

## The Crystal Structure of L-Alanine\*

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The crystal structure of L-alanine,  $C_3H_7O_2N$ , has been determined and refined by analysis of complete three-dimensional diffraction data from copper X-radiation. The crystals are orthorhombic with space group  $P2_12_12_1$ ; the unit-cell dimensions are  $a = 6.032$ ,  $b = 12.343$ ,  $c = 5.784$  Å. Least-squares refinement of the positional parameters of all 13 atoms and of the individual anisotropic temperature factors of the six heavy atoms, using 581 observed reflections of non-zero weight, yielded a final  $R$  index of 0.049.

The structure bears a striking resemblance to that of DL-alanine, and involves the use of all available protons in  $N-H \cdots O$  hydrogen bonds, with lengths of 2.83, 2.85, and 2.81 Å.

### Introduction

The determination of the crystal structure of L-alanine was undertaken as part of a program of research on the structures of compounds of biological importance. Particular interest in this compound arose because of an unusual similarity to DL-alanine, the structure of which has been previously determined (Levy & Corey, 1941; Donohue, 1950). Bernal (1931) found the cell dimensions of L- and DL-alanine to be nearly identical (see Table 1); both are orthorhombic but, of course, their space groups are different ( $P2_12_12_1$  for the D or L crystals,  $Pna2_1$  for the racemate). Furthermore, in a preliminary investigation we noted that zero-level Weissenberg photographs taken about the  $c$  axis are almost identical for the two compounds.

In view of the differences in packing properties which must exist for these two species, it seemed surprising that their cell dimensions and projected structures could be so similar. Accordingly, the structure of L-alanine was determined to provide a comparison with that of DL-alanine.

### Experimental

Crystals of L-alanine were obtained by several procedures, including evaporation of saturated methanol solutions, crystallization from slow cooling of super-saturated aqueous solutions, and slow evaporation of saturated aqueous solutions. The last method was the most successful, producing well-formed needles elongated along  $c$  and with principal faces  $\{110\}$ .

Unit-cell dimensions were obtained from least-squares treatments of spacings of 10 high-angle  $hk0$  reflections and 7 high-angle  $hhl$  reflections measured on Straumanis-type rotation photographs about the  $c$  and  $[110]$  axes. The resulting values are given in Table 1, together with the previously reported values for L- and DL-alanine.

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Table 1. Unit-cell dimensions for L- and DL-alanine

	L-Alanine		DL-Alanine	
	Bernal (1931)	This investigation	Bernal (1931)	Levy & Corey (1941)*
$a$	6.0 kX	6.032(1) Å	6.0 kX	12.04(1) kX
$b$	12.1	12.343(1)	12.0	6.04(1)
$c$	5.75	5.784(1)	5.8	5.81(1)
(Cu $K\alpha = 1.5418$ Å) ( $t = 25 \pm 1$ °C)				

\* Levy & Corey interchanged the  $a$  and  $b$  axes to conform to the space group  $Pna2_1$ .

Complete intensity data for Cu  $K\alpha$  radiation were collected from multi-film, equi-inclination Weissenberg photographs of layer lines 0–5 about the  $a$  and  $c$  axes. Needle-shaped crystals about 0.3 mm in diameter were used, the one oriented along  $a$  having been shaped by dissolution with moist filter paper. By this means, all 589 reflections within an effective copper sphere of  $\sin \theta = 0.99$  were recorded. Of these, eight were too weak to be observed, seven were too strong to be measured reliably, and one (3,14,2) lay at the very edge of the photographs and accordingly was given zero weight. Intensities were estimated visually and corrected for Lorentz and polarization factors; no absorption correction seemed necessary.

Data from the various layers were correlated to a single scale by means of the 434 reflections which were measured about both axes. These 434 reflections also served as a basis for an estimation of the quality of the observations. The best quadratic representation of the standard deviations in  $F^2(\text{obs})$  was found to be

$$\sigma(F_0^2) = 0.25 + 0.083 F_0^2;$$

this relationship was the basis of the weighting scheme used in the final least-squares refinement cycles.

