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Crystal-Structure Analysis of β-Carotene

BY CLARENCE STERLING

Department of Food Science and Technology, University of California, Davis, California, U.S.A.

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The crystals of β-carotene ($C_{40}H_{56}$) are monoclinic ($P2_1/c$), with the unit-cell dimensions $a=7\cdot55$, $b=9\cdot51$, $c=24\cdot8$ Å, and $\beta=105\cdot3°$, and with two molecules in the unit cell. The main chain of the molecule tends to be planar, but the chain is curved in its course. The β-ionone ring is *s-cis* about the C(7)–C(6) bond, thus interrupting the all-*trans* structure of the chain. With photographically registered intensities, refinement of parameters by a least-squares method yielded a discrepancy index, R, of 0·19.

Introduction

Taylor (1937) described the optical properties of single crystals of β-carotene and performed a preliminary X-ray analysis. He gave the dimensions of the monoclinic unit cell as $a=7\cdot75$, $b=9\cdot5$, $c=25\cdot0$ Å, and $\beta=105\cdot5°$. Attempts to resolve the molecular structure were inconclusive. Subsequently Hunter, Lomer, Vand & Williams (1948), using powder diagrams, measured the lattice constants of the unit cell as 7·745, $b=9\cdot44$, $c=25\cdot2$ Å, and $\beta=105\cdot5°$. These workers did not try to analyze the crystal structure. Since Taylor's (1937) work, there have been no further efforts towards a resolution of the structure of the molecule.

Chemical evidence (Isler, Montavan, Ruegg & Zeller, 1956; Isler, Gutmann, Lindlar, Montavan, Ruegg, Ryser & Zeller, 1956) indicates that β-carotene (all-*trans*-β-carotene) is a planar, all-*trans*, polyene chain with conjugated double bonds, attached methyl groups, and a β-ionone ring at each end, also with attached methyl groups. Apparently the molecule has a center of symmetry: this is indicated independently by both chemical and X-ray evidence. However, chemical data cannot distinguish whether the molecule has an *s-cis* or *s-trans* structure (Pullman & Pullman, 1961) about the single bond, C(7)–C(6) (Fig. 1). Moreover, it was shown earlier that the polyene chain of vitamin-A acid is not planar but is curved in several directions (Stam & MacGillavry, 1963) as is the chain of 7,7-dihydro-β-carotene (Sterling, 1964). Because it seemed important to know the structure of a molecule of such biological importance, β-carotene has been made the object of a crystal-structure analysis.

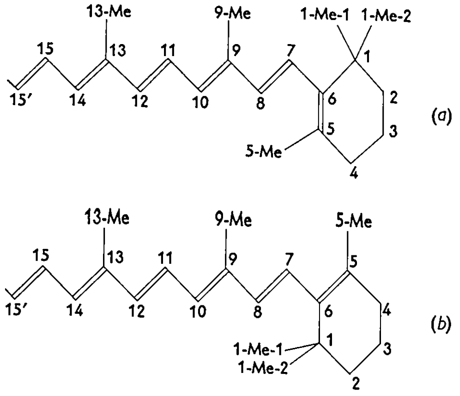

Fig. 1. (*a*) Schematic diagram of a half-molecule of β-carotene which is *s–cis* about the 7–6 bond, showing also the designations of the carbon atoms used here. (*b*) Schematic diagram of a half-molecule of β-carotene which is *s–trans* about the 7–6 bond.

Materials and methods

Single crystals of β-carotene were graciously presented by C. O. Chichester. The density measurements of Taylor were accepted as being correct, and no new determinations were made. X-ray diffraction patterns were registered at room temperature with a Weissenberg apparatus and Cu $K\alpha$ radiation (nickel-filtered). Intensities were recorded by the multi-film technique, in the equi-inclination method, at 7 levels about the b axis. Precession about the a axis gave additional $0kl$ reflections. Cell dimensions were estimated from zero-level photographs. Two individuals read 850 non-zero and 261 'zero' intensities separately, and the values were then averaged. Because of the low mass-absorption coefficient (3·2 g^{-1}), no absorption correction was applied.

Computations were performed on an IBM 7090 computer, with data reduction (INCOR) and Fourier (FOURSUM/FOURPRINT/FOURPEAK) programs kindly provided by A. Zalkin of the Lawrence Radiation Laboratory, Berkeley, California. The least-squares program (LALS1) is that of P. K. Gantzel, R. A. Sparks & K. N. Trueblood, modified by A. Zalkin. Interatomic distances and angles were obtained with the DSTNCE program of A. Zalkin.

Results

The unit-cell dimensions were determined as follows: $a=7\cdot55\pm0\cdot05$, $b=9\cdot51\pm0\cdot1$, $c=24\cdot8\pm0\cdot2$ Å, and

$\beta = 105{\cdot}3° \pm 0{\cdot}3°$. Because these values were in reasonably close agreement with the values given by the other workers, no attempts were made to obtain any greater accuracy in the parameters. The space group is $P2_1/c$, according to the systematic extinctions. With two molecules per unit cell (Taylor, 1937), the calculated density is 1·04 g.cm^{-3}. Because each molecule must have a center of symmetry, it is only necessary to find the parameters of the 20 carbon atoms of the asymmetric unit (half-molecule). The hydrogen atoms were neglected. The designations of the carbon atoms are given in Fig. 1.

