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The Crystal Structure of 15,15′-Dehydrocanthaxanthin

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The crystal structure of the synthetically prepared 15,15′-dehydro derivative of the naturally occurring pigment canthaxanthin has been determined in order to examine the influence which a reinforcement of the carotenoid conjugated system by a carbonyl group in the ring might have on the way in which the rings are attached to the chain. The crystals are triclinic ($P\bar{1}$); one centrosymmetric molecule per unit cell, which has the dimensions $a = 8{\cdot}144$, $b = 10{\cdot}643$, $c = 11{\cdot}138$ Å, $\alpha = 104^\circ 33'$, $\beta = 79^\circ 29'$, $\gamma = 111^\circ 48'$. The structure has been solved by the Patterson technique and refined by Fourier and least-squares procedures, using complete three-dimensional film data from Cu $K\alpha$ radiation. The anisotropically refined heavy atoms and unrefined hydrogen atoms give, after the introduction of some disorder in the ring, a final discrepancy index R of 9·3%. With the exception of the approximate *s-cis* orientation about the single bond from the chain to the cyclohexenone rings, the double bond system of the molecule is in the all-*trans* configuration. The dihedral angle between the planes of the ring and chain (28°) is smaller than that for 15,15′-dehydro-β-carotene. The chain is curved and slightly bent, normal to its plane. The packing can be described as a complete interpenetration of rings and chains, which prevents chain-chain contacts, giving preference to ring-chain contacts.

Introduction

This study is a further step in a series of investigations of vitamin-A-related compounds and carotenoids, carried out in our laboratory and elsewhere.

Zechmeister's (1943, 1944, 1954) work on the *cis-trans* isomerization laid the foundations for the identification of steric isomers which have markedly different light absorption characteristics. The acceptance of the all-*trans* structure for 15,15′-dehydrocanthaxanthin was based on evidence of the melting point and visible, infrared and nuclear magnetic resonance spectra as discussed by Akhtar & Weedon (1959), Isler, Lindlar, Montavon, Rüegg & Zeller (1956) and Zeller, Bader, Lindlar, Montavon, Müller, Rüegg, Ryser, Saucy, Schaeren, Schwieter, Stricker, Tamm, Zürcher & Isler (1959). The numbering of the atoms in the present investigation is shown in Fig. 1.

Some remarkable features of conformation, bond angles and intramolecular distances have been found consistently in all related structures:

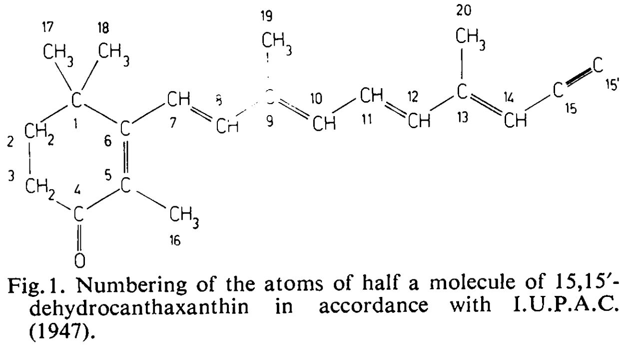

Fig. 1. Numbering of the atoms of half a molecule of 15,15′-dehydrocanthaxanthin in accordance with I.U.P.A.C. (1947).

(*a*) The polyene chain is practically planar as expected. However, it is not a straight zigzag with valence angles of 125° (Drenth & Wiebenga, 1955): wherever a methyl group is attached to the conjugated chain, abnormal valence angles are found, the angle opposite the methyl group being smaller than 125°, whereas the angle opposite the double bond is larger than the expected 110°.

(*b*) The attachment of ring and chain by the single bond C(6)–C(7) has up till now never been found to be such that the double bond system of the cyclohexene ring is coplanar with the conjugated chain. The approximate deviations from the *s-trans* conformation in all-*trans* and 9-*cis*-β-ionylidene-γ-crotonic acid, *trans* vitamin A acid, 15,15′-dehydro-β-carotene and β-carotene are respectively 10°, 100°, 145°, 136° and 145°.

Both anomalies have been interpreted (Stam & MacGillavry, 1963) as being the result of intramolecular Born repulsion between the various methyl groups and atoms not directly bound to the same atom as the methyl group under consideration. It appears that a minimum intramolecular van der Waals distance of about 2·9 to 3·0 Å is maintained. The energies connected with abnormal angles [effect (*a*)] and the loss of conjugation energy [effect (*b*)] will then be compensated by the relief of strain from too-close contacts. Sly (1964) obtained similar results, but left open the possibility that the anomalies could be caused by intermolecular forces.

Professor B. C. L. Weedon drew our attention to canthaxanthin (4,4′-diketo-β-carotene) and derivatives: he pointed out that the extension of the double bond system in the ring by conjugation of the carbonyl group with the double bond C(5)–C(6) might influence the angle between chain and ring.

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The compound under investigation can be isolated during most total syntheses of the naturally occurring polyene pigment canthaxanthin.

X-ray experiments

Cell-constants and space-group

Good crystals of triclinic habit [thin plates (010]) were obtained from a dilute solution of the compound in benzene by slow evaporation at 30° in the dark. The stability of the crystals was found to be good.

The triclinic crystals were orange-red and irregular in habit, although one axis, called [001], could always be easily distinguished. Cell-constants were computed from reflexions with high $\sin\theta$ values on zero-layer Weissenberg diagrams about [001], [100] and [110], calibrated with Al powder lines:

$a = 8{\cdot}144 \pm 0{\cdot}002$ Å $\alpha = 104°33' \pm 3'$
$b = 10{\cdot}643 \pm 0{\cdot}003$ Å $\beta = 79°29' \pm 5'$
$c = 11{\cdot}138 \pm 0{\cdot}003$ Å $\gamma = 111°48' \pm 3'$

(The cell-edge of Al was taken as $a = 4{\cdot}0491$ Å at 20°C.) The density as found by flotation was $1{\cdot}01$ g.cm^{-3}, which corresponds to 1 molecule per unit cell and to a calculated density of $1{\cdot}08$ g.cm^{-3}.

As it is a quite general rule that molecules of symmetry $\bar{1}$ retain this symmetry element in the crystal, the space-group $P\bar{1}$ was assumed. Statistical tests applied to two zones of reflexions also suggested the centric arrangement of the molecules in the crystal. The choice of the space-group was corroborated by the structure determination. With the centre of the molecule at 0,0,0, the positions of the atoms of one half molecule have to be determined.

Optics and polymorphism

The triclinic crystals are highly dichroic; in polarized light, with the incident beam perpendicular to (010), the colour of a thin crystal varies between yellow and red. In the latter case the light vector makes an angle of about 45° with [001] and 35° with [100]. The prediction that the light vector with the highest absorption would coincide in direction with the projection of the chain on the (010) plane was subsequently confirmed [see Fig. 2(*b*)].

Needle-shaped monoclinic crystals ($Z = 4$) are sometimes formed from a solution of benzene. The circumstances under which this modification is likely to occur have not been examined. Without precautions these crystals can only be kept in air or light for a short time. At room temperature they are slowly converted to a triclinic modification. At 80°C the conversion is complete, as could be seen from a series of powder diagrams at different temperatures. The monoclinic crystals could easily be distinguished from the triclinic ones because of their shape or under the polarizing microscope since both are dichroic, but with different angles with respect to the edges. The monoclinic modification was not studied any further.

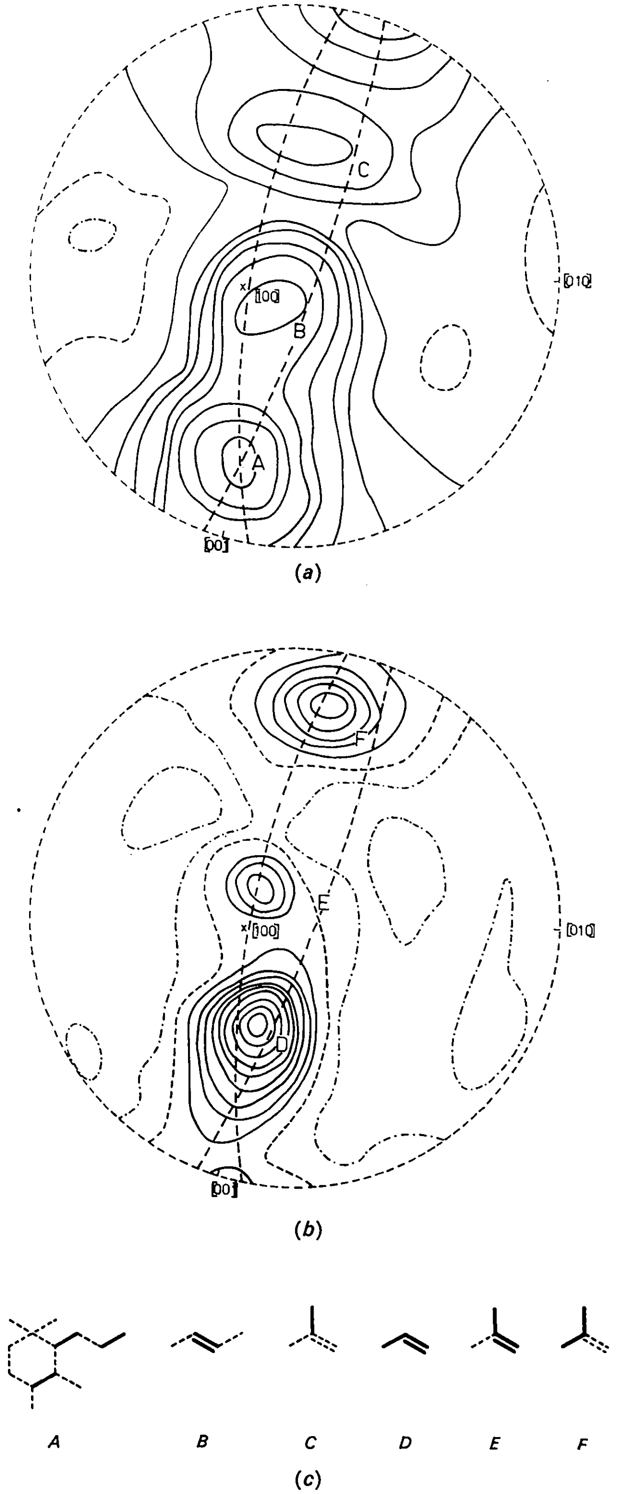

Fig. 2. Stereographic projections of the (*a*) 1·45 Å and (*b*) 2·5 Å spheres around $P(0,0,0)$. The dotted meridian circles indicate the plane of the chain (mostly right) and the plane of the ring (left). Negative contours are indicated by dotted lines. (*c*) Key to the spherical Patterson sections. The direction and length of the vectors is indicated by the beginning- and end-points of the thick lines.

X-ray data

The following intensity data were collected at room temperature with the integrating equi-inclination Weissenberg multifilm technique, using unfiltered Cu radiation: *hk*0 to *hk*9, 0*kl* to 3*kl*. Dimensions of the crystals (thin plates) were $1{\cdot}0\times0{\cdot}4\times0{\cdot}05$ mm and $0{\cdot}5\times0{\cdot}4\times0{\cdot}06$ mm respectively, and the rotation axis in both cases coincided with the largest dimension of the crystals. A total number of 2206 independent reflexions were measured photometrically or recorded directly with a scintillation counter. As the crystals were fairly stable the reliability of the X-ray diffraction data seems to be satisfactory. Data reduction was carried out in the usual way (Lorentz–polarization, $\alpha_1\alpha_2$-splitting, no absorption-correction).

The data were put on a common scale by comparing the reflexions occurring in both zones, according to a least-squares procedure. An approximate overall temperature factor and an absolute scale factor were determined by Wilson's (1949) statistical method.

Patterson synthesis

The interpretation of the unsharpened Patterson function $P(uvw)$ was based on the assumption of a centrosymmetrical molecule with an all-*trans* planar chain, making an unknown angle with the double bond system of the rings. The *P*-values on the surfaces of spheres about the origin with radius 1·45 Å and 2·5 Å respectively were plotted in stereographic projection [Fig. 2(*a*) and (*b*)] in order to obtain a survey of vectors between nearest and next nearest neighbours. On both spheres three major maxima, at angles of about 60° were found. The six vectors are approximately coplanar, those on the second sphere bisecting the ones on the first. They were interpreted as representing nearest and next nearest neighbour distances in the chain C(6)···C(6′). A tentative assignment of the maxima $A-F$ was made as in Fig. 2(*c*), on the basis of the relative frequency of these vectors, correlated with the peak heights. The assignments were in agreement with the optical observations mentioned above.

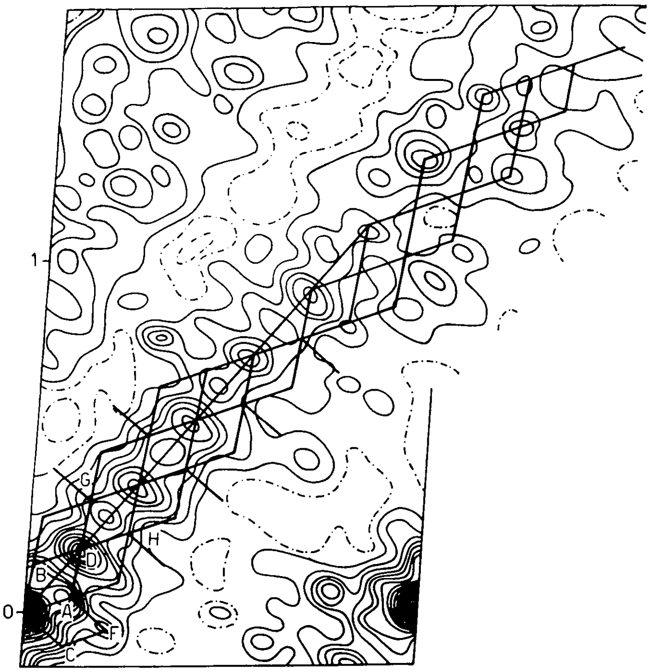

Fig. 3. Section $P(uvw)$ containing the maxima resulting from the separation of the chain atoms. Superimposed is the vector set of a straight chain. Negative contours are dotted. In the horizontal direction the intersections of the vector plane with Patterson sections parallel to (100) are given; the numbers 0 and 1 at the vertical axis refer to relative positions of the intersecting lines with sections at $u=0/360$ and $u=360/360$.

The *P*-values in the central section of this plane were then plotted. A reasonable interpretation of this section could be given on the basis of a straight zigzag chain (Fig. 3). A better fit was however obtained for the vector set of a doubly curved chain; for its construction the results of Sly's structure determination of 15,15′-dehydro-*β*-carotene were used (Sly, 1964). In this way the relative positions of the atoms of the chain were easily derived.

We did not succeed in determining the plane of the ring from the Patterson function.

Solution and refinement

The chain, consisting of 12 atoms in the asymmetric unit, might be regarded hypothetically as a 'heavy atom'. Hence, one can hope to get the signs of about half the structure factors of a chain in a more or less correct position.

From several Fourier syntheses *h*0*l* and 0*kl*, plausible positions of the ring atoms, the methyl groups C(16), C(17) and C(18) and the oxygen atom were determined. Since these positions and especially those of C(2), C(17) and C(18), were rather dubious, four three-dimensional syntheses were subsequently carried out.

In the first block-diagonal least-squares cycles an overall temperature factor was employed. The atomic scattering factors of *International Tables for X-ray Crystallography*, Vol. III, were used. Hydrogen contributions were neglected. When convergence of positional parameters was reached the list of calculated and observed structure factors still showed considerable discrepancies.

A three-dimensional difference synthesis revealed that all the atoms were markedly anisotropic with the largest motion in roughly the [010] direction. C(2), C(17) and C(18) were at minima, whereas three unaccounted for maxima were observed in positions where no atoms had been located (Fig 4.)

Examination of the position of these three maxima revealed that they could be explained by assuming a ring with C(2) on the other side of the plane through C(1), C(3), C(4), C(5) and C(6). Carbons 17 and 18 then swing exactly into positions given by the other two maxima. We have denoted them by C(2*), C(17*) and C(18*). The positions of the *gem* methyl groups are very sensitive to the puckering of the ring. In the next least-squares cycle C(2), C(17) and C(18) were given a larger temperature factor in order to allow for their low electron-density. The parameters of the assumed atoms C(2*), C(17*) and C(18*) were not introduced. After three cycles a three-dimensional difference-Fourier synthesis was calculated, based on terms with $\sin\theta < 0{\cdot}4$. All non-methylic H atoms (0·35–0·45 e.Å^3), could be found although those of C(2) were poorly defined, together with the methylic hydrogens of C(16). Again we noticed three relatively high maxima in exactly the same places as in the first difference synthesis. Anisotropy and the hydrogen atoms so far found were included in fixed positions in the next three least-squares cycles. The positions of the two hydrogen atoms of C(2) were calculated assuming a C_{2v} configuration of the segment C–CH$_2$–C (neglecting the difference in C–C bond lengths), together with a 1·07 Å bond length. Large shifts in the thermal parameters were observed for the methyl carbons, especially for C(17) and C(18), but also for C(2). The standard deviations for these last three atoms were about twice those of the other atoms. From a difference-Fourier synthesis based on reflexions with $\sin\theta < 0{\cdot}4$ reasonable positional parameters of the methyl hydrogens were found. The reliability index R, defined as $100\ \Sigma\ \Delta F(hkl)/\ \Sigma\ F_o(hkl)$, dropped to 12·5.

A difference map based on all the terms showed the following features: hydrogen atoms were systematically in slightly negative regions (we had attributed the same individual isotropic temperature parameters to them as had been found for the carbons to which they are bound); C(2), C(17) and C(18) were in nearly featureless regions; at the positions C(2*), C(17*) and C(18*) significant electron densities ranging from 0·8 to 1·1 e.Å^3 were found.

The SFLS program which we used does not permit the introduction of a variable x expressing the degree of disorder (occupancy factor). Considering that $F_{\rm calc} = (1-x)F_1 + xF_2 + F_3$ in which F_1 is the amplitude based on C(2), C(17) and C(18), F_2 is based on C(2*), C(17*) and C(18*), and the rest of the molecule gives F_3, we can calculate which part of the atoms occupies the new position, by minimizing $\Sigma\ w(F_{\rm obs} - F_{\rm calc})^2$ with respect to x. In this way we calculated that about 15% of C(2), C(17) and C(18) occupy the alternative positions. The same result was obtained by an estimate based on peak heights in the F and ΔF Fourier syntheses. Refinement was continued on the assumption that the structure was disordered in this way. A structure factor calculation including 85% original and 15% alternative orientations yielded an R value of 9·6%.

Table 1. *Influence of disorder on some structure factors*

h	k	l	$F_{\rm calc}(0)$	$F_{\rm calc}(1)$	$F_{\rm calc}(2)$	$F_{\rm calc}(0{\cdot}15)$	$F_{\rm obs}$
4	$\bar{6}$	2	−3·6	+2·2	−2·0	−4·8	−4·6
1	$\bar{5}$	0	+3·7	+4·0	−1·2	+2·7	+2·7
1	$\bar{5}$	1	+12·4	−3·4	+5·3	+14·4	+14·0
$\bar{1}$	$\bar{3}$	3	+12·0	−0·2	+4·4	+13·2	+14·6
0	$\bar{3}$	4	−4·9	−4·0	+4·9	−3·4	−3·2
4	$\bar{3}$	5	−12·8	−3·0	+1·6	−11·8	−10·0
$\bar{3}$	$\bar{2}$	2	+2·4	−0·1	+3·3	+2·9	+3·5
$\bar{3}$	$\bar{2}$	4	−2·3	−0·2	−3·0	−2·9	−3·8
$\bar{2}$	$\bar{2}$	3	+3·7	−2·6	+4·7	+5·9	+6·7
0	$\bar{2}$	4	−3·5	+0·7	−6·4	−5·1	−6·7
$\bar{2}$	$\bar{1}$	3	−2·0	−0·9	−4·9	−3·2	−3·5
$\bar{1}$	$\bar{1}$	4	+5·6	+0·2	−3·9	+4·6	+3·9
1	0	4	+9·2	−3·9	+1·5	+10·0	+10·2
3	0	4	−3·7	+2·8	−3·8	−5·3	−5·2
$\bar{1}$	1	4	−3·8	+1·3	−6·0	−5·0	−6·2
1	1	3	−2·6	+5·4	−5·2	−4·4	−4·7
1	1	5	+11·1	−4·1	+3·3	+12·3	+12·9
3	1	5	+3·8	+2·0	−3·8	+2·6	+2·4
$\bar{2}$	2	2	−8·7	−1·3	+4·5	−7·3	−7·4
$\bar{2}$	2	3	+6·1	−5·6	+1·7	+7·2	+6·8
$\bar{2}$	2	4	+12·8	+2·7	−5·0	+10·7	+11·4
1	2	4	−3·2	+3·9	−4·8	−4·9	−5·1
1	2	8	−2·3	−1·1	+1·2	−1·7	−1·7
2	2	5	−3·1	+1·5	−2·5	−4·3	−4·9
$\bar{3}$	3	2	+2·5	−0·8	+4·5	+3·2	+3·9

In Table 1 some reflexions are collected which were considerably improved by introduction of the disorder. $F_{\rm calc}(0)$ stands for the structure amplitude based on the normal positions ($x=0$); $F_{\rm calc}(1)$ and $F_{\rm calc}(2)$ give the contributions of C(2), C(17), C(18) and C(2*), C(17*), C(18*) respectively; $F_{\rm calc}$ (0·15) is the structure

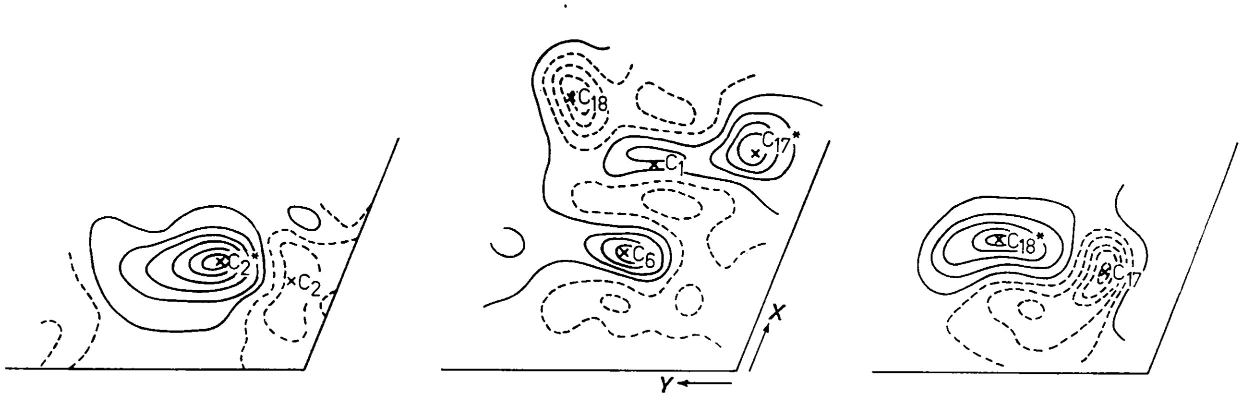

Fig. 4. Sections of the ΔF synthesis calculated with individual isotropic temperature parameters. The three sections, which are parallel to (001) do not pass exactly through the core of all minima and maxima. Contours at intervals of 0·2 e.Å^{-3}. Zero and negative contours are dotted.

factor after introduction of 15% disorder and subsequent refinement. A cycle permitting shifting of the troublesome carbon atoms 2, 17 and 18 only gave a slight improvement to $R=9{\cdot}3\%$. The parameter changes Δx, Δy, Δz for C(2*), C(17*) and C(18*) were within 0·006 Å. The thermal parameters of the atoms of the predominant orientation did not decrease while those of the alternative orientation were strongly reduced. We also calculated structure factors based on 20% disorder. The result was much the same. It is obvious that the parameters of the three alternative atoms (including the probability of their occurrence) have not been determined with accuracy. The possibility had to be considered that residual errors might be prejudicial to the accuracy of the parameters of the predominant orientation. Comparison of the final parameters with those previously obtained for an ordered structure reveals that the effect of considering the alternative orientation is to cause coordinate shifts for C(2), C(17) and C(18) not greater than 0·020 Å. These effects are sufficiently small to suggest that remaining errors in the parameters of C(2*), C(17*) and C(18*) are unlikely appreciably to affect the parameters of the predominant orientation.

