gerite, pharmacolite, and $Na_2HAsO_4.7H_2O$, the dimensions associated with the hydrogen bond of the anionic hydrogen are remarkably similar; the average values for As–O–H, O–H (uncorrected), O$\cdots$O, and O–H$\cdots$O are, respectively, 110°, 1·01 Å, 2·67 Å and 164°.

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The Crystal Structure of All-*trans* Retinal₁

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The crystal structure of all-*trans* retinal₁ has been determined by the symbolic addition method and refined by block-diagonal least-squares calculations with three-dimensional data collected using diffractometers. The crystal is monoclinic, space group $P2_1/n$, with $a = 15\cdot270$, $b = 8\cdot264$, $c = 14\cdot942$ Å, $\beta = 104\cdot73°$, and 4 molecules in the unit cell. The introduction of some disorder in the cyclohexene ring gave the final discrepancy index R of 8·8%. With the exception of the nearly s-*cis* orientation about the single bond from the chain to the cyclohexene ring, the chain is in the all-*trans* configuration. The dihedral angle between the planes of the ring and the chain is 62°. The average values of single and double bonds of this conjugated linear chain are 1·460 and 1·336 Å respectively. The chain is markedly curved in its plane and slightly bent normal to its plane.

Introduction

Retinal (vitamin-A aldehyde) is the chromophore of the visual pigments. It is well known that the only action of light in vision is to isomerize the retinal molecule from 11-*cis* to the all-*trans* configuration (Hubbard & Kropf, 1958; Wald, 1968). To understand the initial process of visual excitation, it is necessary to disclose the mechanism of *cis-trans* isomerization of retinal combined with opsin.

The present study is the first part of a project which has been undertaken in order to explain the photoreceptor process on the basis of the molecular structure of stereoisomers of retinal and retinal-related compounds. The numbering of the atoms is shown in Fig. 1.

Experimental

Crystals of all-*trans* retinal₁ were obtained as pale yellow parallelepipeds from light petroleum below 0°C.

Two sets of three-dimensional intensity data were used in this work. The first set of data was recorded by the Rigaku Denki AFC-I, an automatic four-circle diffractometer operated in a open-loop manner by a

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NEAC-2101 computer. The programs written by Ueki were used for the goniostat setting and the data processing. Integrated intensities were obtained for $2\theta \le 110°$ by the ω–2θ scanning method using Ni-filtered Cu $K\alpha$ radiation and a scintillation counter with pulse height discrimination. A total of 2384 independent reflexions were collected, of which 272 were too weak to be measured. These intensity data were used in the initial stage of the structure determination.

The second set of intensity data was collected for a second crystal on an AFC-III, operated in a closed-loop manner by a FACOM 270-20 computer, with Mo $K\alpha$ radiation monochromatized by the (200) plane of a LiF crystal, detected by a scintillation counter with pulse height discrimination. A total of 5541 independent reflexions were measured for $2\theta \le 60°$ by the ω–2θ scanning mode, and of these, 2729 with intensities less than twice the standard deviation were given values of zero. The measured intensities were corrected for Lorentz and polarization factors, and also corrected for reduction in the intensities of standard reflexions

measured every 50 reflexions during the data collection. As spectroscopic data showed that a crystal did not undergo an appreciable change by light and oxygen during the data collection, this reduction might be attributed to the radiation damage that the crystal suffered. No correction was made for absorption.

Lattice parameters were obtained from measurements of diffraction angles on the diffractometer with Cu $K\alpha$ radiation and the systematic extinctions were examined on the Weissenberg diagrams. The crystal data are as follows (Kuwabara, Hamanaka & Mitsui, 1968):

All-*trans* retinal$_1$, $C_{20}H_{28}O$, M.W. 284·4
Monoclinic
Space group $P2_1/n$, from the systematic absences of $h0l$ for $h+l$ odd, and $0k0$ for k odd

$a = 15·270$ (4) Å, $b = 8·264$ (2), $c = 14·942$ (3)
$\beta = 104·73$ (2)°
$V = 1823·6$ Å^3, $Z = 4$
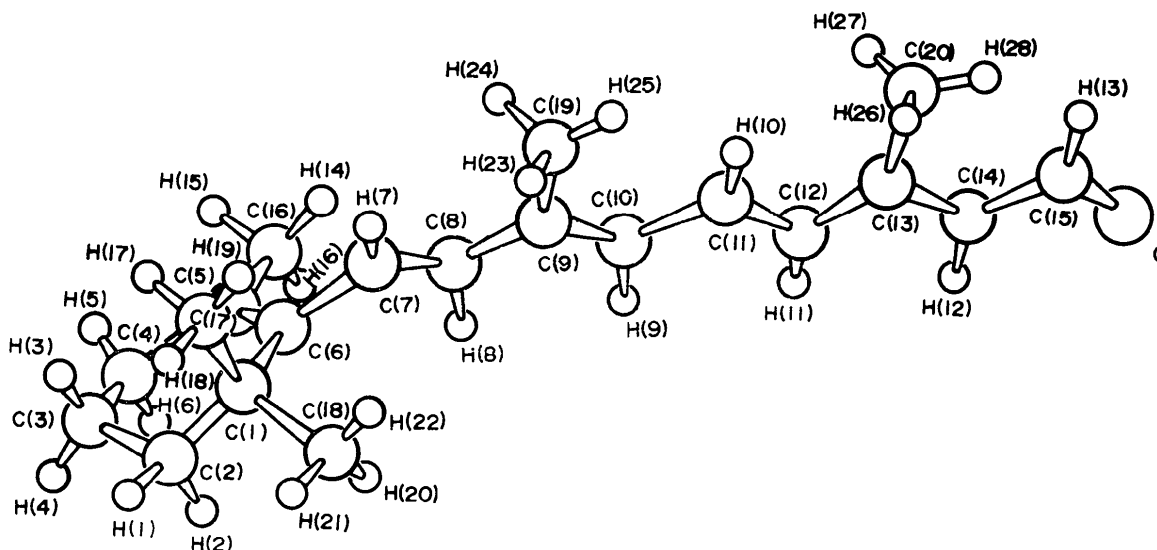$D_m = 1·02$ g.cm^{-3}, $D_x = 1·03$ (5) g.cm^{--3}.
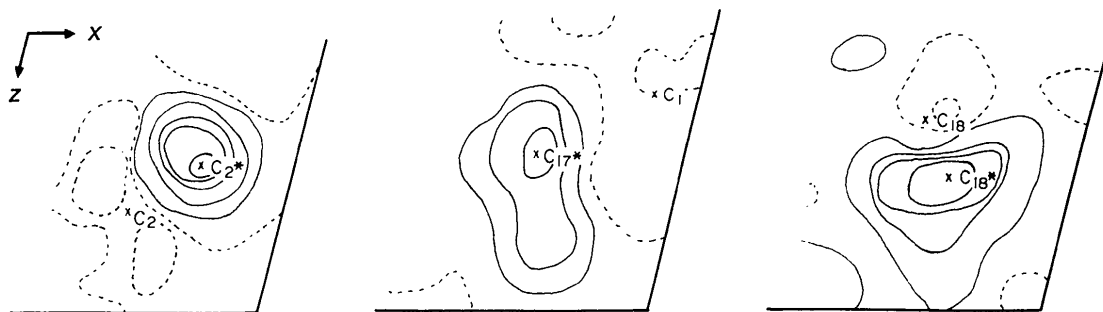

