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The Crystalline Structure of 7,7′-Dihydro-β-carotene

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Synthetically prepared 7,7′-dihydro-β-carotene has been the object of a structure determination by X-ray diffraction methods. The crystals are monoclinic ($P2_1/c$), and the cell dimensions are $a = 20{\cdot}7$, $b = 6{\cdot}04$, $c = 14{\cdot}8$ Å, and $\beta = 108{\cdot}8°$. There are two molecules per unit cell. The final atomic parameters give a discrepancy index, R, of 0·17. Isotropic temperature factors of individual carbon atoms are greatest in the ionone ring and smallest in the polyene chain. Towards the center of the chain, the single-bond lengths are shorter and double-bond lengths greater than towards the ends of the chain. The chain is curved in several directions, and the plane of the ring is at a fairly large angle to any of several arbitrary chain planes.

Introduction

Although the range of biological potentialities of the carotenoids and their derivatives probably is still far from being fully assessed, the stoichiometric relationship of (all-*trans*) β-carotene to vitamin A is now well-known, and the role of vitamin A in animal nutrition and in the formation of photosensitive pigments in the retina has been well elucidated (Moore, 1957; Ames, 1958; Hubbard & Wald, 1952; Wald, 1953; Wald, Brown & Smith, 1955). Other functions have been ascribed to the carotenoid pigments, related similarly to their photochemical properties.

Despite the demonstrably vital significance of the carotenoid compunds, knowledge of their detailed structure is not clear. For the most part, assignments of structure of different isomers have been based on empirical spectral analysis (Pauling, 1939; Zechmeister, 1944; Zechmeister, LeRosen, Schroeder, Polgár & Pauling, 1943). In some cases, there have been uncertainties and even discrepancies in such evaluations. Taylor (1937) described the unit cell, space group, and other crystallographic aspects of (all-*trans*) β-carotene. However, his study of the X-ray intensities of the interplanar spacings was not able to yield the molecular structure. Sly (1955) made a preliminary two-dimensional evaluation of a carotenoid derivative, 15,15′-dehydro-β-carotene. After earlier two-dimensional work (MacGillavry, Kreuger & Eichhorn, 1951), Eichhorn & MacGillavry (1959) reported a three-dimensional analysis of the structure of *trans*-β-ionylidene crotonic acid (C_{17}), a compound with a close structural relationship to half a carotene molecule. Most recently, Stam & MacGillavry (1963) have described the triclinic modification of vitamin-A acid.

The present study describes the structure of the carotenoid derivative, 7,7′-dihydro-β-carotene (Fig. 1(*a*)). In comparison with (all-*trans*) β-carotene (Fig. 1(*b*)), the bond system is shifted. Because the carbon atom at the 7-position has only single bonds to its neighbors in the chain, the conjugated double-bond sequence is interrupted at that point.

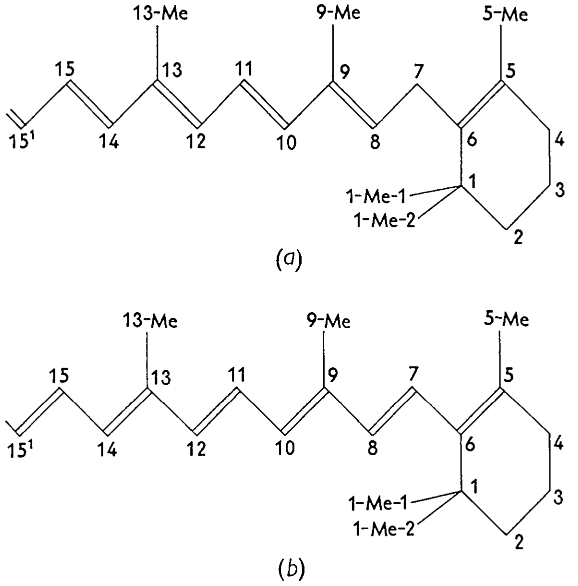

Fig. 1. (*a*) Diagram of the structure of a half-molecule of 7,7′-dihydro-β-carotene, with numbering of the carbon atoms used here. (*b*) Diagram of the structure of a half-molecule of β-carotene, with numbering of the carbon atoms as in (*a*).

Materials and methods

Crystals of 7,7′-dihydro-β-carotene, $C_{40}H_{58}$, prepared in the laboratories of Hoffmann–La Roche Inc., were supplied through the kindness of Dr T. O. M. Nakayama and Dr M. Montavan. Their density was determined by flotation in sucrose solutions of varying concentration. X-ray diffraction data were obtained at room temperature with Cu $K\alpha$ radiation, and intensities were recorded by the multi-film technique. Equi-inclination Weissenberg photographs were taken at nine levels about the *c* axis. Precession about the *b* axis recorded missing $h0l$ reflections. Cell dimensions were estimated from zero-level photographs. A total of 842 non-zero intensities were read independently by two individuals, whose scores were averaged. (The mass-absorption coefficient for the crystal was estimated as 3·2 g^{-1} for Cu $K\alpha$ radiation, and no absorption correction was made.)

For most of the calculations, an IBM 704 computer was used. The programs for the computations were as follows:

1. Reduction of the raw intensities to arbitrary F^2 and F values, together with determination of $(\sin\theta)/\lambda$ values for each reflection; INCOR program of A. Zalkin, Lawrence Radiation Laboratory, Berkeley, Calif.
2. Patterson synthesis and Fourier synthesis: FOURSUM/FOURPRINT programs of A. Zalkin.
3. Structure-factor and least-squares calculations: ORXLS program of W. R. Busing & H. A. Levy 1959*a*).
4. Interatomic distances and angles: ORXFE program of W. R. Busing & H. A. Levy (1959*b*).