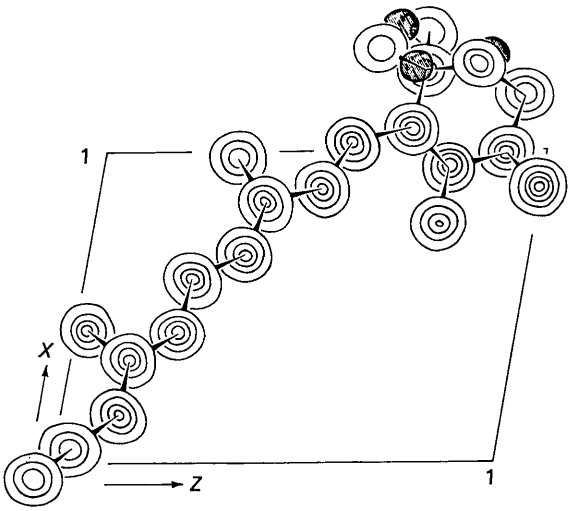

Fig. 5. Final composite Fourier sections parallel to (010). Contours at intervals of 2 e.Å^{-3} starting at 1 e.Å^{-3}. The alternative positions of C(2), C(17) and C(18) are shaded.

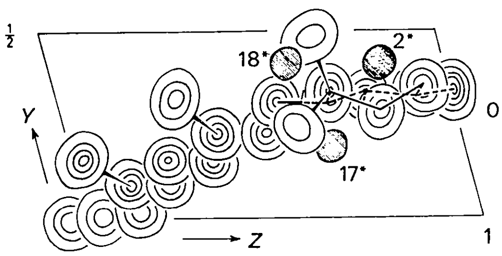

Fig. 6. Composite Fourier sections parallel to (100), calculated with the final structure factors. Contours at intervals of 2 e.Å^{-3} starting at 1 e.Å^{-3}. The shaded atoms are C(2*), C(17*) and C(18*). C(16) is totally obscured by C(5).

Allowance was then made for about 600 unobserved reflexions for which local upper limits of the experimental structure factors were deduced. If $|F_{\text{calc}}| > F_{\text{min}}$, the reflexion was included in the least-squares calculation with an arbitrary value $F_{\text{obs}}=\frac{1}{2}F_{\text{min}}$; those with $|F_{\text{calc}}| < F_{\text{min}}$ were omitted. The weights of the unobserved reflexions were not chosen in accordance with the Cruickshank (1961) scheme (which was used for the F_{obs}) but were taken so that the $\overline{w\Delta^2}$ value was of the same order as for the other reflexions. The reliability factor R of the last cycle including 2206 observed and 228 non-observed reflexions with $|F_{\text{calc}}| > |F_{\text{min}}|$ yielded a value of 10·8%. At this point no significant parameter changes occurred. For x, y and z, the final average and final maximum shifts in parameter values were: 0·0002 – 0·0002 – 0·0002; 0·0008 – 0·0006 – 0·0006. For C(2*), C(17*) and C(18*) these values were 0·0009 – 0·0011 – 0·0012; 0·0020 – 0·0020 – 0·0020. The refinement was terminated here.

The structure factors based on the final parameters are listed in Tables 2(a) and 2(b). Of the calculated 607 non-observed reflexions 52 have $|F_{\text{calc}}| > 2F_{\text{min}}$.

With the final coordinates a last difference synthesis was calculated. Three reflexions suspected of extinction (1$\bar{3}$0, 020 and 030) were omitted. The regions of the *gem* methyl groups and C(2) were now completely featureless.

Figs. 5 and 6 show composite electron density sections viewed along [010] and [100] respectively, based on structure factors calculated with 20% of disorder (the three reflexions liable to extinction were introduced with F_{calc} instead of F_{obs}).

The shaded atoms are C(2*), C(17*) and C(18*). The electron densities at the peaks of the non-disordered carbon atoms varied from 6·2 to 8·4 e.Å^3 with an average value of 7·2 e.Å^3; those of the disordered atoms varied between 4·5 and 5·6 e.Å^3 for the predominant orientation, while the electron densities at the peaks of the alternative atoms reached 1·1 to 1·5 e.Å^3. Finally, oxygen was at 9·7 e.Å^3 whereas the background fluctuation was everywhere less than 0·2 e.Å^3.

Final coordinates and temperature parameters

In Tables 3–5 final positional and thermal parameters of carbon and oxygen are listed, together with their standard deviations. The latter are estimated by the method of least squares, under the assumption that the discrepancies represent random errors.

The final unrefined hydrogen positions with individual isotropic temperature parameters are also given in Table 3.

Structure description

The configuration of the chain is all-*trans*; the ring attachment at the bond C(6)–C(7) is nearer to the *s-cis* than to the *s-trans* conformation. As to the central

Table 2(*a*). *The observed and calculated structure factors of* 15,15′-*dehydrocanthaxanthin*

h	k	l	Fcalc		Fobs
+4	-13	+7	2.9	+	2.2
+5		+3	1.1	+	1.3
		+4	1.5	+	1.7
		+6	1.9	-	1.8
+0	-12	+1	1.4	+	1.4
+1		+0	1.8	+	1.6
+2			0.9	+	1.1
		+1	1.3	+	1.3
+3		+0	1.6	+	1.3
		+6	0.6	-	1.1
		+7	1.5	-	1.5
		+8	1.8	+	2.0
		+9	1.2	-	1.1
+4		+6	1.9	+	2.0
+5		+2	2.0	-	2.1
		+4	2.0	+	2.2
		+6	3.8	-	3.8
		+7	1.9	-	2.2
+6		+2	0.8	+	1.1
		+4	1.8	-	2.1
		+6	2.1	-	2.2
		+8	1.2	+	1.7
+7		+3	1.5	+	1.3
		+4	2.0	-	1.8
		+5	0.9	-	1.1
-2	-11	+2	1.6	-	1.6
		+3	1.7	+	1.9
-1		+1	2.9	+	3.0
		+2	1.3	+	1.6
		+3	1.4	+	1.5
+0		+1	2.1	+	2.0
		+2	1.9	+	1.7
		+6	1.8	-	2.1
		+9	1.4	-	1.0
+1		+0	1.1	-	1.1
		+2	2.1	+	1.6
		+5	2.2	+	1.9
		+6	1.2	+	1.7
+2		+1	2.0	+	2.2
		+2	3.7	+	3.2
		+5	1.7	+	1.6
		+6	1.6	+	1.4
+3		+1	1.9	-	1.7
		+8	3.2	+	3.5
		+9	1.6	-	1.5
+4		+5	2.3	+	2.2
		+6	3.9	+	4.1
		+7	3.8	-	4.2
		+9	1.3	-	1.5
+5		+2	1.9	+	1.9
		+5	1.6	-	2.1
		+6	1.7	+	2.1
		+7	3.6	-	3.8
		+8	2.3	-	2.7
+6		+2	1.7	+	1.9
		+6	1.5	+	1.7
		+7	1.2	-	1.8
		+8	1.3	-	1.7
+7		+4	1.3	+	1.8
		+7	1.9	-	2.2
		+8	2.7	-	2.6
+8		+6	1.0	-	1.2
-3	-10	+3	1.9	-	2.3
		+4	1.1	+	1.5
-2		+1	3.3	-	3.1
		+4	2.0	+	2.6
		+8	1.6	+	1.4
-1		+4	2.2	+	2.3
		+7	2.0	+	2.5
		+8	1.6	+	1.6
		+9	2.1	+	1.8
+0		+1	1.8	-	1.7
		+2	1.2	-	1.8
		+5	1.1	-	1.3
		+9	1.2	+	1.2
+1		+1	2.4	+	2.4
		+3	2.8	+	2.1
		+5	1.6	-	1.6
		+7	2.7	-	2.7
		+9	1.3	+	1.4
		+10	2.4	-	2.4
+2		+1	0.8	+	1.3
		+2	2.1	-	2.5
		+3	0.8	-	1.7
		+5	2.8	-	2.7
		+6	1.9	-	1.8
		+7	1.2	+	1.5
		+8	2.9	-	3.0
		+9	2.6	+	2.6
		+11	2.1	-	2.0
+3		+1	1.9	-	1.9
		+4	0.9	+	1.3
		+6	1.5	-	1.7
		+7	4.9	-	4.7
		+8	0.9	+	1.3
		+9	1.7	-	1.9
+4		+0	2.0	+	1.6
		+1	2.0	-	2.1
		+5	2.9	+	2.9
		+8	1.6	-	2.0
		+9	1.2	-	1.4
+5		+1	2.1	-	1.6
		+3	4.6	+	4.2
		+5	3.8	-	3.0
		+7	3.2	-	3.0
+6		+1	1.5	+	1.5
		+4	2.0	+	2.1
		+7	3.3	+	3.4
		+8	1.7	+	2.2
		+9	1.5	-	1.5
+7		+3	3.8	-	3.5
+8		+4	1.3	-	1.4
		+5	2.0	-	2.2
		+7	2.5	+	2.4
+9		+3	2.0	+	2.0
		+6	2.3	-	1.9
-4	-9	+3	1.7	+	1.8
		+4	2.0	-	2.1
-3		+3	1.4	-	1.6
		+8	2.3	-	1.6
-2		+1	2.6	-	3.0
		+2	3.3	+	2.9
		+3	2.7	+	3.0
		+7	0.6	+	1.2
		+8	1.3	-	1.5
-1		+1	2.0	-	2.3
		+2	2.1	+	2.4
		+3	1.2	+	1.3
		+4	1.5	-	1.5
		+6	1.3	-	1.8
		+7	1.0	-	1.1
		+9	1.6	+	1.6
		+10	2.4	+	2.2
+0		+1	2.1	+	2.2
		+6	1.6	+	2.0
		+9	1.3	+	1.7
		+10	3.5	+	3.1
+1		+0	4.5	+	4.1
		+1	2.8	+	2.9
		+3	4.0	+	4.1
		+4	2.1	+	2.2
		+5	1.2	-	2.1
		+9	0.7	-	1.3
		+10	3.2	+	3.4
		+11	0.2	+	1.2
+2		+0	3.4	+	3.5
		+1	4.5	+	4.6
		+2	3.8	-	3.3
		+3	1.1	-	1.3
		+6	2.2	-	2.5
		+7	2.8	-	2.8
		+9	1.9	+	1.6
+3		+0	1.7	-	1.4
		+1	1.8	+	1.7
		+4	1.6	-	1.7
		+6	2.5	+	2.6
		+7	4.3	+	3.9
		+8	4.3	-	4.6
+4		+0	0.8	-	1.4
		+2	4.0	-	4.2
		+4	0.9	+	1.2
		+5	1.6	+	1.8
		+6	7.1	-	7.2
		+7	1.1	-	1.3
		+8	2.7	-	2.8
		+9	1.3	-	1.4
+5		+2	2.4	-	2.1
		+4	1.5	-	1.8
		+6	5.6	-	5.4
		+7	2.6	-	2.5
		+8	2.0	+	2.1
		+9	1.1	+	1.3
+6		+0	1.1	+	1.0
		+4	2.6	-	2.2
		+5	1.3	-	1.5
		+6	3.0	-	3.1
		+7	2.1	-	1.9
		+9	1.7	-	1.5
+7		+3	2.2	+	2.0
		+4	1.8	-	1.7
		+6	1.9	-	2.0
		+7	2.7	-	2.6
		+8	2.5	+	2.7
		+9	1.0	-	1.6
+8		+1	1.1	+	1.3
		+3	2.4	+	2.6
		+5	3.3	-	3.5
		+6	2.3	+	2.7
		+7	1.1	-	1.4
		+8	1.4	+	1.9
+9		+0	1.0	+	0.8
		+2	2.5	-	2.4
		+3	2.2	-	2.1
		+4	1.8	+	2.0
-5	-8	+3	1.8	+	1.7
		+4	1.3	+	1.4
-4		+1	1.6	+	1.4
		+3	2.5	+	2.6
		+6	1.4	+	1.7
		+7	1.8	+	2.1
-3		+2	5.1	-	4.7
		+4	2.5	+	2.5
		+5	1.6	+	1.6
		+8	0.6	-	1.2
-2		+1	2.9	+	3.3
		+2	2.7	+	2.8
		+3	1.9	+	2.3
		+5	1.3	+	1.6
		+8	1.6	-	1.3
		+9	1.1	-	1.5
-1		+1	1.5	+	1.8
		+2	2.5	+	3.0
		+5	2.6	-	2.7
		+6	3.3	-	2.8
		+9	2.5	-	2.3
		+10	2.0	-	2.0
+0		+1	2.9	+	3.0
		+2	3.6	+	3.4
		+4	3.7	+	4.4
		+6	0.9	-	1.3
		+8	1.8	+	1.8
		+9	3.6	-	3.4
+1		+0	3.4	-	3.0
		+1	3.7	+	3.8
		+2	8.9	+	8.5
		+3	2.4	-	2.5
		+4	1.5	-	1.7
		+5	4.7	+	4.8
		+6	2.6	+	2.9
		+7	3.9	-	4.1
		+8	1.4	+	1.6
		+9	5.1	-	4.5
+2		+0	5.1	+	4.8
		+1	0.8	+	1.5
		+2	1.9	+	2.2
		+5	1.7	+	2.1
		+6	5.7	+	4.9
		+7	2.6	-	2.6
		+8	6.3	+	5.5
		+10	2.5	-	2.6
+3		+0	1.7	-	1.8
		+1	2.4	+	2.8
		+2	2.6	+	2.5
		+3	2.6	+	2.1
		+4	2.0	+	2.4
		+6	7.0	+	6.7
		+7	0.5	-	1.9
		+9	1.9	-	2.0
+4		+0	4.9	-	4.1
		+1	2.1	+	2.1
		+2	2.1	+	2.3
		+4	3.5	+	3.3
		+5	1.1	+	2.3
		+6	1.1	-	1.3
		+7	5.4	-	4.9
+5		+1	3.0	+	2.9
		+2	6.7	+	6.3
		+4	3.0	-	2.7
		+5	2.4	-	2.2
		+6	2.9	+	2.9
		+7	3.6	-	3.4
		+8	3.4	-	3.5
		+9	1.6	+	1.6
+6		+4	2.5	-	2.5
		+7	3.1	-	3.0
		+8	6.0	-	5.7
+7		+1	1.7	-	1.5
		+2	2.0	-	2.2
		+3	1.5	+	1.6
		+4	3.1	+	2.6
		+6	2.4	-	2.6
		+7	1.4	-	1.5
		+8	0.7	-	1.7
		+9	1.5	+	1.7
+8		+1	1.1	-	1.4
		+3	2.7	-	2.1
		+4	3.0	-	2.6
		+6	1.3	-	1.7
		+7	2.1	-	2.6
+9		+0	1.9	-	1.8
		+1	1.2	-	1.2
		+2	1.8	-	1.9
		+3	1.3	-	1.3
		+6	2.5	-	2.6
		+7	1.9	-	1.8
		+8	0.9	-	1.0
+10		+1	2.8	+	1.9
-6	-7	+2	1.9	-	1.8
		+3	2.2	-	2.0
-5			2.2	-	2.5
		+4	3.4	-	3.6
-4		+3	2.9	-	3.0
		+5	2.4	+	2.1
		+6	1.6	-	1.7
		+7	0.2	-	1.6
		+8	2.3	-	2.3
-3		+1	2.3	-	2.0
		+2	2.3	-	2.4
		+3	1.9	-	2.4
		+4	3.4	+	3.4
		+5	1.7	+	1.8
		+6	1.9	+	2.2
		+8	2.7	+	2.6
		+9	0.1	-	0.9
-2		+1	5.0	+	4.7
		+2	2.8	+	3.0
		+3	3.2	+	3.5
		+4	4.2	+	4.1
		+6	1.7	+	1.8
		+9	1.8	+	1.7
-1		+2	1.9	-	2.1
		+3	1.7	-	1.9
		+4	3.5	+	3.7
		+5	1.5	+	2.1
		+6	3.4	-	3.4
		+8	2.7	+	2.6
		+9	2.1	+	2.1
		+10	2.1	-	1.8
		+12	2.7	-	1.8
+0		+1	3.9	-	4.4
		+3	2.3	+	2.1
		+4	2.4	+	2.6
		+5	2.1	+	2.3
		+8	2.5	+	2.9
		+9	3.6	+	3.6
		+10	4.6	-	4.0
+1		+0	1.8	-	2.0
		+1	3.4	-	3.4
		+2	1.2	+	3.0
		+3	3.4	-	3.6
		+4	4.9	-	4.8
		+5	7.5	-	7.1
		+6	0.4	-	1.3
		+7	2.8	+	2.8
		+8	4.1	-	3.8
		+9	1.4	+	1.6
		+11	2.6	-	3.0