Fig. 1. Numbering of the atoms.

Fig. 2. Sections of the difference synthesis calculated with individual isotropic temperature parameters. The three sections, which are parallel to (010), do not pass exactly through the core of all minima and maxima. Contours at intervals of 0·15 e.Å^{-3}. Zero and negative contours are dotted.

(The standard deviations given in parentheses refer to the last figure.)

Structure determination and refinement

The orientation of an all-*trans* planar chain could be deduced from the sharpened three-dimensional Patterson map. However, since further attempts to solve the structure with the map were unsuccessful, solution of the structure with the aid of the symbolic addition procedure (Karle & Karle, 1966) was tried. The program written by one of the authors (TA) was used for a computation of normalized structure factors and a $\sum_2$ listing. Positive signs were given to three reflexions to define the origin and symbols were assigned to the phases of two additional reflexions as follows:

h	k	l	$|E|$	Sign
7	5	$\bar{5}$	4·01	+
1	1	$\overline{12}$	3·19	+
0	3	11	3·83	+
4	4	8	2·99	A
10	4	$\bar{6}$	4·18	B

After several cycles of the phase-determining process the signs of 123 out of 158 reflexions used in this procedure were tentatively assigned. As there were strong indications that B was negative, three-dimensional E maps were computed only for $A = +$, $B = -$ and $A = -$, $B = -$. The coordinates of all the non-hydrogen atoms except for C(18) were obtained from the E map corresponding to $A = +$ and $B = -$. The Fourier map based on these 20 atomic positions revealed the position of the C(18) atom.

After four cycles of isotropic block-diagonal least-squares calculations, using all the intensity data with equal weight, the R value was reduced from 0·42 to 0·20. A further five cycles of refinement employing anisotropic thermal parameters reduced the R value to 0·17.

A three-dimensional difference Fourier synthesis showed all the hydrogen atoms. Three more maxima (about 0·6 e.Å⁻³) were observed in positions where no atoms had been located (Fig. 2). These three peaks could be explained by assuming alternative positions (disorder) of C(2), C(17) and C(18), which have abnormally large thermal parameters. A similar situation is found in 15,15′-dehydrocanthaxanthin (Bart & MacGillavry, 1968). We have denoted them by C(2*), C(17*) and C(18*). It seems appropriate to consider 20% disorder from a difference map and a dependence of R on the degree of disorder.

Further refinement of the structure was done by the use of the data from the second crystal. Unit weight was assigned for all the reflexions, except for those of zero intensity which were not included in the calculation. Several more cycles of anisotropic refinement of the non-hydrogen atoms, with isotropic hydrogen atoms, reduced R to 0·108. Refinement was continued on the assumption that about 20% of C(2), C(17) and

C(18) occupy the alternative positions. The final R value became 0·088. At this stage the maximum shift in the positional parameters was less than a half of the estimated standard deviations for non-hydrogen atoms, and less than the estimated standard deviations for hydrogen atoms. The background fluctuation in the difference synthesis was everywhere less than 0·15 e.Å⁻³. Thus the refinement was terminated.

The atomic scattering factors for C, O and H used were those given in *International Tables for X-ray Crystallography* (1962). The refinement was done with the *HBLS* IV program written by one of the authors (TA).

Table 1. *Final positional parameters (fractional coordinates* $\times 10^4$) *and their standard deviations (in* 10^{-3} Å)

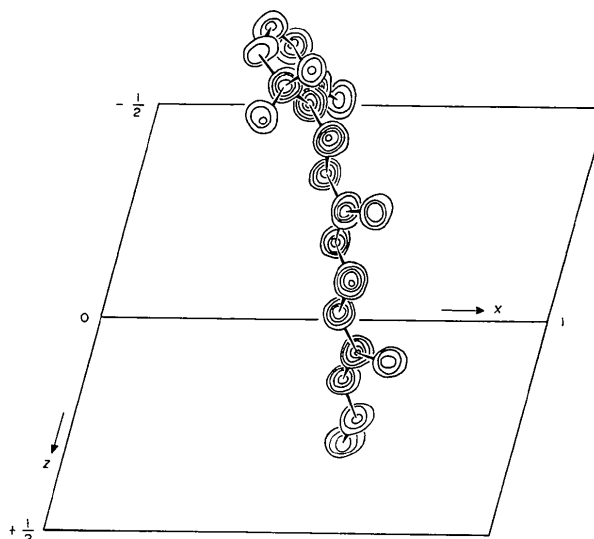|	x	y	z
C(1)	2735(3)	5912 (3)	4571 (3)
C(2)	1888 (5)	5250 (5)	3866 (5)
C(3)	2053 (4)	4067 (5)	3238 (4)
C(4)	2647 (4)	2692 (4)	3668 (3)
C(5)	3354 (3)	3098 (3)	4543 (3)
C(6)	3390 (3)	4526 (3)	4960 (3)
C(7)	4076 (3)	4902 (3)	5833 (3)
C(8)	4180 (3)	4080 (3)	6608 (3)
C(9)	4841 (3)	4415 (3)	7491 (3)
C(10)	4813 (3)	3507 (4)	8231 (3)
C(11)	5403 (3)	3619 (3)	9152 (3)
C(12)	5338 (3)	2652 (4)	9851 (3)
C(13)	5950 (3)	2634 (3)	10773 (3)
C(14)	5797 (3)	1552 (4)	11389 (3)
C(15)	6354 (4)	1320 (5)	12329 (4)
C(16)	4012 (4)	1737 (4)	4878 (4)
C(17)	3212 (5)	7197 (5)	4153 (5)
C(18)	2368 (5)	6673 (5)	5344 (5)
C(19)	5511 (3)	5738 (4)	7521 (4)
C(20)	6734 (4)	3776 (4)	10975 (4)
O	6182 (4)	0344 (4)	12855 (3)
C(2*)	2313 (15)	5614 (18)	3514 (15)
C(17*)	3341 (21)	7575 (18)	4662 (17)
C(18*)	2057 (19)	6175 (20)	5137 (18)