The systematic absence of the odd orders of  $h00$ ,  $0k0$  and  $00l$  confirmed the space group  $P2_12_12_1$  originally derived by Bernal (1931). The density calculated on the basis of four molecules of  $C_3H_7NO_2$  per unit cell is  $1.374 \text{ g.cm}^{-3}$ ; the density of DL-alanine measured by Levy & Corey is  $1.40 \text{ g.cm}^{-3}$ .

Determination and refinement of the structure

The structure was readily derived by analogy with the known structure of DL-alanine (Levy & Corey, 1941; Donohue, 1950). In view of the nearly identical inter-

sities of the *hk0* reflections for the two compounds, the starting *x* and *y* coordinates were those of Levy & Corey, with the origin shifted because of the difference in space group. Initial attempts at refinement by means of difference projections onto (001), for which the am-

Table 2. The final atomic parameters and their standard deviations

The heavy atom values have been multiplied by 10<sup>4</sup>; their temperature factors are in the form exp(-*b*<sub>11</sub>*h*<sup>2</sup>-*b*<sub>22</sub>*k*<sup>2</sup>-*b*<sub>33</sub>*l*<sup>2</sup>-*b*<sub>12</sub>*hk*-*b*<sub>13</sub>*hl*-*b*<sub>23</sub>*kl*). The hydrogen parameters have been multiplied by 10<sup>3</sup>. The hydrogen atoms were assigned fixed isotropic temperature factors with *B*=3.0 for the methyl hydrogen atoms H(5), H(6) and H(7) and *B*=1.0 for H(1)-H(4).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> <sub>11</sub>	<i>b</i> <sub>22</sub>	<i>b</i> <sub>12</sub>	<i>b</i> <sub>13</sub>	<i>b</i> <sub>23</sub>
O(1)	7287(3)	843(1)	6283(3)	206(6)	44(1)	151(6)	59(4)	-47(10)
O(2)	4501(3)	1850(1)	7609(3)	227(7)	53(1)	91(5)	46(4)	-10(3)
C(1)	5606(4)	1418(1)	6016(4)	149(6)	25(1)	119(7)	-6(4)	-8(4)
N	6560(3)	1382(1)	1856(3)	150(6)	36(1)	88(6)	5(4)	12(8)
C(2)	4769(4)	1612(1)	3563(4)	138(6)	28(1)	98(7)	15(4)	-4(4)
C(3)	2746(5)	915(2)	3025(5)	177(8)	58(2)	153(9)	-38(5)	-61(12)
H(1)	699(5)	64(3)	194(6)					
H(2)	769(6)	179(3)	223(6)					
H(3)	599(5)	150(2)	43(6)					
H(4)	442(5)	239(2)	346(6)					
H(5)	222(7)	108(3)	144(8)					
H(6)	153(7)	103(3)	410(9)					
H(7)	315(6)	14(3)	306(8)					

Table 3. Observed and calculated structure factors

Within each group the columns contain the values of *h*, 10*F*<sub>o</sub>, 10*F*<sub>c</sub>, 10*A*<sub>c</sub>, and 10*B*<sub>c</sub>. Reflections designated by an asterisk were omitted from the least-squares and *R*-index calculations.