		+12	2.3	-	2.6
+2		+0	5.9	+	6.4
		+1	7.8	-	7.6
		+2	1.0	-	1.4
		+3	2.6	-	3.4
		+5	3.3	-	3.4
		+6	4.1	-	3.5
		+7	5.4	+	5.3
		+8	4.8	+	4.5
		+9	3.7	-	3.5
		+10	2.2	-	2.3
+3		+0	3.0	+	2.7
		+1	3.5	-	3.9
		+2	1.7	-	1.4
		+3	2.4	-	2.2
		+5	1.7	+	1.7
		+6	3.3	+	3.8
		+7	6.4	-	5.9
		+8	2.7	-	3.0
		+9	3.2	-	2.9
		+10	3.2	-	2.8
		+12	2.1	-	2.4
+4		+1	4.2	-	3.8
		+3	3.1	+	3.1
		+4	6.1	+	6.4
		+5	5.0	-	4.8
		+6	1.5	+	1.6
+5		+0	1.1	+	1.1
		+2	4.0	+	3.5
		+3	2.0	+	1.7
		+4	1.9	+	1.9
		+5	2.9	-	2.7
		+6	1.6	+	1.7
		+7	6.4	+	6.0
		+8	1.7	+	1.8
		+9	0.9	-	1.4
+6		+0	3.2	-	2.6
		+1	1.7	+	1.3
		+2	1.5	-	2.2
		+3	1.6	-	2.0
		+7	4.1	+	4.2
		+8	1.7	-	1.9
+7		+1	3.0	+	3.1
		+3	3.0	+	2.7
		+4	1.6	+	1.7
		+6	4.6	-	4.3
		+7	5.0	-	4.5
		+9	1.2	+	1.4
+8		+3	4.6	-	4.5
		+4	6.0	-	5.1
		+5	3.0	-	3.0
		+6	2.6	-	2.6
		+8	1.8	-	2.0
+9		+1	1.6	-	1.6
		+2	2.1	-	2.0
		+3	2.1	+	2.1
		+7	3.0	+	3.5
		+9	2.7	-	2.3
+10		+3	2.0	-	2.2
		+5	1.0	+	1.1
-6	-6	+2	1.6	+	1.0
		+4	2.6	-	2.6
-5		+2	2.2	+	1.7
		+5	1.3	-	1.5
		+6	1.1	-	1.3
		+8	1.4	-	1.6
-4		+1	1.7	+	1.7
		+2	2.5	+	2.7
		+3	5.3	-	5.5
		+4	3.3	-	3.3
		+5	1.9	+	1.9
		+6	1.7	+	1.8
		+7	1.8	-	1.8
		+8	3.6	-	3.4
-3		+1	7.2	-	6.8
		+2	1.7	+	2.0
		+3	5.8	+	5.5
		+6	1.4	+	2.3
-2		+1	2.3	-	3.0
		+2	3.4	-	3.6
		+3	1.8	+	1.9
		+7	1.9	-	1.6
		+8	1.5	-	1.8
		+9	2.0	+	2.4
		+10	1.9	+	1.9
-1		+1	1.9	+	2.3
		+2	2.0	+	2.1
		+3	2.0	+	2.1
		+4	5.1	-	5.1
		+5	3.2	-	3.6
		+6	4.3	+	4.0
		+8	1.4	-	1.7
		+9	4.1	+	3.7
		+10	3.8	+	3.5
+0		+1	8.8	+	8.1
		+2	1.4	-	2.0
		+3	11.5	-	11.4
		+4	1.9	+	2.1
		+5	2.9	-	3.1
		+6	2.5	+	2.9
		+7	2.8	+	2.6
		+8	4.2	-	4.0
		+9	3.8	+	3.5
		+10	2.3	+	2.2
		+11	1.7	+	2.1
+1		+0	8.6	+	8.7
		+1	13.6	+	11.4
		+2	3.2	+	3.4
		+4	2.7	-	3.0
		+5	1.2	-	1.4
		+6	6.8	-	6.6
		+7	2.1	+	1.7
		+8	4.5	-	4.3
		+9	6.8	+	6.6
		+10	2.4	+	2.2
		+11	2.8	-	2.5
		+12	0.6	-	1.5
		+13	2.4	+	2.4
+2		+0	4.5	+	5.6
		+1	0.4	+	2.0
		+2	1.7	-	1.3
		+3	4.4	+	4.8
		+4	2.3	+	2.3
		+5	3.0	+	2.7
		+6	3.4	-	4.0
		+7	7.9	+	7.4
		+8	1.7	-	1.8
		+9	2.3	-	2.2
+3		+0	1.1	+	1.3
		+1	1.5	-	2.1
		+2	4.0	-	4.6
		+3	3.2	-	3.3
		+4	2.9	-	3.3
		+5	5.4	+	4.9
		+6	3.6	-	4.1
		+7	3.3	-	3.2
		+8	6.1	-	5.8
		+9	3.0	-	3.2
		+11	1.7	-	2.0
		+12	1.6	-	2.7
+4		+0	3.6	+	3.7
		+1	1.8	-	2.6
		+2	4.8	-	4.6
		+3	2.4	+	2.7
		+4	2.0	-	2.1
		+5	3.8	-	3.4
		+6	4.7	-	5.0
		+8	0.4	-	1.5
+5		+0	2.3	+	2.3
		+2	6.7	-	6.8
		+3	2.4	-	2.5
		+5	5.8	-	5.1
		+6	9.3	-	9.3
		+7	3.3	-	3.5
		+8	1.8	+	2.1
		+9	4.4	-	3.7
+6		+0	1.1	-	1.5
		+2	1.1	-	1.2
		+3	1.2	-	1.3
		+6	4.9	-	5.1
		+7	8.0	-	7.2
		+8	2.7	+	2.9
+7		+0	0.9	+	1.1
		+1	1.6	+	1.6
		+2	3.7	+	3.7
		+3	4.4	+	3.8
		+4	3.0	-	2.6
		+5	6.7	-	6.0
		+8	1.2	-	1.6
		+9	1.2	-	1.3
+8		+1	2.6	+	2.5
		+2	2.1	-	2.1
		+3	1.9	-	1.7
		+4	1.1	-	1.1
		+7	2.8	+	3.0
+9		+0	1.4	-	1.2
		+1	1.4	-	1.6
		+3	2.0	+	2.0
		+5	2.2	+	2.3
		+6	1.3	-	1.7
		+8	2.8	+	2.8
+10		+4	2.6	-	2.6
		+5	1.1	-	1.3
		+6	1.1	-	1.0
-7	-5	+3	1.4	+	1.7
-6			3.2	+	3.1
		+5	2.6	+	2.5
-5		+1	1.8	+	1.8
		+3	6.8	+	5.8
		+6	2.7	+	2.7
		+7	3.9	+	3.8
-4		+1	3.1	+	2.8
		+2	4.3	-	4.4
		+3	0.6	-	2.0
		+4	3.4	+	3.6
		+5	2.4	+	2.3
		+7	3.1	+	2.8
		+8	1.1	-	1.3
-3		+1	1.6	-	1.6
		+2	5.2	+	4.7
		+3	2.3	+	2.9
		+4	3.5	+	3.7
		+5	4.2	+	3.5
		+6	1.3	-	1.2
		+9	2.1	-	1.7
-2		+1	1.7	-	1.5
		+2	1.8	+	1.9
		+3	1.4	+	1.6
		+4	3.3	-	3.4
		+5	2.4	-	2.6
		+6	2.1	-	1.6
		+7	4.7	-	4.2
		+8	0.9	-	1.4
		+9	2.2	-	2.4
		+11	3.0	-	2.6
		+12	0.9	+	1.3
		+13	1.2	+	1.1
-1		+1	5.8	+	5.8
		+2	3.0	+	3.4
		+3	1.9	+	2.0
		+4	2.8	+	3.6
		+5	2.3	-	1.9
		+8	1.3	-	1.4
		+9	6.7	-	6.3
		+11	2.4	-	1.8
+0		+1	3.7	+	5.3
		+2	15.7	+	15.9
		+3	2.7	+	3.5
		+4	3.2	-	3.5
		+6	1.4	-	1.7
		+7	4.1	-	3.8
		+8	1.9	+	2.1
		+9	10.0	-	8.9
		+10	2.4	-	2.7
		+12	1.7	-	2.1
		+13	3.8	-	3.8
+1		+0	2.7	-	2.7
		+1	14.4	+	14.0
		+2	0.9	-	1.2
		+3	0.6	-	1.0
		+4	2.1	-	2.8
		+5	7.7	+	7.2
		+6	6.7	+	7.3
		+7	6.1	-	5.4
		+8	4.5	-	3.8
		+9	3.3	+	2.7
		+10	2.4	-	2.2
		+11	2.0	-	2.0
		+13	2.0	-	2.6
+2		+0	10.3	-	11.0
		+1	11.1	+	10.4
		+2	2.9	-	3.4
		+3	1.3	+	1.3
		+4	2.4	-	2.5
		+5	6.0	+	6.6
		+6	10.6	+	10.2
		+7	4.2	-	2.9
		+8	1.9	-	2.1
		+9	2.1	-	2.4
		+10	1.8	-	2.3
+3		+0	5.8	-	6.4
		+2	4.8	+	5.3
		+3	2.1	+	2.1
		+4	1.8	+	2.3
		+5	7.8	+	8.3
		+6	1.6	-	2.1
		+7	2.1	-	1.9
		+9	0.6	+	0.9
		+11	2.6	+	2.8
		+12	3.6	+	3.7
		+13	2.6	+	3.2
+4		+1	7.2	+	8.0
		+2	9.8	+	9.4
		+3	8.5	+	8.3
		+4	2.6	-	2.9
		+5	3.7	+	4.3
		+7	2.8	-	2.1
+5		+0	2.8	-	2.9
		+1	2.2	+	2.1
		+2	4.4	+	4.5
		+3	2.0	-	2.1
		+4	3.6	-	3.7
		+5	4.1	+	4.3
		+6	2.4	+	2.5
		+7	8.8	-	8.0
		+8	5.0	-	4.8
		+9	3.6	-	3.0
+6		+0	4.5	+	4.0
		+1	3.5	-	3.7
		+2	1.7	+	1.9
		+4	1.1	+	1.5
		+5	3.3	+	3.4
		+6	4.1	+	4.1
		+7	8.7	-	8.2
		+9	1.9	+	1.7
+7		+0	1.0	+	0.8
		+1	3.2	-	3.1
		+3	1.5	+	1.7
		+4	3.3	-	3.4
		+5	8.3	-	7.7
		+6	2.6	+	2.6
		+7	2.5	-	2.6
		+9	0.9	-	1.1
+8		+0	1.5	-	1.4
		+2	4.1	-	4.0
		+3	4.4	-	4.1
		+4	2.3	+	1.8
		+5	2.3	-	2.4
		+6	2.0	+	1.9
		+7	3.2	-	3.2
		+8	1.2	+	2.1
		+9	2.2	+	2.2
+9		+0	0.2	+	0.7
		+1	1.9	-	1.5
		+3	2.0	-	2.1
		+6	1.9	+	2.6
		+7	2.8	-	3.2
		+8	4.7	-	5.2
+10		+0	2.4	+	2.2
		+5	1.0	-	1.1
-7	-4	+2	2.3	-	2.2
		+3	2.6	-	2.9
		+5	1.1	-	1.4
-6		+2	2.7	-	2.9
		+3	2.1	-	2.3
		+4	1.8	+	1.6
		+7	0.9	+	1.0
		+8	2.1	-	2.0
-5		+1	2.0	-	1.7
		+2	5.1	-	5.1
		+3	1.3	-	1.3
		+7	1.3	+	1.7
		+8	3.2	+	3.2
		+9	1.2	-	1.3
-4		+2	6.5	-	6.1
		+3	1.4	-	1.9
		+4	6.8	+	6.7
		+5	4.0	+	3.8
		+8	3.8	+	3.6
		+9	2.2	+	2.5
-3		+1	4.3	+	4.3
		+2	5.5	+	5.6
		+3	5.2	+	5.3
		+4	4.8	+	5.0
		+5	2.9	+	3.4
		+6	1.9	+	2.4
		+7	2.3	+	2.3
		+9	0.8	+	1.0
		+11	2.4	+	2.1
-2		+1	8.3	-	8.3
		+2	1.1	-	1.2
		+3	2.3	-	2.5
		+4	6.8	+	7.2
		+5	1.6	+	1.9
		+7	2.5	+	2.5
		+8	3.2	+	3.4
		+11	2.1	+	1.9
		+12	1.9	-	1.8
-1		+1	0.5	-	2.1
		+2	6.4	+	6.5
		+3	2.3	-	3.0
		+4	15.4	+	14.9
		+5	6.3	+	6.9
		+6	1.8	-	1.8
		+7	2.0	+	2.3
		+8	7.3	+	6.5
		+9	2.6	+	3.2
		+10	2.6	-	2.8
		+12	0.2	-	1.9
+0		+1	19.1	-	17.9
		+2	6.3	+	6.4
		+3	4.7	-	5.0
		+4	4.2	-	4.2
		+5	4.8	-	4.4
		+6	3.5	-	4.6
		+7	1.7	-	2.3
		+8	4.3	+	4.3
		+9	1.7	-	1.6
		+12	2.8	-	2.8
		+13	1.9	-	2.1
+1		+0	15.8	+	14.8
		+1	9.0	-	9.8
		+2	5.7	-	5.2
		+3	8.9	-	8.9
		+4	5.8	-	5.2
		+5	6.2	-	6.4
		+6	3.5	+	3.4
		+7	1.2	-	1.4
		+8	10.4	+	9.8
		+9	1.1	-	1.1
		+10	4.2	-	4.0
		+14	1.9	-	1.9
+2		+0	4.1	-	3.3
		+1	7.3	-	8.1
		+2	0.9	-	1.4
		+3	8.3	-	8.5
		+4	6.0	-	6.3
		+5	14.3	-	14.5
		+6	6.8	+	8.1
		+7	2.2	-	1.6
		+8	6.6	-	6.1
		+9	6.4	-	5.4
		+10	5.6	-	4.7
+3		+0	3.0	-	2.6
		+1	5.5	-	5.4
		+2	3.7	-	4.2
		+3	2.7	-	3.1
		+4	13.9	+	14.3
		+5	2.1	-	1.8
		+6	6.9	-	6.9
		+7	1.8	-	1.8
		+10	2.9	-	2.1
+4		+0	0.7	-	1.2
		+1	2.6	-	2.6
		+2	3.5	+	3.2
		+3	4.5	+	4.9
		+4	1.1	+	1.1
		+5	1.3	+	1.5
		+9	1.9	+	1.6
+5		+0	6.5	-	6.3
		+1	1.7	-	2.0
		+4	1.5	-	1.8
		+5	4.4	-	4.4
		+6	5.5	+	5.7
		+7	10.9	+	10.3
		+8	5.8	-	5.4
		+9	1.1	+	1.2
+6		+0	1.3	+	1.5
		+1	3.1	+	3.1
		+2	4.1	+	4.2
		+3	1.6	-	2.0
		+4	2.3	+	2.3
		+6	8.0	-	7.6
		+7	8.9	+	8.8
		+8	3.6	+	3.4
+7		+3	4.8	-	4.2
		+4	8.0	-	7.7
		+7	1.6	-	1.1
		+9	0.8	+	1.0
+8		+0	2.9	+	2.5
		+2	3.4	-	3.4
		+3	2.9	-	2.6
		+4	2.6	+	2.4
		+6	1.7	+	2.1
		+7	1.1	+	1.4
+9		+0	2.7	-	2.2
		+3	2.9	-	2.9
		+7	1.1	+	1.7
		+9	3.2	-	2.7
+10		+0	2.6	-	2.5
		+3	2.5	-	2.8
		+4	0.6	-	1.3
-8	-3	+2	2.0	+	2.1
-7		+1	1.2	-	1.3
		+2	1.9	+	1.8
		+5	2.2	-	2.2
-6		+1	1.3	+	1.2
		+2	5.4	+	5.1
		+3	2.9	-	2.8
		+5	1.9	-	2.0
		+6	1.2	-	1.3
		+8	1.5	+	1.7
-5		+1	4.6	-	3.8
		+2	6.7	+	6.5
		+3	6.5	-	5.7
		+4	8.1	-	7.7
		+6	2.9	+	3.1
		+7	3.9	-	3.7
		+8	2.4	-	2.2
-4		+1	7.1	-	6.6
		+2	4.3	-	3.9
		+3	4.5	+	4.8
		+6	2.8	+	2.6
		+7	3.1	-	2.6
		+8	3.5	-	3.9
-3		+1	4.6	-	4.7
		+2	1.5	+	1.1
		+3	2.9	-	3.0
		+5	2.3	-	1.4
		+6	1.6	-	1.7
		+8	4.4	-	3.9
		+12	1.8	-	2.2
-2		+1	1.6	-	2.1
		+2	4.7	+	4.9
		+3	4.9	+	4.5
		+4	6.6	-	6.5
		+5	1.0	+	1.8
		+6	2.9	+	3.2
		+7	1.6	+	1.5
		+8	1.0	-	1.4
		+9	5.8	+	5.3
		+11	2.5	-	2.3
-1		+1	9.1	+	9.6
		+2	1.7	-	1.9
		+3	13.2	+	14.6
		+4	5.5	+	5.1
		+6	2.0	+	2.1
		+7	2.2	-	2.7
		+8	7.4	-	6.8
		+9	8.7	+	8.1
+0		+1	27.3	+	26.4
		+2	3.9	+	4.6
		+3	3.4	-	4.3
		+4	3.4	-	3.2
		+5	1.2	-	1.0
		+6	1.0	-	1.0
		+7	3.3	+	3.3
		+8	9.2	-	8.8
		+9	6.6	+	6.0
		+10	9.7	+	9.4
		+13	3.5	+	3.4
+1		+0	52.0	+	45.3
		+2	3.5	+	3.6
		+3	15.5	+	14.7
		+4	12.8	+	13.7
		+5	1.8	-	0.9
		+6	5.0	-	5.5
		+7	9.7	+	9.1
		+8	3.7	+	3.4
		+9	1.0	-	0.7
		+11	1.9	-	2.0
		+13	3.7	+	4.4
+2		+0	12.4	+	11.8
		+1	10.2	-	10.5
		+2	2.6	-	2.7
		+3	1.7	+	2.1
		+4	2.4	+	3.2
		+5	3.9	+	3.2
		+6	2.8	-	3.4
		+8	4.3	-	3.8
		+9	2.5	-	1.9
		+11	2.8	-	2.0
		+14	2.4	+	2.4
+3		+0	7.2	+	7.7
		+1	2.3	-	2.7
		+2	8.0	-	7.7
		+3	4.6	+	5.1
		+4	3.6	-	4.2
		+5	2.2	-	2.7
		+7	2.3	-	2.5
		+8	2.3	-	2.8
		+9	0.6	-	1.2
		+10	5.9	+	5.3
+4		+0	7.2	+	7.1
		+2	15.6	-	16.9
		+3	7.7	-	7.3
		+4	2.8	-	2.7
		+5	11.8	-	10.0
		+6	6.5	-	6.1
		+7	1.9	-	2.3
		+8	3.2	-	3.3
		+9	4.2	-	2.8
+5		+0	4.2	-	4.4
		+1	1.8	+	2.1
		+2	5.2	-	5.1
		+3	2.5	-	3.3
		+5	4.2	-	4.5
		+6	11.1	-	10.7
		+7	2.5	-	2.4
		+8	1.7	-	1.6
		+9	1.7	+	1.8
+6		+0	1.1	-	1.3
		+1	1.3	+	1.1
		+3	6.3	+	6.3

