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## The Crystal Structure of the Monoclinic Form of L-Histidine

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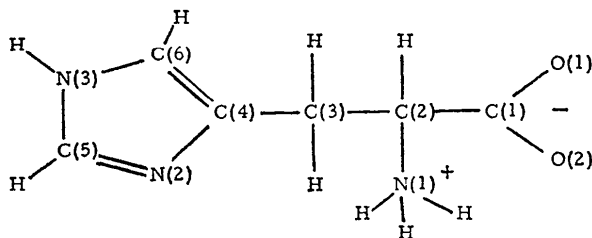
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L-Histidine ( $C_6N_2O_2H$ ) crystallizes from ethanol in the monoclinic space group  $P2_1$ , with  $a=5.172$ ,  $b=7.384$ ,  $c=9.474$  Å,  $\beta=97.162^\circ$  and  $Z=2$ . The structure was solved simultaneously by independent investigations using the tangent formula and from a trial solution based on the structure of the orthorhombic form. The crystals show lamellar twinning, which arises from faults in the stacking of the imidazole residues such that there are two possible orientations of the unit cells. The structures could not be refined below an  $R=0.10$ , but a comparison of the bond distances and angles with those of other free-base histidines shows no significant differences.

### Introduction

Histidine, pictured below, and some of its isostructural analogs, have now been examined as free bases in a series of compounds which includes orthorhombic L-histidine (Madden, McGandy & Seeman, 1972), D,L-histidine (Edington, 1970),  $\beta$ -(pyrazoyl-3)-L-alanine (Seeman, McGandy & Rosenstein, 1972), and mono-

clinic L-histidine which is described in this paper and was studied independently and simultaneously at Edinburgh and Pittsburgh.



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Table 2. Positional parameters for L-histidine

	Edinburgh			Pittsburgh		
	x	y	z	x	y	z
C(1)	0.453 (3)	-0.2314 (*)	0.4968 (7)	0.4475 (17)	0.7429 (15)	0.4966 (6)
C(2)	0.390 (2)	-0.1713 (15)	0.6457 (8)	0.3817 (12)	0.8057 (15)	0.6440 (6)
C(3)	0.357 (3)	-0.3366 (14)	0.7390 (9)	0.3669 (17)	0.6406 (15)	0.7409 (6)
C(4)	0.297 (2)	-0.2860 (13)	0.8835 (9)	0.2974 (15)	0.6916 (13)	0.8837 (6)
C(5)	0.072 (3)	-0.1677 (17)	1.0352 (8)	0.0779 (17)	0.8071 (17)	1.0371 (8)
C(6)	0.433 (3)	-0.3316 (14)	1.0173 (8)	0.4265 (16)	0.6444 (15)	1.0173 (7)
N(1)	0.136 (2)	-0.0681 (13)	0.6251 (6)	0.1331 (13)	0.9079 (14)	0.6240 (7)
N(2)	0.083 (2)	-0.1839 (15)	0.8957 (8)	0.0767 (15)	0.7955 (16)	0.8955 (6)
N(3)	0.279 (2)	-0.2561 (15)	1.1131 (8)	0.2753 (15)	0.7170 (16)	1.1120 (7)
O(1)	0.264 (2)	-0.2603 (15)	0.4004 (6)	0.2652 (13)	0.7179 (18)	0.4028 (6)
O(2)	0.687 (2)	-0.2557 (13)	0.4894 (7)	0.6852 (13)	0.7189 (15)	0.4900 (7)
H(C2)	0.532	-0.0906	0.6927	0.641	0.846	0.674
H(C3)	0.534	-0.4052	0.7510	0.521	0.594	0.737
H(2C3)	0.222	-0.4162	0.6926	0.251	0.549	0.681
H(C5)	-0.067	-0.1006	1.0766	-0.014	0.896	1.076
H(C6)	0.590	-0.4030	1.0366	0.582	0.609	1.035
H(N3)	0.314	-0.2657	1.2189	0.337	0.750	1.176
H(N1)	0.000	-0.0250	0.7120	0.083	0.905	0.698
H2(N1)	0.12	0.0330	0.577	0.149	1.001	0.606
H3(N1)	-0.04	-0.100	0.550	0.008	0.834	0.561

\* C(1) was used to define the origin along y.

