

positions for NH_4ClO_3 in this projection can be considered only approximate.)

The problem here appears more complex than in the examples cited by Bunn, inasmuch as here the entire process takes place in the solid state, and two distinct new phases appear together with the original one. The volume of each new phase must be sufficiently large that it gives sharp diffraction maxima. The only disorder appears to be in the NH_4ClO_3 phase; this is not surprising since it belongs to a non-orthogonal crystal system, in contrast to NH_4Cl and NH_4ClO_2 .

The mechanism by which the process of atomic rearrangement occurs is still completely obscure. However, it appears that it must involve the migration of oxygen atoms through distances of at least the order of 10^1 to 10^2 unit cells. Further study of the phenomenon appears worthwhile.

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References

- ABRAHAMS, S. C. (1956). *Quart. Rev. Chem. Soc. Lond.* **10**, 407.
- ARAVINDAKSHAN, C. (1958). *Z. Kristallogr.* **111**, 35.
- BOWER, J. G., SPARKS, R. A. & TRUEBLOOD, K. (1957). (Unpublished.)
- BUNN, C. W. (1933). *Proc. Roy. Soc. A*, **141**, 567.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.
- CURTI, R., RIGANTI, V. & LOCCHI, S. (1957). *Acta Cryst.* **10**, 687.
- DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.
- DUCHESNE, J. & BURNELLE, L. (1953). *J. Chem. Phys.* **21**, 2005.
- DUNITZ, J. D. & HEDBERG, K. (1950). *J. Amer. Chem. Soc.* **72**, 3108.
- FERRARI, A. & COLLA, C. (1937). *Gazz. Chim. Ital.* **67**, 424.
- GILLESPIE, R. B. & NYHOLM, R. S. (1957). *Quart. Rev. Chem. Soc. Lond.* **11**, 373.
- GILLESPIE, R. B. & TRUEBLOOD, K. N. (1959). To be published.
- KARTHA, G. (1952). *Acta Cryst.* **5**, 845.
- LEE, F. S. & CARPENTER, G. B. (1959). *J. Phys. Chem.* **63**, 279.
- LEUNG, Y. C. & MARSH, R. E. (1958). *Acta Cryst.* **11**, 17.
- LEVI, G. R. & SCHERILLO, A. (1931). *Z. Kristallogr.* **76**, 431.
- LINDQUIST, I. & MÖRTSELL, M. (1957). *Acta Cryst.* **10**, 406.
- MANI, N. V. (1957). *Proc. Indian Acad. Sci.* **16**, 143.
- PAULING, L. (1940). *Nature of the Chemical Bond*, p. 189. Ithaca: Cornell University Press.
- PROSEN, R. (1955). Ph.D. Thesis, Univ. of Calif. at Los Angeles.
- ROLLETT, J. S. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.
- SIEBERT, H. (1954). *Z. anorg. Chem.* **275**, 225.
- SMITH, H. G. & RUNDLE, R. E. (1958). *J. Amer. Chem. Soc.* **80**, 5075.
- SPARKS, R. A., PROSEN, R. J., KRUSE, F. H. & TRUEBLOOD, K. N. (1956). *Acta Cryst.* **9**, 350.
- SPARKS, R. A. (1958). Ph.D. Thesis, Univ. of Calif. at Los Angeles.
- TREFONAS, L. & LIPSCOMB, W. N. (1958). *J. Chem. Phys.* **28**, 54.
- VENKATESAN, K. (1957). *Proc. Indian Acad. Sci.* **16**, 134.
- ZACHARIASEN, W. H. & BUCKLEY, H. E. (1931). *Phys. Rev.* **37**, 1295.

Acta Cryst. (1959). **12**, 872

The Crystal Structure of the *trans* Isomer of β -Ionylidene Crotonic Acid

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The crystal structure of a β -ionylidene crotonic acid, prepared by Arens & Van Dorp (1946), has been determined and refined three-dimensionally. The conjugated side chain is all-*trans*; since this acid was a step in the vitamin *A* synthesis by Arens & Van Dorp, it can be assumed that the corresponding part of the vitamin *A* molecule is also all-*trans*.

Introduction

Preliminary investigations relating to the structure to be described in detail here, were published eight years ago (MacGillavry, Kreuger & Eichhorn, 1951). The

conformation and the more detailed bond distances and angles of this C-17 acid, obtained by Arens & Van Dorp in their vitamin *A* synthesis (Arens & Van Dorp, 1946) were thought to be of much interest in view of the biochemical importance of vitamin *A*. This acid moreover comprises most features found generally in the important group of natural pigments

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mately known from the section ($0\bar{3}1$), the position of this binormal with respect to (010) and [001] could be determined. The axial angle was measured on a Fedorow stage as $54\frac{1}{2}^\circ$. Birefringence is positive, n_γ , nearly parallel to $[\bar{1}13]$. From the indices measured by the Becke method in the various sections, the lengths of the indicatrix axes for Na *D* light have been calculated:

$$n_\alpha = 1.50 \pm 0.01; n_\beta = 1.56 \pm 0.01; n_\gamma = 1.88 \pm 0.01.$$

$$2V \text{ calculated } 57^\circ, \text{ observed } 54\frac{1}{2}^\circ.$$

With two molecules per cell (see next section), and point group $\bar{1}$ the zigzag chains should run antiparallel. The optical investigation then strongly suggests that the plane of the conjugated zigzag should be approximately parallel to ($0\bar{3}1$) and perpendicular to (110), with the chain direction approximately parallel to $[\bar{1}13]$. This is in full agreement with the results of X-ray analysis. From Table 3, which lists the final atomic parameters, it is seen that the differences in *x*, *y* and *z* for the atom pairs 12–15, 15–17, 11–14, 14–16 and 16–18, are, to a close approximation, in the ratio $-1 : 1 : 3$.

X-ray diffraction experiments

Small untwinned crystal fragments were selected under the microscope, and cut parallel to various crystal axes. Twinning was sensitively detected by abnormal interference figures. The unit-cell parameters and the interaxial angles were determined at room temperature and at -150°C . from rotation, oscillation and Weissenberg photographs. Copper *K* radiation was used throughout. In Table 1 the cell data are listed, with the low temperature data in brackets. The density determined by flotation is called d_f ; that found from the unit-cell volume and molecular weight, d_x .

There are no systematic absences: space group $P1$ or $P\bar{1}$. $Z=2$. $d_f=1.091 \text{ g.cm.}^{-3}$ (at 22°C). $d_x=1.093$ (1.188) g.cm.^{-3} .

From the data given in this table expansion coefficients can be calculated. The volume coefficient is found to be 4.9×10^{-4} per degree *K*. For some of the more important planes the linear coefficients of the spacings are:

$d(hkl)$	Linear expansion coefficient $\times 10^4$ per degree C.
100	1.1
010	1.2
001	0.6
$0\bar{3}1$	1.8

The last plane in the list is the plane that was later established to be the plane containing the essentially flat molecules; it is seen that thermal expansion perpendicular to this plane is high.