Patterson distributions were calculated in two dimensions for the (010) and (100) projections. They were calculated in three dimensions as well, with untreated data, with data treated to sharpen the peaks, and with data treated both to sharpen the peaks and to remove the peak at the origin. The best resolution attained in any of these distributions was that of the average vector between alternate carbon atoms, which was also taken to indicate the direction of the chain axis. This vector was given in all but the (010) projection. However, as Taylor (1937) found, the latter distribution did indicate the major direction of the polyene chain in projection. No vector between adjacent carbon atoms was found.

The method of using the strongest reflections in trial-and-error placement of the chain was then followed (Sterling, 1964). In this case, 365 reflections were employed, and a trial molecule based on an all-*trans*, planar, straight chain, with a coplanar ring, was tested by the value of R,* the discrepancy index. (The scale factor approximation was obtained by permitting this value to vary in the least-squares program†; the temperature factor was approximated arbitrarily as $B = 4{\cdot}0$ in the expression $\exp[-B\lambda^{-2}\sin^2\theta]$.) However, with a straight chain, R could not be reduced below 0·53.

Consequently, it was postulated that the chain was curved. A three-dimensional Fourier distribution based on signs of F (calculated) and values of F (observed) from the chain atoms alone gave possible positions of some ring atoms. Successive trial and error placement of the atoms and Fourier syntheses were continued, sometimes accompanied by least-squares refinement in the ring atoms. In this way a structure with $R = 0{\cdot}42$ was obtained. Although a full least-squares variation of all the 60 atomic positional parameters lowered R to 0·34 in 3 cycles, the molecule was unrecognizable as a chemical entity.

At this point, re-study of the electron-density distributions raised the possibility that some neglected, but relatively strong and repeatedly obtained peaks would coincide better with the possibility that the ring was *s-cis* about the C(7)–C(6) bond. A structure postulated on this basis could be refined by the least-squares method to give a discrepancy index with $R = 0{\cdot}29$, but again the molecule was unrecognizable. Because the least-squares program seemed to move the chain atoms into positions that could be interpreted as places in a rather highly curved chain, the chain atoms were placed on a curve of smaller radius. This trial structure could be refined rapidly to $R = 0{\cdot}26$. With 60 positional parameters, 20 isotropic temperature factors, and one overall scale factor being varied in the least-squares program, R was lowered to 0·15. The chain and the ring were both quite recognizable, and the chain (as seen in projection) was smoothly curved. When all the non-zero reflections were used, a final R value of 0·19 was obtained. The average final parameter shifts for x, y, z, and B, respectively, were 0·0005, 0·0003, 0·00004, 0·077. The maximum shifts were 0·0013, 0·0007, 0·0001, 0·349, respectively. A difference Fourier synthesis yielded an essentially featureless map. (The structure with the *s-trans* ring could not be refined.)

The final atomic parameters for the carbon atoms are given in Table 1. The relatively higher temperature

Table 1. *Atomic parameters of the half-molecule of β-carotene*

Carbon atom	x	y	z	Isotropic temperature factor
(15)	0·038	0·059	0·013	4·47
(14)	0·070	0·172	−0·027	5·13
(13)	0·150	0·297	−0·007	5·02
(13–Me)	0·211	0·346	0·054	5·12
(12)	0·171	0·401	−0·053	4·37
(11)	0·251	0·528	−0·039	4·86
(10)	0·247	0·617	−0·088	4·82
(9)	0·317	0·751	−0·082	4·94
(9–Me)	0·389	0·832	−0·025	5·31
(8)	0·297	0·837	−0·135	4·54
(7)	0·344	0·970	−0·135	4·41
(6)	0·338	1·049	−0·190	4·07
(5)	0·209	1·030	−0·235	4·44
(5–Me)	0·039	0·949	−0·244	6·20
(4)	0·217	1·101	−0·294	5·28
(3)	0·383	1·176	−0·290	9·85
(2)	0·486	1·233	−0·239	11·72
(1)	0·496	1·148	−0·181	6·13
(1–Me–1)	0·678	1·076	−0·159	7·91
(1–Me–2)	0·475	1·280	−0·141	7·79

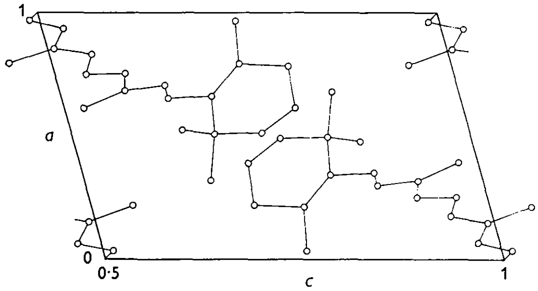

Fig. 2. Projection of half the unit cell of β-carotene on the (010) plane.

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* R is given by the formula, $[\Sigma w(F_o - F_c)^2]^{1/2}/[\Sigma w F_o{}^2]^{1/2}$, with all structure factors assigned an equal weight.

† The function minimized is $[\Sigma(w^{1/2}|F_o - F_c|^2)]^{1/2}$, in which each reflection is given unit weight.

