while their great elasticity and flexibility makes them suitable as monochromatizing crystals with variable curvature.

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The Crystal Structure of 15,15′-Dehydro-β-carotene*

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The crystal structure of 15,15′-dehydro-β-carotene, $C_{40}H_{54}$, at −20 °C has been determined by Fourier and least-squares analysis of complete three-dimensional intensity data from iron $K\alpha$ X-radiation. The crystals are monoclinic with space group $P2_1/c$; the unit cell, which contains two centrosymmetric molecules, has the dimensions $a = 8{\cdot}14_5$, $b = 31{\cdot}8_7$, $c = 8{\cdot}46_5$ Å, $\beta = 128° \; 18{\cdot}_8'$. With the exception of the *s-cis* orientation about the single bond from the chain to the cyclohexene ring the molecule is in the all-*trans* configuration. The central 18 carbon atoms of the structure are coplanar within 0·11 Å and deviations from planarity are consistent with the intermolecular arrangement. The single and double bonds of this highly conjugated linear molecule are distinctly different in length with average values of 1·455 and 1·345 Å, respectively. Despite rather large thermal motions of the molecule it has been possible to assign parameters to all of the hydrogen atoms, there being no evidence for the free rotation of the methyl groups.

Introduction

A previous communication (Sly, 1955) presented a projected structure of 15,15′-dehydro-β-carotene (DHC) (Fig. 1) along with preliminary three-dimensional coordinates and a brief description of the methods of analysis. The present paper on the structure of DHC reports the results of a three-dimensional refinement for this highly conjugated carotene using the previous data, which were collected at −20 °C. Since the refinement procedures used in this work are standard, this report will be concerned principally with the final results.

Solution and refinement

Sly (1955) reported the unit cell and space group given in the abstract above together with three-dimensional atomic coordinates. A three-dimensional Patterson function along with trial and error methods and structure factor maps had led to a well resolved and refined projection of the molecule along [101] onto (101). The preliminary three-dimensional atomic coordinates previously reported were obtained from the refined parameters of the projection with the aid of models and information from the three-dimensional Patterson function.

Since the earlier report the structure of DHC has been intensively refined. The steps of the refinement are outlined below, along with the reliability index, $R = (100)\ (\Sigma|\Delta F_{hkl}|)/(\Sigma|F_{o\,hkl}|)$, which resulted from

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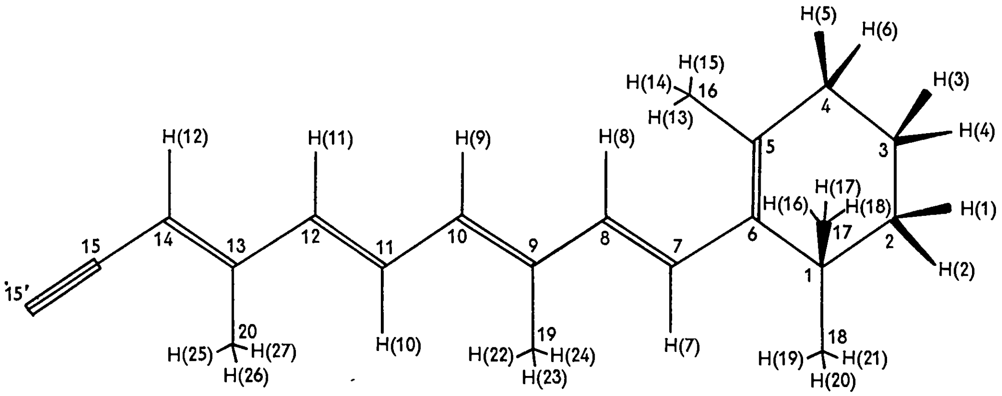

Fig. 1. The half molecule of DHC with the carbon atoms numbered according to the standard carotene system and with the hydrogen atoms numbered arbitrarily. Carbon atom 17 and H(1), H(3), and H(5) are all above the plane of the ring in this figure. The methyl hydrogen atoms are numbered clockwise when viewed along the C–C bond towards the molecule. The primed atoms are derived from the unprimed atoms by inversion through the center of symmetry at the triple bond, which is also at the origin of the unit cell for one of the two molecules in the unit.

each stage of the refinement. Some steps are then discussed in somewhat greater detail in following sections. The calculations of least squares and structure factors were carried out on an IBM 604 electronic computer. All Fourier and Patterson functions were evaluated by standard *M* card procedures with an IBM tabulator and associated equipment (Schomaker, 1949).

1. The coordinates y and $r=z-x$ were refined by electron density projection and least squares using $hk\bar{h}$ reflections. $R=19{\cdot}9$ for $hk\bar{h}$ data.
2. Models plus the three-dimensional Patterson function were used to obtain the x and z coordinates previously reported.
3. The x and z coordinates were refined by electron density projections along [100] and [001]. $R=42$ to $37{\cdot}0$ for $hk0$ and $0kl$ data.
4. Three-dimensional structure factors were calculated and the phases used for the evaluation of a three-dimensional Fourier synthesis that gave refined parameters for all carbon atoms. $R=37{\cdot}2$ (43·3% for $+l$, 32·9% for $-l$) to 25·7.

   All subsequent refinement was in three dimensions using all available data.
5. Carbon atom coordinates were refined by least squares. $R=19{\cdot}3$.
6. Carbon atom coordinates were refined by least squares. Tentative coordinates were calculated for the hydrogen atoms and their contributions included in the structure factors. $R=16{\cdot}7$.

   Hydrogen atom contributions were included in all subsequent structure factor calculations.
7. Carbon atom coordinates were refined by least squares; the scale and average temperature factors were adjusted, and another cycle of least-squares refinement was carried out. $R=16{\cdot}0$.
8. A difference Fourier synthesis was evaluated and used to obtain modified temperature factors and positional coordinates for the hydrogen atoms and anisotropic temperature factors for all carbon atoms. (No parameters were shifted for the carbon atoms.) $R=12{\cdot}2$.
9. Carbon atom coordinates were refined by least squares. The average temperature factor was adjusted and the data were scaled and corrected for extinction. $R=10{\cdot}2$.
10. (*a*) Two cycles of least-squares refinement were carried out on the carbon atom coordinates. The final structure factors (Table 1) were calculated and data obtained for the estimation of standard deviations*. $R=9{\cdot}6$.

    (*b*) The final least-squares refinement of the carbon atom coordinates was carried out.
11. The hydrogen parameters obtained in step 8 were modified to compensate for the refinement of the corresponding carbon atoms.

Step 4. *The three-dimensional Fourier synthesis*

This synthesis confirmed the trial structure previously reported, since no significant spurious peaks were found. The electron densities at the peaks of the carbon atoms varied from 5·8 to 6·9 $e.\text{Å}^{-3}$ with an average value of 6·23 $e.\text{Å}^{-3}$. In the background the electron density was everywhere less than 1·1 $e.\text{Å}^{-3}$. A number of large parameter shifts were obtained from the synthesis, particularly in the direction $a+c$ where the average shift was 0·10 Å. Large shifts were expected in this direction, however, since the $z+x$ parameters had been less thoroughly refined than the y

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* Note that the calculated structure factors in Table 1 are based on the hydrogen coordinates from step 8 and the carbon coordinates from step 10(*a*); for computational convenience the refinement was terminated with a least-squares evaluation and not with a structure-factor calculation.

and $z-x$ parameters; compare the R index for the reflections with positive and negative l.

Steps 5, 6, 7, 9, *and* 10. *Least-squares refinement*

(1) The normal equations were solved by the diagonal approximation, applicable to monoclinic space groups, in which only the $x_i z_i$ cross terms are retained for each atom. Anisotropic temperature factors were included; this reduces the symmetry to $P\bar{1}$, complicates the calculations (Rollett & Davies, 1955) and lowers the reliability of the diagonal approximation.

(2) The three-dimensional data used in this structure analysis were derived from equi-inclination Weissenberg photographs which included all layers about the a and c axes with inclination angles less than 45° and the zero and first layers about the b axis. The correlation coefficients between the various zones of data were refined by an iterative procedure that is essentially equivalent to the method of least squares. During the intensity estimation an effort was made to establish for the unobserved reflections a numerical threshold of observation. When any reflection was absent in more than one zone of data, the smallest value of the threshold intensity was used to obtain $F_{o\,\min}$, which represents both an estimate of the lower limit of observable intensity in the region in question and an estimate of the upper limit for compatible calculated structure factors. The unobserved reflections were retained in the calculation of the normal equations with the provision that when $|F_c| \leq |F_{o\,\min}|$ the error term, ΔF, was taken as zero. This has the effect of slightly damping the shifts obtained from the least-squares refinement.

(3) For 829 of the 1289 observed reflections, independent intensity estimates were made in at least two different zones. The observed value of a structure factor is obtained from

$$F_o^2 = \bar{I} = \sum_{i=1}^{n} I_i/n ;$$

the average error is

$$\overline{\Delta I} = (\sum_{i=1}^{n} |I_i - \bar{I}\,|)/n ,$$

where n is the number of independent measurements of the corresponding reflection. For a group of reflections with nearly the same intensity, a group-average percentage error $100\,\langle\overline{\Delta I}/\bar{I}\rangle$ was calculated and plotted against $\langle F_o \rangle$ for the group. The curve of Fig. 2 resulted; its shape is reasonable for visual data. The curve was used to establish the weighting factor w, as follows:

$$1/w = (\overline{\Delta I}/\bar{I})(F_o)^2$$

for all reflections with $F_o > 2F_{o\,\min}$, and

$$1/w = (\overline{\Delta I}/\bar{I})(2F_{o\,\min})^2$$

for $F_o \leq (2F_{o\,\min})$, where $F_{o\,\min}$ was regarded as a variable in $(\sin\theta)/\lambda$. This system sets the weights as $1/\overline{\Delta I}$ but with a cutoff for weak reflections (Hughes, 1941).

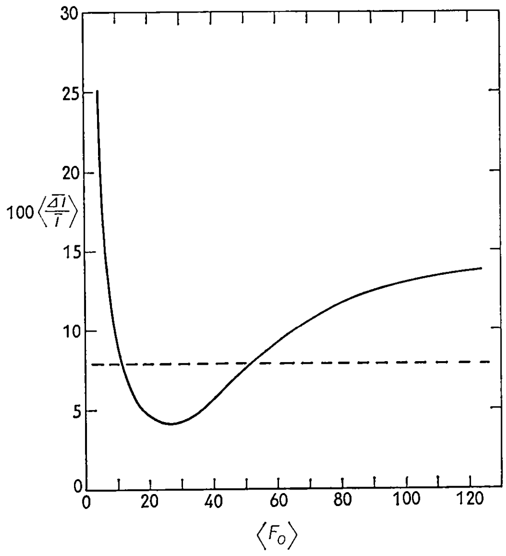

Fig. 2. The group-average percentage error in measured intensity as a function of the group-average structure factor.

Step 8. *The three-dimensional difference Fourier synthesis*

The difference map was calculated from terms which had the contribution of the carbon atoms, calculated with a uniform isotropic value of $4B = 4{\cdot}02$, subtracted from the observed structure factors. Some 27 low-order, strong reflections which appeared to suffer from extinction were arbitrarily left out of the summation. The difference map indicated that, apart from errors introduced by the omitted reflections, the scale factor and the average temperature factor were essentially correct. The background electron density was slightly negative. At the coordinates of the centers of the carbon atoms the algebraic average electron density was $-0{\cdot}013$ e.Å^{-3}, and the average magnitude of the electron density was $0{\cdot}281$ e.Å^{-3}. Within the asymmetric unit ten of the carbon atoms, 14 and 15 and those in the CH_2 and CH_3 groups, were in regions of negative electron density, while the other ten were in regions of positive electron density; if the scale factor is presumed correct the former must have B values larger than the assumed mean while the latter have smaller. The general features of the thermal anisotropy of the carbon atoms, and the resolution of the hydrogen atoms as described in the next paragraphs, suggest that no serious errors have resulted from the omission of the low-order reflections.