Weissenberg equi-inclination photographs were obtained for the first six layers about *c* and for the first nine layers about *a* at room temperature. At low

Table 1. X-ray data

$a = 10.48(10.26)$	} $\pm 0.02 \text{ \AA}$;	$\alpha = 109.1(106.9)$	} $\pm 0.1^\circ$;
$b = 13.63(13.23)$		$\beta = 128.0(127.5)$	
$c = 7.67(7.58)$		$\gamma = 66.4(68.6)$	
$V = 790(727) \pm 2 \text{ \AA}^3$.		(Cu <i>K</i> α , $\lambda = 1.5418 \text{ \AA}$).	

(In our preliminary communication (MacGillavry, Eichhorn & Kreuger, 1951) the cell constants given are slightly in error.)

temperature the first three layers about *c* were recorded for intensities, and the zero layer about *a*. Only the zero layer about the longest axis, *b*, was photographed at both temperatures. The multiple film, visual estimation technique was used for evaluation of the diffraction data.

Since carboxylic acids are almost without exception linked through hydrogen bridges, we assumed that this would be the case here also, with the carboxyl groups hydrogen-bonded across a centre of symmetry. This assumption, borne out also by morphology and by a statistical distribution graph (Howells, Phillips & Rogers, 1950), was subsequently proved correct by the fairly smooth convergence of refinement, to the relatively low value of percentage discrepancy attained.

The first trial model

The *c*-axis being the shortest, the projection (*hk*0) was first looked at for special features. The premise for the trial model was laid by the molecule's assumed stereochemical outlay. We felt certain that the structure would be very nearly planar with the exception of some ring-atoms. A cursory look upon the (*Ok*l) film had already brought information corroborating this assumption: by far the strongest intensity is found for ($0\bar{3}1$); also the higher orders of reflection of this plane up to and including the 4th are outstandingly strong within their region; the lattice spacing of ($0\bar{3}1$) is 3.63 \AA which is a likely value for the thickness of a practically flat molecule. In the (*hk*0) set the strongest reflexion is (120); the trace of this plane on the ($0\bar{3}1$) plane was thought to indicate the overall length-wise direction of the molecule. Fig. 3 shows the two basic arrangements that are feasible. To distinguish between them we looked for reflexions in the far θ ranges that might indicate the zig-zag of the chain. Those were found in (650), (2,13,0) and (3,15,0) and model *A* is seen to fit much better than model *B* of Fig. 3.

Apart from these considerations based on diffraction data and a likely van der Waals model, we also had powerful corroboration from our optical investigation, as explained earlier. We now felt certain about the trial model in all but the position of the ring with respect to the sidechain. At the onset of this investigation we were ignorant of later developments in carotenoid research which to a large extent invalidate the rigid reasoning along 'classical' lines that we then sought to follow.

The acid contains a conjugated bond system that admits of *cis-trans* isomerism. It has, however, been

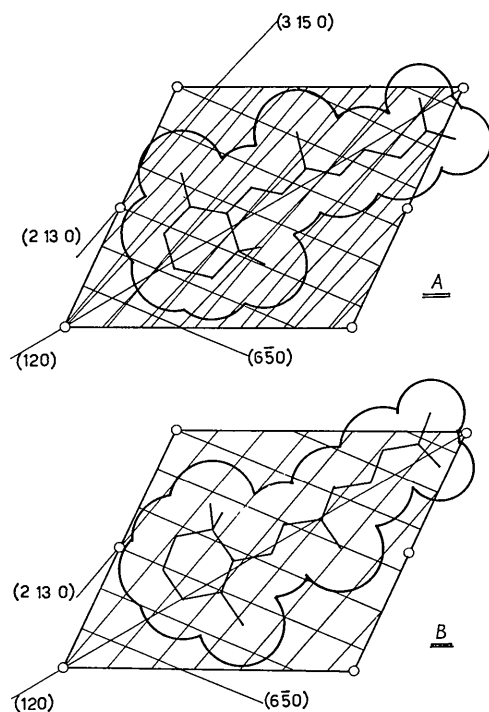


Fig. 3. Two possible ways of fitting an all-*trans* molecule model into the plane (031). Traces of some strongly reflecting planes have been drawn in.

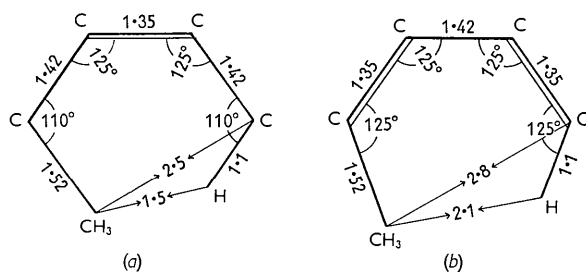


Fig. 4. Steric hindrance in methyl-substituted conjugated chains, *cis* with respect to (a) double bond, (b) single bond.

pointed out long ago (Pauling, 1939) that in the situation drawn in Fig. 4(a) the *cis*-configuration meets with serious steric hindrance, due to the side-chain atoms. It is seen in Fig. 1(b), where the *double* bonds 7=9 and 10=11 are in *cis* position with respect to the (conjugated) *single* bond 9-10, that steric hindrance of the same sort occurs in this case. Conformation C, Fig. 1, was therefore given preference.

We know now, from straightforward X-ray evidence (Sly, 1955; Eichhorn, 1956a), that there are cases in which the inverted ring position does occur. Actually, if conventional bond lengths and angles are assumed, it is seen that the situation is somewhat more favorable for a *cis* position about a single bond (Fig. 4(b)) than for one about a double bond (Fig. 4(a)). This is mainly due to the difference in bond angle distribution. Even

configurations of type 4a have been reported (Lunde & Zechmeister, 1955; Garbers & Karrer, 1953); there is probably large deviation from planarity.

The first projections

The (*hk*0) projection was tackled first. In order to ascertain if the inverted ring position might not prove to be correct after all, two trials with such a model were conducted on the side and discarded when they failed to refine. We knew very little if anything about the puckering of the ionone ring, and there is a considerable amount of latitude in bending the ring; the methyl groups O1 and O2 are very sensitive to puckering. We had to resort to a simultaneous trial of six different internal ring arrangements. The six *F*-sets that emerged were utilized in the following way:

All planes were marked that had the same sign in all six trials, and those planes were used in the first place in the initial density map. A number of other planes was selected the signs of which were indeterminate in some trials and the same in the others; these planes, with the preponderant sign, were also included in the Fourier projection. A very few more planes were included upon various considerations. The

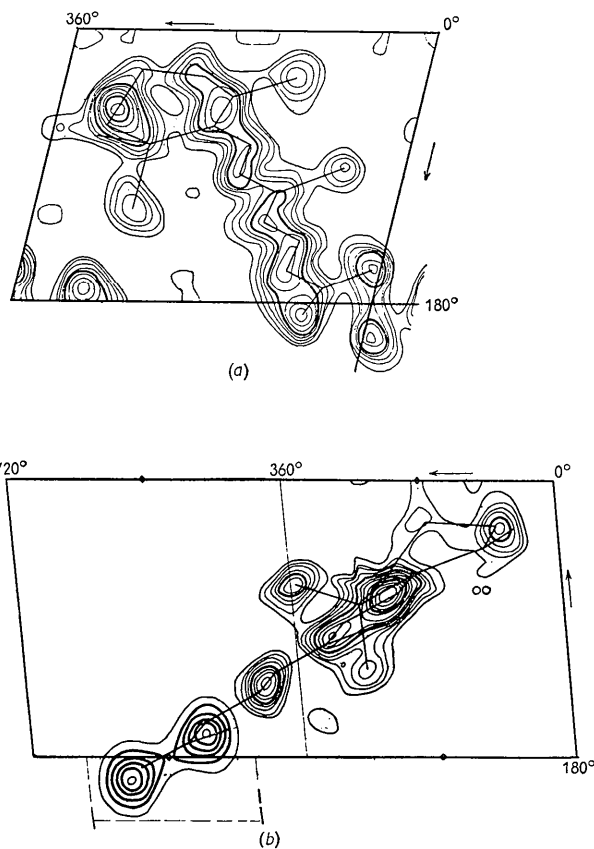


Fig. 5. (a) Fifth density map of the *c*-projection; (b) fourth map of *a*-projection, both calculated from room-temperature diffraction data. Contour levels on arbitrary scale.

first projection was calculated with 50 planes out of a total of 106 observed data.