Table 2. *Interatomic distances in β-carotene*

Between carbon atoms within half-molecule		Distance	Standard deviation
(15)	(15′)	1·35 Å	0·04 Å
(15)	(14)	1·52	0·03
(14)	(13)	1·37	0·03
(13)	(12)	1·54	0·03
(12)	(11)	1·36	0·03
(11)	(10)	1·48	0·03
(10)	(9)	1·38	0·03
(9)	(8)	1·51	0·03
(8)	(7)	1·32	0·03
(7)	(6)	1·56	0·03
(6)	(5)	1·31	0·03
(5)	(4)	1·62	0·03
(4)	(3)	1·47	0·04
(3)	(2)	1·40	0·04
(2)	(1)	1·63	0·03
(1)	(6)	1·52	0·03
(13)	(13–Me)	1·53	0·03
(9)	(9–Me)	1·57	0·03
(5)	(5–Me)	1·50	0·03
(1)	(1–Me–1)	1·55	0·03
(1)	(1–Me–2)	1·65	0·03

Between half-molecules, related through symmetry center ($\bar{x}, \bar{y}, \bar{z}$) of cell translated ($x+1, y+1$)		Distance	Standard deviation
(15)	(1–Me–1)	3·91 Å	0·03 Å
(14)	(1–Me–1)	3·96	0·03
(13)	(9–Me)	3·70	0·03
(10)	(13–Me)	3·91	0·03
(13–Me)	(9–Me)	3·79	0·03
(9–Me)	(9–Me)	3·70	0·04
(11)	(11)	3·90	0·05
Between half-molecules in *same* cell related through symmetry operation ($\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$)			
(8)	(3)	3·81 Å	0·04 Å
(6)	(2)	3·90	0·03
(5)	(2)	3·85	0·03
Between half-molecules in *same* cell related through symmetry operation ($x, \frac{1}{2}-y, \frac{1}{2}+z$)			
(4)	(13–Me)	3·78 Å	0·03 Å
(3)	(13–Me)	3·75	0·03

Table 3. *Bond angles in the half-molecule of β-carotene*

Atomic triangle			Vertex angle	Standard deviation
(15′)	(15)	(14)	113·9°	2·4°
(15)	(14)	(13)	121·6	2·3
(14)	(13)	(12)	114·9	2·2
(13)	(12)	(11)	120·9	2·2
(12)	(11)	(10)	113·0	2·3
(11)	(10)	(9)	120·7	2·2
(10)	(9)	(8)	116·6	2·2
(9)	(8)	(7)	123·2	2·3
(8)	(7)	(6)	121·2	2·2
(7)	(6)	(5)	121·5	2·2
(6)	(5)	(4)	120·2	2·2
(5)	(4)	(3)	112·3	2·3
(4)	(3)	(2)	122·9	2·4
(3)	(2)	(1)	118·3	2·4
(2)	(1)	(6)	109·2	2·2
(1)	(6)	(7)	109·5	2·2
(1)	(6)	(5)	129·0	2·2
(14)	(13)	(13–Me)	127·4	2·2
(12)	(13)	(13–Me)	117·7	2·2
(10)	(9)	(9–Me)	126·1	2·2
(8)	(9)	(9–Me)	116·6	2·2
(6)	(5)	(5–Me)	130·9	2·2
(4)	(5)	(5–Me)	108·9	2·2
(2)	(1)	(1–Me–1)	111·7	2·3
(2)	(1)	(1–Me–2)	99·5	2·3
(6)	(1)	(1–Me–1)	114·7	2·2
(6)	(1)	(1–Me–2)	110·5	2·2
(1–Me–1)	(1)	(1–Me–2)	110·3	2·3

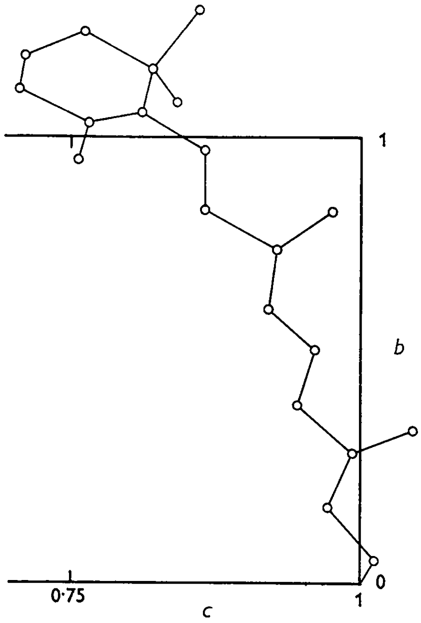

Fig. 3. Projection of one-fourth the unit cell of β-carotene on the (100) plane. Only a single asymmetric unit (half-molecule) is shown, to illustrate molecular form. The symmetry-related molecular segments have been omitted for clarity.

factors for the ring atoms, particularly C(2) and C(3), are notable. Table 2 presents the interatomic distances and their standard deviations. (Between molecules, only the distances below 4 Å are given.) The standard deviations were estimated by the method of least squares, with the assumption that the errors are random. In Table 3 are the interatomic angles. It should be noted that the greater size of angles on one side of the chain indicates that the chain is convex on that side. Table 4 presents the observed and calculated structure factors, with all the unobserved reflections given a value of zero for F_o. Figs. 2 and 3 present the appearance of the asymmetric unit in projections on (010) and (100), respectively.