Fig. 3. Composite electron density sections parallel to (010). Contours at intervals of 1 e.Å⁻³ starting at 2 e.Å⁻³

Table 2. *Final thermal parameters* ($\times 10^4$) *and their standard deviations*

The thermal parameters are of the form: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	64 (1)	145 (4)	65 (1)	10 (4)	16 (2)	−1 (5)
C(2)	67 (2)	234 (9)	86 (3)	34 (8)	−10 (4)	−3 (9)
C(3)	94 (2)	284 (9)	91 (2)	−8 (8)	−53 (4)	−55 (8)
C(4)	77 (2)	203 (6)	65 (1)	−65 (6)	33 (3)	−70 (5)
C(5)	57 (1)	159 (5)	65 (1)	−22 (4)	38 (2)	−8 (5)
C(6)	52 (1)	146 (4)	55 (1)	−14 (4)	21 (2)	14 (4)
C(7)	56 (1)	151 (5)	61 (1)	−20 (4)	14 (2)	−12 (4)
C(8)	53 (1)	178 (5)	62 (1)	−17 (4)	9 (2)	−16 (5)
C(9)	52 (1)	190 (5)	59 (1)	2 (4)	16 (2)	−11 (5)
C(10)	57 (1)	205 (6)	65 (1)	−4 (5)	19 (2)	−25 (5)
C(11)	52 (1)	212 (6)	62 (1)	18 (5)	14 (2)	−31 (5)
C(12)	56 (1)	209 (6)	63 (1)	5 (5)	5 (2)	−23 (5)
C(13)	60 (1)	207 (6)	58 (1)	33 (5)	12 (2)	−36 (5)
C(14)	70 (2)	235 (7)	64 (1)	12 (6)	−4 (3)	−27 (6)
C(15)	98 (2)	293 (9)	83 (2)	−6 (8)	3 (4)	49 (8)
C(16)	81 (2)	162 (6)	98 (2)	30 (6)	32 (3)	−26 (6)
C(17)	94 (3)	166 (7)	87 (3)	−6 (8)	46 (5)	61 (8)
C(18)	78 (2)	258 (10)	85 (3)	54 (8)	33 (4)	−39 (9)
C(19)	60 (1)	247 (7)	72 (2)	−44 (6)	13 (3)	−24 (6)
C(20)	62 (1)	302 (8)	68 (2)	−22 (6)	9 (3)	−35 (7)
O	165 (3)	433 (9)	103 (2)	−85 (9)	−33 (4)	164 (8)
C(2*)	53 (7)	255 (34)	45 (7)	−5 (27)	22 (12)	50 (27)
C(17*)	112 (14)	172 (30)	65 (10)	−70 (34)	33 (19)	53 (29)
C(18*)	82 (11)	247 (38)	71 (10)	119 (34)	21 (17)	24 (33)

Fig. 3 shows a composite electron density section viewed along [010]. In Tables 1–3, final positional and thermal parameters are listed together with their standard deviations. The standard deviations of the par-

Table 3. *Fractional coordinates of the hydrogen atoms* ($\times 10^3$)

	x	y	z	Bonded to
H(1)	152	623	352	C(2)
H(2)	149	452	419	C(2)
H(3)	246	491	290	C(3)
H(4)	153	367	279	C(3)
H(5)	292	224	323	C(4)
H(6)	225	180	379	C(4)
H(7)	441	587	581	C(7)
H(8)	375	310	664	C(8)
H(9)	432	266	815	C(10)
H(10)	588	450	926	C(11)
H(11)	485	186	976	C(12)
H(12)	524	093	1123	C(14)
H(13)	694	201	1249	C(15)
H(14)	458	205	537	C(16)
H(15)	423	130	435	C(16)
H(16)	375	087	514	C(16)
H(17)	348	683	372	C(17)
H(18)	282	804	388	C(17)
H(19)	370	772	457	C(17)
H(20)	218	589	573	C(18)
H(21)	185	737	501	C(18)
H(22)	278	723	573	C(18)
H(23)	521	673	736	C(19)
H(24)	587	556	705	C(19)
H(25)	595	586	809	C(19)
H(26)	656	492	1087	C(20)
H(27)	709	359	1053	C(20)
H(28)	709	373	1159	C(20)

Average estimated standard deviations:
$\sigma_x = 0.03$, $\sigma_y = 0.04$, $\sigma_z = 0.03$ Å
Refined isotropic temperature factor $B = 3.6$ Å^2 for all hydrogen atoms.

ameters were calculated from the sum of the residuals and the diagonal terms of the inverse matrices of the normal equations. The observed and calculated structure factors are listed in Table 4.

Results and discussion

The chain has the all-*trans* configuration, except the bond from the chain to the ring, which has nearly s-*cis* conformation. The structure of retinal shows the same general features as observed in most other related structures (Bart & MacGillavry, 1968).

