable bond lengths of the 1 : 1 molecular complex of formic acid and formamide[12] (Table 7), which match convincingly those of fumaramic acid, enhance the significance of this observation.

Electron Density Distribution.—The electron-density difference-Fourier maps of the molecule (Figures 2 and 3) exhibit features which have been observed in previous structure analyses, such as excess density between the bonded atoms and negative regions antisymmetric to the bonds (see Figure 2).

The peaks in the C–C and C=C bonds are comparatively high (0·2—0·3 eÅ^{-3}) and are compatible with the low thermal vibrations of the carbon atoms. The carbon atoms do not lie on contours of zero density but rather on local peaks (0·14 eÅ^{-3}).

TABLE 7

Comparison of bond lengths (Å) of fumaramic acid, the α- and β-forms of fumaric acid, and the 1 : 1 complex of formic acid with formamide

Bond	Fumaramic acid	α-Fumaric [a] acid	β-Fumaric [b] acid	Complex [c] HCO_2H,	$HCONH_2$
C=C	1·320(2)	1·348(10)	1·315(7)		
C–C	1·497(2)	1·465(8)	1·490(5)		
	1·486(2)				
C–OH	1·310(2)	1·293(6)	1·289(5)	1·320(3)	
C=O	1·209(2)	1·224(10)	1·228(4)	1·202(4)	
	1·247(2)				1·251(1)
C–N	1·323(2)				1·312(2)

The standard deviations of α-fumaric acid and of the 1 : 1 complex of formic acid with formamide were each derived from the ' scatter ' of their chemically equivalent bonds.

[a] From ref. 5. [b] From ref. 6. [c] From ref. 12.

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[12] I. Nahringbauer and G. Larsson, *Arkiv Kemi*, 1968, **30**, 91.

The observed difference-Fourier electron densities of the carboxy- and amide groups are probably adversely affected by the comparatively large out-of-plane motions of the oxygen and nitrogen atoms. There appears to be excess of charge in the O–H and N–H bonds, and in the C=O(amide), C–N, and C–OH bonds. There is a strong peak (0·2 eÅ^{-3}) close to the centre of the carbonyl oxygen of the amide group [O(3)], and there are two satellite

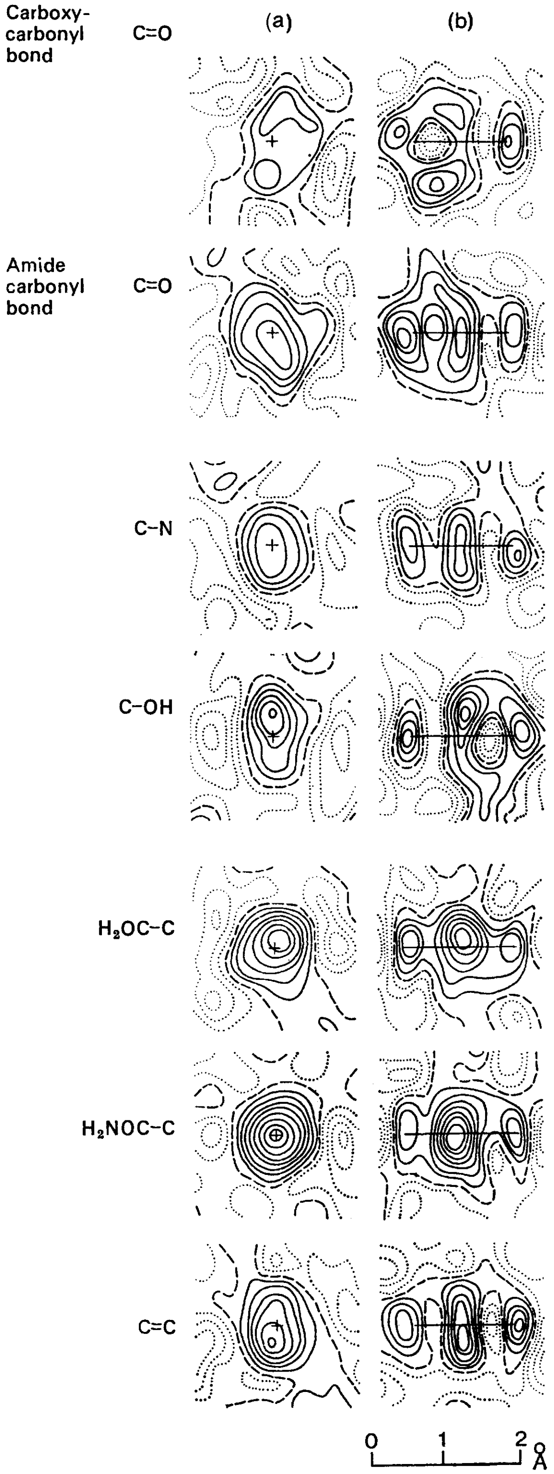

FIGURE 3 Electron density difference sections contoured at intervals of 0·04 eÅ^{-3}: (a) perpendicular to the bond at the centre (marked +), and (b) containing the bond axis and the vector perpendicular to the molecular plane