Table 2(*a*) (*cont.*)

h	k	l	Fcalc		Fobs
		+5	6.4	-	5.7
		+6	13.7	-	14.0
+7		+1	3.8	+	4.1
		+3	3.3	-	3.4
		+4	6.6	-	6.2
		+5	1.6	+	1.7
		+6	1.5	-	1.5
		+7	2.7	+	2.7
		+8	1.6	-	1.4
		+9	1.9	-	1.8
+8		+0	2.1	+	1.8
		+2	0.9	-	1.1
		+3	3.1	+	2.5
		+4	1.8	-	1.6
		+5	2.2	+	2.3
		+7	2.9	+	3.4
		+8	2.0	+	2.3
		+9	2.1	-	2.2
+9		+0	1.7	-	1.3
		+2	2.6	-	2.7
		+3	1.6	+	1.7
		+6	2.5	-	3.4
		+7	0.9	-	1.3
		+8	2.1	+	2.2
-8	-2	+4	1.2	-	1.7
		+5	1.2	+	1.2
-7		+3	2.4	+	2.6
		+5	3.0	+	3.0
		+7	0.9	-	0.9
-6		+2	3.1	+	3.0
		+3	6.6	+	6.8
		+4	2.2	+	2.2
		+7	2.0	+	2.1
		+8	0.8	+	1.0
		+9	2.4	+	1.8
-5		+1	1.7	-	1.8
		+2	2.0	+	2.2
		+5	3.6	+	3.5
		+6	4.0	+	4.3
		+7	4.2	+	4.3
		+8	1.2	-	1.3
-4		+1	3.0	-	2.9
		+2	5.5	+	5.5
		+3	6.3	+	6.3
		+4	4.0	+	4.1
		+5	4.3	+	4.0
		+6	2.9	+	3.2
		+7	3.4	+	3.5
		+8	1.8	+	1.9
		+9	3.8	-	3.6
-3		+1	1.2	-	1.3
		+2	2.9	+	3.5
		+3	1.4	+	1.5
		+4	2.9	-	3.8
		+5	0.6	-	1.0
		+6	1.8	-	2.1
		+7	3.7	-	3.6
		+9	1.1	-	1.5
		+11	2.2	-	2.4
-2		+1	1.9	-	1.6
		+2	1.1	+	1.6
		+3	5.9	+	6.7
		+5	3.1	+	3.5
		+6	1.1	-	1.3
		+7	3.8	-	4.1
		+8	1.1	-	1.5
		+9	1.9	-	2.0
		+11	2.5	-	2.1
-1		+1	6.2	+	6.0
		+2	5.3	+	5.1
		+3	18.3	+	17.9
		+4	9.7	-	8.6
		+5	6.2	-	5.9
		+6	3.1	-	3.0
		+7	3.2	-	3.4
		+8	5.0	-	4.7
		+9	8.9	-	8.0
		+10	4.9	-	4.4
		+13	2.4	-	2.6
+0		+1	52.5	+	49.7
		+2	7.6	+	8.3
		+4	5.1	-	6.7
		+5	0.5	-	1.0
		+6	2.4	+	2.5
		+7	2.6	+	2.8
		+8	2.6	-	2.3
		+9	0.1	-	0.8
		+10	2.5	-	2.7
		+11	2.2	-	2.2
		+12	2.0	-	2.2
		+13	1.4	-	1.3
+1		+0	19.1	-	19.0
		+1	5.3	+	5.6
		+2	12.5	+	13.0
		+3	6.2	-	5.9
		+4	1.7	+	1.4
		+5	18.0	+	17.3
		+6	2.1	-	2.2
		+7	5.7	+	5.6
		+9	3.0	-	3.3
		+10	4.4	-	4.5
		+11	2.2	-	2.6
		+13	2.8	-	3.2
+2		+0	2.5	+	2.8
		+1	8.7	-	9.0
		+2	6.4	-	6.8
		+3	3.1	+	2.8
		+4	8.7	-	8.5
		+5	24.2	+	24.6
		+6	6.6	+	6.6
		+8	1.7	-	2.0
		+9	1.4	+	1.2
		+10	3.1	+	3.0
		+12	2.6	+	2.5
+3		+0	3.0	+	2.5
		+1	18.7	+	18.5
		+2	11.5	+	10.6
		+3	12.5	+	12.5
		+4	4.5	+	4.1
		+5	1.1	-	1.2
		+6	3.3	+	3.2
		+8	1.7	+	1.7
		+9	2.7	-	2.4
		+10	2.2	+	1.6
		+12	1.7	+	2.3
+4		+0	5.0	-	4.9
		+2	18.8	+	19.9
		+3	1.9	-	2.3
		+4	2.3	-	2.0
		+5	2.6	+	2.4
		+6	1.0	-	1.1
		+7	6.0	-	5.8
		+8	2.9	+	3.1
		+9	6.6	-	5.5
+5		+0	4.7	+	4.4
		+2	4.6	+	5.1
		+3	5.6	+	5.6
		+5	8.9	+	8.4
		+6	8.5	+	8.1
		+7	16.3	-	15.0
		+8	1.3	-	1.1
		+9	2.2	+	2.1
+6		+2	4.2	-	4.7
		+5	8.9	-	8.5
		+6	3.6	+	3.7
		+7	4.7		4.9
		+8	2.9		3.1
+7		+0	1.9		1.9
		+1	2.0		2.3
		+2	1.5		1.9
		+3	5.6	-	6.0
		+4	1.5	-	1.8
		+6	1.2	+	1.2
		+9	1.9	+	2.1
+8		+0	1.9	-	1.7
		+1	4.9	-	4.3
		+2	2.0	-	2.0
		+3	1.4	+	1.6
		+4	1.7	-	2.1
		+5	1.3	-	1.9
		+6	0.9	-	1.4
		+7	2.3	-	2.4
		+8	2.0	-	2.5
		+9	0.9	-	1.3
+9		+2	1.8	-	2.0
		+4	1.2	-	1.3
		+5	0.4	-	2.0
		+7	2.4	-	2.6
		+8	2.6	-	2.4
+10		+0	2.6	+	2.1
-9	-1	+2	2.0	-	1.4
-8			1.9	-	1.8
		+4	1.0	-	1.4
-7		+2	4.0	-	3.8
		+3	1.3	+	2.0
		+4	1.2	-	1.7
		+5	1.4	+	1.2
		+7	1.0	-	1.4
-6		+1	4.1	+	3.8
		+2	11.2	-	11.2
		+3	1.6	-	1.7
		+5	2.9	-	2.9
		+6	0.6	+	1.0
		+7	2.6	+	2.4
-5		+1	5.7	+	5.3
		+2	9.6	-	9.4
		+3	7.4	-	7.7
		+4	6.1	+	6.2
		+5	4.3	+	4.2
		+6	1.4	-	1.6
		+7	2.9	+	3.0
		+8	3.2	+	3.4
-4		+1	1.6	+	1.6
		+2	3.8	+	4.3
		+3	5.0	+	4.8
		+4	6.9	+	7.0
		+6	1.7	-	1.3
		+8	4.7	+	5.0
-3		+1	7.6	+	7.6
		+2	5.1	+	5.1
		+3	2.2	-	1.4
		+4	9.5	+	10.3
		+6	2.7	+	2.6
		+7	1.3	+	1.6
		+8	3.2	+	3.3
		+9	1.2	+	1.3
		+10	2.7	+	2.4
-2		+1	14.4	+	14.0
		+2	12.3	+	12.4
		+3	3.2	-	3.5
		+4	16.5	+	15.7
		+5	13.0	+	12.9
		+6	3.9	+	3.6
		+7	2.9	+	3.0
		+8	6.1	+	5.5
		+9	3.1	-	2.7
		+10	3.5	+	3.5
		+11	1.3	-	2.1
-1		+1	7.8	-	7.0
		+2	2.6	+	3.4
		+4	4.6	+	3.9
		+5	3.9	-	3.5
		+6	2.2	-	2.4
		+7	1.8	-	1.1
		+8	13.2	+	12.0
		+9	4.1	-	4.0
		+11	2.8	+	2.5
		+12	2.5	-	2.5
		+13	1.8	-	2.0
+0		+1	2.9	-	3.6
		+3	12.7	-	12.7
		+4	4.4	+	5.4
		+5	1.7	-	2.1
		+6	0.8	+	1.8
		+7	5.1	-	5.3
		+8	12.2	+	11.9
		+9	8.3	+	8.2
		+10	5.5	-	5.6
		+13	2.1	-	1.8
+1		+0	12.5	-	11.9
		+1	20.1	-	20.7
		+2	15.0	-	14.4
		+3	9.6	-	9.5
		+4	17.3	-	16.6
		+5	16.0	-	15.3
		+6	3.7	+	4.7
		+7	2.4	+	2.3
		+8	5.7	-	5.3
		+9	5.5	-	5.5
		+10	4.4	-	3.6
		+13	1.7	-	2.1
+2		+0	15.4	-	14.8
		+1	18.7	+	18.8
		+2	7.8	-	7.7
		+3	12.5	-	12.3
		+4	3.3	+	3.3
		+5	1.4	-	1.7
		+6	2.9	-	3.6
		+7	0.7	-	0.8
		+8	2.3	-	2.1
		+9	3.3	-	3.2
		+10	4.1	-	3.4
		+11	2.9	+	3.0
+3		+0	7.3	-	7.0
		+1	5.1	-	5.2
		+2	7.7	+	8.3
		+3	2.3	-	1.4
		+4	1.1	+	1.7
		+5	2.0	-	2.8
		+6	6.0	-	6.1
		+7	2.4	-	2.5
		+8	2.5	-	3.0
		+9	1.8	+	1.6
		+10	7.7	-	7.7
		+11	2.4	-	2.5
		+12	2.1	-	2.3
		+13	1.8	-	2.1
+4		+0	5.9	-	6.3
		+1	19.3	-	19.3
		+2	1.9	+	2.8
		+3	4.2	+	4.3
		+4	1.4	+	1.1
		+6	1.0	+	1.3
		+7	4.9	+	5.1
		+8	1.7	-	2.0
+5		+0	3.7	+	3.6
		+1	1.6	+	2.1
		+2	3.3	+	3.0
		+6	1.4	+	1.9
		+8	3.4	+	3.5
+6		+0	0.6	+	0.7
		+1	1.9	+	2.1
		+2	4.0	+	4.1
		+3	3.3		3.7
		+4	6.7	-	6.3
		+5	9.6	-	9.4
		+6	4.5	+	4.7
		+7	3.4	+	3.7
		+8	1.4	+	1.8
+7		+0	3.0	+	2.8
		+1	3.1	+	2.6
		+2	1.9	-	1.9
		+3	6.8	-	6.2
		+4	4.1	+	3.7
		+8	1.4	+	1.3
		+9	1.4	+	1.2
+8		+0	1.8	-	1.6
		+1	2.6	-	2.6
		+3	3.8	-	3.3
		+7	1.8	-	2.0
		+8	2.0	-	2.0
		+9	1.2	-	1.1
+9		+0	1.0	-	1.1
		+3	1.6	-	1.9
		+6	1.2	+	1.7
		+7	3.2	+	3.1
+10		+2	1.1	-	0.8
-9	+0		3.3	+	3.6
-8		+1	2.4	-	2.7
		+2	1.5	+	1.9
		+4	1.5	+	1.6
		+5	1.5	+	1.3
		+6	1.3	+	1.6
-7		+1	1.7	+	2.0
		+2	3.6	+	3.8
		+3	1.8	-	2.1
		+4	1.3	-	1.6
		+5	0.9	-	1.1
		+8	1.6	+	1.5
-6		+2	5.4	+	5.9
		+3	2.9	-	3.5
		+4	8.9	-	8.8
		+5	2.7	-	2.6
		+6	1.7	+	1.6
		+9	1.9	-	1.7
-5		+1	2.3	+	2.5
		+2	2.4	-	2.6
		+5	2.5	+	2.6
		+6	1.4	+	1.4
		+7	3.9	-	3.9
		+8	2.4	-	2.0
		+9	1.4	+	1.2
-4		+1	3.1	-	2.8
		+4	1.2	-	1.2
		+5	1.0	-	1.1
		+6	1.0	-	1.5
		+7	5.0	-	5.3
		+8	7.1	-	6.8
		+9	1.5	+	1.7
-3		+1	4.5	-	2.8
		+2	1.3	-	1.8
		+3	2.2	+	1.9
		+4	2.2	+	2.2
		+5	1.6	-	1.8
		+6	2.3	+	2.8
		+7	2.9	-	3.4
		+8	4.0	-	4.5
		+9	2.7	+	2.6
-2		+1	10.7	+	10.3
		+2	4.7	+	4.7
		+3	2.6	+	3.0
		+4	4.4	+	4.4
		+5	2.8	-	2.9
		+6	2.2	-	1.8
		+7	1.0	+	1.3
		+8	1.4	-	1.4
		+9	2.5	+	2.3
-1		+1	10.8	-	9.2
		+2	35.6	+	38.6
		+3	4.8	-	5.3
		+4	4.6	-	4.1
		+5	3.2	-	3.0
		+6	0.8	+	1.3
		+7	2.1	-	2.8
		+8	3.4	-	3.8
		+9	5.4	+	5.5
		+10	7.4	+	6.8
		+11	2.5	+	2.1
+0		+1	9.8	+	9.7
		+2	6.6	-	7.9
		+3	11.7	+	12.2
		+4	9.1	+	9.8
		+5	3.5	+	3.3
		+6	4.0	+	3.9
		+7	0.7	-	1.1
		+8	0.2	+	1.7
		+9	4.1	+	4.4
		+10	3.3	+	3.4
		+11	2.7	-	2.5
		+13	2.6	+	2.6
+1		+0	19.7	+	20.3
		+1	16.0	+	17.2
		+2	11.2	-	11.5
		+3	7.3	+	7.5
		+4	10.0	+	10.2
		+5	7.3	-	8.3
		+6	6.1	+	6.1
		+7	2.0	+	2.4
		+8	2.9	-	2.8
		+9	3.6	-	3.4
		+13	2.8	+	2.9
+2		+0	3.5	+	3.8
		+1	3.7	-	4.8
		+2	8.9	+	9.0
		+3	11.9	+	11.4
		+4	15.7	+	16.5
		+6	4.2	-	4.4
		+9	1.7	+	1.3
+3		+0	12.6	+	12.4
		+1	5.4	-	4.9
		+2	20.1	-	20.3
		+3	1.1	-	1.1
		+4	5.3	-	5.2
		+5	5.4	-	5.0
		+6	6.1	-	6.4
		+8	6.3	-	6.[illegible]
		+9	2.1	+	2.3
+4		+0	2.8	-	3.2
		+1	4.8	+	5.1
		+2	12.0	-	13.0
		+3	3.4	-	3.6
		+4	1.4	-	1.3
		+5	3.2	-	3.6
		+6	5.8	-	6.4
		+7	3.6	+	4.1
		+8	8.9	-	8.1
+5		+0	1.9	+	2.3
		+2	3.1	-	2.9
		+5	5.7	-	5.5
		+6	19.8	-	18.5
		+9	1.6	-	1.4
+6		+0	0.6	-	0.7
		+2	2.8	+	2.6
		+4	7.5	-	7.0
		+5	2.2	-	2.3
		+6	6.5	-	6.0
		+8	1.5	+	1.8
		+9	1.8	-	1.5
+7		+0	3.5	+	2.9
		+2	2.0	-	2.2
		+9	1.9	-	2.1
+8		+2	1.7	-	2.1
		+3	0.8		1.7
		+5	2.0		2.0
		+6	0.8		1.2
+9		+0	0.6		0.9
		+1	0.5	+	2.1
-9	+1		3.2		3.4
-8		+2	1.4	+	1.2
		+3	1.0		1.2
		+4	1.0	+	1.8
-7		+2	6.3	+	6.5
		+4	2.3	+	2.5
		+5	1.2	+	1.3
		+6	2.2	-	2.6
		+8	1.6	+	1.3
-6		+1	6.5	-	6.3
		+2	6.4	+	6.5
		+3	5.1	+	5.4
		+5	3.6	+	3.5
		+6	3.3	+	3.0
		+8	1.9	+	2.0
-5		+1	6.0	-	6.1
		+2	2.3	+	2.1
		+3	10.0	+	10.1
		+4	5.7	+	5.6
		+5	4.1	+	4.1
		+6	5.4	+	5.5
		+7	2.6	+	3.0
-4		+1	1.7	+	2.0
		+2	4.3	+	4.5
		+3	2.4	+	2.4
		+4	3.6	-	3.6
		+5	2.3	+	2.6
		+6	1.2	+	1.5
		+7	3.9	+	4.0
		+8	1.7	-	1.9
		+9	1.1	-	1.1
-3		+1	9.6	+	8.8
		+2	1.2	+	1.1
		+3	9.1	+	8.7
		+4	6.2	-	6.4
		+5	4.5	+	4.5
		+10	1.6	-	2.0
-2		+1	5.0	-	5.1
		+2	8.3	-	8.1
		+3	16.2	+	15.5
		+4	1.6	+	2.1
		+5	5.9	+	6.5
		+6	5.7	-	5.7
		+7	4.7	-	4.7
		+8	7.0	-	6.5
		+10	5.3	-	4.8
		+11	1.7	-	1.9
		+12	1.5	+	1.8
-1		+1	24.7	+	26.0
		+2	19.3	+	18.9
		+3	3.9	+	3.7
		+4	5.0	-	6.2
		+5	0.4	-	1.3
		+6	3.0	-	3.4
		+7	5.8	-	6.1
		+8	10.2	-	9.4
		+9	2.7	-	2.9
		+10	2.0	+	2.5
		+11	2.8	-	2.2
		+12	1.5	-	2.0
+0		+1	18.1	+	18.7
		+2	8.9	+	8.9
		+3	2.6	-	2.9
		+4	9.6	-	9.8
		+5	7.6	+	8.6
		+6	3.6	-	4.3
		+7	5.3	+	5.4
		+8	1.9	+	3.4
		+9	9.0	-	8.6
		+10	3.8	-	4.0
		+11	3.0	-	2.4
		+12	1.6	-	1.5
		+13	1.7	-	1.9
+1		+0	17.2	-	16.2
		+1	6.5	-	7.8
		+2	2.9	+	2.7
		+3	4.4	-	4.7
		+4	4.8	-	4.8
		+5	12.3	+	12.9
		+6	9.3	+	9.3
		+7	4.5	-	4.7
		+8	1.0	-	1.0
		+9	1.4	-	1.5
+2		+0	13.7	+	13.7
		+1	2.5	+	3.1
		+2	6.5	+	7.2
		+3	3.6	+	3.8
		+4	7.8	+	7.6
		+5	6.8	+	6.4
		+6	1.3	+	1.7
		+7	3.8	-	3.8
		+8	1.1	+	1.5
		+9	1.0	-	1.3
		+10	3.7	+	3.6
+3		+0	4.0	+	3.3
		+1	1.7	+	1.1
		+2	2.9	+	3.0
		+3	5.0	+	6.1
		+4	2.2	-	2.5
		+5	2.6	+	2.4
		+6	2.4	+	2.7
		+7	4.7	-	4.8
		+8	3.3	+	3.1
		+9	4.4	-	4.5
		+10	0.5	-	1.7
		+12	2.3	+	2.4
+4		+0	5.7	-	5.8
		+1	14.1	+	13.6
		+2	7.8	+	8.6
		+3	6.1	+	5.9
		+4	2.1	+	2.5
		+5	3.5	+	3.8
		+6	7.2	+	7.0
		+7	5.9	-	6.1
		+8	4.0	-	3.9
+5		+0	4.8	-	4.1
		+1	2.3	+	2.3
		+2	3.1	+	2.8
		+5	0.3	-	2.5
		+6	5.6	-	5.5
		+7	3.5	-	3.6
		+8	1.5	-	1.5
+6		+0	1.6	+	1.5
		+1	2.5	-	2.6
		+4	6.5	-	6.1
		+5	4.7	+	4.6
		+6	2.9	+	3.0
		+7	2.4	-	2.2
		+8	0.9	-	0.9
		+9	2.5	+	2.5
+7		+0	0.3	+	1.1
		+1	3.3	-	2.8
		+2	6.7	-	6.6
		+3	1.5	+	1.5
		+5	2.2	-	2.3
		+8	1.8	-	1.6
		+9	1.2	-	1.2
+8		+0	2.9	-	2.4
		+1	1.6	-	1.6
		+4	1.7	-	1.5
		+6	1.3		1.5
		+7	1.4		1.2
+9		+0	2.0	+	1.9
		+1	1.6	-	1.4
		+2	0.7	-	1.4
		+4	1.5		1.5
-9	+2	+2	4.0		4.2
-8		+1	2.2	+	2.3
		+2	1.4	-	1.8
		+3	1.9	+	2.0
		+4	1.5	-	1.3
7		+2	7.1	-	7.4
		+3	2.6	-	2.4
		+7	1.3	+	1.3
-6		+1	1.5	+	1.8
		+2	9.3	-	9.4
		+3	8.0	-	8.1
		+4	2.7	+	3.0
		+5	2.6	+	2.7
		+6	2.0	+	2.1
-5		+1	3.3	-	3.7
		+2	5.7	-	6.0
		+3	2.8	-	2.7
		+4	6.0	+	6.2
		+6	2.7	-	2.9
		+7	1.3	+	1.4
		+8	2.8	+	2.6
		+9	1.5	-	1.5
-4		+1	5.5	+	5.2
		+2	4.3	+	4.7
		+3	1.6	+	1.7
		+4	4.0	+	3.9
		+6	2.2	-	2.5
		+7	1.4	+	2.0
		+8	6.6	+	6.3
		+9	1.3	-	1.5
-3		+1	8.7	+	9.1
		+2	8.4	+	8.8
		+3	7.3	+	7.1
		+4	8.5	+	7.9
		+5	7.6	+	8.0
		+6	5.0	+	5.2
		+7	1.1	-	1.7
		+8	5.1	+	4.8
		+9	1.3	-	1.5
		+10	1.9	+	2.1
-2		+1	7.9	+	7.6
		+2	7.3	-	7.4
		+3	7.2	+	6.8
		+4	10.7	+	11.4
		+5	2.4	+	2.6
		+6	1.8	+	1.3
		+7	1.5	+	1.9
		+8	4.9	+	5.1
		+11	2.9	+	3.0
-1		+1	41.4	+	41.2
		+2	1.9	+	1.7
		+3	7.4	-	6.0
		+4	0.5	+	2.2
		+5	5.3	+	5.1
		+7	2.3	+	2.4
		+8	7.6	+	7.5
		+9	4.6	+	4.6
+0		+0	32.0	-	24.2
		+1	21.0	-	20.2
		+2	9.6	-	9.9
		+3	3.4	-	4.0
		+4	7.0	-	7.9
		+5	7.1	-	7.4
		+6	4.4	-	3.8
		+7	3.1	+	3.8
		+8	5.4	+	5.3
		+9	1.3	-	1.7
		+10	5.8	-	5.4
+1		+0	10.8	-	9.8
		+1	5.9	-	5.1
		+2	1.2	+	2.3
		+3	9.7	-	9.8
		+4	4.9	-	5.1
		+5	1.2	+	1.9
		+6	0.1	-	1.2
		+7	2.4	-	2.7
		+8	1.7	-	1.7
		+9	0.2	+	1.0
		+10	2.6	-	2.6
		+11	1.2	+	1.7
+2		+1	1.3	-	0.9
		+2	3.0	+	3.8
		+3	8.6	-	8.2
		+4	4.7	-	4.5
		+5	4.3	-	4.9
		+6	2.1	-	2.8
		+7	3.0	-	3.2
		+8	3.0	-	2.6
		+9	3.5	-	3.4
		+10	1.5	-	2.6
		+11	2.3	-	2.1
+3		+0	4.8	-	4.7
		+1	11.6	-	11.9
		+3	1.8	-	2.2
		+4	1.1	+	1.6
		+5	1.2	-	1.6
		+6	0.8	+	1.1
		+7	1.5	-	1.5
		+8	4.2	+	4.4
		+9	5.1	-	5.1
		+10	2.8	-	2.9
+4		+0	3.3	-	3.2
		+1	4.8	-	5.1
		+2	5.6	+	6.0
		+6	4.3	+	4.3
		+7	7.0	-	7.0
		+8	1.9	+	2.0
		+9	2.1	+	2.1
+5		+1	3.2	-	3.4
		+3	1.9	+	2.1
		+4	2.6	-	2.9
		+5	10.1	-	9.5
		+6	3.3	+	3.2
		+7	2.5	+	2.8
		+9	1.4	+	1.4
+6		+0	1.4	+	1.2
		+1	7.0	+	6.7
		+3	7.3	-	6.5
		+6	2.9	+	2.5
		+7	2.6	+	2.1
+7		+0	1.8	-	1.5
		+1	1.6	-	1.3
		+3	3.5	-	3.6
		+4	1.5	-	1.3
		+8	1.4	-	1.4
+8		+6	0 2	-	1.3
-9	+3	+2	2.4	+	2.3
-8			0.9	+	1.6
		+3	2.5	+	2.6
-7		+1	2.9	+	2.9
		+2	2.3	-	2.6
		+4	2.2	-	2.4
		+5	4.2	-	4.3
		+7	1.5	+	1.8
-6		+1	8.5	+	8.2
		+2	3.2	+	3.1
		+3	5.9	-	6.0
		+5	1.2	+	2.0
		+6	1.0	+	1.4
		+8	1.6	-	1.3
-5		+1	3.3		3.1
		+2	5.3	+	5.7
		+4	3.2	-	1.8
		+6	1.1	-	1.7
		+7	4.2	-	4.3
		+8	3.0	-	3.2
-4		+1	2.1	-	2.6
		+2	1.5	-	2.1
		+3	3.3	+	3.4
		+5	2.6		3.0
		+6	1.9	+	1.9
		+7	2.3		2.1
		+8	2.3	-	2.0
		+9	1.2	+	1.1
3		+1	1.5	-	1.3
		+2	3.2	+	3.9
		+3	11.3	-	11.0
		+4	6.2	+	6.1
		+6	1.6	-	1.9
		+7	2.0	-	2.0
		+8	1.8	-	1.7
		+9	1.1	-	1.1
-2		+1	14.8	-	15.3
		+2	22.2	+	21.2
		+3	1.8	+	2.2
		+4	7.4	-	8.1
		+5	3.1	-	2.8
		+7	2.1	-	2.1
		+8	1.9	+	1.7
		+10	2.1	+	2.1
		+11	3.3	+	3.2
-1		+1	27.7	+	25.8
		+3	4.2	+	3.6
		+5	3.1	-	2.8
		+6	4.9	+	4.6
		+7	5.5	-	5.8
		+8	0.8	+	1.8
		+9	5.7	+	5.3
		+11	1.4	-	2.0
+0		+0	23.7	+	20.6
		+1	4.4	+	5.5
		+2	4.6	-	4.4
		+3	1.7	+	1.9
		+4	9.1	+	8.8
		+5	3.7	-	4.5
		+6	2.5	+	2.5
		+7	2.1	+	2.3
		+8	4.4	-	4.3
		+9	1.7	+	2.0
+1		+0	26.6	+	24.6
		+1	7.2	+	6.3
		+3	10.8	+	11.7
		+4	9.4	+	9.2
		+5	4.8	+	4.8
		+6	2.3	-	2.6
		+7	2.4	+	2.4
		+8	2.5	-	2.9
		+9	2.3	+	2.3
+2		+0	2.8	+	2.7
		+1	6.9	+	6.8
		+2	7.5	-	8.4
		+3	1.0	+	1.4
		+4	1.3	+	1.7
		+5	3.7	-	3.7
		+6	3.9	-	4.4
		+7	2.9	+	2.9
		+8	3.4	-	3.3
		+9	1.8	+	2.1
		+10	1.9	-	1.9
+3		+0	2.4	-	2.5
		+1	7.0	-	7.1
		+3	0.7	-	1.5
		+4	1.3	+	1.4
		+5	1.5	-	2.0
		+6	3.9	-	3.9
		+7	4.9	+	4.8
		+8	4.2	+	4.3
		+10	1.7	+	2.1
+4		+0	10.0	+	9.6
		+1	3.4	-	3.0
		+2	5.8	-	6.1
		+5	1.7	-	1.7
		+6	10.4	-	9.7
		+7	5.1	-	4.7
		+8	1.9	-	1.7
+5		+0	1.8	+	1.7
		+1	2.3	+	2.4
		+2	1.6	-	1.9
		+4	2.6	-	2.2
		+5	7.8	-	7.5
		+6	4.4	-	4.3
		+8	1.1	+	1.6
		+9	2.1	-	1.9
+6		+3	2.6	-	2.6
		+5	2.2	-	2.4
		+6	2.9	-	2.6
		+8	1.0	+	1.0
		+9	1.7	-	1.5
+7		+1	1.7	-	1.6
		+5	1.4	-	1.8
		+6	1.7	-	1.3
+8		+1	1.6	+	2.1
-10	+4		3.2	-	2.7
-9			4.2	-	4.4
		+2	2.2	+	2.0
-8		+1	0.1	-	2.1
		+2	2.2	+	2.2
		+3	1.2	-	1.9
		+5	1.4	+	1.5
		+6	1.4	-	1.6
-7		+1	1.8	-	1.8
		+2	5.1	+	5.1
		+3	1.5	+	1.5
		+5	1.6	+	1.8
		+6	1.5	+	1.7
		+8	1.0	+	0.9
-6		+1	4.4	-	4.1
		+2	3.6	+	3.5
		+3	8.0	+	7.9
		+4	1.9	+	2.2
		+5	4.4	+	4.0
		+6	1.8	+	1.8
		+7	1.6	+	2.0
		+9	1.4	+	1.2
-5		+1	3.2	-	3.2
		+2	1.4	+	1.8
		+3	9.6	+	9.4
		+4	0.9	-	1.2
		+5	1.4	+	1.8
		+6	2.9	+	3.0
		+7	2.7	+	2.7
		+8	0.8	-	0.9
-4		+1	6.8	+	6.8
		+2	1.2	+	1.7
		+3	2.8	+	2.6
		+5	1.9	+	2.4
		+6	4.3	+	4.4
		+7	3.6	+	3.3
		+8	2.3	-	2.2
		+9	1.4	+	1.4
3		+1	1.7	-	2.4
		+2	2.2	+	2.5
		+4	0.9	+	1.7
		+5	1.6	+	1.9
		+6	3.2	-	3.6
		+8	4.4	-	4.5
		+9	0.9	+	0.9
		+11	1.7	-	1.5
2		+1	5.8	-	5.2
		+2	15.9	+	15.0
		+3	11.5	+	11.4
		+4	4.9	-	5.2
		+5	3.0	-	3.4
		+6	2.3	-	2.5
		+7	0.8	+	1.4
		+8	3.0	-	3.0
		+9	2.4	-	2.3
		+11	2.0	-	2.0
1		+1	2.8	+	2.5
		+2	1.8	-	1.6
		+5	2.1	-	2.3
		+7	1.0	-	1.7
		+8	1.0	-	1.6
		+9	3.6	-	3.4
		+10	2.1	-	1.7
		+11	3.1	-	2.9
0		+0	3.5	-	5.5