hkl	10F <sub>o</sub>	10F <sub>c</sub>	10A <sub>c</sub>	10B <sub>c</sub>
0 0 0	1000	1000	1000	1000
0 0 1	1000	1000	1000	1000
0 0 2	1000	1000	1000	1000
0 0 3	1000	1000	1000	1000
0 0 4	1000	1000	1000	1000
0 0 5	1000	1000	1000	1000
0 0 6	1000	1000	1000	1000
0 0 7	1000	1000	1000	1000
0 0 8	1000	1000	1000	1000
0 0 9	1000	1000	1000	1000
0 0 10	1000	1000	1000	1000
0 0 11	1000	1000	1000	1000
0 0 12	1000	1000	1000	1000
0 0 13	1000	1000	1000	1000
0 0 14	1000	1000	1000	1000
0 0 15	1000	1000	1000	1000
0 0 16	1000	1000	1000	1000
0 0 17	1000	1000	1000	1000
0 0 18	1000	1000	1000	1000
0 0 19	1000	1000	1000	1000
0 0 20	1000	1000	1000	1000
0 0 21	1000	1000	1000	1000
0 0 22	1000	1000	1000	1000
0 0 23	1000	1000	1000	1000
0 0 24	1000	1000	1000	1000
0 0 25	1000	1000	1000	1000
0 0 26	1000	1000	1000	1000
0 0 27	1000	1000	1000	1000
0 0 28	1000	1000	1000	1000
0 0 29	1000	1000	1000	1000
0 0 30	1000	1000	1000	1000
0 0 31	1000	1000	1000	1000
0 0 32	1000	1000	1000	1000
0 0 33	1000	1000	1000	1000
0 0 34	1000	1000	1000	1000
0 0 35	1000	1000	1000	1000
0 0 36	1000	1000	1000	1000
0 0 37	1000	1000	1000	1000
0 0 38	1000	1000	1000	1000
0 0 39	1000	1000	1000	1000
0 0 40	1000	1000	1000	1000
0 0 41	1000	1000	1000	1000
0 0 42	1000	1000	1000	1000
0 0 43	1000	1000	1000	1000
0 0 44	1000	1000	1000	1000
0 0 45	1000	1000	1000	1000
0 0 46	1000	1000	1000	1000
0 0 47	1000	1000	1000	1000
0 0 48	1000	1000	1000	1000
0 0 49	1000	1000	1000	1000
0 0 50	1000	1000	1000	1000
0 0 51	1000	1000	1000	1000
0 0 52	1000	1000	1000	1000
0 0 53	1000	1000	1000	1000
0 0 54	1000	1000	1000	1000
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0 0 71	1000	1000	1000	1000
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0 0 73	1000	1000	1000	1000
0 0 74	1000	1000	1000	1000
0 0 75	1000	1000	1000	1000
0 0 76	1000	1000	1000	1000
0 0 77	1000	1000	1000	1000
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0 0 88	1000	1000	1000	1000
0 0 89	1000	1000	1000	1000
0 0 90	1000	1000	1000	1000
0 0 91	1000	1000	1000	1000
0 0 92	1000	1000	1000	1000
0 0 93	1000	1000	1000	1000
0 0 94	1000	1000	1000	1000
0 0 95	1000	1000	1000	1000
0 0 96	1000	1000	1000	1000
0 0 97	1000	1000	1000	1000
0 0 98	1000	1000	1000	1000
0 0 99	1000	1000	1000	1000
0 0 100	1000	1000	1000	1000

plitudes were taken as the differences between the  $F_o$  values of L-alanine and DL-alanine, were inconclusive because of overlap. Approximate  $z$  coordinates were then assigned on the basis of hydrogen-bonding and packing considerations, and were adjusted by least-squares calculations based on the  $hk1$  and  $hk2$  data alone. Subsequent refinement was based on the entire set of three-dimensional data.

Aside from preliminary electron-density projections, that were evaluated with the aid of Beevers-Lipson strips, all calculations were carried out on a Burroughs 220 computer using a Fourier code written by Dr K. Hoogsteen and a structure-factor least-squares program for orthorhombic symmetries written by Dr A. Hybl. The least-squares matrix was diagonal for the positional parameters and block-diagonal for the aniso-