Results

The crystals are tabular in the (100) plane, monoclinic, and of rhomboid shape. The long diameter of the rhombus is [001] and the short diameter is [010]. The crystal color is bright orange. Dichroism occurs when light passes through the (100) face, and the crystals are dark red to orange when (010) coincides with the plane of vibration of the electric vector of the polarizer and light yellow to green when (010) is perpendicular to that plane. After 90° rotation of the crystal about [001], the plane of dichroism is about 30° from (100). Since it is expected that the molecule is predominantly linear, this latter direction of dichroism indicates the approximate orientation of the polyene backbone of the molecule.

An approximate specific gravity of 1·06 was ascertained. The space group was determined unequivocally as $P2_1/c$ (systematic absences are $0k0$ when $k=2n+1$, and $h0l$ when $l=2n+1$). The unit-cell dimensions are

$$a=20{\cdot}7\pm0{\cdot}1,\ b=6{\cdot}04\pm0{\cdot}02,$$
$$c=14{\cdot}8\pm0{\cdot}1\ \text{Å};\ \beta=108{\cdot}8^\circ\pm0{\cdot}2^\circ\ .$$

The number of molecules per unit cell was calculated as 2·08, and the value of two molecules per cell was accepted. (On this basis the calculated density is 1·02 $g.cm^{-3}$.) With the general position having multiplicity 4 in this space group, it is apparent that each molecule possesses a center of symmetry — as was expected from the chemical evidence (Fig. 1(*a*)). Hence, if the hydrogen atoms be neglected, the work of structure determination is confined to the establishment of the parameters of the 20 carbon atoms of half a molecule.

I. Both the three-dimensional Patterson synthesis and the Patterson projection on (010) established that the major portion of the molecule (the polyene chain) is essentially planar and that the molecular plane lies nearly in the (201) plane. Although 201 was missing because of space group extinction, 402 was by far the most intense reflection observed. It also appeared that the molecule is either in the (010) plane or but slightly tilted from it. Individual peaks are relatively small and irregular spaced. However, from the above two distributions and from the Harker section at $y=\frac{1}{2}$, it was possible to average certain scattered inter-peak distances and arrive at a 2-carbon interatomic distance of about 2·48 Å, which is approximately that to be expected. No single C–C interatomic distance was obtainable. Atomic parameters for the 11 carbon atoms of the chain were postulated, and then the ring atoms were placed in several possible configurations for structure factor evaluations of the (010) projection of the molecule. The signs of the calculated structure factors and the observed F values of the $h0l$ reflections were then used in an electron-density projection by Fourier synthesis. (For the structure-factor calculations, the temperature factor was estimated by the method of Wilson (1942) and atomic scattering factors for C were taken from *International Tables for X-ray Crystallography* (1962)).

Regardless of the postulated placements of the carbon atoms of the ring, *vis-à-vis* those of the chain, the electron-density projection always gave the chain and the ring in one particular relationship: the ring placed to one side of the chain axis. With the x, z positions of the chain atoms held constant, trials of several ring structures in the indicated position gave structure-factor signs which were used with the observed F values in electron-density projections. Certain atomic positions recurred. Since these positions seemed to outline a reasonable ring, they were used as the basis for a new set of ring atomic positions. Evaluation of the structure factors yielded a discrepancy index R,* of 0·33. The eleven atoms of the chain were held fixed, and the least-squares program was allowed to vary the overall temperature factor, the scale factor, and the x and z parameters of the nine ring atoms†. The refinement of the projected atomic position proceeded until R reached 0·16. At this point, no further refinement was possible with the $h0l$ data alone. It is to be noted that several of the interatomic distances were obviously incorrect; and use of the signs of the calculated structure factors with the magnitudes of the observed values did not reproduce the nine atoms of the ring: only four peaks

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* R is weighted by assigning all structure factors an equal weight in the equation, $R=\surd[\Sigma w(F_o-F_c)^2]/\surd[\Sigma wF_o^2]$.

† The full-matrix program of Busing & Levy (1959*a*) was used directly, the function minimized being $\surd[\Sigma(\surd w|F_o-F_c|^2)]$, with each reflection assigned unit weight.

occurred in the region of the ring, and three of these did not agree with any of the final atomic positions from the least-squares computation.

II. A similar approach was attempted for the (001) projection. However, no useful information was available from the Harker line at 0, y, $\frac{1}{2}$. Because relatively few reflections of the type $hk0$ existed, use of the straight chain and skewed ring to postulate structure-factor signs for an electron-density projection gave a rather featureless density distribution. Only the general area of the ring and the methyl groups at positions 13 and 9 were coarsely indicated. The chain of the molecule was not delimited at all. Various trial-and-error attempts at projected structures gave no pertinent arrangement of atoms which could be refined.

III. Consequently, all the data were used in an attempt to determine the three-dimensional structure directly. Because of the very low R values from the (010) projection, it was assumed the major part of the structure, and particularly the chain, was already correct. After several postulated structures which gave R values above 0·50, one structure was obtained for which R, without zero intensities, was 0·36. This last structure was refined by the least-squares program, in which the overall temperature factor, overall scale factor, and three atomic dimensional parameters for the 20 carbon atoms were allowed to vary. Several successive cycles led to an ultimate R value of 0·24. The structure at this point showed what appeared to be a bent chain, as projected on (001), together with a ring of improbable shape in the same projection. Six of the interatomic distances were too great to be accepted as valid. Although, as the R value indicated and as subsequent work showed, there were elements of correctness in this structure, it was impossible to proceed realistically on a trial-and-error basis.

IV. The success of the earlier work in projection on (010) gave rise to the idea that the chain (which has 11 carbon atoms) might be regarded conceptually as a 'heavy atom'. Hence if the chain were in a reasonably correct position, it could give the signs of at least half the structure factors. Consequently, a new three-dimensional Patterson synthesis was made, minus the origin peak but with the other peaks sharpened. In this synthesis, the approximate single-bond vector between a pair of carbon atoms was clearly indicated, and it was obvious that the molecule was tilted out of the (010) plane. The 2-carbon vector was also delineated, but its exact terminus was not certain because of its closeness to the mirror plane of (010).