Table 4. *Observed* (FOBS) *and calculated* (FCAL) *structure factors for β-carotene*

L	FOBS	FCAL
H,K= 0, 0		
L	FOBS	FCAL
4	792	752
6	208	224
8	166	158
10	244	-225
12	0	-47
14	32	41
16	88	68
18	192	-219
20	0	35
22	115	88
H,K= 1, 0		
L	FOBS	FCAL
0	444	-432
2	1138	1472
4	1239	1331
6	337	-180
8	286	296
10	215	225
12	181	136
14	133	61
16	99	69
18	197	208
20	129	-167
H,K= 2, 0		
L	FOBS	FCAL
0	485	-523
2	523	-570
4	324	304
6	372	441
8	259	280
10	145	39
12	90	78
H,K= 3, 0		
L	FOBS	FCAL
0	200	105
2	113	-59
4	298	-303
6	190	204
8	204	262
10	123	106
12	92	51
14	63	-23
16	0	-18
18	126	-140
H,K= 4, 0		
L	FOBS	FCAL
0	154	214
2	31	38
4	0	-11
6	161	-145
8	94	-83
H,K= 5, 0		
L	FOBS	FCAL
0	0	6
2	0	14
4	187	238
H,K= 6, 0		
L	FOBS	FCAL
0	98	124
2	91	-141
4	59	-66
6	66	56
H,K= 7, 0		
L	FOBS	FCAL
0	78	-123
2	59	103
4	71	-83
H,K= -1, 0		
L	FOBS	FCAL
2	86	38
4	113	140
6	175	-179
8	110	86
10	232	-218
12	0	61
14	150	-176
16	0	-43
18	0	-24
20	405	336
H,K= -2, 0		
L	FOBS	FCAL
2	54	19
4	422	401
6	26	83
8	483	479
10	19	23
12	331	317
14	336	-294
16	213	268
18	0	41
20	169	-193
22	93	-128
H,K= -3, 0		
L	FOBS	FCAL
2	0	44
4	182	-211
6	0	31
8	19	-101
10	0	22
12	62	-31
14	126	113
16	68	-106
18	205	-245
20	161	-179
H,K= -4, 0		
L	FOBS	FCAL
2	295	-306
4	21	15
6	182	-230
8	79	109
10	97	-115
12	34	29
10	0	-13
14	25	87
16	124	-139
18	0	-6
20	110	140
22	136	126
H,K= -5, 0		
L	FOBS	FCAL
2	0	71
4	179	264
6	92	-86
8	0	-11
10	0	-15
12	0	-32
14	110	-138
16	76	92
18	176	199
20	126	146
H,K= -6, 0		
L	FOBS	FCAL
2	0	-8
4	0	-76
6	88	85
8	0	-14
10	0	-37
12	0	46
14	0	-13
16	205	268
H,K= -7, 0		
L	FOBS	FCAL
2	0	27
4	30	19
6	42	28
8	59	111
10	51	36
12	84	128
14	88	137
H,K= 0, 1		
L	FOBS	FCAL
1	123	101
2	264	-236
3	513	-576
4	483	-442
5	366	397
6	213	-79
7	710	641
8	399	387
9	242	198
10	0	-13
11	99	42
12	65	30
13	102	136
14	73	29
15	0	-35
16	162	-147
17	103	79
18	110	73
19	234	-237
20	0	18
21	0	16
22	114	67
23	106	-87
H,K= 1, 1		
L	FOBS	FCAL
0	121	-128
1	309	410
2	87	-34
3	198	-174
4	171	-181
5	47	-28
6	128	31
7	131	-145
8	277	171
9	282	260
10	118	99
11	106	108
12	320	241
13	0	-21
14	0	40
15	0	-107
16	0	-27
17	117	144
18	173	-156
H,K= 2, 1		
L	FOBS	FCAL
0	615	-631
1	470	410
2	129	-88
3	208	228
4	73	-98
5	276	268
6	111	-127
7	398	-329
8	170	-109
9	51	-39
10	0	27
11	95	-71
12	87	-71
H,K= 3, 1		
L	FOBS	FCAL
0	285	-251
1	541	479
2	392	-345
3	97	98
4	62	61
5	193	186
6	85	-26
7	182	177
8	0	-100
9	0	-6
10	164	-124
11	0	-49
12	0	-16
13	0	42
14	113	-85
15	76	99
H,K= 4, 1		
L	FOBS	FCAL
8	221	-123
0	295	316
1	95	-104
2	50	-47
3	109	104
4	199	-225
5	34	8
6	65	-95
7	0	10
8	0	10
9	114	71
10	0	-48
11	0	23
12	0	5
13	0	30
14	0	90
15	0	-60
16	0	33
17	96	117
H,K= 5, 1		
L	FOBS	FCAL
0	0	-24
1	67	-104
2	0	-39
3	0	2
4	85	79
5	0	46
6	150	-145
7	0	-18
8	0	-63
9	65	81
H,K= 6, 1		
L	FOBS	FCAL
0	69	-71
1	143	165
2	0	51
3	159	-173
4	0	-9
5	78	76
6	66	65
H,K= -1, 1		
L	FOBS	FCAL
1	595	-676
2	216	-175
3	921	1004
4	1156	1154
5	200	144
6	389	409
7	132	200
8	221	-123
9	275	232
10	246	225
11	164	-173
13	330	293
14	87	65
15	0	-37
16	210	213
17	164	-186
18	129	135
19	0	3
20	154	136
21	0	-19
22	78	-76
H,K= -2, 1		
L	FOBS	FCAL
1	602	602
2	1437	1366
3	908	783
4	268	205
5	83	116
6	205	199
7	85	-68
8	45	58
9	77	-79
10	46	-61
