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.* B**24**, 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). B**24**, 1587

The Crystal and Molecular Structure of Canthaxanthin

BY J. C. J. BART[*] AND C. H. MACGILLAVRY

Laboratory of Crystallography, University of Amsterdam, Netherlands

(*Received* 16 *October* 1967)

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: $a=14{\cdot}308$, $b=17{\cdot}619$, $c=8{\cdot}591$ Å, $\alpha=98°48'$, $\beta=107°7'$, $\gamma=115°17'$. 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,

---

[*] Present address: Monsanto Research S.A., Zürich, Switzerland.

Schaeren, Schwieter, Stricker, Tamm, Zürcher & Isler (1959). Moreover it is known that most naturally occurring pigments have the all-*trans* structure.

The numbering of the atoms in the present investigation is given in Fig. 1.

The previous paper describes the crystal structure of the 15,15′-dehydro derivative of canthaxanthin (Bart & MacGillavry, 1968).

X-ray experiments

Cell-constants and space-group

Good plate-shaped crystals of triclinic habit were obtained from a mixture of benzene and dimethylformamide by slow evaporation in the dark at +30 °C. The crystals were dark violet, in the form of prisms though not always regular in habit; the prominent face was called (100). The stability of the crystals was found to be somewhat less than in the case of 15,15′-dehydrocanthaxanthin.

Cell constants were computed from high-order reflexions on zero-layer Weissenberg diagrams about the three principal axes, calibrated with Al powder lines:

$a = 14{\cdot}308 \pm 0{\cdot}002$ Å $\quad \alpha = 98°48' \pm 0{\cdot}3'$
$b = 17{\cdot}619 \pm 0{\cdot}002$ Å $\quad \beta = 107°7' \pm 2'$
$c = 8{\cdot}591 \pm 0{\cdot}001$ Å $\quad \gamma = 115°17' \pm 0{\cdot}5'$
($a_{\rm Al} = 4{\cdot}0491$ Å at 20°)
$V = 1771{\cdot}50$ Å^3; $d_{\rm exp} = 1{\cdot}02$ g.cm^{-3}; $d_{\rm calc} = 1{\cdot}06$ g.cm^{-3}; $Z = 2$.

Optics and polymorphism

The crystals were highly dichroic; in polarized light, with the incident beam perpendicular to (100), the colour varied between light red, when the light vector makes an angle of 21° with [001], to dark red.

Occasionally some monoclinic needles were found.

Data for the structure determination

Retigraph diagrams were collected of the layers $l = 0$–6 about [001] and $h = 0$–2 about [100], by means of a Nonius integrating Rimsky retigraph, using Cu $K\alpha$ radiation. The crystal cross sections were $0{\cdot}3 \times 0{\cdot}06$ and $0{\cdot}5 \times 0{\cdot}06$ mm respectively. A total number of 2882 independent reflexions were measured photometrically. Some reflexions were recorded directly on a manually operated single crystal diffractometer. The crystals were stable under the experimental conditions. The intensities were corrected for Lorentz and polarization factors, but not for absorption ($\mu = 5{\cdot}3$ cm^{-1}). The data were put on a common scale by comparing the reflexions occurring in both sets, according to a least-squares procedure (Rollett & Sparks, 1960). The discrepancy index R_1 of the scaled experimental structure factors (defined as

$$R_1 = \frac{\Sigma\, \big||F_{hi}| - |F_{hj}|\big|}{\frac{1}{2}(\Sigma\, |F_{hi}| + \Sigma\, |F_{hj}|)}\,,$$

where $|F_{hi}|$ and $|F_{hj}|$ are the scaled $F_{\rm obs}$ taken from layers i and j) was 0·07.

Structure determination

Statistical tests of the $F_{\rm obs}$ distribution and morphology suggested the space group $P\overline{1}$. The two molecules in the unit cell could be situated either in two non-equivalent symmetry centres [case (*a*)], or in an arbitrary position related by a centre [case (*b*)]. In this last case their orientations are antiparallel and their mutual distance arbitrary; in the first case their mutual orientation is arbitrary, the distance of their centres being fixed. A certain predominance of intensities with even k might point to the first alternative; on the other hand the vector density distribution near the origin points to parallel chains. A very strong Patterson maximum with height somewhat more than half the origin value was found at 6°, 172°, and 20°. The surroundings of this peak are so similar to those around the origin that its corresponding vector was interpreted as the distance between the pseudo-centres of the two molecules related by inversion [case (*b*)]. From here on, the structure determination ran along the same lines as that of 15,15′-dehydrocanthaxanthin (see the preceding paper). Details will be given in the thesis of one of us (J.C.J.B.). With anisotropically refined carbon and oxygen atoms, and hydrogen atom positions determined from difference syntheses, an R value of 11·5% was reached for observed reflexions only; if the 152 non-observed reflexions are included for which $F_{\rm calc}$ is larger than twice the observation limit, R increases to 12·1%. The final calculated structure factors, together with the observed values, are listed in Table 1.

In all later-stage difference syntheses, and even in the final electron density distribution, three maxima of about 0·5 e.Å^{-3} were found in such positions that they can be interpreted as being due to an alternate ring conformation of the same sort as that found in 15,15′-dehydrocanthaxanthin. In the present structure this conformational disorder appears only in one of the two non-equivalent cyclohexenone rings of the molecule. In the final electron density maps, the peak heights of atoms C(2′), C(17′) and C(18′) of this ring are systematically about 12% lower than those of the

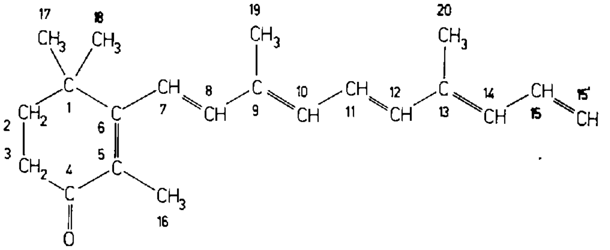

Fig. 1. Numbering of the atoms of half a molecule of canthaxanthin. The molecular centre of symmetry is halfway along the C(15)–C(15′) bond.