Table 3. Vibrational parameters ( $\text{\AA}^2$ ) based on the expression:

$$T = \exp [-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

$$U_{ij} \times 10^3$$

	Edinburgh						Pittsburgh					
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	9	29	12	-2	-4	-4	46	27	17	1	10	4
C(2)	34	29	21	-1	11	-1	24	21	19	-3	2	2
C(3)	67	21	40	0	26	11	41	26	12	-2	2	7
C(4)	17	27	31	5	6	2	34	18	13	4	2	1
C(5)	40	45	17	7	3	13	36	43	24	-18	7	-8
C(6)	58	34	19	-1	15	6	38	26	16	-4	-8	-4
N(1)	26	31	27	2	4	3	23	23	19	-2	-3	-2
N(2)	42	38	35	4	2	11	40	47	20	-14	6	-9
N(3)	36	34	32	3	7	-2	43	39	7	7	-5	-5
O(1)	9	62	32	-6	3	-4	37	44	42	6	14	17
O(2)	13	47	39	-13	6	-1	44	62	24	0	10	7

In contrast to the variety of conformations found among the metal-histidine complexes (Candlin & Harding, 1970) and hydrochloride compounds (Bennett, Davidson, Harding & Morelle, 1970), these free-base histidines are shown to have remarkably uniform conformation angles, bond distances and valence angles.

### Experimental

Striated, platy crystals were prepared from the hydrochloride (Edinburgh) by neutralization with sodium hydroxide, precipitation with ethanol, and recrystallization from aqueous ethanol; and by crystallization from hot aqueous ethanol of the free base (Pittsburgh) purchased from Nutritional Biochemical Corp. All the crystals were laminated twins, and many appeared to be orthorhombic showing *mmm* Laue symmetry. The crystal data given below were measured on a four-circle Picker automatic, card-controlled diffractom-

eter and are in good agreement with less precise values obtained by film methods.

### Crystal data

L-Histidine,  $C_6H_9N_3O_2$ ,  $M = 155.2$ ,  $a = 5.172$  (5),  $b = 7.384$  (7),  $c = 9.474$  (10)  $\text{\AA}$ ,  $\beta = 97.162^\circ$ ,  $V = 359.0$   $\text{\AA}^3$ ,  $D_m = 1.446$   $\text{g.cm}^{-3}$  (24°C),  $Z = 2$ ,  $D_{calc} = 1.446$   $\text{g.cm}^{-3}$ ,  
Space group  $P2_1$ .

### Data collection and structure determination (Pittsburgh)

Crystals which showed no apparent splitting of high-order reflections on upper layer precession photographs were surveyed for twinning and splitting by recording the profiles of reflections along the principal axes by  $\theta/2\theta$  scans on a diffractometer. All crystals

examined showed peak splitting. The crystal finally selected (0.6 × 0.5 × 0.15 mm) for data collection contained a minor component, which accounted for at least 10% of the intensity of each reflection, and which could not be separated from the main peak by adjusting the scan width. The crystal was mounted on its 120 axis on a glass fiber with fast drying epoxy (Bordens).

Intensity data were collected with molybdenum radiation on a Picker four-circle automatic diffractometer with variable width  $\theta/2\theta$  scans and balanced filters (zirconium and yttrium) from  $\lambda d^* = 0.0$  to 0.5, and with variable width  $\theta/2\theta$  scans and a fixed  $\beta$  filter (Zr) from  $\lambda d^* = 0.5$  to 1.0.