The best plane through the side-chain C(6)–O, C(19) and C(20) calculated with the method of least-squares is:

$$-0.710X + 0.647Y + 0.276Z - 2.105 = 0,$$

where X, Y and Z are in Å referred to orthogonal axes a, b, c^*. The distances from this plane are listed in Table 5. The chain is approximately planar and slight overall bending and twisting of the chain are observed. The system of the double bond of the ring is planar and the best plane through the atoms C(1), C(4), C(5), C(6), C(7) and C(16) is:

$$0.772X + 0.341Y - 0.536Z + 0.006 = 0.$$

The deviations of atoms from the plane are given in Table 5. The dihedral angle between the planes of the ring and the chain is 62° from exact s-*cis*. There is considerable puckering of the cyclohexene ring.

The intramolecular bond lengths and bond angles are given in Fig. 4. The bond lengths involving hydrogen atoms are listed in Table 6, and some bond angles involving hydrogen atoms in the chain are shown in Fig. 5. The estimated standard deviations of the bond

Table 4. *Observed and calculated structure factors*

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L=	0	0	2	2	-1	10	2	0	4	17	17	6	3	-3	6	5	-5	1	14	-14	8	2	-2	9	4	-4	2	5	3
2	11	-10	4	4	5	H,L=	1	11	5	9	-9	7	2	2	7	4	-3	2	31	-31	9	2	1	10	4	-4	3	4	-4
4	8	-8	H,L=	0	15	0	10	-10	7	2	1	8	5	-5	8	5	5	3	39	-37	H,L=	6	1	H,L=	7	1	4	11	-11
6	5	-6	2	1	-1	2	6	7	8	3	-3	H,L=	3	5	9	3	2	4	11	11	1	11	11	0	15	-14	5	3	-2
H,L=	0	1	3	2	0	3	20	20	H,L=	2	8	0	67	-66	10	4	3	5	5	4	2	10	10	2	9	-10	6	2	2
1	69	68	4	2	1	4	4	-3	0	4	-3	1	11	-11	H,L=	4	3	6	6	-5	3	6	5	3	19	19	7	2	1
2	48	-48	H,L=	0	16	5	2	2	1	5	-5	2	4	3	1	7	8	7	7	-7	4	7	-7	5	5	-6	9	2	-1
3	24	23	5	1	1	6	2	2	2	6	-6	3	8	-8	2	27	-26	8	2	-2	5	9	8	7	3	-3	H,L=	8	2
4	5	-4	6	0	0	8	2	-1	3	2	2	4	3	4	3	22	-21	9	3	2	6	7	-7	8	3	-2	0	16	-16
5	4	3	7	1	0	H,L=	1	12	4	9	-9	5	3	-3	4	9	-9	H,L=	5	2	7	3	-3	9	3	-2	1	4	2
6	2	0	H,L=	0	17	1	11	12	5	17	17	7	5	-5	8	3	3	1	23	22	8	3	3	H,L=	7	2	2	19	-18
7	6	-7	3	2	0	4	8	8	6	14	-14	8	2	3	11	3	3	2	38	-35	9	3	-4	1	13	-12	4	2	-1
8	5	-5	4	1	2	5	3	3	8	2	-1	10	3	2	H,L=	4	4	3	26	-25	H,L=	6	2	2	12	12	5	4	4
9	2	1	H,L=	0	18	7	1	-1	H,L=	2	9	H,L=	3	6	0	42	42	4	3	-1	0	4	-2	6	1	0	6	5	-4
H,L=	0	2	0	1	-2	8	1	0	1	7	-7	1	22	-22	1	1	0	5	2	-1	1	23	-24	7	3	-3	H,L=	8	3
0	48	47	1	2	1	H,L=	1	13	2	1	2	2	5	3	2	1	0	6	3	-1	2	5	5	8	1	0	1	4	3
1	3	-4	3	2	1	0	2	1	3	6	-6	3	13	-13	3	7	-6	7	1	-1	3	7	-6	H,L=	7	3	2	25	26
2	71	-70	4	1	0	1	2	-2	4	16	16	4	4	4	4	7	-7	8	3	2	4	4	5	0	11	-11	3	2	-2
3	14	-13	H,L=	0	19	2	3	5	5	4	-4	5	4	-3	5	4	4	10	3	2	5	8	-7	1	17	16	4	4	5
4	20	19	2	2	0	3	3	3	6	5	-5	6	3	-5	6	1	0	H,L=	5	3	6	4	-4	2	4	5	5	12	-12
5	8	-7	H,L=	0	20	4	1	1	H,L=	2	10	7	1	0	7	2	1	0	39	40	7	1	1	3	9	9	6	9	9
6	5	4	1	1	0	H,L=	1	14	0	7	-7	8	1	0	9	4	3	1	22	-22	8	1	-1	4	10	-10	7	2	1
7	2	3	H,L=	1	0	2	2	1	1	9	-9	9	3	3	10	1	1	2	32	32	9	2	0	5	5	6	H,L=	8	4
H,L=	0	3	1	66	68	3	1	1	2	13	-13	10	2	0	11	3	-1	3	7	8	H,L=	6	3	6	6	-6	0	34	33
1	2	-2	4	13	14	5	2	2	3	2	0	H,L=	3	7	H,L=	4	5	5	4	2	2	34	34	7	2	2	1	2	-2
2	3	4	5	3	-3	H,L=	1	15	4	9	8	0	5	-5	1	21	22	7	1	1	3	5	-5	H,L=	7	4	2	3	3
3	15	13	6	6	7	0	5	4	5	3	4	1	4	-4	2	4	-4	8	2	-3	4	2	3	1	6	-6	3	12	12
4	10	-9	7	7	-7	1	1	1	6	2	-1	2	11	12	3	2	-1	9	3	3	5	2	2	2	18	19	4	15	-16