Table 1. *The observed and calculated structure factors of canthaxanthin*

h	k	Fcalc	Fobs
	l = 0		
+0	+2	-14.4	-13.2
	+4	-61.6	-58.1
	+5	+8.8	+8.3
	+6	+39.7	+31.8
	+7	+2.6	+3.2
	+8	+4.9	+6.0
	+9	-4.5	-5.8
	+10	-9.7	-8.7
	+11	+7.0	+8.1
	+12	+5.3	+5.7
	+13	+3.1	+3.3
	+14	+7.6	+6.9
	+15	-2.6	-2.5
	+16	-2.1	-2.3
	+17	-1.5	-1.0
+1	-15	-2.5	-2.0
	-14	-4.0	-4.2
	-13	-3.4	-2.7
	-12	+4.8	+5.4
	-11	-0.7	-1.9
	-10	+21.5	+19.4
	-9	-4.6	-4.4
	-8	-21.0	-19.1
	-6	-14.3	-11.7
	-5	+2.4	+3.7
	-4	+45.1	+40.9
	-3	+8.5	+8.4
	-1	+5.4	+5.1
	+1	-3.9	-3.3
	+2	+79.5	+70.9
	+4	+44.6	+43.1
	+5	+3.8	+2.8
	+6	-22.3	-19.5
	+7	+3.4	+3.6
	+8	+3.3	+1.8
	+9	-2.8	-3.4
	+10	+5.6	+6.2
	+11	+8.6	+8.1
	+13	+6.9	+6.6
	+14	+1.6	+1.8
	+16	+1.9	+1.9
+2	-19	+1.3	+1.6
	-18	-1.3	-1.4
	-13	-2.7	-2.9
	-11	-5.1	-5.4
	-10	-8.7	-7.5
	-9	-18.6	-18.4
	-8	+15.2	+13.7
	-7	+0.7	+1.7
	-6	+4.1	+5.2
	-5	+9.2	+9.8
	-4	-40.9	-41.5
	-3	-3.1	-3.4
	-2	+3.4	+4.4
	-1	-1.5	-2.4
	+0	+48.7	+46.8
	+1	+4.3	+4.3
	+2	-21.4	-21.3
	+3	+0.6	+1.9
	+4	-10.9	-12.3
	+6	+19.0	+19.4
	+7	+0.8	+1.5
	+8	+1.7	+2.6
	+9	-2.8	-2.8
	+11	+7.4	+6.9
	+12	-2.1	-2.5
	+13	+6.5	+5.4
	+15	+2.6	+2.0
+3	-12	-2.6	-2.5
	-11	-4.6	-4.7
	-10	-2.5	-3.7
	-9	-16.3	-16.4
	-7	-6.3	-6.6
	-6	-4.3	-3.4
	-5	+2.3	+2.8
	-4	-8.5	-9.3
	-3	+2.8	+3.1
	-2	-22.9	-20.0
	+0	+17.4	+16.8
	+1	+2.2	+1.6
	+2	-39.0	-35.9
	+3	-3.9	-3.9
	+4	-10.3	-11.2
	+5	-1.8	-1.6
	+6	+8.6	+8.8
	+8	-0.9	-2.3
	+9	-2.8	-2.9
	+10	+3.4	+3.7
	+11	+4.4	+3.3
	+13	+3.1	+2.5
	+14	-2.6	-2.4
+4	-19	+2.7	+1.5
	-13	-1.7	-1.8
	-12	+4.3	+3.5
	-10	-0.2	-1.6
	-9	+2.4	+1.8
	-8	-15.5	-15.7
	-7	-14.4	-14.6
	-6	+11.8	+11.0
	-5	-4.9	-6.9
	-4	+6.8	+8.1
	-3	+5.6	+5.9
	-2	-29.5	-32.3
	-1	-3.1	-3.5
	+2	-14.6	-15.5
	+4	-18.8	-16.8
	+6	-7.2	-7.4
	+7	-2.1	-2.5
	+8	+6.2	+7.0
	+9	-3.4	-2.8
	+10	-1.6	-1.6
	+11	+3.2	+3.1
	+12	-1.5	-1.6
+5	-19	+2.3	+2.4
	-18	-2.2	-1.9
	-13	+2.2	+1.8
	-12	+0.1	+1.9
	-11	+4.2	+2.9
	-10	-3.3	-4.3
	-9	-3.4	-5.1
	-8	+16.7	+16.8
	-7	-7.7	-9.0
	-6	+11.6	+12.4
	-5	+11.4	+12.6
	-4	-17.4	-20.3
	-3	-12.0	-13.0
	-2	+7.7	+6.4
	-1	-4.9	-5.6
	+0	+3.7	+5.4
	+1	+3.4	+3.4
	+2	-16.2	-17.4
	+4	-10.1	-9.9
	+5	-2.1	-2.9
	+6	-3.1	-3.1
	+8	-1.2	-2.6
	+9	-2.8	-2.3
	+10	+1.5	+2.4
	+12	-2.1	-2.0
+6	-19	-1.6	-1.9
	-17	-3.1	-3.1
	-15	+3.0	+2.4
	-14	-2.7	-2.7
	-13	-3.4	-2.8
	-12	+2.8	+2.9
	-11	+2.5	+2.6
	10	+4.7	+5.2
	9	+12.9	+12.9
	8	+1.7	+1.6
	-7	-21.0	-22.7
	-6	+6.6	+8.3
	-5	-17.9	-19.3
	-4	+26.2	+26.9
	-3	+13.0	+13.5
	-2	-15.1	-14.4
	-1	-0.8	-1.5
	+0	+5.4	+3.5
	+1	-4.9	-5.7
	+4	-6.9	-7.0
+7	-19	-3.0	-2.7
	-18	-2.1	-1.9
	-17	-9.6	-10.0
	-16	+2.8	+2.0
	-15	-2.7	-2.7
	-14	+3.2	+3.7
	-13	+4.1	+4.8
	-12	-3.7	-3.5
	-11	+2.9	+3.4
	-10	-2.3	-2.4
	-9	-0.3	-1.7
	-8	+6.2	+7.8
	-7	-11.1	-10.4
	-6	-3.7	-5.4
	-5	-5.7	-5.7
	-3	-7.8	-8.6
	-2	+9.3	+9.9
	-1	-2.6	-2.9
	+0	+5.8	+6.9
	+1	+3.6	+3.1
	+2	-3.8	-4.0
	+6	-3.3	-2.9
+8	-18	-1.5	-1.7
	-17	-9.1	-9.1
	-16	+2.7	+3.3
	-15	-6.0	-5.4
	-13	-4.2	-4.4
	-12	+3.1	+3.7
	-11	+4.4	+5.8
	-9	+5.7	+8.1
	-8	-0.7	-1.4
	-7	-10.1	-12.0
	-6	-7.0	-6.1
	-4	-10.0	-10.3
	-3	-2.2	-2.4
	-1	-2.4	-2.6
	+0	+7.3	+7.3
	+2	+4.2	+4.3
	+6	-2.9	-2.3
+9	-19	-1.8	-2.0
	-17	-2.4	-1.7
	-16	+2.3	+2.5
	-13	-8.7	-8.6
	-9	+6.6	+7.7
	-7	-8.0	-6.7
	-6	-8.4	-8.5
	-5	+3.8	+4.4
	-4	-4.3	-4.2
	-3	+7.7	+7.7
	-2	-11.3	-9.9
	-1	-2.3	-2.7
	+0	+2.0	+2.6
	+1	-2.3	-2.6
	+2	+6.5	+5.9
	+3	+1.7	+1.8
	+8	-1.5	-0.6
+10	-19	-2.1	-1.7
	-15	+7.5	+7.4
	-13	+0.9	+2.3
	-12	-1.6	-2.2
	-11	-3.7	-4.3
	-7	-3.5	-3.6
	-6	-6.1	-6.4
	-5	+7.0	+7.7
	-4	-2.9	-3.7
	-3	+10.2	+9.9
	-2	-5.3	-4.8
	-1	+2.3	+2.6
	+0	-5.7	-4.9
	+1	-2.6	-2.6
	+2	+2.5	+2.7
	+5	+1.4	+1.5
	+6	-2.9	-2.0
+11	-17	-0.7	-2.6
	-16	+2.9	+2.8
	-15	+9.3	+9.8
	-14	-2.5	-2.4
	-13	+3.5	+2.7
	-9	+3.9	+4.3
	-8	-2.4	-3.4
	-7	-7.6	-7.4
	-6	-3.7	-3.4
	-5	+2.5	+2.5
	-3	+6.1	+5.6
	-1	+7.3	+7.4
	+0	-1.6	-1.9
	+1	+3.0	+3.1
	+3	-2.7	-2.6
+12	-15	+1.3	+1.9
	-13	+3.7	+3.5
	-11	+4.2	+4.1
	-9	-1.6	-2.7
	-8	+2.5	+2.7
	-7	-5.1	-4.9
	-6	-4.7	-5.2
	-5	+5.0	+4.7
	-3	+3.2	+3.1
	-2	+2.5	+2.8
	+0	+1.3	+1.5
	+2	+2.0	+1.7
+13	-15	+4.4	+4.2
	-13	-2.8	-2.6
	-9	+4.2	+4.0
	-7	-3.3	-3.6
	-4	+3.1	+2.5
	+0	+0.9	+1.2
+14	-16	+1.2	+1.0
	-15	+2.2	+2.5
	-9	+1.3	+1.8
	-7	-2.5	-2.7
	-4	+1.3	+1.5
	-2	+1.4	+1.4
+15	-9	+2.1	+1.8
	-6	-1.1	-0.9
	l = 1		
-16	+5	+3.7	+3.2
	+6	+1.1	+1.2
	+7	-2.1	-2.0
	+11	+1.8	+1.9
	+13	+1.0	+0.9
-15	+2	+1.3	+1.5
	+3	+1.8	+2.0
	+4	+0.9	+1.1
	+5	+1.9	+1.6
	+6	-1.5	-1.8
	+7	-1.9	-1.5
	+8	+1.6	+1.8
	+9	+1.8	+1.7
	+11	+2.8	+2.6
	+13	+1.1	+0.7
-14	-1	+1.3	+1.4
	+0	+1.0	+1.4
	+1	+1.3	+1.5
	+3	+1.3	+1.2
	+4	-1.7	-1.5
	+5	+2.7	+2.5
	+7	-4.3	-3.1
	+8	+2.0	+1.6
	+9	+1.4	+1.4
	+11	+3.2	+3.4
	+13	+3.9	+3.4
	+15	+1.4	+1.9
	+16	+1.5	+1.4
-13	-2	-1.7	-1.7
	-1	+2.4	+2.0
	+1	-1.4	-1.5
	+2	-2.6	-3.1
	+3	+2.4	+2.4
	+4	-3.6	-3.6
	+5	+5.4	+5.4
	+7	-6.0	-6.0
	+9	-2.7	-3.1
	+11	+1.6	+2.0
	+13	+5.7	+5.8
	+15	+2.5	+2.7
	+16	+2.0	+1.5
	+17	-1.3	-1.4
-12	-5	+1.4	+1.2
	-4	+1.3	+1.6
	-3	-2.7	-2.4
	-2	-0.7	-1.4
	-1	-2.6	-2.6
	+0	-6.2	-6.0
	+1	+3.8	+4.3
	+2	-3.7	-2.8
	+4	-7.1	-6.8
	+5	-3.0	-4.3
	+6	-6.0	-7.0
	+7	-3.3	-4.1
	+8	+5.8	+6.2
	+9	+1.2	+1.0
	+11	-2.9	-4.2
	+12	-1.9	-1.6
	+13	-1.6	-1.4
	+15	+1.8	+1.4
	+17	-0.7	-1.1
-11	-7	-1.0	-1.0
	-5	-1.4	-1.4
	-4	-5.1	-4.8
	-3	+3.4	+4.0
	-2	+5.4	+5.3
	+0	+2.2	+2.5
	+1	-7.9	-8.2
	+2	-10.9	-12.3
	+3	-1.8	-2.3
	+4	-7.6	-7.5
	+5	+3.4	+3.5
	+6	-3.5	-3.5
	+7	-8.9	-10.3
	+9	-1.3	-1.8
	+12	+1.8	+2.7
	+13	-2.7	-4.4
	+14	-1.0	-1.7
	+15	-6.3	-6.4
	+16	+1.2	+1.1
	+17	-6.0	-5.7
	+18	-1.9	-1.6
-10	-8	-3.5	-2.4
	-4	+2.4	+3.1
	-3	-2.0	-2.5
	-2	-4.7	-5.6
	-1	+2.6	+2.8
	+0	+3.9	+4.4
	+1	+0.4	+1.5
	+2	+6.2	+6.6
	+3	-7.9	-8.1
	+4	-12.2	-13.6
	+5	-5.7	-6.6
	+6	-1.3	-2.5
	+7	-6.4	-7.5
	+8	+2.7	+3.7
	+9	+1.7	+1.4
	+10	-4.0	-4.0
	+12	+2.5	+2.2
	+13	-1.7	-2.0
	+14	+2.8	+3.1
	+15	-8.6	-8.5
	+16	+0.5	+1.5
	+17	-9.7	-9.1
	+18	-2.9	-3.2
-9	-8	+0.9	+1.2
	-4	+2.0	+1.4
	-2	-2.4	-2.6
	-1	+1.6	+1.9
	+0	+2.0	+2.4
	+1	+2.7	+2.7
	+2	+3.8	+4.9
	+3	-1.4	-2.0
	+4	+4.7	+5.6
	+5	-7.1	-7.4
	+6	-3.1	-4.0
	+7	-7.4	-8.5
	+8	+6.8	+6.4
	+10	-1.1	-2.2
	+12	-4.3	-4.2
	+13	+3.0	+3.4
	+14	+3.2	+3.3
	+15	-4.2	-4.5
	+16	+2.1	+1.9
	+17	-9.6	-9.1
	+18	-2.9	-2.7
-8	-11	+1.0	+1.2
	-6	+5.2	+5.0
	-2	-0.6	-2.3
	+0	+5.4	+5.7
	+1	+0.9	+1.6
	+2	+2.6	+3.6
	+4	+4.2	+4.8
	+5	+1.4	+1.0
	+6	+6.4	+7.6
	+7	3.1	-2.6
	+8	+9.7	+12.4
	+9	+4.1	+5.0
	+10	+1.3	+1.6
	+11	-4.0	-4.0
	+12	-3.6	-4.9
	+13	+1.8	+2.9
	+14	-2.0	-2.5
	+15	+2.3	+1.9
	+16	+3.7	+3.6
	+17	-5.3	-4.7
	+18	-2.0	-2.0
-7	-11	+2.0	+1.4
	-8	-3.8	-3.9
	-5	+1.6	+2.0
	-4	+5.7	+4.8
	-3	-1.0	-1.8
	-2	-5.5	5.2
	-1	-0.7	-1.9
	+0	+0.3	+1.4
	+1	+3.5	+3.7
	+2	+5.9	+5.4
	+3	+3.3	+3.4
	+4	+4.3	+5.1
	+5	+4.2	+5.8
	+6	+10.0	+10.4
	+7	-1.3	1.9
	+8	+1.0	+1.8
	+9	+10.9	+11.7
	+10	-2.6	3.2
	+11	+2.1	+3.4
	+12	+6.9	+7.7
	+13	-1.4	1.7
	+14	-1.8	-2.0
	+15	-2.9	2.9
	+17	+4.1	+3.7
	+20	+2.2	+1.7
-6	-11	+2.5	+2.5
	-9	-1.9	-2.0
	6	-2.0	-2.4
	-4	-5.8	-7.8
	-3	+1.6	+2.4
	-2	-7.2	-10.3
	-1	+3.3	+4.8
	+0	+20.6	+21.8
	+1	-2.7	-2.9
	+2	+8.0	+9.0
	+3	-6.6	-7.7
	+4	-15.9	-14.6
	+5	+5.3	+4.3
	+6	-4.6	-4.2
	+7	+12.6	+12.9
	+8	+22.1	+23.0
	+9	+2.7	+2.5
	+10	-1.8	-1.7
	+12	-8.9	-10.1
	+13	+6.5	+6.9
	+14	+5.2	+6.1
	+16	+1.9	+1.6
	+17	-2.4	-1.9
	+18	-3.7	-3.2
	+19	+4.6	+4.5
-5	-14	-1.7	-1.8
	-12	+2.6	+2.3
	-11	+3.0	+2.5
	-10	+3.4	+2.8
	-9	-2.9	-2.0
	-8	-10.2	-10.4
	-7	-1.3	-1.4
	-6	+5.0	+6.5
	-5	+2.1	+2.5
	-4	+3.1	+2.8
	-3	+2.2	+2.5
	-2	-16.9	-15.4
	-1	-2.4	-3.5
	+0	+1.9	+2.2
	+1	+4.5	+5.1
	+2	+10.8	+11.6
	+3	-2.5	-3.2
	+4	+20.3	+15.7
	+5	-5.5	-5.1
	+6	-5.6	-5.4
	+8	-3.1	-2.8
	+9	+3.0	+2.9
	+10	+3.0	+4.4
	+11	-2.0	-2.6
	+12	+3.0	+2.9
	+13	+1.0	+2.2
	+14	-3.0	-3.3
	+15	+3.1	+2.8
	+19	+2.4	+2.4
-4	-15	+2.4	+2.0
	-13	+3.2	+3.3
	-11	+2.0	+2.4
	-10	+4.4	+5.2
	-9	-4.2	-4.8
	-8	-3.1	-3.4
	-6	-4.7	-6.0
	-5	-3.0	-3.1
	-4	+8.8	+9.6
	-3	+1.8	+2.3
	-2	+7.6	+5.3
	-1	+3.5	+3.7
	+0	-5.9	-6.1
	+2	+3.6	+4.7
	+3	-5.2	-5.8
	+4	-7.4	-5.4
	+5	-2.3	-1.9
	+8	+11.1	+12.5
	+9	-4.9	-6.4
	+10	+6.2	+6.1
	+11	-1.7	-2.0
	+13	+2.2	+1.9
	+14	+0.1	+1.7
	+19	+1.8	+1.5
-3	-16	+0.7	+1.2
	-14	+3.4	+3.5
	-13	+2.4	+2.3
	-12	+4.9	+5.4
	-11	+3.5	+3.9
	-10	+2.3	+1.9
	-9	-5.0	-5.0
	-7	-2.1	-2.5
	-6	-2.7	-3.2
	-5	-4.2	-4.5
	-4	+5.5	+6.0
	-2	-1.3	-1.8
	+0	+61.3	+56.0
	+1	+5.9	+6.2
	+2	-7.1	-8.8
	+3	-3.7	-3.1
	+4	-20.2	-19.6
	+5	-5.4	-6.1
	+6	-6.3	-7.3
	+8	+4.2	+3.7
	+9	-2.7	-2.8
	+10	+14.3	+14.7
	+11	+1.8	+2.0
	+12	-0.6	-1.6
	+13	+1.0	+1.2
	+18	-1.3	-0.9
-2	-12	+6.6	+6.0
	-11	-1.4	-1.4
	-10	+11.8	+10.1
	-9	-1.7	-2.9
	-8	-10.1	-8.7
	-6	+1.5	+2.3
	-5	-5.5	5.4
	-4	+7.8	+7.7
	-3	-4.2	4.9
	-2	+11.2	+11.8
	-1	-3.4	-4.5
	+0	+57.4	+53.8
	+1	+8.7	+8.7
	+2	-18.4	-17.0
	+3	-3.8	-2.7
	+4	+18.3	+15.5
	+6	-9.0	-9.3
	+7	+1.3	-1.9
	+8	-14.6	-14.7
	+9	-3.5	-3.3
	+10	+5.4	+4.0
	+11	+4.2	+5.8
	+12	+6.0	+7.4
	+13	+3.1	+3.2
	+14	-0.1	-1.6
	+17	-2.1	-1.5
-1	-14	-2.2	-2.7
	-13	-4.5	-4.5
	-12	+4.1	+4.4
	-11	-2.9	-3.2
	-10	+4.2	+5.7
	-9	-6.4	6.7
	-8	-2.0	3.9
	-7	+0.6	+1.6
	-6	+11.2	+12.1
	-4	+10.6	+10.2
	3	+3.1	+3.4
	-2	-19.4	-19.3
	1	-10.6	9.9
	+0	+10.4	+11.2
	+1	8.0	-9.3
	+2	+43.8	+33.3
	+3	+14.7	+14.4
	+4	30.2	30.1
	+5	1.4	1.7
	+6	[illegible]	16.4
	+7	[illegible]	-4.2
	+8	+19.0	+17.7
	+10	-5.0	-5.1
	+11	+5.9	+6.8
	+12	-9.1	-9.2
	+13	+1.5	+2.7
	+14	+3.2	+2.9
	+16	+2.6	+2.7
	+17	-1.1	-1.1
+0	-16	+2.2	+1.9
	-15	+4.3	+3.7
	-14	-4.0	-3.7
	-13	-1.6	-1.9
	-12	-2.9	-4.3
	-11	-7.7	-8.5
	-10	+2.9	+3.4
	-9	-8.0	-8.5
	-8	+1.3	+1.5
	-7	+13.3	+12.6
	-6	-17.3	-15.0
	-5	-9.9	-10.5
	-4	+19.1	+18.9
	-3	-3.5	-3.3
	-2	+38.6	+26.7
	-1	+16.9	+17.1
	+0	31.2	28.8
	+2	-73.9	-67.7
	+3	-16.7	-17.1
	+4	+31.0	+28.5
	+5	+5.9	+7.0
	+6	+1.1	+1.2
	+7	+9.1	+8.8
	+8	-20.1	-19.7
	+9	-4.3	-4.5
	+10	+10.0	+9.4
	+11	+2.8	+3.4
	+12	-2.7	-3.1
	+13	+2.2	+1.8
	+14	-8.0	-6.8
	+15	+1.0	+1.4
+1	-17	-1.8	-1.9
	-14	+2.2	+2.4
	-13	+1.4	+1.1
	-12	-3.5	-3.1
	-11	-2.6	-2.4
	-10	-7.0	-7.7
	-9	-4.5	-6.1
	-8	-20.4	-18.0
	-7	-3.8	-2.9
	-6	+12.3	+11.5
	-5	+4.8	+4.5
	-4	+24.9	+23.7
	-3	+20.3	+19.6
	-2	-28.1	-21.2
	-1	-14.4	-9.3
	+0	+25.1	+25.2
	+1	+4.8	+5.6
	+2	-35.7	-36.0
	+3	+7.1	+6.8
	+4	-25.2	-24.2
	+5	-4.1	-6.1
	+6	+0.5	+1.9
	+7	-2.2	-2.3
	+8	+6.9	+7.7
	+9	+4.4	+3.7
	+10	-1.7	-2.4
	+11	+4.1	+3.7
	+12	-4.1	-4.0
	+13	-2.5	-2.3
	+14	-2.7	-2.4
	+16	-2.5	-1.8
+2	-19	-1.5	-1.1
	-17	-3.1	-3.2
	-15	+1.2	+1.7
	-13	-2.3	-1.8
	-12	-0.7	-1.7
	-11	-1.3	-1.8
	-10	-3.5	-2.0
	-9	+3.6	+4.7
	-8	-14.2	-14.4
	-7	+6.3	+6.0
	-6	-13.4	-12.7
	-5	+3.9	+3.9
	-4	-9.6	-9.0
	-3	-8.4	-7.7
	-2	+26.5	+24.3
	-1	+13.9	+12.9
	+0	-6.9	-6.9
	+1	+2.3	+2.9
	+2	-19.0	-17.8
	+3	-7.2	-6.4
	+4	+4.4	+2.2
	+5	+1.5	+1.4
	+6	-8.9	-8.6
	+7	+1.6	+1.6
	+8	+1.8	+1.4
	+10	+3.4	+3.3
	+11	+3.3	+3.2
	+13	-1.7	-2.0
	+14	-2.0	-1.7
	+15	-2.1	-1.7
+3	-19	-1.3	-1.7
	-17	4.2	-4.1
	-15	+2.8	+2.7
	-14	-2.6	-2.0
	-13	-6.9	-7.6
	-12	+3.5	+3.7
	-11	-2.6	-1.6
	-9	+10.1	+8.8
	-8	-6.4	-5.8
	-7	+2.3	+2.5
	6	-18.5	-17.6
	-5	-15.0	-13.6
	-4	+8.8	+8.6
	-3	+13.0	+12.9
	-2	-1.3	-3.2
	-1	+14.0	+13.3
	+0	-19.7	-17.4
	+1	-11.4	-12.1
	+4	+8.3	+9.1
	+5	+1.5	+2.0
	+6	-2.7	-2.4
	+8	-3.6	-3.6
	+9	-1.3	-1.5
	+10	+5.6	+5.2
	+11	+3.5	+3.1
	+12	-1.8	-1.5
	+13	-2.0	-1.8
+4	-19	-2.1	-2.2
	-17	-6.6	-7.4
	-16	+1.4	+1.9
	-15	+1.0	+1.8
	-14	+1.8	+1.7
	-13	+2.3	+2.0
	-12	-3.0	-3.6
	-11	-6.3	-7.3
	-9	-6.7	-6.8
	-8	+7.7	+6.7
	-7	-3.9	-5.6
	-6	-6.3	-5.9
	5	+2.8	+2.8
	-4	7.9	-8.6
	-3	3.6	3.9
	2	18.4	17.8
	1	15.9	-16.0
	+0	+9.6	+8.7
	+1	+12.2	+12.0
	+2	-11.3	-11.6
	+4	+2.0	+2.7
	+5	-5.5	-5.6
	+5	+5.3	+7.4
	+13	-2.2	-1.6
+5	-19	-3.0	-3.2
	-17	-6.5	-7.5
	-16	+2.4	+2.4
	-15	+4.4	+4.9
	-14	-2.0	-2.2
	-13	-2.8	-4.1
	-11	-5.9	-7.3
	-10	+6.2	+7.0
	-9	+8.5	+9.1
	-8	-2.2	-3.3
	-7	-13.3	-16.2
	-6	-28.1	-28.1
	-5	-26.5	-29.6
	-4	+3.4	+3.9
	-2	+12.0	+11.7
	-1	+21.6	+19.2
	+0	-25.2	-23.0
	+1	-13.3	-13.6
	+2	-4.4	-4.7
	+3	-6.2	-6.0
	+4	+11.0	+11.8
	+5	+7.1	+6.6
	+6	-5.0	-5.4
	+7	-2.3	-1.6
	+9	-2.4	-2.4
	+10	+3.8	+3.2
	+11	+2.1	+1.4
+6	-19	+2.3	+2.9
	-18	-2.0	-1.4
	-17	-6.9	-7.6
	-16	+3.2	+4.5
	-15	+4.3	+4.3
	-13	+3.1	+3.7
	-11	+3.1	+2.6
	-10	-3.3	-4.2
	-9	-8.2	-9.6
	-8	+8.8	+9.3
	-7	-4.1	-6.5
	-6	-10.4	-10.7
	-5	+19.2	+20.9
	-4	-29.1	-24.5
	-3	-16.1	-17.2
	-2	-2.2	-2.2
	-1	-14.0	-12.3
	+0	+8.8	+7.9
	+1	+8.6	+8.3
	+2	-7.0	-8.2
	+3	+2.5	+2.0
	+4	-2.9	-2.4
	+5	-4.9	-5.6
	+6	+2.7	+3.7
	+7	+1.7	+1.7
	+8	-3.6	-3.3
+7	-20	+1.1	+1.4
	-19	-0.7	-1.2
	-18	+1.3	+1.7
	-17	+3.1	+5.0
	-16	+1.4	+1.6
	-15	+12.6	+12.8
	-14	-2.5	-2.0
	-11	-2.6	-2.7
	-10	+3.7	+4.0
	-9	+6.5	+7.3
	-7	-1.5	-1.9
	-6	-8.7	-10.7
	-4	+6.3	+6.5
	-3	+14.5	+15.2
	-2	-6.6	-7.1
	-1	+3.2	+2.3
	+0	-6.2	-5.4
	+1	-8.4	-8.2
	+2	+2.6	+2.7
	+5	+2.8	+3.1
	+6	-2.9	-2.7
	+8	-1.5	-1.7
+8	18	+1.2	+1.7
	-16	+3.4	+3.9
	-15	+18.5	+21.0
	-14	-2.3	-2.7
	-13	+10.6	+11.6
	-12	-2.2	-2.8
	-11	-2.1	-2.8
	-10	+0.6	+1.2
	-9	+0.8	+1.7
	-8	+2.6	+3.5
	-6	-4.4	-4.7
	-5	+10.0	+11.6
	-4	+3.2	+4.0
	-3	+4.7	+6.2
	-2	+8.4	+8.1
	-1	+5.9	+6.6
	+0	-1.7	-2.5
	+2	-3.3	-3.2
	+3	-3.5	-3.6
	+4	+2.3	+2.3
+9	-20	+0.4	+0.9
	-17	-3.3	-3.7
	-16	+2.6	+2.7
	-15	+11.6	+12.9
	-14	-2.5	-2.4
	-13	+12.7	+13.7
	-11	+2.7	+4.0
	-9	-1.9	-2.0
	-7	+1.7	+2.3
	-6	-4.1	-3.9
	-5	+9.9	+10.5
	-4	+5.6	+6.6
	-2	+10.7	+11.6
	-1	+6.4	+6.1
	+0	+3.3	+3.2
	+1	+3.9	+3.9
	+2	-1.2	-2.0
	+3	-0.8	-1.4
	+4	-0.9	-1.1
+10	-17	-1.8	-2.4
	-13	+2.2	+2.8
	-11	+4.2	+5.2
	-10	-1.7	-1.9
	-8	+2.0	+2.5
	-7	+2.2	+2.7
	-6	-4.7	-4.9
	-5	+4.1	+4.8
	-4	+5.1	+4.8
	-2	+7.1	+6.0
	+0	+6.5	+6.7
	+1	+2.7	+2.3
	+2	+2.9	+2.4
	+3	+2.2	+1.8
	+4	-2.0	-1.9
	+5	-1.3	-1.2
	+6	+1.4	+1.1
+11	19	-1.9	-2.2
	-14	-2.5	-1.9
	-13	-9.0	8.7
	-11	-1.9	-2.3
	-10	+1.1	+4.3
	-9	+1.9	+2.2
	-8	-2.2	-2.4
	-7	2.6	-3.2
	-6	-2.7	-2.3
	-5	+6.6	+6.6
	-4	+2.9	+2.8
	2	+4.1	+3.6
	-1	-4.4	-4.0
	+0	+2.5	+2.2
	+1	-1.4	-1.7
	+2	+2.5	+2.0
+12	-19	+2.7	+2.9
	17	-4.1	-5.0
	-15	+2.3	+2.7
	-14	-2.4	-1.8
	-11	-11.2	-11.0
	-9	-3.8	-3.7
	-7	+3.4	+3.5
	-6	-3.1	-3.2
	-5	+2.5	+1.8
	-4	+1.7	+2.0
	-3	-4.8	-4.8
+13	-17	+1.9	+2.0
	-15	-1.5	-2.3
	-13	-2.2	-2.7
	-11	+1.2	+1.9
	-9	-5.1	-5.3
	-8	+1.5	+1.8
	-7	-4.0	-4.8
	-5	+3.5	+3.2
	-3	-2.2	-1.8
	-1	-1.9	-1.7
	+0	-1.4	-1.4
+14	-14	-1.6	-1.7
	-13	+1.8	+2.4
	-11	-1.7	-1.9
	-9	-2.3	-2.2
	-3	-3.2	-2.8
+15	-7	-2.0	-2.2
	l = 2		
-17	+6	-2.2	-1.5
	+7	+0.7	+0.8
	+8	+2.0	+1.5
	+9	-1.7	-1.4
-16		+3.4	+2.4
-15	+0	-2.4	-1.6
	+1	+1.3	+1.2
	+6	-2.2	-2.5
	+8	+2.3	+2.2
	+9	+2.0	+1.4
	+17	-1.9	-1.5
-14	+0	-1.9	-1.7
	+2	-1.9	-1.7
	+4	-2.7	-2.3
	+8	+4.5	+4.0
	+9	+2.2	+2.0
	+17	-2.7	-1.8
-13	-2	+4.8	+4.1
	-1	-2.0	-2.5
	+0	-3.9	-4.1
	+4	+4.5	+4.3
	+5	-8.3	-7.3
	+6	-2.6	-2.3
	+7	-5.6	-4.8
	+8	-2.2	-2.2
	+9	+9.3	+7.4
	+10	+5.6	+4.5
	+12	+2.2	+1.6
	+13	-3.8	-3.4
	+14	-2.6	-2.4
	+15	-1.8	-1.8
	+17	-2.2	-1.9
-12	-4	-1.2	-1.5
	-2	-3.8	-4.5
	-1	+3.2	+3.2
	+0	+7.8	+9.0
	+1	-3.0	-2.5
	+2	+3.5	+3.5
	+3	-6.3	-6.0
	+4	-7.6	-7.9
	+5	-2.7	-3.1
	+6	+9.0	+7.9
	+7	-3.1	-3.3
	+8	+8.4	+7.6
	+10	-6.9	-5.7
	+13	+3.0	+2.8
	+14	+5.1	+4.8
	+15	-3.0	-2.6
	+17	-4.9	-4.0
	+18	-2.8	-2.2
	+19	+1.0	+1.1
-11	-6	-1.6	-1.8
	-4	+6.1	+6.5
	+0	-14.3	-14.3
	+1	+4.4	+3.9
	+2	+5.8	+5.2
	+4	+17.8	+15.2
	+5	-9.3	-8.2
	+6	-7.7	-6.9
	+7	-3.8	-3.4
	+8	+3.0	+2.9
	+9	+7.4	+6.8
	+10	+7.4	+6.4
	+11	-2.5	-4.3
	+12	-4.4	-3.6
	+14	-1.6	-2.3
	+15	+3.7	+3.7
	+16	+3.6	+2.9
	+17	-1.4	-1.8
-10	-8	+2.5	+2.3
	-6	+4.5	+4.1
	-4	-0.1	-1.8
	+2	-8.7	-8.3
	+3	+2.4	+2.4
	+6	+14.8	+12.3
	+7	-2.5	-2.0
	+9	+5.3	+4.5
	+10	-2.2	-2.6
	+11	-3.3	-2.8
	+12	+2.3	+2.3
	+14	-3.2	-2.9
	+15	+3.1	+2.8
	+17	+1.9	+2.3
	+19	+4.3	+3.2
	+20	+1.2	+1.1
-9	-3	-0.7	-3.9
	-2	+3.4	+2.8
	+1	-1.2	-1.5
	+2	-5.8	-4.9
	+3	+1.7	+1.6
	+4	-5.3	-5.4
	+5	+2.5	+3.1
	+6	+1.1	+1.5
	+7	+4.6	+5.3
	+8	+5.7	+4.3
	+9	+8.7	+8.3
	+11	-3.8	-4.3
	+13	-3.9	-4.2
	+15	+1.2	+1.5
	+17	+2.6	+1.9
	+19	+4.0	+3.9
	+20	+1.4	+1.4
-8	-10	+2.5	+2.6
	-8	-4.0	-3.4
	-7	+2.1	+2.6
	-4	+4.2	+4.7
	-2	+3.2	+3.5
	+0	+2.6	+2.2
	+1	+2.7	+2.8
	+3	+2.6	+2.2
	+4	+1.6	+2.9
	+6	-12.5	-11.3
	+7	+3.9	+4.4
	+8	-1.1	-1.8
	+9	+8.7	+9.1
	+10	-2.5	-2.0
	+12	-1.2	-2.3
	+13	-3.1	-2.9
	+14	+2.4	+2.9
	+15	-1.9	-2.6
	+18	-3.0	-2.6

Table 1 (*cont.*)