A Wilson plot and normalized structure factors,  $E$ , were calculated (Shiono, 1970) and the  $E^2$  values were renormalized on all parity, reflection zone and  $\sin \theta$  groups as described by Madden, McGandy & Seeman (1972). The 125 reflections with the highest  $E$  values were used in the tangent formula programs DP3 and DP5 (Hall, Maslen & Berman, 1967). Three origin-determining reflections (108, 203, and 117) and one enantiomorph-determining reflection (137), plus two arbitrary reflections (411 and 114) were chosen for symbolic addition such that phases could be generated for all 125 reflections. After phase refinement by ap-

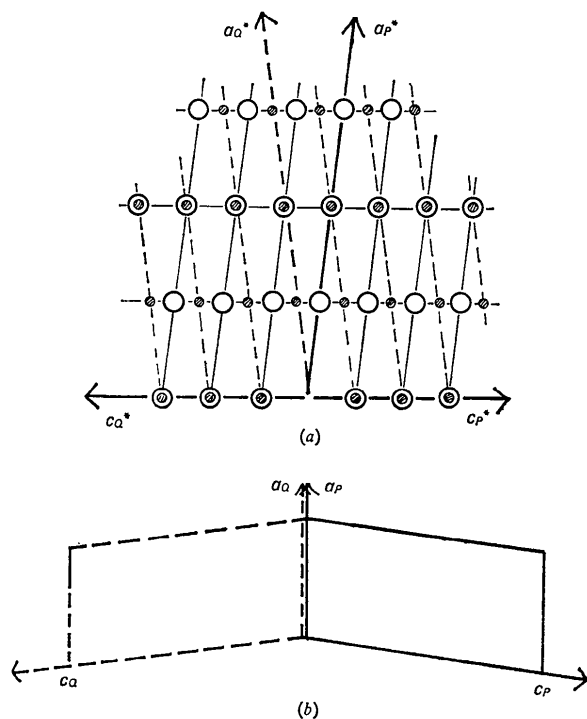


Fig. 1. (a) The positions of the observed reflections in twinned monoclinic L-histidine. Open circles are attributed to the orientation  $P$ , whose reciprocal lattice is shown by solid lines, and shaded circles to the orientation  $Q$  whose reciprocal lattice is shown by broken lines.  $b_p^*$  is directed upwards and  $b_q^*$  downwards. (b) The orientations,  $P$  and  $Q$ , of the unit cells.

Table 4. Distances calculated for the histidine free-base series

Reference	Space group	Cell dimensions $a, b, c$	$\beta$	Data collection	$R$ (percent)
	C(1)-O(1)	1.26 (2) Å		10.0	C(1)-O(1)
	C(1)-O(2)	1.23 (2)		11.1	C(1)-O(2)
	C(1)-C(2)	1.55 (2)		3.4	C(1)-C(2)
	C(2)-N(1)	1.51 (2)		3.4	C(2)-N(1)
	C(2)-C(3)	1.53 (2)		3.4	C(2)-C(3)
	C(3)-C(4)	1.49 (2)		3.4	C(3)-C(4)
	C(4)-N(2)	1.36 (2)		3.4	C(4)-N(2)
	N(2)-C(5)	1.33 (2)		3.4	N(2)-C(5)
	C(5)-N(3)	1.38 (2)		3.4	C(5)-N(3)
	N(3)-C(6)	1.40 (2)		3.4	N(3)-C(6)
	C(6)-C(4)	1.40 (2)		3.4	C(6)-C(4)
					1.247 (2) Å
					1.250 (2)
					1.545 (2)
					1.493 (2)
					1.536 (3)
					1.505 (3)
					1.382 (2)
					1.327 (3)
					1.339 (3)
					1.374 (3)
					1.361 (3)
					1.248 (6) Å
					1.252 (6)
					1.529 (6)
					1.482 (6)
					1.537 (6)
					1.472 (9)
					1.348 (9)
					[1.323 (9)]
					[1.332 (10)]
					[1.344 (11)]
					1.369 (10)
					8.983, 8.087, 9.415 Å
					97.65°
					10.8
					1.248 (6) Å
					1.252 (6)
					1.529 (6)
					1.482 (6)
					1.537 (6)
					1.472 (9)
					1.348 (9)
					[1.323 (9)]
					[1.332 (10)]
					[1.344 (11)]
					1.369 (10)
					4.623, 7.548, 10.063 Å
					98.61°
					7.8
					1.219 (9) Å
					1.243 (8)
					1.525 (9)
					1.477 (9)
					1.498 (9)
					1.472 (9)
					1.348 (9)
					[1.323 (9)]
					[1.332 (10)]
					[1.344 (11)]
					1.369 (10)

