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The Crystal and Molecular Structure of Crocetinindialdehyde

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Crystals of 2,6,11,15-tetramethylhexadeca-2,4,6,8,10,12,14-heptaen-1,16-dial (crocetinindialdehyde) are triclinic, space group $P\bar{1}$, with $a = 5.136(2)$, $b = 8.369(2)$, $c = 11.146(3)$ Å, $\alpha = 87.30(5)$, $\beta = 92.63(5)$, $\gamma = 112.28(5)^\circ$. Data were collected on an automated diffractometer using Cu $K\alpha$ radiation. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares methods to an R value of 0.047 based on 1142 observed reflexions. The molecules are all *trans* and nearly planar and are stacked in layers nearly parallel to the (577) plane. The packing of the molecules is probably determined by the aldehyde and methyl groups, as the shortest intermolecular distances involve such groups. The molecules show significant deviations from planarity, also within the double bond systems. Calculations of torsion angles show that the aplanarity decreases towards the middle of the chain. This is probably due to a higher degree of conjugation in this part of the chain, as the differences between single and double bond lengths also decrease towards the middle of the chain.

Introduction

Crocetin is a C_{20} -carotenoid and its digentiobiose ester, crocin, is the principal pigment of saffron (*Crocus sativus*) and has also been observed in several other flowers and in some fruits. Saffron has been used for artificial colouring of food since ancient times. Crocetinindialdehyde can be synthesized as described by Isler, Gutman, Lindlar, Montavon, Rüegg, Ryser & Zeller (1956). Recently it has also been isolated from the leaves of *Jacquinia angustifolia* by Eugster, Hürlimann & Leuenberger (1969). Crocetinindialdehyde is commonly used in syntheses of carotenoids according to the method of Wittig & Schöllkopf (1954).

It was shown by Karrer, Benz, Morf, Raudnitz,

Stoll & Takahashi (1932) that crocetin is a dicarboxylic acid that has a polyene chain structure with seven double bonds and four side chain methyl groups. The numerous conjugated double bonds in the carotenoids are responsible for their colour and allow exceptional opportunities for *cis-trans*-isomerism as discussed by Zechmeister (1962).

The all-*trans* form is generally the more stable. It is found by ultraviolet spectroscopy that this form also dominates in solutions of crocetinindialdehyde. One of the aims of this investigation was therefore to establish that the all-*trans* conformation is retained in the crystalline state. Furthermore I was interested in studying the packing and bonding effects of long-chain aldehydes.

Experimental

Crystal data

Crystals grown from methylene chloride at -20°C were supplied by Siv.ing. H. Kjösen at the Organic Chemistry Laboratories of NTH. They are bright orange-red thin plates [face (010)] and usually elongated in the [100] direction. The {101} forms are also well developed.

Crystallographic data:

Crocetindialdehyde (2,6,11,15-Tetramethylhexadeca-2,4,6,8,10,12,14-heptaen-1,16-dial), $\text{C}_{20}\text{H}_{24}\text{O}_2$

F.W. 296.41; triclinic, $Z=1$; $\lambda_{\text{CuK}\alpha}=1.5418 \text{ \AA}$

$a=5.136 \pm 0.002 \text{ \AA}$

$b=8.369 \pm 0.002$

$c=11.146 \pm 0.003$

$\alpha=87.30 \pm 0.05^{\circ}$

$\beta=92.63 \pm 0.05$

$\gamma=112.28 \pm 0.05$

$V=442.6 \text{ \AA}^3$

$D_x=1.11 \text{ g.cm}^{-3}$ for $Z=1$.

$\mu=5.6 \text{ cm}^{-1}$ for $\text{Cu K}\alpha$.

No systematic absences.

Space group: $P1$ or $P\bar{1}$. The latter was indicated by the statistical distribution of intensities and confirmed by the final solution of the structure.

Intensity measurements

A crystal of dimensions $0.035 \times 0.16 \times 0.30 \text{ mm}$ was used for the intensity measurements. Its greatest length was in the direction of the a axis, and it was mounted on a Picker FACS-1 automatic diffractometer with this axis approximately parallel to the goniometer head axis. Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) was used. The lattice parameters given above were obtained by least-squares refinement of the setting angles for 12 reflexions with $2\theta > 70^{\circ}$.