Table 2(*a*) (*cont.*)

h	k	l	Fcalc	Fobs
		+ 1	1.2	+ 2.0
		+ 2	1.1	+ 2.0
		+ 3	4.1	− 3.9
		+ 4	2.8	− 2.7
		+ 5	2.8	+ 3.6
		+ 6	5.5	+ 5.8
		+ 7	2.3	+ 2.5
		+ 8	3.8	− 3.7
		+ 9	4.9	− 5.0
+ 1		+ 0	1.4	− 1.4
		+ 1	7.8	+ 8.6
		+ 2	1.4	+ 1.7
		+ 3	2.3	+ 2.1
		+ 5	5.8	+ 6.0
		+ 7	2.4	− 2.7
		+ 8	0.9	+ 1.3
		+ 9	2.2	− 2.2
+ 2		+ 0	1.0	+ 1.8
		+ 1	0.9	+ 1.1
		+ 2	5.6	− 6.5
		+ 3	2.7	+ 2.9
		+ 5	1.2	+ 1.8
		+ 6	1.0	+ 1.7
		+ 7	2.4	− 2.3
		+ 9	2.2	+ 2.3
+ 3		+ 0	2.4	− 2.3
		+ 1	6.7	+ 5.9
		+ 2	2.6	+ 2.7
		+ 3	4.4	+ 4.8
		+ 4	3.2	+ 2.8
		+ 5	3.2	+ 3.4
		+ 7	2.1	+ 2.2
		+ 8	5.9	− 5.5
		+ 9	1.5	− 1.6
		+10	1.9	+ 2.3
+ 4		+ 0	2.6	− 2.8
		+ 1	5.7	+ 4.7
		+ 2	3.3	+ 3.5
		+ 5	4.1	+ 4.2
		+ 6	6.2	− 5.8
		+ 7	2.6	− 2.6
		+ 9	1.3	− 1.2
+ 5		+ 2	3.8	+ 3.9
		+ 3	2.2	+ 2.1
		+ 4	5.4	− 4.8
		+ 5	2.4	+ 2.3
		+ 6	2.3	+ 2.2
		+ 7	1.3	− 1.5
		+ 9	1.2	+ 1.0
+ 6		+ 0	2.0	+ 1.9
		+ 1	2.7	− 2.6
		+ 2	5.3	− 5.1
		+ 7	2.1	− 2.1
+ 7		+ 1	2.3	− 1.8
		+ 2	1.4	− 1.5
− 9	+ 5		2.3	− 2.3
− 8		+ 1	0.6	+ 1.5
		+ 3	2.4	− 2.4
− 7		+ 1	3.9	− 3.6
		+ 3	2.3	− 2.4
		+ 4	2.5	− 2.7
		+ 6	2.1	+ 2.3
− 6		+ 1	2.4	− 2.2
		+ 2	11.4	− 11.5
		+ 4	2.9	+ 3.4
		+ 6	1.6	− 1.9
− 5		+ 1	3.6	+ 3.5
		+ 2	4.1	− 4.3
		+ 3	2.1	− 1.8
		+ 4	2.4	+ 2.6
		+ 6	2.9	− 2.9
		+ 8	3.4	+ 3.0
− 4		+ 1	4.1	+ 3.9
		+ 2	2.1	+ 2.3
		+ 3	4.4	+ 4.2
		+ 4	0.9	− 1.7
		+ 5	3.0	+ 2.9
		+ 6	1.3	+ 1.7
		+ 7	1.1	+ 1.7
		+ 8	2.3	+ 1.7
− 3		+ 1	8.6	+ 8.2
		+ 2	6.0	− 7.0
		+ 3	10.3	+ 9.2
		+ 4	5.2	+ 5.7
		+ 5	1.3	+ 1.9
		+ 7	1.8	+ 1.8
		+ 8	1.7	+ 2.0
− 2		+ 1	18.5	+ 18.2
		+ 2	5.3	+ 5.3
		+ 4	4.7	+ 4.8
		+ 5	3.7	+ 3.6
		+ 7	3.0	+ 2.7
		+ 8	2.0	+ 1.9
		+ 9	1.7	+ 1.8
		+10	2.4	+ 2.4
− 1		+ 1	4.7	− 4.6
		+ 2	2.1	− 3.0
		+ 3	6.0	− 6.1
		+ 5	2.0	+ 1.8
		+ 6	3.5	− 3.8
		+ 7	3.0	+ 3.3
		+ 8	5.7	+ 5.1
		+ 9	0.5	− 1.0
		+10	2.6	− 2.6
+ 0		+ 0	11.3	− 9.9
		+ 1	4.5	− 5.3
		+ 2	4.7	+ 4.4
		+ 3	2.7	− 2.6
		+ 4	4.6	− 4.2
		+ 6	1.6	+ 2.1
		+ 7	0.7	− 1.3
		+ 8	3.7	+ 3.5
		+ 9	1.1	− 1.2
+ 1		+ 0	3.1	− 3.4
		+ 1	5.4	− 5.8
		+ 2	3.5	+ 4.3
		+ 3	3.6	− 3.7
		+ 4	4.0	− 4.1
		+ 5	4.4	− 4.6
		+ 7	3.6	− 3.8
		+ 8	1.0	+ 1.5
		+ 9	2.6	− 2.5
+ 2		+ 0	1.3	+ 1.4
		+ 1	5.0	− 4.9
		+ 2	3.6	− 3.8
		+ 3	3.1	− 3.5
		+ 6	1.2	+ 1.6
		+ 7	2.9	− 2.8
		+ 8	2.4	+ 2.3
		+ 9	2.9	− 2.8
		+10	2.0	− 2.1
+ 3		+ 0	7.3	− 6.7
		+ 2	2.7	+ 2.3
		+ 4	1.3	− 1.3
		+ 6	3.9	+ 3.7
		+ 7	4.3	− 4.1
		+ 8	1.3	− 1.3
+ 4		+ 0	4.5	− 4.2
		+ 1	3.2	− 3.3
		+ 2	0.9	+ 1.4
		+ 3	1.7	+ 2.0
		+ 5	5.1	− 5.1
		+ 6	1.3	− 1.9
		+ 8	1.4	+ 1.3
		+ 9	1.9	+ 1.4
+ 5		+ 2	1.3	+ 1.8
		+ 3	2.1	− 2.1
		+ 4	3.0	− 2.8
		+ 6	2.0	+ 1.6
		+ 7	1.5	+ 1.6
+ 6		+ 2	1.8	− 1.8
		+ 3	2.1	− 2.4
		+ 4	2.1	− 1.7
− 9	+ 6	+ 1	3.9	+ 3.8
− 8			0.9	+ 1.8
		+ 5	2.7	− 2.4
− 7		+ 1	3.8	+ 3.9
		+ 3	1.6	− 1.9
− 6		+ 1	2.6	+ 2.5
		+ 2	2.0	+ 2.1
		+ 3	3.2	− 3.4
		+ 7	2.0	− 1.6
− 5		+ 1	1.6	+ 1.7
		+ 2	5.8	+ 5.8
		+ 3	4.4	− 4.4
		+ 4	1.0	+ 1.3
		+ 6	0.7	+ 1.3
		+ 7	1.6	− 1.4
− 4		+ 1	6.1	− 5.5
		+ 3	1.6	− 1.7
		+ 7	3.3	− 2.7
		+ 9	1.0	− 0.9
− 3		+ 1	3.1	− 3.4
		+ 2	3.3	− 3.7
		+ 3	4.9	+ 4.7
		+ 4	1.9	+ 2.0
		+ 5	3.2	− 3.1
		+ 7	3.0	− 3.0
		+ 8	1.2	+ 1.3
− 2		+ 1	15.9	+ 14.7
		+ 2	5.3	+ 5.1
		+ 3	5.8	− 5.7
		+ 4	1.8	− 2.1
		+ 7	1.2	− 1.7
		+ 8	1.7	− 1.7
		+ 9	2.6	+ 2.4
− 1		+ 2	1.2	+ 1.6
		+ 4	2.3	− 2.3
		+ 9	1.5	+ 1.7
+ 0		+ 0	13.8	+ 12.6
		+ 1	4.2	+ 4.7
		+ 3	6.2	+ 6.3
		+ 4	5.6	+ 5.9
		+ 8	2.7	− 2.6
		+ 9	3.2	+ 3.0
+ 1		+ 0	7.4	+ 7.4
		+ 1	3.4	+ 3.4
		+ 3	2.4	− 2.3
		+ 4	4.5	+ 4.9
		+ 6	2.6	− 2.8
		+ 7	2.0	+ 1.6
		+ 8	2.1	− 1.8
+ 2		+ 0	4.0	+ 3.9
		+ 1	4.8	− 5.3
		+ 2	2.2	+ 2.6
		+ 3	1.1	+ 1.4
		+ 4	0.9	+ 1.7
		+ 6	0.7	− 1.7
		+ 7	1.9	+ 2.1
		+ 8	1.6	+ 1.6
		+ 9	2.2	− 1.7
+ 3		+ 0	3.8	+ 3.2
		+ 1	2.0	− 2.2
		+ 2	1.9	− 1.4
		+ 4	0.2	− 2.1
		+ 5	2.6	− 2.9
		+ 7	4.6	− 4.1
		+ 8	1.9	− 1.6
		+ 9	1.1	+ 0.8
+ 4		+ 0	2.5	+ 2.2
		+ 2	2.5	− 2.6
		+ 4	2.2	+ 2.1
		+ 5	6.3	− 6.1
		+ 6	3.4	− 3.3
		+ 8	0.2	− 0.6
+ 5		+ 0	1.6	+ 1.5
		+ 1	1.9	+ 2.0
		+ 3	3.4	− 2.8
		+ 5	1.6	− 1.7
		+ 6	2.6	− 2.1
+ 6		+ 0	1.8	− 1.4
		+ 5	1.6	− 1.4
− 9	+ 7	+ 1	1.8	− 1.5
		+ 2	1.9	+ 1.9
− 7		+ 4	1.0	+ 1.2
		+ 5	3.3	+ 2.7
− 6		+ 1	4.5	− 4.3
		+ 2	4.6	+ 4.7
		+ 3	4.5	+ 4.2
		+ 6	2.2	+ 2.0
− 5		+ 1	2.1	− 2.5
		+ 2	4.5	+ 4.5
		+ 3	3.8	+ 3.6
		+ 6	2.4	+ 2.2
		+ 7	3.5	+ 3.2
		+ 8	0.9	− 1.0
− 4		+ 1	2.0	− 2.2
		+ 2	1.4	+ 2.3
		+ 3	1.9	− 2.2
		+ 4	1.6	+ 1.6
		+ 5	2.5	+ 2.6
		+ 8	1.4	− 1.4
− 3		+ 1	4.3	− 4.2
		+ 2	7.4	+ 7.3
		+ 3	3.6	+ 3.6
		+ 8	0.7	− 1.1
		+ 9	1.1	− 0.9
− 2		+ 2	2.1	+ 2.2
		+ 3	2.3	+ 2.3
		+ 4	2.9	− 3.4
		+ 5	1.5	− 1.9
		+ 8	1.0	− 1.6
− 1		+ 2	2.7	− 3.0
		+ 3	4.0	+ 4.0
		+ 5	1.3	− 1.4
		+ 6	2.0	+ 2.1
		+ 7	2.0	+ 2.3
		+ 8	2.5	− 2.0
		+ 9	2.1	− 2.0
+ 0		+ 0	0.3	+ 1.1
		+ 1	5.9	+ 5.6
		+ 2	1.4	− 1.7
		+ 5	2.4	+ 2.9
		+ 8	2.6	− 2.2
+ 1		+ 1	3.2	+ 3.7
		+ 2	2.3	− 2.7
		+ 3	2.2	− 2.6
		+ 4	1.4	− 2.0
		+ 5	2.0	+ 2.4
		+ 8	1.8	− 1.6
		+ 9	1.2	+ 1.1
+ 2		+ 0	1.1	− 2.0
		+ 3	2.9	+ 3.1
		+ 4	1.5	+ 1.7
		+ 5	1.7	+ 2.0
		+ 6	1.0	− 1.5
		+ 7	2.0	+ 2.1
		+ 8	2.1	− 1.6
		+ 9	1.4	− 1.0
+ 3		+ 0	1.2	+ 0.9
		+ 1	1.2	+ 1.6
		+ 5	2.8	+ 3.0
		+ 6	2.8	− 2.4
		+ 7	2.7	− 2.5
+ 4		+ 0	1.6	+ 1.3
		+ 1	2.2	+ 2.3
		+ 2	2.4	+ 2.3
		+ 3	1.3	+ 1.7
		+ 4	1.3	− 1.5
+ 5		+ 3	1.7	− 1.6
+ 6		+ 1	2.0	− 1.8
− 8	+ 8	+ 4	2.2	− 1.8
− 7		+ 2	3.8	− 3.6
		+ 3	1.1	− 1.4
− 6		+ 1	1.6	− 2.1
		+ 2	4.2	− 4.3
− 5		+ 1	2.7	+ 2.9
		+ 2	6.0	− 5.5
		+ 3	2.1	+ 1.4
− 4		+ 1	3.7	+ 3.6
		+ 4	3.3	+ 3.6
		+ 6	1.1	− 1.2
− 3		+ 2	7.8	+ 6.9
		+ 3	3.4	+ 3.1
		+ 7	2.1	+ 2.1
		+ 8	1.3	+ 1.0
− 2		+ 2	4.0	− 4.3
		+ 3	0.8	− 1.4
		+ 4	2.2	+ 2.5
		+ 8	3.1	+ 3.0
− 1		+ 3	2.4	− 2.7
		+ 5	1.2	+ 1.4
		+ 8	2.4	+ 2.1
		+ 9	1.4	− 0.8
+ 0		+ 0	2.8	− 2.7
		+ 1	2.0	− 2.2
		+ 2	2.9	+ 3.3
		+ 4	3.8	− 4.0
		+ 8	2.5	+ 1.8
+ 1		+ 0	1.6	− 2.0
		+ 2	2.5	− 3.0
		+ 4	1.5	− 1.8
		+ 8	1.0	+ 1.1
+ 2		+ 0	5.8	− 5.2
+ 3			2.6	− 2.3
		+ 3	0.8	− 1.3
		+ 6	2.2	− 1.5
+ 4		+ 0	1.3	− 1.4
		+ 2	2.1	+ 2.1
		+ 4	3.5	− 2.8
+ 5		+ 1	1.4	− 1.4
− 9	+ 9		1.9	+ 1.5
− 8			1.5	+ 1.4
− 6			3.7	+ 3.5
		+ 2	1.3	+ 1.7
		+ 3	1.3	− 1.8
		+ 5	1.2	+ 1.3
− 5		+ 1	2.2	+ 2.5
		+ 4	1.5	− 1.9
		+ 6	1.3	+ 1.4
− 4		+ 2	2.3	− 2.3
		+ 3	2.0	+ 2.3
		+ 4	2.3	+ 2.2
		+ 6	1.1	− 1.2
− 3		+ 1	3.7	+ 3.8
		+ 2	1.9	+ 1.8
		+ 6	1.0	− 1.2
− 2		+ 3	2.4	− 2.7
		+ 4	0.6	− 0.9
− 1		+ 1	1.5	+ 2.1
		+ 2	3.0	+ 3.4
+ 0		+ 0	4.9	+ 4.7
		+ 2	1.5	+ 1.8
+ 1		+ 0	5.7	+ 5.1
		+ 1	1.7	− 1.8
		+ 2	1.3	− 1.2
		+ 3	1.5	+ 1.2
		+ 4	1.9	+ 2.1
+ 2		+ 5	1.6	− 1.5
+ 4		+ 0	1.3	+ 1.2
		+ 3	0.6	− 0.8
− 8	+10	+ 2	1.2	+ 1.4
− 7		+ 1	1.8	− 1.7
		+ 2	1.2	+ 1.0
− 6		+ 1	1.4	− 1.4
		+ 2	3.8	+ 3.4
− 5		+ 1	3.6	− 3.1
		+ 2	2.8	+ 2.6
− 4		+ 3	3.1	+ 2.8
− 3		+ 1	3.0	+ 3.2
		+ 2	1.4	+ 1.6
		+ 4	1.5	− 1.2
− 2		+ 3	2.4	+ 2.3
− 1			1.2	+ 1.4
		+ 5	0.2	− 3.4
+ 0		+ 1	1.8	+ 1.8
		+ 3	1.8	− 2.1
+ 1		+ 0	1.6	+ 1.3
		+ 5	1.2	+ 1.3
+ 3		+ 0	1.1	+ 1.1
− 7	+11	+ 2	1.5	− 1.7
− 6			2.4	− 2.2
− 5		+ 1	0.8	− 1.3
		+ 3	1.2	− 1.3
− 4			2.1	+ 1.8
− 3		+ 1	1.9	+ 1.9
− 2		+ 4	0.7	+ 1.0
+ 0		+ 0	2.0	− 1.6
		+ 1	1.8	+ 2.1
+ 1		+ 0	2.7	− 2.4
		+ 1	1.3	− 1.1
+ 2		+ 0	0.8	− 0.7
− 6	+12	+ 1	2.2	+ 1.9
− 5			1.5	+ 1.5
+ 0		+ 0	2.7	+ 2.3

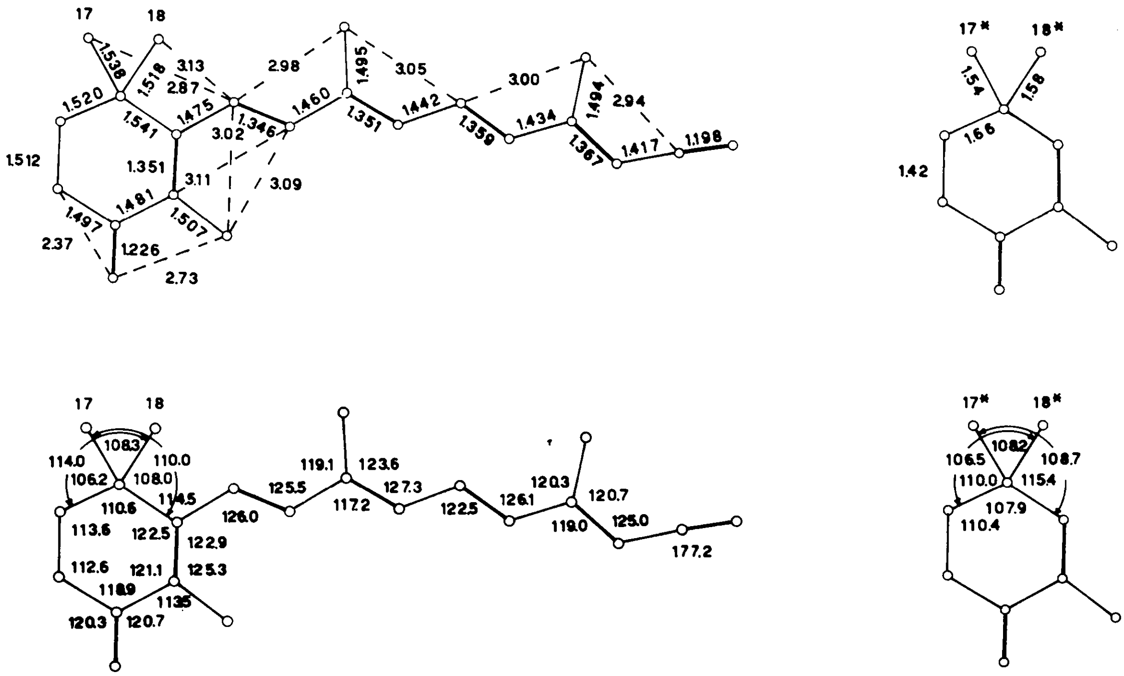

Fig. 7. Bond lengths and bond angles of 15,15′-dehydrocanthaxanthin.

part of the chain, according to Pauling (1960) the eclipsed orientation (*cis*) of the two groups adjacent to the triple bond should have a slightly lower energy, about 0·4 kcal.mol^{-1}, than the *trans* configuration. In fact the *trans* configuration about C(15)≡C(15′), which follows directly from the space group $P\bar{1}$, has also been found for 15,15′-dehydro-β-carotene in the crystal phase, although spectroscopic studies (Inhoffen, Bohl-

Table 2(*b*). *The unobserved and calculated structure factors*

F_{min} has not been indicated where the reflexion was omitted from the least-squares refinement.