The difference map was used to obtain rotational orientation for the methyl groups, some angular parameters associated with the hydrogen atoms along the chain, temperature-factor exponents for the hydrogen atoms, and anisotropic temperature factors for the

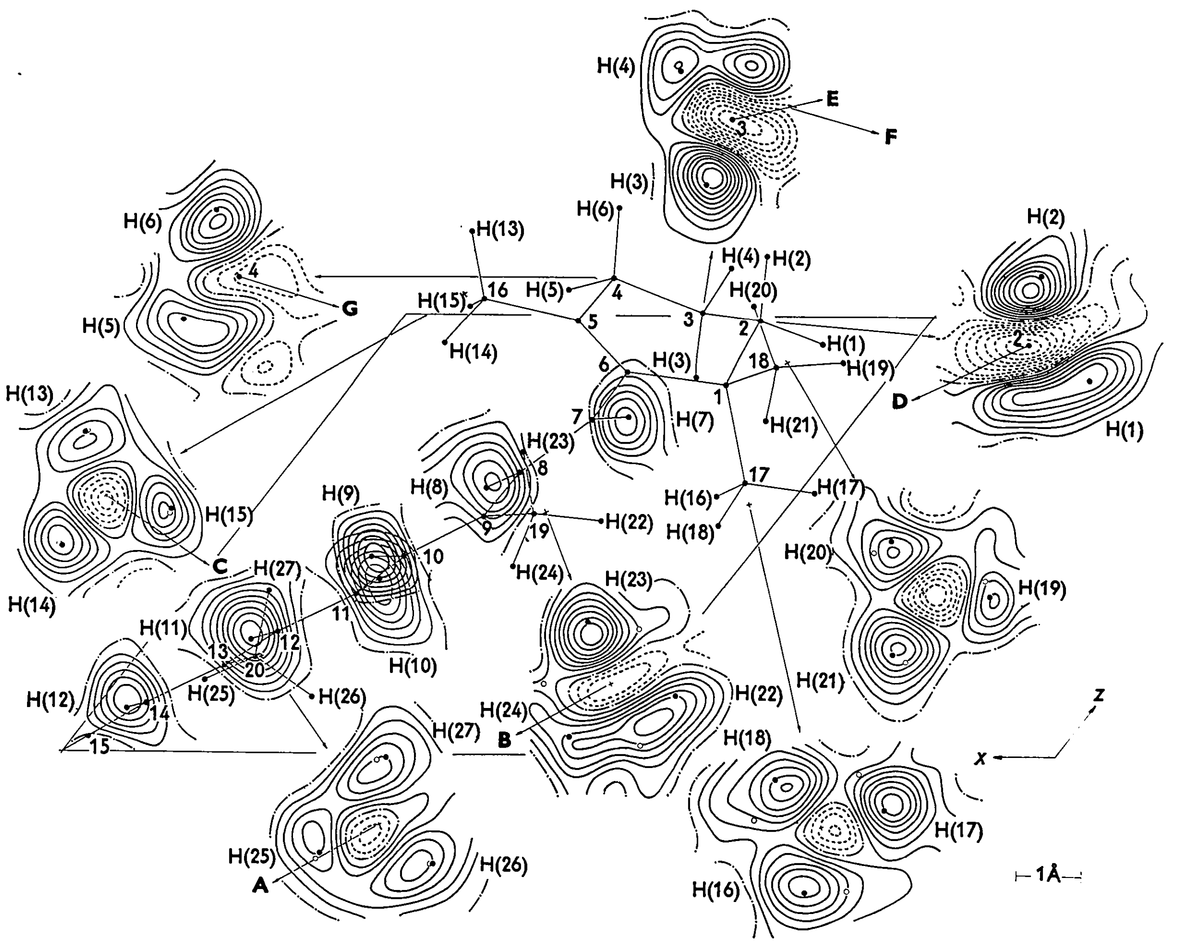

Fig. 3. A b-axis projection of the half-molecule of DHC, where numbers indicate carbon atoms, with sections from the difference Fourier synthesis superimposed upon it. The sections pass through the various hydrogen atoms but are not in all cases parallel to (010). The dash–dot lines are zero-amplitude contours. The solid lines are contours of positive electron density while the dashed lines are negative electron density contours, all with an interval of 0·07 e.Å^{-3}.

carbon atoms. In all, some 131 parameters were derived; they served to establish the model of the molecule which was subsequently refined by least squares.

The coordinates for the hydrogen atoms of DHC were based on assumed carbon–hydrogen bond lengths, 1·07 Å for the CH and CH_3 groups, and 1·08 Å for the CH_2 groups*. The methyl groups were assumed to be regular tetrahedrons and only the rotational orientations were obtained from the difference map. The two hydrogen atoms of each CH_2 group and the three carbon atoms of the segment C–CH_2–C were assumed to lie in a C_{2v} configuration (with neglect of difference in C–C bond lengths). A 1·08 Å bond length and a tetrahedral angle H–C–H then suffice to determine the coordinates of the CH_2 hydrogen atoms. For the CH groups, the assumed bond length of 1·07 Å and the angle parameters determined from the difference map serve to locate the hydrogen atoms.

In Fig. 3 the half molecule with positive y coordinates is shown projected along the b axis onto the ac plane. Superimposed upon the projection are sections through the hydrogen atoms; the sections are cut in various planes chosen to be as informative as possible. For the hydrogen atoms of the CH groups, atoms H(7) through H(12), the sections are projected identically with the molecule and have y coordinates at the nearest 1/120th to the calculated parameters based on the assumed 1·07 Å C–H bonds. The sections through the methyl hydrogen atoms are planes perpendicular to the C–CH_3 bonds and intersect the C–CH_3 vectors 0·357 Å beyond the methyl carbon atoms. The points of intersection of the C–CH_3 vectors with the planes passing through the hydrogen peaks are indicated by crosses both in the projected molecule and in the sections through the methyl

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* It had been my intent to set all of these distances the same, but final calculations of interatomic distances revealed that 1·08 Å had accidentally been assumed for the CH_2 groups.

hydrogen atoms; these crosses serve as a reference between the different projections which occur in Fig. 3. All of the methyl groups of Fig. 3 are viewed looking away from the molecule; hence the hydrogen atoms appear numbered counterclockwise to be consistent with Fig. 1. Vectors **A**, **B**, and **C** represent the projections of the double bonds of the carbon atoms to which the methyl groups are bonded. Each section through a CH_2 group passes through the carbon atom and bisects the angle between the carbons adjacent to the CH_2. Vector **D** is the intersection of the plane of 1–2–3 with the section passing through 2, H(1), and H(2). Vectors **G** and **E** are similar intersections for the sections through 4 and 3, respectively. The vector **F** represents the intersection of the plane of 1–6–5 with the section through 3, H(3), H(4).

Peaks for all of the hydrogen atoms are present in Fig. 3 and for the most part they are well resolved. Some of the peaks are markedly influenced by the anisotropic thermal motion of the carbon atoms, for example the hydrogen atoms H(22), H(23), and H(24) of the methyl group 19, and those in the CH_2 groups. The locations assigned to all hydrogen atoms are shown in Fig. 3 as solid dots. The open circles in the methyl sections show the tentative coordinates assigned to the hydrogen atoms during step 6; the difference map changed the rotational orientation about the C–CH_3 bonds. Considerable correction is observed to have occurred in the orientation of methyl 18, while 17 and 19 have almost the completely opposite configuration. It is apparent that not many phases of the structure factors are determined by the hydrogen atoms, since the methyl groups come out well resolved in the difference map even though the provisional coordinates used during the least-squares refinements were in error.

The maximum electron densities for the hydrogen atoms of DHC, approximately corrected for the effect of anisotropic vibrations of the carbon atoms, range from 0·32 to 0·64 e.Å^{-3}, with an average value of 0·45 e.Å^{-3}. Some generalizations about temperature factors could be made from the peak values of electron density, but the work of McDonald (1956) on the radial distribution of hydrogen atoms as a function of temperature factor makes possible a more quantitative estimate of their thermal motion. B values for the various hydrogen atoms were derived from a consideration of both the maximum magnitudes of the electron density and the radial distribution of electron density. The use of the radial distribution function rather than just the peak amplitudes helps to eliminate errors introduced by the omission of the low-order reflections suffering from extinction. It is doubtful that the ΔF Fourier is reliable enough to warrant individual temperature factors for the hydrogen atoms. Accordingly average values were assumed for all of the hydrogens of each CH_2 and CH_3 group. Several of the groups furthermore had temperature factors so nearly identical that only four different B values were necessary; these are listed along with the coordinates of the atoms in Table 2.

Anisotropic temperature factors for all of the carbon atoms were derived from the electron densities and the curvatures along the principal axes of the ellipsoids of vibration, determined graphically, by a straightforward application of Fourier transforms carried out by numerical integration (Schomaker, 1956; Leung, Marsh & Schomaker, 1957).

For several reasons, no parameters of carbon atoms were corrected as a result of the difference map. First, the parameters had had several refinements and they were expected to be nearly correct. Second, the slopes of the electron density at the centers of the carbon atoms were very nearly zero. Finally, the weighting of the data is different in the difference Fourier synthesis from that in the least-squares treatment, and it was deemed desirable to continue the refinement of positional parameters by the method of least squares.

Step 9. *Scale factor, temperature factor, and extinction corrections*

Following the adjustment of the average temperature factor exponent and the scale factor by standard computational methods, $(F_c/F_o)_{avg}$ was plotted against $(F_o)_{avg}$ (Fig. 4) and a second-order correction evaluated. The resulting changes in the structure factors are summarized by the equations:

$$F'_o = 0{\cdot}7263 F_o + 0{\cdot}007802 F_o^2$$
$$F'_c = F_c \exp\{-1{\cdot}13(\sin^2\theta)/\lambda^2\}$$

where F'_o and F'_c are the modified values of the observed and calculated structure factors, respectively. The second-order term suggests a correction for extinction, but it is entirely empirical. It is considered, however, that no error in the structural model could be responsible for the type of systematic behavior of

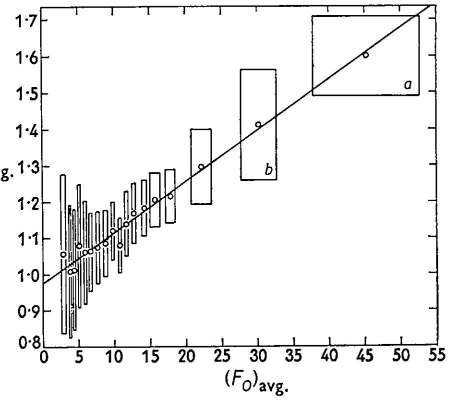

Fig. 4. A plot of $(F_c/D_o)_{avg}$ *versus* $(F_o)_{avg}$ that shows a systematic variation. The eight points for lowest F_o are averages over 100 reflections; points a and b are averages over 20 and 30 reflections respectively; the remainder are averages over 50 reflections. The rectangles indicate average deviations. A second-order correction was made on the basis of this graph.