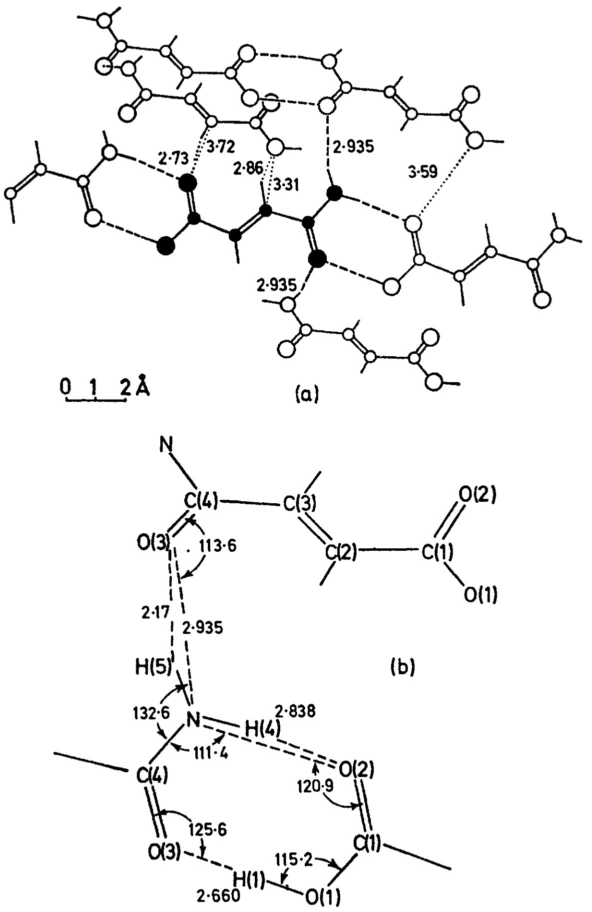

FIGURE 4 (a) Packing arrangement seen along the normal to the best plane of the shaded molecule. Some intermolecular contacts (Å) are shown. (b) Interatomic distances (Å) and angles (°) of the hydrogen-bonded system

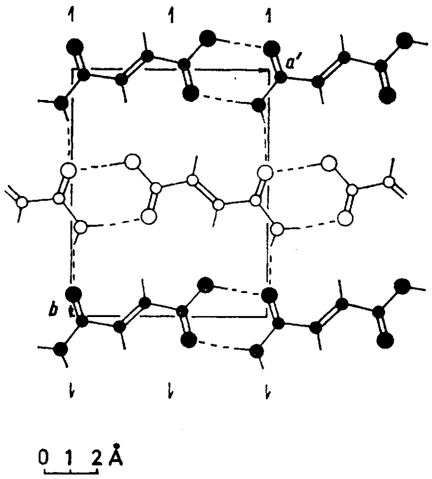

FIGURE 5 Packing arrangement seen along [001]. $a' = a \sin \beta$

TABLE 8

Intermolecular contacts * (Å)

$A(000)$† $A(\bar{1}0\bar{1})$		
	C(4) ··· O(1)	3·54
	C(4) ··· O(2)	3·54
	N ··· O(2)	2·84
	N ··· H(1)	3·02
	O(3) ··· C(1)	3·43
	O(3) ··· O(2)	3·42
	O(3) ··· O(1)	2·66
	H(4) ··· O(1)	3·07
$B(101)$		
	O(2) ··· O(1)	3·59
	H(3) ··· O(1)	2·89
$A(\bar{1}00)$		
	N ··· O(2)	3·57
	N ··· O(1)	3·54
	O(3) ··· O(1)	3·51
$A(00\bar{1})$		
	C(1) ··· O(2)	3·36
	C(2) ··· C(1)	3·46
	C(2) ··· O(2)	3·34
	C(4) ··· C(3)	3·48
$A(000)$ $B(00\bar{1})$		
	N ··· O(3)	3·31
	H(5) ··· O(3)	3·17
$B(000)$		
	N ··· O(3)	2·94
	N ··· H(2)	3·18
	H(5) ··· O(3)	2·17
	H(5) ··· C(4)	2·92
$B(1\bar{1}0)$		
	H(2) ··· O(2)	2·73
$B(100)$		
	C(3) ··· O(1)	3·31
	N ··· O(1)	3·51
	N ··· H(1)	3·19
	H(3) ··· O(1)	2·86
	H(5) ··· O(1)	3·14

* Limiting radii of C, N, and O 1·8 and H 1·4 Å.

† Co-ordinates of equivalent positions:

A x, y, z B $-x, \frac{1}{2}+y, -z$

$A(pqr)$ denotes fractional co-ordinates $p+x$, $q+y$, $r+z$.

peaks on either side of O(3), at *ca.* 0·7 Å, probably due to the lone-pair electrons of this atom.

Packing.—The hydrogen-bond network is two-dimensional (see Figures 4 and 5). The amide and carboxy-groups of molecules related by translation along [101] form hydrogen-bonded asymmetric pairs (OH ··· O, 2·660, NH ··· O, 2·838 Å) generating chains which are interlinked, along the two-fold screw axis, by NH ··· O (2·935 Å) bonds between amide groups.

These hydrogen-bonded amide groups do not form a coplanar system (see Figures 4 and 5): the pleated nature of the hydrogen-bond arrangement follows from the dihedral angle of 65·9° between the *ac* plane and that of the amide group.

The interatomic lengths and angles of the hydrogen-bonded network are shown in Figure 4(b). Short intermolecular contacts are listed in Table 8, some of which are shown in Figure 4(a).

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