The 11 carbon atoms of the chain were placed according to the chain's newly indicated position, and structure factors for 344 of the most intense reflections were calculated. The signs of the most trustworthy values were used in a three-dimensional Fourier synthesis to establish the positions of some of the ring carbon atoms. Those which appeared to be too far wrong were not used; those which agreed more or less with the original projected atomic positions on (010) determined in section I, and with an atomic model, were used in a new structure-factor determination. By continuing cycles of this sort, four acceptable ring carbon atoms were obtained. The remainder of the carbon atoms were placed in approximately reasonable positions, according to the model and the parameters of section I.

In the postulated structure, R was 0·39. The structure was subjected to a least-squares variation of the overall scale and temperature factors and the atomic positional parameters. After six cycles, R had attained a value of 0·18, with the 344 reflections. At this juncture, little shifting of the atoms was occurring, and some very small discrepancies in interatomic distances were apparent. Nevertheless, the structure of the ring looked correct, and the chain — although somewhat arched in (001) projection — was continuously smooth.

Next, the full set of 842 non-zero intensities were used in a least-squares program, in which nine scale factors (corresponding to nine sets of Weissenberg films), three positional parameters, and an isotropic temperature factor of the form, $\exp(-B\lambda^{-2}\sin^2\theta)$, for each carbon atom were varied. (The positions of the hydrogen atoms were not postulated in the least-squares refinement.) Although the initial R value was 0·23, in five cycles it had reached 0·17, at which point no significant atomic parameter changes were occurring. (For x, y, z, and β, final average and final maximum shift in parameter values: 0·0001, 0·0005, 0·0001, 0·091; 0·0004, 0·001, 0·0003, 0·196.) Final calculated structure factors are presented in Table 1. It may be seen that the calculated values for 299 unobserved intensities are negligible on the whole. However, because of the uncertainty of these intensities, they were omitted from the least-squares computation. The essential correctness of the structure was verified with a three-dimensional Fourier synthesis, based on the signs of the calculated structure factors and the magnitudes of the observed structure factors. Although the shape of the atoms was not quite spherical, the interatomic regions were completely featureless.

The final parameters for the carbon atoms are given in Table 2. It may be noted that the atoms of the chain have approximately the same temperature factor. However, the atoms of the ring — which presumably are freer to experience thermal motion — have significantly higher temperature factors. The lowest temperature factor in the ring is that of C(6), which is connected directly to the chain atom C(7), and the next lowest ones are those of C(5) and C(1), which are linked to C(6).

Interatomic distances and angles are presented in Tables 3 and 4 respectively. The standard deviations listed are those estimated by the method of least squares, under the assumption that the discrepancies represent random errors. It is apparent that towards

Table 1. *Observed* (FOB) *and calculated* (FCA) *structure factors for* 7,7′-*dihydro-β-carotene*