h	k	Fcalc	Fobs
	+19	+3.5	+3.1
	+20	+1.6	+1.6
-7	-13	+1.8	+1.6
	-10	+2.6	+2.4
	-7	+2.5	+2.8
	-6	+2.7	+3.2
	-5	+1.7	+1.7
	-4	-3.5	-3.9
	-2	+11.2	+11.1
	+0	+15.0	+14.5
	+1	+0.6	+1.2
	+2	-4.0	-4.2
	+3	-2.0	-1.4
	+4	+4.3	+4.0
	+5	+3.5	+3.4
	+6	-2.6	-2.3
	+7	+2.9	+3.5
	+8	-8.8	-8.5
	+9	+5.1	+5.6
	+11	-2.9	-2.7
	+14	-4.4	-4.8
	+16	+3.1	+2.8
	+17	-2.1	-2.0
-6	-13	+1.4	+1.8
	-12	+1.3	+1.4
	-10	+3.4	+3.4
	-9	-3.1	-3.5
	-8	-2.5	-2.5
	-7	+4.3	+4.3
	-6	-4.7	-5.6
	-5	-1.3	-1.7
	-4	+12.5	+12.1
	-3	+1.9	+2.7
	-2	+15.4	+14.1
	-1	+2.7	+2.8
	+0	+8.4	+7.9
	+2	+2.2	+2.3
	+3	+3.0	+2.3
	+4	+6.6	+7.6
	+5	-3.9	-3.9
	+6	+7.7	+6.7
	+8	-4.7	-4.7
	+9	+6.0	+6.6
	+10	-3.0	-2.8
	+11	+1.3	+2.4
	+12	+3.4	+4.2
	+13	-1.1	-2.5
	+16	-2.6	-2.5
-5	-15	-1.4	-1.6
	-14	+2.7	+2.9
	-11	-3.2	-3.5
	-9	-6.9	-6.8
	-7	+4.6	+4.5
	-6	-2.8	-4.2
	-5	+1.9	+2.5
	-4	-6.9	-8.5
	-3	-2.1	-3.5
	-2	+15.1	+16.4
	+0	+30.0	+26.0
	+1	+4.7	+3.6
	+2	-19.6	-17.1
	+4	+13.3	+12.4
	+5	+3.5	+2.9
	+6	-1.7	-1.8
	+7	-2.4	-2.7
	+8	+0.1	+1.5
	+9	+2.1	+1.7
	+10	+5.7	+7.5
	+11	+8.9	+8.3
	+13	+2.1	+2.6
-4	-16	-0.7	-1.2
	-15	-1.8	-2.2
	-14	+0.7	+1.5
	-13	-3.6	-4.0
	-12	+1.7	+2.2
	-11	-7.5	-8.4
	-10	+2.5	+3.5
	-9	-6.9	-7.5
	-8	-3.8	-5.0
	-7	+2.1	+2.0
	-5	+2.1	+1.8
	-4	-17.9	-16.3
	-3	-3.2	-2.2
	-2	+3.6	+2.3
	-1	-2.1	-2.9
	+0	+19.0	+18.0
	+1	+3.4	+2.8
	+2	-16.6	-13.4
	+3	-2.8	-3.4
	+5	-4.0	-2.9
	+6	+7.1	+6.7
	+8	-1.9	-1.7
	+9	+2.7	+3.5
	+10	-3.9	-3.4
	+11	+7.9	+7.3
	+12	+3.6	+4.1
	+13	+2.9	+2.9
	+15	+1.4	+1.9
-3	-15	+1.1	+1.2
	-14	-3.0	-3.2
	-13	-4.7	-5.4
	-11	-8.4	-9.1
	-9	-10.5	-11.1
	-8	-2.7	-2.7
	-7	+4.1	+4.8
	-6	-3.9	-5.2
	-5	-4.3	-4.5
	-4	-3.5	-2.9
	-2	-9.1	-9.3
	-1	+4.6	+4.9
	+0	-35.5	-34.8
	+1	-6.5	-6.8
	+2	-46.3	-46.7
	+3	-5.2	-4.7
	+4	+1.7	+5.1
	+6	+8.4	+8.1
	+7	-3.4	-3.7
	+8	+0.1	+1.5
	+9	-1.9	-1.8
	+10	-4.3	-3.7
	+11	+6.4	+6.8
	+12	-1.9	-3.1
-2	-15	+3.2	+2.7
	-13	+3.4	+3.2
	-12	-5.8	-5.8
	-11	-6.7	-7.1
	-10	-6.0	-6.0
	-9	-11.8	-11.7
	-7	+6.1	+7.0
	-6	+3.3	+3.1
	-4	-11.9	-12.9
	-3	-6.9	-7.6
	-2	-12.1	-10.7
	-1	-8.5	-8.1
	+0	-14.2	-11.8
	+1	+11.5	+10.3
	+2	-92.4	-88.1
	+3	-6.8	-6.2
	+4	-16.6	-14.4
	+5	-3.4	-2.5
	+6	-0.3	-2.0
	+7	-3.0	-4.0
	+8	+1.4	+1.7
	+9	-3.8	-3.3
	+10	+4.7	+4.5
	+11	+4.3	+4.4
	+12	-6.4	-6.1
	+13	-3.3	-3.6
	+14	-3.9	-4.2
	+15	-1.9	-2.3
-1	-17	-2.4	-2.2
	-15	+1.4	+1.8
	-14	+2.3	+2.7
	-13	+6.6	+6.9
	-12	-4.3	-4.5
	-10	-2.0	-2.9
	-9	+1.8	+1.6
	-8	-11.5	-11.1
	-7	+3.8	+3.9
	-6	+3.9	+4.4
	-5	-7.1	-6.1
	-4	+5.5	+6.2
	-3	-1.4	-1.1
	-2	+12.8	+12.9
	-1	+8.9	+9.3
	+0	-17.5	-17.7
	+1	+6.7	+5.7
	+2	-86.7	-81.3
	+3	-17.3	-15.9
	+4	-5.8	-6.7
	+5	+1.1	+2.3
	+6	+2.6	+4.0
	+7	+2.8	+4.1
	+8	-6.5	-8.6
	+9	-2.3	-2.5
	+10	-1.8	-1.7
	+12	+5.3	+4.4
	+13	-3.9	-4.1
	+14	-3.1	-3.2
	+15	-2.4	-2.4
	+16	-4.2	-3.5
+0	-14	+1.8	+2.2
	-12	+4.4	+4.4
	-11	+11.2	+11.5
	-10	-8.6	-9.0
	-9	+1.2	+2.4
	-8	-2.9	-3.1
	-7	+14.3	+13.6
	-6	+9.3	+9.9
	-5	+11.6	+11.9
	-4	-18.2	-16.4
	-3	-25.9	-25.9
	-2	+29.6	+27.7
	-1	-2.2	-10.8
	+0	+22.3	+19.6
	+1	+7.9	+6.7
	+2	-20.4	-20.1
	+3	+10.0	+9.6
	+4	-12.5	-14.2
	+5	-1.3	-1.2
	+6	-4.8	-4.8
	+7	-4.6	-6.6
	+8	+3.6	+4.1
	+9	+1.0	+1.7
	+10	-2.6	-3.1
	+11	+3.4	+3.4
	+12	-2.0	-2.3
	+13	-6.4	-5.9
	+14	+3.3	+2.7
	+15	-4.2	-3.2
+1	-19	-0.7	-1.4
	-17	-4.5	-4.1
	-15	+3.0	+4.0
	-14	-2.2	-2.3
	-10	+4.3	+4.9
	-9	+9.6	+9.5
	-8	+3.2	+2.8
	-7	+25.1	+25.8
	-6	+1.6	+1.1
	-5	+2.2	+2.4
	-4	+7.8	+8.5
	-3	+9.4	+10.4
	-2	-8.3	-9.4
	-1	-11.3	-13.0
	+0	+19.0	+19.2
	+2	+2.0	+2.3
	+3	-4.8	-6.2
	+4	+17.2	+20.4
	+5	+2.5	+3.3
	+6	+6.0	+5.0
	+7	+6.1	+6.2
	+8	-7.0	-8.1
	+9	-1.9	-3.2
	+10	+0.5	+1.7
	+13	-2.4	-2.0
	+15	-2.4	-2.2
+2	-17	-3.4	-3.7
	-15	-2.8	-2.5
	-14	+1.9	+2.2
	-13	+1.9	+2.7
	-12	-3.3	-3.4
	-9	+3.6	+3.1
	-8	+5.4	+.8
	-7	+3.0	+3.9
	-6	+2.6	+1.8
	-5	+7.3	+7.1
	-4	+2.7	+2.8
	-3	+6.3	+4.3
	-2	+9.7	+10.0
	-1	+6.4	+7.1
	+0	+7.0	+7.4
	+2	-5.1	-6.2
	+3	-5.2	-4.9
	+4	+16.7	+18.8
	+5	+3.2	+2.6
	+6	+9.8	+11.0
	+9	+1.3	+2.0
	+10	-3.1	-2.7
	+11	+1.8	+2.2
	+13	-2.1	-2.3
	+14	+0.9	+1.2
+3	-17	-5.1	-5.3
	-16	+2.3	+2.4
	-15	+3.2	+3.4
	-14	-1.2	-1.5
	-10	-3.8	-3.6
	-9	-7.6	-7.7
	-8	+1.4	+2.2
	-6	-5.0	-5.8
	-5	+28.6	+27.8
	-4	-15.4	-15.4
	-3	-12.2	-12.3
	-2	+7.7	+6.6
	-1	+1.0	+1.1
	+0	+5.4	+5.2
	+1	+5.1	+5.1
	+2	+7.4	+8.8
	+3	-2.3	-1.9
	+6	+6.0	+5.9
	+8	+4.5	+4.4
	+11	+2.3	+2.3
+4	-21	+0.6	+0.9
	-19	+2.4	+3.2
	-16	+2.6	+3.2
	-15	+4.9	+6.4
	-13	-4.4	-4.3
	-12	+0.4	+1.6
	-11	+2.6	+3.3
	-10	-3.0	-3.9
	-9	-2.0	-2.4
	-7	-4.8	-6.1
	-6	-9.5	-9.9
	-5	+15.4	+15.4
	-4	-13.4	-12.6
	-3	+5.7	+4.2
	-2	-7.8	-8.2
	-1	+2.2	+1.5
	+0	+5.2	+6.2
	+1	+2.6	+3.5
	+2	-5.2	-4.3
	+3	-4.8	-3.9
	+4	+3.1	+2.3
	+6	+4.9	+5.7
	+7	+3.3	+3.1
+5	-21	-2.4	-2.4
	-19	+2.7	+3.2
	-17	+7.3	+8.5
	-15	+7.5	+8.3
	-11	+1.7	+1.6
	-10	+1.4	+2.0
	-9	-4.7	-5.1
	-8	-3.0	-3.5
	-7	-9.4	-8.7
	-6	-6.8	-7.6
	-5	+19.8	+20.4
	-4	+6.0	+7.4
	-3	+18.9	+19.5
	-2	-8.2	-9.1
	-1	-9.9	-10.4
	+0	-3.2	-3.6
	+3	+5.5	+5.2
	+4	-0.3	-1.8
	+7	-3.3	-3.1
	+8	+2.5	+2.9
	+9	+1.8	+1.9
+6	-21	+1.5	+1.8
	-19	-2.5	-2.4
	-17	+2.9	+2.4
	-15	+21.2	+25.1
	-14	-3.3	-3.4
	-13	+3.1	+4.0
	-11	-5.4	-6.5
	-8	+2.4	+3.6
	-7	-2.9	-3.5
	-6	-1.5	-2.2
	-5	+8.0	+9.1
	-4	+4.2	+5.3
	-3	-4.6	-4.7
	-2	+7.0	+7.3
	-1	+11.4	+12.1
	+0	-1.1	-1.7
	+1	+1.1	+1.8
	+2	-5.7	-5.6
	+3	-6.5	-5.9
	+5	+2.1	+2.2
	+8	+2.2	+2.0
+7	-21	-1.9	-1.7
	-19	+5.3	+5.3
	-16	+1.8	+2.5
	-15	+4.2	+3.9
	-14	-2.8	-3.9
	-13	+7.3	+7.4
	-11	+11.2	+11.1
	-9	-6.8	-6.9
	-7	-8.6	-9.4
	-5	+5.0	+6.5
	-4	+9.5	+11.0
	-3	-1.5	-2.0
	-2	+6.0	+7.0
	-1	-4.7	-5.8
	+0	+4.2	+4.2
	+1	+1.9	+2.9
	+2	-2.0	-2.0
	+3	+3.5	+3.7
	+4	-4.1	-3.7
	+5	-3.6	-3.6
+8	-22	-1.6	-1.0
	-20	+1.7	+1.8
	-19	-2.2	-2.9
	-17	+4.4	+5.2
	-14	-1.4	-2.3
	-13	-9.3	-10.3
	-12	+1.5	+2.4
	-11	+4.8	+5.1
	-9	+3.4	+2.0
	-5	+4.3	+4.8
	-4	+8.7	+8.5
	-3	-7.6	-7.6
	-2	+4.1	+3.6
	-1	-10.1	-9.4
	+0	+5.0	+5.0
	+2	+1.9	+1.9
	+4	-2.9	-2.4
+9	-18	+1.2	+1.8
	-16	+2.7	+2.6
	-14	-2.4	-2.5
	-13	-14.3	-14.2
	-11	-3.5	-3.7
	-9	+5.6	+6.4
	-7	-4.0	-4.7
	-5	+5.9	+5.8
	-4	+3.8	+4.2
	-3	-3.1	-3.2
	-2	+1.5	+1.8
	-1	-6.8	-6.5
	+1	-5.7	-4.5
+10	-21	-1.8	-2.5
	-19	+1.2	+2.5
	-17	-1.6	-2.0
	-15	+1.4	+2.0
	-13	-5.4	-6.2
	-11	-7.7	-7.3
	-9	-1.3	-1.8
	-7	+1.8	+2.4
	-5	+4.8	+4.4
	-4	+5.0	+4.4
	-3	-2.3	-2.3
	-1	-2.4	-1.8
	+0	-2.2	-2.6
	+1	-3.4	-2.8
+11	-20	-0.7	-1.4
	-17	+2.5	+2.7
	-15	-4.5	-4.7
	-13	-3.0	-3.1
	-11	+4.2	+4.1
	-9	-5.5	-5.2
	-8	-1.4	-2.3
	-5	+5.7	+5.2
	-4	+2.7	+2.5
	-3	-1.8	-1.6
	-2	-2.2	-2.2
	+0	-2.3	-2.5
+12	-19	-1.1	-1.6
	-18	-1.9	-1.7
	-13	-4.8	-4.7
	-9	+5.1	+5.2
	-7	-4.2	-4.0
	-2	-1.7	-1.8
+13	-18	-2.0	-2.2
	-15	-1.9	-1.5
	-9	-1.3	-2.6
	-5	+1.5	+2.0
	-2	-2.1	-1.6
+14	-16	-1.5	-1.4
	-15	+1.9	+1.6
	-7	-1.9	-2.0
	-5	-1.4	-1.6
+15	-17	-1.3	-1.2
	-12	-0.6	-1.2
	-7	-2.7	-4.0
l = 3			
-18	+10	+0.9	+0.7
-17	+5	-1.9	-1.5
	+7	-2.6	-2.6
	+9	+2.4	+2.4
	+12	+1.3	+1.7
	+13	-2.7	-2.4
-16	+0	-1.4	-1.4
	+7	-2.3	-2.3
	+9	+2.3	+1.8
	+15	-2.4	-2.2
-15	-2	+1.8	+1.7
	+0	+2.9	+3.1
	+1	-1.6	-2.2
	+6	+4.0	+4.2
	+9	+3.8	+3.9
	+15	-2.3	-2.6
	+17	-1.3	-1.5
	+18	-1.9	-1.4
-14	-4	+1.1	+1.4
	+2	+2.8	+3.4
	+4	+6.7	+6.9
	+5	-2.2	-2.7
	+6	+5.1	+4.8
	+9	+5.3	+6.1
-13	-6	+2.8	+3.1
	+2	+5.6	+4.9
	+4	+2.4	+2.7
	+5	+3.1	+3.4
	+6	+3.6	+4.1
	+8	+8.9	+9.5
	+9	+2.6	+4.2
	+10	-2.0	-3.1
	+12	-5.3	-5.3
	+13	+3.0	+4.2
	+15	+1.8	+2.0
	+16	+1.8	+2.2
	+18	-2.2	-1.9
	+19	+2.6	+2.6
-12	-2	+4.8	+5.2
	+0	-3.9	-4.2
	+2	-10.6	-10.9
	+4	+7.8	+8.3
	+6	+10.3	+11.2
	+7	+3.7	+4.1
	+8	-7.0	-8.1
	+9	+6.9	+7.9
	+12	+5.6	+6.2
	+14	-5.5	-5.8
	+15	+2.9	+3.6
	+17	+4.9	+4.9
	+18	+1.7	+2.0
	+19	+4.2	+3.6
-11	-6	+2.9	+2.9
	-2	-5.7	-6.0
	+0	+5.2	+6.2
	+1	-2.7	-3.2
	+4	-12.9	-14.7
	+5	+2.9	+3.7
	+8	+10.0	+10.0
	+9	+4.0	+5.2
	+10	-6.8	-7.3
	+14	+4.8	+5.1
	+16	-3.1	-3.2
	+17	+3.5	+3.2
	+18	-2.2	-2.3
	+19	+4.9	+5.1
-10	-8	-2.4	-2.2
	-4	-4.8	-4.9
	+0	+2.8	+3.4
	+2	-7.4	-8.4
	+3	-5.4	-6.1
	+5	-6.2	-7.7
	+7	+4.1	+3.4
	+8	-7.4	-7.6
	+11	-3.9	-4.4
	+19	+2.8	+2.3
-9	-6	+1.8	+2.6
	-2	-3.3	-3.1
	+1	-1.9	-2.2
	+6	-2.2	-2.7
	+7	-2.8	-2.6
	+8	-9.0	-9.9
	+10	-5.6	-7.1
	+11	-4.9	-4.8
-8	-9	-4.2	-3.6
	-6	+5.0	+5.0
	-1	-2.6	-2.9
	+0	+13.8	+15.5
	+1	+4.1	+4.9
	+2	-8.9	-9.4
	+4	-9.5	-10.2
	+5	-3.0	-3.6
	+6	+3.8	+6.5
	+8	+3.9	+3.1
	+10	-7.3	-8.7
	+11	-5.0	-4.5
-7	-8	-4.7	-5.3
	-6	+3.4	+3.4
	-4	+2.5	+4.4
	-2	+6.0	+6.7
	-1	+2.3	+2.8
	+1	3.8	-3.3
	+2	-5.7	-8.8
	+3	-4.9	-5.6
	+4	+12.4	+11.2
	+5	+9.9	+9.3
	+6	-6.7	6.8
	+8	-3.3	-4.1
	+9	-4.3	-4.8
	+10	+2.7	+3.7
-6	-13	-3.0	-2.6
	-10	-4.2	-3.9
	-9	-3.7	-3.9
	-8	-4.2	-3.4
	-7	+1.9	+2.4
	-6	+9.4	+9.6
	-5	+6.7	+7.1
	-4	-6.0	-7.9
	-2	-7.3	-7.7
	-1	-8.8	-9.4
	+0	+17.0	+16.7
	+1	+7.7	+7.6
	+2	-10.1	11.1
	+3	+3.2	+1.7
	+4	-17.1	-15.9
	+5	-7.4	-6.4
	+6	+13.0	+12.4
	+7	+4.4	+4.3
	+8	+3.6	+4.4
	+9	+4.1	+4.3
	+10	-9.9	-10.9
-5	-14	-2.8	-2.6
	-13	-4.0	-3.9
	-11	-3.3	-3.1
	-10	-3.5	-4.4
	-9	-2.7	-2.9
	-8	-6.5	-7.1
	-7	+5.0	+5.7
	-6	+2.3	+2.5
	-4	+4.9	+6.2
	-3	+6.3	+6.5
	-2	-11.6	-12.8
	-1	+3.1	+3.3
	+0	-13.5	-14.5
	+1	-9.2	-7.6
	+2	-8.1	-10.8
	+3	-1.8	-2.2
	+4	+7.3	+5.8
	+5	+7.9	+5.7
	+6	-7.7	-7.0
	+7	-1.8	2.2
	+8	+6.6	+7.5
	+11	+4.6	+5.3
	+12	-8.5	-9.0
-4	-12	-4.4	-3.7
	-10	5.5	-5.4
	-8	9.0	10.1
	-6	+4.4	+4.9
	-4	+3.0	+2.8
	-3	+10.2	+8.8
	-2	-4.9	-5.1
	-1	+4.0	+4.0
	+0	-15.8	-15.1
	+1	+5.2	+3.9
	+2	-46.7	-39.6
	+3	-16.0	-14.6
	+4	+12.2	+11.1
	+5	+2.3	+2.7
	+6	+3.6	+6.0
	+7	+4.1	+5.0
	+10	+3.5	+3.3
	+12	-2.8	-2.7
	+13	-1.5	-2.6
	+14	-2.4	-2.6
-3	-11	+5.7	+6.1
	-10	-5.5	-5.1
	-8	-7.6	-7.6
	-7	+4.7	+4.5
	-6	+8.0	+7.3
	-5	+5.3	+4.9
	-4	-10.6	-11.2
	-3	-8.6	-8.3
	+0	+7.6	+6.8
	+1	+15.4	+13.6
	+2	-89.2	-85.0
	+4	-4.6	-4.3
	+5	-6.8	-6.5
	+6	+3.3	+4.7
	+8	+4.2	+6.6
	+9	+2.5	+2.3
	+13	-3.4	-2.8
-2	-13	-3.4	-4.9
	-12	+4.6	+5.0
	-11	+8.5	+7.8
	-9	+7.3	+7.3
	-8	-3.5	-2.8
	-7	+7.2	+7.9
	-6	+7.0	+7.4
	-5	-5.8	-6.4
	-4	-1.7	-1.7
	-3	+2.8	+2.9
	-2	-14.2	-14.0
	-1	-4.7	-4.4
	+0	+7.3	+5.6
	+1	-5.3	-3.7
	+2	+11.4	+10.5
	+3	+4.7	+4.9
	+4	+11.8	+11.3
	+5	+3.0	+3.1
	+8	+3.4	+3.1
	+13	-3.9	-3.9
	+14	+4.5	+4.1
-1	-17	+2.4	+2.5
	-15	+2.7	+2.6
	-14	-2.1	-2.2
	-13	-5.9	-5.9
	-12	+1.3	+2.2
	-10	+7.2	+7.4
	-9	+11.7	+11.3
	-6	+10.6	+11.1
	-5	-7.6	-7.9
	-4	+13.6	+12.9
	-3	+21.6	+20.9
	-2	-20.8	-20.0
	-1	-17.2	-16.3
	+0	-5.2	-6.2
	+1	-11.0	-10.9
	+2	+12.2	+10.8
	+4	+28.9	+29.9
	+5	+8.6	+8.2
	+7	-2.8	-2.2
	+9	-2.4	-2.9
	+10	+3.1	+2.7
	+11	+2.0	+2.8
	+12	-2.7	-3.3
	+13	-2.3	-2.6
	+14	+1.1	+1.5
	+16	+3.9	+3.4
+0	-15	+4.2	+3.7
	-13	+6.4	+6.4
	-12	-3.1	-3.3
	-11	-8.7	-8.6
	-10	+2.0	+2.4
	-9	-4.5	-4.5
	-8	+11.2	+11.9
	-7	+13.6	+14.7
	-6	+11.5	+11.6
	-5	-3.0	-2.8
	-3	-25.4	-22.9
	-2	+8.6	+8.1
	-1	+13.3	+14.5
	+0	-3.8	-5.0
	+1	+6.3	+5.0
	+2	-6.6	-6.6
	+3	-12.7	-12.8
	+4	+17.7	+18.5
	+6	+5.3	+6.6
	+7	+5.2	+5.1
	+11	-3.1	-2.6
	+15	+2.2	+2.3
+1	-17	+4.0	+3.9
	-15	+5.0	+4.4
	-13	-10.1	-9.3
	-12	+2.5	+2.6
	-11	+16.8	+16.2
	-10	-2.0	-3.7
	-9	+1.7	+2.4
	-8	-1.2	-1.7
	-7	-32.0	-29.7
	-6	+14.1	+14.9
	-5	+9.7	+10.2
	-4	+7.6	+7.6
	-3	+17.5	+15.2
	-2	-2.6	-1.9
	-1	-11.7	-13.3
	+0	+4.0	+4.4
	+1	-9.3	-8.4
	+2	+1.0	+2.7
	+3	+7.5	+6.7
	+4	+3.6	+3.1
	+5	+2.2	+1.7
	+6	-1.8	-2.0
	+7	-3.8	-3.3
	+8	+2.5	+2.7
	+11	+2.1	+1.9
	+12	-2.6	-2.4
	+13	-2.8	-2.2
+2	-15	+9.1	+8.8
	-14	-1.3	-1.7
	-11	-4.6	-4.0
	-9	+3.2	+4.2
	-8	-4.0	-4.2
	-7	+18.6	+18.4
	-6	-6.1	-6.4
	-5	-3.7	-6.2
	-4	+16.7	+17.0
	-3	-1.4	-1.6
	+0	+2.6	+2.7
	+1	+4.8	+4.8
	+2	+2.8	+3.3
	+4	+2.9	+3.7
	+6	-3.7	-4.8
	+8	-1.8	-2.0
+3	-17	+5.7	+4.9
	-15	+6.5	+6.5
	-13	-5.7	-5.2
	-9	+11.9	+11.5
	-7	-6.5	-6.9
	-6	-5.4	-5.4
	-5	+9.6	+10.4
	-4	+12.4	+12.7
	-3	+19.3	+18.4
	-2	+4.2	+4.9
	-1	+2.5	+2.5
	+0	+2.0	+1.9
	+1	-3.5	-6.9
	+2	+3.0	+4.2
	+4	+3.0	+4.1
	+5	+3.3	+4.5
	+6	-4.1	-4.7
+4	-19	-3.0	-2.8
	-17	+10.9	+10.3
	-14	-2.4	-2.3
	-13	-8.1	-8.4
	-8	-2.0	-2.0
	-6	-2.5	-2.8
	-5	+15.1	+15.5
	-4	+14.3	+15.9
	-3	-6.2	-6.1
	-2	+7.6	+8.5
	-1	+6.4	+7.9
	+4	+4.0	+4.4
+5	-17	-5.2	-4.7
	-16	-2.6	-2.7
	-15	+2.8	+2.5
	-14	-3.4	-3.3
	-13	-9.3	-9.4
	-12	+2.3	+2.4
	-11	-6.9	-6.9
	-8	-4.1	-3.4
	-7	+3.0	+1.8
	-6	-2.1	-2.6
	-5	-7.5	-8.2
	-4	+11.1	+12.6
	-3	-2.5	-4.1
	-1	-1.4	-2.5
	+2	+1.3	+2.3
+6	-17	+5.5	+4.9
	-16	+2.1	+2.2
	-15	-10.3	-9.6
	-14	-2.5	-2.9
	-13	-21.2	-21.8
	-12	-3.3	-4.0
	-10	+2.8	+2.8
	-9	-1.9	-2.0
	-8	+2.1	+2.4
	-7	-4.7	-4.5
	-6	-6.1	-5.9
	-5	+4.0	+3.4
	-4	+3.2	+3.6
	-3	-12.0	-11.5
	-1	-8.4	-8.8
	+0	-2.3	-3.1
+7	-21	+2.9	+2.4
	-20	+2.5	+2.7
	-16	-4.3	-4.0
	-15	+8.1	+8.3
	-13	-20.5	-21.4
	-12	+4.8	+5.4
	-11	-18.5	-20.5
	-10	-3.1	-4.4
	-9	+4.3	+5.3
	-8	-1.8	-2.2
	-7	-2.6	-2.9
	-6	+1.3	+1.6
	-4	+4.4	+4.5
	-3	-4.1	-5.2
	-2	-7.9	-7.9
	-1	-4.0	-3.5
	+0	-6.1	-5.9
	+1	-6.9	-6.5
+8	-19	+3.0	+2.3
	-11	-4.5	-4.9
	-10	+2.2	+2.7
	-9	-7.3	-7.4
	-4	+4.1	+3.4
	-3	-5.4	-4.5
	-2	-5.0	-4.7
	+0	-6.4	-6.0
	+2	-3.9	-2.9
+9	-20	+2.8	+2.6
	-19	-2.6	-2.7
	-12	+2.8	+2.7
	-11	+6.2	+5.7
	-4	+4.0	+4.1
	-3	-3.5	-3.1
	-2	-3.5	-3.3
	-1	+1.9	+2.4
	+0	-4.1	-3.5
	+1	+3.3	+2.6
+10	-20	+2.4	+2.5
	-17	-2.5	-2.6
	-15	+2.4	+2.5
	-11	+4.9	+5.0
	-9	+8.5	+8.1
	-3	-2.3	-2.5
	+1	+2.9	+2.4
+11	-9	+3.2	+2.6
	-7	+6.1	+4.7
	-1	+3.4	+2.4
+12	-20	+3.5	+1.0
	-19	-3.7	-3.5
+13	-18	+3.3	+3.6
	-17	-3.5	-3.2
	-11	-3.0	-3.2
+14	-17	+1.7	+0.9
l = 4			
-16	+2	+2.8	+1.7
-15	+0	-3.3	-2.8
	+4	+2.1	+2.4
	+7	+2.9	+2.0
-14	+4	-3.4	-3.4
	+5	+2.8	+2.6
	+7	+4.3	+3.9
-13	+6	-2.4	-2.6
	+7	+3.3	+3.2
	+8	-3.8	-3.4
	+9	+3.1	+2.8
	+10	-3.3	-2.2
	+11	-2.8	-2.6
-12	-8	-3.5	-3.4
	-2	-6.4	-5.9
	+2	+8.0	+7.1
	+6	-6.4	-7.1
	+12	-4.2	-2.5
-11	-11	-1.5	-2.0
	-7	+2.0	+2.6
	-6	-3.0	-3.2
	+0	-3.0	-2.9
	+4	+5.0	+4.9
	+5	-3.3	-3.9
	+8	-5.1	-5.1
	+11	-5.4	-4.2
-10	-6	+4.1	+3.6
	-2	-3.6	-3.1
	+0	-5.5	-5.6
	+2	-4.0	-3.1
	+3	-2.1	-2.4
	+4	+4.7	+5.3
	+7	-3.1	-2.9
	+8	+2.8	+1.8
	+9	-3.6	-2.9
	+11	-3.4	-2.4
-9	-8	-3.3	-5.1
	-6	+2.8	+2.8
	-1	-2.9	-3.4
	+1	+2.4	+3.2
	+2	-7.2	-7.7
	+4	-6.6	-6.7
	+5	-3.3	-3.3
	+8	+5.9	+5.1
	+10	+2.1	+2.3
	+11	-3.5	-3.4
-8	-8	-3.2	-3.7
	-7	+3.9	+3.1
	-5	-3.0	-3.0
	-4	+2.8	+3.1
	-2	-2.5	-3.6
	-1	+2.1	+3.3
	+0	-10.1	-10.7
	+1	-2.4	-2.6
	+2	-6.4	-6.0
	+3	-3.7	-3.3
	+4	+2.7	+2.6
	+6	-4.8	-4.8
	+8	-3.1	-2.7
	+10	+3.0	+2.6
	+11	-3.3	-2.9
-7	-10	-2.8	-2.6
	-8	-2.8	-3.1
	-7	+3.7	+3.4
	-6	+4.3	+4.0
	-4	+3.4	+4.8
	-3	+3.8	+4.3
	-2	-2.8	-3.4
	-1	-3.3	-3.7
	+0	-7.8	-8.5
	+1	-4.4	-4.3
	+2	-7.4	-8.2
	+3	+2.1	+8.3
	+4	+6.2	+5.8
	+5	+3.8	+3.3
	+6	-4.7	-5.9
	+7	-4.4	-3.6
	+12	-3.8	-3.6
	+13	-5.3	-3.5
-6	-15	+3.2	+2.9
	-13	+2.8	+3.1
	-12	-2.9	-2.2
	-9	+8.2	+8.3
	-7	+4.9	+8.2
	-5	-3.8	-3.2
	-4	+2.7	+2.4
	-3	-4.8	-6.0
	-2	+11.1	+12.7
	-1	+9.1	+9.5
	+0	-2.1	-3.2
	+1	+9.8	+8.6
	+2	-14.7	-14.3
	+3	-14.6	-14.1
	+4	+13.3	+13.3
	+5	+8.2	+8.9
	+7	+7.1	+6.7
	+8	-5.3	-6.6
	+9	-1.9	-2.3
	+10	+2.5	+3.8
	+11	-2.2	-2.0
	+14	-2.7	-2.7
-5	-15	-2.4	-2.4
	-11	+8.2	+7.7
	-9	+6.4	+5.8
	-7	+6.0	+6.6
	-6	+4.8	+6.0
	-3	+3.6	+5.0
	-2	+4.3	+6.5
	-1	-0.8	-1.8
	+0	+5.5	+5.3
	+1	-4.6	-3.1
	+2	+8.0	+7.0
	+3	+9.0	+8.5
	+4	+13.1	+13.2
	+6	+3.3	+1.8
	+7	-2.5	-3.1
	+9	+3.5	+4.1
	+13	-3.8	-3.5
-4	-13	-6.5	-5.7
	-10	+4.3	+4.4
	-9	+8.4	+8.3
	-8	+3.8	+3.4
	-7	+11.5	+12.1
	-5	-4.6	-4.2
	-4	-0.9	-2.2
	-3	-1.3	-2.8
	-2	+1.8	+2.2
	-1	-1.3	-1.7
	+0	+6.6	+6.9
	+1	+4.3	+2.6
	+2	+15.6	+15.0
	+4	+31.1	+40.4
	+5	+7.4	+7.7
	+6	+1.9	+1.8
-3	-11	-9.6	-9.0
	-10	+4.0	+4.7
	-9	+4.0	+4.1
	-8	+5.1	+4.9
	-7	+3.1	+2.6
	-6	+6.4	+6.9
	-5	-8.2	-8.6
	-4	-2.7	-3.9
	-3	+7.0	+8.1
	-2	-3.5	-2.4
	-1	+4.7	+4.8
	+0	-6.0	-5.9
	+1	-9.6	-7.8
	+2	+9.0	+9.5
	+3	-9.3	-8.3
	+4	+35.0	+47.8
	+5	+8.8	+9.1
	+6	+5.3	+5.8
	+7	+1.7	+2.8
-2	-15	+4.4	+3.5
	-12	-2.3	-2.4
	-11	-6.5	-6.6
	-9	-7.2	-7.9
	-8	+5.7	+6.1
	-6	+4.1	+4.7
	-5	-8.5	-10.4
	-4	-5.9	-6.5
	-3	-9.2	-10.0
	-2	+5.0	+4.7
	-1	+11.6	+11.5
	+0	-9.5	-8.6
	+1	+1.2	+1.4
	+2	-9.3	-8.8
	+3	-8.3	-7.1
	+4	+15.4	+15.7
	+6	+4.1	+5.0
	+15	+2.5	+2.4
-1	-15	+3.0	+2.9
	-11	+5.9	+6.1
	-9	-13.7	-13.0
	-8	-1.8	-1.9
	-7	-10.4	-10.9
	-6	+2.2	+2.7
	-5	+0.3	+1.4
	-4	-2.4	-2.7
	-3	-9.4	-9.4
	-2	-3.5	-6.2
	-1	-7.4	-8.4
	+0	-1.9	-2.8
	+1	+8.8	+9.0
	+2	-6.8	-6.8
	+3	-3.7	-3.8
	+4	-4.1	-3.4
	+13	-1.8	-1.7

