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# The Crystal Structure of the Triclinic Modification of Vitamin-A Acid

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The crystal structure of the triclinic modification of vitamin-A acid has been determined from a sharpened three-dimensional Patterson synthesis and refined by three-dimensional least-squares methods. The all-trans-conjugated side chain is markedly curved in its plane because of the presence of the methyl groups.

#### Introduction

Some years ago an investigation was started in this laboratory into the crystal structures of two vitamin-A related compounds namely trans  $\beta$ -ionylidene  $\gamma$ -crotonic acid and vitamin-A acid. The main object was to provide a direct proof of the generally accepted all-trans configuration of the double-bond system in these compounds.



Fig. 1. Numbering of the atoms.

The crystal structure of trans  $\beta$ -ionylidene  $\gamma$ -crotonic acid has been published in 1956 (Eichhorn, 1956; Eichhorn & MacGillavry, 1959). The structure determination of Vitamin-A acid forms the subject of this paper. The numbering of the atoms is analogous to the one adopted in the paper on trans  $\beta$ -ionylidene  $\gamma$ -crotonic acid (Fig. 1).

### Crystal data and space group

Vitamin-A acid was found to crystallize in two modifications. Usually well developed monoclinic crystals were obtained; occasionally some poorly developed triclinic ones were found. The monoclinic crystals are metastable; at about  $120^{\circ}$  they transform irreversibly into the triclinic form. This was established by means of powder diagrams at a series of increasing temperatures. The triclinic crystals melt at 180 °C. Eventually the following procedure was found to yield rather good triclinic crystals:

The (monoclinic) acid was powdered and heated in vacuo for several hours at about 120 °C., to effect the transformation to the triclinic form. A hot saturated solution in ethyl alcohol was then prepared ( $\pm$ 70 °C.) which was allowed to cool very slowly in a Dewar flask filled with water of the same temperature.

The following unit cell was chosen for the triclinic crystals:

$$a = 8.04 \pm 0.02, \ b = 28.49 \pm 0.04, \ c = 5.996 \pm 0.007 \text{ Å}.$$
  
$$\alpha = 50^{\circ} 58' \pm 10', \ \beta = 71^{\circ} 38' \pm 9', \ \gamma = 95^{\circ} 7' \pm 12'.$$

The cell dimensions were obtained by means of zero-layer Weissenberg diagrams about the three principal axes, calibrated with Al powder lines. The density as found by flotation is 1.09 g.cm.<sup>-3</sup>; for Z=2 the calculated density is 1.07. With two molecules in the unit cell the most probable space group is  $P\overline{1}$ , as it might be expected that the carboxyl groups of every two molecules would be linked by hydrogen bridges on either side of a centre of symmetry. This choice of space group was confirmed by the eventual solution of the structure. The crystals are in the shape of tablets parallel to (010), elongated along [001]. There is a rather good cleavage plane parallel to (100) and a bad one parallel to (201). The crystals are dichroic; in polarized light, incident perpendicular to (010), the colour varies between yellow, when the light vector is parallel to  $[10\overline{2}]$ , to light vellow.

#### Intensities

The intensities for the three-dimensional refinement were obtained from equi-inclination Weissenberg

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diagrams. The following films were made at room temperature using Cu  $K\alpha$  radiation:

The total number of independent reflexions measured is 1127 out of about 4300 within the reflexion sphere.

Attempts to obtain the diagrams at liquid-air temperature failed because after a short time at this temperature the crystals invariably cracked. With much effort reasonable zero layer diagrams about a- and c-axis were obtained at about -150 °C, the intensities of which were used in the refinement of the corresponding projections.

## Solution of the structure

The starting point was the high intensity of the reflexion 201 which, together with the corresponding

spacing of 3.67 Å, made it probable that a large part of the molecule, possibly the conjugated side chain, would be in the (201)-plane. An approximate direction of the side chain in the (201)-plane could be deduced from the Patterson projections hk0 and 0kl. In order to obtain more information about the mutual positions of the side chains in the (201)-plane, a Patterson section through this plane was calculated. This section was sharpened by using as coefficients in the Patterson summation:  $\sin^2 \theta F^2 \exp(-2\cdot 3 \sin^2 \theta)$  and is shown in Fig. 2. It confirms the assumption that the side chain is in the (201)-plane. A very reasonable interpretation of this Patterson section could be given in terms of straight conjugated chains connected by hydrogen bonds across a centre of symmetry as indicated in Fig. 2. After many vain attempts to refine this structure it had to be abandoned and a new start was made, this time using the complete three-dimensional Patterson, sharpened as indicated above. Attention was



Fig. 2. Sharpened Patterson section through (201), with, in the bottom part of the figure, the wrong interpretation in terms of straight conjugated chains (hatched parts indicate low value regions).