In  $\beta$ -(Pyrazolyl-3)-L-alanine, N(3) and C(5) are reversed from their positions in histidine, but all other atoms are in identical positions, making pyr-ala an isostructural analogue of histidine. All bonds involving these reversed atoms are marked by squared brackets.

plication of the tangent formula, an *E*-map revealed the eleven non-hydrogen atoms as the eleven highest peaks.

Anisotropic full-matrix least-squares refinement converged at  $R=0.128$  using a constant weight in each of 15 equal-sized groups of reflections based on  $\sin \theta/\lambda$ . In each group,  $w=1/\langle \Delta F|^2 \rangle$  for observed and  $w=0$  for unobserved reflections. The hydrogen atoms, with the exception of those bonded to N(1), were placed at tetrahedral positions around C(2) and C(3) and trigonal positions around N(3), C(5), C(6), at distances of 1.06 Å from the nitrogen atoms and 1.08 Å from the carbon atoms. After a cycle of refinement, a difference map showed the position of one of the N(1) hydrogen atoms. The two remaining N(1) hydrogen atoms were placed in tetrahedral positions as above. A final cycle of full-matrix least-squares gave an *R* value of 0.11 for the observed reflections and 0.14 for all reflections. The positional and thermal parameters are listed in Tables 1, 2 and 3.

#### Data collection and structure determination (Edinburgh)

Although many of the crystals examined appeared to be orthorhombic, there were systematic absences

additional to those of any conventional space group [Fig. 1(a)] suggesting twinning (Dornberger-Schiff & Dunitz, 1965). On close inspection the reflections with high even values of *h* were seen to be doubled. In a few crystals the symmetry of the intensity pattern was no more than  $2/m$ , and there were pronounced sharp streaks along some row lines parallel to  $c^*$ .

These observations can be accounted for by lamellar twinning of an essentially monoclinic structure, and when the nature of the twinning had been established it was possible to extract intensity data corresponding to a single crystal. The unit cells may be in either of the orientations *P* or *Q* in Fig. 1(b), and each contributes to the reciprocal lattice as shown in Fig. 1(a); because  $c \sin(\beta-90^\circ)$  is very nearly equal to  $a/4$  the two contributions are nearly superposed when *h* is even. Most 'crystals' are composed of approximately equal proportions of *P* and *Q* and so appear to have Laue symmetry *mmm*, but some contain very unequal amounts and are more obviously monoclinic. In the  $c^*$  direction several layers of orientation *P* are followed by several layers in the orientation *Q* – as indicated by the streaking.

One 'crystal' with very unequal proportions of components *P* and *Q* was selected. Intensities were estimated visually on multiple film Weissenberg photo-