Table 1. *The observed and calculated structure factors for* DHC

The symbol < that precedes some of the observed structure factors indicates the estimate of $10F_{o\,\min}$ for unobserved reflections. Minus signs follow negative calculated structure factors

h	k	ℓ	$\lvert 10F_o \rvert$	$10F_c$
0	2	0	22	30-
0	4	0	65	95
0	6	0	253	275
0	8	0	305	304-
0	10	0	38	28-
0	12	0	83	92-
0	14	0	239	234-
0	16	0	450	404
0	18	0	87	100-
0	20	0	< 22	30-
0	22	0	199	187
0	24	0	< 18	12-
0	26	0	178	174-
0	1	1	81	101
0	2	1	412	526
0	3	1	386	467-
0	4	1	868	890-
0	5	1	1470	1300
0	6	1	722	707-
0	7	1	196	225
0	8	1	319	332
0	9	1	133	151
0	10	1	141	147
0	11	1	58	51-
0	12	1	225	220
0	13	1	49	58-
0	14	1	51	49-
0	15	1	34	23
0	16	1	103	105
0	17	1	55	52
0	18	1	177	167
0	19	1	178	179-
0	20	1	37	6-
0	21	1	48	28-
0	22	1	63	65-
0	23	1	< 19	10
0	24	1	262	242
0	25	1	176	178
0	26	1	149	151
0	27	1	< 9	12
0	28	1	48	53-
0	29	1	27	19
0	30	1	< 26	8-
0	31	1	81	77-
0	32	1	< 16	12
0	0	2	568	597
0	1	2	88	108-
0	2	2	539	539-
0	3	2	145	172
0	4	2	182	228
0	5	2	350	378-
0	6	2	170	186-
0	7	2	88	86-
0	8	2	177	169-
0	9	2	120	105-
0	10	2	267	257
0	11	2	207	194-
0	12	2	80	80
0	13	2	47	31
0	14	2	187	191-
0	15	2	114	127
0	16	2	30	19-
0	17	2	< 22	27
0	18	2	60	50-
0	19	2	213	205
0	20	2	286	276
0	21	2	117	109
0	22	2	< 18	35
0	23	2	107	109-
0	24	2	66	64-
0	25	2	66	68
0	26	2	38	41-
0	27	2	129	118-
0	28	2	85	82-
0	29	2	40	50-
0	30	2	59	61-
0	31	2	41	44
0	1	3	101	111-
0	2	3	124	137
0	3	3	134	170-
0	4	3	105	124-
0	5	3	207	231
0	6	3	< 20	22
0	7	3	183	197-
0	8	3	43	32
0	9	3	72	87
0	10	3	246	231-
0	11	3	< 22	14
0	12	3	43	48-
0	13	3	34	8-
0	14	3	61	85-
0	15	3	382	338
0	16	3	21	37
0	17	3	30	38
0	18	3	63	51-
0	19	3	125	123-
0	20	3	< 17	17
0	21	3	32	24
0	22	3	85	85-
0	23	3	164	171-
0	24	3	< 42	21-
0	25	3	< 40	11
0	26	3	< 35	40-
0	27	3	< 31	29
0	28	3	53	68-
0	29	3	29	31-
0	0	4	< 22	26
0	1	4	130	128-
0	2	4	43	31
0	3	4	< 22	20-
0	4	4	111	109
0	5	4	93	116-
0	6	4	106	109-
0	7	4	62	58-
0	8	4	78	85
0	9	4	46	43
0	10	4	229	207
0	11	4	140	145
0	12	4	26	26
0	13	4	68	64-
0	14	4	45	42
0	15	4	28	28
0	16	4	46	23
0	17	4	40	49-
0	18	4	106	96-
0	19	4	132	138-
0	20	4	121	108
0	21	4	48	46-
0	22	4	87	79-
0	23	4	98	94-
0	24	4	36	40-
0	25	4	40	40-
0	26	4	< 12	5-
0	1	5	69	60
0	2	5	88	67-
0	3	5	< 18	10-
0	4	5	141	147
0	5	5	157	160
0	6	5	33	36
0	7	5	25	9
0	8	5	50	38-
0	9	5	39	38
0	10	5	40	38
0	11	5	81	87
0	12	5	62	77-
0	13	5	91	93-
0	14	5	70	78-
0	15	5	63	48
0	16	5	43	35
0	17	5	< 20	20-
0	18	5	82	90-
0	19	5	22	37-
0	20	5	< 16	18
0	21	5	30	20
0	22	5	21	24
1	0	0	960	890-
1	1	0	110	140
1	2	0	422	479
1	3	0	508	575
1	4	0	535	565
1	5	0	632	671
1	6	0	632	667
1	7	0	51	53-
1	8	0	300	307-
1	9	0	229	236-
1	10	0	291	287
1	11	0	165	161-
1	12	0	45	56-
1	13	0	43	31-
1	14	0	< 29	10
1	15	0	82	80-
1	16	0	42	44-
1	17	0	98	99-
1	18	0	50	61-
1	19	0	134	117-
1	20	0	48	49-
1	21	0	44	49-
1	22	0	31	4-
1	23	0	37	44
1	24	0	65	68-
1	25	0	228	237-
1	26	0	174	193
1	27	0	< 13	2
1	1	1	1560	1500
1	2	1	615	701-
1	3	1	501	550
1	4	1	288	321-
1	5	1	132	166-
1	6	1	498	541
1	7	1	98	87-
1	8	1	129	122-
1	9	1	105	122-
1	10	1	177	192-
1	11	1	64	67-
1	12	1	129	135
1	13	1	32	38-
1	14	1	31	33
1	15	1	47	59
1	16	1	72	82-
1	17	1	75	66
1	18	1	77	68
1	19	1	36	26
1	20	1	96	84-
1	21	1	51	56
1	22	1	178	176
1	23	1	81	78
1	24	1	155	143-
1	25	1	151	163-
1	26	1	90	102-
1	27	1	< 32	8
1	28	1	214	202
1	29	1	< 26	27
1	30	1	46	43-
1	31	1	60	52
1	0	2	138	116
1	1	2	45	44-
1	2	2	41	23-
1	3	2	98	88-
1	4	2	53	88-
1	5	2	181	195-
1	6	2	568	553
1	7	2	392	377-
1	8	2	345	351
1	9	2	< 31	31
1	10	2	129	123-
1	11	2	141	121
1	12	2	122	124-
1	13	2	79	75
1	14	2	63	55
1	15	2	41	37
1	16	2	< 33	9
1	17	2	70	69
1	18	2	< 32	21-
1	19	2	50	44-
1	20	2	226	230-
1	21	2	< 26	4-
1	22	2	150	156
1	23	2	187	199
1	24	2	96	112
1	25	2	< 40	27
1	26	2	< 37	8-
1	27	2	94	75
1	28	2	< 29	4-
1	29	2	34	40-
1	1	3	88	100
1	2	3	124	109
1	3	3	209	201-
1	4	3	136	126-
1	5	3	49	42
1	6	3	80	88-
1	7	3	< 34	16-
1	8	3	< 34	9
1	9	3	39	49-
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6	14	2-	<38	2
6	15	2-	63	61
6	16	2-	41	21-
6	17	2-	49	40
6	18	2-	42	41
6	19	2-	<26	12
6	20	2-	<22	19
6	1	3-	56	59
6	2	3-	<46	13
6	3	3-	<46	39
6	4	3-	<46	42
6	5	3-	187	166
6	6	3-	139	112-
6	7	3-	161	136-
6	8	3-	180	184-
6	9	3-	72	64-
6	10	3-	135	129
6	11	3-	84	77
6	12	3-	<43	44-
6	13	3-	<42	35-
6	14	3-	<41	46
6	15	3-	155	140
6	16	3-	127	111
6	17	3-	<36	25
6	18	3-	80	77
6	19	3-	<32	24
6	20	3-	<29	21-
6	21	3-	<25	10-
6	22	3-	82	91
6	0	4-	94	68
6	1	4-	<26	11
6	2	4-	<26	27
6	3	4-	<26	7
6	4	4-	82	60-
6	5	4-	52	57
6	6	4-	85	63
6	7	4-	148	144-
6	8	4-	35	48
6	9	4-	178	165
6	10	4-	189	194
6	11	4-	86	83-
6	12	4-	195	199-
6	13	4-	203	195-
6	14	4-	46	40-
6	15	4-	<24	19
6	16	4-	38	38-
6	17	4-	134	126
6	18	4-	187	174-
6	19	4-	76	75
6	20	4-	84	71
6	21	4-	<16	0
6	22	4-	82	83
6	1	5-	68	54
6	2	5-	<24	8-
6	3	5-	<24	4
6	4	5-	67	70-
6	5	5-	<24	3
6	6	5-	<24	0
6	7	5-	<24	14-
6	8	5-	<24	12-
6	9	5-	66	58-
6	10	5-	<24	24
6	11	5-	225	222-
6	12	5-	177	175
6	13	5-	248	254-
6	14	5-	174	183
6	15	5-	188	176
6	16	5-	101	100-
6	17	5-	83	80-
6	18	5-	97	92-
6	19	5-	<17	24-
6	20	5-	35	36-
6	21	5-	20	27
6	0	6-	94	97
7	1	1-	34	35-
7	2	1-	41	37-
7	3	1-	<17	5-
7	4	1-	<16	5
7	5	1-	<14	2
7	0	2-	<34	33
7	1	2-	46	37
7	2	2-	72	65
7	3	2-	67	50
7	4	2-	<33	6
7	5	2-	94	97-
7	6	2-	45	37-
7	7	2-	58	51-
7	8	2-	<29	17
7	9	2-	<28	21-
7	10	2-	41	29-
7	11	2-	<24	21
7	12	2-	<21	16
7	1	3-	58	51
7	2	3-	<39	5-
7	3	3-	65	52-
7	4	3-	<38	28-
7	5	3-	<38	10
7	6	3-	<37	27
7	7	3-	121	98
7	8	3-	70	73
7	9	3-	<35	19
7	10	3-	128	122-
7	11	3-	<32	17-
7	12	3-	<30	35-
7	13	3-	78	69-
7	14	3-	63	52-
7	15	3-	<22	5-
7	16	3-	<18	18
7	0	4-	39	52
7	1	4-	70	49-
7	2	4-	<24	9-
7	3	4-	<24	22
7	4	4-	<24	27
7	5	4-	50	71-
7	6	4-	<24	1
7	7	4-	<23	21
7	8	4-	50	50-
7	9	4-	67	65-
7	10	4-	127	114-
7	11	4-	71	59
7	12	4-	48	30-
7	13	4-	189	187
7	14	4-	129	131-
7	15	4-	32	35
7	16	4-	34	39-
7	17	4-	76	82-
7	1	5-	28	42
7	2	5-	25	33
7	3	5-	73	72-
7	4	5-	25	16-
7	5	5-	<22	2-
7	6	5-	112	95
7	7	5-	89	85-
7	8	5-	204	211
7	9	5-	149	135-
7	10	5-	<21	35
7	11	5-	<20	1
7	12	5-	67	61
7	13	5-	45	47
7	14	5-	113	115-
7	15	5-	62	58-
7	16	5-	24	28
7	17	5-	38	39
8	0	4-	<15	2-
8	1	4-	<15	7
8	2	4-	27	21
8	3	4-	<14	21-
8	4	4-	41	37-
8	5	4-	35	35
8	6	4-	<12	17-
8	7	4-	57	81
8	1	5-	<16	13
8	2	5-	56	54
8	3	5-	<15	9-
8	4	5-	62	74
8	5	5-	45	50-
8	6	5-	127	138
8	7	5-	22	18-
8	8	5-	27	29-
8	9	5-	<10	2

the structure factors illustrated in Fig. 4, and that the correction is therefore admissible.