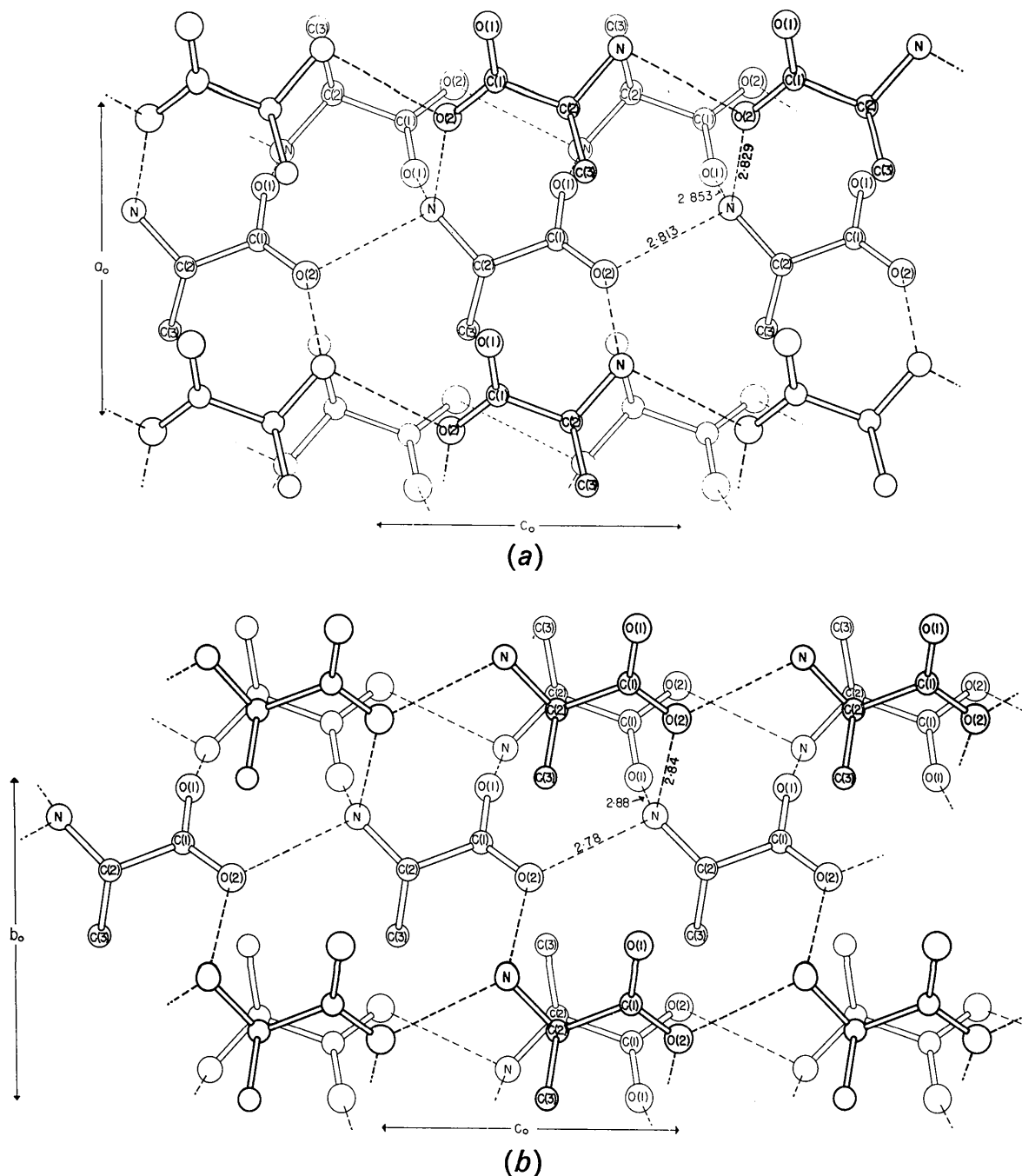


Fig. 1. (a) The structure of L-alanine viewed down the  $b$  axis. (b) The structure of DL-alanine (Levy & Corey, 1941) viewed down the  $a$  axis. The structure of L-alanine can be generated from that of DL-alanine by reversing the sense and direction of the columns of  $\mathbf{D}$  molecules [(heavy lines, (b))].

tropic temperature parameters; the quantity minimized was

$$\sum w(F_o^2 - K^2F)^2$$

where  $w$  is the weight and  $K$  is a refinable scale parameter. Atomic form factors for C, N and O were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for H from McWeeny (1951).