Table 1 (*cont.*)

h	k	Fcalc	Fobs
+0	-15	+5.8	+5.1
	-13	-2.7	-2.5
	-12	-1.5	-2.0
	-11	-5.1	-4.3
	-9	+15.1	+14.6
	-8	+2.1	+2.8
	-7	-6.1	-6.1
	-6	-8.3	-7.6
	-5	-33.9	-40.7
	-4	-1.1	-2.6
	-3	+12.6	+13.0
	-2	+1.5	+2.3
	-1	+3.4	+4.9
	+0	-1.3	-1.9
	+1	-10.0	-8.5
	+2	-3.8	-6.1
	+3	+1.7	+2.0
	+4	-1.6	-1.4
	+5	+5.8	+5.3
	+6	-6.7	-8.4
	+7	-3.1	-3.1
	+8	-3.7	-4.3
	+9	-2.9	-2.7
+1	-15	+3.9	+3.2
	-14	-2.3	-2.4
	-13	+2.5	+2.5
	-12	+2.1	+2.0
	-10	+1.7	+1.7
	-9	-9.7	-8.4
	-8	-1.3	-2.2
	-7	+10.9	+11.9
	-6	-3.4	-2.6
	-5	+17.7	+17.7
	-4	+6.6	+7.4
	-3	-27.7	-26.5
	-2	+2.2	+3.9
	+0	-3.6	-3.2
	+1	+5.9	+6.0
	+2	-0.8	-1.9
	+3	-3.5	-3.9
	+4	+2.6	+2.0
	+6	-5.7	-6.6
	+8	-4.3	-4.3
+2	-17	-2.5	-2.2
	-15	+5.7	+4.7
	-13	-10.2	-9.5
	-12	-1.3	-1.7
	-11	+4.4	+4.4
	-9	+3.5	+4.3
	-8	+4.7	+4.1
	-7	-2.9	-3.7
	-6	+1.9	+2.3
	-4	+5.6	+5.8
	-3	-0.9	-1.7
	-2	+4.3	+4.4
	-1	+1.7	+1.4
	+0	+3.0	+3.5
	+1	-4.2	-4.1
	+2	-2.0	-2.3
	+8	-2.0	-2.5
+3	-17	-2.4	-2.7
	-15	-5.7	-9.1
	-13	-8.1	-7.8
	-9	-1.5	-1.6
	-7	+6.8	+8.3
	-6	-2.0	-2.6
	-5	-1.5	-1.4
	-4	+9.6	+10.5
	-3	-12.7	-12.9
	-2	+1.6	+1.2
	-1	-5.9	-6.0
	+1	+2.8	+3.3
+4	-15	-8.2	-7.6
	-13	-13.2	-12.5
	-12	+3.0	+3.1
	-11	-3.6	-3.7
	-10	-2.1	-1.8
	-9	-2.4	-3.7
	-8	-1.7	-2.2
	-7	+8.0	+7.8
	-5	+9.5	+9.9
	-4	+3.1	+2.8
	-3	-14.8	-15.8
	-2	-7.0	-7.9
	-1	-3.4	-4.0
	+3	-1.6	-2.6
+5	-14	+4.0	+3.6
	-13	-21.4	-22.8
	-12	-3.0	-3.3
	-9	+3.8	+5.0
	-8	+5.2	+5.2
	-7	-9.6	-9.9
	-6	-4.8	-5.1
	-5	+6.5	+7.0
	-3	+5.3	+5.1
	-2	-4.4	-6.0
	-1	-2.4	-3.4
	+0	-3.6	-4.5
	+1	-3.3	3.9
	+2	-2.4	-2.6
	+3	+1.2	+2.3
+6	-17	-4.4	-3.5
	-16	-4.8	-4.4
	-14	-3.0	-2.5
	-13	+6.4	+6.7
	-12	+10.5	+10.4
	-11	-5.4	-5.9
	-9	-9.0	-9.9
	-8	-8.8	-9.2
	-7	+13.9	+14.7
	-6	+4.2	+4.4
	-5	-5.5	-5.6
	-4	+3.2	+3.2
	-3	6.6	-6.6
	-2	10.0	-10.4
	-1	+10.7	+11.0
	+0	-3.9	-4.4
	+1	+3.7	+3.9
	+3	-3.4	-3.9
+7	-22	+2.5	+0.5
	-18	-2.2	-1.9
	-17	+3.6	+2.9
	-16	+3.8	+3.6
	-15	-5.4	-5.2
	-12	-5.4	-5.9
	-11	+19.8	+22.0
	-10	+4.7	+4.5
	-9	-2.5	-2.4
	-8	+6.5	+6.8
	-7	-10.7	-10.4
	-6	-6.5	-6.7
	-5	+7.8	+7.0
	-3	-2.7	-3.5
	-2	-1.6	-2.4
	+0	-2.0	-2.2
	+1	+7.8	+7.5
	+2	-1.9	-2.7
	+3	+2.8	+2.6
+8	-21	+2.0	+1.5
	-20	+2.2	+2.5
	-16	-3.1	-2.9
	-15	+2.7	+2.8
	-12	+2.0	+2.7
	-11	+7.0	+6.2
	-10	-3.4	-3.4
	-9	+8.5	+9.5
	-6	+3.3	+3.3
	-5	-3.1	-2.9
	-3	-4.3	-4.1
	-2	-6.0	-5.2
	-1	+2.8	+2.5
	+3	+3.0	+2.2
+9	-19	+2.3	+1.9
	-18	+2.2	+1.9
	-12	-1.1	-2.3
	-11	+4.6	+4.7
	-7	+3.1	+3.2
	-3	-2.9	-2.2
+10	-22	-1.0	-1.5
	-20	+1.7	+1.2
	-16	+2.5	+2.5
	-11	+2.0	+1.9
	-3	-2.8	-2.7
	+2	+1.6	+1.4
	+3	-1.6	-1.5
+11	-20	+2.9	+2.6
	-19	+1.8	+2.4
	-18	+3.0	+2.3
+12	-19	+1.4	+1.4
	-17	+2.0	+1.7
	-16	+3.8	+3.6
	-12	-2.2	-2.3
	-11	+1.5	+2.0
	-10	+2.0	+2.3
+13	-17	+2.1	+2.3
	-16	-2.2	-2.0
	-14	+2.2	+1.9
	-15	+1.5	+1.1
+14	-14	-1.9	-1.8
	-11	-2.1	-1.5
l = 5			
-15	+4	-3.2	-1.8
	+6	-3.4	-1.8
-14	+2	+2.6	+2.4
	+4	+1.9	+1.7
	+8	-4.2	-2.6
-13	+2	+1.8	+1.7
	+4	+5.8	+4.7
	+9	-2.0	-2.0
-12	-4	-2.7	-2.5
	-3	-1.8	-2.2
	-2	+5.4	+4.7
	-1	+2.3	+2.2
	+0	+2.7	+2.3
	+1	+3.2	+3.2
	+2	-6.0	-6.1
	+3	-2.7	-3.2
	+4	+2.5	+2.7
	+6	+7.1	+6.6
	+11	-2.7	-2.0
	+12	+3.1	+2.0
-11	-7	-1.4	-1.4
	-6	+2.2	+2.3
	-3	+3.0	+3.2
	-1	-1.8	-1.8
	+3	+2.3	+2.9
	+8	+3.4	+3.7
	+10	+4.3	+2.6
-10	-7	+5.3	+4.9
	-6	-1.2	-1.6
	-5	-2.0	-2.3
	-4	-4.7	-4.4
	3	-3.0	3.1
	1	+1.5	+2.4
	+0	1.3	1.8
	+2	-5.5	4.4
	+4	+2.6	+2.6
-9	-6	+3.1	+2.9
	-4	-4.5	-4.0
	+0	-3.0	-3.4
	+2	-4.3	-5.2
	+3	-3.9	-4.5
	+4	+5.4	+6.6
	+5	+2.6	+3.2
	+8	-2.3	-2.7
-8	-11	+2.7	+2.2
	-9	+2.8	+2.4
	-8	+2.0	+2.2
	-6	+4.7	+4.4
	-4	-2.7	-3.5
	-3	2.1	-2.2
	-2	+1.7	+2.4
	+0	-0.1	-1.5
	+1	+2.7	+2.9
	+2	-3.3	-3.7
	+4	+2.6	+4.9
	+6	+2.5	+2.2
-7	-11	+2.9	+2.8
	-8	+5.6	+6.0
	-7	+7.0	+6.6
	-6	+4.5	+5.3
	-5	-3.1	-3.7
	-4	-4.8	-5.4
	-3	-6.8	-6.2
	-2	+3.2	+2.9
	+0	+5.7	+6.5
	+1	+0.9	+1.4
	+2	+3.1	+4.2
	+3	+1.3	+2.0
	+4	+7.3	+8.1
	+5	+2.5	+2.4
	+6	1.4	-1.7
	+10	-1.8	-1.8
-6	-13	-3.2	-2.9
	-11	+4.8	+4.2
	-10	+2.4	+2.6
	-9	+2.0	+2.5
	-8	+3.9	+4.0
	-7	-5.4	-4.7
	-6	+7.8	+7.8
	-4	-3.6	-2.9
	-3	+3.4	+3.5
	-1	-5.5	-5.2
	+0	+5.1	+5.4
	+1	-2.1	-3.3
	+2	+6.8	+7.4
	+3	-3.4	-2.7
	+4	+16.0	+15.0
	+5	+8.0	+8.1
	+6	-2.0	-1.4
	+8	-2.1	-2.9
-5	-15	+2.9	+2.5
	-11	-9.4	-8.5
	-8	+4.2	+4.9
	-7	+3.0	+2.7
	-6	+5.6	+6.5
	-5	-3.4	-4.4
	-4	-5.0	-5.3
	-3	-3.5	-3.2
	-2	+1.9	+2.3
	+0	+1.8	+1.5
	+1	+1.3	+1.2
	+2	+3.7	+3.2
	+3	-1.6	-3.9
	+4	+13.1	+12.4
	+5	+0.8	+2.8
	+8	-1.2	-1.8
	+10	-2.1	-2.4
-4	-15	-2.9	-2.4
	-11	+6.8	+6.6
	-10	-1.8	-2.3
	-9	-12.1	-11.9
	-8	+1.0	+1.4
	-7	-8.3	-7.7
	-6	+2.9	+2.7
	-4	-6.6	-5.8
	-3	+1.4	+1.5
	-2	+1.6	+1.2
	-1	+3.4	+3.4
	+0	+0.7	+1.6
	+1	-1.1	-1.8
	+2	-3.5	-3.4
	+3	-3.9	-3.6
	+4	+2.1	+2.4
	+5	+2.5	+2.7
	+6	-4.9	-5.3
	+7	-2.1	-1.9
-3	-13	-2.8	-2.8
	-11	+5.0	+5.0
	-10	-2.3	-2.5
	-8	-2.8	-3.4
	-7	-6.3	-7.9
	-6	-1.4	-2.7
	-5	-0.5	-7.1
	-4	-8.5	-8.4
	-3	+2.3	+2.3
	-1	-0.8	-3.1
	+0	+3.8	+4.0
	+1	+9.4	+7.7
	+2	-4.7	-3.6
	+3	+1.4	+1.0
	+4	-5.1	-4.5
	+5	-2.7	-2.4
	+6	-9.3	-9.2
	+7	-2.1	-2.3
-2	-15	-1.9	2.0
	-13	-1.8	2.2
	-9	+3.6	+3.5
	-8	3.2	2.7
	-7	-1.1	2.0
	+6	4.4	5.0
	-5	+0.9	+2.8
	4	8.5	8.8
	2	3.7	4.8
	-1	-8.4	-6.4
	+0	+2.3	+2.5
	+1	+3.0	+3.2
	+2	+1.7	+2.3
	+3	+7.3	+6.7
	+4	-2.8	-2.7
	+5	+0.7	+2.2
	+6	-8.6	-8.6
	+7	-3.9	-3.7
-1	-13	-8.3	-7.7
	-11	+3.9	+3.7
	-9	-2.9	-2.6
	-6	2.1	2.4
	-5	+8.7	+6.8
	4	5.8	6.0
	3	2.4	2.3
	2	4.9	5.7
	-1	+5.1	+5.0
	+1	-6.0	-6.7
	+2	+0.2	+1.2
	+3	-2.6	-2.2
	+4	+0.8	+1.5
	+5	+4.7	+6.0
	+6	-3.9	-4.7
+0	-13	-8.3	-7.5
	-11	+2.1	+2.2
	-10	+0.9	+1.8
	-9	-4.9	-5.3
	-7	-1.2	-1.4
	-6	+1.0	+2.6
	-5	+4.8	+4.8
	-4	+3.2	+2.9
	-3	-4.3	-2.2
	-2	-4.4	-4.9
	-1	-6.3	-6.0
	+0	-4.0	-4.5
	+1	+7.1	+6.7
	+2	-0.8	-1.7
	+3	+0.1	+1.6
	+4	+1.5	+1.9
	+5	-4.0	-4.1
	+6	-1.4	-1.9
	+10	+0.2	+1.8
+1	-16	+1.7	+2.0
	-15	-7.6	-6.6
	-14	-3.7	-3.1
	-13	-4.7	-4.9
	-12	+0.9	+1.6
	-11	+4.4	+5.0
	-9	-3.5	-3.4
	-8	+0.5	+1.1
	-7	-4.5	-4.1
	-6	+2.1	+2.3
	-5	-0.8	-1.2
	-4	+1.2	+2.0
	-3	-4.3	-3.6
	-2	-7.0	-7.3
	-1	-5.0	-5.1
	+1	-2.8	-3.1
	+2	-1.1	-1.9
	+3	+2.3	+2.8
	+4	-1.8	-2.5
	+7	-2.7	-2.7
	+8	+2.2	+1.6
+2	-17	+2.7	+2.7
	-14	+3.4	+2.6
	-13	-12.8	-11.6
	-11	+8.1	+8.2
	-9	+5.3	+5.4
	-8	+1.3	+2.3
	-7	-6.9	-7.1
	-5	+2.8	+4.3
	-4	+2.9	+3.5
	-3	-6.8	-6.5
	-2	-9.0	-8.4
	-1	-3.0	-2.5
	+0	-3.9	-3.6
	+6	-1.7	-1.8
+3	-15	+3.1	+3.1
	-14	+1.1	+2.0
	-13	-4.8	-5.1
	-12	+2.5	+2.2
	-11	+10.7	+10.9
	-10	+3.0	+2.7
	-9	+2.5	+2.7
	-8	-3.2	-2.8
	-5	+2.7	+2.5
	-4	+3.6	+3.9
	-3	+2.8	+3.3
	-2	-6.2	-6.4
	+0	-2.0	-2.0
	+3	+1.4	+1.9
+4	-18	-2.0	-2.4
	-14	+2.5	+2.5
	-13	+5.9	+6.2
	-12	+2.0	+2.3
	-11	+12.1	+12.6
	-10	-2.1	-2.3
	-9	+5.5	+5.4
	-8	+3.0	+3.6
	-7	+5.5	+4.9
	-6	+4.0	+3.5
	-5	-4.7	-4.8
	-4	-3.4	-2.9
	-3	+2.1	+2.7
	-2	-3.9	-4.8
	-1	+9.5	+9.1
	+0	+4.0	+3.6
	+1	+1.9	+2.4
+5	-15	-3.9	-4.2
	-14	-4.2	-4.4
	-13	+2.7	+2.8
	-11	+23.1	+23.1
	-10	+6.6	+6.6
	-9	+3.7	+3.7
	8	3.8	3.5
	7	-4.0	4.5
	6	4.3	-4.9
	-5	+10.7	+9.5
	-4	+9.3	+8.5
	-3	-4.6	-4.3
	-2	-3.9	-4.1
	-1	+1.4	+2.0
	+1	+8.0	+7.4
	+2	+5.0	+4.2
	+3	+1.7	+2.6
+6	-18	-3.3	-2.9
	-15	+1.8	+1.7
	-14	+6.0	+5.6
	13	7.6	-7.6
	-12	6.7	-6.1
	11	+6.4	+6.7
	-10	6.0	6.8
	9	+13.2	+13.6
	8	+8.2	+7.9
	7	[illegible]	2.2
	-6	+1.9	+2.0
	-5	-4.4	-4.8
	-4	-6.9	-6.4
	-3	+4.9	+5.1
	-1	+1.6	+1.8
	+0	+7.1	+6.0
	+1	-2.3	-2.5
	+3	+4.1	+3.7
+7	-12	+3.6	+3.3
	-11	-2.8	-1.9
	-9	-5.7	-5.7
	-8	-7.5	-7.3
	-7	+4.2	+4.5
	-4	+4.2	+3.6
	-3	-2.7	-2.4
	-2	-5.2	-4.5
	-1	+2.9	+2.8
	+2	+4.5	+3.3
+8	-18	-2.5	-2.6
	-13	-1.7	-1.4
	-9	-5.1	-4.2
	-8	+2.2	+2.6
	-7	-6.4	-5.9
	-6	-1.9	-2.6
+9	-18	-1.7	-1.9
	-15	+1.7	+2.2
	-7	-4.8	-4.0
	-5	-2.6	-2.3
+10	-17	+1.9	+1.7
	-6	+2.3	+1.2
	-5	-2.6	-2.3
l = 6			
-13	+4	-3.7	-4.0
-12	+1	-4.7	-4.4
	+2	+3.9	+3.9
	+4	+3.6	+3.1
	+5	+4.4	+4.0
	+6	-3.6	-3.3
-11	-4	-3.8	-3.5
	-3	-2.2	-2.7
	-1	-1.2	-2.2
	+0	+2.6	+2.9
	+1	+5.6	+5.9
	+3	-1.6	-2.6
	+4	+3.0	+3.3
-10	-6	+3.2	+2.9
	-5	-3.5	-3.2
	-3	+4.7	+5.2
	+1	-3.5	-4.4
	+2	+4.6	+4.9
	+3	+2.3	+2.4
	+4	+3.7	+3.5
	+5	+2.5	+2.6
-9	-5	-2.7	-2.8
	-4	-2.5	-2.7
	+2	+2.2	+3.7
	+4	+4.5	+4.5
-8	-7	-4.8	-4.7
	-6	+2.9	+2.8
	-5	-2.9	-2.6
	-4	-4.2	-4.7
	-2	-4.2	-4.2
	-1	-2.4	-3.7
	+2	+3.3	+4.0
	+4	+2.0	+2.8
	+6	-5.8	-4.8
-7	-7	-10.8	-11.3
	-5	-8.3	-9.4
	-4	-2.1	-2.2
	-3	+9.1	+9.2
	+0	-5.6	-6.5
	+1	-9.6	-9.0
	+5	+4.0	+3.4
	+6	-7.3	-7.4
	+7	-3.8	-4.3
-6	-9	-7.3	-8.1
	-8	-3.3	-3.2
	-7	+1.5	+2.5
	-5	-6.1	-5.2
	-4	-2.8	-3.6
	-3	-8.3	-8.7
	-1	+7.4	+6.9
	+1	+5.8	+5.0
	+2	3.2	-4.7
	+3	-6.7	-6.7
	+4	-5.7	-5.8
	+6	-11.4	-10.3
-5	-11	+8.7	+8.7
	-9	+7.9	+7.9
	-7	-11.8	-12.8
	-6	-5.2	-5.8
	-4	-4.6	-4.7
	-3	+10.8	+10.7
	-2	+4.9	+4.3
	-1	-9.9	-9.2
	+0	+1.6	+1.5
	+1	+1.3	+1.9
	+3	+7.6	+7.1
	+4	-4.7	-5.9
	+6	-12.5	-11.6
	+7	-5.0	-5.0
	+8	-2.8	-2.9
-4	-13	-3.6	-3.6
	-12	+2.1	+2.7
	-11	-3.5	-3.6
	-9	+10.2	+10.3
	-8	-2.3	-2.9
	-7	+7.9	+9.0
	-5	-4.0	-4.4
	-4	-2.6	-2.7
	-1	+6.8	+4.3
	+1	-5.0	-5.4
	+2	+4.5	+4.4
	+3	+1.9	+1.9
	+5	+5.6	+6.0
	+6	8.2	-7.9
	+7	-2.9	-3.1
-3	-13	-4.7	-4.9
	-10	+2.3	+2.4
	-9	-1.7	-2.9
	-7	+6.6	+7.6
	-6	-2.4	-3.3
	-5	+9.1	+9.8
	-3	+4.2	+3.4
	-2	+2.1	+3.2
	-1	+3.0	+2.6
	+1	-2.3	-2.6
	+2	+2.7	+3.4
	+3	-2.3	-2.4
	+4	+4.7	+4.8
	+5	+4.0	+3.4
	+6	-2.2	-2.5
-2	-13	-4.8	-5.1
	-5	+1.5	+1.9
	-3	+8.0	+9.1
	-1	+3.4	+3.1
	+1	+3.2	+3.3
	+3	-2.5	-3.1
	+4	+2.9	+3.5
	+8	+2.6	+3.2
-1	-16	-1.7	-1.5
	-15	-1.5	-1.4
	-13	-2.3	-2.3
	-12	+3.5	+3.5
	-10	-0.8	-1.7
	-8	-2.5	-2.7
	-7	-2.0	-2.5
	-4	+3.9	+3.5
	-2	-3.5	-3.3
	+3	+3.5	+3.6
	+7	-3.2	-3.2
	+8	+2.2	+2.7
	+9	+1.4	+1.9
	+10	+1.7	+1.6
+0	-15	+1.7	+1.6
	-14	+2.3	+2.5
	-13	-6.5	-6.0
	-12	-3.7	-3.9
	-11	+7.1	+6.6
	-10	+3.2	+2.6
	-9	+1.9	+2.5
	-8	+2.9	+2.9
	-7	-4.0	-4.8
	-6	-4.0	-3.4
	-5	-4.2	-4.5
	-2	-5.0	-5.1
	-1	+6.0	+5.9
	+1	-1.2	-2.4
	+3	-2.0	-2.2
	+5	+2.3	+2.9
	+8	+1.9	+1.8
+1	-16	-3.2	-2.9
	-15	+4.3	+4.5
	-14	+2.7	+2.8
	-13	+2.6	+3.3
	-12	+4.2	+4.1
	-11	+5.1	+5.8
	-10	-2.1	-1.6
	-8	-2.1	-3.2
	-7	+4.6	+5.8
	-6	+2.9	+4.0
	-5	-5.5	-6.7
	-2	-5.1	-4.8
	-1	+4.9	+4.7
	+1	+1.5	+2.7
+2	-14	-3.6	-4.1
	-13	+8.2	+7.9
	-12	+1.7	+2.4
	-11	+12.3	+11.9
	-10	+2.8	+2.8
	-6	-1.8	-2.2
	-4	+1.3	+2.0
	-3	-1.7	-2.2
	-2	-2.6	-2.9
	-1	+6.3	+6.4
	+0	+3.3	+4.2
	+1	+2.0	+2.0
+3	-13	+2.5	+2.4
	-12	-3.6	-3.5
	-11	+13.7	+14.2
	-9	+3.4	+4.3
	-8	+2.3	+2.5
	-4	+1.6	+2.0
	-3	-4.4	-4.4
	-2	-2.1	-2.2
	-1	+2.2	+2.5
	+0	+4.7	+4.8
	+1	+2.6	+2.6
	+2	+2.3	+2.9
+4	-11	+2.6	+2.8
	-10	-2.8	-2.7
	-7	+5.7	+3.9
	-5	-2.2	-1.6
	+0	+3.5	+4.2
	+1	-2.6	-2.7
+5	-12	+3.7	+4.4
	-11	-4.4	-3.9
	-10	-2.5	-2.6
	-9	-9.4	-10.0
	-8	-4.1	-4.4
	-7	+3.0	+2.5
	-6	+2.0	+2.3
	-2	-2.8	-2.4
	-1	+2.9	+2.8
	+0	+5.9	+3.2
	+1	-3.0	-2.8
+6	-12	+1.8	+2.7
	-11	-2.4	-2.9
	-9	-7.5	-7.9
	-7	-4.2	-4.2
	-6	-3.9	-4.0
+7	-10	+2.6	+2.7
	-9	-5.1	-5.6
l = 7			
-2	-11	+6.4	+5.9
	-9	-2.8	-2.7
	-8	-3.4	-3.2
	-7	+4.4	+4.3
	-4	+2.0	+2.3
	-3	-6.1	-5.7
	-1	+2.1	+1.6
	+0	+2.1	+2.4
	+1	+2.7	+2.9
-1	-13	+3.0	+3.3
	-11	+6.0	+5.7
	-9	-4.2	-4.0
	-5	+3.6	+3.3
	-4	-2.1	-2.3
	+0	+2.9	+2.7
	+1	+2.3	+2.0
+0	-14	-2.0	-2.4
	-13	+2.4	+2.3
	-11	+6.3	+5.9
	-9	-5.4	-4.8
	-7	-2.2	-2.3
	-2	-4.7	-3.9
	-1	+4.2	+3.5
	+0	+5.4	+4.9
	+2	+1.6	+1.7
+1	-15	-1.6	-1.5
	-12	-4.5	-4.4
	-11	+5.7	+4.7
	-10	+2.2	+2.4
	-9	-8.2	-7.7
	-7	-3.5	-3.3
	-6	-2.4	-2.3
	-5	+1.3	+1.4
	-3	-3.0	-2.6
	+0	+1.7	+1.4
+2	-17	+1.2	+0.9
	-16	+2.2	+1.8
	-13	-1.9	-2.3
	-12	-2.0	-1.7
	-10	-3.0	-2.5
	-9	-9.5	-9.0
	-7	-2.8	-2.4
	-4	-2.5	-2.5
	-1	-2.3	-2.7
	+0	+3.4	+4.0
	+1	-3.3	-3.4
	+2	-1.4	-2.2
l = 8			
-2	-12	-2.8	-2.6
	-11	+2.4	+2.5
	-9	-3.0	-3.9
	+0	+4.1	+3.6
-1	-13	-2.7	-2.2
	-9	-5.0	-4.9
	-8	-2.5	-2.4
	-3	+2.4	+2.3
+0	-13	-3.0	-2.6
	-11	-4.2	-3.7
	-10	-1.9	-2.0
	-9	-6.5	-6.2
	-4	-2.5	-2.4
	-3	+2.5	+2.0
	+0	+2.8	+2.8
	+1	-3.5	-2.6
	+2	-3.3	-2.5
+1	-14	+1.7	+1.6
	-12	+2.3	+1.9
	-11	-4.6	-4.0
	-9	-8.0	-7.1
	-8	-2.7	-2.0
	-4	+1.7	+1.8
	-2	-2.9	-2.6
	-1	+2.2	+2.3
	+1	-1.7	-1.7
	+3	-1.7	-1.4
+2	-10	+3.5	+3.3
	-9	-4.4	-4.0
	+2	-2.8	-2.2
l = 9			
-2	-11	-1.6	-1.5
	-9	-3.5	-3.5
	-7	+4.0	+3.9
	-6	+1.6	+1.8
	+0	+1.5	+1.5
-1	-10	+1.6	+1.7
	-9	-3.2	-2.6
	-8	-2.7	-2.2
	-7	+4.9	+3.7
	-5	+3.0	+2.0
	-4	+2.0	+2.4
+0	-9	-0.3	-1.0
	-7	+4.9	+4.3
	-5	+2.1	+1.8
	-2	+0.8	+1.0
+1	-10	-0.7	-0.8
	-9	+1.4	+1.9
	-8	+1.1	+1.2
	-7	+5.6	+5.1
	-6	+2.6	+2.9
	-5	+1.7	+1.6
+2	-10	-1.7	-1.5
	-8	-1.1	-1.2
	-7	+4.4	+4.4
	-5	+1.7	+1.9
	-4	+1.0	+1.4
l = 10			
-2	-7	+3.7	+2.4
	-6	+1.4	+1.5