The sidechain was discernible with fair resolution of methyl group 13. The ring lay on a density blob of the right shape but could of course not be differentiated into separate atoms. Methyl group 08 was also resolved and had shifted considerably in the first map. A scale model of the molecule was now projected with a parallel light beam onto the Fourier map, and the model was adjusted for best fit. Three subsequent trial-and-Fourier-cycles were thus effected and progress was measurable but slow. After a 6th refinement from (*hk0*) maps we decided to start on the (*0kl*) projection also; this was handled in much the same way. Refinement of this projection was discontinued after four cycles, as it had yielded methyl group 02 but did not otherwise show much detail. Fig. 5 shows the 5th (*hk0*) projection which was computed with 88 out of the 106 available data; and the 4th (*0kl*) map which includes 70 out of the available 83 data.

Three-dimensional refinement, first stage

All 1158 room temperature diffraction data were now evaluated and the F_c -set calculated for it. The density section through the plane ($0\bar{3}1$) was first organized. For this purpose the crystal axes were transformed as follows:

$$\begin{aligned} a' &= a, & b' &= b + 3c, & c' &= c; \\ h' &= h, & k' &= k + 3l, & l' &= l. \end{aligned}$$

The first summation of Fourier coefficients is carried out over the last index. It is convenient then to arrange sets of structure factors with the same value of the first two indices such that the last index is listed in increasing natural order. If the molecules are nearly planar, normal decline in coefficient value should be observable in these sets. In many such sets the signs for coefficients of indeterminate phase (resulting from the imperfectness of the input model) can then be inferred from the rest of the set, if the general trend of signs can be recognized. This method of extrapolation, using normal decline, in our case proved extremely powerful and sped our progress substantially.

The first density section of the molecular plane confirmed the assumption regarding planarity and the all-*trans* zigzag of the sidechain. The ring still showed dubious features. As a further aid to refinement we now calculated a bounded projection $\parallel b$, covering one third of the unit cell from $y=0$ to $y=\frac{1}{3}$. This section contains all the ring atoms and the first part of the chain. The 'adjoining' bounded projection extending from $y=\frac{1}{3}$ to $y=\frac{2}{3}$ gives the end of the chain. Although far from perfect, the model of the molecule could again be corrected from this operation and the parameters thus revised were used for a start in the next step.

We were now able to use a large digital computer, built by Messrs. Ferranti Ltd. for the University of Manchester. The necessary programs for the refine-

ment of structures belonging to the centric triclinic space group had been prepared by the computer group at the University of Leeds (Ahmed, 1953) and were kindly made available to us through Prof. E. G. Cox, F.R.S., and Dr D. W. J. Cruickshank. The programs make use of backshift corrected differential syntheses. Viervoll & Øgrim (1949) scattering factors were utilized in the first cycle, and were then replaced by McWeeny (1951) *f*-values. The methyl groups were given a somewhat heavier scattering weight than the carbons. Heat movement was in first approximation taken to be isotropic.

The ring parameters as they emerged from the 4th refinement cycle showed a systematic shift in the position of atoms 04 and 05 and we had to rebend the ring accordingly. An electron-density section $\parallel (0\bar{3}1)$ at plus and minus $\frac{1}{4}$ of the spacing of that plane was now calculated and showed carbons 04 and 05 neatly resolved. The sectional planes do not cut precisely through the density cores of both atoms but the information obtained from them enabled us to compute line sections from which the *z*-coordinates could be determined. Methyl group 02 was also visible in one of the sectional planes and its position was affirmed. Finally an electron-density section $\parallel (001)$ was computed at $z=0.500$, which showed carbon 05 in full resolution; the peak was slightly oval in shape and small corrections in the parameters were effected therefrom.

The low temperature data

In spring 1954 the results of our work so far were reassessed in the light of experiments carried out with new X-ray equipment; at that time the pilot model of the now commercially available Nonius Weissenberg instrument for low temperatures was built and tested in our laboratory in Amsterdam (Kreuger, 1955). We were fairly certain that if we could extend the number of available diffraction data for the two reasonably accessible projections by using the same radiation at -150°C ., resolution of the atoms would be good enough to permit further two-dimensional refinement and to shorten substantially any three-dimensional operations on the room temperature set of data. For the (*hk0*) projection in fact 172 planes were observed at low temperature as against 106 at room temperature; for the other projection, $\parallel a$, 167 data were found as against 83 at room temperature:

Fourier refinement was carried out for both projections at first by means of successive density maps, starting from the best model obtained by previous operations. Then difference maps were applied, with curvatures deduced by use of the Booth-Costain formula from the F_o maps. While applying this procedure it occurred to us that a similar method could also be utilized for the sums which one obtains in the differential synthesis, and the concept of their graphical derivation was worked out. Slope maps and in one case curvature maps were found especially useful

in our case where a great number of sums are to be determined in each differential refinement (Eichhorn, 1955).

When X-RAC became available to one of us (E. L. E.), two slope map refinements were carried out from oscillograms of the projection along a , while one hand-calculated slope map refinement was done for the projection along c . The structure factors were in part computed at Pennsylvania State University with an I.B.M. 604 computer and in part still in Manchester on the Ferranti digital machine.

We found in the end that the ring atoms had shifted

appreciably, especially the two sensitive methyl groups 01 and 02. Some atoms of the side chain also had moved a little. It was obvious from the difference maps that a different temperature factor should be applied to the oxygens, but we omitted to do this since we did not think that it would improve the positional parameters noticeably. In the projection $\parallel a$ the hydrogen contributions were neglected and the methyl groups were treated as carbons. In the projection $\parallel c$ the non-methyl hydrogens, however, were included, and again the methyl groups were treated as carbons. McWeeny (1951) scattering curves were utilized.

In the $(hk0)$ projection the atoms 02, 03, 04 and 05 overlap appreciably and a least-squares procedure was adopted to correct the shifts. The labour involved was considerable since 32 sums of the type

$$\Sigma_H (\delta F / \delta m_r) \cdot (\delta F / \delta n_s)$$

and 8 sums of the type $\Sigma_H \Delta F \cdot (\delta F / \delta m_r)$ have to be computed (m, n coordinates; r, s atoms). The determinant then has to be set up and the 8 parameter shifts must be solved by tedious arithmetic. The summations were carried out on I.B.M. equipment. The determinant was set up and solved by hand computation.