Table 5. Angles calculated for the histidine free-base series

	L-Histidine (Edinburgh) <i>P</i> 2 <sub>1</sub>	L-Histidine (Pittsburgh) <i>P</i> 2 <sub>1</sub>	L-Histidine (Pittsburgh) <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	DL-Histidine (Edinburgh) <i>P</i> 2 <sub>1</sub> / <i>c</i>	β(Pyrazolyl-3)- L-alanine (Pittsburgh) <i>P</i> 2 <sub>1</sub>
O(1)–C(1)–O(2)	127.1°	127.4 (9)°	126.7 (2)°	124.9 (3)°	125.2 (6)°
O(1)–C(1)–C(2)	117.8	117.1 (8)	117.1 (2)	119.3 (3)	117.4 (6)
O(2)–C(1)–C(2)	115.0	115.4 (8)	116.3 (2)	115.7 (3)	117.3 (6)
C(1)–C(2)–N(1)	108.4	109.5 (6)	109.5 (1)	110.3 (3)	108.2 (5)
C(1)–C(2)–C(3)	110.4	109.6 (6)	110.6 (1)	110.5 (3)	113.9 (6)
N(1)–C(2)–C(3)	108.3	111.4 (7)	109.8 (1)	110.6 (3)	110.2 (5)
C(2)–C(3)–C(4)	112.5	112.3 (7)	112.7 (2)	112.9 (3)	114.9 (6)
N(2)–C(4)–C(6)	111.7	111.0 (7)	109.6 (2)	109.7 (3)	109.7 (6)
C(3)–C(4)–C(6)	128.8	127.9 (7)	129.9 (2)	129.0 (3)	128.7 (6)
C(3)–C(4)–N(2)	119.5	121.0 (7)	120.5 (2)	121.4 (3)	121.7 (6)
C(4)–N(2)–C(5)	106.3	103.1 (8)	104.9 (2)	105.7 (3)	[104.3 (6)]
N(2)–C(5)–N(3)	110.5	113.1 (9)	112.2 (2)	111.6 (3)	[113.1 (6)]
C(5)–N(3)–C(6)	108.2	108.0 (8)	106.9 (2)	107.4 (3)	[105.9 (7)]
N(3)–C(6)–C(4)	103.3	104.5 (7)	106.4 (2)	105.6 (3)	[107.0 (6)]

Table 6. Conformational angles calculated for the histidine free-base series

A positive angle represents a clockwise rotation of atom *l* with respect to atom *i* looking down the *jk* bond, from *j* to *k*, in the atomic group *ijkl*.

<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>	L-Histidine (Edinburgh) <i>P</i> 2 <sub>1</sub>	L-Histidine (Pittsburgh) <i>P</i> 2 <sub>1</sub>	L-Histidine (Pittsburgh) <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	DL-Histidine (Edinburgh) <i>P</i> 2 <sub>1</sub> / <i>c</i>	β(Pyrazolyl-3)- L-alanine (Pittsburgh) <i>P</i> 2 <sub>1</sub>
O(1)–C(1)–C(2)–N(1)				–30°	–28.1°	–26.8°	–9.7°	25.4°
O(2)–C(1)–C(2)–N(1)				154	153.8	155.1	170.7	203.7
O(1)–C(1)–C(2)–C(3)				89	94.4	94.4	112.9	148.4
O(2)–C(1)–C(2)–C(3)				–87	–83.6	–83.8	–66.7	–33.3
N(1)–C(2)–C(3)–C(4)				–62	–57.1	–59.3	–86.7	–72.9
C(1)–C(2)–C(3)–C(4)				180	181.4	179.8	150.8	165.2
C(2)–C(3)–C(4)–C(6)				–123	–128.3	–123.2	114.1	–103.5
C(2)–C(3)–C(4)–N(2)				58	53.2	56.8	–68.1	74.7

graphs (Cu  $K\alpha$  radiation) of the layers  $h0l$ , and  $0kl$  to  $4kl$ . Intensity data corresponding to the stronger component,  $P$ , were then derived; the interpretation of the photographs is based on the relationships shown in Fig. 1. For  $h$  odd, the reflections of the  $P$  and  $Q$  components occur separately and can be used to find the ratio,  $r$ , of the intensities of the two components;

39 pairs of reflections in the layers  $1kl$  and  $3kl$  gave a mean ratio  $r = I_P/I_Q = 8.8$  with a consistency which may be expressed as an  $R$  value,  $(\sum |I_P - 8.8I_Q|)/\sum I_P$ , of 0.08. This ratio  $I_P/I_Q$  therefore represents the relative volumes of the two components. In the layer  $2kl$  reflections from  $P$  and  $Q$  are superimposed. Pairs of measured intensities may be selected corresponding to