Fig. 3. Sharpened Patterson section parallel to (201) at 1.5 Å above this plane.

now directed towards the vectors from the C-atoms 1 and 2, protruding from the ring, to the side-chain atoms. It was hoped that these vectors would give rise to peaks more or less free from overlap. While looking for these vectors, at about 1.6 Å above (201) we encountered a row of peaks which could very well be attributed to vectors from C8 to the side-chain and to part of the ring. In Fig. 3 the Patterson section parallel to and at about 1.6 Å above (201) is shown with the above-mentioned vectors indicated, and also those of C8 to the next molecule. A probable conformation of the ring could also be found. If this interpretation were correct the side-chain would not be straight but markedly curved in its plane, which would account for the failure of our first attempts at solving the structure. And further, the double bond in the ring would not be in the plane of the side-chain but make an angle of about  $40^{\circ}$  with it. The trial structure based on this assumption gave very reasonable agreement between  $F_o$  and  $F_c$  and refinement of this structure proceeded without difficulty. First the a-axis projection, giving the best resolution for the sidechain atoms, was refined to an R of 18% using one overall isotropic temperature factor. The c-axis projection was refined in the same way to an R of 22%. A three-dimensional least-squares refinement was then started; after three cycles with individual isotropic temperature factors R had dropped from 32 to 25%. A difference synthesis at this stage clearly revealed anisotropic thermal motion of the side-chain atoms, with the largest displacement roughly perpendicular to (201). In the next cycle individual anisotropic temperature parameters were introduced. After five more cycles R had dropped to 13.3%. The refinement was terminated here; the last drop in R was 0.4%, the last average coordinate shift 0.003 Å. The discrepancy factors are for the 1127 observed reflexions only.

Fig. 4 shows the electron density in the (201) plane calculated from the last cycle. The corresponding

In all calculations the hydrogen atoms were left out

of consideration.



Fig. 4. Final electron-density section through (201) on arbitrary scale.

section of the difference synthesis is reproduced in Fig. 5; only terms for which  $\sin \theta < 0.5$  were used. This last section was calculated in order to see whether indications would be found for the presence of hydrogen atoms, especially those in the plane of the sidechain. There are indeed positive regions where H-atoms are expected to be.

### Results

In Table 1 the final coordinates and temperature parameters are given, together with their calculated standard deviations. Fig. 6 shows the bond distances and angles calculated from the coordinates of Table 1. The bond distances are also given in Table 2 together with their approximate standard deviations. As the standard deviations of the coordinates are anisotropic, the proper calculation of the standard deviations of the atomic positions in the bond directions is tedious. The standard deviations for the bond lengths listed in Table 2 were therefore calculated for isotropic positional standard deviations equal to the largest of the three axial ones of every atom. The standard deviations for the bond angles are about 1.5° throughout. The best plane through the side-chain: C9-C20, O1 and O2, calculated with the method of Schomaker et al. (1959) is:



Fig. 5. (201) section of  $\Delta F$  projection;  $F_c$  for C and O only. Terms for which  $\sin \theta > 0.5$  omitted. The crosses indicate C and O atoms in or near (201). Dotted contours are negative. Arbitrary scale.  $\Delta F(000)$  omitted.





Fig. 6. (a) Bond distances. (b) Bond angles.



Fig. 7. Packing of the molecules viewed perpendicularly to (201).

# $7 \cdot 274x - 0 \cdot 273y + 3 \cdot 703z = 3 \cdot 625$ (fractional coordinates).

The distances from this plane are listed in Table 3. The best plane through the atoms C3, C6, C7, C8, C9 and C10, forming the system of the double bond in the ring, has also been calculated. The equation of this plane is:

$$4 \cdot 092x + 2 \cdot 611y + 4 \cdot 977z = 3 \cdot 165$$

The distances of the atoms from this plane are given in Table 4. The angle between the two planes is  $34^{\circ}$ . The packing of the molecules is drawn in Fig. 7.

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In Fig. 8 the shorter intermolecular distances in a layer parallel to (201) are shown and in Fig. 9 the distances between molecules of adjacent layers.