Step 10. *Final refinement*

The final tabulated structure factors for DHC are listed in Table 1. As indicated in the foregoing outline the calculated structure factors listed in Table 1 were used for the final least-squares refinement of parameters and so were not obtained from the final coordinates of the atoms. The parameter shifts for the last three sets of least squares are as follows:

	L.S. $10a_1$	L.S. $10a_2$	L.S. $10b$
$\langle \lvert \Delta x \rvert \rangle$	0·0029 Å	0·0012 Å	0·0013 Å
$\langle \lvert \Delta y \rvert \rangle$	0·0031	0·0012	0·0003
$\langle \lvert \Delta z \rvert \rangle$	0·0035	0·0015	0·0011

The maximum shifts are generally about 2 to 3 times the above average values. The fact that the average standard deviation, *ca.* 0·006 Å, is larger than the above shifts, while interesting, is not really a valid basis for judging the degree of convergence of least-squares refinements. The decision to stop calculations with step 10(*b*) was based upon limitations of time, data, and equipment and not upon the belief that only insignificant changes in parameters *could* result from further stages of refinement.

Step 11. *Final hydrogen coordinates*

During steps 9 and 10, the coordinates of the carbon atoms were refined by least squares. In step 11, the parameters of each hydrogen atom, obtained from the difference Fourier synthesis in step 8, were adjusted by the cumulative shift in the parameters of the carbon atom to which it is bonded. The average and maximum magnitudes of these shifts are given below.

	Average	Maximum
$\lvert\Delta x\rvert$	0·0048 Å	0·022 Å
$\lvert\Delta y\rvert$	0·0072	0·023
$\lvert\Delta z\rvert$	0·0078	0·022

These shifts are sufficiently small that it was not deemed necessary to recalculate the contributions of the hydrogen atoms to the structure factors, especially in view of the assumptions made in deriving their coordinates in the first place. The C–H distances are left at the assumed values after the shifts. The bond angles, however, may be slightly changed; these were therefore calculated from the final parameters, and it was found that all of the angles were within 1° of the values assumed in step 8. The final parameters for the atoms of DHC are listed in Table 2.

Table 2. *Final parameters for the carbon and hydrogen atoms of* DHC

Hydrogen parameters are based on assumed bond lengths and bond angles; see text

Atom	x	y	z
1	$-0{\cdot}7056_5$	0·17324	$0{\cdot}8442_5$
2	$-0{\cdot}6777_3$	0·20644	$0{\cdot}9902_0$
3	$-0{\cdot}5565_0$	0·24400	$1{\cdot}0090_4$
4	$-0{\cdot}3381_5$	0·23132	$1{\cdot}0865_1$
5	$-0{\cdot}3350_4$	0·19251	$0{\cdot}9879_3$
6	$-0{\cdot}5008_3$	0·16715	$0{\cdot}8722_6$
7	$-0{\cdot}5024_5$	0·13103	$0{\cdot}7619_3$
8	$-0{\cdot}4431_8$	0·13160	$0{\cdot}6452_6$
9	$-0{\cdot}4398_7$	0·09502	$0{\cdot}5425_9$
10	$-0{\cdot}3507_8$	0·09871	$0{\cdot}4520_8$
11	$-0{\cdot}3170_3$	0·06413	$0{\cdot}3623_9$
12	$-0{\cdot}2259_9$	0·06826	$0{\cdot}2743_7$
13	$-0{\cdot}1779_1$	0·03439	$0{\cdot}1951_1$
14	$-0{\cdot}0858_9$	0·04355	$0{\cdot}1105_2$
15	$-0{\cdot}0254_2$	0·01278	$0{\cdot}0328_9$
16	$-0{\cdot}1242_8$	0·18471	$1{\cdot}0354_8$
17	$-0{\cdot}8838_0$	0·18572	$0{\cdot}6249_4$
18	$-0{\cdot}7725_8$	0·13244	$0{\cdot}8878_2$
19	$-0{\cdot}5301_6$	0·05451	$0{\cdot}5502_1$
20	$-0{\cdot}2212_5$	−0·01039	$0{\cdot}2151_6$

Atom	x	y	z	4B
H(1)	$-0{\cdot}831_0$	$0{\cdot}2163_8$	$0{\cdot}937_4$	$6{\cdot}1_9$
H(2)	$-0{\cdot}595_2$	$0{\cdot}1923_5$	$1{\cdot}137_3$	$6{\cdot}1_9$
H(3)	$-0{\cdot}637_5$	$0{\cdot}2583_6$	$0{\cdot}862_7$	$6{\cdot}7_3$
H(4)	$-0{\cdot}544_4$	$0{\cdot}2662_5$	$1{\cdot}112_1$	$6{\cdot}7_3$
H(5)	$-0{\cdot}270_4$	$0{\cdot}2567_0$	$1{\cdot}059_6$	$5{\cdot}3_7$
H(6)	$-0{\cdot}244_7$	$0{\cdot}2257_1$	$1{\cdot}246_4$	$5{\cdot}3_7$
H(7)	$-0{\cdot}567_4$	$0{\cdot}1024_9$	$0{\cdot}768_2$	$6{\cdot}1_9$
H(8)	$-0{\cdot}401_3$	$0{\cdot}1601_4$	$0{\cdot}611_6$	$6{\cdot}1_9$
H(9)	$-0{\cdot}288_8$	$0{\cdot}1283_6$	$0{\cdot}452_6$	$5{\cdot}3_7$
H(10)	$-0{\cdot}337_1$	$0{\cdot}0334_7$	$0{\cdot}399_7$	$5{\cdot}3_7$
H(11)	$-0{\cdot}187_7$	$0{\cdot}0991_7$	$0{\cdot}257_3$	$5{\cdot}3_7$
H(12)	$-0{\cdot}056_2$	$0{\cdot}0756_2$	$0{\cdot}098_3$	$6{\cdot}1_9$
H(13)	$-0{\cdot}002_0$	$0{\cdot}1935_7$	$1{\cdot}188_3$	$5{\cdot}3_7$
H(14)	$-0{\cdot}113_7$	$0{\cdot}2026_1$	$0{\cdot}935_4$	
H(15)	$-0{\cdot}108_3$	$0{\cdot}1520_6$	$1{\cdot}018_4$	
H(16)	$-0{\cdot}850_1$	$0{\cdot}2155_4$	$0{\cdot}592_9$	$5{\cdot}6_6$
H(17)	$-1{\cdot}027_9$	$0{\cdot}1874_8$	$0{\cdot}602_7$	
H(18)	$-0{\cdot}896_8$	$0{\cdot}1625_0$	$0{\cdot}526_2$	
H(19)	$-0{\cdot}894_1$	$0{\cdot}1392_6$	$0{\cdot}898_4$	$5{\cdot}6_6$
H(20)	$-0{\cdot}642_3$	$0{\cdot}1186_5$	$1{\cdot}025_8$	
H(21)	$-0{\cdot}830_1$	$0{\cdot}1109_5$	$0{\cdot}766_2$	
H(22)	$-0{\cdot}668_4$	$0{\cdot}0610_9$	$0{\cdot}534_4$	$5{\cdot}6_6$
H(23)	$-0{\cdot}418_1$	$0{\cdot}0393_2$	$0{\cdot}691_0$	
H(24)	$-0{\cdot}568_8$	$0{\cdot}0344_1$	$0{\cdot}430_1$	
H(25)	$-0{\cdot}161_1$	$-0{\cdot}0309_7$	$0{\cdot}162_3$	$6{\cdot}7_3$
H(26)	$-0{\cdot}387_0$	$-0{\cdot}0148_5$	$0{\cdot}126_5$	
H(27)	$-0{\cdot}148_7$	$-0{\cdot}0171_4$	$0{\cdot}369_0$	

The intermolecular arrangement

Resolution into plane strips and sections

The mean direction of the molecular chain of DHC is steeply inclined at 64° to the b axis. The molecule is oriented and inclined in such a direction that the conjugated chains of molecules related by the translation $c-a$ are nearly coplanar and are in van der Waals contact with one another. As a result it is convenient to describe the structure of DHC in terms of *sections* and *plane strips*. The sections are separated by the c-glide planes, since of the molecule centered at the origin all of the atoms with the exception of three hydrogen atoms on each of the two cyclohexene rings lie within the section bounded by the glide planes at $y=\pm\frac{1}{4}$. One such section is illustrated in the projection along [010] shown in Fig. 5. Within the sections the conjugated chains are arranged into plane strips with period $c-a$ and are closely packed together in an arrangement that is almost unaffected by the cyclohexene rings.

The a and c axes of DHC are nearly equal, 8·145 and 8·465 Å respectively, and the β angle of 128·3° is near enough to 120° for the structure to be described in terms of either a pseudohexagonal lattice or a pseudo-orthorhombic lattice. The hexagonal arrangement of the cyclohexene rings in which each ring has six nearest neighbors at the same level in y is apparent in Fig. 5. A similar sixfold coordination about each molecular chain will be apparent in some of the illustrations which follow. The two hexagonal sections related by the c-glide plane are not superimposed in closest packing; instead four nearest neighbors are produced by the translation.

The base diagonals of the unit cell of DHC, $c-a$ and $c+a$, 14·95 and 7·25 Å respectively, form an almost orthogonal unit cell that is centered in the basal plane. These base diagonals form the basis of the simplified representation of the DHC structure shown in Fig. 6. This illustration shows how the glide planes which are penetrated by the cyclohexene rings also divide the structure into sections of offset plane strips. Molecules C and D and all molecules derived from them by the translation $c-a$ are in one plane strip; similarly A and B and related molecules are from the layer immediately behind that containing C and D. Every molecular chain has six nearest neighbors, two in the

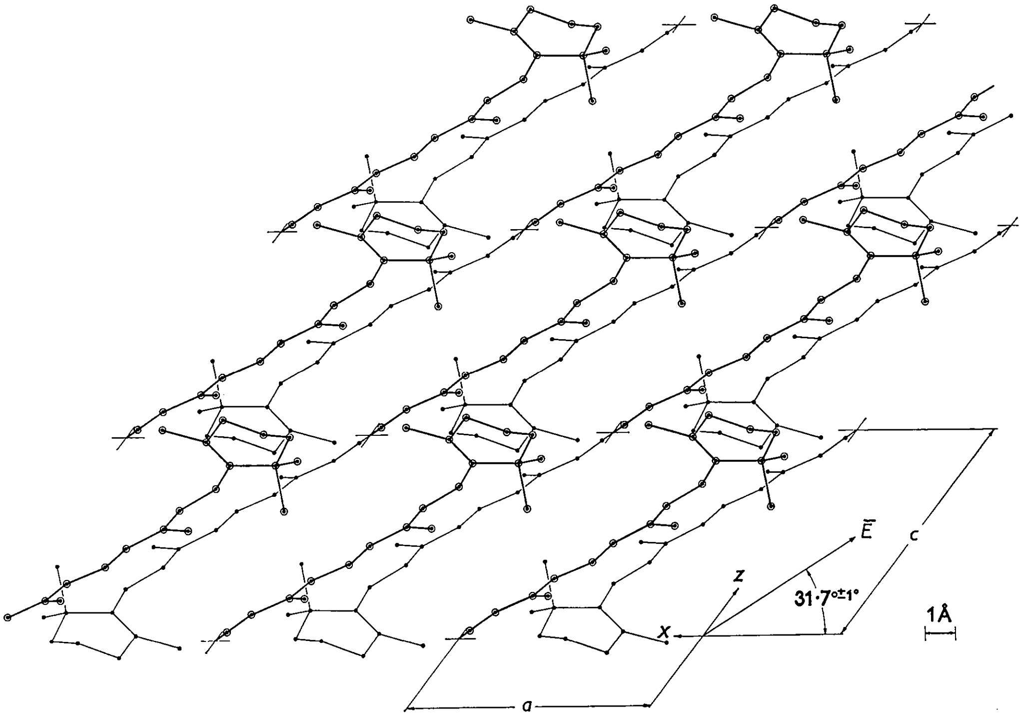

Fig. 5. The b-axis projection onto (010) of the molecules lying within the section bounded by the glide planes at $y = \pm \frac{1}{4}$. $\bar{E}$ is the observed direction of the electric vector for maximum absorption in the visible.