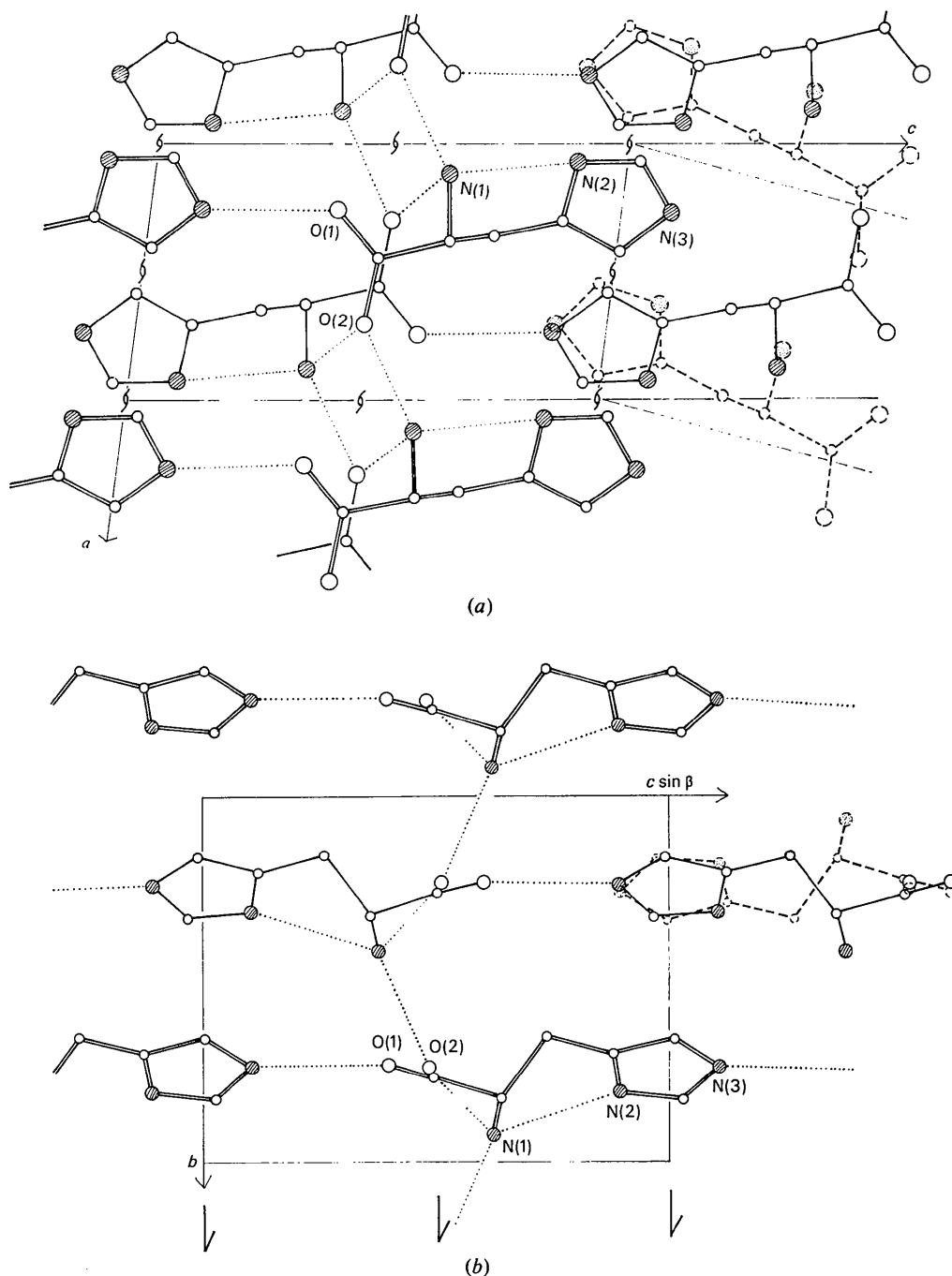


Fig. 2. (a)  $b$ -Axis projection of monoclinic L-histidine. The full lines show the structure when only one orientation,  $P$ , is present. Dotted lines represent hydrogen bonds, while broken lines show how it is proposed that the molecules in the alternative orientation,  $Q$ , are stacked. (b)  $a$ -Axis projection of (a).