The percentage discrepancy for the $(hk0)$ low temperature data was 20.0%, including 85 non-observed reflections. For the other projection the percentage discrepancy was 17.8%, also including all possible reflections. The Debye-Waller constant was 1.66 Å² for the $\parallel c$ projection and 1.60 Å² for the $\parallel a$ projection, assuming isotropic heat movement.

Our object was thus achieved and structural refinement pushed to the degree visualized when we undertook the low temperature work. We now reverted to the three-dimensional data set, collected at room temperature. Fig. 6 shows the last two low temperature projections. Comparison with Fig. 5 shows that the ring configuration has changed considerably during the refinement. It also shows the much better resolution that is achieved with the low temperature diffraction data.

Terminal refinement

Again differential syntheses, corrected for termination-of-series error, were chosen as the refinement procedure. Actual evaluation of the refinement stage is somewhat easier than in other methods, since one has to compute curvatures also. An atomic position found in a region of positive curvature will of course immediately signal an error in the input. But even if the curvature value is negative at the input position and its absolute magnitude is low, a mistake is apparent. The magnitude of the curvature of an atom will thus be an indication of the positional refinement of the particular atom to which it refers, as will the increment in curvature in subsequent refinements. If a curvature value is still low, the shift computed from it may have an exaggerated magnitude and one has to take this

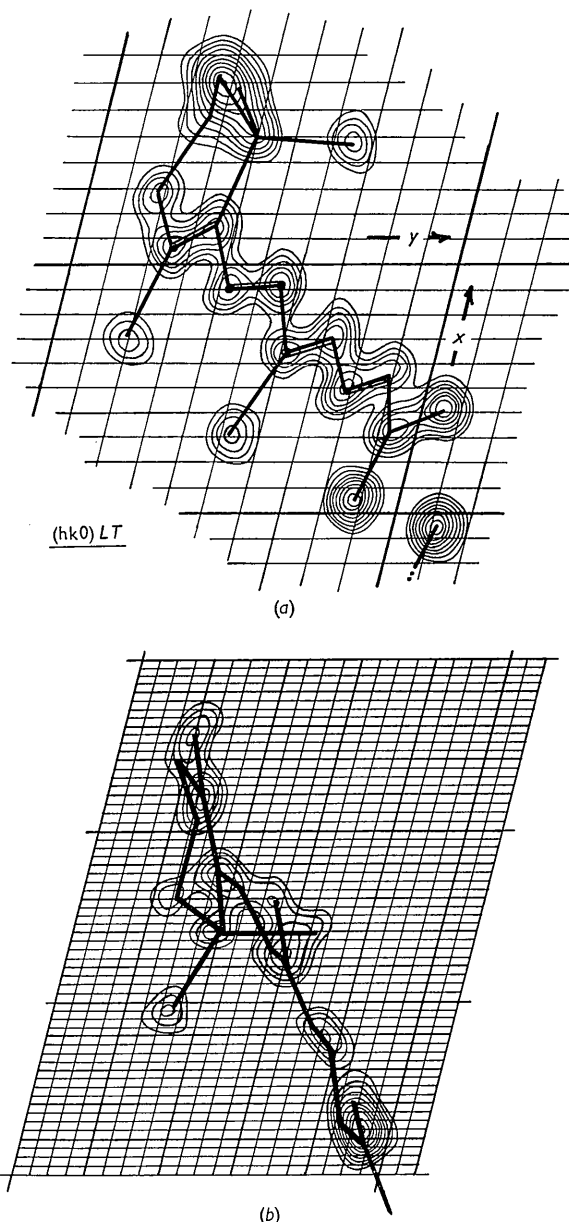


Fig. 6. Final electron-density projections (a) along c -axes and (b) along a -axes calculated on X-RAC from -150 °C. diffraction data.

Table 2. Room temperature data

Observed reflections only. Negative Miller indices are indicated by a minus sign after the appropriate number. The full set of data, including low temperature values is given by Eichhorn (1956a)