corresponding atoms in the other ring, whereas all other corresponding atoms in both halves of the molecule show random differences in electron density of about 4%. From the height of the electron density maxima in the last difference synthesis, ascribed to the alternate position of atoms C(2′), C(17′) and C(18′), we estimate an occupancy rate of roughly 8% for these positions. Considering their low accuracy, these lead to reasonable interatomic distances and valency angles (Table 2). It seems therefore that there is enough evidence for about 10% conformational disorder in the 'primed' ring.

A still smaller degree of disorder might well have escaped detection. Such disorder would then presumably have been concealed by errors in the thermal motion and the geometry. The disorder was not included in any least-squares cycle. In view of similar results in the structure determination of 15,15′-dehydrocanthaxanthin a further drop in *R* to about 10% might be possible upon allowance for disorder. It is not impossible that significant parameter changes might have occurred on further refinement, especially in the thermal parameters of C(2′), C(17′) and C(18′) which are probably too high (Table 4). On the other hand, introduction of 15% disorder in the acetylenic derivative did not lead to significant changes in the positional parameters. We believe therefore that our geometric results are only very slightly in error, if at all.

Figs. 2 and 3 show the final Fourier synthesis in sections viewed along [001] and [010]. A few reflexions suspected of having suffered from extinction were included with F_{calc} instead of F_{obs}. The electron densities at the peaks of the carbon atoms of the chain varied from 5·6 to 7·7 $e.\text{Å}^{-3}$ with an average value of 6·7 $e.\text{Å}^{-3}$; in the rings average values of 5·1 $e.\text{Å}^{-3}$ were reached. This lower value is related to the larger temperature factors of the ring atoms. The oxygen atoms were at 6·5 $e.\text{Å}^{-3}$. The electron densities of the methyl groups of the ring were considerably lower than the densities of those attached to the chain; the *gem*-methyl groups especially were diffuse. At the C(17′*), C(2′*) and C(18′*) positions a higher electron density was found than was expected from the difference synthesis. The background fluctuation everywhere else was less than 0·25 $e.\text{Å}^{-3}$.

Molecular parameters and discussion

Assessment of the final structure

Tables 3–6 list final carbon and oxygen positional and thermal parameters with their standard deviations, obtained by least-squares methods from Cruickshank's (1961) formulae, also the unrefined hydrogen parameters. The numbering of the hydrogen atoms is indicated in Fig. 4.

Conformation of the molecule

The chain has the all-*trans* configuration. The chain is doubly curved as can be observed in Figs. 2 and 3. The angle between the best planes through the double bond system of the chain and the planar part of both rings is 43° from *s-cis*, as compared with 28° in the 15,15′-dehydro derivative. Comparison of the angles between chain and rings with the angle in β-carotene (35°) indicates that reinforcement of the conjugated system by the introduction of an extra carbonyl grouping does not give enough compensation for tolerance of steric hindrance. On the contrary, it seems likely that at rather large angles the total energy is not much dependent on the conjugation energy. A change anywhere in the molecule causes changes in the inter-

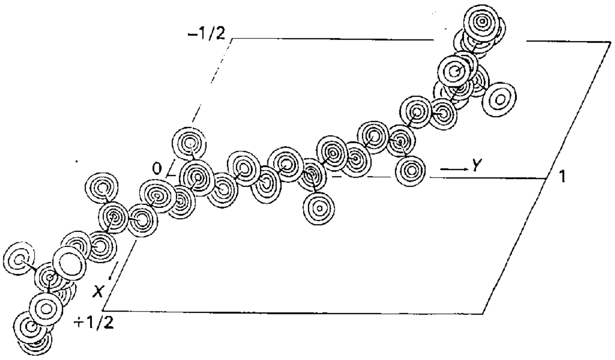

Fig. 2. Final composite electron density sections parallel to (001). Contours at intervals of 1·5 $e.\text{Å}^{-3}$, starting at 1 $e.\text{Å}^{-3}$.

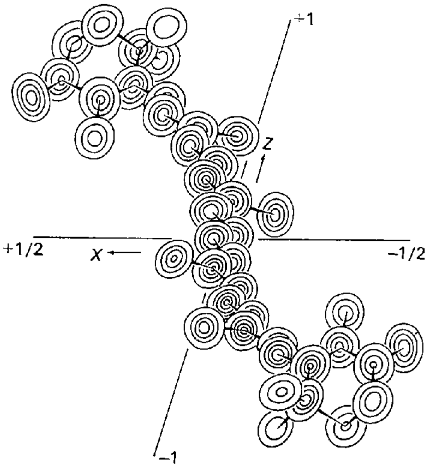

Fig. 3. Composite electron density sections parallel to (010) based on final structure factors. Contours at intervals of 1·5 $e.\text{Å}^{-3}$ starting at 1·0 $e.\text{Å}^{-3}$.

Table 2. *Disordered ring; positional parameters of the disordered atoms*

	x	y	z
C(2′*)	−0·442	+0·722	−0·747
C(17′*)	−0·420	+0·586	−0·888
C(18′*)	−0·255	+0·743	−0·780

Distances	
C(1′)—C(2′*)	1·68 Å
C(1′)—C(17′*)	1·55
C(1′)—C(18′*)	1·55
C(2′*)-C(3′)	1·34

Angles	
C(1′)—C(2′*)-C(3′)	111·0°
C(2′*)—C(1′)—C(6′)	104·2
C(2′*)—C(1′)—C(17′*)	113·1
C(2′*)—C(1′)—C(18′*)	110·5
C(6′)—C(1′)—C(17′*)	98·9
C(6′)—C(1′)—C(18′*)	118·7
C(17′*)-C(1′)—C(18′*)	110·3

molecular packing arrangement. Therefore it is probable that the angle between chain and ring is also partly determined by the intermolecular interaction (see the discussion of packing arrangements).

The conformation of the hydrogen atoms of the methyl groups C(17), C(18) of both rings is fairly well staggered with respect to C(2), C(6), C(18) and C(2), C(6), C(17). The other methyl groups, which are directly bonded to the conjugated system, do not have a configuration as in propylene (Herschbach & Krisher, 1958), where the double bond eclipses a hydrogen atom from the methyl group; see *e.g.* Fig. 4 and Table 10. Only methyl group C(19′) has the orientation predicted by Pauling.

Planarity of the molecule

Best planes were calculated by using a least-squares criterion (Schomaker, Waser, Marsh & Bergman, 1959), after transformation of the coordinates to a standard set x,y,z of orthogonal axes, in which y coincides with b, x is the projection of a on a plane perpendicular to y, and z is perpendicular to x and y (Cruickshank, 1961).

(*a*) *The chain*

Displacements of the atoms from the least-squares plane through the chain are given in Table 7 (x, y and z in the formulae of the planes are orthogonal coordinates in Å).

These deviations denote a bending of the chain normal to its plane. The angle between the chain plane and the plane of $(\bar{5}66)$, which is the closest lattice plane, is 2·5°.

The results of an analysis of the planarity of the separate double bond systems of the molecule are summarized in Table 8.

Most chain double bond systems are planar within the limits of error. An exception is the double bond C(9′)=C(10′) which shows significant deviations from planarity. Some parts of the chain are reasonably flat. The best plane through atoms C(14) to C(11′) including the methyl group C(20′) gives a maximum displace-

Table 3. *Final positional parameters for* C *and* O *atoms*; *fractional coordinates*

	x	y	z		x	y	z
C(1)	+0·3750	−0·1836	+0·8588	C(1′)	−0·3580	+0·6785	−0·7525
C(2)	+0·5008	−0·1471	+0·9726	C(2′)	−0·4808	+0·6466	−0·8502
C(3)	+0·5618	−0·1684	+0·8768	C(3′)	−0·5405	+0·6614	−0·7458
C(4)	+0·5423	−0·1483	+0·7116	C(4′)	−0·5098	+0·6460	−0·5782
C(5)	+0·4409	−0·1440	+0·6250	C(5′)	−0·4059	+0·6394	−0·5056
C(6)	+0·3647	−0·1578	+0·6947	C(6′)	−0·3368	+0·6530	−0·5892
C(7)	+0·2590	−0·1561	+0·6105	C(7′)	−0·2350	+0·6456	−0·5250
C(8)	+0·2550	−0·0894	+0·5560	C(8′)	−0·2340	+0·5747	−0·4887
C(9)	+0·1542	−0·0855	+0·4744	C(9′)	−0·1333	+0·5663	−0·4190
C(10)	+0·1643	−0·0157	+0·4157	C(10′)	−0·1489	+0·4919	−0·3755
C(11)	+0·0739	−0·0014	+0·3258	C(11′)	−0·0590	+0·4763	−0·2862
C(12)	+0·0944	+0·0689	+0·2675	C(12′)	−0·0830	+0·4016	−0·2397
C(13)	+0·0102	+0·0862	+0·1640	C(13′)	+0·0001	+0·3822	−0·1385
C(14)	+0·0480	+0·1609	+0·1210	C(14′)	−0·0402	+0·3033	−0·1044
C(15)	−0·0187	+0·1927	+0·0201	C(15′)	+0·0266	+0·2709	−0·0088
C(16)	+0·4258	−0·1318	+0·4541	C(16′)	−0·3841	+0·6230	−0·3327
C(17)	+0·3239	−0·1454	+0·9648	C(17′)	−0·3123	+0·6422	−0·8717
C(18)	+0·3118	−0·2844	+0·8096	C(18′)	−0·2885	+0·7791	−0·7058
C(19)	+0·0413	−0·1578	+0·4556	C(19′)	−0·0216	+0·6385	−0·3952
C(20)	−0·1142	+0·0217	+0·1123	C(20′)	+0·1215	+0·4456	−0·0822
O	+0·6107	−0·1386	+0·6446	O′	−0·5691	+0·6381	−0·4941

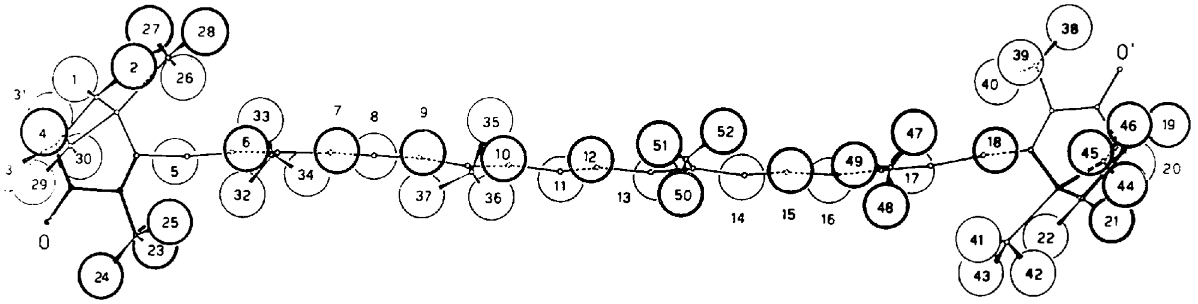

Fig. 4. Positions of hydrogen atoms in canthaxanthin. The molecule is viewed looking at the chain on edge, roughly normal to the mean direction of the molecule. 'Heavy' atoms are shown as small circles, hydrogens as larger ones. Only the hydrogen atoms are numbered.

ment of 0·02 Å, while the plane defined by C(11) to C(15) including C(20) has a maximum displacement of 0·01 Å. These two planes make an angle of 3·2°.

In the chain, the deviations from planarity (which do not appreciably increase the intramolecular distances between non-bonded atoms) are somewhat smaller than in 15,15′-dehydrocanthaxanthin. This may result from better balanced opposing forces exerted on the molecule by its various neighbours.

Small rotations have taken place about most single bonds of the chain [except C(12)–C(13) and C(15′)–C(14′)]. The angles made by the double bond systems of the chain with the best plane of the chain are 6·1°, 1·4°, 4·3°, 7·1°, 9·6°, 8·2°, 6·4°, 4·2° and 11·0° respectively from C(7)=C(8) to C(8′)=C(7′), while the angles of intersection of the successive planes along the chain are 5·0°, 3·3°, 3·3°, 3·7°, 1·2°, 2·1°, 6·2° and 6·7°.

(*b*) *The cyclohexenone ring*

The best planes of the planar parts of the rings I and II are given by the following expressions:

$$+0{\cdot}310x+0{\cdot}813y+0{\cdot}492z+1{\cdot}147=0\,, \text{ and}$$

$$+0{\cdot}344x+0{\cdot}794y+0{\cdot}501z-8{\cdot}296=0\,, \text{ respectively.}$$

The elevations of the ring atoms above these planes are as follows:

Ring I		Ring II	
C(1)	+0·06 Å	C(1′)	+0·09 Å
C(3)	−0·00	C(3′)	−0·07
C(4)	−0·03	C(4′)	−0·01
C(5)	−0·04	C(5′)	−0·03
C(6)	−0·04	C(6′)	−0·00
C(7)	−0·02	C(7′)	−0·04
C(16)	+0·06	C(16′)	+0·02
O	+0·01	O′	+0·04

The deviations from planarity are significant. This holds too for the distances of the atoms from the double bond systems C(5)=C(6) and C(5′)=C(6′) (see Table 8). The carbonyl groupings, however, form essentially planar configurations. In the first ring the angle between the planes of the double bond and the carbonyl group is 3·5° against 1·4° in the second ring.