$[I_p(2, k, l) + I_Q(2, k, -l - 1)]$  and  $[I_p(2, k, -l - 1) + I_Q(2, k, l)]$ ; using  $I_p(2kl) = 8.8I_Q(2kl)$ , intensity values corresponding to the separate components may be found. Their accuracy is undoubtedly poorer than those for the other layers. The  $0kl$  reflections were used directly;  $L_p$  corrections were applied;  $h0l$  reflections were used to find approximate layer scale factors, and a set of 492 observed intensities was obtained.

Inspection of a drawing of the orthorhombic structure of Madden & McGandy (1970) allowed us to set up a trial structure for the monoclinic form. This was checked by structure factor and Fourier calculations ( $R = 31\%$ ), then positional and isotropic temperature parameters were refined by the full-matrix least-squares program *XFLS* (Busing, Martin & Levy, 1962).

For weighting purposes  $\sigma(F)$  was taken as  $0.05(F_{obs})$  or  $0.15$ , whichever was greater, in the layers  $h = 0, 1, 3$ , and twice this value in the layer  $h = 2$  (in which the contributions of the two orientations were superimposed). Form factors were taken from *International Tables for X-ray Crystallography* (1962). Adjustment of positional and isotropic thermal parameters and the four layer scale factors brought  $R$  to  $0.12$ , with no shifts in the last cycle greater than  $0.25\sigma$ . Six hydrogen atoms in the stereochemically expected positions were then included in the structure factor calculations and two cycles of refinement including anisotropic thermal parameters brought  $R$  to  $0.10$ . In a difference Fourier series, maxima of  $0.4 \text{ e.}\text{\AA}^{-3}$  allowed us to locate two hydrogens of the amino group and the electron density in the expected position of the third hydrogen was positive. Observed and calculated structure factors are given in Table 1 and positional and thermal parameters in Tables 2 and 3.

### Description of the structure

The position of the two equivalent histidine molecules in the cell is shown in Fig. 2. Tables 4, 5 and 6 give the bond distances, valence and conformational angles and other pertinent data for the histidines (free bases) which have been studied by crystal structure analysis. None of the bond distances and valence angles vary by more than  $3\sigma$ , those from the orthorhombic form being the most accurate.

The molecules are extended in the  $c$  direction, and linked, in this direction, by  $N(3)\text{--}H\cdots O(1)$  hydrogen bonds. Near  $z = \frac{1}{2}$  there is a hydrogen bond network (see Table 7) linking the carboxyl and imidazole groups as shown in Fig. 2. Near  $z = 0$ , the imidazole groups are stacked at an angle of  $66^\circ$  to each other and their planes are related by the monoclinic twofold screw axis. Stacking faults which would result in lamellar twinning may readily occur in these imidazole layers while the packing of the carboxyl and amino groups remains intact. If, throughout a whole layer, neighboring imidazole rings in the  $c$  direction are placed in the alternative orientation (dotted lines in Fig. 2) the stacking is scarcely affected except that  $C(4)$  and  $N(2)$

are interchanged, as are  $C(5)$  and  $C(6)$ .  $N(3)$  is still able to participate in the hydrogen bond to  $O(1)$  and  $C(5)$  and  $N(2)$  are only  $0.25$  and  $0.45 \text{ \AA}$  from the positions of  $C(6)$  and  $C(4)$  which they replace.