### Discussion

The bond distances found are all normal in view of the calculated standard deviations, except for the single bond C4–C5 in the ring. The length of this bond is significantly smaller than the average single-bond distance in the ring. It is not clear how to account for this. Curiously enough this is also found for the corresponding bond in a further refinement of the

	æ	я	N	$v_{\mathbf{n}}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
౮	$5 \cdot 200(0 \cdot 017)$	$4 \cdot 014 (0 \cdot 025)$	1.782(0.025)	0.108(0.012)	0.217(0.017)	0.158(0.014)	0.241(0.024)	-0.317(0.029)	-0.192(0.022)
<u>°</u>	5.294(0.016)	6.151(0.020)	-1.546(0.020)	0.096(0.011)	0.097(0.010)	0.077(0.009)	0.063(0.017)	-0.113(0.017)	-0.006(0.016
ບິ	$4 \cdot 298(0 \cdot 013)$	$4 \cdot 406(0 \cdot 016)$	0.682(0.017)	0.078(0.009)	0.074(0.008)	0.080(0.008)	0.065(0.013)	-0.132(0.015)	-0.060(0.014)
5	3.826(0.017)	2.818(0.020)	0.772(0.024)	0.112(0.012)	0.092(0.010)	0.143(0.013)	0.061(0.018)	-0.190(0.022)	-0.011(0.020)
<b>ں</b>	2.496(0.017)	1.158(0.021)	2.575(0.027)	0.096(0.011)	(110.0)660.0	0.194(0.017)	0.052(0.018)	-0.238(0.026)	-0.046(0.022)
లి	1.070(0.015)	1.606(0.018)	2.965(0.022)	0.094(0.010)	0.079(0.009)	0.133(0.012)	0.062(0.015)	-0.180(0.019)	-0.086(0.018)
ర	1.416(0.013)	3.361(0.016)	2.612(0.018)	0.073(0.008)	0.062(0.007)	0.080(0.009)	0.034(0.013)	-0.109(0.014)	-0.048(0.014)
ືບຶ	-0.030(0.013)	3.555(0.019)	$3 \cdot 427 (0 \cdot 020)$	0.051(0.008)	0.103(0.010)	0.117(0.011)	0.062(0.014)	-0.177(0.019)	-0.070(0.015
లి	2.857(0.013)	4.636(0.015)	1.561(0.016)	0.078(0.008)	0.067(0.007)	0.066(0.007)	0.081(0.013)	-0.113(0.014)	-0.074(0.013)
C <sub>10</sub>	$3 \cdot 215(0 \cdot 013)$	6.365(0.015)	1.129(0.017)	0.068(0.008)	0.065(0.007)	0.078(0.008)	0.059(0.012)	-0.119(0.014)	-0.063(0.013)
C <sub>11</sub>	2.509(0.013)	6.516(0.016)	$2 \cdot 415(0 \cdot 018)$	0.074(0.008)	0.068(0.007)	0.085(0.009)	0.057(0.013)	-0.127(0.015)	-0.072(0.014)
$C_{12}$	2.857(0.013)	8.245(0.014)	1.962(0.017)	0.071(0.008)	0.050(0.008)	0.068(0.008)	0.006(0.012)	-0.086(0.013)	-0.035(0.013)
C13	$4 \cdot 192(0 \cdot 015)$	10.057(0.017)	-0.110(0.018)	0.098(0.010)	0.073(0.008)	0.080(0.009)	0.016(0.015)	-0.116(0.016)	0.001(0.015)
$C_{14}$	1.953(0.014)	8.227(0.016)	3.311(0.017)	0.083(0.009)	0.076(0.007)	0.080(0.008)	0.066(0.014)	-0.132(0.015)	-0.053(0.014)
C <sub>15</sub>	2.109(0.013)	9.856(0.015)	3.011(0.017)	0.084(0.009)	0.059(0.007)	0.067(0.008)	0.032(0.013)	-0.100(0.014)	-0.039(0.013)
$c_{16}$	1.151(0.014)	9.789(0.015)	$4 \cdot 386(0 \cdot 017)$	0.090(0.009)	0.053(0.007)	0.072(0.008)	0.035(0.013)	-0.096(0.013)	-0.022(0.014)
с1,	1.254(0.014)	11.364(0.016)	$4 \cdot 202(0 \cdot 018)$	0.087(0.009)	0.068(0.008)	0.079(0.009)	0.044(0.014)	-0.119(0.015)	-0.037(0.014)
ပ ပ	2.451(0.017)	13.288(0.017)	2.251(0.020)	0.121(0.012)	0.063(0.008)	0.084(0.010)	-0.007(0.016)	-0.112(0.016)	0.042(0.017)
c" C	0.276(0.014)	11.047(0.017)	5.731(0.018)	0.085(0.009)	0.087(0.009)	0.089(0.009)	0.050(0.015)	-0.150(0.017)	-0.025(0.015
$C_{20}$	0.181(0.015)	12.462(0.017)	5.770(0.018)	0.099(0.010)	0.072(0.008)	0.068(0.008)	0.018(0.014)	-0.110(0.015)	0.022(0.014)
o'	-1.034(0.010)	11.804(0.012)	7.367(0.013)	0.103(0.007)	0.089(0.006)	0.100(0.007)	0.005(0.011)	-0.154(0.012)	0.039(0.011)
02	1.092(0.011)	14.047(0.011)	4.622(0.013)	0.118(0.007)	0.069(0.005)	0.093(0.006)	-0.025(0.010)	-0.131(0.011)	0.064(0.011)

