165. The Crystal and Molecular Structures of Tiglic and Angelic Acids. Part II.[1] Angelic Acid.

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Crystals of angelic acid are monoclinic, space-group C_{2h}^5–$P2_1/a$, with four molecules of $C_5H_8O_2$ per unit cell. The crystal structure was solved by use of molecular Fourier transforms, and the analysis confirms that the acid is 2-methyl-*cis*-but-2-enoic acid. Difficulties due to a high temperature factor and possible disorder restrict the accuracy with which the atomic co-ordinates can be measured. The manner in which the molecule overcomes the intramolecular overcrowding is discussed.

In the preceding paper [1] it was shown how the method of *X*-ray analysis, and especially the method of the molecular Fourier transform, may be used to assign configurations to geometrical isomers. In this way tiglic acid was shown to be 2-methyl-*trans*-but-2-enoic acid and the spatial positions of all the atoms were accurately determined. For angelic acid it has not been possible to make a very accurate structure determination. There is a high temperature factor and possible disorder. As a result only about one third of the possible *X*-ray reflections can be observed. However, the overall agreement index of 23% indicates that the structure described below is probably correct in all essential features. The molecule is found to have the *cis*-configuration. The distortions from a strictly coplanar configuration are somewhat greater than in tiglic acid but are in a direction which tends to relieve the intramolecular overcrowding.

Crystal Data.—Angelic acid, $C_5H_8O_2$; *M*, 100·1; m. p. 45·5°; *d*, calc. 1·139, found 1·141. Monoclinic, $a = 7{\cdot}66 \pm 0{\cdot}02$, $b = 11{\cdot}60 \pm 0{\cdot}02$, $c = 6{\cdot}67 \pm 0{\cdot}02$ Å, $\beta = 100 \pm 0{\cdot}5°$. Absent spectra, ($h0l$) when h is odd, ($0k0$) when k is odd. Space-group, $C_{2h}^5 - P2_1/a$. Four molecules per unit cell. No molecular symmetry is required but a centre of symmetry must lie between each pair of molecules. Volume of the unit cell = 584 Å^3. Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}542$ Å) $\mu = 8{\cdot}39$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 216.

The unit-cell dimensions agree approximately with those found by Schimper,[2] who gives $a : b : c = 0{\cdot}6494 : 1 : 1{\cdot}1393$, $\beta = 100° 33'$. On doubling the c axis we obtain $a : b : c = 0{\cdot}660 : 1 : 1{\cdot}150$, $\beta = 100° \pm 0{\cdot}5°$.

Crystals of angelic acid were obtained as thin plates, developed on (001), by slow recrystallisation from light petroleum. The crystals are soft and very volatile, with pronounced cleavage on $(20\bar{1})$.

Structure Analysis.—The projection of the structure along the *a* axis was first studied. There are four molecules of angelic acid in the unit cell and it was assumed that these formed two centrosymmetric dimers with hydrogen bonding between the carboxyl groups. A simplified planar model was therefore set up as shown at the bottom of Fig. 1. In this, it was assumed that all the bond lengths were 1·4 Å and that the hydrogen bonded O···O distance was 2·8 Å. The Fourier transform

$$T(X^*Y^*) = 2\sum \omega \cos 2\pi(X^*\xi + Y^*\eta)$$

was evaluated and is plotted in Fig. 1. Since the unit cell now contains two centrosymmetric dimers of angelic acid, the weighted ($0kl$) reciprocal lattice net cannot be obtained merely by sampling the T(X*Y*) function but must be obtained by sampling the sum of two such transforms correctly oriented with respect to each other. By making use of the symmetry properties of the space group $P2_1/a$, it is easy to show that

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[1] Part I, Porte and Robertson, preceding paper.

[2] Schimper, *Z. Kryst.*, 1881, **5**, 296.

this weighted reciprocal lattice net and the transform of one dimer are related by the expression

$$\frac{F(0kl)}{f_O} = T(0kl) + (-1)^k T(0k\bar{l}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this, the origin of the reciprocal lattice net coincides with the origin of the transform; f_O is the atomic scattering factor for a carbon atom, and T(0*kl*) is the value of the transform sampled by the point (0*kl*) of the correctly oriented reciprocal lattice.

With Cu radiation, 46 independent (0*kl*) reflections were observed out of a possible 102. Phase angles for these were obtained by orienting the (0*kl*) reciprocal lattice net on the T(X*Y*) contour map until equation (1) was satisfied. Combination of these phase angles with the observed values of the corresponding structure factors, followed by summation of the appropriate Fourier series, then gave the approximate electron density as projected on to a plane perpendicular to the *a* axis of the unit cell. (For the final electron density map, see Fig. 2.) Owing to lack of resolution this map is difficult to interpret, and two structures, each of which was approximately consistent with the postulated *cis*-butenoic acid configuration for angelic acid, could have been accepted at this stage. Furthermore, both these structures were approximately consistent with the 22 (*h*0*l*) reflections which were observed and estimated, but only one of them was consistent with the observed (*hk*0) structure factors. On the basis of this structure the *a*, *b*, and *c* axial projections were now refined independently by means of successive difference syntheses.