Table 7. *Hydrogen bonds*

$i$	$j$	$k$	D	$\angle_{ijk}$
N(3)	H	O(1), at $x, y, -1+z$	2.73 Å	133.6°
N(1)	H	O(2), at $-1+x, y, z$	2.85	155.2
N(1)	H	O(2), at $1-x, \frac{1}{2}+y, -1+z$	2.76	162.3
N(1)	H	N(2), (intramolecular)	2.75	151.9

The conformation of the molecule is stabilized by an intramolecular hydrogen bond between  $N(1)\text{--}H\cdots N(2)$ , in a manner identical to that in the orthorhombic form. In all four compounds, the alanine backbone maintains a staggered conformation across the  $C(1)\text{--}C(2)$  bond, the imidazole and the carboxyl groups being *trans* rather than *gauche* as found in L-histidine hydrochloride (Donohue & Caron, 1964). In the latter compound, the histidine folds into a more compact form with the imidazole group *gauche* to both the amino and carboxyl groups. The prevalence of the extended form in the structure here described and in the rest of the free base series indicates that it is the form of lowest energy in the absence of other packing forces, such as those due to a chloride ion in the lattice. However, since the hydrochloride crystallizes in both the extended and tight-packed forms (Edington & Harding, 1970), the energy difference between them cannot be large.

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## Crystal and Molecular Structure of Diethyl Ether at 128°K

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Three-dimensional single-crystal X-ray diffraction data of the stable form of diethyl ether have been collected at 128°K. The unit cell is orthorhombic,  $a = 11.81(2)$ ,  $b = 8.07(2)$ ,  $c = 10.85(3)$  Å, space group  $P2_12_12_1$ ,  $Z = 8$ ; there are two molecules in the asymmetric unit. The acentric structure has been solved by direct methods and refined to an  $R$  index of 0.052. Both molecules have approximately ( $C_{2v}$  *trans-trans*) symmetry and the rigid-body model is a good approximation to the thermal motion. For a planar molecule with five atoms, the normal equations matrix is singular and the molecular tensors have been found by a technique of regression on principal components. The packing is loose and this might explain the strong tendency of diethyl ether to give a vitreous form on cooling.

Solid diethyl ether [formula  $(\text{CH}_3\text{CH}_2)_2\text{O}$ ] has been investigated by various techniques. This compound crystallizes in a metastable form (triple point 149.86°K) which, on further cooling, transforms into the stable form (triple point 156.92°K) (Counsell, Lee & Martin, 1971). A glassy state is obtained by depositing vapours or liquid on a surface held near liquid nitrogen temperature (Snyder & Zerbi, 1967; Grude, Haupt & Müller-Warmuth, 1966; Perchard, 1968). A preliminary report of crystallographic data on the stable form has been published (André, Fourme, Kahn & Renaud, 1971). We describe here the crystalline and molecular structure of this form.

### Experimental

Merck spectroscopic quality grade diethyl ether kept over sodium was used. Single crystals were grown in sealed Lindemann glass capillaries (diameter 0.3 mm) directly on the goniometer head of Weissenberg and Buerger instruments. The attached cooling system gave a quasi-laminar flow of cold nitrogen which prevented

any frosting of the sample (Renaud & Fourme, 1967); the goniometer head was held near room temperature by means of a built-in furnace. The temperature of the gas was monitored and the overall long-range fluctuations were estimated to be at most  $\pm 0.5^\circ\text{K}$ . The calibration curve  $T = f(mV)$  of the thermocouple was corrected by checking the melting point of several pure organic compounds sealed in capillaries.

Either by slow cooling of the liquid or by pouring liquid nitrogen on the sample, a glassy state was always obtained. At this point, a crystalline powder was induced through thermal shocks, using a small electrically heated manganine coil. From the powder, good single crystals were grown by a zone melting technique at 150°K (Renaud & Fourme, 1966); after a slow cooling down to 128°K, the crystals were grossly oriented between crossed 'Polaroids'.

Cell parameters and space group were determined from precession photographs (Zr-filtered Mo radiation  $\lambda = 0.7107$  Å). Crystal data are: formula  $(\text{CH}_3\text{CH}_2)_2\text{O}$ , M.W. 74.12; orthorhombic,  $a = 11.81(2)$ ,  $b = 8.07(2)$ ,  $c = 10.85(3)$  Å,  $V = 1034$  Å<sup>3</sup>, space group  $P2_12_12_1$ ;