K,L= 0, 0		
H	FOB	FCA
2	34	-28
3	67	56
4	43	-46
5	41	37
6	25	-19
7	28	-27
8	15	-15
9	11	5
10	12	-7
11	5	4
12	0	4
13	0	-4
14	0	1
15	12	15
16	0	2
17	7	-10
18	5	5
K,L= 1, 0		
H	FOB	FCA
1	33	-45
2	114	-116
3	4	1
4	33	-22
5	18	10
6	24	-28
7	0	-0
8	0	7
9	6	-0
10	11	10
11	12	-9
12	5	3
13	6	6
14	4	3
15	4	-5
16	0	-4
17	5	-4
18	2	-2
K,L= 2, 0		
H	FOB	FCA
0	28	26
1	22	19
2	4	6
3	30	36
4	9	-9
5	12	11
6	25	28
7	29	-31
8	0	-4
9	5	8
10	0	-0
11	7	-7
12	6	4
13	2	4
14	7	-6
15	5	-5
16	6	-6
K,L= 3, 0		
H	FOB	FCA
1	24	-30
2	17	-14
3	5	-7
4	5	-5
5	21	-18
6	7	-11
7	0	1
8	2	-2
9	0	-3
10	2	4
11	0	3
12	0	-3
13	0	-4
14	7	-7
K,L= 4, 0		
H	FOB	FCA
0	5	-2
1	3	-4
2	0	-4
3	0	1
4	0	0
5	4	3
6	3	2
7	0	-3
8	0	-1
9	0	1
10	0	-0
11	0	-4
12	2	-6
13	3	-6
K,L= 5, 0		
H	FOB	FCA
1	0	-4
2	0	-4
3	0	-2
4	0	2
5	0	1
6	5	-4
7	4	-6
8	0	4
9	0	1
10	5	-6
K,L= 1, 1		
H	FOB	FCA
0	41	-47
1	73	70
2	63	-62
3	24	18
4	21	22
5	31	24
6	4	-1
7	3	-3
8	13	14
9	0	4
10	9	9
11	11	13
12	10	-13
13	0	-3
14	10	10
15	5	-5
16	0	-1
17	0	-3
18	6	-8
K,L= 2, 1		
H	FOB	FCA
0	31	42
1	39	45
2	10	-7
3	25	-26
4	26	-35
5	3	2
6	0	0
7	20	-17
8	10	11
9	0	2
10	11	-10
K,L= 3, 1		
H	FOB	FCA
0	7	2
1	7	-3
2	23	-21
3	20	-15
4	24	23
5	6	4
6	4	1
7	6	5
8	0	0
9	4	1
10	0	4
11	0	3
12	6	-6
K,L= 4, 1		
H	FOB	FCA
0	9	-7
1	9	-7
2	4	4
3	6	2
4	7	7
5	0	-1
6	4	-4
7	0	5
8	0	-0
9	0	1
10	0	-1
11	6	-8
12	0	-4
13	0	1
14	0	-1
15	4	-6
16	4	-7
K,L= 1, 1		
H	FOB	FCA
-1	25	24
-2	44	53
-3	59	-64
-4	41	47
-5	23	27
-6	4	-13
-7	44	44
-8	17	-17
-9	23	-19
-10	26	21
-11	0	-1
-12	8	-9
-13	11	-9
-14	9	-11
-15	0	-3
-16	0	6
-17	0	6
-18	0	-2
-19	4	1
K,L= 2, 1		
H	FOB	FCA
-1	0	3
-2	4	-4
-3	3	4
-4	7	2
-5	7	-12
-6	0	4
-7	20	21
-8	3	3
-9	0	-4
-10	15	13
-11	0	9
-12	5	5
-13	3	11
K,L= 3, 1		
H	FOB	FCA
-1	27	28
-2	6	1
-3	3	-5
-4	13	10
-5	0	-1
-6	0	2
-7	8	6
-8	8	-7
-9	4	-8
-10	0	-2
-11	0	2
-12	9	-5
-13	11	-13
K,L= 4, 1		
H	FOB	FCA
-1	9	3
-2	0	1
-3	0	-2
-4	0	-2
-5	0	-0
-6	0	2
-7	9	8
-8	9	11
-9	0	1
-10	0	-1
-11	10	11
-12	11	12
-13	0	4
-14	6	-6
-15	6	-8
K,L= 5, 1		
H	FOB	FCA
-1	0	-0
-2	0	0
-3	0	-4
-4	0	-3
-5	4	-5
-6	5	-6
-7	0	-4
-8	0	-2
-9	0	-3
-10	0	-5
-11	0	-4
-12	0	1
-13	6	5
-14	5	4
K,L= 0, 2		
H	FOB	FCA
0	63	68
1	84	-75
2	2	-2
3	106	105
4	247	210
5	64	53
6	16	-3
7	5	11
8	6	-9
9	13	17
10	6	-9
11	13	-20
12	9	3
13	3	2
14	19	-7
15	8	7
16	0	-2
17	0	-4
18	5	6
K,L= 1, 2		
H	FOB	FCA
0	21	-18
1	39	43
2	69	72
3	65	67
4	20	-16
5	47	-46
6	27	-31
7	9	-8
8	25	-19
9	5	1
10	6	-5
11	0	-2
12	0	-1
13	4	3
14	0	4
15	4	-6
K,L= 2, 2		
H	FOB	FCA
0	7	10
1	0	4
2	8	14
3	33	30
4	11	9
5	6	7
6	12	12
7	13	13
8	9	-2
9	7	9
10	5	6
11	3	-11
12	7	4
K,L= 3, 2		
H	FOB	FCA
0	12	10
1	9	10
2	12	9
3	21	22
4	9	2
5	20	-22
6	3	-10
7	0	-3
8	3	-5
9	11	-10
K,L= 4, 2		
H	FOB	FCA
0	0	2
1	0	-3
2	0	1
3	7	-4
4	10	-7
K,L= 0, 2		
H	FOB	FCA
-1	22	-15
-2	38	-40
-3	50	45
-4	105	-94
-5	2	9
-6	11	14
-7	7	2
-8	9	-4
-9	7	4
-10	0	3
-11	22	24
-12	13	14
-13	19	-19
-14	7	6
K,L= 1, 2		
H	FOB	FCA
-1	28	-31
-2	83	79
-3	47	-44
-4	6	-1
-5	5	7
-6	15	-17
-7	11	11
-8	16	-18
-9	5	9
-10	17	-15
-11	6	5
-12	16	14
-13	11	9
-14	8	7
K,L= 2, 2		
H	FOB	FCA
-1	34	34
-2	9	-6
-3	18	-14
-4	15	-10
-5	6	-7
-6	23	26
-7	29	-28
-8	6	5
-9	14	14
-10	20	-16
-11	15	-10
-12	13	-11
K,L= 3, 2		
H	FOB	FCA
-1	10	9
-2	19	15
-3	8	9
-4	6	-4
-5	5	3
-6	6	-6
-7	0	-4
-8	6	3
-9	0	5
-10	9	9
-11	7	10
-12	0	1
-13	7	-8
K,L= 4, 2		
H	FOB	FCA
-1	0	1
-2	0	1
-3	0	3
-4	0	-5
-5	0	-3
-6	0	3
-7	0	-5
-8	13	-11
-9	6	-10
K,L= 5, 2		
H	FOB	FCA
-1	0	-3
-2	5	3
-3	9	9
-4	0	-5
-5	0	-2
-6	8	7
K,L= 1, 3		
H	FOB	FCA
0	28	25
1	18	-11
2	13	15
3	8	0
4	13	-17
5	59	53
6	29	31
7	17	8
8	26	23
9	2	4
10	0	1
11	8	6
12	0	-4
13	4	7
K,L= 2, 3		
H	FOB	FCA
0	6	-5
1	0	0
2	12	-12
3	7	9
4	24	27
5	26	23
6	0	-2
7	17	-16
8	8	-10
9	0	-0
10	6	-7
11	4	-4
12	5	5
K,L= 3, 3		