FIG. 1. *Fourier transform of idealised dimer of angelic acid with the* b * *and* c * *reciprocal axes superimposed.*

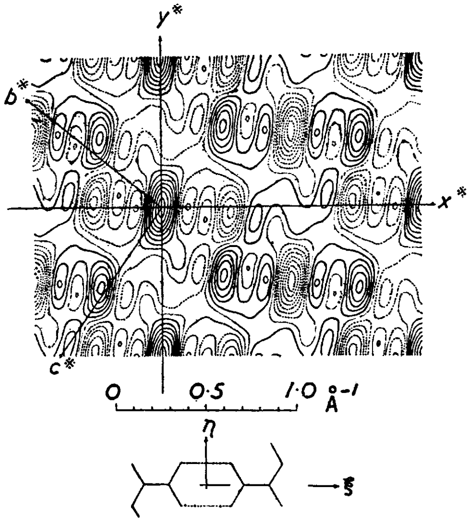
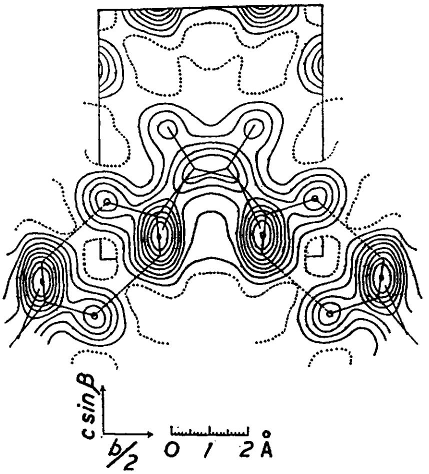


FIG. 2. *Electron-density projection on a plane normal to the* a *axis.*

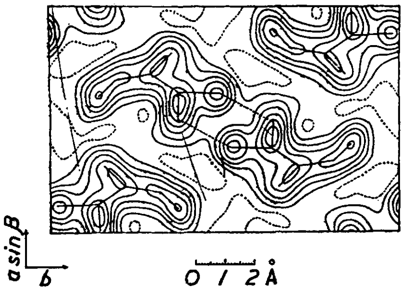


(Contour interval 1 e Å⁻², with one-electron line dotted.)

Structure factors calculated from the average co-ordinates obtained from the final difference maps resulted in average discrepancies (*R*) of 24·0% for the (0*kl*) zone, 14·4% for the (*h*0*l*) zone, and 25·4% for the (*hk*0) zone. Although these figures are still quite high, the refinement processes were not carried further because it became impossible to interpret the difference maps unambiguously for small shifts of the atoms. In addition, the Debye factor (*B*) was found to be about 10×10^{-16} cm.², which made the refinement processes extremely slow. However, when the (*h*1*l*) structure factors were calculated and compared with the corresponding observed values, the average discrepancy for these was found to be only 26·4%. There are no gross discrepancies between any of the observed and calculated structure factors and all those reflections which were not observed give low calculated values. We therefore conclude that this structure is essentially correct.

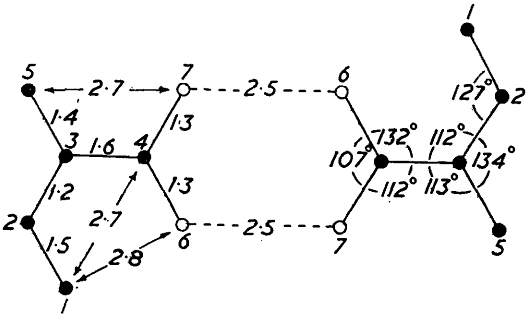
The final electron-density projections on the planes perpendicular to the *a* and *c* axes are shown in Fig. 2 and Fig. 3 respectively. These maps show conclusively that angelic acid is 2-methyl-*cis*-but-2-enoic acid.

FIG. 3. *Electron-density projection on a plane normal to the* c *axis.*



(Contour interval 1 e Å^{-2}, with one-electron line dotted.)