11	430	311
12	74	-20
13	306	-246
14	60	3
15	34	-59
16	50	67
17	78	84
18	0	-44
19	68	62
20	128	-143
21	0	-30
22	0	-41
23	106	109
H,K= -3, 1		
L	FOBS	FCAL
1	5,9	444
2	219	-270
3	371	-239
4	246	-140
5	31	-13
6	70	55
7	76	117
8	0	93
9	92	-131
10	0	-46
11	133	-105
12	112	107
13	150	-162
14	41	-20
15	160	180
16	136	-151
17	0	6
18	172	-188
19	89	110
20	41	32
21	117	118
22	0	37
23	66	53
H,K= -4, 1		
L	FOBS	FCAL
1	173	-179
2	0	58
3	42	-66
4	55	-46
5	96	131
13	0	55
6	108	113
7	0	53
8	0	28
9	0	41
10	121	172
11	58	43
12	34	-25
13	165	187
14	111	-127
15	79	99
16	90	-93
H,K= -5, 1		
L	FOBS	FCAL
1	105	-72
2	0	-55
3	225	241
4	0	45
5	85	-100
6	101	-146
7	70	96
8	71	-63
9	84	89
10	109	-128
11	114	131
12	119	-121
13	98	96
H,K= -6, 1		
L	FOBS	FCAL
1	0	-49
2	0	53
3	0	-52
4	73	-64
5	48	-62
H,K= 0, 2		
L	FOBS	FCAL
0	151	11
1	332	565
2	258	-350
3	281	-258
4	163	121
5	109	97
6	14	4
7	254	269
8	77	-29
9	655	-563
10	150	-146
11	0	35
12	134	-70
13	0	55
14	143	-145
15	0	-21
16	102	58
17	70	-119
18	0	6
19	0	-65
20	87	54
H,K= 1, 2		
L	FOBS	FCAL
0	578	539
1	109	104
2	310	-249
3	205	170
4	188	156
5	177	175
6	0	-19
7	80	41
8	152	136
9	118	82
10	0	-12
11	222	-174
12	0	-1
13	108	-86
14	150	-145
15	210	236
16	134	-141
17	0	15
18	0	-33
19	65	68
H,K= 2, 2		
L	FOBS	FCAL
0	354	-393
1	311	-327
2	238	278
3	50	68
4	141	156
5	269	-260
6	137	-107
7	173	-173
8	0	-8
9	0	-37
10	63	54
11	121	79
12	0	-1
13	0	-71
14	112	146
15	0	2
16	0	-28
17	115	118
18	0	6
19	77	116
H,K= 3, 2		
L	FOBS	FCAL
0	277	299
1	183	-153
2	77	-125
3	75	59
4	157	-153
5	115	-105
6	94	83
7	0	13
8	52	-22
9	0	-13
10	83	-126
11	0	23
12	0	-21
13	0	30
14	0	-50
15	0	-70
16	109	114
5	316	-247
17	77	-69
H,K= 4, 2		
L	FOBS	FCAL
0	117	79
1	76	-112
2	59	104
3	115	-84
4	81	94
5	0	-45
6	0	-67
7	114	155
H,K= 5, 2		
L	FOBS	FCAL
0	110	132
1	172	-146
2	0	-95
3	124	-129
4	111	108
5	0	-26
6	0	-34
7	106	-129
8	0	30
9	0	-24
10	0	-40
11	0	-16
12	0	20
13	86	-111
H,K= 6, 2		
L	FOBS	FCAL
0	0	-1
1	0	-16
2	0	26
3	71	-87
4	41	-46
5	65	-55
6	41	14
7	65	-61
H,K= 7, 2		
L	FOBS	FCAL
0	50	-60
H,K= -1, 2		
L	FOBS	FCAL
1	640	-717
2	331	-364
3	485	499
4	380	372
5	316	-247
6	503	-544
7	57	-152
8	333	235
9	420	321
10	358	-245
11	475	426
12	295	209
14	171	169
15	0	-87
16	213	184
17	0	-53
18	0	-33
19	128	-154
20	81	100
H,K= -2, 2		
L	FOBS	FCAL
1	63	-82
2	231	268
3	122	-106
4	193	-260
5	278	-236
6	60	-16
7	385	372
8	34	77
9	227	211
10	378	303
11	132	-69
12	391	358
13	44	8
14	65	-10
15	191	-180
16	115	174
17	74	-109
18	71	63
19	62	-52
20	49	30
21	133	-156
H,K= -3, 2		
L	FOBS	FC
1	132	-98
2	53	-56
3	149	55
4	290	247
5	51	74
6	606	531
7	184	177
8	469	431
9	228	-172
10	174	129
11	136	-122
12	102	115
13	87	-109
14	83	101
15	114	119
16	90	93
H,K= -4, 2		
L	FOBS	FCAL
1	345	287
2	212	216
3	428	394
4	579	473
5	392	346
6	0	59
7	111	31
8	66	35
9	68	-96
10	40	61
11	34	46
12	0	-9
13	0	-76
13	266	207
14	0	75
15	0	28
16	77	-100
H,K= -5, 2		
L	FOBS	FCAL
1	307	228
2	70	10
3	133	119
4	82	-82
5	0	-15
6	145	-149
7	43	-66
8	71	115
9	0	-11
10	0	0
11	0	12
12	89	83
13	102	-130
H,K= -6, 2		
L	FOBS	FCAL
1	0	-1
2	128	-128
3	112	-107
4	0	3
5	128	-123
6	79	85
7	108	151
H,K= -7, 2		
L	FOBS	FCAL
1	88	-111
2	83	64
3	0	11
4	65	43
H,K= 0, 3		
L	FOBS	FCAL
1	42	94
2	0	-13
3	392	-249