H	FOB	FCA
0	4	-5
1	7	9
2	0	-5
3	20	13
4	14	15
5	17	-16
6	9	-10
7	0	-1
8	0	6
9	7	1
10	4	4
K,L= 4, 3		
H	FOB	FCA
0	0	-5
1	0	-3
2	4	6
K,L= 1, 3		
H	FOB	FCA
-1	2	-5
-2	39	47
-3	21	14
-4	23	-17
-5	11	13
-6	5	-12
-7	12	19
-8	5	-7
-9	43	-33
-10	14	-13
-11	6	-5
-12	6	7
-13	19	14
-14	0	-1
-15	0	-1
-16	6	6
K,L= 2, 3		
H	FOB	FCA
-1	0	3
-2	8	-8
-3	9	10
-4	30	34
-5	22	-28
-6	13	24
-7	24	21
-8	0	-3
-9	20	22
-10	0	2
-11	9	-8
K,L= 3, 3		
H	FOB	FCA
-1	4	4
-2	10	6
-3	0	0
-4	7	-6
-5	8	-9
-6	8	-7
-7	0	-3
-8	0	0
-9	18	-21
-10	13	-13
-11	5	4
-12	6	9
K,L= 4, 3		
H	FOB	FCA
-1	0	4
-2	0	-1
-3	10	8
-4	12	14
-5	4	6
-6	0	-1
-7	11	13
-8	15	16
-9	6	7
-10	8	-8
-11	15	-16
K,L= 5, 3		
H	FOB	FCA
-1	6	-8
-2	0	-2
-3	6	-8
-4	0	-5
-5	0	-1
-6	6	-8
-7	5	-4
-8	0	2
-9	7	7
-10	7	7
K,L= 0, 4		
H	FOB	FCA
0	57	-59
1	10	3
2	4	-5
3	27	21
4	27	3
5	45	-48
6	24	18
7	44	49
8	54	61
9	30	29
10	9	-0
11	0	2
12	3	3
K,L= 1, 4		
H	FOB	FCA
0	16	-14
1	0	-4
2	28	35
3	8	-9
4	12	-11
5	13	11
6	46	41
7	29	30
8	7	-11
9	16	-15
10	10	-2
11	4	-3
12	9	-7
K,L= 2, 4		
H	FOB	FCA
0	14	-14
1	21	-19
2	7	8
3	6	10
4	9	11
5	5	4
6	9	5
7	12	14
8	0	4
9	8	7
10	0	1
11	6	3
12	6	6
K,L= 3, 4		
H	FOB	FCA
0	0	1
1	11	11
2	12	11
3	6	2
4	4	4
5	11	9
6	5	6
7	10	10
8	0	-0
9	9	-10
K,L= 4, 4		
H	FOB	FCA
0	4	-7
1	0	-4
2	9	9
3	0	-3
4	0	-4
5	6	4
6	0	0
7	6	-5
K,L= 5, 4		
H	FOB	FCA
0	0	1
1	3	5
K,L= 0, 4		
H	FOB	FCA
-1	17	-15
-2	29	24
-3	6	6
-4	11	-13
-5	2	1
-6	7	8
-7	50	47
-8	0	5
-9	7	-9
-10	12	12
-11	4	-7
-12	12	13
-13	7	-5
-14	5	-7
-15	0	-1
-16	8	-8
-17	4	2
K,L= 1, 4		
H	FOB	FCA
-1	6	2
-2	14	9
-3	28	-27
-4	7	-6
-5	23	24
-6	27	-29
-7	9	-3
-8	32	26
-9	32	27
-10	6	3
-11	5	2
-12	7	6
-13	5	7
-14	4	5
K,L= 2, 4		
H	FOB	FCA
-1	16	18
-2	17	-10
-3	4	-11
-4	14	20
-5	20	-19
-6	0	-3
-7	16	-13
-8	28	-25
-9	6	9
-10	10	7
-11	10	11
-12	11	10
K,L= 3, 4		
H	FOB	FCA
-1	3	-10
-2	9	-1
-3	7	6
-4	7	-3
-5	10	11
-6	7	12
-7	6	7
-8	5	7
-9	16	-18
-10	9	-5
-11	10	14
-12	[illegible]	6
-13	6	6
-14	7	7
K,L= 4, 4		
H	FOB	FCA
-1	3	4
-2	0	-5
-3	0	-3
-4	5	-7
-5	15	-17
-6	0	3
-7	5	5
-8	7	-5
-9	5	3
-10	9	-2
-11	8	-7
-12	0	1
-13	7	6
K,L= 5, 4		
H	FOB	FCA
-1	0	-3
-2	0	3
-3	7	7
K,L= 1, 5		
H	FOB	FCA
0	3	4
1	20	15
2	9	17
3	0	1
4	15	10
5	0	2
6	5	-2
7	7	-3
8	0	-0
9	13	14
10	13	14
11	7	5
12	4	6
13	7	6
K,L= 2, 5		
H	FOB	FCA
0	23	23
1	5	7
2	10	-14
3	10	9
4	5	-2
5	11	-10
6	0	-2
7	5	3
8	11	13
9	15	15
10	0	-5
11	0	-4
12	0	-1
13	5	-4
K,L= 3, 5		
H	FOB	FCA
0	4	-2
1	7	7
2	4	-5
3	5	4
4	0	1
5	0	-2
6	0	-1
7	16	16
8	0	3
K,L= 4, 5		
H	FOB	FCA
0	11	10
1	7	5
K,L= 5, 5		
H	FOB	FCA
0	4	-4
1	3	-4
2	6	-5
3	4	-5
K,L= 1, 5		
H	FOB	FCA
-1	20	-16
-2	12	12
-3	14	16
-4	23	-26
-5	8	-9
-6	39	-34
-7	17	-12
-8	32	24
-9	18	15
-10	0	2
-11	6	2
-12	0	4
-13	14	9
-14	8	8
-15	8	-6
K,L= 2, 5		
H	FOB	FCA
-1	16	-16
-2	15	18
-3	18	13
-4	20	20
-5	7	8
-6	6	5
-7	10	4
-8	18	-19
-9	12	14
-10	10	7
-11	3	1
-12	5	4
-13	0	0
-14	5	4
-15	8	6
-16	0	-1
-17	0	1
-18	6	6
K,L= 3, 5		
H	FOB	FCA
-1	14	-17
-2	0	-2
-3	5	-2
-4	11	-11
-5	3	-10
-6	14	-16
-7	10	-11
-8	25	28
-9	0	0
-10	6	-6
-11	17	14
-12	0	1
-13	0	5
-14	3	5
K,L= 4, 5		
H	FOB	FCA
-1	7	9
-2	0	1
-3	10	9
-4	14	14
-5	11	11
-6	10	-11
-7	21	-20
-8	9	-5
-9	4	2
-10	6	7
-11	0	-2
-12	0	1
-13	7	5
-14	9	4
-15	5	5
K,L= 5, 5		
H	FOB	FCA
-1	6	-6
-2	0	-2
-3	5	-4
-4	0	-3
-5	14	12
-6	9	6
-7	0	-0
-8	0	-3
-9	9	-7
K,L= 0, 6		
H	FOB	FCA
0	8	-6
1	9	1
2	16	9
3	3	2
4	29	-31
5	7	-8
6	15	17
7	0	5
8	11	-4
9	14	-16
10	1	-2
11	17	26
12	14	18
13	6	7
14	5	4
K,L= 1, 6		
H	FOB	FCA
0	17	-15
1	0	-8
2	0	3
3	12	-10
4	8	4
5	2	2
6	2	6
7	3	-1
8	4	-7
9	7	6
10	13	15
11	11	10
12	0	-3
13	5	-7
K,L= 2, 6		
H	FOB	FCA
0	0	3
1	5	-7
2	5	4
3	3	2
4	5	-11
5	0	-1
6	0	4
7	0	-1
8	5	7
9	6	5
10	0	-2
11	5	6
12	4	5
K,L= 3, 6		
H	FOB	FCA
0	5	-5
1	6	6
2	4	4
3	8	-11
4	0	1
5	9	9
6	3	4
7	0	2
8	0	0