6	2	2	8	2	2	2	2	3	7	1	0	3	25	25	4	2	1	10	2	1	6	2	-2	3	3	-2	5	10	11
7	3	2	9	1	2	3	2	-1	8	1	2	4	13	-14	5	10	10	H,L=	5	4	7	2	-2	5	7	-7	6	3	-3
8	2	0	H,L=	1	1	5	2	2	H,L=	2	11	6	3	-4	6	8	-9	1	46	44	8	3	3	6	8	8	7	1	0
9	2	-3	0	20	-18	6	2	0	1	6	-5	7	1	0	7	4	4	2	29	-28	9	3	-3	7	3	-3	8	1	1
H,L=	0	4	1	43	45	7	2	1	2	8	8	10	3	2	8	3	2	3	2	-1	H,L=	6	4	8	2	1	H,L=	8	5
0	26	26	2	44	45	H,L=	1	16	4	7	7	H,L=	3	8	H,L=	4	6	4	3	3	0	30	28	H,L=	7	5	1	4	-4
1	10	-11	4	2	-1	1	2	2	5	1	1	1	10	10	0	30	29	5	9	9	1	1	-1	0	14	-13	2	10	-10
2	18	16	6	10	11	2	3	2	6	3	-3	3	2	-2	1	9	-9	8	2	2	2	11	-11	1	12	11	3	11	12
4	3	2	7	3	4	H,L=	1	18	H,L=	2	12	4	5	5	2	8	-9	H,L=	5	5	3	7	7	2	20	21	4	2	-3
5	17	-17	8	4	-3	2	1	1	0	16	17	7	7	-8	3	3	-3	0	31	-32	4	14	13	3	12	-12	5	5	-6
6	3	-3	9	2	1	3	2	-2	1	4	4	8	1	1	4	8	9	1	24	-24	10	3	-3	5	7	8	6	6	6
7	6	5	10	2	2	4	1	0	2	3	-4	9	2	1	5	12	-12	2	7	6	H,L=	6	5	6	2	-3	7	3	-3
8	7	-8	H,L=	1	2	5	1	0	3	5	6	H,L=	3	9	6	5	4	3	8	-8	2	13	-14	7	2	2	H,L=	8	6
9	3	-2	1	37	-37	H,L=	1	19	5	3	1	2	6	-6	7	3	-3	4	14	14	3	9	9	8	2	-1	1	10	-10
H,L=	0	5	2	56	-56	0	2	2	6	2	-2	3	3	2	8	4	4	5	9	-9	4	14	-14	9	2	1	3	8	8
2	16	16	3	10	9	2	2	-1	7	2	1	4	14	-15	H,L=	4	7	6	6	6	5	4	4	H,L=	7	6	4	2	-1
3	13	-12	4	19	-18	3	2	1	8	2	1	5	9	-10	1	9	9	8	1	0	6	2	3	1	16	16	5	7	-7
4	12	-12	5	7	8	H,L=	2	0	H,L=	2	13	6	3	2	2	10	-10	H,L=	5	6	7	1	2	2	22	23	7	2	3
5	22	-21	7	9	9	0	9	-6	1	7	8	9	2	1	3	15	-14	1	9	-9	8	2	-1	3	4	4	H,L=	8	7
7	1	-1	8	8	9	1	33	-32	2	5	-5	H,L=	3	10	4	6	6	2	5	5	H,L=	6	6	4	5	-5	1	4	-4
8	3	2	9	3	1	2	8	8	6	3	2	1	11	-11	5	1	-1	3	1	3	0	9	-9	6	3	-3	2	1	1
9	1	-1	H,L=	1	3	3	15	14	7	2	1	2	20	-21	6	2	-2	4	18	-18	1	1	0	7	2	2	3	2	3
H,L=	0	6	0	2	-2	4	7	-7	H,L=	2	14	3	10	-10	7	3	4	5	21	21	2	9	-9	8	2	3	4	2	2
0	16	-17	1	34	-33	5	5	5	0	2	2	5	3	4	H,L=	4	8	6	8	-8	3	7	-7	H,L=	7	7	5	3	2
1	29	29	2	6	7	6	3	3	1	1	1	6	3	3	1	3	-3	7	1	1	4	12	13	0	3	4	6	2	3
2	19	-18	3	17	-17	7	13	13	2	1	0	H,L=	3	11	2	7	-8	H,L=	5	7	5	4	-4	1	2	3	H,L=	8	8
3	10	11	4	26	-26	8	2	1	3	2	-1	0	10	-9	3	5	-4	0	12	13	7	2	0	2	11	12	0	2	2
4	11	-11	5	7	6	9	3	-3	H,L=	2	15	1	2	0	4	18	18	1	2	2	H,L=	6	7	3	2	2	1	6	-6
5	6	-7	6	14	14	10	2	-2	2	2	-2	2	4	4	5	2	-3	2	8	8	1	4	3	4	4	-4	2	0	-1
7	10	11	7	13	13	H,L=	2	1	3	2	-1	3	6	-6	6	11	-11	3	9	-10	2	4	5	5	14	14	3	6	6
8	3	-4	10	4	-2	1	62	-62	4	1	1	5	1	1	7	2	2	4	6	-6	3	9	9	6	5	6	4	2	2
H,L=	0	7	H,L=	1	4	2	27	-27	6	2	1	6	2	-1	H,L=	4	9	6	7	8	4	6	6	7	3	-2	H,L=	8	9
1	23	22	1	7	7	3	36	35	H,L=	2	16	9	2	1	1	3	3	7	3	-2	5	2	-3	H,L=	7	8	1	3	3
4	5	-5	2	13	12	4	16	15	0	2	1	H,L=	3	12	2	2	-2	8	1	1	6	10	10	1	3	3	2	2	2
5	6	-6	3	28	27	5	10	-9	1	2	1	1	1	0	3	4	-4	9	3	-2	7	2	3	2	8	8	3	4	-4
6	6	4	4	25	24	6	11	11	2	1	1	2	3	3	4	19	-19	H,L=	5	8	8	4	-4	3	8	8	4	2	-2
8	3	3	5	2	0	7	4	6	H,L=	2	17	3	2	-3	6	4	-4	1	2	1	H,L=	6	8	4	9	9	H,L=	8	10
H,L=	0	8	6	5	6	9	1	1	1	2	-1	H,L=	3	13	H,L=	4	10	2	5	7	0	3	4	5	1	1	0	3	3
0	12	13	7	2	-2	10	1	1	2	2	-1	0	6	-6	0	8	-9	3	2	-3	1	9	10	H,L=	7	9	1	5	-4
1	20	19	9	4	-3	11	1	1	4	1	0	4	2	-2	1	2	-2	4	3	-4	2	13	13	0	5	6	2	1	0
2	6	4	11	2	-1	H,L=	2	2	5	1	1	H,L=	3	14	2	13	-14	5	2	2	3	20	20	2	6	6	3	1	-1
3	20	-19	H,L=	1	5	0	69	-70	H,L=	2	18	3	1	-2	3	12	-12	H,L=	5	9	4	10	11	3	2	-1	5	3	2
4	4	5	0	34	35	1	7	7	0	3	-2	4	3	-1	5	7	-7	0	2	-2	6	4	-4	4	4	4	H,L=	8	11
6	2	0	1	7	8	2	37	37	1	3	2	6	2	0	6	3	-2	1	5	4	H,L=	6	9	H,L=	7	10	2	2	1