FIG. 4. *Approximate bond lengths* (Å) *and bond angles in angelic acid.*



Co-ordinates, Molecular Dimensions, and Orientation.—The final co-ordinates are given in Table 1; *x*, *y*, *z* are expressed as fractions of the axial lengths and *X*, *Y*, *Z* in Ångstrøm units referred to the monoclinic crystal axes; *X'*, *Y'*, *Z'*, also in Ångstrøm units, are referred to rectangular axes with *OZ'* coincident with *Oc* and *OY'* coincident with *Ob*. These are obtained from the monoclinic frame by means of the transformations

$$X' = X \sin \beta,\ Y' = Y, \text{ and } Z' = Z + X \cos \beta.$$

Two independent estimates of *x*, *y*, and *z* were obtained from the three axial projections. The averages of these are given in Table 1. The bond lengths and bond angles derived from these co-ordinates are shown in Fig. 4. Quite large errors may be associated with these co-ordinates and we therefore do not feel justified in quoting bond lengths to more than 0·1 Å. The equation of the mean plane through the molecule, referred to the rectangular frame *X'*, *Y'*, *Z'* is $0{\cdot}8X' - 0{\cdot}6Z' - 0{\cdot}03 = 0$. This plane is very nearly the (20$\bar{1}$) plane of the crystal and accounts for the very pronounced cleavage in this plane which is characteristic of the crystals. The distances of the various atoms from this plane are given in Table 2.

TABLE 1. *Co-ordinates.*

Atom	*x*	*y*	*z*	*X*	*Y*	*Z*	*X'*	*Y'*	*Z'*
C(1)	0·105	0·360	0·117	0·81	4·18	0·78	0·79	4·18	0·64
C(2)	0·181	0·310	0·318	1·38	3·60	2·12	1·36	3·60	1·88
C(3)	0·207	0·213	0·361	1·58	2·47	2·41	1·56	2·47	2·14
C(4)	0·134	0·126	0·170	1·03	1·47	1·13	1·01	1·47	0·95
C(5)	0·299	0·154	0·530	2·29	1·78	3·54	2·25	1·78	3·14
O(6)	0·006	0·137	0·015	0·05	1·59	0·10	0·05	1·59	0·09
O(7)	0·124	0·017	0·231	0·95	0·20	1·54	0·94	0·20	1·38

TABLE 2. *Distances of atoms from mean molecular plane.*

Atom	C(1)	C(2)	C(3)	C(4)	C(5)	O(6)	O(7)
d (Å)	+0·21	−0·07	−0·06	+0·18	−0·11	−0·10	−0·05

Accuracy.—The resolution of the structure is poor in each of the three axial projections, and therefore Cruickshank's statistical methods [3] for estimating the standard deviations of the atomic co-ordinates cannot be applied. However, these three axial projections were refined independently of one another and therefore two independent estimates of each co-ordinate are available. The mean deviation from the mean of the two values obtained for the X and Z co-ordinates is only 0·02 Å. The deviations in the Y co-ordinates are much greater, the mean being 0·06 Å, and the largest, 0·11 Å. Probable errors of the order 0·1 Å in the bond lengths must be accepted.

Intermolecular Distances.—The closest approach occurs between the hydrogen-bonded oxygen atoms in the dimers, and was found to be 2·5 Å. The closest approach of dimers is approximately 3·3 Å and occurs between atoms C(1) of the dimer at the origin of the unit cell, and atom O(6) of the dimer centred at $\frac{1}{2}$, $\frac{1}{2}$, 0. All other non-bonded distances are of the expected order of magnitude, and the minimum values between adjacent molecules lie in the range 3·3—4·0 Å.

Discussion.—Only about one third of the reflections from the ($0kl$), ($h0l$), ($hk0$), and ($h1l$) reciprocal lattice points lying within the Cu-K_α sphere of reflection have been observed, and it is this that restricts the accuracy with which the atomic co-ordinates can be determined. The small number of observed reflections is due to the extensive overlapping of atoms in each of the projections, and especially to the high Debye factor ($B = 10 \times 10^{-16}$ cm.^{2}). Crystals of angelic acid melt at 45·5°, are extremely volatile, and appear distorted in the polarising microscope. Although no direct evidence of disorder was obtained from an examination of the X-ray photographs, it seems necessary to assume some stacking irregularities in order to account for the abnormally high temperature factor.