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

The angles between the planar part of rings I and II and the overall plane of the chain are 43·3° and 42·8° respectively, which is not a significant difference. However, the planes of the double bonds of the rings C(5)=C(6) and C(5′)=C(6′) make angles of 51·8° and 55·5° respectively with the first and last double bond system of the chain, and this is a significant difference.

Bond lengths and bond angles

The final bond data are given in Table 9 and Fig. 5. Approximate standard deviations were calculated by taking the highest values of the set $\sigma(x)$, $\sigma(y)$, $\sigma(z)$.

Table 4. *Final thermal parameters for* C *and* O *atoms* (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$		U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_3$
C(1)	+0·0774	+0·0925	+0·0835	+0·1136	+0·1053	+0·0697	C(1′)	+0·0698	+0·0618	+0·0579	+0·0903	+0·0427	+0·0343
C(2)	+0·0867	+0·1189	+0·0900	+0·1247	+0·1139	+0·0493	C(2′)	+0·1001	+0·1691	+0·1088	+0·1740	+0·1416	+0·0518
C(3)	+0·0521	+0·1231	+0·1267	+0·0867	+0·1467	+0·0583	C(3′)	+0·0662	+0·1134	+0·1070	+0·1188	+0·0804	+0·0350
C(4)	+0·0667	+0·0810	+0·1141	+0·0795	+0·1037	+0·0922	C(4′)	+0·0568	+0·0686	+0·1028	+0·0668	+0·0769	+0·0670
C(5)	+0·0700	+0·0679	+0·0840	+0·0783	+0·0862	+0·0876	C(5′)	+0·0551	+0·0629	+0·0906	+0·0654	+0·0775	+0·0537
C(6)	+0·0579	+0·0576	+0·0710	+0·0671	+0·0762	+0·0458	C(6′)	+0·0483	+0·0463	+0·0564	+0·0556	+0·0491	+0·0321
C(7)	+0·0567	+0·0695	+0·0717	+0·0777	+0·0916	+0·0522	C(7′)	+0·0543	+0·0616	+0·0604	+0·0719	+0·0649	+0·0370
C(8)	+0·0560	+0·0608	+0·0610	+0·0704	+0·0620	+0·0441	C(8′)	+0·0445	+0·0556	+0·0661	+0·0607	+0·0737	+0·0425
C(9)	+0·0554	+0·0551	+0·0566	+0·0617	+0·0632	+0·0475	C(9′)	+0·0464	+0·0547	+0·0659	+0·0641	+0·0563	+0·0414
C(10)	+0·0572	+0·0543	+0·0625	+0·0660	+0·0620	+0·0446	C(10′)	+0·0542	+0·0602	+0·0719	+0·0725	+0·0801	+0·0465
C(11)	+0·0567	+0·0581	+0·0623	+0·0666	+0·0683	+0·0485	C(11′)	+0·0531	+0·0597	+0·0690	+0·0739	+0·0587	+0·0542
C(12)	+0·0614	+0·0558	+0·0543	+0·0771	+0·0564	+0·0493	C(12′)	+0·0654	+0·0574	+0·0691	+0·0854	+0·0753	+0·0598
C(13)	+0·0627	+0·0493	+0·0456	+0·0662	+0·0392	+0·0518	C(13′)	+0·0564	+0·0684	+0·0732	+0·0905	+0·0635	+0·0428
C(14)	+0·0602	+0·0531	+0·0583	+0·0748	+0·0488	+0·0392	C(14′)	+0·0617	+0·0595	+0·0673	+0·0741	+0·0792	+0·0556
C(15)	+0·0642	+0·0561	+0·0552	+0·0740	+0·0536	+0·0399	C(15′)	+0·0715	+0·0651	+0·0598	+0·0973	+0·0550	+0·0480
C(16)	+0·1236	+0·1144	+0·0975	+0·1643	+0·1357	+0·1434	C(16′)	+0·0992	+0·1125	+0·1006	+0·1393	+0·1280	+0·1182
C(17)	+0·1606	+0·1913	+0·1003	+0·2524	+0·1716	+0·1533	C(17′)	+0·2366	+0·2265	+0·0889	+0·3742	+0·1337	+0·1336
C(18)	+0·0737	+0·1042	+0·1388	+0·0899	+0·1654	+0·0799	C(18′)	+0·1319	+0·0966	+0·1167	+0·0477	+0·1562	+0·0256
C(19)	+0·0625	+0·0518	+0·0720	+0·0578	+0·0726	+0·0661	C(19′)	+0·0476	+0·0610	+0·0811	+0·0583	+0·0855	+0·0643
C(20)	+0·0564	+0·0705	+0·0723	+0·0800	+0·0720	+0·0594	C(20′)	+0·0655	+0·0696	+0·0743	+0·0867	+0·0724	+0·0569
O	+0·0835	+0·1188	+0·1658	+0·1101	+0·1363	+0·1505	O′	+0·0734	+0·1011	+0·1579	+0·0953	+0·1126	+0·1248

The e.s.d. are somewhat higher than in the case of 15,15′-dehydrocanthaxanthin. The chain has lower standard deviations than the ring, owing to smaller heat movement. The highest e.s.d. are found for bonds and angles connected with C(2), C(17) and C(18) in both rings. The e.s.d. of the angles vary from 0·7° to 1·1°, with average value of 0·8° to 0·9°. The lowest values are found in the chain. No significant differences exist between bond lengths and valency angles related by the centre of symmetry of the molecule, except for the bonds C(13)–C(20) and C(13′)–C(20′).

The bond lengths in the chain show the same general features as in most other related structures. As in the case of 15,15′-dehydrocanthaxanthin the difference between the longest and shortest single bond of the chain is significant, and that between the longest and shortest double bond is possibly significant.

Several of the bonds from the chain to the methyl groups C(19) and C(20) and the bonds in the ring appear to be rather short. A more detailed discussion cannot be given, since the bond lengths have not been corrected for thermal vibrations (see below). From Table 4 it can be seen that thermal effects will be more likely to affect these bonds than those along the conjugated system of the chain.

The carbonyl bond lengths do not deviate from the accepted value.

The bond angles in the chain show the same features as in previously determined structures, again confirming the hypothesis that their deviations from normal values can be interpreted as due to steric hindrance from the methyl groups C(19) and C(20) with the backbone hydrogen atoms. This can be seen in Table 10, where short intramolecular H---H distances are listed, and in Fig. 7 where short non-bonded intramolecular carbon distances are given. The resulting curvature of the chain of canthaxanthin (see Figs. 2 and 3) is less than the one reported in β-carotene, but more than in its acetylenic derivative, which was somewhat more curved than 15,15′-dehydro-β-carotene (see Fig. 5).

The C(5)–C(16) bonds are tilted out of the cyclohexenone planes in senses opposed to the one of the

Table 5. *Standard deviations of positional and thermal parameters* (× 10⁴) *in* Å *and* Å²

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(U_{11})$	$\sigma(U_{22})$	$\sigma(U_{33})$	$\sigma(2U_{12})$	$\sigma(2U_{23})$	$\sigma(2U_{31})$
C(1)	104	104	101	54	60	63	101	106	101
C(2)	115	121	107	63	76	68	122	124	111
C(3)	102	122	122	48	78	84	106	139	109
C(4)	101	102	110	50	56	75	92	112	107
C(5)	95	91	96	49	50	61	86	96	96
C(6)	86	82	86	41	42	52	71	81	81
C(7)	88	89	88	43	46	54	78	87	83
C(8)	85	82	84	42	43	51	74	81	79
C(9)	84	80	81	41	40	46	70	75	77
C(10)	85	79	82	41	39	48	70	75	78
C(11)	84	82	84	41	40	51	70	79	78
C(12)	84	77	79	42	40	46	72	74	76
C(13)	84	76	76	42	37	42	69	69	73
C(14)	85	78	83	41	38	49	70	75	78
C(15)	87	80	81	43	41	48	73	76	79
C(16)	132	124	113	84	79	73	142	131	137
C(17)	165	172	134	120	136	86	229	187	177
C(18)	112	114	126	58	66	92	105	136	123
C(19)	87	80	89	43	40	55	70	82	84
C(20)	86	87	93	40	45	56	75	87	83
O	78	83	89	43	53	69	84	103	96
C(1′)	91	83	83	47	42	53	77	80	84
C(2′)	129	151	125	72	107	83	155	159	131
C(3′)	108	115	113	55	68	75	108	120	109
C(4′)	94	93	102	46	49	66	83	97	95
C(5′)	90	88	99	43	46	65	77	93	91
C(6′)	78	72	76	36	35	44	62	69	70
C(7′)	84	84	83	40	43	48	72	78	76
C(8′)	77	77	80	35	39	50	65	77	73
C(9′)	77	78	82	36	39	51	66	78	74
C(10′)	84	81	85	41	42	53	73	83	81
C(11′)	83	82	85	40	41	51	72	79	79
C(12′)	88	80	85	43	41	51	74	80	81
C(13′)	85	85	89	41	45	55	76	85	81
C(14′)	86	81	83	43	42	51	74	81	81
C(15′)	90	84	83	46	44	49	80	81	83
C(16′)	125	120	112	73	75	73	131	129	128
C(17′)	199	189	135	160	151	86	281	191	199
C(18′)	152	123	131	99	67	86	134	134	150
C(19′)	80	83	89	38	42	57	69	84	81
C(20′)	93	92	94	47	50	58	85	92	89
O′	73	76	86	38	45	65	73	93	87

Table 6. *Final positional and thermal parameters of the hydrogen atoms*

	x	y	z	B		x	y	z	B
H(1)	+0·507	−0·173	+1·078	+3·0	H(27)	+0·350	−0·158	+1·079	+3·0
H(2)	+0·542	−0·077	+1·030	+3·0	H(28)	+0·368	−0·074	+1·002	+3·0
H(3)	+0·537	−0·237	+0·852	+3·0	H(29)	+0·348	−0·311	+0·741	+3·0
H(4)	+0·650	−0·134	+0·956	+3·0	H(30)	+0·225	−0·311	+0·730	+3·0
H(5)	+0·183	−0·210	+0·590	+0·0	H(31)	+0·319	−0·303	+0·924	+3·0
H(6)	+0·333	−0·034	+0·576	+0·0	H(32)	+0·019	−0·215	+0·353	+1·0
H(7)	+0·247	+0·032	+0·435	+0·0	H(33)	+0·042	−0·169	+0·575	+1·0
H(8)	−0·009	−0·046	+0·306	+0·0	H(34)	−0·020	−0·138	+0·441	+1·0
H(9)	+0·181	+0·117	+0·302	+0·0	H(35)	−0·146	+0·031	+0·209	+1·0
H(10)	+0·133	+0·199	+0·165	+0·0	H(36)	−0·161	+0·025	−0·007	+1·0
H(11)	−0·108	+0·152	−0·036	+0·0	H(37)	−0·116	−0·040	+0·093	+1·0
H(12)	+0·116	+0·311	+0·042	+0·0	H(38)	−0·428	+0·647	−0·272	+3·0
H(13)	−0·126	+0·264	−0·150	+0·0	H(39)	−0·295	+0·657	−0·266	+3·0
H(14)	−0·170	+0·354	−0·283	+0·0	H(40)	−0·424	+0·552	−0·358	+3·0
H(15)	+0·029	+0·526	−0·251	+0·0	H(41)	−0·225	+0·644	−0·802	+3·0
H(16)	−0·232	+0·442	−0·409	+0·0	H(42)	−0·321	+0·666	−0·980	+3·0
H(17)	−0·313	+0·519	−0·516	+0·0	H(43)	−0·359	+0·571	−0·917	+3·0
H(18)	−0·158	+0·700	−0·503	+0·0	H(44)	−0·298	+0·799	−0·819	+3·0
H(19)	−0·523	+0·729	−0·722	+3·0	H(45)	−0·201	+0·802	−0·634	+3·0
H(20)	−0·629	+0·623	−0·818	+3·0	H(46)	−0·316	+0·792	−0·626	+3·0
H(21)	−0·490	+0·676	−0·950	+3·0	H(47)	−0·009	+0·702	−0·334	+1·0
H(22)	−0·500	+0·575	−0·917	+3·0	H(48)	−0·011	+0·639	−0·515	+1·0
H(23)	+0·340	−0·151	+0·380	+3·0	H(49)	+0·042	+0·627	−0·335	+1·0
H(24)	+0·464	−0·156	+0·383	+3·0	H(50)	+0·156	+0·453	−0·171	+1·0
H(25)	+0·461	−0·063	+0·466	+3·0	H(51)	+0·167	+0·426	+0·022	+1·0
H(26)	+0·237	−0·175	+0·878	+3·0	H(52)	+0·142	+0·511	−0·014	+1·0

Table 7. *Distances in* Å *of chain atoms to their best plane*: $+0{\cdot}227x-0{\cdot}403y-0{\cdot}886z+1{\cdot}818=0$

C(6)	−0·05	C(12)	−0·07	C(13′)	+0·09	C(7′)	−0·29
C(7)	−0·03	C(13)	+0·09	C(12′)	+0·23	C(6′)	−0·44
C(8)	−0·14	C(14)	+0·07	C(11′)	+0·16	C(19)	−0·09
C(9)	−0·13	C(15)	+0·20	C(10′)	+0·20	C(20)	+0·25
C(10)	−0·15	C(15′)	+0·10	C(9′)	+0·06	C(19′)	−0·02
C(11)	−0·10	C(14′)	+0·19	C(8′)	−0·04	C(20′)	−0·11

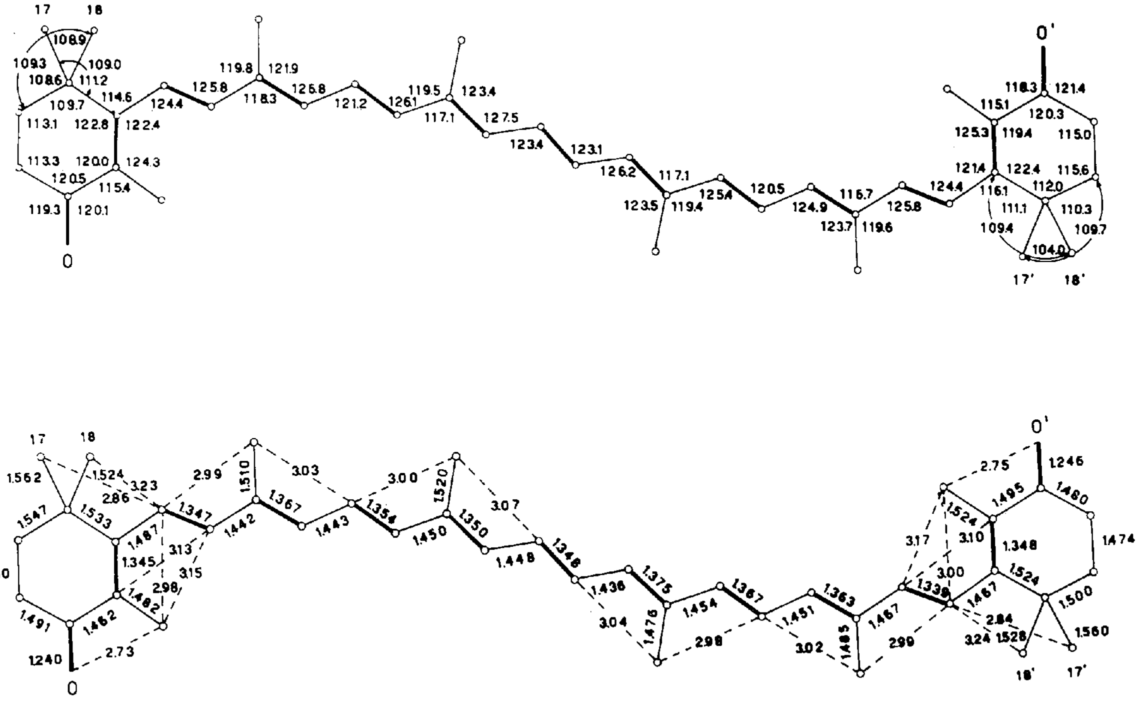

Fig. 5. Canthaxanthin. Final bond lengths and angles.

mean direction of the chain. The angles C(16,5,6) are significantly larger than their counterparts C(4,5,6). Angles C(5,6,7) are equal to angles C(1,6,5).

Differences between the intramolecular bond data of canthaxanthin and its dehydro derivative are smaller than the experimental errors. Since it has been observed (Hirshfeld & Schmidt, 1957) that a difference in molecular environment hardly influences bond lengths and angles, though it may significantly influence molecular planarity, we regard this identity as a confirmation of the accuracy of the experimental results.

Packing of the molecules

Fig. 6 shows a scheme of the string-like arrangement of the canthaxanthin molecules in the unit cells. C---C distances smaller than 4 Å were computed and are listed in Table 11, together with H---H distances. No C---H contacts were calculated.

The chains of the molecules are arranged in fairly close-packed rows extending along [010], with intermolecular contacts across centres 000 and $0\frac{1}{2}0$. These contacts, which are partly due to interlock of the methyl groups of the chain, are listed under *A*---*D* and *A*---*E* in Table 11 and illustrated in Fig. 7. The first two molecules have numerous contacts over part of the chain, whereas the *A*---*E* contacts are more spread out along the molecules.

The chains run roughly in the direction $[1\bar{1}1]$ and their planes are approximately perpendicular to the plane (100). The rings of such rows of chains, along $[0y0]$ and $[1y1]$ interlock in a staggered row along $[\frac{1}{2}y\frac{1}{2}]$. The best contact is between the upper and lower rings respectively of molecules translated along $[1\bar{1}1]$, as listed under *A–J*/*K* (see Figs. 8 and 9). These molecules, which are related by translation, can be considered to form a string. They have interesting interannular distances. C---O and O---O distances are not very short, but the relative orientation of the carbonyl groups suggests dipole–dipole interaction.

Further contact in the row $[\frac{1}{2}y\frac{1}{2}]$ is achieved across the centres of symmetry $-\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}$ and $\frac{1}{2}, 0, \frac{1}{2}$. These contacts, listed under *A–L* and *A–H* respectively, are comparable but not equal and are mainly from an oxygen atom of one molecule to chain atoms of the other and *vice versa*. Together with the *A–D* and *A–E*

Table 8. *Planes through various parts of the molecule*

Double bond system	Formula
5 = 6	$+0\cdot307x+0\cdot814y+0\cdot493z+1\cdot473=0$
7 = 8	$+0\cdot300x-0\cdot330y-0\cdot895z+2\cdot172=0$
9 = 10	$+0\cdot251x-0\cdot400y-0\cdot882z+1\cdot923=0$
11 = 12	$+0\cdot279x-0\cdot441y-0\cdot853z+1\cdot782=0$
13 = 14	$+0\cdot334x-0\cdot437y-0\cdot835z+1\cdot756=0$
15 = 15′	$+0\cdot382x-0\cdot395y-0\cdot835z+1\cdot637=0$
14′ = 13′	$+0\cdot364x-0\cdot393y-0\cdot845z+1\cdot621=0$
12′ = 11′	$+0\cdot331x-0\cdot385y-0\cdot861z+1\cdot551=0$
10′ = 9′	$+0\cdot247x-0\cdot337y-0\cdot908z+0\cdot954=0$
8′ = 7′	$+0\cdot273x-0\cdot226y-0\cdot935z-0\cdot415=0$
6′ = 5′	$+0\cdot344x+0\cdot784y+0\cdot517z-8\cdot080=0$
4 = O	$+0\cdot329x+0\cdot803y+0\cdot497z+1\cdot266=0$
4′ = O′	$+0\cdot377x+0\cdot800y+0\cdot468z-8\cdot356=0$

Distances of atoms to several double bond systems (Å)

5=6		7=8		9=10		11=12		13=14	
C(1)	+0·06	C(6)	−0·00	C(8)	+0·01	C(10)	+0·03	C(12)	−0·00
C(4)	−0·03	C(7)	+0·00	C(9)	−0·00	C(11)	−0·02	C(13)	+0·01
C(5)	−0·04	C(8)	+0·00	C(10)	−0·02	C(12)	−0·03	C(14)	−0·00
C(6)	−0·04	C(9)	−0·00	C(11)	+0·01	C(13)	+0·03	C(15)	−0·00
C(7)	−0·02	C(10)	+0·10	C(19)	−0·00			C(20)	−0·00
C(16)	+0·06	C(11)	+0·16						
		C(19)	−0·11						

15=15′		14′=13′		12′=11′		10′=9′		8′=7′	
C(14)	−0·01	C(15′)	+0·00	C(13′)	−0·03	C(11′)	−0·05	C(9′)	−0·01
C(15)	+0·01	C(14′)	+0·00	C(12′)	+0·03	C(10′)	+0·06	C(8′)	+0·01
C(15′)	+0·01	C(13′)	−0·01	C(11′)	+0·02	C(9′)	+0·02	C(7′)	+0·01
C(14′)	−0·01	C(12′)	+0·00	C(10′)	−0·03	C(8′)	−0·04	C(6′)	−0·01
		C(20′)	+0·00			C(19′)	+0·00		

6′=5′		4=O		4′=O′	
C(7′)	−0·03	C(3)	−0·00	C(3′)	−0·00
C(6′)	−0·01	C(4)	+0·02	C(4′)	+0·00
C(5′)	−0·03	C(5)	−0·01	C(5′)	−0·00
C(4′)	−0·03	O	−0·01	O′	−0·00
C(1′)	+0·05				
C(16′)	+0·05				

contacts they form the links between the strings. Figs. 8 and 9 show where there are short spacings.

Strongest van der Waals contacts are thus in puckered layers and intermolecular contacts between these layers are formed by translations [001] and $[0\bar{1}1]$; see distances *A–B/C* and *A–M/N* respectively. The arrangement of these molecules does not permit close packing of the chains. Contacts are reduced to some short distances between methyl groups of the rings and those of the chains. There is stronger interaction between molecules related by the centres $00\frac{1}{2}$ (distances *A–F*) and $0\frac{1}{2}\bar{\frac{1}{2}}$ (distances *A–G*) where CH_3 groups of the chain of one molecule interlock with the backbone of the chain of the other.