 Table 2. Bond lengths and corresponding standard deviations

	Distance	σ		Distance	σ
$C_1 - C_3$	1·525 Å	0.030	C19-C19	1·567 Å	0.025
$C_2 - C_3$	1.548	0.026	$C_{12}^{-}-C_{14}^{+}$	1.353	0.024
$C_3 - C_4$	1.552	0.029	$C_{14} - C_{15}$	1.442	0.024
$C_4 - C_5$	1.451	0.036	$C_{15} - C_{16}$	1.362	0.024
$C_5 - C_6$	1.535	0.032	$C_{16} - C_{17}$	1.456	0.025
$C_6 - C_7$	1.536	0.028	$C_{17} - C_{18}$	1.526	0.027
$C_{7} - C_{8}$	1.516	0.027	$C_{17}^{}-C_{19}^{}$	1.337	0.025
$C_7 - C_9$	1.355	0.024	$C_{19} - C_{20}$	1.451	0.025
$C_9 - C_3$	1.554	0.023	$C_{20} - O_1$	1.331	0.022
$C_{9} - C_{10}$	1.468	0.023	$C_{20}^{-}-O_{2}^{-}$	1.205	0.022
C10-C11	1.367	0.025	$0_{1}^{*} - 0_{2}^{*}$	2.647	0.018
$C_{11}^{-1} - C_{12}^{-1}$	1.458	0.025			

Table 3. Distances from the plane

	$7 \cdot 274x - 0 \cdot 273y$	+3.703z =	3.625
C,	2·140 Å	C19	0·092 Å
С,	0.120	C13	0.003
$C_3$	0.642	C14	0.107
Č₄_	0.286	C15	0.048
C <sub>5</sub>	0.206	C16	0.030
C <sub>6</sub>	-0.842	C17	-0.005
$C_7$	-0.763	$C_{18}^{11}$	-0.145
C's	-1.570	Cin	0.058
C,	-0.121	C.0	-0.018
Cin	-0.080	0,	-0.124
C11	0.073	O,	0.083

Table 4. Distances of atoms  $C_3$  and  $C_6-C_{10}$ from the plane 4.092x+2.611y+4.977z=3.165

C <sub>3</sub>	−0·008 Å	C <sub>8</sub>	-0.013 Å
C <sub>6</sub>	-0.015	C <sub>9</sub>	0.009
C7	0.032	C <sub>10</sub>	-0.008

structure of trans  $\beta$ -ionylidene  $\gamma$ -crotonic acid (Eichhorn, 1961). As can be seen from Table 3 the sidechain as a whole is not exactly planar, the deviations from planarity being for the greater part significant. The separate double-bond systems of the side-chain, however, are planar within the limits of accuracy. The best plane through the side-chain does not deviate much from (201). The side-chain is appreciably curved in its plane. The reason for this is clear from Fig. 10, where the shorter non-bonding intramolecular distances involving the CH<sub>3</sub>-groups are given. The angles opposite the CH<sub>3</sub>-groups 13 and 18 are reduced by the steric interaction of these with the side-chain, as a consequence of which it is no longer straight. The angles opposite the double bonds C12-C14 and C17-C19 are increased for the same reason. This effect was already noticeable in trans  $\beta$ -ionylidene  $\gamma$ -crotonic acid and has also been found in 15,15'dehydro  $\beta$ carotene (Sly, private communication).

The configuration of the cyclohexene ring is the same as in trans  $\beta$ -ionylidene  $\gamma$ -crotonic acid and corresponds to the chair form of cyclohexane. (The configuration corresponding to the bed form of cyclohexane is not free from strain).

The position of the ring relative to the side-chain is quite different from that in trans  $\beta$ -ionylidene



Fig. 8. Intermolecular distances in a layer parallel to (201).



Fig. 9. Intermolecular distances between adjacent layers parallel to (201).

 $\gamma$ -crotonic acid, where the double bond in the ring is a continuation of the zigzag of the side-chain and is approximately in the same plane with it. In vitamin-A acid, the ring is rotated from this position by an angle of approximately 145° about the C9–C10 bond. A similar situation is found in 15,15'dehydro  $\beta$ -carotene (Sly, 1960), and in cis 12–14  $\beta$ -ionylidene  $\gamma$ -crotonic acid (Koch & MacGillavry, 1961). Both conformations are about equally favourable as far as steric effects between ring and side-chain are concerned.