<i>h</i>	<i>k</i>	<i>l</i>	F(obs)	F(c)	<i>h</i>	<i>k</i>	<i>l</i>	F(obs)	F(c)	<i>h</i>	<i>k</i>	<i>l</i>	F(obs)	F(c)	<i>h</i>	<i>k</i>	<i>l</i>	F(obs)	F(c)	<i>h</i>	<i>k</i>	<i>l</i>	F(obs)	F(c)
00 01 00	8,8	7,2-	05 00 00	6,4	6,1	06 03- 00	2,9	2,4	04 09 01	5,5	5,1-	05- 05 01	4,3	3,1	07 01- 01	2,2	1,1-							
00 02 00	11,5	11,1-	05 02 00	5,3	4,2	06 05- 00	8,1	7,7-	04 12 01	2,4	3,0	05- 06 01	3,2	1,3	07 02- 01	2,9	4,8-							
00 03 00	28,3	26,4-	05 03 00	12,6	10,5-	06 07 00	2,2	2,8	04 14 01	2,6	3,1-	01- 01 01	3,2	1,8	01- 01 01	5,0	6,0							
00 04 00	11,7	10,3-	05 04 00	8,1	5,4	07 01- 00	4,4	2,7	05 00 01	4,6	6,4-	06- 02 01	10,3	8,5	01- 02- 01	18,5	17,2-							
00 05 00	9,3	8,7-	05 05 00	3,9	3,7	07 02- 00	1,5	4,0-	05 01 01	3,8	2,4	06- 03 01	4,6	2,4	01- 03- 01	33,7	30,1-							
00 06 00	2,7	1,3	05 06 00	2,2	0,3	07 03- 00	6,4	4,7-	05 03 01	3,4	2,9-	06- 05 01	5,3	4,3	01- 04- 01	44,5	41,9-							
00 07 00	5,8	5,7	05 08 00	2,3	2,6-	07 04- 00	2,4	3,5	05 05 01	1,5	0,3-	07- 00 01	8,4	7,0	01- 05- 01	30,1	29,1							
00 08 00	3,3	2,0-	05 11 00	3,7	4,6	07 05- 00	4,4	4,3	05 07 01	1,7	1,8-	07- 01 01	7,2	6,8	01- 06- 01	7,7	6,5							
00 09 00	2,9	2,9	06 01 00	3,5	3,3				05 13 01	4,5	3,7	07- 02 01	7,5	6,6	01- 07- 01	10,3	9,6							
00 10 00	4,6	3,7	06 02 00	5,0	3,4				05 15 01	2,7	1,4-	07- 04 01	3,2	2,5	01- 08- 01	4,5	2,7-							
00 12 00	1,9	3,4-	06 03 00	5,4	3,5-	00 00 01	13,1	12,4-	05 14 01	2,1	3,0-	07- 05 01	3,6	2,9	02- 01 01	16,8	16,7							
01 00 00	11,5	11,3-	06 07 00	3,7	4,0	00 01 01	13,9	15,1	06 03 01	3,8	4,3-	08- 00 01	5,5	5,4	02- 02 01	11,1	10,2							
01 01 00	12,5	11,7-	06 08 00	2,4	0,7	00 02 01	12,0	11,7-	06 06 01	3,2	3,3	08- 01 01	6,5	7,3	02- 03- 01	12,0	12,8-							
01 02 00	46,9	48,4	06 10 00	6,2	4,9-	00 03 01	14,6	14,8-	06 07 01	4,1	3,1-	08- 02 01	3,2	2,1	02- 04- 01	13,2	13,6							
01 03 00	9,3	6,8-	07 00 00	2,4	0,6	00 04 01	2,1	2,8	06 08 01	4,1	4,3	08- 03 01	5,6	5,0	02- 05- 01	17,6	16,1-							
01 04 00	3,3	0,1-	07 01 00	5,4	5,3	00 05 01	5,3	3,3-	07 00 01	2,4	3,9	08- 06 01	3,4	3,0	02- 06- 01	8,0	6,1-							
01 05 00	10,4	9,4-	08 01 00	1,5	2,0	00 06 01	9,0	7,6	07 01 01	4,1	5,0	09- 00 01	4,1	3,0	02- 07- 01	8,1	7,7							
01 07 00	14,6	12,6	08 05 00	2,7	4,0-	00 07 01	4,1	1,0	09 00 01	1,3	1,4-	09- 01 01	3,4	4,1	02- 08- 01	2,9	3,3							
01 08 00	5,0	2,8-	10 00 00	9,9	2,9-	00 08 01	7,3	5,2	01- 00 01	14,4	13,0	09- 03 01	2,4	2,0	02- 09- 01	1,5	2,0-							
01 10 00	1,9	3,1-	01 01- 00	18,5	20,0-	00 09 01	8,6	7,2-	01- 01 01	11,3	13,0	01- 01 01	15,7	16,5-	03- 01 01	7,3	8,4							
02 00 00	20,6	21,5-	01 02- 00	14,6	13,9	01 00 01	7,7	13,9-	01- 02 01	12,0	11,2	00 02- 01	21,4	24,2-	03- 02 01	16,1	17,1							
02 01 00	19,8	21,5	01 03- 00	7,6	6,5	01 01 01	8,8	8,8	01- 03 01	5,3	3,9	00 03- 01	66,6	69,3	03- 03 01	4,5	1,8-							
02 02 00	5,2	3,6	01 04- 00	9,8	9,3	01 02 01	6,9	6,9	01- 05 01	3,4	0,4	00 04- 01	14,8	13,9-	03- 04 01	6,0	5,0-							
02 03 00	4,4	2,4	01 05- 00	13,2	12,7	01 03 01	8,6	6,3-	01- 06 01	4,3	2,7	00 05- 01	13,0	12,4	03- 06 01	8,4	5,2							
02 04 00	5,3	1,7	01 07- 00	1,5	1,4-	01 04 01	12,3	11,2	01- 07 01	12,2	11,7-	00 06- 01	6,5	5,3	03- 07 01	8,4	6,2							
02 05 00	3,9	3,2	01 10- 00	3,3	6,5-	01 05 01	6,0	5,2	01- 08 01	4,1	3,4	00 07- 01	7,9	4,7	03- 08 01	6,2	5,0							
02 06 00	9,8	8,3-	02 02- 00	9,1	6,6-	01 07 01	4,6	4,4-	01- 09 01	5,5	5,7	03- 10 01	6,2	6,5	03- 10 01	3,4	2,3-							
02 07 00	6,8	4,9	02 03- 00	5,0	3,2-	01 09 01	1,7	2,0-	02- 00 01	3,8	3,1-	00 09- 01	1,7	2,2-	04- 01 01	6,7	6,3-							
02 13 00	5,4	5,4-	02 04- 00	1,3	1,1	01 10 01	3,8	1,6	02- 01 01	14,7	14,7-	01 01- 01	23,1	23,8	04- 02 01	6,0	4,2-							
03 00 00	9,7	9,1-	02 05- 00	7,4	8,5	01 11 01	3,8	2,6-	02- 02 01	12,7	9,9	01 02- 01	17,6	18,5-	04- 03 01	9,7	9,9							
03 01 00	8,7	9,8-	02 06- 00	2,2	3,2-	02 00 01	4,5	4,8-	02- 04 01	2,4	0,9	01 03- 01	10,8	7,3	04- 04 01	7,5	5,2-							
03 02 00	11,9	10,7	03 01- 00	3,3	3,4	02 01 01	3,2	0,0	02- 05 01	1,3	1,5-	01 05- 01	1,3	1,2	04- 05 01	2,2	0,8-							
03 03 00	23,9	24,6	03 03- 00	7,4	6,8	02 02 01	8,2	7,4	02- 06 01	2,9	0,5-	01 07- 01	4,8	3,1	04- 06 01	15,6	16,4-							
03 04 00	8,1	5,6-	03 04- 00	5,4	4,5-	02 03 01	7,7	6,9	02- 08 01	4,4	4,0	01 08- 01	4,6	2,1	04- 07 01	3,6	1,4-							
03 05 00	6,4	3,4-	03 05- 00	5,0	3,9	02 04 01	7,7	6,9	03- 00 01	5,3	4,2	01 08- 01	3,6	3,0	04- 08 01	3,9	2,9							
03 06 00	5,8	5,8-	03 06- 00	1,6	4,4-	02 07 01	1,5	1,7	03- 01 01	11,6	10,6-	02 01- 01	14,2	13,3-	04- 09 01	6,7	6,6							
03 07 00	6,8	6,8-	03 08- 00	7,7	8,6-	02 08 01	4,1	3,1	03- 02 01	9,2	6,6	02 02- 01	6,2	5,0	05- 02 01	9,9	7,5-							
03 09 00	3,9	5,1	04 01- 00	4,2	4,4-	02 09 01	2,4	0,6	03- 03 01	10,5	10,0-	02 03- 01	5,3	2,9	05- 03 01	10,1	11,3							
03 15 00	5,2	6,0-	04 02- 00	1,7	2,7	02 10 01	9,6	10,2-	03- 05 01	13,0	12,2-	02 04- 01	9,9	7,9	05- 05 01	11,6	9,7							
04 00 00	3,9	2,6	04 03- 00	7,6	7,4	02 11 01	4,8	4,5	03- 06 01	4,8	4,8	02 05- 01	3,6	3,5-	05- 06 01	6,0	4,9-							
04 01 00	14,4	13,9-	04 04- 00	1,5	2,4-	03 00 01	12,5	12,3	03- 07 01	5,5	5,4	02 07- 01	1,7	0,9-	05- 07 01	5,8	2,4							
04 02 00	6,8	4,2-	04 05- 00	5,0	4,6-	03 01 01	11,7	12,7-	03- 08 01	5,1	4,4	03 01 01	6,2	5,2	05- 08 01	11,6	12,2-							
04 03 00	10,8	11,6-	04 07- 00	5,3	4,5-	03 02 01	10,6	6,9	04- 00 01	5,1	4,4	03 01 01	5,5	5,8	05- 09 01	3,9	2,9							
04 04 00	8,9	10,3	05 01- 00	3,3	4,0	03 03 01	6,7	4,9-	04- 01 01	4,5	3,4-	04 01- 01	1,3	1,6	05- 10 01	4,9	3,7							
04 05 00	13,3	12,1	05 02- 00	1,3	2,9	03 04 01	5,5	5,0	04- 03 01	10,8	8,5-	04 02- 01	3,6	4,7	06- 01 01	3,9	3,0							
04 06 00	7,4	6,6	05 03- 00	2,7	2,4-	03 12 01	8,0	10,0-	04- 04 01	14,7	14,4	04 03- 01	2,9	3,3	06- 02 01	3,6	2,6-							
04 07 00	2,6	2,7-	05 04- 00	2,4	3,0	04 00 01	10,8	9,5-	04- 05 01	3,2	3,4-	05 01 01	6,0	6,8	06- 03 01	3,2	1,5							
04 08 00	4,6	4,3-	05 05- 00	4,6	3,7	04 01 01	5,3	5,1	04- 08 01	4,8	4,5-	05 04- 01	2,9	3,6	06- 04 01	3,2	2,1-							
04 09 00	2,6	1,5	05 07- 00	3,1	2,2	04 02 01	5,8	4,6	04- 09 01	3,2	3,5-	05 06 01	2,4	3,4	06- 05 01	3,2	3,6							
						04 03 01	3,4	3,6	05- 00 01	1,5	1,0-	05 08 01	3,2	4,2	06- 06 01	1,3	0,4							
						04 04 01	2,9	2,0	05- 01 01	5,6	4,8-	05 04- 01	2,2	3,3	06- 07 01	4,5	3,8							
						04 06 01	4,5	2,4	05- 02 01	5,2	5,0	06 08 01	2,6	3,6	06- 08 01	3,6	3,6							
						04 08 01	5,1	5,4-	05- 04 01	6,3	3,6-	06 08- 01	2,4	4,5	06- 09 01	4,8	5,0-							