h	k	l	Fcalc	Fmin
+5	-13	+5	+0.8	0.4
+3	-12	+1	+0.5	
		+2	-1.1	0.6
		+3	-0.4	
		+4	-0.9	0.5
		+5	-0.5	
+5		+3	-0.8	0.5
		+5	-0.1	
+6		+3	-0.4	
		+5	+0.4	
		+7	-1.0	0.4
+0	-11	+3	-0.2	
		+4	-0.2	
		+5	-0.1	
		+7	+0.1	
		+8	+0.7	0.4
+1		+1	+1.1	0.6
		+3	-0.0	
		+4	+0.2	
+2		+3	-0.4	
		+4	-0.5	
+3		+2	+1.2	0.7
		+3	+0.3	
		+4	+0.3	
		+5	-0.2	
		+6	+0.5	
		+7	+0.2	
+4		+8	-0.7	0.5
+5		+3	+0.0	
		+4	+0.0	
+6		+3	-0.3	
		+4	+0.2	
		+5	-0.8	0.6
+7			-0.2	
		+6	-0.3	
-2	-10	+2	+0.6	0.6
		+3	+1.2	0.5
		+5	+0.5	
		+6	+0.0	
		+7	-0.1	
-1		+5	+1.1	
		+6	+0.8	0.6
+0		+3	-0.6	0.6
		+4	-0.0	
		+6	+0.1	
		+7	+0.4	
		+8	+0.6	0.5
+1		+2	-0.2	
		+4	-0.6	
		+6	+0.8	0.7
		+8	+0.4	
+2		+4	-0.8	0.6
		+10	-1.3	0.5
+3		+2	-1.2	0.7
		+3	-1.3	0.7
		+5	+0.4	
+4		+3	+0.6	
		+4	+0.3	
		+6	-0.1	
		+7	-0.5	
+5		+2	+0.4	
		+4	+0.7	0.6
		+6	-0.0	
+6		+2	+0.0	
		+3	-1.1	0.6
		+5	-1.1	0.6
		+6	+0.3	
+8			-0.6	0.5
+9		+4	-0.3	
		+5	+0.3	
-3	-9	+4	+0.8	0.5
		+5	+1.1	0.5
		+6	-0.5	
		+7	+0.0	
-2		+4	+0.1	
		+5	+1.2	0.6
		+6	+0.6	
-1		+5	+0.2	
		+8	-0.9	0.6
+0		+2	-0.2	
		+3	+0.2	
		+4	-0.7	0.6
		+5	-0.8	0.7
		+7	+0.6	
		+8	-0.3	
+1		+2	+0.4	
		+5	-0.5	
		+7	+0.0	
		+8	-0.0	
+2		+4	-0.1	
		+5	+0.6	
		+8	+0.5	
+3		+2	-0.5	
		+3	+0.5	
		+5	-0.3	
+4		+1	+0.2	
		+3	-1.1	0.7
+5		+0	-0.2	
		+1	+0.3	
		+3	+0.5	
		+5	+0.5	
+6		+1	-0.4	
		+2	-0.6	
		+3	-0.3	
		+8	-0.1	
+7		+5	-1.4	0.6
+8		+2	+1.1	0.6
		+4	-1.0	0.5
+9		+1	-0.3	
-4	-8	+2	+0.8	0.6
		+4	-0.6	0.5
		+5	+1.0	0.5
-3		+3	+0.6	
		+6	-0.4	
		+7	-0.5	
-2		+4	+1.5	0.6
		+6	-0.9	0.7
		+7	+0.8	0.6
-1		+3	+1.1	0.7
		+4	-1.4	0.6
		+8	+0.2	
+0		+3	+0.2	
		+5	+1.1	0.6
		+7	+0.8	0.6
+2		+3	-0.1	
		+4	-0.9	0.6
		+9	+0.2	
+3		+5	+0.6	
		+8	-0.6	
+4		+3	-0.2	
+5			-0.6	
+6		+5	+0.4	
		+6	+1.3	0.7
+7		+5	-0.4	
+8		+2	+0.8	0.7
		+5	-0.9	0.6
+9		+4	-0.2	
		+5	-1.1	0.5
-4	-7	+4	+0.5	
-3		+7	-0.3	
-2		+5	+0.6	
		+7	+0.6	
		+8	+0.3	
-1		+11	+0.8	0.6
+0		+2	-0.9	0.7
		+6	+0.4	
		+7	+1.2	0.6
+1		+10	-0.5	
+2		+4	-0.2	
+3			-0.4	
		+11	-0.7	0.6
+4		+2	+0.3	
+5		+1	-1.0	0.6
+6		+4	-0.2	
		+5	-1.4	0.7
		+6	+0.9	0.7
+7		+2	+0.4	
		+5	+0.2	
		+8	+0.5	
+8		+7	+0.9	0.6
+9		+4	-0.9	0.5
		+5	+0.6	0.5
		+6	-0.4	
+10		+4	-0.0	
-6	-6	+3	-0.5	
-5			-0.7	0.6
		+4	-1.3	0.5
		+7	+0.5	0.4
-3		+4	+1.6	0.6
		+5	-0.7	
-2		+4	+0.1	
		+5	-0.5	
		+6	+0.2	
+1		+3	-0.6	0.5
+3		+10	+1.0	
+4		+7	-0.3	
+5		+1	-0.4	
		+4	-0.3	
+6		+1	+0.4	
		+4	-0.3	
		+5	-1.2	0.6
+7		+6	+0.3	
		+7	+0.8	0.6
+8		+5	+0.2	
		+6	-1.1	0.6
+9		+2	-1.1	0.6
		+4	+0.5	
		+7	+0.6	
-6	-5	+4	+0.5	
-5		+2	+0.5	
		+4	-1.0	0.6
		+5	-0.7	0.6
-4		+6	+0.6	
-3		+7	+0.7	0.6
		+8	+0.2	
-2		+10	-0.1	
-1		+6	-0.5	
		+10	+0.5	
+0		+5	+0.6	0.5
		+11	+0.9	0.5
+1		+12	+0.1	
+3		+8	-0.6	0.5
		+10	-0.9	0.5
+4		+0	-0.4	0.3
		+6	-0.4	
+6		+3	+0.6	
		+8	-0.7	0.6
+7		+2	-1.1	0.7
		+8	+0.4	
+8		+1	-1.3	0.6
+9		+2	+1.2	0.6
		+4	+0.7	0.5
		+5	-0.6	0.6
+10		+1	-0.4	
		+3	+0.4	
		+4	+0.3	
-7	-4		+0.5	0.4
-6		+5	+1.0	0.6
		+6	-0.4	
-5		+4	-0.0	
		+5	-0.3	
		+6	+0.6	
-4			-0.0	
		+7	+0.5	
-3		+8	-0.1	
		+10	+1.4	0.7
-2		+6	-0.1	
		+9	+0.8	0.5
		+10	-0.1	
-1		+11	-1.3	0.5
+0		+10	+1.0	0.5
		+11	-1.2	0.5
+1			+0.0	
		+12	-0.3	0.3
		+13	-0.4	0.2
+3		+8	-0.3	
+4		+6	+1.0	0.5
		+7	-0.3	
		+8	-0.4	
+5		+2	+1.2	0.6
		+3	+0.4	
+6		+5	+1.0	0.6
+7			+0.9	0.7
		+6	-0.6	
		+8	+0.8	0.6
+8		+1	-0.2	
		+5	+0.5	
+9		+1	-0.7	0.6
		+2	+1.4	0.6
		+4	-0.6	0.5
		+5	-0.8	0.5
		+6	-1.0	0.5
+10		+1	-0.3	
-7	-3	+3	-1.0	0.6
		+4	-0.5	
-6			+0.3	
		+7	+0.9	0.5
-5		+5	+1.1	0.7
-4		+4	+1.4	0.6
		+5	+0.6	
-3		+4	-0.9	0.5
		+7	-1.1	0.6
		+9	+0.1	
		+10	-0.1	
		+11	+0.3	
-2		+10	-0.8	0.6
-1		+5	+0.5	
+0		+11	-0.6	0.4
		+12	-0.9	0.3
+1		+1	+0.5	0.3
		+10	-0.9	0.3
		+12	-0.3	
+2		+10	+0.2	
		+12	-0.4	0.2
		+13	+0.5	0.1
+3		+6	+1.0	0.4
+4		+1	+0.8	0.4
+6		+2	-0.4	
		+4	-0.5	
+7		+2	+0.5	
+8		+1	-0.2	
		+6	-0.5	
+9		+1	-0.6	0.5
		+4	-0.8	0.5
		+5	-1.2	0.5
-7	-2	+4	+0.1	
		+6	-0.3	
-6		+5	-0.3	
		+6	+0.6	
-5		+3	+0.5	
		+4	+1.3	0.6
-3		+8	+0.4	
		+10	+0.5	
-2		+4	-0.5	0.1
		+10	+0.4	
-1		+11	+0.2	
		+12	+0.3	
+0		+3	+0.4	0.3
+1		+8	-0.1	
		+12	-1.0	0.2
+3		+7	-0.3	
		+11	+0.6	0.5
+4		+1	-0.4	
+5			+0.3	
+6		+3	+0.5	
		+4	-0.0	
+7		+5	-0.5	
		+7	-0.0	
		+8	+0.6	
+9		+6	+0.5	
-8	-1	+3	-1.1	0.5
-7		+1	+0.8	0.6
		+6	+0.9	0.5
-6		+4	+0.1	
-4		+5	+0.8	0.6
		+7	+0.6	
-3		+5	+1.0	0.5
-1		+3	+1.5	0.3
		+10	-1.1	0.5
+0		+2	-0.8	0.2
		+6	+0.8	0.2
		+11	-1.5	0.4
+1			-0.3	
		+12	-0.0	
+2			-1.0	0.3
+4		+5	+0.2	
+5		+3	-0.2	
		+5	+1.0	0.6
		+7	+0.2	
+7		+5	+0.8	0.7
		+6	+0.5	
		+7	+0.8	0.6
+8		+2	+0.4	
		+4	-0.3	
		+5	+0.2	
		+6	-0.2	
+9		+1	-0.2	
		+2	-0.1	
		+4	-0.3	
		+5	-1.2	0.5
-8	+0	+3	-0.2	
-7		+6	-0.7	0.6
		+7	+0.7	0.5
-6			+0.2	
		+8	-0.1	
-5		+3	+0.1	
		+4	-0.2	
-4		+2	+0.6	
		+3	+0.0	
+1		+10	+1.3	0.4
		+11	-0.6	0.4
		+12	-0.2	
+2		+5	-1.2	0.3
		+7	+1.6	0.4
		+8	+0.4	
+3		+7	-0.6	0.5
+5		+1	+1.0	0.5
		+3	-0.2	
		+7	-0.4	
		+8	-0.1	
+6		+1	-0.2	
		+3	-0.1	
		+7	+0.9	0.6
+7		+1	+0.2	
		+3	+1.6	0.7
		+4	-1.3	0.6
		+5	+0.6	
		+6	+0.2	
		+7	-0.0	
		+8	+0.7	0.5
+8		+4	+0.0	
-7	+1	+3	+0.5	
		+7	+0.6	0.5
-6		+4	-1.1	0.6
		+7	+1.1	0.6
-3		+6	+1.0	0.5
		+7	-0.3	
		+8	+0.1	
		+9	+0.2	
-2			+0.9	0.5
+3		+11	+0.7	0.6
+5		+3	+0.1	
+6		+2	-0.7	
		+3	-0.8	0.7
+7		+4	-1.2	0.6
		+6	-0.1	
		+7	-0.9	0.5
+8		+2	-0.6	
		+3	-0.8	0.6
+9			+1.0	0.4
-7	+2		-0.4	
		+4	-0.3	
		+6	-1.0	0.6
-5		+5	-0.9	0.6
-4			+0.6	
-2		+9	-0.4	
		+10	-0.5	
-1		+6	+0.3	
+3		+2	+0.8	0.5
+4		+3	+0.8	0.6
		+4	+1.1	0.5
		+5	+0.5	
+5		+2	+0.5	
		+8	+0.6	
+6		+2	-0.3	
		+4	+0.2	
		+5	-0.4	
+7		+2	+0.7	
		+5	-0.0	
		+6	-0.7	0.6
		+7	-0.3	
-7	+3	+3	+0.6	
		+6	+1.0	0.6
-6		+4	-0.2	
		+7	+0.2	
-5		+3	-0.6	
		+5	-0.4	
-4		+3	+0.0	
-3		+5	-0.1	
-2		+6	-0.1	
		+9	-0.7	0.5
-1		+2	+0.2	
		+4	-0.2	
		+10	+1.4	0.6
+1		+2	+0.9	0.5
+3			-0.3	
		+9	-0.5	
+4		+3	-1.2	0.6
		+4	+0.0	
+5		+3	-0.4	
		+7	+0.8	0.6
+6		+4	+0.5	
		+7	+0.0	
+7		+2	-0.3	
		+3	-0.5	
		+4	-0.4	
-8	+4		+0.6	0.5
-7			-1.1	0.6
		+7	+0.7	0.5
-6		+8	+0.4	
-4		+4	+0.5	
-3		+3	-0.7	0.5
		+7	-0.1	
		+10	-1.7	0.6
-2			+1.6	0.6
-1		+3	+0.3	
		+4	+0.1	
		+6	-0.4	
+1		+4	-0.3	
		+6	+0.8	0.6
+2		+4	-0.2	
		+8	-0.4	
+3		+6	+1.2	0.7
+4		+3	-0.1	
		+4	+0.1	
		+8	-0.1	
+5			+0.1	
+6		+3	+0.1	
		+4	+0.1	
		+5	+0.2	
		+6	-0.6	0.5
-7	+5	+2	-1.2	0.7
		+5	+0.9	0.6
-6		+3	-0.9	0.7
		+5	-0.1	
-5			+0.8	0.7
		+7	+0.4	
-3		+6	-0.6	
-2		+3	-0.3	
		+6	+0.6	
-1		+4	+0.4	
+0		+5	+0.5	
+1		+6	-0.2	
+2		+4	-0.4	
		+5	-0.2	
+3		+1	+0.9	0.6
		+3	-0.7	
		+5	+0.3	
+4		+4	-0.5	
		+7	+0.6	
+5		+5	-0.1	
-8	+6	+3	+1.1	0.6
		+4	+0.5	
-7		+2	+0.7	
-6		+4	+0.6	
		+5	-1.0	0.6
		+6	+0.2	
-5		+5	-0.1	
-4		+4	-0.3	
		+5	+1.4	0.7
		+6	-0.4	
		+8	-0.4	
-3		+6	-0.3	
-2		+5	-1.4	0.6
		+6	+0.9	0.7
-1		+3	+0.7	0.6
		+5	-0.2	
		+6	-0.7	
		+7	+0.5	
+0		+5	+0.5	
		+6	+0.7	
		+7	-1.3	0.6
+1		+5	-1.2	0.7
+2			+0.6	
+3		+3	+0.8	0.7
		+6	-1.0	0.6
+4		+1	+0.2	
		+3	+0.1	
		+7	+0.6	0.5
+5		+2	-0.5	
		+4	-0.1	
+6		+1	-0.4	
		+2	-0.3	
		+3	-0.3	
		+4	-0.5	0.4
-6	+7		+0.3	
		+5	-0.1	
-5		+4	+1.2	0.6
		+5	-0.1	
-4		+6	+1.0	0.7
		+7	-0.3	
-3		+4	-0.3	
		+5	-0.7	
		+6	+0.6	
		+7	-0.2	
-2		+6	-0.1	
		+7	-1.3	0.6
-1		+4	-0.4	
+0		+3	-0.5	
		+4	+0.4	
		+6	+0.3	
		+7	+0.5	
+1		+6	-0.1	
		+7	+0.8	0.6
+2		+1	-0.7	0.6
		+2	+0.9	0.7
+3			+0.4	
		+3	+0.4	
		+4	+0.8	0.6
-4	+8	+3	-0.6	
		+5	+0.8	0.6
-3		+1	+1.1	0.6
		+4	-0.1	
		+5	+0.8	0.6
		+6	-0.3	
-2		+5	+0.9	0.7
		+6	-0.5	
		+7	+0.3	
-1		+4	+1.1	0.6
		+6	+0.7	0.6
		+7	+0.9	0.5
+0		+3	-0.4	
		+5	-1.1	0.6
		+6	-0.6	
		+7	-1.2	0.5
+1		+1	-0.2	
		+3	-0.1	
		+5	-0.7	0.6
		+6	+1.1	0.6
		+7	-1.2	0.5
+3		+1	-0.6	
		+2	+0.4	
		+4	-0.4	
+4		+1	-0.4	
		+3	+0.3	
-6	+9	+4	-0.4	
-5		+2	-0.1	
		+3	-1.3	0.6
		+5	+0.8	0.5
-4			-0.4	
-3		+3	-0.8	0.7
		+4	-0.5	
		+5	-0.8	0.6
+4		+1	+0.5	0.4
		+2	-0.7	0.4
-3	+10	+3	-0.2	
-1		+4	+0.4	
+0		+2	-0.4	
+1		+1	-1.1	0.6
		+2	-0.0	
		+3	-0.2	
		+4	+0.7	0.4
-5	+11	+2	-0.8	0.6

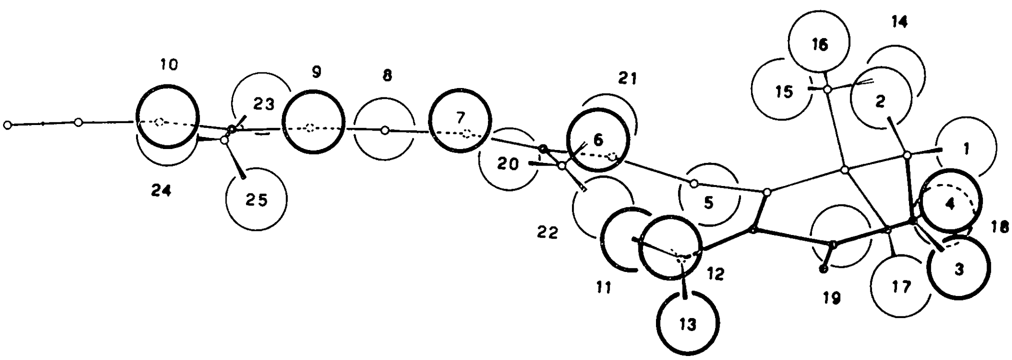

Fig. 8. Hydrogen atoms of 15,15′-dehydrocanthaxanthin. The molecule is viewed parallel to the best fit plane of the chain, perpendicular to the mean direction of the zigzag. 'Heavy' atoms are shown as small circles, hydrogens as larger ones. The numbers refer to the hydrogen atoms.

Table 3. *Final positional parameters (fractional coordinates) for the atoms of* 15,15′-*dehydrocanthaxanthin*

	x	y	z
C(1)	+1·26433	+0·33404	+0·69370
C(2)	+1·2758	+0·2898	+0·8105
C(3)	+1·18334	+0·35334	+0·92692
C(4)	+0·99712	+0·33608	+0·91079
C(5)	+0·95075	+0·32191	+0·78438
C(6)	+1·07153	+0·31940	+0·68379
C(7)	+1·03308	+0·31111	+0·55710
C(8)	+0·88255	+0·22938	+0·50491
C(9)	+0·84106	+0·22856	+0·38251
C(10)	+0·67288	+0·15619	+0·35376
C(11)	+0·59580	+0·15186	+0·24539
C(12)	+0·41841	+0·09286	+0·23438
C(13)	+0·32982	+0·08963	+0·13301
C(14)	+0·15072	+0·02095	+0·13347
C(15)	+0·04690	+0·00760	+0·03882
C(16)	+0·76542	+0·32055	+0·78309
C(17)	+1·3265	+0·2366	+0·5834
C(18)	+1·3821	+0·4813	+0·6861
C(19)	+0·98023	+0·31492	+0·30048
C(20)	+0·43257	+0·15863	+0·02776
O	+0·88545	+0·33433	+1·00114
C(2*)	+1·3143	+0·4178	+0·8371
C(17*)	+1·2765	+0·1886	+0·6696
C(18*)	+1·4100	+0·4182	+0·6015

Table 3 (*cont.*)

	x	y	z	B
H(1)	+1·413	+0·318	+0·823	+3·7
H(2)	+1·225	+0·181	+0·797	+3·7
H(3)	+1·257	+0·461	+0·955	+3·9
H(4)	+1·181	+0·306	+1·002	+3·9
H(5)	+1·133	+0·376	+0·502	+3·0
H(6)	+0·786	+0·159	+0·557	+3·2
H(7)	+0·588	+0·097	+0·418	+3·3
H(8)	+0·681	+0·196	+0·171	+3·1
H(9)	+0·337	+0·044	+0·308	+3·2
H(10)	+0·084	−0·026	+0·210	+3·8
H(11)	+0·736	+0·292	+0·692	+3·6
H(12)	+0·672	+0·256	+0·842	+3·6
H(13)	+0·761	+0·425	+0·819	+3·6
H(14)	+1·464	+0·253	+0·592	+5·5
H(15)	+1·308	+0·247	+0·494	+5·5
H(16)	+1·256	+0·133	+0·594	+5·5
H(17)	+1·350	+0·553	+0·761	+5·5
H(18)	+1·517	+0·494	+0·692	+5·5
H(19)	+1·367	+0·503	+0·600	+5·5
H(20)	+0·942	+0·300	+0·211	+4·0
H(21)	+1·097	+0·289	+0·289	+4·0
H(22)	+1·006	+0·419	+0·347	+4·0
H(23)	+0·547	+0·133	−0·006	+3·6
H(24)	+0·350	+0·133	−0·044	+3·6
H(25)	+0·472	+0·267	+0·064	+3·6

mann, Bartram, Rummert & Pommer, *et al.*, 1950), might indicate the. *cis* configuration as the stable one in ether solution. However the spectral evidence presented is not quite convincing. In the same way, the positions of the absorption maxima of 15,15′-dehydrocanthaxanthin in solution might seem to denote a *cis* configuration: $\lambda_{\max}=438$ mμ; $\lambda_{\max}$ canthaxanthin $=467$ mμ in light petroleum.

Planarity of the molecule

Planes were calculated by using a least-squares criterion (Schomaker, Waser, Marsh & Bergman, 1959), after transformation of the coordinates to a standard set of orthogonal axes x,y,z, in which y coincides with b; x is the projection of a on the plane perpendicular to y, and z is perpendicular to x and y.

(*a*) *The molecular chain*

The best plane through the atoms of the chain turned out to be $-0·091x+0·921y+0·378z=0$ (x, y and z are the orthogonal coordinates in Å). Displacements of the atoms from this plane (Table 6) show that the chain is bent normal to the plane (see Fig. 8). The largest distortion stake place at C(10) and C(6).

Table 4. *Final thermal parameters for carbon and oxygen atoms* (Å^2)

Atom number	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
1	+0·0322	+0·0610	+0·0392	+0·0336	+0·0306	−0·0009
2	+0·0410	+0·0791	+0·0429	+0·0566	+0·0262	−0·0197
3	+0·0480	+0·0851	+0·0351	+0·0602	+0·0214	−0·0285
4	+0·0365	+0·0526	+0·0316	+0·0343	+0·0195	−0·0034
5	+0·0278	+0·0496	+0·0377	+0·0294	+0·0269	−0·0054
6	+0·0292	+0·0425	+0·0326	+0·0189	+0·0211	−0·0170
7	+0·0311	+0·0600	+0·0346	+0·0373	+0·0272	−0·0123
8	+0·0444	+0·0560	+0·0290	+0·0322	+0·0239	−0·0150
9	+0·0380	+0·0510	+0·0305	+0·0284	+0·0210	−0·0183
10	+0·0429	+0·0470	+0·0376	+0·0215	+0·0165	−0·0255
11	+0·0415	+0·0471	+0·0319	+0·0212	+0·0110	−0·0301
12	+0·0398	+0·0477	+0·0372	+0·0192	+0·0237	−0·0192
13	+0·0345	+0·0421	+0·0415	+0·0155	+0·0160	−0·0242
14	+0·0432	+0·0506	+0·0571	+0·0111	+0·0385	−0·0268
15	+0·0344	+0·0525	+0·0633	+0·0038	+0·0274	−0·0313
16	+0·0359	+0·0726	+0·0488	+0·0516	+0·0304	−0·0048
17	+0·0698	+0·1421	+0·0578	+0·1376	−0·0166	−0·0234
18	+0·0380	+0·0868	+0·1168	−0·0151	+0·0940	−0·0497
19	+0·0442	+0·0789	+0·0352	+0·0234	+0·0420	−0·0185
20	+0·0396	+0·0618	+0·0439	+0·0118	+0·0426	−0·0293
O	+0·0484	+0·0805	+0·0322	+0·0439	+0·0258	+0·0057
2*	+0·0275	+0·0292	+0·0178	+0·0150	+0·0159	−0·0265
17*	+0·0227	+0·0770	+0·0149	+0·0189	−0·0165	−0·0157
18*	+0·0612	+0·0676	+0·0370	+0·0370	−0·0480	−0·0119

The angle between the chain plane and the strongest reflecting lattice plane ($\bar{1}30$) is about 8°.

The central part of the molecule is reasonably flat: the best plane passing through atoms C(10) *via* the centre to C(10′), including the methyl groups 20 and 20′, gives a maximum displacement of 0·045 Å. Another fairly well defined plane is C(6)–C(10) including C(19), having a maximum displacement of 0·09 Å. The last two planes make an angle of about 12°. See Fig. 8.

An analysis of the planarity of each separate double bond system gives the following planes and distances:

C(6) to C(9): $-0{\cdot}372x+0{\cdot}844y+0{\cdot}387z+1{\cdot}947=0$

C(6)	+0·022 Å	C(10)	+0·232 Å
C(7)	−0·023	C(11)	+0·455
C(8)	−0·022	C(19)	−0·067
C(9)	+0·022		

C(8) to C(11): $-0{\cdot}221x+0{\cdot}873y+0{\cdot}435z+0{\cdot}707=0$

C(8)	+0·036 Å	C(12)	+0·231 Å
C(9)	−0·036	C(13)	+0·382
C(10)	−0·040		
C(11)	+0·037		
C(19)	+0·004		

C(10) to C(13): $-0{\cdot}076x+0{\cdot}891y+0{\cdot}447z-0{\cdot}050=0$

C(10)	+0·016 Å
C(11)	−0·014
C(12)	−0·018
C(13)	+0·016

C(12) to C(15): $-0{\cdot}119x+0{\cdot}866y+0{\cdot}486z-0{\cdot}014=0$

C(12)	−0·005 Å
C(13)	+0·006
C(14)	+0·005
C(15)	−0·005
C(20)	−0·001

The displacements of the atoms C(8) to C(11) from their plane are significant, and the departures of C(6) to C(9) are possibly significant. The other systems must be considered planar within the limits of error, in accordance with the flat central portion of the chain. The angles of the above mentioned planes with the 'best' plane through the chain are 15°, 7°, 4°, 6°, while the angles of intersection of the successive planes along the chain are 9°, 8°, 4°. In an ideal conjugated molecule one would expect them to be zero. The distances of C(10) and C(11) from the plane of the double bond C(7)–C(8), *etc.* indicate rotations about successive single bonds of the chain. The bending and twisting of the chain can be observed in Fig. 8.

Deviations from planarity may be due to the fact that it is more difficult to deflect the bonds in directions parallel to the chain plane than perpendicular to it. However they may also be due to close-packing requirements.