The intensities were measured in the $\theta-2\theta$ scan mode with a scan speed of 1° per min in 2θ and a scan width of 2.0° plus a dispersion correction. The background was measured for 40 sec at each side of the reflexions. Two standard reflexions (230 and 104) were measured every 20 reflexions. They did not show any significant changes during the data collection period. The intensities of all 1453 reflexions with $2\theta < 128^{\circ}$ were measured. 1147 reflexions which had net intensity I greater

than $2\sigma(I)$ were regarded as observed, $\sigma(I)$ being defined as $\sqrt{(\sigma_N + (0.01 \cdot N)^2)}$ where the last term accounts for a 1% instrumental instability; σ_N is the statistical counting error and N is the sum of peak and background counts.

The intensities were corrected for Lorentz and polarization effects. The program *SCALER* was used to determine the scale factor and a common temperature factor by a least-squares fit of a straight line to a Wilson plot. The values obtained were used for calculation of normalized structure factor amplitudes, $|E_h|$'s. The values of $\langle |E_h| \rangle = 0.798$ and $\langle |E_h|^2 - 1 \rangle = 1.018$ compare well with the theoretical values for the centric case, 0.798 and 0.968 respectively. This confirms space group $P\bar{1}$, which requires a centre of symmetry in the molecule since there is only one molecule in the unit cell. The molecule must then be in a *trans* configuration around the central C(8)-C(8') double bond. Fig. 1 shows the numbering of the atoms as used in this paper.

Determination and refinement of the structure

The structure was solved by the symbolic addition method (Karle & Karle, 1963). The first trials were not successful, however, and the failure was later traced to an unfavourable choice of starting reflexions. This particular set gave a wrong sign for the 002 reflexion early in the sign generation process, and this ruined the remainder of the procedure. In the final starting set 111, 454 and 362 were chosen as origin-defining reflexions, and, in addition, symbols were assigned to the 355, 238 and 543 reflexions. Signs of 137 reflexions with $E > 1.50$ were generated and E maps were calculated for the eight possible sign combinations of the three symbols. All the maps contained maxima corresponding to zigzag chains or parts of chains. A model with C(1)-C(8) positions based on the third map with sign combination $-, -, +$ for the three unknowns in the starting set, had an R_1 index ($R_1 = \frac{\sum |F_o| - F_c|}{\sum |F_o|}$) of 0.468 and a difference map gave the correct positions for C(9), C(10) and O. It is interesting to note that the R_1 index for this model was not significantly lower than for the incorrect models based on the first two maps, namely 0.471 and 0.496 respectively. The symbolic addition program *SYMBOL* and the Σ_2 -relationships program *PHASE* of *XRAY67* (Stewart, 1967) were used in the calculations of signs.

The full-matrix least-squares program *ORFLS* was used for parameter refinement. It minimizes $\sum w(|F_o| - |F_c|)^2$, and $w=1$ during this part of the refinement. The scattering factors used are those of Doyle & Turner (1968) for carbon and oxygen and from Stewart, Davidson & Simpson (1965) for hydrogen. Refinement with individual isotropic temperature factors converged at $R_1=0.168$. Conversion to anisotropic temperature factors and refinement gave $R_1=0.105$. A difference map revealed the positions of all hydrogen atoms.

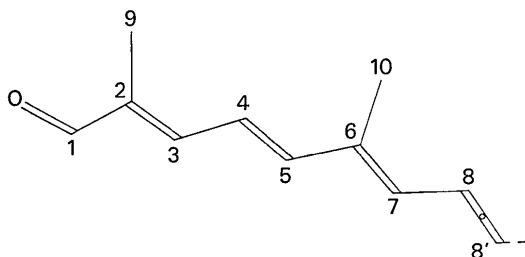


Fig. 1. Numbering of the atoms in crocetindialdehyde as used in this paper.

Refinement proceeded with isotropic temperature factors for hydrogen and all parameters were allowed to vary. The refinement converged at a value of $R_1 = 0.055$. Inspection of the observed and calculated structure factors showed that the observed $|F|$'s were systematically too small for the highest $|F|$ values. This is probably due to secondary extinction which may be corrected by the method given by Zachariasen (1963). Since there are so few strong reflexions in this data set it is difficult to determine the extinction coefficient in a reliable way. Therefore it was decided simply to remove the five strongest reflexions (111, $10\bar{1}$, 012, $11\bar{1}$ and $00\bar{2}$) from the data set. These reflexions had $|F_{\text{obs}}|$ ranging from 90.0 for 111 to 39.1 for $00\bar{2}$. Subsequent refinement gave a final R_1 index of 0.047. The final least-squares cycles were calculated with the weight factor $w = 1/\sigma^2(I)$ where $\sigma(I)$ is as defined earlier. The final weighted reliability index $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ is 0.036. All reliability indexes given are based on 1142 observed reflexions. A final difference map showed only a few maxima of $0.05\text{--}0.10 \text{ e.}\text{\AA}^{-3}$ and no significant features could be found.