7	3	3	2	14	14	3	34	33	H,L=	2	19	H,L=	3	15	H,L=	4	11	2	3	3	1	7	7	1	4	5	3	2	0
8	3	-3	3	10	10	4	18	19	1	1	0	1	2	0	1	7	-8	3	11	-10	2	10	10	2	8	-9	4	3	3
9	2	1	9	4	-4	5	16	-17	2	2	1	4	2	2	2	2	3	4	11	-11	3	3	4	3	2	4	7	3	2
10	3	-2	10	2	-2	6	4	4	H,L=	3	0	H,L=	3	16	3	5	-5	5	3	3	4	5	-5	4	1	-2	H,L=	8	12
H,L=	0	9	H,L=	1	6	7	12	13	1	50	49	3	2	-1	4	4	-4	6	2	3	6	2	-2	5	3	-3	0	5	-5
1	7	-7	1	30	-30	8	5	6	2	58	58	4	2	-1	5	3	-3	7	3	-2	7	1	2	6	2	0	1	1	0
2	3	-2	2	11	11	10	2	1	4	31	30	H,L=	3	17	6	3	3	H,L=	5	10	H,L=	6	10	7	2	-2	3	1	0
3	5	5	7	2	3	H,L=	2	3	5	12	-10	0	1	0	H,L=	4	12	1	1	-2	0	5	6	H,L=	7	11	6	2	2
4	4	-5	8	4	-4	1	40	40	6	2	-1	1	1	-2	1	3	3	2	5	-5	1	9	-10	0	2	1	H,L=	8	13
5	4	3	11	2	-1	2	18	-19	7	6	6	2	2	-2	2	3	-3	3	1	-2	4	1	-1	1	1	1	2	2	-3
6	3	2	H,L=	1	7	3	36	36	8	2	1	4	2	1	3	4	4	4	2	-3	5	1	-1	3	2	2	H,L=	8	14
7	3	2	0	19	-18	4	9	8	H,L=	3	1	H,L=	3	18	4	2	-3	5	1	1	H,L=	6	11	4	1	-2	2	1	-2
H,L=	0	10	1	7	-7	6	8	8	0	31	30	1	2	-1	H,L=	4	13	H,L=	5	11	2	1	0	5	1	1	H,L=	8	15
0	4	-3	2	6	-7	7	7	7	1	39	39	2	1	0	1	5	-4	0	13	-14	3	3	2	6	4	-4	1	2	-2
1	7	6	4	4	-4	8	1	0	2	40	38	4	2	-1	4	3	-3	1	2	2	H,L=	6	12	H,L=	7	12	2	2	2
2	3	4	5	7	8	H,L=	2	4	4	5	-5	H,L=	3	19	5	3	3	4	3	3	0	3	4	1	2	-2	H,L=	8	16
3	15	-15	6	2	-1	0	18	-18	6	2	-1	2	3	0	H,L=	4	14	H,L=	5	12	1	4	-4	2	1	1	0	4	3
4	6	7	7	5	6	1	40	40	7	2	-2	H,L=	4	0	0	1	-1	2	4	4	H,L=	6	13	5	2	-2	2	3	-3
5	10	10	H,L=	1	8	2	6	7	8	5	5	0	9	-8	1	2	-2	3	1	-2	1	1	0	6	3	2	3	2	2
6	3	2	3	15	15	3	22	21	9	2	-3	1	8	8	2	2	-1	5	2	0	2	1	1	H,L=	7	13	H,L=	9	0
8	2	3	5	2	-2	4	17	17	10	2	1	2	23	-22	3	1	-1	H,L=	5	13	3	2	-1	1	1	0	1	15	-15
H,L=	0	11	6	7	7	8	3	2	H,L=	3	2	3	36	34	H,L=	4	16	2	2	0	6	2	-1	2	1	0	2	2	1
1	5	-5	7	5	-5	9	2	-2	1	16	-16	4	13	-12	0	3	2	4	2	2	H,L=	6	14	H,L=	7	14	3	9	9
2	4	5	H,L=	1	9	H,L=	2	5	2	12	11	5	3	-2	1	1	0	5	2	-2	0	2	-1	1	2	-1	6	4	4
3	22	22	0	14	-13	1	52	-49	3	6	-6	6	9	-9	2	2	2	H,L=	5	14	2	2	0	H,L=	7	15	7	1	1
5	3	2	1	9	7	2	3	3	5	3	-3	7	5	-5	3	3	-2	1	2	2	5	3	3	2	3	1	9	3	2
6	3	-2	2	4	4	3	12	11	6	9	-9	9	4	-4	4	2	1	4	2	-3	6	2	-2	3	2	2	H,L=	9	1
7	2	-1	3	7	7	4	10	10	7	6	6	H,L=	4	1	H,L=	4	17	H,L=	5	15	H,L=	6	15	H,L=	7	16	1	6	-6
8	1	1	4	5	-5	5	7	7	8	2	-2	1	21	-21	2	1	0	1	2	1	2	2	1	1	3	3	2	12	11
9	1	0	5	10	-10	7	2	3	9	4	4	2	9	-9	3	1	1	3	2	3	3	2	1	H,L=	7	17	3	18	-18
H,L=	0	12	6	7	8	8	6	-7	H,L=	3	3	3	8	-9	H,L=	4	18	H,L=	5	16	H,L=	6	16	1	2	-2	4	3	-4
0	16	16	7	2	1	H,L=	2	6	0	18	-18	4	5	6	0	3	-2	1	3	2	0	2	2	2	1	2	5	5	6
1	10	9	8	2	-1	0	17	-16	1	31	31	6	3	-2	H,L=	5	0	H,L=	5	17	H,L=	6	17	H,L=	8	0	6	1	0
2	5	5	9	1	2	1	47	45	2	7	-7	7	6	-5	1	17	16	1	4	-3	1	2	1	0	10	-10	7	2	-3
3	2	2	H,L=	1	10	2	14	-13	3	7	-7	8	8	-8	2	10	-10	2	2	3	2	2	-2	1	2	-1	8	2	1
H,L=	0	13	1	7	-7	3	2	-1	4	12	12	10	2	2	3	37	-36	H,L=	6	0	H,L=	7	0	2	2	-2	9	3	2
1	3	2	2	3	-3	6	3	3	5	11	11	H,L=	4	2	4	8	7	0	8	-9	2	6	5	3	10	9	H,L=	9	2
2	1	0	3	13	-13	7	7	-7	6	3	-1	0	25	25	5	2	1	1	5	-5	3	11	-11	5	5	4	1	8	-8
3	2	2	4	11	11	8	3	3	8	4	4	1	13	14	6	2	-2	2	3	2	4	1	1	6	1	2	2	10	-10
4	5	5	5	1	0	H,L=	2	7	H,L=	3	4	2	4	-6	8	2	-2	3	4	4	5	7	7	7	3	3	3	10	10
6	3	-2	6	2	3	1	2	1	1	27	28	3	25	-25	9	4	-4	5	5	6	6	2	3	9	3	-2	5	6	-6
H,L=	0	14	7	4	4	2	14	-16	3	2	0	4	11	-11	H,L=	5	1	6	2	2	7	1	0	H,L=	8	1	9	3	2
1	2	-1	8	2	-2	3	15	-16	4	12	11	5	13	-12	0	53	-53	7	3	3	8	2	2	1	9	-9	H,L=	9	3