(*b*) *The cyclohexenone ring*

The systems of the two double bonds of the ring are planar within the limits of error. The best plane of the atoms C(1,4,5,6,7,16) is: $+0{\cdot}321x+0{\cdot}936y+0{\cdot}143z-0{\cdot}267=0$. The distances of these atoms from the plane are:

C(1)	+0·031 Å	C(6)	−0·029 Å
C(4)	−0·002	C(7)	−0·001
C(5)	−0·030	C(16)	+0·032

For the keto grouping we have the following analytical expression: $+0{\cdot}268x+0{\cdot}953y+0{\cdot}143z-1{\cdot}791=0$ and distances to the plane:

C(3)	−0·000 Å	C(5)	−0·000 Å
C(4)	+0·002	O	−0·001

Table 5. *Standard deviations for positional and thermal parameters* (Å *and* Å^2)

Atom number	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
1	0·0045	0·0054	0·0046	0·0021	0·0028	0·0024	0·0040	0·0041	0·0035
2	0·0061	0·0076	0·0060	0·0029	0·0042	0·0031	0·0057	0·0057	0·0046
3	0·0053	0·0062	0·0047	0·0026	0·0036	0·0023	0·0050	0·0045	0·0039
4	0·0044	0·0050	0·0042	0·0021	0·0027	0·0021	0·0038	0·0036	0·0033
5	0·0041	0·0048	0·0043	0·0019	0·0024	0·0022	0·0034	0·0036	0·0032
6	0·0041	0·0045	0·0041	0·0019	0·0023	0·0021	0·0033	0·0033	0·0031
7	0·0043	0·0051	0·0043	0·0019	0·0027	0·0022	0·0037	0·0037	0·0032
8	0·0047	0·0051	0·0043	0·0023	0·0027	0·0021	0·0040	0·0037	0·0035
9	0·0045	0·0049	0·0042	0·0021	0·0025	0·0021	0·0037	0·0036	0·0034
10	0·0048	0·0050	0·0045	0·0023	0·0025	0·0023	0·0038	0·0038	0·0037
11	0·0046	0·0048	0·0042	0·0022	0·0025	0·0021	0·0037	0·0035	0·0034
12	0·0046	0·0048	0·0044	0·0021	0·0025	0·0023	0·0037	0·0037	0·0035
13	0·0044	0·0047	0·0045	0·0020	0·0023	0·0023	0·0035	0·0036	0·0034
14	0·0052	0·0054	0·0052	0·0025	0·0028	0·0030	0·0042	0·0045	00·043
15	0·0048	0·0057	0·0054	0·0023	0·0028	0·0031	0·0041	0·0047	0·0039
16	0·0047	0·0058	0·0050	0·0023	0·0032	0·0027	0·0045	0·0047	0·0039
17	0·0084	0·0108	0·0077	0·0046	0·0077	0·0043	0·0101	0·0089	0·0070
18	0·0071	0·0092	0·0097	0·0034	0·0054	0·0065	0·0069	0·0098	0·0077
19	0·0051	0·0059	0·0046	0·0025	0·0034	0·0024	0·0047	0·0045	0·0039
20	0·0048	0·0055	0·0048	0·0023	0·0030	0·0026	0·0041	0·0043	0·0039
O	0·0035	0·0041	0·0031	0·0018	0·0025	0·0016	0·0034	0·0031	0·0027
2*	0·0233	0·0251	0·0223	0·0117	0·0126	0·0117	0·0196	0·0189	0·0184
17*	0·0296	0·0360	0·0270	0·0150	0·0214	0·0145	0·0287	0·0266	0·0233
18*	0·0382	0·0402	0·0381	0·0210	0·0224	0·0239	0·0346	0·0367	0·0353

Table 6. *Distances of chain atoms from plane* $-0{\cdot}091x+0{\cdot}921y+0{\cdot}378z=0$

	Distance		Distance
C(6)	+0·349 Å	C(12)	−0·221 Å
C(7)	+0·226	C(13)	−0·085
C(8)	−0·124	C(14)	−0·135
C(9)	−0·156	C(15)	−0·035
C(10)	−0·321	C(19)	+0·093
C(11)	−0·245	C(20)	+0·089

The angle between these two double bond systems is 3°.

(*c*) *Attachment of ring to chain*

The double bond of the ring –C(5)=C(6)– makes an angle of 43° with the plane of the first double bond of the chain –C(7)=C(8)–. However the angle between the best planes through the double bond system of the chain and the planar part of the ring is only 28°. We will come back to this point in the following paper.

Bond lengths and bond angles

The final intramolecular bond angles and bond lengths are given in Fig. 7 and in Table 7, together with the most interesting non-bonded distances.

The appropriate standard deviations were calculated from the standard deviations of the atomic coordinates which are isotropic to a good approximation (Jeffrey & Cruickshank, 1953).

It is noted that the central double bond has a fairly high σ value, which is due to the fact that this bond is formed across a centre of symmetry. In the bonds C(1)–C(17) and C(1)–C(18), however, the high value is the result of high individual σ contributions of the methyl carbon atoms. Very high σ values are of course found for bonds in which one of the bound atoms is C(2*), C(17*) or C(18*). The standard deviations of the angles are 0·4°–0·5° throughout. Somewhat greater is σ(14–15–15′)=0·7°, while those connected with C(2*), C(17*) or C(18*) are between 1·0° and 1·5°.

The bond lengths and angles calculated with the coordinates of C(2), C(17) and C(18) before the introduction of disorder were as follows:

C(1)–C(2)	1·511 Å	∠C(6)–C(1)–C(2)	110·4°
C(1)–C(17)	1·547	C(6)–C(1)–C(17)	109·4
C(1)–C(18)	1·527	C(6)–C(1)–C(18)	107·6
C(2)–C(3)	1·508	C(2)–C(1)–C(17)	106·2
		C(2)–C(1)–C(18)	114·0
		C(17)–C(1)–C(18)	108·1
		C(1)–C(2)–C(3)	114·1

The final results are not significantly different.

The results obtained with the coordinates of C(2*), C(17*) and C(18*) as determined from the difference map are:

C(1)–C(2*)	1·65 Å	∠C(6)–C(1)–C(2*)	105°
C(1)–C(17*)	1·52	C(6)–C(1)–C(17*)	106
C(1)–C(18*)	1·65	C(6)–C(1)–C(18*)	111
C(2*)–C(3)	1·44	C(2*)–C(1)–C(17*)	114
		C(2*)–C(1)–C(18*)	111
		C(17*)–C(1)–C(18*)	107
		C(1)–C(2*)–C(3)	109

The bond distances in the chain show the expected alternation of shorter and longer bonds, derived theoretically by Labhart (1957) even for a long conjugated chain. As in 15,15′-dehydro-β-carotene (Sly, 1964), there is a tendency for the single bonds to decrease and the double bonds to increase, towards the centre of the chain. The maximum differences along the chain, both in the single and in the double bonds, though small, are more than three times the standard deviations and are thus considered to be significant.

The three C–CH$_3$ bond distances, C(5)–C(16), C(9)–C(19) and C(13)–C(20), and also C(4)–C(3), which are single bonds attached to the conjugated system, appear to be significantly shortened, their average bond length being 1·498 Å. This agrees well with Sly's (1964) results. On the other hand, the bond C(6)–C(1), with length 1·541 Å, is slightly long. It is to be noted that the bond lengths have not been corrected for thermal movement. Table 4 shows that C(16), C(19), C(20) and C(3) have considerably larger thermal parameters than C(1), so that the differences in the sp^3-sp^2 bond lengths may be spurious.

The other single bonds of the ring have greater standard deviations caused by the less accurate posi-

Table 7. *Bond lengths and standard deviations*

	Bond length	σ		Bond length	σ
C(1)–C(2)	1·520 Å	0·009 Å	C(10)–C(11)	1·442 Å	0·007 Å
C(1)–C(6)	1·541	0·007	C(11)–C(12)	1·359	0·007
C(1)–C(17)	1·538	0·012	C(12)–C(13)	1·434	0·007
C(1)–C(18)	1·518	0·011	C(13)–C(14)	1·367	0·007
C(2)–C(3)	1·512	0·010	C(13)–C(20)	1·494	0·007
C(3)–C(4)	1·497	0·008	C(14)–C(15)	1·417	0·008
C(4)–C(5)	1·481	0·007	C(15)–C(15′)	1·198	0·011
C(5)–C(6)	1·351	0·007	C(1)—C(17*)	1·54	0·036
C(5)–C(16)	1·507	0·007	C(1)—C(18*)	1·58	0·040
C(6)–C(7)	1·475	0·007	C(1)—C(2*)	1·66	0·026
C(7)–C(8)	1·346	0·007	C(2*)–C(3)	1·42	0·026
C(8)–C(9)	1·460	0·007	C(4)—O	1·226	0·007
C(9)–C(10)	1·351	0·007			
C(9)–C(19)	1·495	0·008			

tions of C(2), C(17) and C(18). They are not significantly shorter than the expected value 1·54 Å. This holds also for the bonds connected with C(2*), C(17*) and C(18*). The carbonyl bond length, 1·226 Å, does not deviate from the accepted normal value.

The bond angles along the chain, with the exception of those around C(9), C(11) and C(13), show no significant deviation from the mean value of 125·4°. The bond angles opposite the methyl groups are notably decreased. This is due to repulsion between the methyl groups and H(5) and H(8), as can be seen in Table 8, where short intramolecular H---H distances are listed; see also Fig. 7 where short non-bonded intramolecular carbon–carbon distances are given. The conformation of the hydrogen atoms is depicted in Fig. 8. H(8)---H(20) is shorter than H(5)---H(21) and H(5)---H(22), due to the eclipsing of the bonds C(19)–H(20) and C(9)=C(10). For the same reason H(8)---H(23) and H(8)---H(25) are not very short. H(24)---C(15) = 2·46 Å does not result in much repulsion between these two atoms. H(5) has short contacts to H(15) and H(19), which are bound to C(17) and C(18) respectively.

With bond angles of 125° along the chain and 110° between the methyl groups and the adjacent single bonds in the chain, greater release of steric hindrance is necessary between, say, C(19) and C(7) than between C(19) and C(11). This is what actually happens, at the expense of the valency angles of the atoms to which methyl-groups are attached. For C(19) the result is in good agreement with other related structures. The rather small angle C(20, 13, 14) = 120·7°, as compared with C(19, 9, 10) = 123·6° may be due to the different bonding situation of C(15) and the absence of a hydrogen on this atom. Much the same angles are found around C(13) and C(14) in 15,15′-dehydro-*β*-carotene. On the other hand, the release of strain by decreasing the bond angles opposite the methyl group brings the hydrogen atoms H(6)---H(7) and H(9)---H(10) closer together than H(7)---H(9).

The result of the angular differences is in-plane bending of the chain. This can be observed in the composite Fourier map (Fig. 5).

The bond angles around C(4) are normal. The deviations from tetrahedral values for some angles around C(1), C(2) and C(3) are slight, but may be significant.

If significant, the tilting of the C(5)–C(16) bond out of the cyclohexenone plane, in a sense opposed to that of the mean direction of the chain, could be interpreted as a consequence of repulsion forces between C(8) and C(16) and their hydrogen atoms. The angle C(6)–C(5)–C(16) is much larger than its counterpart C(4)–C(5)–C(6) and the difference is significant (e.s.d. in the angle 0·4°, so a difference between two angles is significant when larger than 1·8°). Angle C(5)–C(6)–C(7) is equal to angle C(1)–C(6)–C(5). It is interesting to note that H(6) is 0·065 Å away from the plane C(6, 7, 8, 9); this increases its distance to C(16). Though the inaccuracy in the hydrogen positions is very large, this substantial difference suggests a real deformation. On the other hand the position of H(11) is unexpected as it lies 0·17 Å out of the plane of the double bond of the ring in a direction which decreases the distances to H(6) and C(8) to 1·89 and 2·28 Å respectively.

A more detailed comparison of distances and angles will be deferred to the next paper (Bart & MacGillavry, 1968), where the results of the structure determination of canthaxanthin and 15,15′-dehydrocanthaxanthin will be compared with each other and with formerly determined structures.

Conformation of the hydrogen atoms in the CH$_2$ and CH$_3$ groups

The conformation of the hydrogen atoms in the methyl groups C(17) and C(18) can be described as staggered with respect to C(2), C(6), C(18) and C(2), C(6), C(17) respectively. This result may not seem surprising as the staggered conformation has been established as the stable one for ethane *etc.* One must bear in mind, however, that deviations are quite possible because the rotational orientations of these groups are easily influenced by intra- (and probably also inter-)molecular non-bonding interactions. Small intramolecular distances are listed in Table 8.

The rotational orientations of the methyl groups C(16), C(19) and C(20) agree approximately with Pauling's bent-bond model for double bonds (Pauling, 1960).

The environment of C(20) is not much different from the situation in propene, for which the equilibrium conformation is such that the double bond eclipses a hydrogen atom of the methyl group [Herschbach & Krisher (1958)]. Methyl group (20) has this predicted orientation (see Fig. 8) with a deviation smaller than 10°.

In view of a still greater number of additional interactions it is not immediately clear which rotational orientation should be expected for the other two

Table 8. *Short intramolecular* H---H, H---C *and* H---O *distances*

H(1)–H(3)	2·38 Å	H(5)–H(19)	2·18 Å	H(8)—H(25)	2·66 Å
H(1)–H(4)	2·47	H(5)–H(21)	2·34	H(9)—H(10)	2·27
H(1)–H(14)	2·49	H(5)–H(22)	2·37	H(14)–H(18)	2·43
H(1)–H(18)	2·47	H(6)–H(7)	2·24	H(15)–H(19)	2·58
H(2)–H(4)	2·37	H(6)–H(11)	1·89	H(11)–C(8)	2·28
H(2)–H(16)	2·18	H(7)–H(9)	2·39	H(12)–O	2·48
H(3)–H(17)	2·47	H(8)–H(20)	2·07	H(13)–O	2·92
H(5)–H(15)	2·30	H(8)–H(23)	2·27	H(24)–C(15)	2·46

methyl groups, C(16) and C(19). The situation as determined is such that C(19) gives exactly the double-bond eclipsed configuration and C(16) a slightly rotated one (10°) – see Fig. 8.

The puckering of the ring gives a staggered conformation for H(1) and H(2) with H(3) and H(4), and a nearly eclipsed one for H(1) and H(2) with H(14) and H(16).

Packing of the molecules

Crystals built up from organic molecules with an inversion centre mostly fall in space groups $P2_1/c$, $C2/c$, $Pbca$ or $P\bar{1}$, which allow closest packing. In most organic crystals of lath- or rod-shaped molecules, layers of molecular coordination number 6 can be identified, which are stacked so that the ends of the molecules of subsequent layers fit together. It is impossible, however, to describe the present crystal structure in terms of layers as described above. This is seen immediately from Fig. 9, where one is looking along [010]. The long molecules stretch through more than two cells, so that there is a complete interpenetration of rings and chains. As a result there are only occasional contacts between chains.

For the sake of clarity, only intermolecular carbon and oxygen distances are shown in Figs. 10–13; any such distances not marked are longer than 4 Å. The intermolecular H---H distances, listed in Table 9, are not included in these figures; C---H distances were not computed. In our notation the first atom always belongs to the molecule at 000, and the second to the molecule forming the contact.

The chain direction (Fig. 9) is roughly along [412], and the plane of the chains is tilted at 28° to the *xz* plane. The tilt towards the *a* axis is such that chains on the row [*u*00] interlock, leading to C---C distances < 4 Å from the methyl groups 19 and 20 to atoms of the neighbouring chain (molecules *A* and *B*). 'Backbone' distances are all longer than 4 Å. Moreover there are some ring-chain contacts from C(17) through H(14) and (15) to C(10) and C(12) respectively (see Fig. 10 and Table 9); and finally inter-annular contact mainly from C(2) to C(16) through H(1).

Along the row [00*w*] molecules come close together only where the rings of *A* touch the chain of molecule *C* between the methyl groups C(19) and C(20), as illustrated in Fig. 10. A short H---H contact is found from C(16) to C(20) through H(12)---H(23) = 2·26 Å. The oxygen atom falls in the hollow formed by C(20), C(11) and C(19) and forms short contacts with some hydrogen atoms of the chain: distances O to H(20), H(8), H(23) are respectively 2·60, 2·64 and 2·79 Å. The posi-

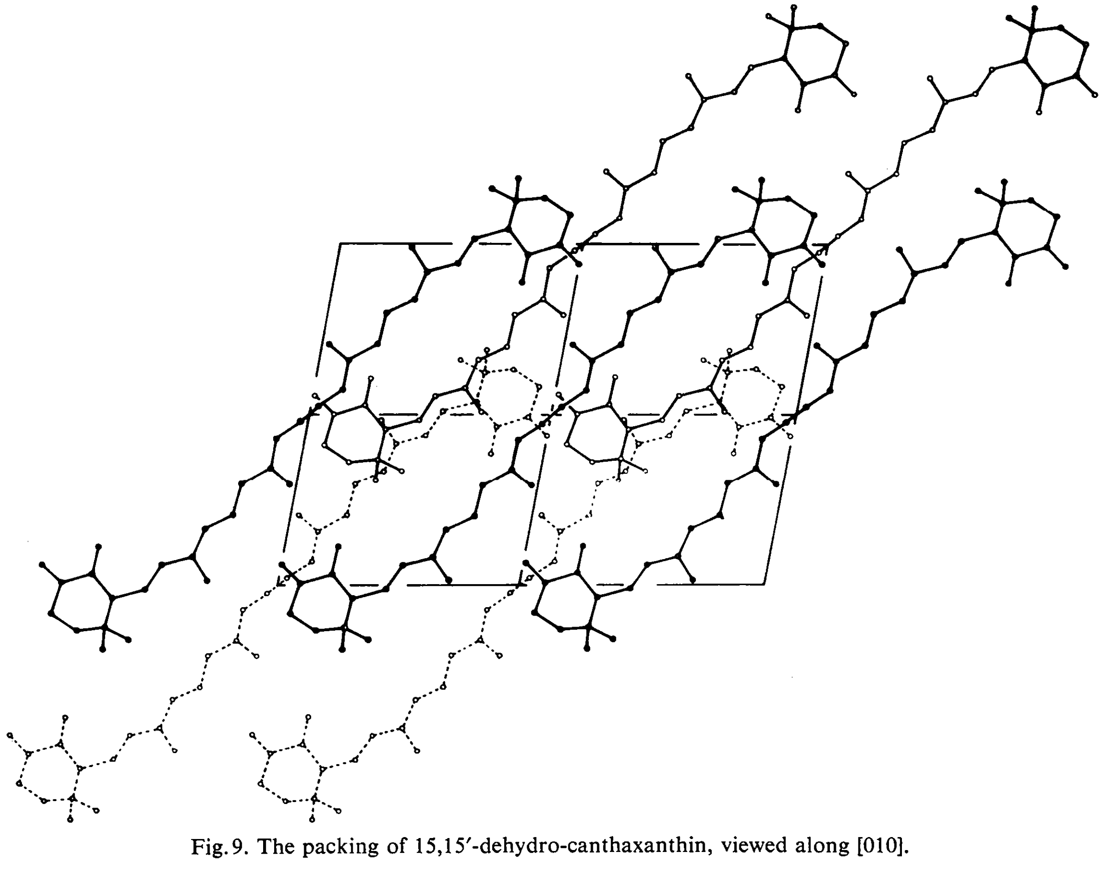

Fig. 9. The packing of 15,15′-dehydro-canthaxanthin, viewed along [010].

Table 9. *List of the shorter intermolecular* H---H *distances, with corresponding* C---C *distances*

The first mentioned atom belongs to the original molecule

The superscripts refer to the positions:

A	*x*,	*y*,	*z*
B	*x*+1,	*y*,	*z*
C	*x*,	*y*,	*z*+1
D	*x*+2,	*y*+1,	*z*+2
E	*x*+1,	*y*,	*z*+1
G	*x*+2,	*y*+1,	*z*+1
H	*x*+3,	*y*+1,	*z*+1

A	*B*	Distance (Å)	*A*	*B*	Distance (Å)
H(1)	H(11)	2·84	C(2)	C(16)	3·84
H(1)	H(12)	2·48	C(2)	C(16)	3·84
H(1)	H(13)	2·62	C(2)	C(16)	3·84
H(14)	H(7)	2·54	C(17)	C(10)	3·65
H(14)	H(11)	2·51	C(17)	C(16)	>4·0
H(15)	H(9)	2·64	C(17)	C(12)	3·85
H(23)	H(23′)	2·67	C(20)	C(20′)	3·79
A	*C*		*A*	*C*	
H(4)	H(20)	2·74	C(3)	C(19)	>4·0
H(12)	H(23)	2·26	C(16)	C(20)	3·73
H(12)	H(24)	2·70	C(16)	C(20)	3·73
H(12)	H(25)	2·70	C(16)	C(20)	3·73
A	*D*		*A*	*D*	
H(3)	H(13′)	2·51	C(3)	C(16′)	>4·0
H(4)	H(13′)	2·97	C(3)	C(16′)	>4·0

Table 9 (*cont.*)

A	*E*		*A*	*E*	
H(6)	H(9′)	2·73	C(8)	C(12′)	>4·0
H(7)	H(7′)	2·90	C(10)	C(10′)	>4·0
H(10)	H(2′)	2·44	C(14)	C(2′)	3·90
H(1)	H(24)	2·60	C(2)	C(20)	3·69
H(2)	H(24)	2·44	C(2)	C(20)	3·69
H(4)	H(24)	2·59	C(3)	C(20)	3·85
H(4)	H(25)	2·78	C(3)	C(20)	3·85
A	*G*		*A*	*G*	
H(3)	H(25′)	2·95	C(3)	C(20′)	>4·0
H(5)	H(22′)	2·86	C(7)	C(19′)	>4·0
H(8)	H(17′)	2·68	C(11)	C(18′)	>4·0
H(13)	H(22′)	2·77	C(16)	C(19′)	>4·0
H(17)	H(25′)	2·58	C(18)	C(20′)	>4·0
A	*H*		*A*	*H*	
H(19)	H(19′)	2·82	C(18)	C(18′)	>4·0

tions of C(2*), C(17*) and C(18*) do not result in impermissible short intermolecular distances between the molecules related by translations **a** or **c**.