TABLE 3. *Observed and calculated structure factors.*

Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_o	Plane	F_o	F_o	Plane	F_o	F_c
000	—	216	023	8·4	−12·9	065	2·6	−0·3	$40\bar{1}$	13·3	−11·5	250	2·2	2·6	111	5·2	5·0
001	19·0	15·7	024	5·2	7·2	072	3·6	2·3	$40\bar{2}$	25·2	29·3	280	4·0	4·5	112	15·4	−13·2
004	6·3	4·8	031	6·0	−7·9	073	4·3	2·7	$40\bar{3}$	8·5	10·6	290	5·6	−2·4	113	18·9	14·4
020	20·7	−19·1	032	21·8	−23·6	074	2·3	−0·9	$40\bar{4}$	3·5	1·8	2100	2·4	−1·4	114	5·9	9·6
040	24·1	−30·0	033	3·2	1·8	081	6·6	7·2	602	4·2	3·7	320	10·2	6·0	$11\bar{1}$	26·8	35·8
060	17·2	22·0	041	24·7	−22·2	091	3·8	−2·4	$60\bar{1}$	3·7	−1·3	330	16·9	−23·1	$11\bar{2}$	6·1	2·2
080	11·1	8·0	042	28·4	−28·3	092	4·6	−4·6	$60\bar{2}$	6·7	−3·5	340	4·6	−7·7	$11\bar{3}$	11·0	−7·9
0100	4·1	−0·8	043	3 0	3·4	0101	2·7	−1·4	110	26·8	27·5	370	4·5	3·6	$11\bar{4}$	9·1	5·3
200	9·7	−12·6	044	3·6	−0·1	0102	4·1	−2·7	120	22·1	−18·4	390	2·8	−2·4	211	10·3	−4·9
400	10·2	−7·1	051	6·3	3·6	201	16·4	−11·7	130	5·1	9·1	420	8·9	−9·2	$21\bar{1}$	32·1	−29·4
011	47·8	−54·2	052	10·0	11·5	203	3·9	4·8	150	1·8	0·4	430	9·2	−6·8	$21\bar{2}$	16·5	22·0
012	11·9	−6·5	053	3·0	4·2	204	4·5	5·5	170	7·2	6·6	440	2·0	−4·3	311	7·6	−6·2
013	8·2	−4·8	054	4·1	2·5	$20\bar{1}$	113·8	117·9	180	2·8	−1·7	450	6·5	3·9	312	8·9	15·5
014	3·8	−6·0	055	5·7	−1·3	$20\bar{2}$	24·6	24·7	210	32·6	−36·9	480	3·6	−1·6	$31\bar{1}$	14·7	15·3
015	3·9	4·1	061	3·0	2·1	$20\bar{3}$	6·3	3·9	220	17·2	19·0	490	4·4	−2·0	$31\bar{2}$	11·9	19·9
021	13·1	17·0	062	4·7	−1·1	401	4·0	5·3	230	13·8	−11·2	510	4·9	−1·5	$41\bar{1}$	9·3	−8·9
022	16·3	−15·9	063	4·3	−3·8	403	6·4	6·4	240	11·8	−13·0	520	2·7	—	$41\bar{2}$	19·6	−14·2

Although the *cis*-configuration of the acid has been confirmed, we cannot on the results of this analysis be precise about the finer details of the structure. However, it is possible to obtain a qualitative picture of the molecule from our results. In the idealised structure implied by the chemical formula, and used in the calculation of the Fourier transform shown in Fig. 1, the methyl groups lie very close to the oxygen atoms of the carboxyl group, the distance C(1)—O(6) being only 2·4 Å. The resultant steric strain might be relieved by rotating the carboxyl group out of the plane of the rest of the molecule, but this is not indicated by our results. Instead, a balance appears to be maintained between maximum overlap of π-orbitals, and hence maximum resonance, and minimum steric strain. The results show that this is achieved by a displacement of C(1), and probably also C(4), from the plane of the rest of the molecule, coupled with distortion of bond angles until the methyl groups and oxygen atoms are about 2·8 Å apart. The steric strain is not relieved by gross distortion at one particular site in the molecule but rather by smaller distortions spread over the molecule as a whole.

The intramolecular overcrowding must account in part for the differences in relative stabilities of tiglic and angelic acids and of their derivatives. If any additional strain

[3] Cruickshank, *Acta Cryst.*, 1949, **2**, 65; 1954, **7**, 519.

should be placed on the angelic acid molecule by an attempted substitution reaction, then it may well be sufficient to cause the molecule to become completely unstable. The instability will then be overcome by rotation of the bond C(1)–C(2) about the double bond C(2)–C(3) with resultant isomerisation to tiglic acid. The ready isomerisation of angelic acid, and its derivatives, to tiglic acid, and its derivatives, has been observed.[4]

Experimental.—Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å, was used in all the *X*-ray measurements. The reflections were recorded on rotation, oscillation, and moving-film photographs, and the intensities were measured visually, use being made of the multiple film technique. Unit-cell dimensions were determined from rotation and equatorial layer line moving-film photographs.

The observed structure factors, F_o, were estimated by the usual mosaic crystal formulæ and the calculated values, F_c, were obtained from the co-ordinates and the temperature-corrected scattering factors based on the calculations of McWeeny.[5]

Table 3 contains all the measured structure factors. Those too weak to be estimated have been omitted but in these cases the calculated values were in general found to be of the expected order. The overall discrepancy $100\sum|(|F_o| - |F_c|)|/\sum|F_o|$ for all the measured structure factors is 22·8%.

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[4] Buckles, Mock, and Locatell, *Chem. Rev.*, 1955, **55**, 659, and references therein.

[5] McWeeny, *Acta Cryst.*, 1951, **4**, 513.