Some additional short H---H distances exist from the reference atom H(22) to H(43) at $\bar{x}-1,\bar{y}+1,\bar{z}-2$ (2·34 Å); from H(3) to H(21) and from H(4) to H(44) at $x+1,y-1,z+2$ (2·46 and 2·51 Å respectively); from

Table 9. *Bond lengths and angles and standard deviations* (Å)

	Bond length	σ		Bond length	σ
C(1)—C(2)	1·547	0·016	C(1′)—C(2′)	1·500	0·017
C(1)—C(6)	1·533	0·013	C(1′)—C(6′)	1·524	0·012
C(1)—C(17)	1·562	0·019	C(1′)—C(17′)	1·560	0·021
C(1)—C(18)	1·524	0·016	C(1′)—C(18′)	1·528	0·017
C(2)—C(3)	1·480	0·017	C(2′)—C(3′)	1·474	0·018
C(3)—C(4)	1·491	0·016	C(3′)—C(4′)	1·480	0·015
C(4)—C(5)	1·462	0·014	C(4′)—C(5′)	1·495	0·014
C(5)—C(6)	1·345	0·013	C(5′)—C(6′)	1·348	0·012
C(5)—C(16)	1·482	0·016	C(5′)—C(16′)	1·524	0·016
C(6)—C(7)	1·487	0·012	C(6′)—C(7′)	1·467	0·012
C(7)—C(8)	1·347	0·012	C(7′)—C(8′)	1·339	0·011
C(8)—C(9)	1·442	0·012	C(8′)—C(9′)	1·467	0·011
C(9)—C(10)	1·367	0·012	C(9′)—C(10′)	1·363	0·011
C(9)—C(19)	1·510	0·012	C(9′)—C(19′)	1·485	0·012
C(10)-C(11)	1·443	0·012	C(10′)-C(11′)	1·451	0·012
C(11)-C(12)	1·354	0·012	C(11′)-C(12′)	1·367	0·012
C(12)-C(13)	1·450	0·011	C(12′)-C(13′)	1·454	0·012
C(13)-C(14)	1·350	0·012	C(13′)-C(14′)	1·375	0·012
C(13)-C(20)	1·520	0·012	C(13′)-C(20′)	1·476	0·013
C(14)-C(15)	1·448	0·012	C(14′)-C(15′)	1·436	0·012
C(15)-C(15′)	1·348	0·012	C(4′)—O′	1·246	0·013
C(4)—O	1·240	0·014			

	Angle	σ(angle)		Angle	σ (angle)
C(1)—C(2)—C(3)	113·1°	1·0°	C(1′)—C(2′)—C(3′)	115·6°	1·1°
C(1)—C(6)—C(7)	114·6	0·7	C(1′)—C(6′)—C(7′)	116·1	0·7
C(2)—C(3)—C(4)	113·3	1·0	C(2′)—C(3′)—C(4′)	115·0	1·0
C(3)—C(4)—C(5)	120·5	0·9	C(3′)—C(4′)—C(5′)	120·3	0·9
C(3)—C(4)—O	119·3	1·0	C(3′)—C(4′)—O′	121·4	0·9
C(4)—C(5)—C(6)	120·0	0·9	C(4′)—C(5′)—C(6′)	119·4	0·8
C(4)—C(5)—C(16)	115·4	0·9	C(4′)—C(5′)—C(16′)	115·1	0·9
C(5)—C(6)—C(1)	122·8	0·8	C(5′)—C(6′)—C(1′)	122·4	0·8
C(5)—C(6)—C(7)	122·4	0·8	C(5′)—C(6′)—C(7′)	121·4	0·7
C(6)—C(1)—C(2)	109·7	0·8	C(6′)—C(1′)—C(2′)	112·0	0·8
C(6)—C(7)—C(8)	124·4	0·8	C(6′)—C(7′)—C(8′)	124·4	0·8
C(7)—C(8)—C(9)	125·8	0·8	C(7′)—C(8′)—C(9′)	125·8	0·7
C(8)—C(9)—C(10)	118·3	0·8	C(8′)—C(9′)—C(10′)	116·7	0·7
C(8)—C(9)—C(19)	119·8	0·7	C(8′)—C(9′)—C(19′)	119·6	0·7
C(9)—C(10)-C(11)	126·8	0·8	C(9′)—C(10′)-C(11′)	124·9	0·8
C(10)-C(11)-C(12)	121·2	0·8	C(10′)-C(11′)-C(12′)	120·5	0·8
C(11)-C(12)-C(13)	126·1	0·8	C(11′)-C(12′)-C(13′)	125·4	0·8
C(12)-C(13)-C(14)	117·1	0·7	C(12′)-C(13′)-C(14′)	117·1	0·8
C(12)-C(13)-C(20)	119·5	0·7	C(12′)-C(13′)-C(20′)	119·4	0·8
C(13)-C(14)-C(15)	127·5	0·8	C(13′)-C(14′)-C(15′)	126·2	0·8
C(14)-C(15)-C(15′)	123·4	0·8	C(14′)-C(15′)-C(15)	123·1	0·8
C(16)-C(5)—C(6)	124·3	0·9	C(16′)-C(5′)—C(6′)	125·3	0·9
C(17)-C(1)—C(2)	108·6	1·0	C(17′)-C(1′)—C(2′)	109·7	1·0
C(17)-C(1)—C(6)	111·2	0·9	C(17′)-C(1′)—C(6′)	111·1	0·9
C(17)-C(1)—C(18)	108·9	1·0	C(17′)-C(1′)—C(18′)	104·0	1·1
C(18)-C(1)—C(2)	109·3	0·9	C(18)′-C(1′)—C(2′)	110·3	1·0
C(18)-C(1)—C(6)	109·0	0·8	C(18′)-C(1′)—C(6′)	109·4	0·8
C(19)-C(9)—C(10)	121·9	0·8	C(19′)-C(9′)—C(10′)	123·7	0·7
C(20)-C(13)-C(14)	123·4	0·7	C(20′)-C(13′)-C(14′)	123·5	0·8
O——C(4)—C(5)	120·1	1·0	O′——C(4′)—C(5′)	118·3	0·9

H(2) to H(28) at $\bar{x}+1,\bar{y},\bar{z}+2$ (2·51 Å). No distances were found to be appreciably shorter than the sum of the van der Waals radii.

Table 10. *Short intramolecular* H---H, H---C *and* H---O *distances*

Distances between hydrogen atoms in CH_3 or CH_2 groups are not given here

H(1)—H(3)	2·34 Å	H(15)–H(49)	1·98 Å
H(1)—H(4)	2·46	H(15)–H(52)	2·32
H(1)—H(31)	2·44	H(16)–H(17)	2·26
H(2)—H(4)	2·34	H(18)–H(41)	2·33
H(2)—H(28)	2·44	H(18)–H(45)	2·45
H(3)—H(29)	2·23	H(18)–H(47)	2·18
H(5)—H(26)	2·26	H(19)–H(21)	2·30
H(5)—H(30)	2·47	H(20)–H(21)	2·49
H(5)—H(33)	2·40	H(21)–H(44)	2·42
H(6)—H(7)	2·26	H(22)–H(43)	2·05
H(6)—H(25)	2·48	H(26)–H(30)	2·44
H(7)—H(9)	2·35	H(27)–H(31)	2·48
H(8)—H(34)	2·11	H(42)–H(44)	2·37
H(8)—H(37)	2·06	H(5)—C(19)	2·62
H(9)—H(10)	2·20	H(8)—C(19)	2·74
H(10)–H(12)	2·44	H(8)—C(20)	2·66
H(11)–H(13)	2·42	H(11)–C(20)	2·77
H(11)–H(36)	2·11	H(12)–C(20′)	2·73
H(12)–H(51)	1·90	H(15)–C(19′)	2·73
H(13)–H(14)	2·26	H(15)–C(20′)	2·64
H(14)–H(16)	2·34	H(18)–C(19′)	2·63

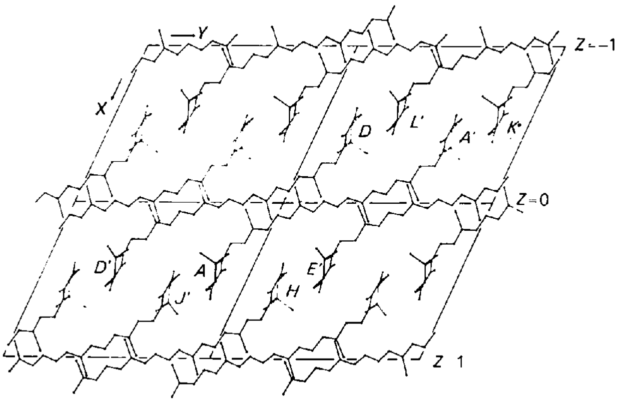

Fig. 6. The arrangement of the canthaxanthin molecules viewed in the direction of [001].

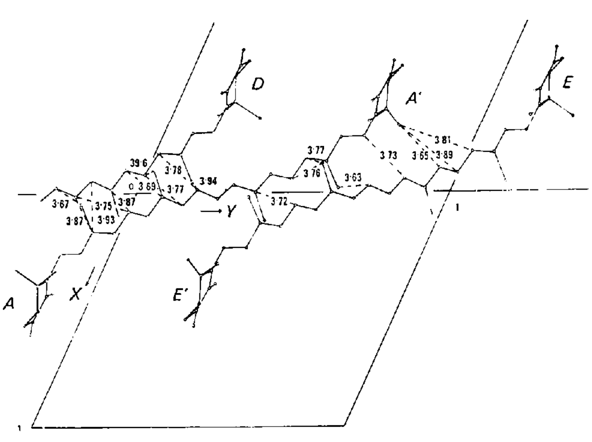

Fig. 7. Packing of molecules at x, y, z (*A*); $\bar{x}, \bar{y}, \bar{z}$ (*D*) and $\bar{x}, \bar{y}+1, \bar{z}$ (*E*).

Vibrational parameters

The direction cosines of the principal axes of the ellipsoids describing the anisotropic temperature factors and the mean square displacements, calculated according to Waser (1955), are given in Table 12. **L**, **M** and **N** denote the coordinate axes of the chain, while $\bar{\mathbf{R}}$ is the average of the two normals to the planes of the double bond systems of the rings. There is a fairly good quantitative agreement between the mean square displacements of atoms related by the molecular centre of symmetry.

The directions of the largest mean square displacements for the ring atoms deviate considerably from $\bar{\mathbf{R}}$, while in most cases neither of the other axes of the ellipsoids coincides with the plane of the ring. The lowest temperature factors in the rings are those of the C(6) atoms, which are connected directly to the chain. The greatest u^2 for ring atoms are found for C(2,2′) and C(3,3′). However the thermal motion of the substituents of the rings, including the oxygen atoms, is still greater, and much larger than that of the methyl groups of the chain. The directions of smallest u^2 of the O atoms deviate not more than 20° from the direction of the C(4)–O bonds. The same holds for the C(16) atoms with respect to the C(5)–C(16) bonds, but not for the other terminal atoms.

It is worth noting that the vibration ellipsoids of most chain atoms coincide quite well with the **LMN** directions: the smallest component coincides with **N** and the largest principal axis with **L**. (Although the precise directions which the principal axes make with the molecular axes were determined they will not be listed here.) The agreement between the direction of greatest mean square displacement and **N** is in most cases better than 20°, except for C(12) to C(15′). The ellipsoids of C(6) to C(11) and C(14′) to C(6′) are roughly in the same direction, with small mutual differences. For these atoms the vibrational amplitudes in the same direction are of the same order of magnitude. In spite of this it did not seem particularly useful to carry out a further analysis in terms of rigid

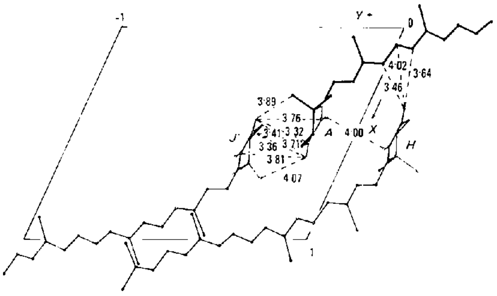

Fig. 8. Shortest intermolecular distances between molecules at x, y, z (*A*); $\bar{x}+1, \bar{y}, \bar{z}+1$ (*H*) and $x+1, y-1, z+1$ (*J*).

body vibrations. The bond data given above are therefore uncorrected for thermal vibrations.

Comparison of various structures of vitamin A related compounds and carotenoids

It is of interest to try to distinguish between, on the one hand, molecular features which are similar in all the structures determined so far, and which accordingly appear to be dictated by intramolecular influences, and on the other hand, features which seem to be influenced by the various packing schemes.

Structure of the polyene chains

In Table 13, where the bond lengths in the chains of the most accurately determined structures are com-

Table 11. *Intermolecular contacts*

Reference molecule	Molecule	Distance (Å)	Reference molecule	Molecule	Distance (Å)
A	*C*		*A*	*E*	
C(17)	C(16)	3·94	C(10)	C(18′)	3·81
C(16′)	C(17′)	3·69	C(11)	C(18′)	3·89
H(27)	H(23)	2·62	C(12)	C(18′)	3·65
H(27)	H(24)	2·63	C(14)	C(7′)	3·73
H(38)	H(42)	2·41	C(15)	C(19′)	3·75
H(39)	H(42)	2·58	C(15′)	C(9′)	3·72
			C(15′)	C(19′)	3·63
A	*D*		C(14′)	C(19′)	3·99
C(9)	C(15)	3·87	C(13′)	C(11′)	3·72
C(9)	C(15′)	4·00	C(12′)	C(20′)	3·88
C(9)	C(14′)	3·93	C(11′)	C(20′)	3·76
C(10)	C(15)	3·78	C(10)′	C(20′)	3·77
C(11)	C(13)	3·87	H(9)	H(46)	2·62
C(11)	C(14)	3·77	H(10)	H(39)	2·39
C(11)	C(15)	3·75	H(12)	H(39)	2·47
C(11)	C(20)	3·96			
C(12)	C(13)	3·69	*A*	*F*	
C(12)	C(20)	3·56	C(9)	C(20)	3·83
C(13)	C(13)	3·66	C(12)	C(19)	4·00
C(13)	C(20)	3·82	C(13)	C(19)	3·70
C(18)	C(10′)	4·00	C(20)	C(19)	3·66
C(19)	C(15)	3·94	H(33)	H(35)	2·34
C(19)	C(15′)	3·67			
C(19)	C(14′)	3·65	*A*	*G*	
H(13)	H(23)	2·70	C(12′)	C(19′)	3·94
			C(11′)	C(19′)	3·88
			C(17′)	C(20′)	3·74
			H(41)	H(50)	2·32
			H(41)	H(51)	2·62
			H(48)	H(50)	2·59
A	*H*		*A*	*M*	
C(10)	O	3·46	C(19)	C(19′)	3·82
C(11)	O	4·02	H(5)	H(48)	2·66
C(12)	O	3·64	H(30)	H(49)	2·21
C(16)	C(16)	4·00	H(33)	H(18)	2·59
H(25)	H(25)	1·90	H(33)	H(47)	2·40
			H(34)	H(45)	2·17
A	*J*				
C(3)	O′	3·61			
C(4)	C(4′)	3·71			
C(4)	O′	3·32			
C(5)	O′	3·76			
C(18)	O′	3·89			
O	C(5′)	3·81			
O	C(4′)	3·36			
O	C(3′)	3·72			
O	C(18′)	4·01			
O	O′	3·41			
H(3)	H(38)	2·46			
H(24)	H(19)	2·19			
A	*L*				
C(16′)	C(5′)	3·99			
O′	C(10′)	3·37			
O′	C(9′)	3·98			
O′	C(8′)	3·54			
H(40)	H(40)	2·48			

Contacts of molecules *B*, *K* and *N* are not given as they can easily be derived from *C*, *J* and *M* respectively.

The superscripts refer to the positions:

A	x,	y,	z
B	x,	y,	$z-1$
C	x,	y,	$z+1$
D	$\bar{x}$,	$\bar{y}$,	$\bar{z}$
E	$\bar{x}$,	$\bar{y}+1$,	$\bar{z}$
F	$\bar{x}$,	$\bar{y}$,	$\bar{z}+1$
G	$\bar{x}$,	$\bar{y}+1$,	$\bar{z}-1$
H	$\bar{x}+1$,	$\bar{y}$,	$\bar{z}+1$
J	$x+1$,	$y-1$,	$z+1$
K	$x-1$,	$y+1$,	$z-1$
L	$\bar{x}-1$,	$\bar{y}+1$,	$\bar{z}-1$
M	x,	$y-1$,	$z+1$
N	x,	$y+1$,	$z-1$

pared, one notices a systematic decrease in the alternative character of the single and double bonds towards the centre of the molecule only for the two acetylenic derivatives, and not for the canthaxanthin. In the former two, the effect seems to be enhanced by the shortening of the single bond C(14)–C(15), which may well be due to the neighbouring triple bond. This last bond has not been lengthened in spite of a presumed decrease in bond order.

The same bond angle anomalies are found in all structure determinations of this class of compound. For the part of the chain between C(7) and C(13) especially, excellent agreement is found in all the more accurate determinations to-date, as shown in Table 14. In particular, angles C(8,9,10) and C(12,13,14), which are opposite methyl-groups of the chain, are significantly smaller than 125°, thereby increasing the angles opposite the double bonds at C(9,9′) and C(13,13′). This results in distances C(7)---C(19), C(19)---C(11), C(11)---C(20) and C(20)---C(15) being about 3·0 Å instead of 2·8 Å in the case of a straight zigzag chain. However, the angles C(10,11,12) and C(14,15,15′) of canthaxanthin, which are on the same side of the chain, are also smaller than those at the opposite side of the zigzag whose average value is slightly above 125°. Sterling (1964) found very pronounced distortions at C(11) and C(15) in the case of β-carotene and 7,7′-dihydro-β-carotene but the standard deviations of the values quoted are rather high. The explanation of the effect might be non-bonded interactions of the side-chain methyl groups with the hydrogens at C(11) and C(15). From C(13) on, the different bonding situation of C(15) appears to have some influence on the angles at C(13) and C(14), but in this region there is again good agreement among the two independent halves of canthaxanthin, and among the two dehydro-compounds. Note the significant difference in the angles C(20,13,14) and C(13,14,15) of both groups, and consequently the shorter distance C(20---C(15) in the dehydro-compounds.

The in-plane bending of the chain away from the CH_3 groups (19) and (20) is thus a well established stereochemical effect. Twisting of the planes of the successive double bonds is a second, though probably less important, factor in releasing steric hindrance in the polyene chain caused by the methyl-groups.

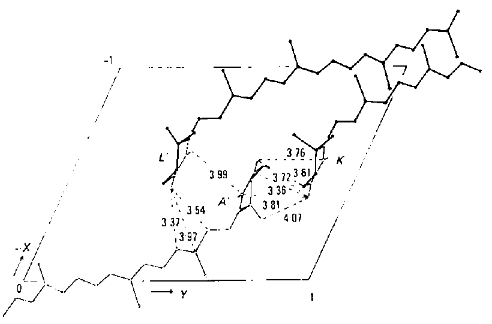

Fig. 9. Contacts between molecules situated at x, y, z (A), $x-1$, $y+1$, $z-1$ (K) and $\bar{x}-1$, $\bar{y}+1$, $\bar{z}-1$ (L).

Since large differences in the packing type are found among the compounds (see below), it seems now beyond doubt that the in-plane bending of a fully conjugated polyisoprenoid chain is due to intramolecular forces so it can therefore be expected to exist also in solution. The major differences between the free and the 'crystallized' molecule will be found where the packing forces may be involved in other features of the structure, *e.g.* in the rotation angle about C(6)–C(7) and in the rotational orientations of the methyl groups.

Structure of the rings

Table 15 compares angles in the rings and Table 16 compares the bond distances. Considering that the positions of the atoms C(2) and C(3) are less well defined in all the structures, the angles within the rings agree well, except those at C(4), where the influence of the carbonyl oxygen in the canthaxanthins on the hybridization of the orbitals of C(4) is clearly evident. This influence is also reflected in the bond lengths C(3)–C(4) and C(4)–C(5). In the 'pure' single bonds a tendency towards ring angles somewhat larger than the tetrahedron angle might be connected with the rather heavy substitution on the rings. To some extent these increased angles in the cyclohexenone ring can probably be attributed to strain.

As already pointed out elsewhere (Sly, 1964) a correction for thermal movement might well lengthen the abnormally short C(2)–C(3) bond and thereby decrease somewhat the valency angles at these atoms. Moreover it is difficult to assess whether or not the shortening of a bond is real in structures suffering from disorder of one of the atoms connected with that bond. However, the bond lengths C(1)–C(2) and C(3)–C(4) appear to be fairly normal. The difference between C(1)–C(17) and C(1)–C(18) is not considered to be significant. C(4)=O is a normal carbonyl bond.

So far, small differences in the chain and the ring are thus easily interpreted in terms of the chemical differences between the individual compounds.

Ring-chain attachment

When considering the attachment of ring and chain, a fairly wide range of interplanar angles is found. In Table 17 we have distinguished between the angle of the double bond system C(5)=C(6) (or C(6)=C(5)–C(4)=O for the canthaxanthins) with the overall 'best' plane of the chain (column 2) and with the double bond system C(7)=C(8) (column 3). There is a difference of the order of 10° between the two sets of values.

