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# A preliminary report on the crystal-structure determination of 15,15'-dehydro-β-carotene.*

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This report on the structure determination of 15,15'-dehydro-β-carotene, communicates, in a preliminary stage of refinement, the first conclusive analysis of a structure of one of the extensively conjugated carotenes.†

The compound 15,15'-dehydro-β-carotene, $C_{40}H_{54}$, Fig. 1(*a*), hereafter referred to as DHC, crystallizes in thin, orange, monoclinic rhomboids, platy on (010), with edges parallel to [100] and [001].‡ By transmitted polarized light the crystals are dark orange-red if the electric vector of the incident light is approximately parallel to [$\bar{1}$01], but otherwise a pale yellow-green. At −20° C. the unit cell has the parameters:

$$a\ 8{\cdot}14_5,\quad b\ 31{\cdot}8_7,\quad c\ 8{\cdot}46_5\ \text{Å};\quad \beta\ 128°\ 18{\cdot}_8'\,.$$

From systematic absences the space group was uniquely determined to be $C^5_{2h}$–$P2_1/c$. Rough measurements of density require the unit cell to contain two molecules of DHC, which accordingly must be centrosymmetric.

Weissenberg photographs about all three axes were taken with copper, iron and chromium radiations with the crystals in air at −20° C. Oxidation of the crystals, which proceeds rapidly in air at room temperature, was negligible at the lower temperature. Complete three-dimensional data were collected, using chromium radiation for the zero layers and iron radiation for all others. The high temperature factor limits the data obtainable with copper radiation.

From the method of synthesis (Inhoffen *et al.*, 1950) the molecule was expected to have an all-*trans* chain structure with either a 'V' or an extended *trans* configuration about the three collinear central bonds. Since the molecule is centered, the 'V' form is impossible and the molecule was presumed to be completely *trans*. Early attempts were made to pack models of the half molecule into a structure which would be consistent with the observed dichroism and would account for the strong reflections in the three zero-layer photographs. These attempts, while giving the general orientation of the molecule, did not lead to a completely satisfactory structure. A sharpened three-dimensional Patterson, with the peak at the origin removed, was calculated using IBM punched-card techniques. The location of peaks in the Patterson agreed with the orientation previously determined for the molecule and indicated that the molecule is almost completely planar and that its projection on to the plane (101) would be essentially resolved and relatively undistorted. Attention therefore turned to the projection along the zone [101], which is only 2·9° from the normal to (101). A two-dimensional trial structure consistent with the Patterson was found by the use of models and of the $hk\bar{h}$ data, together with appropriate structure-factor maps. Some help was also obtained from a modification of the mapping method first used by Lonsdale (1929) on hexamethylbenzene and later by White & Robertson (1945) on coronene. Refinement of the projection was completed with two-dimensional Fouriers followed by a least-squares calculation.

At an early stage in the Fourier refinement it was found necessary to invert the cyclohexene ring from the

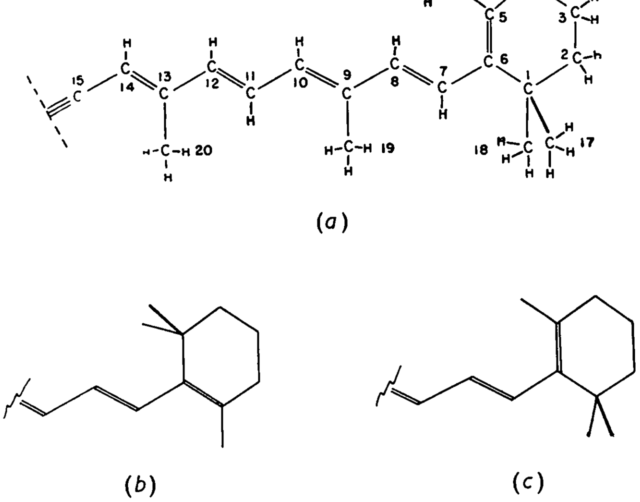

Fig. 1. (*a*) The structural formula of 15,15'-dehydro-β-carotene. The other half of the molecule is obtained by inversion through the center at the triple bond. The numbering is consistent with Table 1.