into account and reduce the computed shift by a modulant. This procedure was worked out in detail in the refinement of the *trans* isomer of 4-azopyridine-N-oxide (Eichhorn, 1959). Here it is assumed for a start that all atoms are in their approximately correct position in the asymmetric unit, but that some positions are more refined than others. All curvatures of equal atoms are summed and the mean value obtained. The individual discrepancies from the mean are listed as percentage deviations, plus or minus. The 'straight shift' as obtained from the true curvatures is then modified according to the percentage deviation from the mean and the absolute magnitude of the shift. The table worked out for this method is empirical but it was found to work very well with several compounds. The convergence was checked by several parallel computations and found to be much sharper on application of this method. A similar procedure for the modification of temperature corrections was published recently (Cruickshank, 1956).

The straight shifts are first grouped as follows:

- group A: $\Delta X = 0.03 \text{ \AA}$ or smaller
- group B: $\Delta X = 0.03\text{--}0.08 \text{ \AA}$
- group C: $\Delta X = 0.08 \text{ \AA}$ or larger

where ΔX stands for a shift in an arbitrary direction, (either x , y or z). Shifts from group A were not reduced. Whenever the true curvature exceeded the mean curvature in magnitude, the straight shift also was adopted without modification. In our structure moreover we decided that in no case ought a positional correction to exceed 0.1 \AA and whenever straight or modified shifts came out larger than this distance, it was arbitrarily reduced to 0.1 \AA . The table below gives the reduction factor to be applied to the straight shift:

Group	Percentage deviation from mean curvature			
	%	-1 to -15	-16 to -45	-46 or less
B		0.9	0.7	0.5
C		0.8	0.6	0.4

Four three-dimensional refinement cycles were thus carried through. In the first cycle it seemed appropriate to ascertain whether it would be permissible to neglect non-spherical shape of density peaks, and the shifts were computed initially by application of Booth's complete formula, and afterwards by use of the reduced formula. It was found that the influence of ellipsoidal peak-shape upon the magnitude of the vectorial shifts was so small as to be negligible. The form to be applied then becomes:

$$\begin{aligned}\Delta x + \Delta y \cdot \cos \gamma + \Delta z \cdot \cos \beta &= dX \\ \Delta x \cdot \cos \gamma + \Delta y + \Delta z \cdot \cos \alpha &= dY \\ \Delta x \cdot \cos \beta + \Delta y \cdot \cos \alpha + \Delta z &= dZ\end{aligned}$$

where dX signifies the straight shift obtained by neglecting both anorthogonality of axial directions and non-spherical shape of density peaks, i.e.:

$$dX_r = -(\partial \rho / \partial X)_r / (\partial^2 \rho / \partial X^2)_r, \text{ for atom } r$$

and the quantities Δx are the shifts corrected for non-orthogonality of the axes.

The positional corrections are then found from relations of the type:

$$\begin{aligned}\Delta x_r &= p_x \cdot dX_r + q_x \cdot dY_r + s_x \cdot dZ_r \text{ etc. ,} \\ & p, q, s \text{ being constants.}\end{aligned}$$

To assess the progress made in refinement, optimization for scale and for heat movement (isotropic) was carried out after each cycle. In the last two cycles in particular, neither n nor B changed notably. Bond lengths and valency angles were also checked.

In computing the structure factors, the non-methylic hydrogens were finally all included by putting them in reasonable positions at 1 \AA distance from the respective carbon atoms. The hydrogen of the carboxyl group was placed halfway between the oxygens involved in the bridge. An attempt was made to account for the 12 methylic hydrogens by the assumption that the methyl groups are free rotators; we felt that the difference between this assumed state of affairs and the true one would not be large enough to justify a more sophisticated analysis of the methylic hydrogen positions. The free rotator scattering curves were calculated from McWeeny (1951) scattering values for hydrogen in the usual way (James, 1948, p. 230).

The set of 1158 observed reflections gave an optimal percentage discrepancy $R_{21\Omega} = 18.72\%$.* If this set is extended to include the non-observed terms within the Cu $K\alpha$ limiting sphere, the value rises to 25.75% . The complete set of observed structure factors is given in Table 2, along with their calculated counter-parts.

Assessment of the final structure

The positional parameters as they emerged from the last refinement cycle are given in Table 3; they are

Table 3. *Positional parameters*

Atom type	Code number	x	y	z
Methyl	01	0.7352	0.3240	0.8038
Methyl	02	0.8351	0.1644	1.0070
Carbon	03	0.7506	0.1998	0.7852
Carbon	04	0.8660	0.1339	0.7031
Carbon	05	0.7891	0.1349	0.4626
Carbon	06	0.6383	0.0909	0.3186
Carbon	07	0.5313	0.1274	0.4079
Methyl	08	0.3597	0.0983	0.2287
Carbon	09	0.5739	0.1776	0.6095
Carbon	10	0.4513	0.2116	0.6729
Carbon	11	0.4545	0.2749	0.8460
Carbon	12	0.3256	0.3033	0.8926
Methyl	13	0.1657	0.2646	0.7065
Carbon	14	0.3496	0.3625	1.0845
Carbon	15	0.2372	0.3911	1.1550
Carbon	16	0.2722	0.4449	1.3538
Carbon	17	0.1575	0.4693	1.4204
Oxygen	18	0.2008	0.5282	1.6153
Oxygen	19	0.0279	0.4378	1.3022

* For an explanation of the R_{21} and $R_{21\Omega}$ nomenclature see Eichhorn (1956b).

relating to atoms in the same molecule and some of the z values therefore appear modulo one.