4	103	-62
5	51	18
6	48	64
7	302	-249
8	44	-18
9	286	177
10	482	-355
11	0	-2
12	0	-35
13	266	207
14	41	-59
15	158	156
16	141	-128
17	54	108
18	0	3
19	75	99
H,K= 1, 3		
L	FOBS	FCAL
0	71	-95
1	164	123
2	75	78
3	77	-54
4	122	-128
5	0	-7
6	0	-11
7	318	-289
8	324	259
9	128	-131
10	0	-15
11	61	-32
12	120	-86
13	173	135
14	0	-93
15	0	-33
16	71	-117
17	152	141
H,K= 2, 3		
L	FOBS	FCAL
0	151	-129
1	138	-63
2	82	-40
3	46	-79
4	112	81
5	0	-5
6	62	-37
7	166	139
8	62	-93
9	65	78
10	128	112
11	58	-86
12	158	181
13	0	38
14	106	-111
15	73	59
H,K= 3, 3		
L	FOBS	FCAL
0	73	81
1	154	-136
2	105	-70
3	192	-154
4	61	-58
5	0	-46
6	66	-60
7	45	-36
8	0	-40
9	0	-2
10	107	-121
11	0	24
12	0	8
13	123	-170
H,K= 4, 3		
L	FOBS	FCAL
0	62	45
1	78	-11
2	270	-237
3	70	71
4	0	-17
5	85	-64
6	128	-133
10	340	-270
7	0	-23
8	0	13
9	61	-71
10	96	-122
H,K= 5, 3		
L	FOBS	FCAL
0	0	66
1	58	52
2	53	-64
3	65	-113
4	0	0
5	0	17
6	124	-137
7	123	-151
H,K= 6, 3		
L	FOBS	FCAL
0	0	-75
1	102	128
2	57	72
H,K= -1, 3		
L	FOBS	FCAL
1	93	116
2	106	-151
3	419	394
4	262	250
5	349	288
6	389	-382
7	352	339
8	395	-288
9	263	155
10	274	164
11	368	241
12	366	-299
13	160	-63
14	61	-86
15	59	-34
H;K= -2, 3		
L	FOBS	FCAL
1	168	-223
2	155	-106
3	82	172
4	0	-53
5	226	-290
6	42	87
7	333	318
8	0	-60
9	0	-20
10	340	-270
11	180	-128
12	0	-14
13	0	-54
14	70	-66
H,K= -3, 3		
L	FOBS	FCAL
1	120	-140
2	420	370
3	354	-324
4	255	-239
5	182	186
6	102	68
7	43	-50
8	150	-127
9	71	-57
10	0	-58
11	324	260
12	0	78
13	118	122
14	0	7
15	131	142
H,K= -4, 3		
L	FURS	FCAL
1	31	-20
2	0	-22
3	172	173
4	61	-58
5	68	-88
6	66	-63
7	77	-61
8	0	47
9	178	170
10	152	194
11	0	25
12	126	95
13	136	126
H,K= -5, 3		
L	FOBS	FCAL
1	116	113
2	0	-34
3	0	21
4	0	65
5	71	63
6	140	123
7	107	81
8	147	148
9	77	80
10	131	147
11	0	18
12	71	-76
13	0	-23
14	104	68
H,K= -6, 3		
L	FOBS	FCAL
1	0	50
2	115	101
3	128	125
4	96	95
5	124	126
6	133	166
7	145	194
H,K= 0, 4		
L	FOBS	FCAL
0	42	-44
1	105	85
2	163	-142
3	62	31
4	0	73
7	106	103
5	304	-286
6	94	-103
7	0	50
8	373	302
9	0	-34
10	99	-83
11	58	45
12	148	103
H,K= 1, 4		
L	FOBS	FCAL
0	153	-106
1	308	-316
2	69	92
3	281	-264
4	37	-33
5	276	-277
6	288	272
7	172	-105
8	45	-42
9	343	-292
10	148	120
11	49	-47
H,K= 2, 4		
L	FOBS	FCAL
0	0	105
1	314	-252
2	157	-167
3	106	108
4	149	-121
5	0	-14
6	0	-57
7	173	-185
8	0	16
9	91	-113
10	77	30
11	87	-100
12	0	-5
13	187	-250
14	60	99
H,K= 3, 4		
L	FOBS	FCAL
0	164	131
1	124	48
2	56	65
3	93	95
4	89	-97
5	162	-155
6	187	-221
7	106	103
8	227	-240
9	133	-156
10	0	-30
11	111	-130
H,K= 4, 4		
L	FOBS	FCAL
0	0	-43
1	0	61
2	66	50
3	63	71
4	121	162
5	0	-36
6	0	-34
7	0	-25
8	0	40
9	0	16
10	172	-159
H,K= 5, 4		
L	FOBS	FCAL
0	0	-65
1	0	-59
2	91	-106
3	53	-53
4	0	6
5	116	121
6	123	106
H,K= -1, 4		
L	FOBS	FCAL
1	189	139
2	201	-185
3	63	-24
4	268	200
5	33	27
6	0	-62
7	251	-167
8	41	21
9	144	-136
10	50	38
11	45	-17
12	165	128
13	84	-126
H,K= -2, 4		
L	FOBS	FCAL
1	465	-370
2	244	107
3	252	224
4	40	-38
5	233	-231
6	179	-151
7	126	133
8	105	39
9	65	-74
10	148	-117
11	0	-30
12	78	-68
13	0	5
14	92	75
15	60	-13
H,K= -3, 4		
L	FOBS	FCAL
1	41	-9
2	0	59
3	71	85
4	0	-33
5	0	49
6	133	173
7	171	221
8	155	-172
9	0	-61
10	106	114
11	74	64
12	0	-16
13	0	-14
14	0	-28
15	99	-44
H,K= -4, 4		
L	FOBS	FCAL
1	63	-18