9	4	4
10	5	5
K,L= 4, 6		
H	FOB	FCA
0	5	-3
1	5	-6
2	3	3
3	8	1
4	5	-7
5	0	-2
6	5	6
7	5	-5
K,L= 5, 6		
H	FOB	FCA
0	5	3
1	3	5
K,L= 0, 6		
H	FOB	FCA
-1	10	7
-2	5	10
-3	13	16
-4	27	32
-5	3	-3
-6	2	-4
-7	19	12
-8	3	2
-9	8	7
-10	8	-6
-11	11	-18
-12	0	2
-13	0	0
-14	0	0
-15	9	5
-16	6	-6
-17	0	-2
-18	12	8
-19	11	9
K,L= 1, 6		
H	FOB	FCA
-1	18	26
-2	15	-21
-3	18	-18
-4	35	41
-5	20	21
-6	9	5
-7	3	4
-8	9	6
-9	12	14
-10	0	-1
-11	0	-1
-12	0	3
-13	0	-3
-14	0	-2
-15	0	-0
-16	0	3
-17	5	-4
-18	7	-7
-19	7	6
-20	9	8
K,L= 2, 6		
H	FOB	FCA
-1	0	-3
-2	18	-18
-3	4	-6
-4	6	-6
-5	18	-16
-6	23	19
-7	25	30
-8	0	-2
-9	4	5
-10	8	5
-11	7	-6
-12	5	4
-13	0	0
-14	6	-3
-15	8	5
-16	0	-0
-17	4	-4
K,L= 3, 6		
H	FOB	FCA
-1	7	10
-2	7	9
-3	3	5
-4	0	2
-5	8	-16
-6	7	-4
-7	9	12
-8	11	11
-9	9	12
-10	9	9
K,L= 4, 6		
H	FOB	FCA
-1	4	-7
-2	5	-4
-3	0	2
-4	5	4
-5	4	-5
-6	3	-3
-7	0	-1
-8	8	-6
-9	12	10
-10	10	9
-11	4	-4
-12	7	5
-13	6	5
K,L= 5, 6		
H	FOB	FCA
-1	0	-2
-2	4	-2
-3	0	0
-4	0	-0
-5	0	-2
-6	0	-2
-7	0	-1
-8	0	-0
-9	0	1
-10	0	2
-11	5	3
K,L= 1, 7		
H	FOB	FCA
0	7	-10
1	11	14
2	2	0
3	6	-8
4	6	10
5	3	3
6	0	4
7	4	6
8	0	1
9	0	1
10	0	1
11	5	-5
12	0	1
13	4	6
K,L= 2, 7		
H	FOB	FCA
0	18	21
1	4	7
2	3	5
3	3	-0
4	7	9
5	3	-1
6	0	-3
7	4	4
8	4	-2
9	4	-4
10	0	-2
11	3	2
12	4	6
13	4	4
K,L= 3, 7		
H	FOB	FCA
0	7	-6
1	2	0
2	4	-5
3	11	-12
4	3	3
5	0	1
6	5	-5
7	9	8
8	6	-4
9	0	-4
10	7	6
K,L= 4, 7		
H	FOB	FCA
0	9	10
1	5	4
2	3	2
3	5	7
4	5	3
5	4	4
K,L= 5, 7		
H	FOB	FCA
0	0	-2
1	0	-1
2	2	-3
3	3	-5
4	0	-1
5	3	-4
6	3	-4
K,L= 1, 7		
H	FOB	FCA
-1	17	-16
-2	17	-17
-3	2	-6
-4	4	7
-5	29	28
-6	8	5
-7	11	-9
-8	13	12
-9	7	11
-10	10	10
-11	0	-0
-12	6	-5
-13	3	3
-14	3	4
-15	7	-6
-16	3	-2
-17	0	2
-18	0	-2
-19	6	-4
-20	7	-6
-21	6	-5
K,L= 2, 7		
H	FOB	FCA
-1	0	-0
-2	3	4
-3	10	8
-4	17	-18
-5	10	9
-6	10	11
-7	0	1
-8	0	2
-9	0	2
-10	4	1
-11	9	12
-12	0	1
-13	2	-2
-14	12	9
-15	0	0
-16	3	-2
-17	0	2
-18	10	7
-19	5	5
K,L= 3, 7		
H	FOB	FCA
-1	5	-10
-2	6	-9
-3	6	-7
-4	12	15
-5	14	12
-6	0	-1
-7	2	-1
-8	12	13
-9	7	6
-10	6	-3
-11	2	9
-12	5	-6
-13	6	-2
-14	8	7
-15	6	-2
K,L= 4, 7		
H	FOB	FCA
-1	5	7
-2	6	-6
-3	16	-17
-4	11	-12
-5	5	6
-6	8	9
-7	0	-1
-8	0	2
-9	2	2
-10	7	7
-11	7	7
K,L= 5, 7		
H	FOB	FCA
-1	0	6
-2	9	7
-3	0	0
-4	6	-6
-5	6	-5
-6	2	-2
-7	0	1
-8	3	3
-9	0	-0
-10	0	-1
-11	3	3
K,L= 0, 8		
H	FOB	FCA
0	15	18
1	10	7
2	2	1
3	3	5
4	2	-2
5	2	1
6	7	7
7	7	-7
8	4	-7
9	3	-2
10	0	4
11	6	7
12	7	-6
13	5	-7
14	3	4
15	2	7
16	4	5
17	2	3
K,L= 1, 8		
H	FOB	FCA
0	11	13
1	0	-6
2	4	-3
3	2	3
4	0	-2
5	0	-1
6	3	-2
7	4	-4
8	3	2
9	4	4
10	4	-1
11	0	-2
12	0	-2
13	0	2
14	4	6
K,L= 2, 8		
H	FOB	FCA
0	3	-1
1	7	-8
2	3	-4
3	0	-1
4	8	-9
5	5	5
6	2	3
7	6	-6
8	0	-0
9	0	0
10	3	-1
11	2	2
K,L= 3, 8		
H	FOB	FCA
0	2	-2
1	2	2
2	6	5
3	6	5
4	4	-1
5	4	3
6	2	2
7	4	-5
8	0	1
9	5	4
K,L= 4, 8		
H	FOB	FCA
0	5	6
1	3	-2
2	0	-2
3	0	-2
4	7	-9
5	0	-1
6	0	1
7	3	-3
K,L= 5, 8		
H	FOB	FCA
0	0	1
1	9	0
2	4	-4
3	9	-1
4	3	3
K,L= 0, 8		
H	FOB	FCA
-1	3	9
-2	3	-4
-3	10	-6
-4	24	20
-5	9	9
-6	21	-23
-7	3	-1
-8	5	-5
-9	4	-2
-10	0	4
-11	0	-1
-12	2	3
-13	5	-4
-14	6	6
-15	19	17
-16	6	4
-17	18	-13
-18	16	-15
-19	14	-7
K,L= 1, 8		
H	FOB	FCA
-1	17	19
-2	9	5
-3	2	-2
-4	10	12
-5	3	3
-6	3	1
-7	9	7
-8	7	-4
-9	0	-2
-10	2	-2
-11	0	-0
-12	0	2
-13	3	-3
-14	9	-7
-15	9	6
-16	18	14
-17	10	7
K,L= 2, 8		
H	FOB	FCA
-1	5	-7
-2	11	12
-3	22	25
-4	4	4
-5	3	-2
-6	4	5
-7	0	1
-8	0	-3
-9	4	-1
-10	5	6
-11	0	-1
-12	4	-7
-13	0	1
-14	8	-4
K,L= 3, 8		
H	FOB	FCA
-1	4	-7
-2	4	-4
-3	4	5
-4	12	15
-5	13	13
-6	5	7
-7	3	4
-8	0	-2
-9	0	3
-10	3	3
-11	6	-4
-12	5	3
-13	0	3
-14	3	-3
-15	9	2
-16	5	5
-17	6	5
K,L= 4, 8		
H	FOB	FCA
-1	0	-2
-2	6	-6
-3	0	-1
-4	0	-1
-5	5	6
-6	8	7
-7	5	7
-8	0	1
-9	4	4
-10	4	3
K,L= 5, 8		
H	FOB	FCA
-1	0	-2
-2	9	-2
-3	0	0
-4	0	0
-5	0	0
-6	3	3
-7	3	3
-8	3	1
-9	0	1
-10	0	1
-11	4	2