(*b*)–(*c*) The configuration of the cyclohexene ring (*b*) in *trans*-β-ionylidene crotonic acid, (*c*) in 15,15'-dehydro-β-carotene.

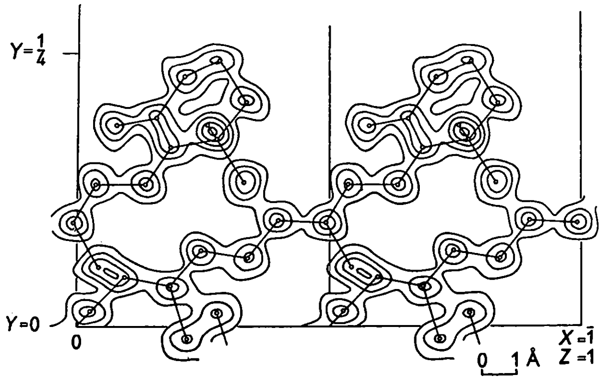

Fig. 2. Fourier projection of the structure of 15,15'-dehydro-β-carotene along [101] on to (101); contours are drawn equally spaced on an arbitrary scale.

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* Contribution No. 1951 from the Gates and Crellin Laboratories.

† An X-ray investigation of β-carotene was carried out by Taylor (1937). However, despite considerable effort, sparsity of data prevented a detailed structure determination. Recently MacGillavry, Kreuger & Eichhorn (1951) have reported the structure of a compound related to part of one end of the β-carotene molecule, *trans*-β-ionylidene crotonic acid.

‡ I am indebted to Prof. H. Inhoffen, through the courtesy of Prof. L. Zechmeister, for the crystals used in this work.

Table 1. *Coordinates of the carbon atoms of* 15,15′-*dehydro-β-carotene*

| Atom number | $y$ | $r = z - x$ | $x$ | $z$ |
|---|---|---|---|---|
| 1 | $0\cdot172_4$ | $0\cdot554_9$ | $-0\cdot703$ | $0\cdot852$ |
| 2 | $0\cdot206_3$ | $0\cdot670_4$ | $-0\cdot673$ | $0\cdot997$ |
| 3 | $0\cdot243_7$ | $0\cdot565_1$ | $-0\cdot558$ | $0\cdot007$ |
| 4 | $0\cdot229_4$ | $0\cdot425_1$ | $-0\cdot340$ | $0\cdot085$ |
| 5 | $0\cdot191_0$ | $0\cdot312_9$ | $-0\cdot340$ | $0\cdot973$ |
| 6 | $0\cdot165_2$ | $0\cdot371_9$ | $-0\cdot513$ | $0\cdot859$ |
| 7 | $0\cdot130_1$ | $0\cdot271_2$ | $-0\cdot528$ | $0\cdot743$ |
| 8 | $0\cdot130_2$ | $0\cdot075_8$ | $-0\cdot438$ | $0\cdot638$ |
| 9 | $0\cdot095_6$ | $0\cdot986_6$ | $-0\cdot440$ | $0\cdot547$ |
| 10 | $0\cdot097_9$ | $0\cdot797_1$ | $-0\cdot338$ | $0\cdot459$ |
| 11 | $0\cdot062_5$ | $0\cdot677_7$ | $-0\cdot312$ | $0\cdot366$ |
| 12 | $0\cdot069_2$ | $0\cdot495_1$ | $-0\cdot205$ | $0\cdot290$ |
| 13 | $0\cdot036_1$ | $0\cdot373_5$ | $-0\cdot172$ | $0\cdot202$ |
| 14 | $0\cdot044_6$ | $0\cdot193_2$ | $-0\cdot068$ | $0\cdot125$ |
| 15 | $0\cdot013_9$ | $0\cdot054_4$ | $-0\cdot015$ | $0\cdot039$ |
| 16 | $0\cdot184_3$ | $0\cdot155_6$ | $-0\cdot122$ | $0\cdot034$ |
| 17 | $0\cdot185_0$ | $0\cdot516_8$ | $-0\cdot883$ | $0\cdot634$ |
| 18 | $0\cdot132_2$ | $0\cdot662_8$ | $-0\cdot780$ | $0\cdot883$ |
| 19 | $0\cdot054_5$ | $0\cdot089_1$ | $-0\cdot548$ | $0\cdot541$ |
| 20 | $-0\cdot012_9$ | $0\cdot439_9$ | $-0\cdot237$ | $0\cdot203$ |