Observed and calculated structure factors are listed in Table 1. Final positional and thermal parameters are given in Table 2.

Results and discussion

Fig. 2 shows the molecules as viewed down the a axis and Fig. 3 shows the molecular packing as seen along the c axis. The conformation is all-*trans* and nearly planar, but the molecular chains are slightly bent, both in the molecular plane and out of this plane.

Equations of mean least squares through various parts of the molecule have been calculated and the results are given in Table 3. The best plane through the conjugated chain is very nearly parallel to the (577) plane. Table 3 shows the results of calculations of best planes through each double bond system and also through the methyl carbon atoms and the three chain atoms nearest to them. Ideally the angle between successive double bond systems should be zero in a conjugated bond system, but Table 4 shows that there are angles of $2.4\text{--}8.3^\circ$ between them. Furthermore, each double bond system shows significant deviation from planarity. On the other hand the C(1)–C(2)–C(3)–C(9) and the C(5)–C(6)–C(7)–C(10) groups of atoms are planar. To investigate further the non-planarity of the conjugated chain, torsion angles have been calculated for alternating single and double bonds through the chain, and the results are given in Table 5. The torsion angles are $1\text{--}2^\circ$ higher for single bonds than

Table 2. *Final atomic parameters of crocetindialdehyde*

E.s.d.'s of the parameters are given in parentheses.

The first number in the index of an H atom refers to the number of the C atom to which it is bonded.

Thermal parameters, $\beta_{ij} (\times 10^4)$, are defined by: $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.5763 (4)	−0.3527 (2)	0.2630 (3)	541 (13)	181 (5)	148 (3)	156 (6)	42 (5)	31 (3)
C(2)	0.4320 (4)	−0.2476 (2)	0.3069 (2)	469 (11)	151 (4)	97 (2)	121 (5)	2 (4)	13 (2)
C(3)	0.3671 (4)	−0.1443 (2)	0.2251 (2)	537 (12)	176 (4)	91 (2)	153 (6)	36 (4)	18 (2)
C(4)	0.2400 (4)	−0.0223 (2)	0.2443 (2)	496 (11)	166 (4)	83 (2)	143 (5)	13 (4)	7 (2)
C(5)	0.2033 (4)	0.0826 (2)	0.1563 (2)	632 (13)	197 (4)	82 (2)	201 (6)	25 (4)	15 (2)
C(6)	0.0920 (4)	0.2160 (2)	0.1656 (2)	549 (12)	172 (4)	76 (2)	164 (6)	2 (4)	5 (2)
C(7)	0.0835 (4)	0.3123 (3)	0.0653 (2)	796 (14)	211 (4)	77 (2)	258 (7)	18 (4)	9 (2)
C(8)	−0.0083 (4)	0.4535 (2)	0.0524 (2)	793 (13)	212 (4)	77 (2)	262 (7)	−3 (4)	3 (2)
C(9)	0.3714 (9)	−0.2609 (5)	0.4368 (2)	1323 (26)	315 (7)	91 (2)	440 (13)	−23 (6)	14 (3)
C(10)	−0.0022 (6)	0.2439 (3)	0.2845 (2)	667 (14)	188 (5)	83 (2)	194 (4)	15 (4)	8 (2)
O	0.6683 (3)	−0.4438 (2)	0.3244 (1)	760 (10)	245 (3)	208 (2)	284 (5)	11 (3)	46 (2)

Table 2 (cont.)

	x	y	z	B
H(11)	0.601 (4)	−0.344 (2)	0.168 (2)	7.4 (0.5) \AA^2
H(31)	0.414 (3)	−0.148 (2)	0.145 (1)	4.6 (0.4)
H(41)	0.185 (3)	−0.009 (2)	0.328 (1)	4.1 (0.4)
H(51)	0.263 (3)	0.072 (2)	0.077 (1)	4.8 (0.4)
H(71)	0.154 (3)	0.283 (2)	−0.007 (1)	4.6 (0.4)
H(81)	−0.095 (3)	0.485 (2)	0.127 (1)	4.7 (0.4)
H(91)	0.403 (5)	−0.354 (4)	0.477 (2)	10.3 (0.7)
H(92)	0.260 (6)	−0.210 (4)	0.459 (2)	12.1 (1.0)
H(93)	0.526 (8)	−0.173 (5)	0.474 (3)	17.5 (1.6)
H(101)	−0.083 (4)	0.328 (2)	0.282 (1)	6.5 (0.5)
H(102)	0.165 (4)	0.285 (3)	0.344 (2)	8.4 (0.6)
H(103)	−0.115 (4)	0.144 (3)	0.324 (2)	7.5 (0.6)

for neighbouring double bonds, and the torsion angles seem to decrease towards the middle of the chain.