Table 4 (cont.)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC

H,L= 6 -1

Table 5. *Distances from the plane*

$$-0.710X + 0.647Y + 0.276Z - 2.105 = 0$$

C(6)	−0.050 Å	C(1)	1.142 Å
C(7)	−0.011	C(4)	−1.090
C(8)	−0.048	C(5)	−1.055
C(9)	0.004	H(7)	0.123
C(10)	0.042	H(8)	−0.078
C(11)	0.076	H(9)	0.063
C(12)	0.095	H(10)	0.101
C(13)	0.038	H(11)	0.140
C(14)	0.035	H(12)	0.201
C(15)	−0.066	H(13)	−0.225
C(19)	0.004		
C(20)	−0.067		
O	−0.051		

$$0.772X + 0.341Y - 0.536Z + 0.006 = 0$$

C(1)	0.028 Å	C(2)	−0.406 Å
C(4)	−0.022	C(3)	0.122
C(5)	−0.006	C(17)	1.401
C(6)	−0.007	C(18)	−1.012
C(7)	−0.021	C(2*)	0.580
C(16)	0.028	C(17*)	1.115
		C(18*)	−1.307

lengths and angles involving non-hydrogen atoms are 0.004–0.007 Å and 0.3–0.4°. Very high σ values are found for bonds in which one of the bonded atoms is C(2*), C(17*) or C(18*). Their values are about 0.02 Å for bond lengths and 1.0° for bond angles. Average σ values are 0.04 Å for C–H bonds and 2° for $\angle$C–C–H. The bond distances in the chain show the alternation of shorter and longer bonds (bond alternation), and a systematic decrease in the alternative character of the single and double bonds towards the centre of the molecule (size effect). Those are expected from theoretical investigations by Labhart (1957), Ooshika (1957), Longuet-Higgins & Salem (1959), Suzuki & Mizuhashi (1964) and others.

The bond angles in the chain, with the exception of those around C(9) and C(13), show a characteristic feature descibed below. The C–C–C bond angles along the chain have a mean value of 125.1°. The mean values of the C–C–H bond angles opposite the single and double bonds are 119° and 115° respectively. The dif-

Table 6. *Bond lengths involving the hydrogen atoms*

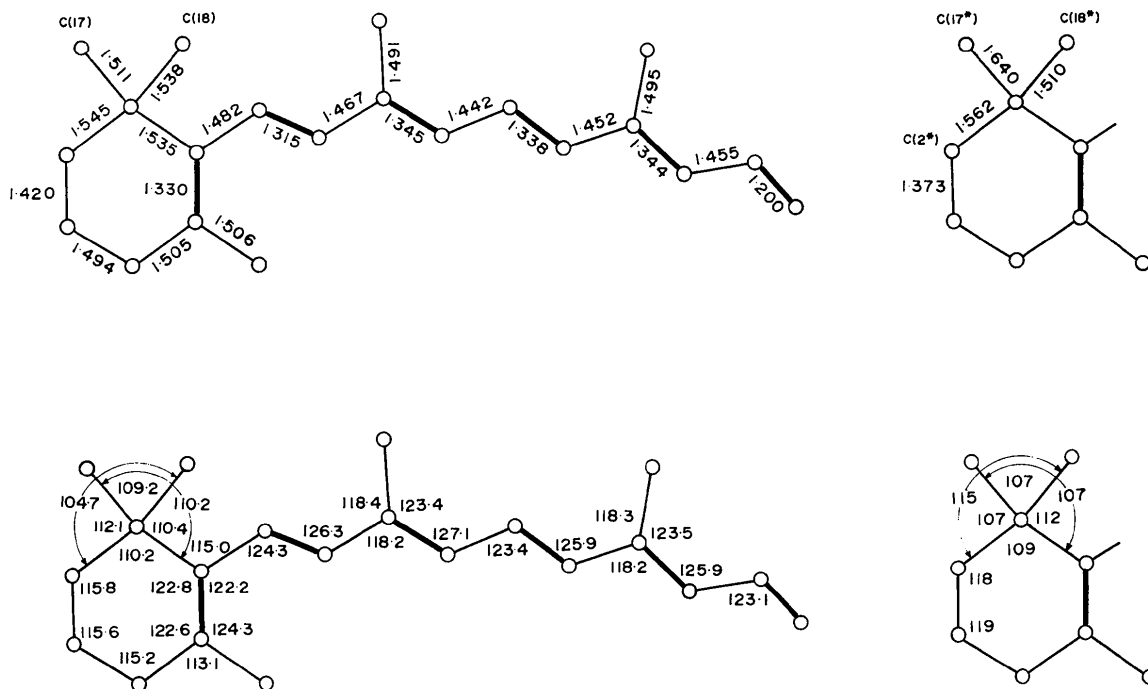|					
C(2)–H(1)	1.05 Å	C(10)–H(9)	1.02 Å	C(17)–H(19)	0.95 Å
C(2)–H(2)	1.05	C(11)–H(10)	1.02	C(18)–H(20)	0.96
C(3)–H(3)	1.13	C(12)–H(11)	0.98	C(18)–H(21)	1.00
C(3)–H(4)	0.96	C(14)–H(12)	0.97	C(18)–H(22)	0.88
C(4)–H(5)	0.94	C(15)–H(13)	1.04	C(19)–H(23)	0.94
C(4)–H(6)	1.00	C(16)–H(14)	1.03	C(19)–H(24)	1.01
C(7)–H(7)	0.96	C(16)–H(15)	1.00	C(19)–H(25)	0.94
C(8)–H(8)	1.06	C(16)–H(16)	0.95	C(20)–H(26)	0.99
		C(17)–H(17)	0.90	C(20)–H(27)	0.98
		C(17)–H(18)	0.95	C(20)–H(28)	0.95