Table 2. *Atomic parameters of the half-molecule of 7,7′-dihydro-β-carotene*

Carbon atom	*x*	*y*	*z*	Isotropic temperature factor
15	0·013	0·092	−0·020	5·85
14	0·041	0·019	−0·089	6·71
13	0·069	0·174	−0·145	6·55
13–Me	0·069	0·423	−0·127	7·32
12	0·099	0·078	−0·206	6·37
11	0·129	0·209	−0·267	7·07
10	0·159	0·092	−0·323	5·98
9	0·198	0·202	−0·379	5·99
9–Me	0·199	0·459	−0·384	6·37
8	0·229	0·071	−0·424	7·05
7	0·269	0·156	−0·491	7·17
6	0·332	−0·010	−0·475	7·45
5	0·384	−0·026	−0·385	8·89
5–Me	0·378	0·116	−0·304	11·57
4	0·435	−0·173	−0·374	13·37
3	0·436	−0·319	−0·450	14·50
2	0·390	−0·316	−0·547	14·98
1	0·329	−0·129	−0·566	7·89
1–Me–1	0·266	−0·252	−0·596	10·62
1–Me–2	0·339	0·047	−0·635	9·54

the center of the chain the bond lengths tend to have an intermediate character, *i.e.*, the single-bond lengths are shorter and the double-bond lengths longer. A second fact is also significant, namely, the chain tends to be curved. Note that the interior angles on one side of the chain are uniformly larger than those on the other. This aspect is represented in Fig. 2, a projection of the molecule on (001). Fig. 4 shows that the chain may feature other curvatures, in the projection on (010).

Table 3. *Interatomic distances in 7,7′-dihydro-β-carotene*

Carbon atoms Within half-molecule		Distance	Standard deviation
15	15′	1·45 Å	0·03 Å
15	14	1·40	0·02
14	13	1·48	0·03
13	12	1·37	0·02
12	11	1·48	0·03
11	10	1·37	0·02
10	9	1·50	0·01
9	8	1·32	0·02
8	7	1·59	0·03
7	6	1·61	0·03
6	5	1·42	0·02
5	4	1·35	0·04
4	3	1·43	0·04
3	2	1·45	0·04
2	1	1·65	0·03
1	6	1·52	0·03
13	13–Me	1·53	0·03
9	9–Me	1·55	0·03
5	5–Me	1·52	0·03
1	1–Me–1	1·45	0·03
1	1–Me–2	1·54	0·03
7	1–Me–1	2·90	0·03
7	1–Me–2	3·02	0·03
8	1–Me–1	3·48	0·03
8	1–Me–2	>4·00	—
Between half-molecules, cell translated (*y*−1)			
14	13–Me	3·72	0·03
8	9–Me	3·83	0·03
1–Me–1	7	3·89	0·03
All other intermolecular distances		>4·00	—