*trans* configuration of Fig. 1(*b*) to the *cis* form of Fig. 1(*c*). (The *trans* configuration of Fig. 1(*b*) is reported to occur in *trans-β*-ionylidene crotonic acid (MacGillavry *et al.*, 1951).) The last Fourier projection is shown in Fig. 2, with a superimposed projection of the molecule drawn from the parameters determined by the least-squares refinement. The atomic coordinates $y$ and $r$, where $r = z - x$, are listed in Table 1, along with preliminary $x$ and $z$ coordinates determined from models and from measurements in the three-dimensional Patterson.

Three-dimensional Fourier and least-squares refinements are in progress. A more precise description of the structure and the details of its solution and refinement will be reported later.

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## References

Inhoffen, H. H., Bohlmann, F., Bartram, K., Rummert, G. & Pommer, H. (1950). *Liebigs Ann.* **570**, 54.
Lonsdale, K. (1929). *Proc. Roy. Soc.* A, **123**, 494.
MacGillavry, C. H., Kreuger, A. & Eichhorn, E. L. (1951). *Proc. K. Ned. Akad. Wet.* B, **54**, No. 5.
Taylor, W. H. (1937). *Z. Kristallogr.* **96**, 150.
White, J. G. & Robertson, J. M. (1945). *J. Chem. Soc.* p. 607.

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## The unit cell, powder pattern, and space group of phenyl carbonate.

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About a year ago, structure investigations of certain organic carbonates were begun in this Laboratory. The study of ethylene carbonate had proceeded to the point of verification of parameters, when its complete structure was reported (Brown, 1954). Cell dimensions obtained in this Laboratory were

$$a = 8\cdot95,\ b = 6\cdot285,\ c = 7\cdot04\ \text{Å},\ \beta = 99°\ 43',$$

in excellent agreement with the reported values. The space group was verified as $C2/c$, and predicted parameters were close enough to those of Brown that the study was not continued.

A preliminary X-ray survey of phenyl carbonate, $(C_6H_5)_2CO_3$, has determined the unit cell and space group from precession photographs of two specimens of its orthorhombic, lath-shaped crystals.

$$a = 7\cdot52,\ b = 6\cdot09,\ c = 23\cdot47\ \text{Å}\,.$$

These data lead to a calculated density of 1·323 g.cm.$^{-3}$ for 4 molecules in the unit cell, to be compared with the reported specific gravity of 1·272. The only absent types of reflections are the odd orders of the three pinacoids. Accordingly, the space group is uniquely determined as $P2_12_12_1$. Atomic positions (exclusive of the hydrogen atoms) for the four molecules in the cell are thus fixed by 48 parameters.

The powder pattern of phenyl carbonate was recorded with nickel-filtered copper radiation in a Debye–Scherrer camera of 57·3 mm. radius. After measuring the $d$ spacings with the appropriate Nies scale, line intensities were obtained by comparing microphotometer traces of the powder pattern and a graded intensity scale. These data are presented in Table 1.

Table 1. *Principal lines of the powder pattern of phenyl carbonate*

| $d$ | $I/I_0$ | $d$ | $I/I_0$ |
|---|---|---|---|
| 11·5 | < 5 | 2·82 | 20 |
| 7·2 | 25 | 2·72 | 15 |
| 6·3 | 50 | 2·48 | 10 |
| 5·8 | 65 | 2·40 | 5 |
| 5·3 | 15 | 2·32 | 15 |
| 4·7 | 95 | 2·17 | 10 |
| 4·35 | 90 | 2·10 | 10 |
| 4·00 | 80 | 2·00 | 10 |
| 3·70 | 50 | 1·91 | 10 |
| 3·55 | 100 | 1·88 | 15 |
| 3·35 | 30 | 1·81 | 5 |
| 3·18 | 70 | 1·77 | 5 |
| 3·05 | 15 | 1·74 | 5 |
| 2·92 | 5 | | |

Because of the non-centrosymmetric space group observed, the effort necessary for a complete structure determination did not seem warranted at this time.

## Reference

Brown, C. J. (1954). *Acta Cryst.* **7**, 92.