Fig. 10. Intramolecular distances involving the methyl groups.

As in trans  $\beta$ -ionylidene  $\gamma$ -crotonic acid the double C-O bond is not in line with the zigzag of the sidechain. The reason for this is obvious from Figs. 6 and 10. A planar configuration with the carboxyl group 180° rotated about the C17-C19 bond would be virtually impossible because the smaller C-C-O angle would bring the O too near to C17 and C19. Even in the configuration as found in vitamin-A acid the carboxyl group is twisted away from the methyl group C18. For the best plane through the atoms C16-C20 one finds:

### $7 \cdot 484x + 0 \cdot 721y + 3 \cdot 614z = 3 \cdot 975$ .

The distances of  $O_1$  and  $O_2$  from this plane are -0.20and 0.18 Å respectively, which amounts to a twist of about 10°. The accuracy of the thermal parameters in Table 1 is low. Therefore not too much importance is to be attached to the individual values. In Table 5 the direction of the axes of the vibration ellipsoid and the corresponding mean square displacements are given as calculated from the average  $B_{ij}$ 's of the sidechain atoms C9-C20. The largest vibration is in a

Table 5. Direction cosines of the axes of the average vibration ellipsoid of the side-chain atoms C<sub>9</sub>-C<sub>20</sub> relative to a-, b- and c-axis respectively and the corresponding mean square displacements

$\overline{u}^2$ (Å <sup>2</sup> )	$\cos \alpha$	$\coseta$	$\cos \gamma$
0.129	0.901	-0.042	0.606
0.042	-0.189	+0.945	+0.767
0.067	0.392	0.325	-0.214

direction nearly perpendicular to the plane of the side-chain; the smallest is roughly parallel to it. This is in agreement with the first difference synthesis.

Our thanks are due to Dr D. A. van Dorp who suggested the investigation and provided the first samples.

Later, through the courtesy of Dr P. H. van Leeuwen of Philips-Duphar, Weesp, The Netherlands, larger amounts of very pure vitamin-A acid were obtained.

The three-dimensional least-squares calculations were done on the Leeds University Pegasus computer. We are very indebted to Dr D. W. J. Cruickshank who made this possible and who took a personal interest in the work. Further we have to thank Dr J. C. Schoone who was kind enough to calculate a three-dimensional difference synthesis on the Zebra computer of the University of Utrecht.

One of us (C. H. S.) has to acknowledge the tenure of a Ramsay Memorial Fellowship; he is very grateful to Prof. E. G. Cox in whose laboratory he spent the two years of this Fellowship.

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## **Short Communications**

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1963). 16, 68

## **Tabulation of interplanar spacings of cementite Fe<sub>3</sub>C.** By K. W. ANDREWS, The United Steel Companies Limited, Research & Development Department, Swinden Laboratories, Moorgate, Rotherham, Yorkshire, England

(Received 12 June 1962)

A table of interplanar spacings for cementite, Fe<sub>3</sub>C, has been prepared and is available on request from this laboratory. A copy has also been deposited in the editorial files of *Acta Crystallographica*. The table was required in connexion with the interpretation of electron-diffraction diagrams in which spacings could occur down to 0.5 Å (kX.), but would also be useful in connexion with identification by X-ray diffraction methods.

The unit cell is orthorhombic and the lattice parameters have been taken as

a = 4.515, b = 5.078, c = 6.728 kX.

These values are between those reported by Lipson & Petch (1940) and Hume-Rothery, Raynor & Little (1942).

The space group is Pbnm (No. 62, Pnma), so that h0l reflexions are expected if h+l is even, 0kl reflexions require k even, and h00, 0k0, 00l should also be even. The systematic absences are expected to apply to X-ray diffraction patterns, but some of these reflexions may not

be missing from electron-diffraction patterns, so it was desirable to cover all reciprocal-lattice points in the calculation. This was effected by a programme using the Pegasus 'Autocode'.

The tabulation gives 792 interplanar spacings above 0.5 kX. and the corresponding values of  $1/d^2$ . This set of data represents 5,133 reciprocal-lattice points (including 000) contained within the sphere of 2 kX.<sup>-1</sup> radius. The points immediately outside the sphere are also included, giving an additional 93 spacings (622 points). The tabulation lists the points in reciprocal lattice rows parallel to the  $c^*$  axis and in successive planes perpendicular to the  $a^*$  axis.

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