Table 4. *Bond angles in the half-molecule of 7,7′-dihydro-β-carotene*

Carbon atoms			Angle	Standard deviation
15′	15	14	111·4°	2·3°
15	14	13	122·7	2·0
14	13	12	116·2	2·1
13	12	11	123·1	2·1
12	11	10	117·0	2·2
11	10	9	122·7	2·0
10	9	8	117·1	2·0
9	8	7	124·1	2·1
8	7	6	105·5	1·7
7	6	5	121·5	2·0
6	5	4	119·0	2·8
5	4	3	120·9	3·0
4	3	2	127·5	3·4
3	2	1	113·4	2·9
2	1	6	111·2	2·0
1	6	7	111·1	1·9
1	6	5	127·4	2·2
14	13	13–Me	120·0	2·0
12	13	13–Me	123·5	2·1
10	9	9–Me	118·4	1·8
8	9	9–Me	124·5	2·1
6	5	5–Me	118·1	1·9
4	5	5–Me	122·9	2·4
2	1	1–Me–1	105·8	2·1
2	1	1–Me–2	109·1	2·0
6	1	1–Me–1	106·6	2·0
6	1	1–Me–2	107·0	2·0
1–Me–1	1	1–Me–2	117·2	2·1

As was expected from steric hindrance in the construction of atomic models, the plane of the ring cannot be coincident with the plane of the chain (*cf.* Figs. 2 and 3). If the ring plane be considered as defined by the atoms C(1), C(6), and C(5), and the chain plane by C(9), C(8), and C(7), the dihedral angle between these two planes in 102·6°. The angle between the ring plane and the plane of C(8), C(7), and C(6) is 61·9°. Carbon atom C(3) is out of the plane of the ring.

The closest approach between atoms of different

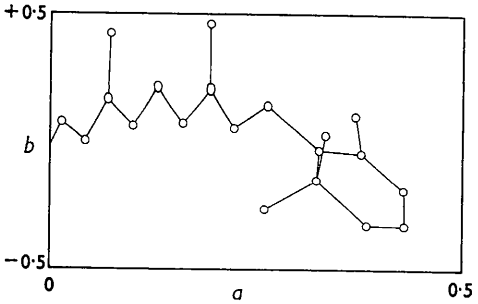


Fig. 2. Projection of a half-molecule (asymmetric unit) of 7,7′-dihydro-β-carotene on (001). Portions of other molecules that belong in this projection (*p*2*mg*) have been removed for clarity.

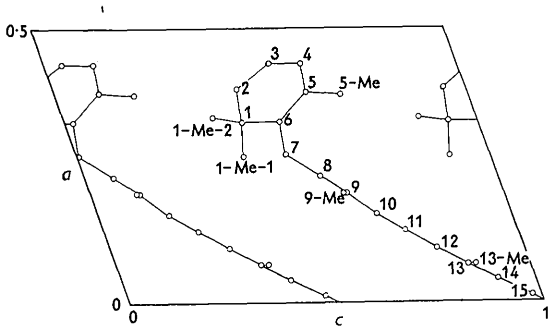


Fig. 3. Projection of half-molecules of 7,7′-dihydro-β-carotene on (010).

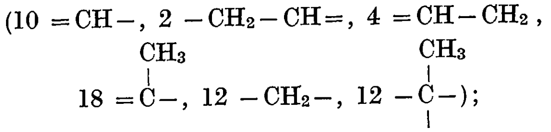
molecules is 3·7 Å (between a methyl group and CH group). This distance is about the value of the sums of their respective van der Waals radii and again serves to reinforce the general correctness of the molecular structure.

Discussion

From the chemical standpoint, the multiple curvature of the polyene chain is unexpected. However, a critical re-examination of the findings of Eichhorn & MacGillavry (1959) indicated that in *trans*-β-ionylidenecrotonic acid the interior angles on the methyl side of the chain are consistently somewhat larger than those on the opposite side, leading to a curvature in the chain plane of the same kind as is to be found in 7,7′-dihydro-β-carotene. A very definite curvature has also been described for the chain of vitamin-A acid (Stam & MacGillavry, 1963). These authors suggest that the curvature is due to a steric interaction between the methyl groups at C(13) and C(9) and the nearby carbon atoms in the chain.

A particularity of some interest is the relationship between bond length and the position of the bond with respect to the center of the chain. As has been shown above, the single bonds become smaller and the double bonds larger toward the center of the chain. This relationship has been reported in diphenylpolyenes (Drenth, 1954; Drenth & Wiebenga, 1955) and has been predicted by Coulson (1938) for conjugated polyenes generally. Its verification in a carotenoid compound would seem to validate its applicability.

The relatively short single-bond distances within the β-ionone ring could be due to its bonds' having a somewhat aromatic character here, to its large amount of thermal motion (*cf.* Eichhorn & MacGillavry, 1959), or to a cumulative error in the intensity readings. It might appear, from the values for the interatomic distances alone, that the double bond in the ring is essentially in the 5–4 position rather than in a 6–5 position. However, the approximate bond-length error of 2% and the large amount of thermal motion militate against too strict a reliance on these values for such a decision. Moreover, two other types of evidence are in favor of the ring's β-ionone structure: (1) Analysis of the protons by nuclear magnetic resonance shows that these can only accord with the structure of 7,7′-dihydro-β-carotene



$$(10\ {=}\mathrm{CH}{-},\ 2\ {-}\mathrm{CH_2}{-}\mathrm{CH}{=},\ 4\ {=}\mathrm{CH}{-}\mathrm{CH_2},\ 18\ {=}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}{-},\ 12\ {-}\mathrm{CH_2}{-},\ 12\ {-}\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}{-});$$

(2) the sum of the angles about carbon atoms 5 and 6 totals 360° for each, indicating that the bonds about each atom lie in a plane and that a double bond very likely connects them.

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