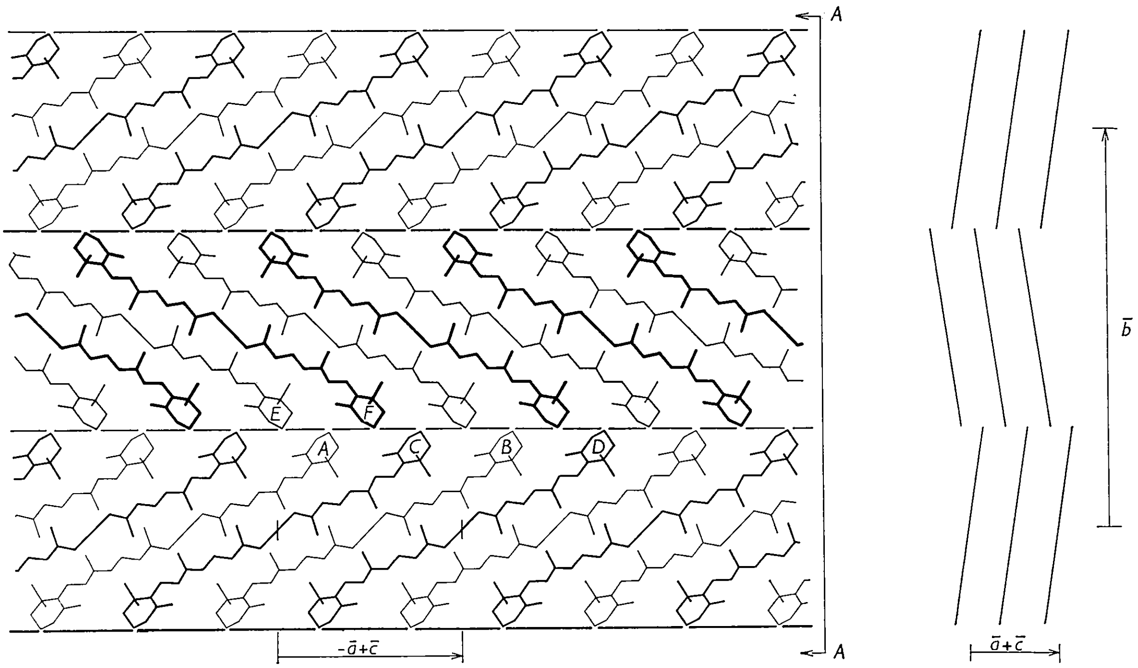

Fig. 6. A simplified drawing of the DHC molecules illustrating the close-packed plane strips and sections that constitute the structure. Left: a view looking along $\bar{a}+\bar{c}$. Right: section A–A.

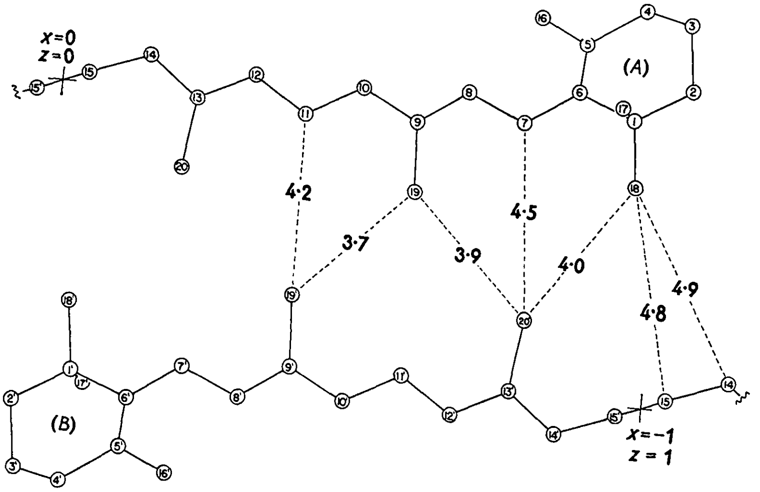

Fig. 7. Two adjacent molecules from one plane strip.

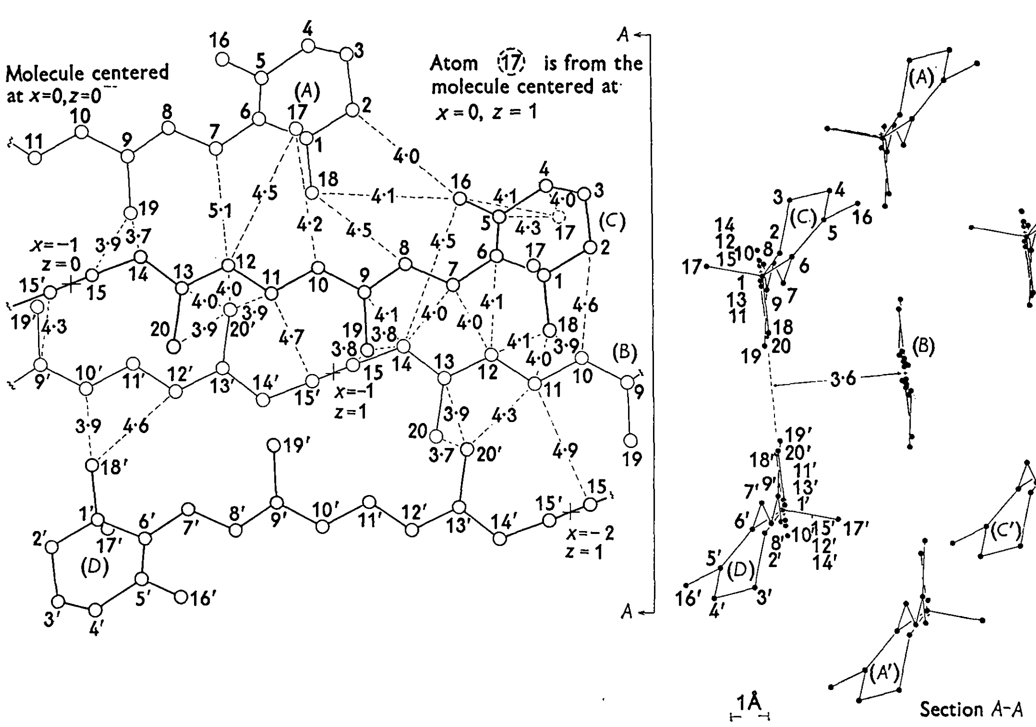

Fig. 8. The relative positions of molecules in two adjacent and parallel plane strips.

same plane strip and two in each of the adjacent layers, all arranged in what may be called a two-dimensionally close-packed array. In describing the detailed arrangement of the molecules it will be convenient to consider in turn the intermolecular configuration within one plane strip (Fig. 7) the relative positions of molecules in two adjacent strips (Fig. 8) and the packing of the ring structures related by the *c*-glide planes (Fig. 9). On the detailed diagrams that illustrate these points the molecules are lettered in accordance with Fig. 6*.

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* This figure, the preceding drawing, and some of those which follow were made from atomic parameters derived from the three-dimensional Fourier synthesis, step 4; though the general features are quite correct, some of the detailed dimensions are slightly in error. Fig. 10 and the *A–A* Section of Fig. 8 have been constructed from the final parameters and should be consulted for structural detail.

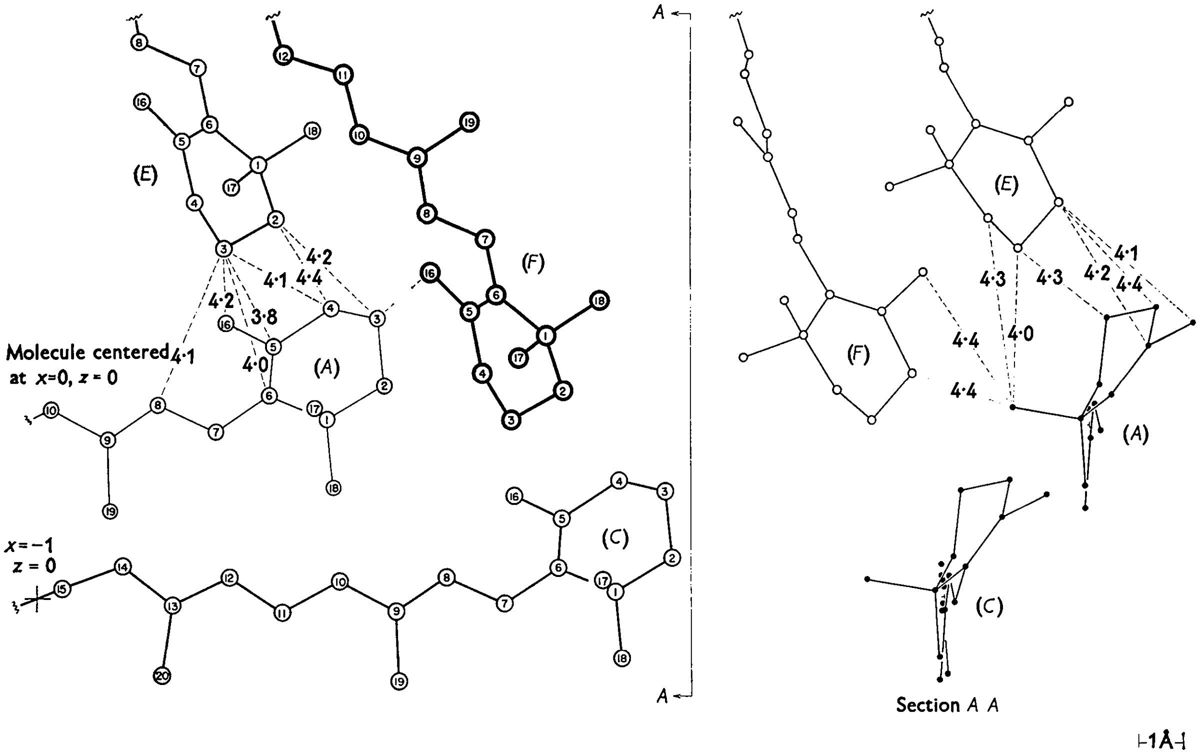

Fig. 9. The packing of the rings along the glide plane at $y = \frac{1}{4}$.

For the sake of clarity only intercarbon distances are shown in Figs. 7–9; any such distances not shown on these figures are greater than 4 Å. Intermolecular carbon–hydrogen and hydrogen–hydrogen distances are not listed in this paper since they are based on assumed C–H bond lengths; the shortest values for such interactions are 2·8 and 2·0 Å respectively.