In order to study the balance of the opposed effects of conjugation and steric hindrance one has to look at each pair of double bonds separately and at the deviations in their angles. In the case of the ring-chain attachment the release of steric hindrance between the methyl groups C(17) and C(16) of the ring with the

Table 12. *Direction cosines of the principal axes of the vibration ellipsoids of* C *and* O *atoms* (*relative to the crystal axes*) *with mean square displacements* (Å^2)

	u^2	cos *a*	cos *b*	cos *c*		u^2	cos *a*	cos *b*	cos *c*
C(1)	0·0427	+0·531	−0·797	+0·550	C(1′)	0·0374	+0·665	−0·868	+0·343
	0·1070	−0·066	+0·603	+0·519		0·0829	−0·736	−0·274	+0·583
	0·0751	+0·845	+0·043	−0·654		0·0604	+0·126	−0·414	−0·736
C(2)	0·0487	+0·552	−0·648	+0·610	C(2′)	0·0517	+0·660	−0·581	+0·518
	0·1311	−0·365	+0·717	+0·543		0·1746	−0·175	+0·803	+0·316
	0·1020	+0·750	+0·256	−0·577		0·1304	+0·730	+0·133	−0·795
C(3)	0·1713	−0·416	+0·615	+0·670	C(3′)	0·0421	+0·858	−0·560	+0·235
	0·0773	+0·181	+0·713	−0·731		0·1256	−0·491	+0·119	+0·958
	0·0461	+0·891	−0·337	+0·130		0·1132	−0·137	−0·820	+0·165
C(4)	0·1203	−0·156	+0·337	+0·805	C(4′)	0·1067	−0·242	+0·222	+0·900
	0·0660	−0·674	+0·888	−0·298		0·0602	−0·145	+0·943	−0·411
	0·0564	−0·721	−0·311	+0·512		0·0536	+0·959	−0·246	−0·142
C(5)	0·0920	+0·089	+0·328	+0·672	C(5′)	0·0992	−0·357	+0·327	+0·872
	0·0610	−0·966	+0·645	+0·188		0·0556	−0·705	−0·330	+0·306
	0·0459	−0·241	−0·690	+0·717		0·0466	+0·613	−0·886	+0·381
C(6)	0·0843	−0·451	+0·460	+0·803	C(6′)	0·0317	+0·531	−0·882	+0·465
	0·0588	−0·806	−0·143	+0·184		0·0649	−0·575	+0·311	+0·884
	0·0333	+0·382	−0·876	+0·567		0·0502	−0·622	−0·354	+0·052
C(7)	0·0915	−0·301	+0·572	+0·677	C(7′)	0·0328	+0·564	−0·780	+0·534
	0·0566	−0·853	−0·108	+0·411		0·0739	−0·417	+0·532	+0·744
	0·0318	+0·426	−0·813	+0·610		0·0599	−0·713	−0·329	+0·400
C(8)	0·0384	+0·529	−0·814	+0·539	C(8′)	0·0790	−0·338	+0·488	+0·762
	0·0707	−0·280	+0·548	+0·692		0·0455	−0·765	−0·256	+0·409
	0·0582	+0·801	+0·195	−0·481		0·0293	+0·549	−0·835	+0·502
C(9)	0·0349	+0·209	−0·808	+0·698	C(9′)	0·0711	−0·297	+0·327	+0·860
	0·0674	−0·304	+0·582	+0·669		0·0522	+0·548	+0·522	−0·441
	0·0547	−0·929	+0·087	+0·255		0·0339	+0·782	−0·788	+0·259
C(10)	0·0355	+0·417	−0·883	+0·541	C(10′)	0·0852	−0·347	+0·464	+0·782
	0·0707	−0·413	+0·444	+0·809		0·0563	−0·785	−0·222	+0·362
	0·0583	−0·810	−0·153	+0·229		0·0301	+0·513	−0·857	+0·508
C(11)	0·0360	+0·332	−0·842	+0·628	C(11′)	0·0380	+0·837	−0·804	+0·119
	0·0733	−0·309	+0·539	+0·710		0·0722	−0·053	+0·343	+0·751
	0·0563	−0·891	−0·021	+0·318		0·0559	+0·544	+0·486	−0·649
C(12)	0·0343	+0·486	−0·878	+0·504	C(12′)	0·0291	+0·485	−0·919	+0·445
	0·0656	+0·459	+0·407	+0·189		0·0774	+0·068	+0·394	+0·632
	0·0553	+0·743	−0·252	−0·842		0·0620	+0·872	−0·010	−0·635
C(13)	0·0629	+0·768	+0·096	+0·023	C(13′)	0·0305	+0·798	−0·782	+0·236
	0·0429	+0·639	−0·751	−0·531		+0·0794	−0·295	+0·305	+0·872
	0·0407	+0·031	−0·653	+0·847		0·0715	+0·526	+0·544	−0·430
C(14)	0·0338	+0·603	−0·903	+0·365	C(14′)	0·0320	+0·310	−0·862	+0·612
	0·0667	−0·793	−0·104	+0·712		0·0794	−0·224	+0·505	+0·707
	0·0611	−0·084	−0·417	−0·600		0·0600	−0·924	+0·050	+0·353
C(15)	0·0361	+0·450	−0·844	+0·566	C(15′)	0·0359	+0·654	−0·883	+0·336
	0·0687	−0·888	−0·002	+0·557		0·0795	+0·651	+0·388	−0·250
	0·0624	+0·090	−0·536	−0·608		+0·0627	+0·387	−0·265	−0·908
C(16)	0·1434	+0·400	+0·375	+0·320	C(16′)	0·1308	+0·148	+0·522	+0·433
	0·0756	+0·902	−0·738	−0·311		0·0725	+0·988	−0·538	−0·328
	0·0547	−0·159	−0·561	+0·895		0·0622	−0·040	−0·662	+0·840
C(17)	0·2058	+0·295	+0·616	+0·101	C(17′)	0·2894	+0·564	+0·481	−0·220
	0·0990	+0·953	−0·667	−0·276		0·0945	+0·773	−0·709	−0·529
	0·0670	−0·064	−0·418	+0·956		0·0747	+0·290	−0·515	+0·819
C(18)	0·1763	−0·419	+0·517	+0·756	C(18′)	0·2547	−0·863	+0·570	+0·596
	0·0720	−0·883	+0·035	+0·125		0·1022	−0·502	−0·216	−0·359
	0·0530	+0·208	−0·855	+0·641		0·0406	+0·055	−0·793	+0·718
C(19)	0·0349	−0·058	−0·822	+0·618	C(19′)	0·0912	−0·237	+0·451	+0·756
	0·0776	−0·158	+0·384	+0·774		0·0454	−0·889	+0·635	−0·150
	0·0625	−0·986	+0·421	+0·138		0·0382	−0·391	−0·627	+0·636
C(20)	0·0815	−0·083	+0·522	+0·618	C(20′)	0·0432	+0·625	−0·857	+0·405
	0·0563	+0·558	+0·415	−0·756		0·0822	−0·109	+0·472	+0·679
	0·0434	+0·825	−0·745	+0·217		0·0670	+0·773	+0·208	−0·612
O	0·1694	−0·009	+0·211	+0·812	O′	0·1587	−0·051	+0·105	+0·887
	0·1063	−0·385	+0·976	−0·357		0·0933	−0·294	+0·985	−0·299
	0·0585	−0·922	+0·053	+0·461		0·0575	+0·955	−0·138	−0·353

	cos *a*	cos *b*	cos *c*
L	+0·559	−0·883	+0·438
M	+0·766	+0·259	−0·326
N	−0·358	+0·391	+0·829
$\bar{\mathbf{R}}$	−0·035	+0·799	+0·191

hydrogen atoms on C(7) and C(8) is mainly accomplished by the rotation α about C(6)–C(7) (column 3). Some extra relief appears to be gained by the angles C(16,5,6), C(5,6,7) and C(6,7,8) (column 6). Although the angles II vary between 40° and 56° (TADA is a different case), the length of the bond C(6)–C(7) does not appear to be significantly influenced by the out-of-plane rotation. If the shortening of the bond by conjugation is proportional to $\cos^2$ of the angle between adjacent double bond systems, one would expect bond distances of about 1·49 and 1·51 Å respectively. The experimental values lie somewhat below this, except for TADA, which has the most planar conformation. As a result of the out-of-plane rotation and the bending of the *exo* angles the distances C(16)---C(8) are very similar. There is a linear correlation with the rotation angle II. On the other hand, distances C(17)–C(7) are consistently 0·1 Å shorter in the canthaxanthin structures than in other compounds. The *exo* C=O bond will stiffen the ring. All release from angular strain within the ring is effected through C(2) moving out of the plane C(1,2,3,4,5,6,7,16), whereas in a cyclohexene ring there are more degrees of freedom for release from strain. This fixes the positions of C(17) and C(18). Accordingly, though the larger conjugated bond system of the canthaxanthins would prefer a planar conformation of the molecule, the stiffening of the ring would then give even more strain by repulsion of non-bonded groups. Possibly a balance of these two effects may be the reason why a significant difference has not been found in the angle between the bond systems C(5)=C(6) and C(7)=C(8) in β-carotene and the canthaxanthins.

If we list the principal angles connected with the ring-chain attachment (Table 18) we notice much larger deviations from the expected 125° and 110°

Table 13. *Comparison of distances in the chain* (*in Å*)

Bond	TADA	VITA	CANTHI	CANTHII	$\overline{\text{CANTHA}}$	Mean I	DHCAR	DHCANT	Mean II	Mean III
C(6)—C(7)	1·519	1·468	1·487	1·467	⟨1·477⟩	⟨1·485⟩	1·477	1·475	⟨1·476⟩	⟨1·482⟩
C(7)=C(8)	1·333	1·367	1·347	1·339	⟨1·343⟩	⟨1·346⟩	1·342	1·346	⟨1·344⟩	⟨1·346⟩
C(8)—C(9)	1·473	1·458	1·442	1·467	⟨1·454⟩	⟨1·460⟩	1·464	1·460	⟨1·462⟩	⟨1·461⟩
C(9)=C(10)	1·362	1·353	1·367	1·363	⟨1·365⟩	⟨1·361⟩	1·348	1·351	⟨1·350⟩	⟨1·357⟩
C(10)–C(11)	1·447	1·442	1·443	1·451	⟨1·447⟩	⟨1·446⟩	1·458	1·442	⟨1·450⟩	⟨1·447⟩
C(11)=C(12)	1·369	1·362	1·354	1·367	⟨1·360⟩	⟨1·363⟩	1·344	1·359	⟨1·352⟩	⟨1·359⟩
C(12)–C(13)	1·438	1·456	1·450	1·454	⟨1·452⟩	⟨1·450⟩	1·447	1·434	⟨1·440⟩	⟨1·447⟩
C(13)=C(14)		1·337	1·350	1·375	⟨1·362⟩	⟨1·354⟩	1·351	1·367	⟨1·359⟩	⟨1·356⟩
C(14)–C(15)		1·451	1·448	1·436	⟨1·442⟩	⟨1·445⟩	1·427	1·417	⟨1·422⟩	⟨1·436⟩
C(15)≡C(15′)			1·348	1·348			1·196	1·198		
C(9)—C(19)	1·535	1·567	1·510	1·485	⟨1·497⟩		1·507	1·495		⟨1·516⟩
C(13)–C(20)		1·526	1·520	1·476	⟨1·498⟩		1·505	1·494		⟨1·504⟩

Notation:

TADA = all *trans*-β-ionylidene-γ-crotonic acid (unpublished refined values; Eichhorn, 1960)
VITA = *trans* vitamin-A acid
CANTHI = canthaxanthin (one side of chain)
CANTHII = canthaxanthin (other side of chain)
$\overline{\text{CANTHA}}$ = canthaxanthin (average value)
DHCAR = 15,15′-dehydro-β-carotene
DHCANT = 15,15′-dehydrocanthaxanthin
Mean I = mean value of the first four columns
Mean II = mean value over DHCAR and DHCANT
Mean III = overall mean value

Table 14. *Comparison of angles in the chain* (*in degrees*)

Angle			VITA	CANTHI	CANTHII	$\overline{\text{CANTHA}}$	DHCAR	DHCANT	Mean
6	7	8	125·3	124·4	124·4	⟨124·4⟩	126·1	126·0	⟨125·2⟩
7	8	9	124·8	125·8	125·8	⟨125·8⟩	125·0	125·5	⟨125·4⟩
8	9	10	118·2	118·3	116·7	⟨117·5⟩	118·8	117·2	⟨117·8⟩
8	9	19	118·3	119·8	119·6	⟨119·7⟩	117·9	119·1	⟨118·9⟩
19	9	10	123·4	121·9	123·7	⟨122·8⟩	123·2	123·6	⟨123·2⟩
9	10	11	124·1	126·8	124·9	⟨125·8⟩	124·9	127·3	⟨125·6⟩
10	11	12	122·4	121·2	120·5	⟨120·8⟩	124·2	122·5	⟨122·2⟩
11	12	13	125·4	126·1	125·4	⟨125·7⟩	125·8	126·1	⟨125·8⟩
12	13	14	118·2	117·1	117·1	⟨117·1⟩	118·9	119·0	⟨118·1⟩
12	13	20	117·8	119·5	119·4	⟨119·4⟩	120·3	120·3	⟨119·5⟩
20	13	14	124·0	123·4	123·5	⟨123·4⟩	120·7	120·7	⟨122·5⟩
13	14	15	125·4	127·5	126·2	⟨126·9⟩	124·0	125·0	⟨125·6⟩
14	15	15′		123·4	123·1	⟨123·2⟩			⟨123·2⟩

Notation: see table 13

values for the compound with *s-trans* structure about C(6)–C(7) (TADA) than for the roughly *s-cis* structures. These considerable distortions, necessary in order to create an *s-trans* configuration, may be a reason for the more frequent occurrence of an *s-cis* arrangement around C(6)–C(7).

Thus, the expectation was not fulfilled that ring-chain conjugation would be increased by the extension of the ring system through the carbonyl group. In fact, the angle of twist in canthaxanthin is one of the largest found thus far (Table 17), although in dehydrocanthaxanthin this angle is much smaller. It strengthens us in our opinion that conjugation and steric effects hold each other in balance over quite a wide range of angles. Moreover, as will be discussed in connexion with the molecular packing of the various related compounds studied so far, we think that the angle between the ring and the 'best' plane of the whole chain (Table 17, column 2) is correlated with the packing scheme of the molecules.

Packing principles

There is some similarity in the packing of vitamin A acid, dehydro-*β*-carotene, *β*-carotene and canthaxanthin. The chain centres (the centres of the hydrogen-bonded pairs in vitamin A acid) are packed in a grid so that there is contact between approximately coplanar chains through interlock of the side-chain methyl groups C(19) and C(20). There is also very good backbone contact between a chain and the one above and/or below. See molecules marked *A,D* and *A,E* in Fig. 7 and compare also Figs. 8 and 9 in the paper by Stam & MacGillavry (1963) and Sly's (1964) Figs. 7 and 8. The chains run skew with respect to the grid: the angles between the overall chain direction and the grid planes [(100) for canthaxanthin and *β*-carotene, (010) for

Table 15.

(*a*) Comparison of the *endo*-angles in the ring (°)

Angle at	TADA	VITA	DHCAR	DHCANT	CANTHI	CANTHII	Average
C(1)	109·1	110·3	110·9	110·6	109·7	112·0	110·4
C(2)	117·3	115·4	113·4	113·6	113·1	115·6	114·7
C(3)	109·7	111·9	110·6	112·6	113·3	115·0	112·2
C(4)	112·7	112·3	113·4	118·9	120·5	120·3	*sp*^{3}: 112·8 *sp*^{2}: 119·9
C(5)	124·5	122·7	123·1	121·1	120·0	119·4	121·8
C(6)	123·1	122·8	122·6	122·5	122·8	122·4	122·7

(*b*) Comparison of the *exo*-angles in the ring (°)

Angle	TADA	VITA	DHCAR	DHCANT	CANTHI	CANTHII	Mean
C(3)—C(4)–O				120·3	119·3	121·4	120·3
C(5)—C(4)–O				120·7	120·1	118·3	119·7
C(4)—C(5)–C(16)	(109·7)	112·1	113·1	113·5	115·4	115·1	113·8
C(6)–C(5)–C(16)	(125·5)	125·0	123·7	125·3	124·3	125·3	124·7
C(5)—C(6)–C(7)	(116·2)	123·7	122·8	122·9	122·4	121·4	122·6
C(7)—C(6)–C(1)	(120·6)	113·5	114·5	114·5	114·6	116·1	114·6
C(6)—C(1)–C(17)	(111·9)	110·9	111·5	110·0	111·2	111·1	110·9
C(2)—C(1)–C(17)	(107·1)	103·0	106·7	106·2	108·6	109·7	106·8
C(6)—C(1)–C(18)	(111·0)	109·7	109·8	108·0	109·0	109·4	109·2
C(2)—C(1)–C(18)	(107·3)	111·2	110·6	114·0	109·3	110·3	111·1
C(17)–C(1)–C(18)	(110·3)	111·6	107·3	108·3	108·9	104·0	108·0

Notation: see Table 13.

Table 16. *Comparison of bond lengths in the ring* (Å)

Distance	TADA	VITA	DHCAR	DHCANT	CANTHI	CANTHII	Mean
C(1)–C(2)	1·543	1·552	1·533	1·520	1·547	1·500	1·533
C(2)–C(3)	1·483	1·451	1·496	1·512	1·480	1·474	1·483
C(3)–C(4)	1·556	1·535	1·520	1·497	1·491	1·480	sp^3: 1·537 sp^2: 1·489
C(4)–C(5)	1·515	1·536	1·501	1·481	1·462	1·495	sp^3: 1·517 sp^2: 1·479
C(5)–C(6)	1·350	1·355	1·340	1·351	1·345	1·348	1·348
C(6)–C(1)	1·527	1·554	1·545	1·541	1·533	1·524	1·537
C(1)–C(17)	1·544	1·548	1·541	1·538	1·562	1·560	1·549
C(1)–C(18)	1·587	1·525	1·540	1·518	1·524	1·528	1·537
C(4)–O				1·226	1·240	1·246	1·237
C(5)–C(16)	1·563	1·516	1·521	1·507	1·482	1·524	1·519

Notation: see Table 13.

dehydro-β-carotene and vitamin A acid] are respectively about 21°, −24°, 27°, and 32°. In the case of canthaxanthin, where the grid can be thought of as being formed by the pseudo-unit $\frac{1}{2}b \times c$ with a mesh of about 8·8 by 8·6 Å including an angle of 99°, the rings of opposite ends of subsequent layers meet halfway. The grid is wide enough for rings from opposite chain ends to interlock, giving some close contacts between rings (*A–J′* and *A′–K* in Figs. 8 and 9) and between rings and chain (*A–H* and *A′–L′*). In β-carotene, whose packing type resembles 15,15′-dehydro-β-carotene, except for the position of the molecules with respect to the glide plane, approximately parallel rings are present, comparable with the canthaxanthin packing. However, the interlock of these rings is less effective than in the case of canthaxanthin.

In 15,15′-dehydro-β-carotene and in the all-*trans* C_{20}-acid the grid of the molecule centres is so narrow that rings of neighbouring layers only touch edgewise, but do not interlock (see Sly, Figs. 6, 7 and Stam & MacGillavry, Figs. 7, 8, 9). The inclination angle of the chain with respect to the grid is also larger than in the previous cases. If we define a new *a* axis for dehydro-β-carotene, namely $\mathbf{a}' = \mathbf{a} + \mathbf{c}$, the direction of the chain with respect to [100] and [010] coincides well with the one in vitamin A acid. As mentioned before, there is no great difference in inclination angles with respect to (010), so that the two chain directions of these two compounds are fully comparable.

The packing of 15,15′-dehydrocanthaxanthin is of a completely different type. The molecules run through more than two cells (Fig. 9 in the preceding paper), so that there is a complete interpenetration of rings and chains. As a result, there is no contact between chains, except occasionally through the methyls C(19) and C(20). On the other hand, strong van der Waals contact exists between the central part of the chain and the two adjacent rings across its centre of symmetry (Fig. 11, preceding paper). The packing is somewhat similar to that of all-*trans* β-ionylidenecrotonic acid, in which there are also many contacts between ring and chain of neighbouring molecules [Fig. 8 of the paper by Eichhorn & MacGillavry (1959)]. The angle of inclination of the chain with respect to the 'grid' plane of the molecular layers is 16° in the case of dehydrocanthaxanthin and 22° in the structure of *trans*-ionylidenecrotonic acid. The grid plane is (010) in both cases. These angles appear to be somewhat smaller than the ones in the first-mentioned packing type with ring–ring and chain–chain contacts. It is evident that interleaving of rings and chains is more effective if the angle between ring and chain is not too large. On the other hand, the contacts between rings in canthaxanthin and β-carotene appear to be favoured by the larger deviation from planarity.

Some conformational topics

If the β-ionone double bond system were completely planar, no difference in energy should exist between (dehydro)canthaxanthin molecules with C(2) on opposite sides of the planar part of the cyclohexenone rings. However, when the ring is rotated about C(6)–C(7) with respect to the chain, then the two resulting con-

Table 17. *Comparison of some structural features connected with the ring-chain attachment*

	Angle I	Angle II	C(6)—C(7)	C(16)—C(8)	Σ angles	C(17)—C(7)
TADA	3°	11°	1·519 Å			
CANTHI	−43	−52	1·487	3·15 Å	371·1°	2·86 Å
CANTHII	−43	−56	1·467	3·17	371·1	2·84
DHCAR	44	51	1·477	3·14	372·6	2·98
VITA	35	43	1·468	3·08	374·0	2·97
DHCANT	−28	−44	1·475	3·09	374·2	2·87
CAR	35	40	1·56	3·07	373·4	2·92

Notation:

For abbreviation of names of compounds see table 13.

CAR = β-carotene.

Angle I = angle between best plane through double bond systems of ring and chain.

Angle II = angle between the best planes of the double bond systems C(7)=C(8) and C(5)=C(6) (cyclohexene ring) and C(6)=C(5)–C(4)=O (cyclohexenone ring).

Σ angles = sum of the angles C(16, 5, 6), C(5, 6, 7) and C(6, 7, 8).

Except for TADA the angles I and II are deviations from the planar *s-cis* situation around C(6)–C(7).

Table 18. *Angle distortions due to the ring-chain attachment* (*degrees*)

	Expected	TADA	VITA	DHCAR	DHCANT	CANTHI	CANTHII
C(8)–C(7)–C(6)	125	128·9	125·3	126·1	126·0	124·4	124·4
C(7)–C(6)–C(1)	110	120·6	113·5	114·5	114·5	114·6	116·1
C(7)–C(6)–C(5)	125	116·2	123·7	122·8	122·9	122·4	121·4
C(5)–C(6)–C(1)	125	123·1	122·8	122·6	122·5	122·8	122·4
C(6)–C(5)–C(16)	125	125·5	125·0	123·7	125·3	124·3	125·3

Notation: see Table 13.

formations are no longer equivalent. These two conformations can also be described as resulting from a rotation of the ring with a given C(2) position, either clockwise or anti-clockwise, as indicated in Table 17.

From Fig. 4 in the present paper and Fig. 8 in the previous communication as compared with Sly's Fig. 10, it can be seen that the rings in the canthaxanthin structures are rotated in the opposite sense to dehydro-β-carotene. Vitamin A acid and β-carotene correspond to this latter structure. In the carotene structures C(2) and C(8) are on opposite sides of the C(5)=C(6) double bond plane, but on the same side in the canthaxanthins. The alternative conformation of 15,15′-dehydrocanthaxanthin corresponds with the position of C(2) in the carotenes. The result is that in the carotenes the C(2) swings back close to the best plane of the chain, whereas in the canthaxanthins C(2) is further away from the chain-plane than it would be if the cyclohexenone ring were planar.

Although the molecules of canthaxanthin occupy general positions, C(2) and C(2′) are related by the pseudo-centre at C(15)–C(15′), so both rings have the same conformation.

The influence of the packing conditions on the positions of C(2) is not known. A different packing arrangement might favour a flip-over of C(2) and consequently of the two *gem* methyl groups. We cannot say whether the degree of disorder is constant in the crystals of one batch, or whether it depends on the conditions of crystallization.

We are grateful to Professor B. C. L. Weedon for supplying us with enough material to carry out the crystallizations. Thanks are due to Mr A. Kreuger who carried out the experimental work. We are grateful to the Directors of the 'Mathematisch Centrum' in Amsterdam and of 'Centraal Rekeninstituut' in Leiden for use of computer equipment and time. The programs used are listed in the Appendix.

Part of the present investigation has been done under the auspices of the Netherlands Foundation for Pure Research with X-rays and Electron-rays (FOMRE) and with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

Appendix

The following computer programs, devised by the authors mentioned below, were used in the course of the structure determination of canthaxanthin and its 15,15′-dehydro derivative.

Cell constants	J. M. v. d. Berg (Univ. Amsterdam)
Data reduction and Wilson plot	H. J. V. H. Geise, B. Hesper (Univ. Leiden)
Correlation of intersecting layers of X-ray intensity data	W. Rutten, B. Hesper (Univ. Leiden)
Averaging and sorting of reflexions on different levels	W. Rutten, E. W. M. Rutten-Keulemans (Univ. Leiden)
Fourier synthesis	E. W. M. Keulemans (Univ. Amsterdam)
Calculation of hydrogen positions	W. Rutten, H. J. V. H. Geise (Univ. Leiden)
Structure factors least-squares (SFLS)	E. W. M. Rutten-Keulemans (Univ. Leiden)
Intra- and intermolecular distances and angles	H. L. Jonkers, J. v. Loenen
Geometry of the molecule	W. Rutten, H. J. V. H. Geise, B. Hesper (Univ. Leiden)
Vibration ellipsoids	C. H. Stam (Univ. Amsterdam)

References

AKHTAR, M. & WEEDON, B. C. L. (1959). *J. Chem. Soc.* 4058.

BART, J. C. J. & MACGILLAVRY, C. H. (1968). *Acta Cryst.* B**24**, 1569.

CRUICKSHANK, D. W. J. (1961). *Computing methods and the Phase Problem in X-ray Crystal Analysis.* p. 45. Oxford: Pergamon Press.

EICHHORN, E. L. & MACGILLAVRY, C. H. (1959). *Acta Cryst.* **12**, 872.

HAXO, F. (1950). *Bot. Gaz.* **112**, 228.

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

HIRSHFELD, F. L. & SCHMIDT, G. M. J. (1957). *J. Chem. Phys.* **26**, 923.

ISLER, O., LINDLAR, H., MONTAVON, M., RÜEGG, R. & ZELLER, P. (1956). *Helv. Chim. Acta*, **39**, 449.

ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.

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.

STERLING, C. (1964). *Acta Cryst.* **17**, 500, 1224.

WARREN, C. K. & WEEDON, B. C. L. (1958). *J. Chem. Soc.* 3986.

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

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.