Initial refinement included only the six heavy atoms with isotropic temperature factors. When the  $R$  index reached 0.13, the four non-methyl hydrogen atoms were assigned coordinates consistent with tetrahedral bond angles and optimum N-H...O hydrogen bonding; the hydrogen atoms of the methyl group were located from a difference map calculated in their plane. The final least-squares cycles included as refinable parameters the coordinates of all 13 atoms and the anisotropic temperature factors of the heavy atoms; the hydrogen atoms were assigned constant isotropic temperature factors with  $B=3.0$  for those of the methyl group and  $B=1.0$  for the remainder. Different weighting functions were used, depending upon the stage of the refinement; during the final cycles the function was

$$\sqrt{w} = 1/\sigma(F_o^2) = (0.25 + 0.083F_o^2)^{-1}$$

(see *Experimental*). During the final cycle no parameter shift was greater than 30% of its standard deviation. The final parameters are given in Table 2, and the observed and calculated structure factors in Table 3. The  $R$  index for 573 reflections of non-zero weight is 0.049.

#### Accuracy of the results

The value of the quantity  $[\sum w(F_o^2 - KF_o^2)^2/(n-p)]^{1/2}$  – the standard deviation of an observation of unit weight – is 1.36, indicating small but significant systematic errors in the data. We suspect that at least some of the errors may have been introduced by the effect of double reflection, which was evidenced on several of the photographs. The standard deviations in the positional parameters (Table 2) were calculated from the sum of the residuals and the diagonal terms of the least-squares normal equations; they correspond to about 0.002–0.003 Å for the heavy atoms and about 0.04 Å for the hydrogen atoms. The standard deviations in the bond distances, then, are about 0.004 Å for bonds between heavy atoms and about 0.04 Å for bonds involving the hydrogen atoms.

The standard deviations of the temperature-factor parameters were calculated from the diagonal coefficients of the inverse matrices of the normal equations and include interactions among the six temperature parameters of the same atom.

#### Discussion of the results

##### *The intermolecular environment*

The most interesting result of this investigation lies, we believe, in the close relationship between the structures of L- and DL-alanine. Drawings of the two structures are shown in Fig. 1.

In both structures all three available protons are used to form N-H...O hydrogen bonds, two to O(2) atoms and one to an O(1) atom. One of the N-H...O(2) hydrogen bonds links molecules together lengthwise to form columns along the  $c$  direction; the other two hydrogen bonds link columns together in a three-dimensional network. The geometry of the hydrogen bonds is nearly identical in the two structures, the only difference being a slight change in the angle of attack of one of the hydrogen atoms on O(2). The two sets of hydrogen bond distances are equal within the limits of error (0.03 Å) in the more approximate determination (Levy & Corey, 1941) and refinement (Donohue, 1950) of the structure of DL-alanine.

As can be seen in Fig. 1, the structure of L-alanine can be derived from that of DL-alanine by reflecting the columns of D molecules [the heaviest lines in Fig. 1(b)] through the (001) plane, thus producing L molecules, and translating them along  $c$  until the oxygen atoms O(2) are in the proper position to accept the N-H...O(2) hydrogen bonds between columns.

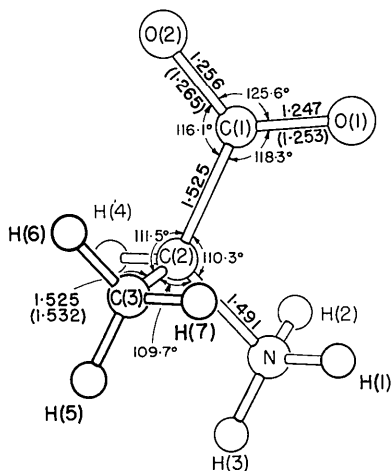


Fig. 2. Bond distances and angles. Values in parentheses have been corrected for effects of thermal vibration (see text).

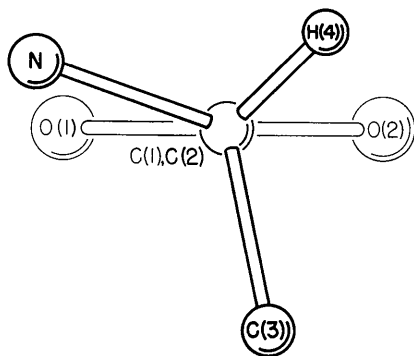


Fig. 3. A view down the C(2)–C(1) bond, showing conformation of the heavy atoms.

When viewed down the  $c$  axis, the two structures are essentially indistinguishable, giving rise to the nearly identical  $hk0$  intensity distributions that prompted this investigation.