Fig. 4. Bond lengths and bond angles.

ferences among these angles are due to bond alterna-
tion. The bond angles opposite the methyl groups are
significantly decreased and the above mentioned sys-
tematic property is lost. This is owing to repulsion be-
tween the methyl groups and H(7), H(10) and H(13),
and causes the in-plane bending of the chain which is
also seen in related structures. The above situations
coincide qualitatively with the results of CNDO cal-
culation (Suzuki, Takizawa & Komatsu, 1971). The
three C–CH₃ bond distances, C(5)–C(16), C(9)–C(19)
and C(13)–C(20), which are single bonds attached to
the conjugated system, appear to be significantly
shortened, their average bond length being 1·497 Å.
The bond length C(2)–C(3) is unusually short as a
single bond. This is also observed in all structures of
this class of compound. It is not clear how to account
for this, though the C(2) atom suffers from disorder.
The deviations from tetrahedral values for some angles
around C(1), C(2), C(3) and C(4) may be significant.
The puckering of the ring gives a staggered conforma-
tion for H(1) and H(2) with H(3) and H(4). The con-
formation of the hydrogen atoms in the methyl groups
C(17) and C(18) can be described as staggered with
respect to C(2), C(16), C(18) and C(2), C(6), C(17)
respectively. These situations are similar in 15,15'-de-
hydrocanthaxanthin (Bart & MacGillavry, 1968).

A view of the packing of the molecules in the crystal
is shown in Fig. 6, a projection of the structure
along [010]. The chain direction is roughly parallel to
[225], and the plane of the chains is tilted at 50° to the
xz plane. The ring is on the plane which passes roughly
through the origin. All intermolecular distances less
than 4·0 Å between non-hydrogen atoms and those
less than 3·0 Å involving hydrogen atoms have been
calculated. None of the contacts is less than the normal
van der Waals seperation.

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laboratory of the Institute for Protein Research, Osaka
University. The authors are also indebted to Dr T.
ried out on the HITAC 5020E Computer of the Com-
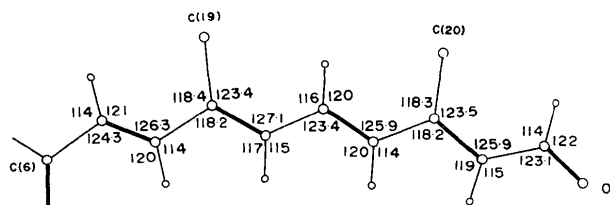puter Centre of the University of Tokyo.

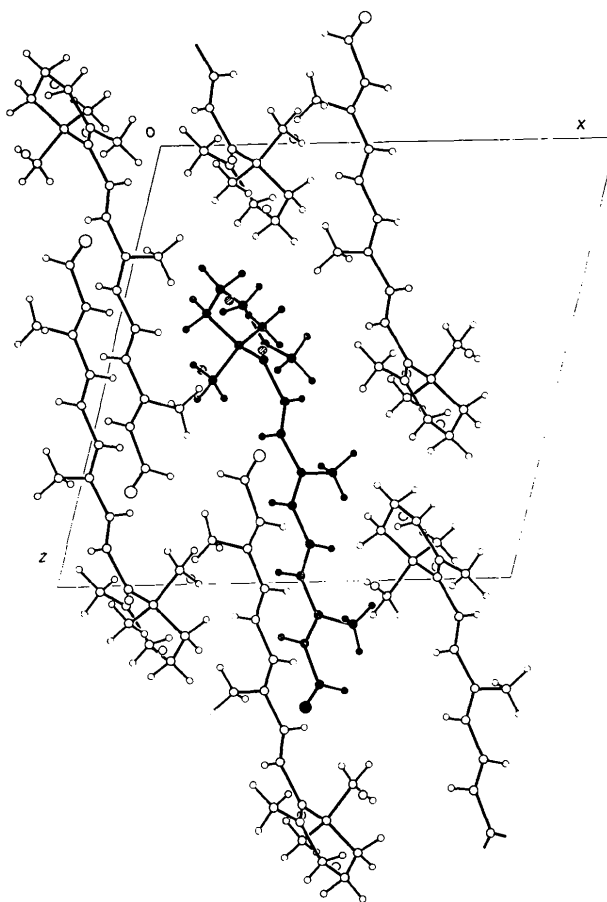Fig. 5. Bond angles involving hydrogen atoms in the chain.

Fig. 6. Projection of the structure along [010]. The shaded
atoms are C(2*), C(17*) and C(18*).

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