The estimated standard deviations of the atomic parameters were computed from Cruickshank's formulas. They are given in Table 4. The peak densities given in this table were computed along with the curvatures and slopes in the last run of differential syntheses. The e.s.d. value for the electron density is $0.12 \text{ e.}\text{\AA}^{-3}$.

Table 4. *Estimated standard deviations*

Atom code number	σ_x	σ_y	σ_z in \AA	Peak density in $\text{e.}\text{\AA}^{-3}$
01	0.015	0.018	0.019	12.4
02	0.015	0.021	0.015	12.0
03	0.013	0.015	0.013	14.9
04	0.016	0.025	0.017	10.5
05	0.021	0.027	0.017	9.2
06	0.013	0.014	0.010	16.0
07	0.010	0.010	0.009	20.6
08	0.015	0.017	0.013	12.8
09	0.009	0.010	0.008	21.4
10	0.009	0.010	0.008	21.8
11	0.010	0.010	0.008	21.4
12	0.009	0.011	0.009	21.0
13	0.012	0.016	0.015	14.5
14	0.010	0.011	0.009	20.0
15	0.009	0.011	0.009	21.0
16	0.010	0.011	0.009	19.5
17	0.010	0.012	0.008	19.5
18	0.009	0.010	0.008	22.1
19	0.009	0.013	0.008	20.2
Average value	0.012	0.014	0.011	

Table 5 lists all distances of nearest and next nearest neighbours within the molecule, with their most probable errors; they are set out moreover in Fig. 7. The bond angles have also been tabulated. The hydrogen bridge is also given in the list. (The atoms 20 and 21 are related by a centre of symmetry to the atoms 18 and 19 respectively.) The data are those computed for room temperature.

With the exception of the hydrogen bridges, all intermolecular approaches are larger than 3.5 \AA and

are therefore not mentioned. We did, however, compute all intramolecular distances below 5 \AA and their most probable error.

The average probable error for the double bond in the conjugated chain is 0.010 \AA and the mean bond length is 1.332 \AA . The lowest and the highest value for this set of bond lengths differ by about three times the mean probable deviation, and this difference is

Table 5. *Bond distances in the trans isomer of β -ionylidene crotonic acid*

Atoms	Distance	Atoms	Distance
01-02	$2.577 \pm 0.022 \text{ \AA}$	09-10	$1.499 \pm 0.010 \text{ \AA}$
01-03	1.601 ± 0.019	09-11	2.550 ± 0.010
01-04	2.517 ± 0.024	10-11	1.314 ± 0.010
01-09	2.592 ± 0.016	10-12	2.484 ± 0.010
02-03	1.500 ± 0.017	11-12	1.479 ± 0.011
02-04	2.429 ± 0.018	11-13	2.565 ± 0.013
02-09	2.551 ± 0.014	11-14	2.444 ± 0.011
03-04	1.537 ± 0.018	12-13	1.548 ± 0.013
03-05	2.565 ± 0.018	12-14	1.346 ± 0.011
03-07	2.528 ± 0.013	12-15	2.484 ± 0.011
03-09	1.564 ± 0.013	13-14	2.560 ± 0.015
03-10	2.639 ± 0.013	14-15	1.452 ± 0.011
04-05	1.493 ± 0.020	14-16	2.449 ± 0.011
04-06	2.462 ± 0.017	15-16	1.339 ± 0.011
04-09	2.520 ± 0.015	15-17	2.437 ± 0.011
05-06	1.502 ± 0.022	16-17	1.463 ± 0.011
05-07	2.507 ± 0.020	16-18	2.355 ± 0.010
06-07	1.500 ± 0.013	16-19	2.376 ± 0.011
06-08	2.518 ± 0.017	17-18	1.325 ± 0.010
06-09	2.514 ± 0.011	17-19	1.244 ± 0.012
07-08	1.566 ± 0.015	18-19	2.251 ± 0.011
07-09	1.327 ± 0.010	19-20	2.673 ± 0.010
07-10	2.440 ± 0.010		
08-09	2.558 ± 0.014		

The third column lists the most probable error in \AA per \AA of bond length. 20 denotes the oxygen atom obtained by symmetry operation from 18. It is the atom that forms the hydrogen bridge 19-20.

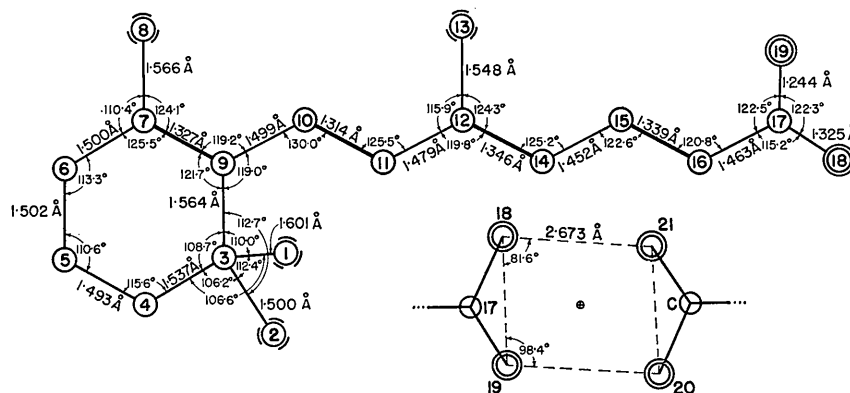


Fig. 7. Bond distances and bond angles of *trans*- β -ionylidene crotonic acid at room temperature.

therefore 'possibly significant'. Anyhow, these bonds show pronounced double bond character.

The methyl-carbon bonds and the bonds in the ring 9-3-4-5-6 are probably all pure single bonds, viewed in the light of their most probable errors. Bond 06-07 may be an exception, since it forms as it were the termination of the conjugation within the ring. The fairly low curvature and peak density values for atoms not belonging to the conjugated system point to rather larger heat movement.

The mean probable error and the mean bond length for the single bonds in the conjugation also suggest that the bond length difference of 06-07 and 14-15 is possibly significant; since the single bonds tend to become shorter and the double bonds to become larger, going from 06 to 17, this might indicate that the conjugation grows stronger going from the ring towards the carboxyl group.

Table 5 (cont.)

Bond angles in the <i>trans</i> isomer of β -ionylidene crotonic acid		
Triangle atoms	Obtuse angle	M. P. error (over whole angle)
01-03-02	112.35°	± 0.87°
01-03-04	106.63	0.82
01-03-09	109.95	0.67
02-03-04	106.19	0.73
02-03-09	112.70	0.66
04-03-09	108.72	0.63
03-04-05	115.65	0.88
04-05-06	110.59	0.86
05-06-07	113.28	0.84
06-07-09	125.46	0.69
06-07-08	110.42	0.64
08-07-09	124.12	0.76
03-09-07	121.74	0.69
03-09-10	119.00	0.61
07-09-10	119.25	0.55
09-10-11	129.99	0.68
10-11-12	125.51	0.65
11-12-13	115.89	0.59
11-12-14	119.79	0.60
13-12-14	124.30	0.76
12-14-15	125.17	0.67
14-15-16	122.63	0.63
15-16-17	120.76	0.61
16-17-18	115.19	0.55
16-17-19	122.54	0.69
18-17-19	122.26	0.71
18-19-20	98.43	± 0.24

The difference between the two C-O bonds in the carboxyl group is pronounced and significant. It is surprising to find the C=O bond to be the one which is not in line with the all-*trans* positioning of double bonds in the chain.