#### The temperature factors

The magnitudes and direction cosines of the principal axes of thermal motion of the heavy atoms, as derived from the anisotropic temperature parameters of Table 2, are listed in Table 4. As expected, the largest thermal motions are associated with the oxygen atoms and the methyl carbon atom C(3). The major axes of the oxygen atoms are oriented approximately perpendicular to the plane of the carboxyl group, and the major axis of C(3) is approximately perpendicular to the C(2)–C(3) bond. Accordingly, we feel justified in correcting the C–O and C(2)–C(3) bond distances for the implied rocking effects, assuming riding motions (Busing & Levy, 1964).

A noticeable trend is the relatively small magnitude in the  $c$  direction of the thermal motion of each of the atoms. This direction is approximately parallel to the long dimension of the molecule, and to the strong N–H $\cdots$ O(2) hydrogen bond which links the molecules into columns.

#### The geometry of the molecule

The distances and angles involving the heavy atoms are shown in Fig. 2; values in parentheses have been corrected for the implied effects of thermal motion (see above). With the exception of the C(2)–N and C(1)–O(1) bonds, all values agree with those found in DL-alanine by Levy & Corey (1941) and by Donohue (1950) within their estimated limits of error, 0.03 Å and 3°. The value of the C–N bond length, 1.49 Å, is 0.07 Å longer than the value reported by Levy & Corey; it is in good agreement with the value 1.50 Å found by Donohue (1950) in a refinement based on the data of Levy & Corey, and with values observed in other amino acids. The value of the C(1)–O(1) bond length is 0.04 Å longer than the value reported by Donohue.

The carboxyl group is planar within experimental error, the central carbon atom C(1) lying 0.004 Å to one side and O(1), O(2) and C(2) less than 0.002 Å to the other side of the plane

$$0.5744X + 0.8161Y - 0.0626Z = 3.148 \text{ \AA};$$

here, the coefficients are direction cosines relative to the crystallographic axes. An edge-on view of this plane, as seen along the C(2)–C(1) bond, is shown in Fig. 3 to illustrate the conformation about C(2).

Table 4. The magnitudes  $B$ , root mean-square displacements  $\mu$ , and direction cosines  $q$  relative to the crystallographic axes, of the principal axes of the thermal vibration ellipsoids

Atom	Axis $i$	$B_i(\text{\AA}^2)$	$q_i^a$	$q_i^b$	$q_i^c$	$\mu_i(\text{\AA})$
O(1)	1	3.74	0.778	0.624	-0.066	0.218
	2	2.37	-0.385	0.558	0.735	0.173
	3	1.59	-0.496	0.546	-0.675	0.142
O(2)	1	3.95	0.730	0.683	0.000	0.224
	2	2.59	-0.677	0.723	-0.135	0.181
	3	1.19	-0.093	0.099	0.991	0.123
C(1)	1	2.20	0.976	-0.107	-0.188	0.167
	2	1.68	-0.074	0.653	-0.754	0.146
	3	1.42	0.203	0.750	0.630	0.134
N	1	2.27	0.726	0.684	0.069	0.169
	2	2.10	-0.684	0.729	-0.039	0.163
	3	1.17	-0.077	-0.019	0.997	0.122
C(2)	1	2.14	0.872	0.490	0.005	0.164
	2	1.62	-0.479	0.854	-0.204	0.143
	3	1.30	-0.104	0.176	0.979	0.128
C(3)	1	3.80	-0.417	0.909	-0.009	0.219
	2	2.68	0.726	0.326	-0.606	0.184
	3	1.68	0.547	0.259	0.796	0.146