The relative positions of molecules in two adjacent and parallel plane strips are illustrated in Fig. 8. Molecules *C* and *D*, respectively, are derived from *A* and *B* by the translation $-a$. Except for atom 17 of molecule *D′*, molecules *A′*, *C′*, and *D′* on the extreme right of Fig. 8, which are derived from *A*, *C*, and *D* by inversion at the center of molecule *B*, are not repeated to the left of the section line *A*−*A*. The puckering of the cyclohexene ring by displacement of atom 3 and the rotation of the ring about the 7–6 bond are obvious in the *A*–*A* section of Fig. 8. The right-hand section of Fig. 8 also illustrates the degree of coplanarity of the molecules contained in the various plane strips. The effective thickness of the chain for packing purposes is 3·6 Å; all of the intercarbon distances are acceptable van der Waals contacts.

The rotation of the cyclohexene ring about the 7–6 bond, while providing intramolecular clearance between methyl group 16 and the hydrogen atom bonded to atom 8, also produces a very satisfactory intermolecular arrangement, particularly with regard to methyl groups 16, 17, and 18 and the molecular chain of DHC. Molecules *A* and *B* form a compact strip beneath molecule *C*. Molecule *B* extends under atoms 19 and 18 but molecule *A* ends at about atom 9 of *C*. The chain and ring simply twist down into the remaining space, bringing atom 16 into contact with 18 and 2 of *A*, and atoms 16 and 4 into contact with 17 of *D′*, in the layer beneath *A* and *B*. The *A*–*A* section of Fig. 8 shows how the methyl groups of molecules *C* and *D′* come together to box the central portion of molecule *B* above the cyclohexene ring of molecule *A*; this joining of the methyl groups occurs along the side of the conjugated chain where there are only hydrogen atoms. In summary, the molecules are interlocked into strips by the merging of the protruding methyl groups; the strips of molecules are closely packed side by side but with the chains displaced along their length sufficiently for the bulky cyclohexene rings to fit at the ends; the central portion of each molecular chain is tightly boxed by its six neighboring molecules.

Fig. 9 shows the packing of the rings along the glide planes of the unit cell. Molecules *E* and *F* are related to *A* and *C* respectively by the *c* glide in the direction $-c/2$. The lengths of the packing vectors are all sufficiently long. One possible reason for the non-occurrence of the alternative puckered form of the cyclohexene ring is illustrated in Fig. 9; that is, atom 3 of molecule *E* cannot be displaced to the other side of

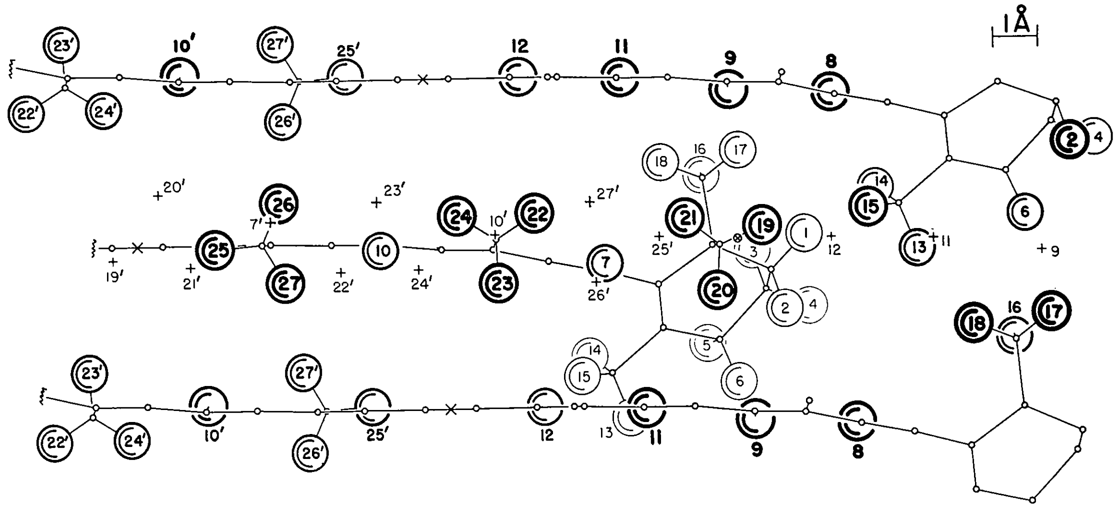

Fig. 10. The interpacking at the hydrogen atoms of DHC as viewed looking at the chains on edge roughly normal to the mean length of the molecule. The upper and lower molecules are derived from the central molecule by the translations $-a$ and c, respectively. For the sake of clarity only the hydrogen atoms that are in contact are shown; also only the hydrogen atoms are numbered. The crosses in the central portion of the figure are the projected positions for the hydrogen atoms from the molecule related by the translation $c-a$, the center of which is indicated by the symbol ⊗. Thus the figure shows the hydrogen interactions within a plane strip and between plane strips of the structure.

the ring, because of the proximity of atoms 4, 5, 6, 16, and 17 of *A*.

The packing of the hydrogen atoms within a section

The packing of the hydrogen atoms of DHC is illustrated in Fig. 10, which shows the hydrogen contacts of the molecules *C*, *A*, and *D′* of the *A–A* section of Fig. 8. Superimposed as crosses are the hydrogen atoms of molecule *B*. Many of the features of the packing of the hydrogen atoms along the chain and around the cyclohexene ring, particularly as regards the methyl groups, are evident in Fig. 10.

Molecular parameters

Conformation of the DHC *molecule*

Apart from the *s-cis* orientation about the bond from the chain to the ring, DHC is in the all-*trans* configuration. Other significant structural detail involves the conformation of the methyl groups of the molecule. Figs. 3 and 10 illustrate some details of the molecular geometry. Two of the methyl groups, 17 and 18, are bonded to tertiary carbon atoms, and the rotational orientation of these groups should at least in part be dictated by intramolecular nonbonding carbon–hydrogen interactions. Methyl group 17 has almost exactly a staggered conformation with respect to atoms 2, 6, and 18. Methyl group 18 also has a staggered conformation relative to the appropriate carbon atoms, 2, 6, and 17, but with some distortion from ideality (see Fig. 10). The rotational displacement, which also improves the intermolecular packing with molecules related by the translations $-a$ and c (Figs. 8 and 10), is probably caused by the close proximity of atom H(21) of the methyl group to atoms 7 and H(7) of the molecular chain.

The other three methyl groups, 16, 19 and 20, are bonded to carbon atoms that are part of the conjugated system and thus have a local environment similar to that of the methyl group of propylene but with additional interactions stemming from the greater molecular complexity. Theoretical predictions and experimental evidence (Pauling, 1960) indicate that in the stable configuration for propylene the double bond eclipses a hydrogen atom from the methyl group. Methyl group 20 has exactly the predicted orientation (see Fig. 3). The other methyl groups, 16 and 19, are somewhat rotated from the predicted stable conformations; in Fig. 3, atoms H(15) and H(24) lie off the projected double-bond vectors **C** and **B**, respectively. It is easy to justify the deviations from the ideal conformations in terms of intramolecular interactions, those between H(15) and atoms 6, 7, and 8 in the case of methyl group 16, and those between H(24) and atoms 11 and H(10) for methyl group 19. To conclude that the orientations found for the methyl groups of DHC supports the bent-bond model for double bonds (Pauling, 1960) would, however, require the always tenuous assumption that the conformation which exists in the crystal is the stable arrangement for the free molecule. The importance of intermolecular forces may be illustrated by the fact that *trans*-β-ionylidene-γ-crotonic acid (Eichhorn & MacGillavry, 1959), which is similar to one end of the DHC molecule, is entirely *trans*.

The rotational orientations of methyl groups 18 and 16, along with the puckering of the ring, give a nearly staggered conformation for 5 pairs of hydrogen atoms around the cyclohexene ring; namely, H(19) and H(20) with H(1) and H(2), H(1) and H(2) with H(3) and H(4), H(3) and H(4) with H(5) and H(6), and H(5) and H(6) with H(13) and H(14). Work with models reveals that the cyclohexene ring with the methyl groups and chain attached is so encumbered with hydrogen atoms that almost no variation of any part of the structure is possible without a change of the entire intramolecular arrangement. In view of the large number of hydrogen interactions in and around the cyclohexene ring it is probable that the conformation found for the carbon atoms is as much a consequence of intramolecular forces as it is a result of the intermolecular arrangement.

Planarity of the DHC *molecule*

The atoms 15, 14, 13, and 20 and the corresponding primed atoms are all within 0·004 Å of a common plane. The remainder of the molecular chain is bent normal to this plane and is also twisted as it comes from the origin. These features can be seen in the carbon skeleton of the upper molecule of Fig. 10, where the bending is downwards and the twist is clockwise as viewed from the ring towards the origin; see also the *A–A* section of Fig. 8. The configuration of the molecule can be described either with the departure, in Å, of the various atoms from the plane indicated above or with the angle of intersection of successive plane sections along the chain, both of which are given in Table 3. The angles are a measure of the rotations about successive bonds along the chain; they would be zero in an ideal conjugated molecule. The positive angles are clockwise rotations and the negative are counter-clockwise for an observer who looks from the first listed atom towards the second, that is, towards the origin. The central portion of the molecule is reasonably flat; in fact a plane can be found which passes within ±0·11 Å of the entire central portion of the molecule, from atoms 9 to 15 inclusive (and indeed to 9′), including the methyl groups 19 and 20. Section *A–A* of Fig. 8 is a projection along an axis contained in such a plane. The deviations of the molecule from planarity are consistent with the intermolecular packing of the molecules, with the largest distortions beginning at the 9–10 bond, as pointed out previously.

Table 3. *Configuration of the 15,15′–dehydro–β–carotene molecule*

Displacement from plane		Bond	Angular distortion		
			Bond type (Sing., Dbl.)	Rotation	Atom located
15	−0·001 Å	13–14	*D*	1° 58′	12
				− 43′	20
14	−0·003	12–13	*S*	2′	11
13	0·004	11–12	*D*	4° 8′	10
12	−0·042	10–11	*S*	− 42′	9
20	−0·002				
11	−0·040	9–10	*D*	6° 34′	8
				4° 17′	19
10	−0·175	8–9	*S*	−8° 46′	7
9	−0·188	7–8	*D*	2° 5′	6
8	−0·475	6–7	*S*	48° 40′	5
19	0·030			48° 25′	1
7	−0·685	5–6	*D*	5° 18′	4
				6° 16′	16
6	−1·017				
5	−1·983				
1	−0·166				

Bond lengths and bond angles

The final intercarbon bond angles and the bond

Table 4. *The bond lengths and bond angles for the carbon atoms of* DHC

Atom Nos.	Bond lengths	σ
15–15′	1·196 Å	0·010 Å
15–14	1·427	0·007
14–13	1·351	0·008
13–12	1·447	0·007
12–11	1·344	0·008
11–10	1·458	0·007
10–9	1·348	0·008
9–8	1·464	0·007
8–7	1·342	0·008
7–6	1·477	0·007
6–5	1·340	0·007
6–1	1·545	0·007
4–5	1·501	0·007
5–16	1·521	0·007
9–19	1·507	0·008
13–20	1·505	0·008
1–2	1·533	0·008
2–3	1·496	0·008
3–4	1·520	0·008
1–17	1·540	0·008
1–18	1·541	0·007
Atom Nos.	**Bond angles**	**σ**
15′–15–14	180·5°	0·9°
15–14–13	124·0	0·5
14–13–12	118·9	0·5
14–13–20	120·7	0·5
12–13–20	120·3	0·5
13–12–11	125·8	0·5
12–11–10	124·2	0·5
11–10–9	124·9	0·5
10–9–8	118·8	0·5
10–9–19	123·2	0·5
8–9–19	117·9	0·5
9–8–7	125·0	0·5
8–7–6	126·1	0·5
7–6–5	122·8	0·4
7–6–1	114·5	0·4
1–6–5	122·6	0·4
6–5–4	123·1	0·5
6–5–16	123·7	0·5
4–5–16	113·1	0·4
6–1–2	110·9	0·4
6–1–17	109·8	0·4
6–1–18	111·5	0·4
17–1–18	107·3	0·4
17–1–2	110·6	0·4
18–1–2	106·7	0·5
1–2–3	113·4	0·5
2–3–4	110·6	0·5
3–4–5	113·4	0·5