The deviations from the mean plane of the molecule, the lattice plane (031), were also computed and they are listed in Table 6. These values $T_r = (3y_r - z_r) \cdot d_{031}$ which we called 'elevations' give an indication of the planarity of the atom foursomes 09-10-11-12, 11-12-13-14, 14-15-16-17 and 16-17-18-19 and also the set of 06-07-08-09-03. Of the valency angles at atoms

Table 6. Elevations of the atoms in Å

$T_r = (3y_r - z_r) \cdot d_{031}$			
Atom	T_r	Atom	T_r
01	+0.61	11	-0.07
02	-1.87	12	+0.06
03	-0.67	13	+0.31
04	-1.09	14	+0.01
05	-0.21	15	+0.06
06	-0.17	16	-0.07
07	-0.09	17	-0.04
08	+0.24	18	-0.11
09	-0.28	19	+0.04
10	-0.14		

07, 12 and 17 the least obtuse is always between the two single bonds. This was also found by Sly (1955) in the case of deshydrocarotene and was assumed by us in Fig. 4.

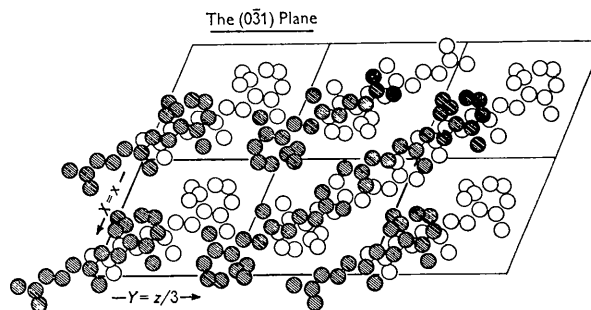


Fig. 8. Stacking of subsequent layers of molecules in the structure of β -ionylidene crotonic acid, viewed perpendicularly to these layers.

Fig. 8 shows two layers of molecules seen perpendicular to the mean molecular plane. The stringlike arrangement of molecules is quite pronounced. The striking correlation between molecular stacking and optical properties has already been mentioned. Fig. 9 shows the density map of the molecular plane section after the last refinement cycle.

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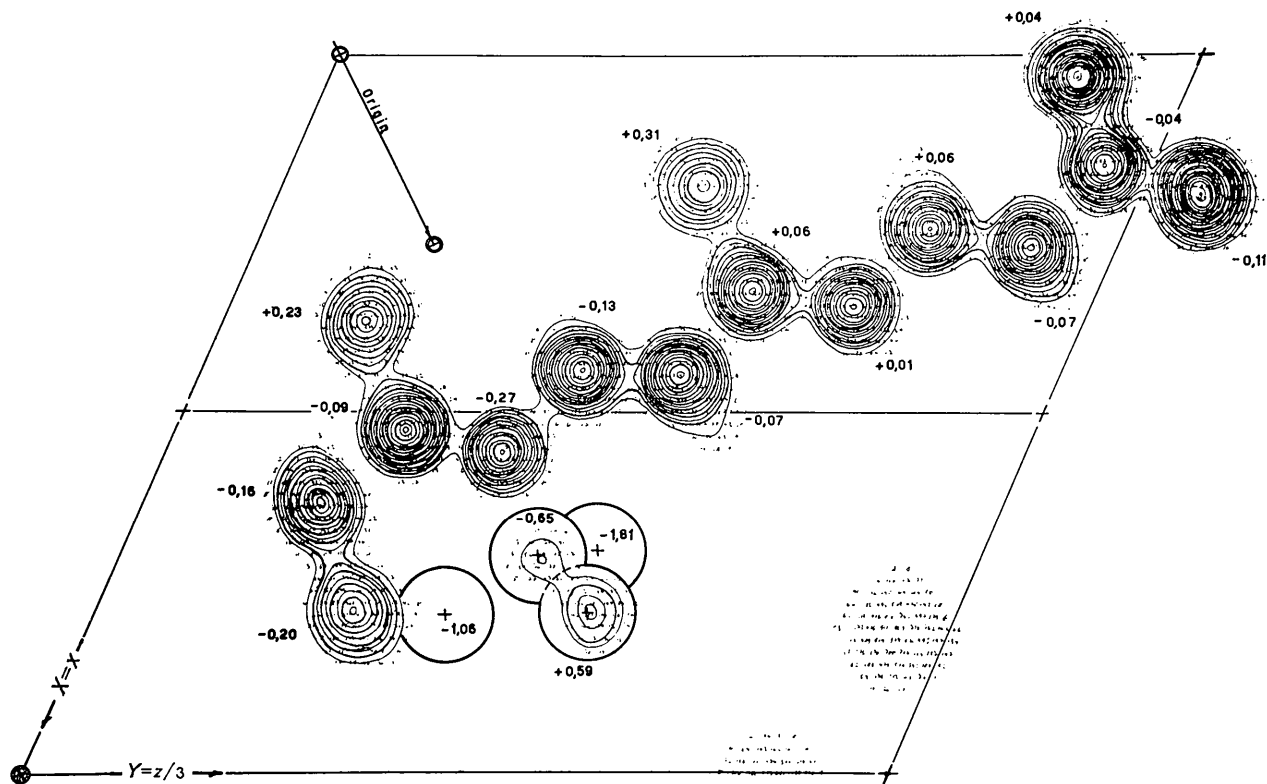


Fig. 9. Final section through the plane $(0\bar{3}1)$; room temperature. Contour levels on arbitrary scale. Numbers indicate approximate vertical distance of atomic centre from plane of section, in Å.

References

- AHMED, F. A. (1953). Thesis, University of Leeds.
 ARENS, J. F. & VAN DORP, D. A. (1946). *Rec. Trav. chim. Pays-Bas*, **65**, 338.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.
 EICHHORN, E. L. (1955). *Acta Cryst.* **8**, 63.
 EICHHORN, E. L. (1956a). Thesis, University of Amsterdam.
 EICHHORN, E. L. (1956b). *Acta Cryst.* **9**, 787.
 EICHHORN, E. L. (1959). *Acta Cryst.* **12**, 746.
 GARBERS, C. F. & KARRER, P. (1953). *Helv. Chim. Acta*, **36**, 828.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
 JAMES, R. W. (1948). 'The Crystalline State', Vol. II. London: Bell.
 KREUGER, A. (1955). *Acta Cryst.* **8**, 348.
 LUNDE, K. & ZECHMEISTER, L. (1955). *J. Amer. Chem. Soc.* **77**, 1647.
 MACGILLAVRY, C. H., KREUGER, A. & EICHHORN, E. L. (1951). *Proc. K. Ned. Akad. Wet. Amsterdam, B*, **54**, 449.
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 PAULING, L. (1939). *Fortschritte Chem. Org. Naturst.* **3**, 203.
 PERDOK, W. G. (1949). Private communication.
 SLY, W. G. (1955). *Acta Cryst.* **8**, 115.
 VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.