Table 5. Distances and angles involving the hydrogen atoms

Distance	Angle	Angle			
N–H(1)	0.95 Å	C(2)–N–H(1)	110°	H(1)–N–H(2)	110°
N–H(2)	0.88	C(2)–N–H(2)	107	H(2)–N–H(3)	116
N–H(3)	0.90	C(2)–N–H(3)	107	H(1)–N–H(3)	107
C(2)–H(4)	0.98	C(1)–C(2)–H(4)	106	N–C(2)–H(4)	108
		C(3)–C(2)–H(4)	111		
C(3)–H(5)	0.99	C(2)–C(3)–H(5)	109	H(5)–C(3)–H(6)	109
C(3)–H(6)	0.98	C(2)–C(3)–H(6)	113	H(6)–C(3)–H(7)	108
C(3)–H(7)	0.99	C(2)–C(3)–H(7)	110	H(5)–C(3)–H(7)	107
H(1) $\cdots$ O(1)	1.92	N–H(1) $\cdots$ O(1)	166	H(1)–N $\cdots$ O(1)	10
H(2) $\cdots$ O(2)	2.00	N–H(2) $\cdots$ O(2)	157	H(2)–N $\cdots$ O(2)	16
H(3) $\cdots$ O(2)	1.91	N–H(3) $\cdots$ O(2)	173	H(3)–N $\cdots$ O(2)	5

The difference between the two C–O bond distances, 0.01 Å, is possibly significant; however, it is far less than the difference of 0.06 Å found by Donohue (1950) in DL-alanine. This difference was interpreted by Donohue to represent the effect of the hydrogen bonds on the resonance character of the carboxyl group. Since the hydrogen bonding is essentially identical in the two structures, it now appears that its effect on the dimensions of the carboxyl group is slight.

The bond distances and angles involving the hydrogen atoms are given in Table 5. It is interesting to note that the positions of the hydrogen atoms, as determined from a difference map and refined by least-squares methods, are very nearly the same (after appropriate transformations due to the different space groups and choices of axes) as those in DL-alanine as deduced by Levy & Corey from packing considerations. As in DL-alanine, methyl carbon atoms C(3) related to one another by screw axes along *c* are separated by only 3.68 Å – considerably less than the value 4.0 Å usually taken as the diameter of a methyl group (see, *e.g.*,

Pauling, 1960). Accordingly, the hydrogen atoms mesh in the manner described by Levy & Corey; the closest H–H approaches are 2.5 Å between H(5) and H(7) and 2.7 Å between H(6) and H(7).

The work described here was carried out as an undergraduate research project (HJS). We are grateful to Mr Earl Ubell for his assistance.

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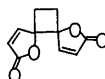
## The Crystal and Molecular Structure of Anemonin, C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>

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Anemonin,

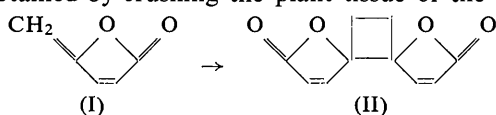


is the dimer of protoanemonin, a substance found in the plants of the crowfoot family (Ranunculaceae). While the structural formula of anemonin was fairly well established, the stereochemical relationship of the lactone rings was not. The material crystallizes in the orthorhombic system, space group *Pbca*, with eight molecules in the unit cell and cell parameters  $a = 11.65$ ,  $b = 13.86$ ,  $c = 11.07$  Å. The crystal structure analysis has established that the lactone rings are in the *trans* configuration. Furthermore, it has been shown that the cyclobutane ring is bent with a dihedral angle of 152° and that the C–C bond lengths in the cyclobutane ring have normal single-bond values near 1.54 Å.

The structure was solved by obtaining the phases directly from the structure factor magnitudes by means of the symbolic addition procedure.

### Introduction

Protoanemonin (I), a disagreeable vesicant liquid, may be obtained by crushing the plant tissue of the crow-



foot family (Ranunculaceae) (Heyer, 1792; Hill & Van Heyningen, 1951). It undergoes spontaneous dimerization in aqueous solution to yield crystalline anemonin

(II) (Asahina & Fujita, 1920). Only one cyclodimer is formed where several different combinations seem equally possible. While the structural formula of anemonin was fairly well established, the stereochemical relationship of the lactone rings was not. It had been assumed that the lactone rings were in the *cis* configuration (Harris, 1959). The crystal structure investigation was carried out in order to establish the stereo-configuration. A short note concerning the chemical properties and the configuration of anemonin has been published (Moriarty, Romain, Karle & Karle, 1965).