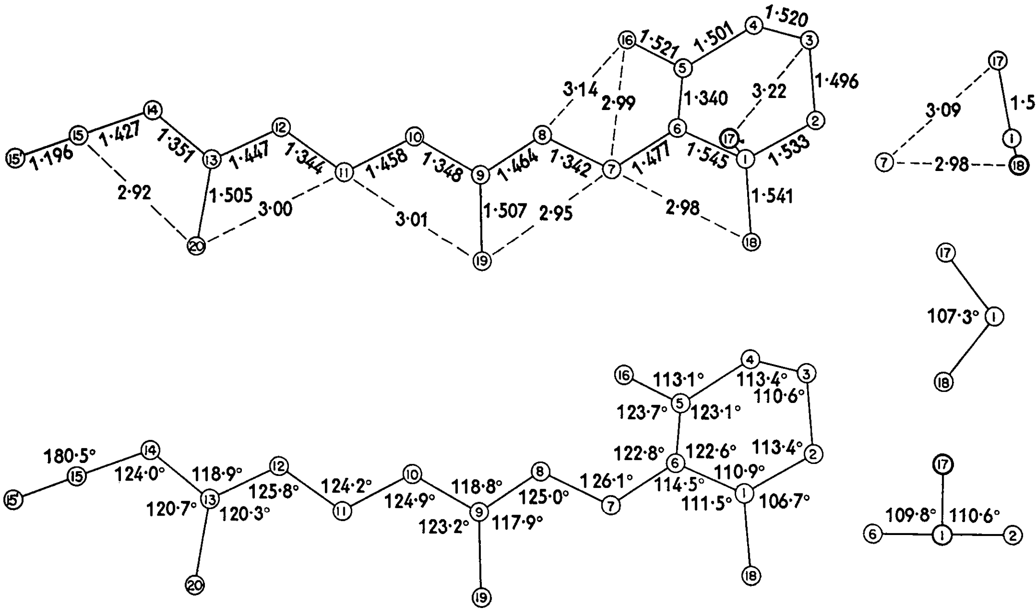

Fig. 11. The bond lengths and bond angles of DHC.

lengths between carbon atoms in the molecule of DHC are shown in Fig. 11 and are listed along with the appropriate standard deviations in Table 4.

Four of the single bonds which are attached to but not part of the conjugated system, namely the 13–20, 9–19, 5–16, and 4–5 bonds, are all significantly shorter than a normal single bond; their average length is 1·508 Å. Similar shortening has been reported for epuivalent bonds in other compounds (McHugh & Schomaker, 1955). That the 1–6 bond is not similarly shortened is probably due to steric effects associated with the two methyl groups bonded to atom 1, although both of the bonds to the methyl groups are normal length single bonds. Two of the normally single bonds in the cyclohexene ring are significantly shorter than the predicted 1·542 Å; a possible explanation of this anomaly will be given when the vibrational parameters are discussed.

Fig. 12 shows the bond lengths along the conjugated chain plotted successively from the end; the numbering is such as to give the total number of atoms in the conjugated system for the last plotted bond-length. Data for *trans-β*-ionylidene-γ-crotonic acid (Eichhorn & MacGillavry, 1959)* and for 1,8-diphenyl-1,3,5,7-octatetraene (Drenth & Wiebenga, 1955) are included in the figure. In comparing the latter two compounds with DHC it has been assumed that the conjugation associated with the C=O of an acid and the conjugation associated with a phenyl group are approximately equivalent to that of a carbon–carbon double bond. All of the data have been plotted with lengths equal to twice the standard deviation given

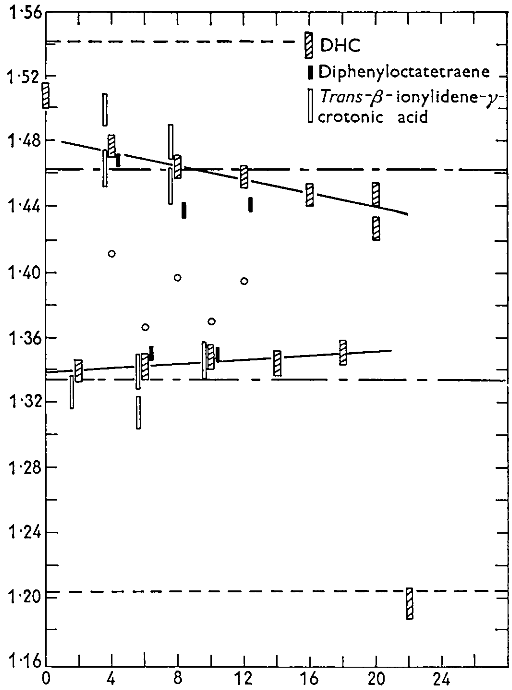

Fig. 12. Bond lengths along the conjugated chains of DHC, trans-β-ionylidene-γ-crotonic acid (Eichhorn & MacGillavry, 1959), and diphenyloctatetraene (Drenth & Wiebenga, 1955). The dash–dot lines represent the values of the single and double bonds, 1·462 and 1·334 Å respectively, of the non-aromatic compound cyclo-octatetraene, as determined by electron diffraction (Bastiansen, Hedberg & Hedberg, 1957), while the dashed lines are the predicted bond lengths of isolated single and triple bonds. The small circles represent the theoretical molecular orbital values reported by Drenth & Wiebenga (1955) for diphenyloctatetraene.

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* *Note added March* 1963. The crystal structure of a second compound related to Vitamin *A* has recently been published (Stam & MacGillavry, 1963).

by the respective authors. The bond lengths of cyclo-octatetraene are included because they are very reliable, with a quoted standard deviation of 0·001 Å, and because they represent a system that is presumably less strongly conjugated than butadiene. It may be noted that the three values for the single bonds at $n=4$ that are longer than the value from cyclo-octatetraene are all bonds from a ring system to a chain. Deviations from planarity and/or steric factors are probably the reason for the long bonds. All of the remaining single bonds are within limits of error either the same as or shorter than the value for cyclo-octatetraene.

In order to compare the 14–15 bond length with the other distances along the chain of DHC two corrections must be made. First, the proximity of the triple bond is expected to decrease the bond length by about 0·037 Å. Second, as will be discussed shortly, it is probable that the bond has been artificially lengthened by the refinement procedure. A rough estimate leads to the corrected value of 1·45 Å, which is plotted in Fig. 12 along with the observed distance of 1·427 Å.

Early theoretical treatments of linear conjugated systems predicted rather rapid convergence of the bond lengths to a mean value of 1·395 Å (Coulson, 1939) as the chain length is increased. For example the small circles plotted on Fig. 12 represent the theoretical molecular orbital values reported by Drenth & Wiebenga (1955) for diphenyloctatetraene. The data reported in Fig. 12 are in considerably better agreement with more recent theoretical treatments which predict that the difference between single and double bonds should be the same order of magnitude for very long polyenes as it is for shorter ones. See for example Simpson (1951), Labhart (1957), Ooshika (1957), Longuet-Higgins & Salem (1959) and Kuhn (1959).

The average of the six bond angles along the chain, neglecting those opposite the methyl groups 19 and 20, is 125.0°, with no significant differences from the mean value. The bond angles opposite the methyl

Table 5. *Vibrational parameters for the carbon atoms of* DHC

At. No.	Direction cosines relative to orthogonal axes					
	x_0	y_0	z_0	B_i	u_i	u_H
1	−0·9693	0·2233	0·1033	0·615 Å²	0·177 Å	
	0·2372	0·9595	0·1519	1·188	0·245	—
	−0·0652	0·1717	−0·9830	1·465	0·272	
2	−0·8883	0·2869	0·3587	1·109	0·237	
	0·3974	0·8717	0·2867	1·374	0·264	0·280 Å
	−0·2304	0·3973	−0·8883	1·884	0·309	
5	−0·9281	0·3225	0·1862	0·943	0·219	
	0·3614	0·9008	0·2408	1·050	0·231	—
	−0·0901	0·2907	−0·9526	1·368	0·263	
6	−0·8482	0·5153	0·1227	0·533	0·164	
	0·5297	0·8279	0·1844	1·223	0·249	—
	−0·0066	0·2214	−0·9752	1·382	0·265	
3	−0·5455	0·7907	0·2780	1·081	0·234	
	0·8176	0·5750	−0·0309	1·271	0·254	0·292
	−0·1842	0·2104	−0·9601	1·908	0·311	
4	−0·6507	0·5798	0·4903	1·033	0·229	
	0·7208	0·6747	0·1588	1·239	0·251	0·261
	−0·2387	0·4568	−0·8569	1·670	0·291	
7	−0·7023	0·5371	0·4672	0·877	0·211	
	0·6259	0·7785	0·0460	1·132	0·239	0·280
	−0·3390	0·3247	−0·8830	1·376	0·264	
8	−0·7558	0·5613	0·3371	0·847	0·207	
	0·4031	0·8046	−0·4360	1·273	0·254	0·280
	−0·5160	−0·1936	−0·8344	1·444	0·270	
9	−0·8610	0·3793	0·3388	0·870	0·210	
	0·4017	0·9158	−0·0044	1·040	0·230	—
	−0·3119	0·1323	−0·9409	1·464	0·272	
10	−0·7602	0·5235	0·3847	0·825	0·204	
	0·4102	0·8460	−0·3407	1·329	0·259	0·261
	−0·5038	−0·1012	−0·8579	1·472	0·273	
11	−0·7814	0·4423	0·4402	0·854	0·208	
	0·4964	0·8680	0·0090	1·555	0·281	0·261
	−0·3781	0·2256	−0·8979	1·249	0·252	
12	−0·6802	0·6154	0·3982	0·622	0·178	
	0·2808	0·7206	−0·6340	1·249	0·252	0·261
	−0·6771	−0·3194	−0·6630	1·631	0·287	

Table 5 (*cont.*)