The most intimate intermolecular contact is between molecules shifted along [101]. The arrangement of these molecules does not permit close packing of the chains. Fig. 11 shows that the upper ring of *A* comes close to the central part of the molecule at *x*+1, *y*, *z*+1 (mol-

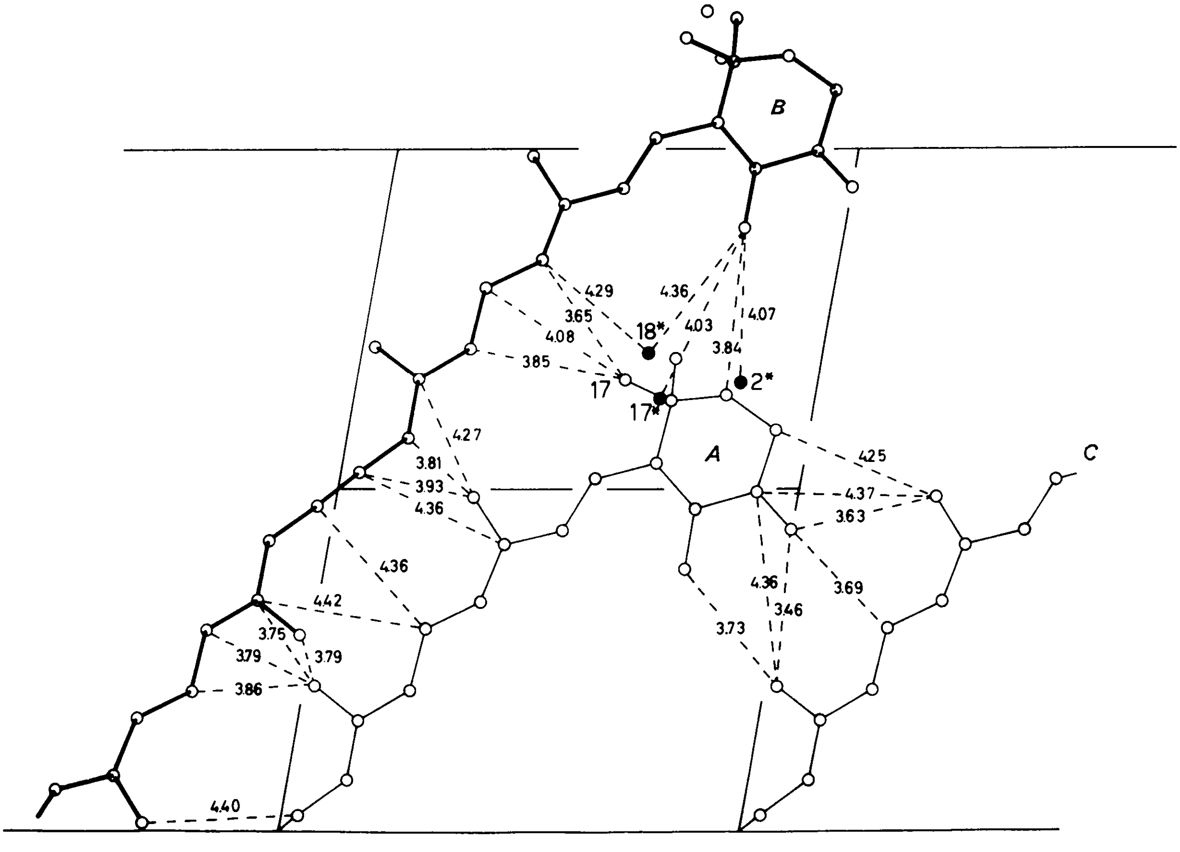

Fig. 10. Packing of adjacent molecules related by translations **a** and **c**.

ecule *E*); the same holds, by the symmetry centre at $\frac{1}{2}0\frac{1}{2}$, for the lower ring of *E* and the central part of *A*. In total, thirteen C---O, C---C and O---O distances smaller than 4 Å can be counted in these small contact regions. The shortest computed distance between one of the positions C(2*), C(17*) or C(18*) of ring *A* and chain *E* is C(14)---C(17*) = 3·97 Å. Short H---H contacts are mainly from C(2) and C(3) to C(20) through H(1), H(2), H(4) to H(24) and H(25). Moreover, since the centre of the molecule is on a symmetry centre, this situation occurs both at $+y$ and at $-y$.

Proceeding further along the y axis, we see in Fig. 13 that the two rings at y (molecule *A*) and $1-y$ (*D′*) have an interesting contact mainly through their oppositely oriented C=O groups. C(4), O, C(4′) and O′ form quite a good rectangle (O–C(4)–O′ = 85°), which makes an angle of 84° with the plane of the ring. The C(4)---O′ distance however is 3·21 Å, a fairly normal value, equal to the sum of generally accepted van der Waals radii. The situation is similar to that discussed by Klug (1965) and is interpreted by him as an indication of charge transfer. In our case, since the C=O groups are related by a symmetry centre, this interpretation is not applicable. The situation, however, suggests dipole–dipole interaction. The shortest hydrogen distances are H(3)---H(13′) = 2·51 Å and O---H(3′) = 2·74 Å.

Some weaker chain-ring contacts are seen in Figs. 11 (*A* and *F*) and 12 (*A* and *G*) across the centres $1,0,\frac{1}{2}$ and $1,\frac{1}{2},\frac{1}{2}$ respectively.

So far, all intermolecular distances are compatible with generally accepted van der Waals radii. Consider now the spacings between molecules *A* and *H*, related by translation $3\mathbf{a}+\mathbf{b}+\mathbf{c}$. The shortest distance is between the *gem* methyl groups: C(18)---C(18′) = 4·28 Å. We must conclude that there are no contacts between these molecules. If we take into account the C(2*), C(17*) and C(18*) positions we find a permissible distance C(18*)---C(18′) = 3·56 Å. H---H distances could not be computed because the positions of the H atoms of C(18*) are unknown. This means that it is possible to find two molecules in positions *A* and *H* with the three troublesome atoms of the opposite rings in different positions. It is worth noting, however, that an impermissible distance C(18*)---C(18*′) = 3·03 Å arises when the three atoms of both rings take the abnormal positions. This implies that

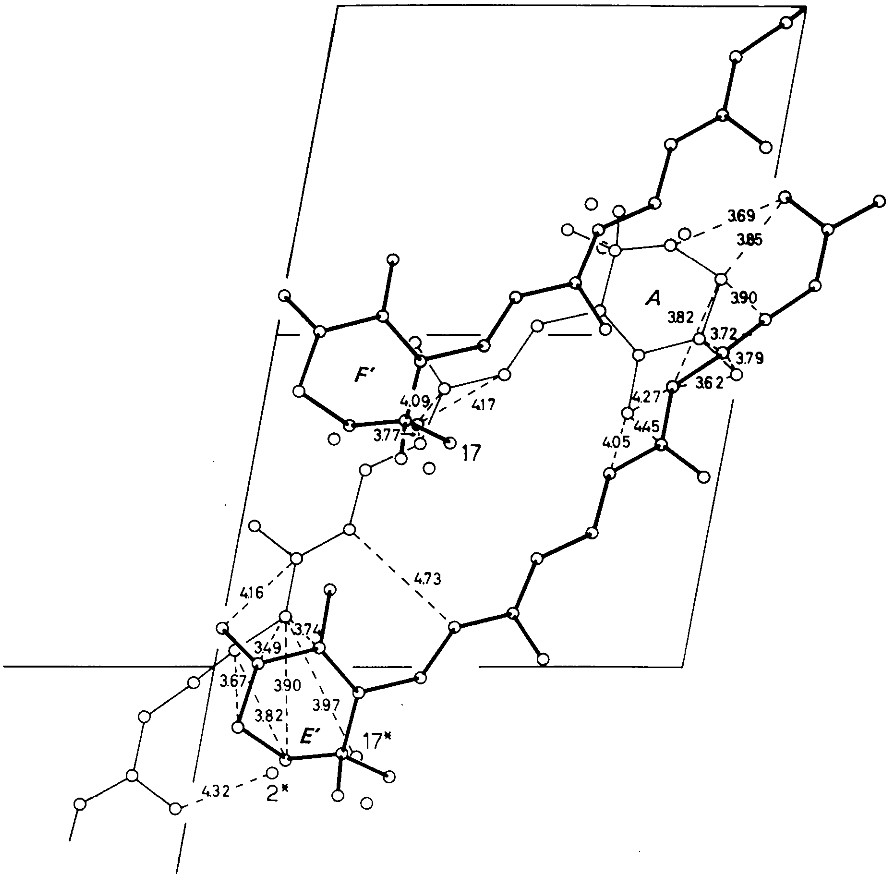

Fig. 11. Contacts between molecules related by translation $\mathbf{a}+\mathbf{c}$.

such an arrangement is impossible and sets an upper limit to the occurrence ratio of the molecules in alternate ring conformation in the present crystal structure.

Vibrational parameters

The direction cosines of the principal axes of the ellipsoid describing the anisotropic temperature factors, together with the mean square displacements, are listed in Table 10 (calculated relative to the original system of axes, following the method described by Waser).

Table 10. *Direction cosines of the principal axes of the vibration ellipsoids of* C *and* O *atoms* (*relative to the crystal axes*) *with mean square displacements* (Å²)

Atom number	u²	cos *a*	cos *b*	cos *c*
1	+0·0618	−0·1200	+0·9196	+0·0924
	+0·0372	−0·3164	+0·3605	−0·9876
	+0·0308	−0·9410	+0·1563	+0·1265
2	+0·0794	+0·0311	+0·9100	−0·0776
	+0·0467	+0·4751	−0·0943	−0·7740
	+0·0273	+0·8794	−0·4038	+0·6284
3	+0·0860	+0·0352	+0·9129	−0·1298
	+0·0495	+0·7407	−0·2599	−0·5151
	+0·0228	+0·6710	−0·3147	+0·8472
4	+0·0526	−0·0618	+0·9372	−0·0494
	+0·0352	−0·9950	+0·3251	−0·2560
	+0·0310	−0·0780	−0·1262	+0·9654
5	+0·0505	−0·0796	+0·8660	+0·2184
	+0·0348	+0·0579	+0·3791	−0·9418
	+0·0258	+0·9951	−0·3261	+0·2555
6	+0·0455	−0·3898	+0·8785	+0·2281
	+0·0341	+0·4680	+0·3945	−0·6495
	+0·0232	+0·7931	−0·2695	+0·7254
7	+0·0602	−0·0622	+0·9158	+0·0563
	+0·0357	+0·4919	+0·0613	−0·7617
	+0·0234	+0·8684	−0·3969	+0·6455
8	+0·0248	+0·3582	−0·2937	+0·9832
	+0·0569	−0·2679	+0·9558	+0·0371
	+0·0450	+0·8944	−0·0114	−0·1787
9	+0·0242	+0·5617	−0·3033	+0·9134
	+0·0520	−0·2608	+0·9510	+0·0524
	+0·0405	+0·7852	+0·0597	−0·4037
10	+0·0299	+0·6115	−0·1225	+0·8435
	+0·0533	−0·7069	+0·7477	+0·2270
	+0·0450	+0·3554	+0·6526	−0·4868
11	+0·0228	+0·5772	−0·0952	+0·8566
	+0·0522	−0·6828	+0·8270	+0·1294
	+0·0461	+0·4478	+0·5541	−0·4996
12	+0·0540	−0·5860	+0·8361	+0·2059
	+0·0401	+0·5445	+0·4898	−0·4183
	+0·0309	+0·6000	−0·2471	+0·8847
13	+0·0280	+0·7943	+0·0110	+0·5711
	+0·0492	−0·6071	+0·6541	+0·4210
	+0·0423	+0·0222	+0·7563	−0·7047
14	+0·0706	−0·5352	+0·6113	+0·5065
	+0·0433	−0·2855	+0·7609	−0·8164
	+0·0379	+0·7950	+0·2175	+0·2772
15	+0·0286	+0·8192	+0·1820	+0·2709
	+0·0706	−0·4891	+0·5764	+0·5603
	+0·0568	−0·2996	+0·7967	−0·7827
16	+0·0726	+0·0272	+0·8940	+0·0301
	+0·0475	−0·0102	+0·2139	−0·9847
	+0·0298	−0·9996	+0·3938	−0·1716
17	+0·1598	−0·1211	−0·8592	+0·3554
	+0·0551	−0·3137	−0·0190	−0·9320
	+0·0399	−0·9418	+0·5113	+0·0710
18	+0·1418	−0·3739	+0·5697	+0·6135
	+0·0722	−0·3826	+0·8028	−0·7780
	+0·0308	+0·8449	+0·1759	+0·1351
19	+0·0868	−0·4054	+0·9428	+0·0734
	+0·0447	+0·8187	+0·1587	−0·2236
	+0·0274	+0·4066	−0·2933	+0·9719
20	+0·0761	−0·5126	+0·8206	+0·2788
	+0·0413	+0·5037	+0·4940	−0·4924
	+0·0276	+0·6953	−0·2872	+0·8245
O	+0·0823	−0·2225	+0·9821	−0·1266
	+0·0506	−0·9452	+0·1777	−0·3933
	+0·0301	−0·2388	−0·0627	+0·9107
2*	+0·0059	+0·6018	−0·3835	+0·8949
	+0·0364	−0·7302	+0·5282	+0·4137
	+0·0278	+0·3233	+0·7576	−0·1672
17*	+0·0938	+0·3279	−0·9910	+0·3666
	+0·0246	+0·8495	−0·0987	−0·3469
	+0·0103	+0·4134	+0·0901	+0·8633
18*	+0·1070	+0·4246	−0·8982	+0·6479
	+0·0611	+0·9037	+0·0376	−0·0561
	+0·0201	−0·0553	+0·4381	+0·7596
L		+0·8090	−0·1392	+0·6561
M		+0·3746	+0·3907	−0·7314
N		−0·4848	+0·9304	+0·0872
R		−0·0349	+0·9397	−0·0872

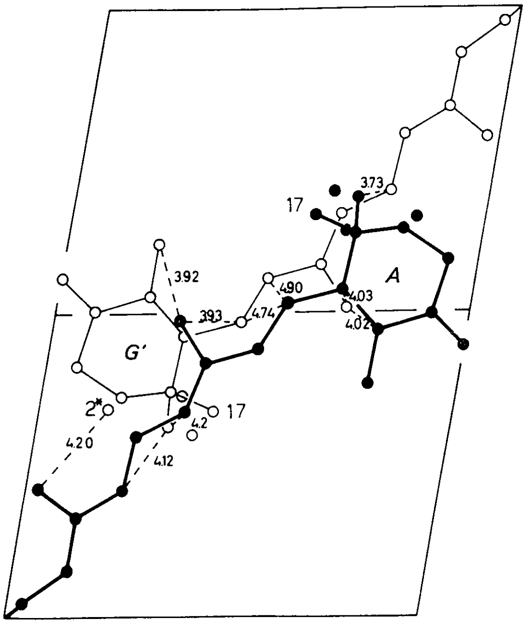

Fig. 12. Contacts between molecules centred at (0,0,0) and (2,1,1).

The reference vectors **L**, **M** and **N** denote the coordinate axes of the molecular chain: **L** is the mean direction of the chain, **M** is perpendicular to **L** in the plane of the chain, and **N** is normal to both. **R** is normal to the plane of the double bond system of the ring.

The directions of greatest mean square displacements for the ring atoms including C(2) are parallel to **R**, with greatest deviations (25°) for C(5) and C(6). Both the other axes of the ellipsoids are lying in the plane of the ring with small deviations, except for C(6). The greatest mean square displacements of ring atoms are found at C(2) and C(3), whose ellipsoids are parallel. The thermal movement of the oxygen atom is also rather large. The lowest temperature factor in the ring is that of C(6), which is connected directly to the chain.

There is a fairly good directional agreement between the vibration ellipsoids of the atoms of the chain and the vectors **L**, **M** and **N** in the expected sense: the shortest axis coincides with **N**, the largest one with **L**. (The shortest axis of the vibration ellipsoid is in the direction of the largest displacement.) With the exception of C(14), C(15) and C(19) the axes lie within 30° of the corresponding vector triplet **LMN**. The agreement between the direction of greatest mean square displacement and **N** is in most cases better than 15°; the other two axes of the ellipsoid are within 20° in the plane of the chain [except for C(14) and C(15)].

The direction of smallest $\mathbf{u}^2$ of C(4) and O deviate about 25° from the direction of the bond. The axis of smallest $\mathbf{u}^2$ of the ellipsoid of C(16) is directed along the C---C bond but the same is not true for the other methyl groups. One expects $\mathbf{u}^2$'s of the same order of magnitude for C(2), C(17), C(18) and C(2*), C(17*), C(18*). The difference – very large for the first set of carbon atoms and much smaller in the second case – probably indicates that the percentage of disorder introduced (15%) is not quite right. The calculated thermal parameters of these atoms are probably very inaccurate since there must be considerable correlation with the occupancy parameters. The vibrational parameters of the other three methyl groups are much smaller, and all of roughly the same order.

The ellipsoids of C(10,11,12) are in the same direction. This holds too for C(8,9,19), C(14,15), for C(5,16) and for C(4) and O. In general the vibrational amplitudes in the same direction are roughly the same. It is felt that parts of the molecule might have small internal vibrations, while undergoing vibrations as a rigid body.

As the data given above do not permit an exhaustive rigid body treatment we did not correct the bond distances and angles for thermal-movement effects.

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The calculations were carried out on the Electrologica X-1 computers of the 'Mathematisch Centrum' in Amsterdam and of 'Centraal Rekeninstituut' in

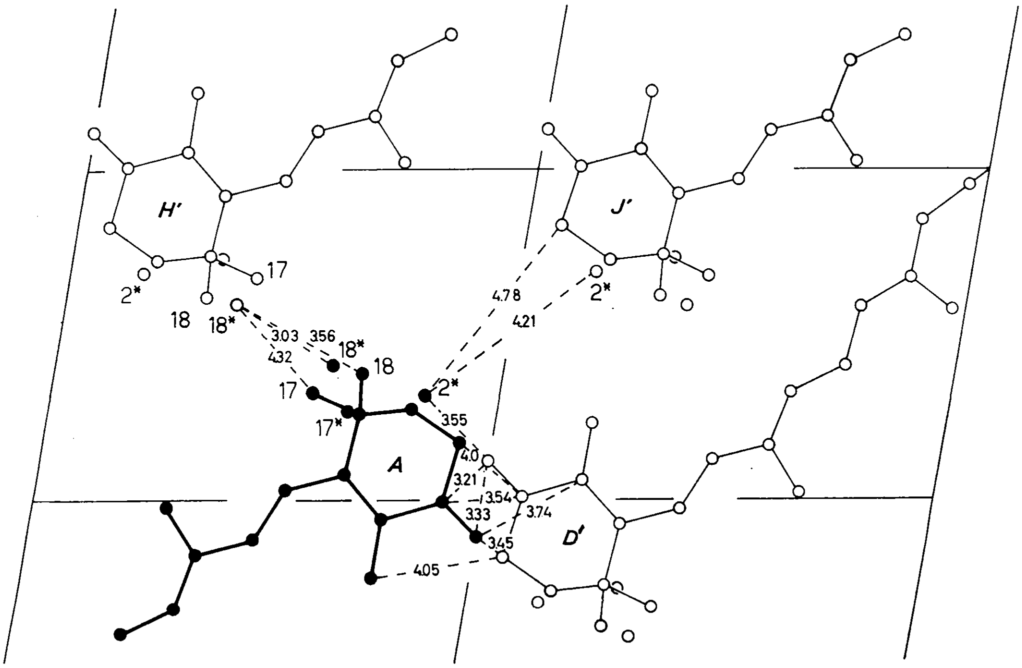

Fig. 13. Contacts between two rings (*A* and *D*) related by a centre of symmetry, and the relative position of the molecule centred at (3,1,1).

Leiden; the cooperation of Mr J. van Loenen and Mrs E. Rutten-Keulemans is gratefully acknowledged. The programs used and their authors are listed in the next paper.

References

Akhtar, M. & Weedon, B. C. L. (1959). *J. Chem. Soc.* 4058.

Bart, J. C. J. & MacGillavry, C. H. *Acta Cryst.* **B24**, 1587.

Cruickshank, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press. pp. 45, 70.

Drenth, W. & Wiebenga, E. H. (1955). *Acta Cryst.* **8**, 755.

Herschbach, D. R. & Krisher, L. C. (1958). *J. Chem. Phys.* **28**, 728.

Inhoffen, H. H., Bohlmann, F., Bartram, K., Rummert, G. & Pommer, H. (1950), *Liebigs Ann.* **570**, 54.

Isler, O., Lindlar, H., Montavon, M., Rüegg, R. & Zeller, P. (1956). *Helv. Chim. Acta*, **39**, 449.

Jeffrey, G. A. & Cruickshank, D. W. J. (1953). *Quart. Rev. Chem. Soc., Lond.* **7**, 335.

Klug, H. P. (1965). *Acta Cryst.* **19**, 983.

Koch, B. & MacGillavry, C. H. (1963). Program and Abstracts, I.U.C. Summer Meeting, Roma.

Labhart, H. (1957). *J. Chem. Phys.* **27**, 957.

Pauling, L. (1960). *The Nature of the Chemical Bond*, p. 136. Ithaca: Cornell Univ. Press.

Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.

Sly, W. G. (1964). *Acta Cryst.* **17**, 511.

Stam, C. H. & MacGillavry, C. H. (1963). *Acta Cryst.* **16**, 62.

Waser, J. (1955). *Acta Cryst.* **8**, 731.

Wilson, A. J, C. (1949). *Acta Cryst.* **2**, 318.

Zechmeister, L., Le Rosen, A. L., Schroeder, W. A., Polgar, A. & Pauling, L. (1943). *J. Amer. Chem. Soc.* **65**, 1940.

Zechmeister, L. (1944). *Chem. Rev.* **34**, 267.

Zechmeister, L. & Polgar, A. (1954). *J. Amer. Chem. Soc.* **65**, 1522.

Zeller, P., Bader, F., Lindlar, L., Montavon, M., Müller, P., Rüegg, R., Ryser, G., Saucy, G., Schaeren, S. F., Schwieter, U., Stricker, K., Tamm, R., Zürcher, P. & Isler, O. (1959). *Helv. Chim. Acta*, **42**, 841.

Acta Cryst. (1968). **B24**, 1587

The Crystal and Molecular Structure of Canthaxanthin

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The crystal structure of the polyene canthaxanthin, 4,4′-diketo-β-carotene, has been determined at 20°C by Fourier and least-squares analysis of the complete three-dimensional intensity data from Cu $K\alpha$ radiation. The crystals are triclinic, spacegroup $P\bar{1}$; the unit cell, which contains two molecules in general positions, has the dimensions: $a=14\cdot308$, $b=17\cdot619$, $c=8\cdot591$ Å, $\alpha=98^\circ 48'$, $\beta=107^\circ 7'$, $\gamma=115^\circ 17'$. The all-*trans* configuration of the conjugated bond system is interrupted at the attachment of the cyclohexenone rings to the chain. The dihedral angles, between the planes of the rings and the chain, are 43° from *s-cis*. The chain is curved and slightly bent normal to its plane due to small twists about the single bonds. The packing arrangement is quite different from that of 15,15′-dehydrocanthaxanthin; it is more similar to that of vitamin A acid, 15,15′-dehydro-β-carotene and β-carotene with interlocking of side methyl groups and good backbone contact between the chains. Rings from opposite chain ends in neighbouring layers interlock. The results have been compared with the structures of related vitamin A and carotene derivatives.

Introduction

In view of our interest in the molecular structures of carotenes and related substances we carried out a crystal structure determination of the polyene pigment canthaxanthin (4,4′-diketo-β-carotene). This carotenoid, which does not show provitamin A activity, had originally been isolated from the edible mushroom *Cantharellus cinnabarinus* (Haxo, 1950) and has subsequently been found to be the main pigment in the plumage of a great number of birds.

We analysed synthetically prepared material (Warren & Weedon, 1958). The acceptance of the all-*trans* structure for the chain of canthaxanthin was based on evidence of the melting point, and visible, infrared and nuclear magnetic resonance (n.m.r.) spectra as discussed by Akhtar & Weedon (1959), Isler, Lindlar, Montavon, Rüegg & Zeller (1956), and Zeller, Bader, Lindlar, Montavon, Müller, Rüegg, Ryser, Saucy,

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