2	0	-13
3	0	-5
4	0	56
5	49	-45
6	0	8
7	111	-130
8	0	83
9	0	6
10	0	-19
11	101	68
12	50	-63
13	229	-232
14	0	-56
15	113	115
H,K= -5, 4		
L	FOBS	FCAL
1	0	11
2	0	-29
3	62	-58
4	0	-18
5	0	-45
6	67	-29
7	0	48
8	63	23
9	0	-60
10	98	-56
11	80	-38
12	97	90
13	133	118
14	0	15
15	0	22
16	118	98
H,K= 0, 5		
L	FOBS	FCAL
1	78	83
2	46	97
3	70	-41
4	148	-145
5	129	-84
6	47	14
7	193	-186
8	79	-60
9	70	20
10	96	15
11	76	-84
12	59	-108
H,K= 1, 5		
L	FOBS	FCAL
0	51	49
1	98	151
2	123	109
3	88	41
4	83	-38
5	39	16
6	110	-151
7	94	-124
8	178	-183
9	0	-11
10	280	-258
11	106	-145
12	58	-85
H,K= 2, 5		
L	FOBS	FCAL
0	83	35
1	151	-135
2	52	-84
3	133	184
4	143	155
5	170	147
6	66	-37
7	62	73
8	53	-63
9	50	-59
H,K= 3, 5		
L	FOBS	FCAL
0	0	-7
1	39	37
2	109	-165
3	0	-10
4	145	-204
5	0	31
6	32	-52
7	278	255
8	77	104
9	66	78
10	44	-64
11	90	112
12	70	106
H,K= 4, 5		
L	FOBS	FCAL
0	51	57
1	47	21
2	53	-21
3	42	-28
4	65	59
5	50	-68
6	151	-188
7	0	-27
8	0	7
9	75	92
10	0	-38
11	81	110
H,K= 5, 5		
L	FOBS	FCAL
0	0	2
1	58	-11
2	0	12
3	0	-19
4	92	127
5	0	40
6	81	98
H,K= -1, 5		
L	FOBS	FCAL
1	170	-127
2	294	-185
3	332	-240
4	34	35
5	34	-31
6	52	-47
7	0	-18
8	35	15
9	169	-136
10	98	-66
H,K= -2, 5		
L	FOBS	FCAL
1	0	16
2	91	-153
3	100	111
4	0	-8
5	40	-54
6	152	-158
7	35	82
8	32	11
9	28	-56
10	54	22
11	71	87
12	0	33
13	40	-42
14	87	78
H,K= -3, 5		
L	FOBS	FCAL
1	60	30
2	141	170
3	66	67
4	124	-158
5	103	-102
6	76	98
7	0	47
8	0	-34
9	0	20
10	141	-98
11	94	-92
12	131	91
13	0	30
14	109	-92
H,K= -4, 5		
L	FOBS	FCAL
1	56	-63
2	45	48
3	110	-57
4	0	25
5	122	136
6	0	-39
7	69	-98
8	134	-146
9	71	61
10	108	77
11	0	23
12	347	-220
13	112	69
14	58	12
15	84	-64
16	53	80
H,K= -5, 5		
L	FOBS	FCAL
1	57	66
2	44	44
3	0	-8
4	0	-21
5	0	11
6	72	102
7	0	9
8	51	53
9	0	17
10	0	5
11	37	-34
12	84	-65
13	117	-96
14	120	138
15	114	-63
H,K= -6, 5		
L	FOBS	FCAL
5	60	-61
6	54	61
7	54	-36
8	54	37
9	118	-100
10	111	96
11	101	-80
12	85	75
13	66	-75
H,K= 0, 6		
L	FOBS	FCAL
0	42	62
1	29	-49
2	59	89
3	80	-99
4	55	53
5	128	87
6	116	114
7	45	73
8	36	69
9	0	-26
10	41	-63
11	0	-13
12	68	-126
13	0	-26
14	0	-56
15	96	-94
H,K= 1, 6		
L	FOBS	FCAL
0	27	-54
1	20	-31
2	48	37
3	59	79
4	134	-161
5	171	-231
6	76	-97
7	143	138
8	86	110
9	51	70
10	82	130
H,K= 2, 6		
L	FOBS	FCAL
0	0	-4
1	115	-133
2	83	-50
3	71	93
4	18	-63
5	19	19
6	35	62
7	56	-58
8	190	-225
H,K= 3, 6		
L	FOBS	FCAL
0	44	-6
1	0	34
2	29	4
3	0	-19
4	53	103
5	22	-20
6	33	49
7	62	79
8	94	100
9	55	-102
10	35	-42
11	25	-44
H,K= 4, 6		
L	FOBS	FCAL
0	0	-22
1	23	-71
2	24	52
3	24	-33
4	24	0
5	0	-37
6	0	-20
7	0	-65
8	44	50
9	36	61
10	44	3
H,K= -1, 6		
L	FOBS	FCAL
1	15	-2
2	23	-21
3	88	103
4	76	107
5	50	23
6	15	-3
7	104	-128
8	80	-120
9	43	-67
10	196	-205
11	82	-118
12	0	-0
13	130	-173
H,K= -2, 6		
L	FOBS	FCAL
1	0	-43
2	22	32
3	59	46
4	0	16
5	109	-93
6	52	-32
7	84	-66
8	47	-27
9	82	-143
10	153	133
11	104	-104
H,K= -3, 6		
L	FOBS	FCAL
1	28	-9
2	19	5
3	48	25
4	175	-155
5	146	-157
6	45	-43
7	97	138
8	0	-12
9	90	-115
10	50	-41
11	212	176
12	212	-214
H,K= -4, 6		
L	FOBS	FCAL
1	32	-38
2	94	-67
3	39	36
4	45	-93
5	79	64
6	33	-2
7	90	53
8	182	-212
9	139	125
10	153	-122
11	101	114
H,K= -5, 6		
L	FOBS	FCAL
1	43	58
2	0	0
3	79	60
4	35	-5
5	56	45
6	109	-129
7	43	64
8	44	-22
9	57	62
10	0	-27
11	57	-72