At. No.	Direction cosines relative to orthogonal axes					
	x_0	y_0	z_0	B_i	u_i	u_H
13	−0·7000	0·5840	0·4111	0·575 Å²	0·171 Å	
	0·5457	0·8087	−0·2197	1·506	0·276	—
	−0·4608	0·0706	−0·8847	1·329	0·259	
14	−0·7281	0·5842	0·3586	0·957	0·220	
	0·4956	0·8100	−0·3135	1·339	0·260	0·280 Å
	−0·4736	−0·0505	−0·8793	1·584	0·283	
15	−0·6372	0·6801	0·3625	0·958	0·220	
	0·5205	0·7267	−0·4483	1·521	0·278	—
	−0·5684	−0·0970	−0·8171	1·712	0·294	
16	−0·9638	0·1618	−0·2118	1·002	0·225	
	0·2595	0·7504	−0·6079	1·621	0·287	0·261
	0·0606	−0·6409	−0·7652	1·568	0·282	
17	−0·9735	0·0742	0·2162	1·361	0·263	
	0·1249	0·9649	0·2312	1·637	0·288	0·268
	−0·1914	0·2521	−0·9486	1·223	0·249	
18	−0·8598	0·5102	−0·0185	1·419	0·268	
	0·5056	0·8459	−0·1697	0·996	0·225	0·268
	−0·0710	−0·1553	−0·9853	1·717	0·295	
19	−0·7241	0·4592	0·5146	1·181	0·245	
	0·5176	0·8549	−0·0347	1·224	0·249	0·268
	−0·4559	0·2412	−0·8567	1·744	0·297	
20	−0·8419	0·3119	0·4403	1·070	0·233	
	0·3071	0·9479	−0·0843	1·192	0·246	0·292
	−0·4437	0·0643	−0·8939	1·729	0·296	
A	−0·7880	0·4380	0·4327	—	—	—
B	0·4213	0·8961	−0·1397	—	—	—
C	−0·4489	0·0722	−0·8907	—	—	—
R	0·1718	0·5911	−0·7881	—	—	—

groups 19 and 20 are approximately six degrees smaller than the mean value along the chain. As a result of this angular disparity the molecule bends in its own plane; that is to say that atoms such as 14, 12, 10, 8, and 6 are not on a straight line even though they are nearly coplanar; see for example Figs. 8 and 11. This in-plane bending is consistent with the asymmetry of the molecule with methyl groups on one side of the chain and hydrogen atoms on the other; it is also consistent with the intermolecular packing of the methyl groups along the chains. The geometry of the molecule appears to be largely the result of repulsion between methyl groups 18, 19, and 20 and atoms 7, 11, and 15. It may be noted that the average bond angles along the chains in *trans*-β-ionylidene-γ-crotonic acid and in diphenyloctatetraene are 124·8° and 124·4° respectively, and that the bond angle opposite the methyl group of the crotonic acid is also small, being 119·8°. It could be that the state of hybridization of the bonds of the carbons attached to methyl groups is different from that of the other atoms along the chain, but the fact that the $\mathrm{C{=}C}\Big\langle\begin{array}{l}\mathrm{C}\\ \updownarrow\\ \mathrm{H}\end{array}$ bond angles are 116° seems to be evidence against such a possibility; it is probable that the observed bond angles are simply the result of intermolecular and intramolecular van der Waals forces.

The bond angles around atoms 5 and 6 of the cyclohexene ring are nearly equal. The deviations from the values reported for tetramethylethylene, 111·5° ± 2° and 124·2° (Pauling & Brockway, 1937), are doubtless the result of ring formation. The bond angles around atom 1 deviate from tetrahedral values in a way that is consistent with the rotational orientation of the methyl groups 17 and 18 and with the environment of the ring structure.

As expected, there is considerable puckering of the cyclohexene ring in the region opposite the double bond. The atoms of the ring deviate from the plane of atoms 1, 5, and 6 as follows:

2	−0·231 Å
3	0·531
4	0·122
16	−0·144

where the positive direction is defined by the cross product 6 → 1 × 6 → 5. The displacements of atoms 4 and 16 are in agreement with the 5°–6° rotation about the 5–6 bond previously noted, but the major displacements are in atoms 2 and 3, particularly the latter.

Vibrational parameters

Table 5 lists for the carbon atoms of DHC the direction cosines of the principal axes of vibration, the associated temperature-factor coefficients, B_i, and the root-mean-square vibrational amplitudes, u_i, where an isotropic temperature factor has the form $\exp[-B_i(4\sin^2\theta)/\lambda^2]$ and the u_i are given by $u_i=\sqrt{(B_i/2\pi^2)}$. The last column of the table gives the root-mean-square vibrational amplitudes assigned to the hydrogen atoms bonded to the corresponding carbon atoms. The orthogonal set of axes used for the direction cosines is defined with i and j parallel to a and b respectively and k completing a right-handed triple. Four reference vectors are listed at the end of Table 5. The vectors **A**, **B**, and **C** are roughly the coordinate axes of the molecular chain; **A** lies along the mean direction of the chain from the origin towards the ring, **C** is normal to the central portion of the chain, and **B** is orthogonal to **A** and **C**. **R** is normal to atoms, 1 5, and 6 of the cyclohexene ring.

In Table 5 the axes of the ellipsoid for each atom are listed in the order of nearest parallelism with vectors **A**, **B**, and **C**; for all atoms except 3, 12, and 16, the axes lie within 30° of the corresponding vectors **A**, **B**, and **C**. Moreover, if the axes of a vibration ellipsoid are called $\alpha<\beta<\gamma$ the above listing also results in sequential ordering of α, β, and γ, with the exception of atoms 11, 13, 17, and 18. If attention is focused on the atoms along the chain, 7 to 14 inclusive, and the two methyl groups 19 and 20, there is, apart from atom 12, even better directional agreement between the vibration ellipsoids and the vector triple **ABC**.

As might be expected, α of atom 15 lies along the triple bond and β and γ are about equal in magnitude. One axis of the ellipsoid of vibration of the methyl carbon atoms has been assumed to lie along the vector direction of the C–C bond; the hydrogen peaks confuse the electron density in the region and require some initial assumption. The α's lie along the C–C bonds for the methyl groups 16, 17, and 18, while the intermediate amplitudes, β, lie along the equivalent directions for the methyl groups 19 and 20.

For all of the ring atoms the γ's are approximately parallel and lie between 25° and 32° from the normal **R** to the ring atoms 1, 5, and 6. The α's are within 16° of perpendicularity to **R** and thus roughly in the plane of the ring. For atoms 1, 2, 5, and 6, the α's and β's are approximately parallel; they lie 60° from the corresponding axes, also parallel, for atoms 3 and 4.

In general the vibrational amplitudes in or near the same direction are roughly the same; therefore the molecule probably undergoes fairly large translatory vibrations as a rigid body, and only moderate amplitude vibrations involving rotations of the molecule as a whole or of isolated atoms or groups of atoms relative to one another. There is some evidence that the positions of the atoms around the origin and in the cyclohexene ring may have been affected by the asymmetric vibrations of the atoms. Atom 15 has two components of high vibration normal to the triple bond. If atoms 15–15′ vibrate with appreciable rocking motion about the center of symmetry some false shortening of the triple bond would be expected from the least-squares refinement (Cruickshank, 1956). The bond is not significantly shorter, on statistical grounds, than a normal triple bond; however, conjugation should leave the bond longer than normal and not shorter. Atoms 2 and 3 have the largest components of vibration of any of the carbon atoms, and as previously noted their ellipsoids of vibration are not in coincidence. It is very probable that the short 2–3 and 3–4 bonds are at least in part the result of an incorrect model for the electron density of the asymmetrically vibrating atoms in this region of the molecule; note that these two bonds were shortened by 0·021 Å and 0·007 Å respectively as a result of the least-squares refinement which followed the inclusion of the anisotropic temperature factors. It could be argued that the 1–2 bond should also be similarly shortened. The 1–6 bond is predicted to be 1·50–1·52 Å, since it is adjacent to a double bond. If the lengthening to 1·545 Å is presumed to be due to steric effects associated with the two methyl groups bonded to atom 1, it is reasonable to assume that the 1–2 bond should be lengthened for the same reason. The value of 1·533 Å for this bond may be the result of a compromise between a real lengthening on steric grounds and some false shortening associated with vibrational parameters. It is beyond the scope of this paper to treat the subject in greater detail; but it is doubtful that the short distances found in the ring are real despite the fact that short bond lengths have also been reported for the same ring system, although differently oriented, in *trans*-β-ionylidene-γ-crotonic acid (Eichhorn & Mac Gillavry, 1959) although with somewhat larger standard deviations (Table 6).

Table 6. *Bond lengths in the cyclohexene ring*

	Sly	σ	Eichhorn & MacGillavry
1–6	1·545	0·007	1·564 ± 0·013
1–2	1·533	0·008	1·537 ± 0·018
2–3	1·496	0·008	1·493 ± 0·020
3–4	1·520	0·008	1·502 ± 0·022
4–5	1·501	0·007	1·500 ± 0·013
5–6	1·340	0·007	1·327 ± 0·010

Variances and covariances

The standard deviations of the bond angles and bond lengths as given in Table 4 were derived from the equations given by Cruickshank & Robertson (1953) using the variances and covariances determined from the standard least-squares expression

$$\sigma_{ij}^2=\frac{\Sigma(\Delta F)^2 w}{s-m}\,c_{ij}\,,$$

where $\Sigma(\Delta F)^2w$ is the sum of the squares of the residuals with w the weight as previously defined, s is the number of independent reflections, m is the number of parameters, and c_{ij} is the term in the inverse

Table 7. *The variances and covariances,* $\sigma_{ij}^2(10^6)$, *in* Å^2, *for the carbon atoms of* DHC *in terms of the previously defined orthogonal coordinates*

1	21·7	1·4	−1·3	6	22·1	3·2	−1·2	11	28·6	3·7	−0·5	16	30·9	1·3	−4·1
		24·9	−0·8			22·8	−1·0			29·9	−0·8			35·3	−0·2
			30·2				28·3				29·3				38·1
2	34·8	0·2	0·4	7	27·3	0·8	−0·3	12	28·2	4·0	1·9	17	36·4	0·5	−3·0
		34·8	−3·2			24·7	−1·5			24·6	−1·0			36·2	1·5
			41·6				29·7				30·0				34·7
3	34·3	0·6	−0·3	8	28·4	2·3	−0·3	13	26·6	4·5	−0·3	18	34·1	−2·6	−1·6
		30·6	−2·0			26·4	−0·5			25·4	−2·6			28·8	1·3
			41·7				31·0				27·8				39·0
4	31·4	0·4	−0·4	9	25·4	0·5	−0·3	14	31·4	2·3	0·1	19	35·0	−0·5	0·7
		29·7	−3·3			23·9	−0·9			28·9	−0·8			30·7	−1·9
			35·6				30·2				34·9				38·6
5	25·6	0·5	−1·8	10	27·8	2·5	0·2	15	34·0	5·7	1·8	20	32·2	0·4	1·3
		24·3	−1·0			27·1	−1·2			30·2	−2·6			29·6	−1·0
			29·6				31·6				37·6				36·7

matrix of the normal equations. Unobserved reflections have been included in the least-squares treatment but with the provision that when $|F_c| < F_{o\,\min}$, the error term, ΔF, is set equal to zero. The unobserved reflections have not, however, been included in s; therefore it has the value 1723 − 434 (unobs.) = 1289. Although the least-squares refinement was carried out only on 60 positional parameters, m was taken as the total number of parameters derived from the structure, *viz.* 191: 180 parameters for the carbon atoms, 5 orientational parameters for the methyl groups, 4 temperature factor exponents for the hydrogens and 2 parameters for scale and extinction. The σ_{ij}^2 values were evaluated from the working equation

$$\sigma_{ij}^2 = \frac{\Sigma(\Delta F)^2 w}{s-m} \cdot \frac{(D_{ij}(-1)^{i+j})}{D},$$

where D is the determinant of the normal equations and D_{ij} is the same determinant with the ith row and jth column suppressed. This expression has been evaluated neglecting all interatomic off-diagonal elements in the matrix; that is, by the use of a three-by-three matrix for each atom. The resulting variances of parameters have been converted to Ångström units and transformed to the orthogonal axes previously defined; the resulting orthogonal variances and covariances are given in Table 7.

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