Discussion

The large standard deviations in most of the interatomic distances (0·03 Å) and the rather deviant values for some of these distances in the ring are undoubtedly due to two factors: (1) the error in reading photographic intensities visually and (2) the relatively high temperature factors — indicating a large amount of thermal motion, particularly in the atoms of the ring. The same relationship of results was also obtained in the derivative molecule, 7,7′-dihydro-β-carotene (Sterling, 1964). However, in both molecules, the values of the interatomic distances in the chain are reasonable, and the temperature factor is considerably lower in the chain atoms than in the ring atoms.

If, despite the large standard deviations, the intrachain distances be accepted as approximately correct, a curious relationship is found. Whereas in 7,7′-dihydro-β-carotene the interatomic carbon–carbon distances in the center of the conjugated chain tend toward a uniform intermediate length, indicating bonds of a mixed character (*cf.* Coulson, 1939), in β-carotene, the shorter and larger bond lengths are clearly alternating: there is little sign of bonds of mixed nature. (Note that the polyene chains in all-*trans*-β-ionylidenecrotonic acid (Eichhorn & MacGillavry, 1959) and in vitamin-A acid (Stam & MacGillavry, 1963) likewise have no bonds of mixed character). Neither the bond distances nor the bond angles support the speculated values given by Pauling (1939) in developing his concept of stable and unstable *cis* configurations.

Although it was expected that the β-ionone ring of all-*trans*-β-carotene should continue the all-*trans* relationship from the chain (similarly to that in all-*trans*-β-ionylidenecrotonic acid, Eichhorn & MacGillavry, 1959), an *s-cis*-arrangement about the C(7)–C(6) bond was found instead. (Precedence for such a structure is given in Sly's (1955) two-dimensional resolution of 15,15′-dehydro-β-carotene and in the structure of vitamin-A acid (Stam & MacGillavry, 1963)). The *s-cis* arrangement is confirmed not only by the relatively low *R* value obtained and the short length of the C(6)–C(5) bond (1·35 Å), but also by the fact that the angles about the atoms at each end of the C(6)–C(5) bond total 360·0°. Thus, there is little question about this aspect of the molecular structure.

The final structure confirms Taylor's (1937) interpretation of the optical data to the effect that the double bonds in the chain are more or less parallel to [010] (Fig. 3). However, these bonds are sufficiently anti-parallel so that the assumption of their parallelism is not adequate for the structure resolution. It is noteworthy that the polyene chain is curved, with the methyl groups on the convex side. This relationship was found in vitamin-A acid (Stam & MacGillavry, 1963), in 7,7′-dihydro-β-carotene (Sterling, 1964), and in androsterone (High, 1962).

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