The molecule exhibits an in-plane bending as can be clearly seen from the bond angles in Fig. 4. These results agree well with earlier investigations on polyene chains, such as those discussed by Bart & MacGillavry (1968), Braun, Hornstra & Leenhouts (1971) and Hamanaka, Mitsui, Ashida & Kakudo (1972). The in-plane bending may be explained as a result of intramolecular repulsion between methyl groups and neighbouring hydrogen atoms. Some of the short $\text{H}\cdots\text{H}$ approach distances are given in Table 6. The $\text{H}(81)\cdots$

Table 3. *Planarity of the molecule*

(a) Equations for best planes

Plane A: C and O in the conjugated chain
 $3.023x + 3.518y + 4.531z = 1.759$ Plane B: C(1), C(2), C(3), C(4)
 $3.383x + 3.562y + 1.957z = 1.192$ Plane C: C(3), C(4), C(5), C(6)
 $3.572x + 3.105y + 2.269z = 1.357$ Plane D: C(5), C(6), C(7), C(8)
 $3.695x + 2.791y + 2.426z = 1.352$ Plane E: C(7), C(8), C(8'), C(7')
 $3.687x + 2.666y + 2.950z = 1.333$ Plane F: C(1), C(2), C(3), C(9)
 $3.318x + 3.689y + 1.964z = 1.127$ Plane G: C(5), C(6), C(7), C(10)
 $3.683x + 2.844y + 2.326z = 1.345$

(b) Deviations (Å) from planes defined above

	A	B	C	D	F	G
O	0.170					
C(1)	-0.066	0.016			0.001	
C(2)	0.066	-0.012			-0.004	
C(3)	-0.137	-0.023	0.017		0.001	
C(4)	-0.005	0.019	-0.015			
C(5)	-0.146		-0.020	0.009		0.002
C(6)	0.029		0.018	-0.007		-0.007
C(7)	-0.112			-0.013		0.002
C(8)	0.049			0.011		
C(9)	0.425				0.001	
C(10)	0.381					0.002

Table 4. *Angles between best planes*

The planes are defined in Table 3; angles are given in degrees.

Planes	B	C	D	E	F	G
A	13.9	12.9	13.1	11.2	13.8	13.4
B		3.7	6.1	8.3	1.0	5.6
C			2.4	4.7	4.6	1.9
D				2.9	7.0	0.6
E					9.0	3.5
F						6.5

Table 5. *Torsion angles for bonds in the conjugated chain*

Bonds	Angle
O—C(1)—C(2)—C(3)	5.4°
C(2)—C(3)—C(4)—C(5)	4.8
C(4)—C(5)—C(6)—C(7)	2.6
C(6)—C(7)—C(8)—C(8')	3.8
C(1)—C(2)—C(3)—C(4)	3.5
C(3)—C(4)—C(5)—C(6)	3.4
C(5)—C(6)—C(7)—C(8)	2.0

H(101) distance of 2.13 Å probably causes strain which is responsible for the C(6)—C(7)—C(8) and C(10)—C(6)—C(7) angles being larger than 120° so as to make the C(10) methyl group bend away from H(81) to release some of the strain. There are also short intramolecular distances between H(41) and the two methyl groups. This causes H(41) to be bent away from

C(10) and C(9) away from H(41), so that the whole chain is bent in the molecular plane. The H...H distances on the side of the chain opposite the methyl groups are also short and the only way that the strain can be released is by a bending out of the molecular plane as observed above.

Table 6. *Short intramolecular distances*

E.s.d.'s are given in parentheses.

H(11)···H(31)	2.20 (3) Å
H(31)···H(51)	2.34 (3)
H(51)···H(71)	2.20 (3)
H(71)···H(81')	2.41 (2)
H(81)···H(101)	2.13 (2)
H(41)···H(103)	2.34 (3)
H(41)···H(92)	2.31 (4)
O···H(91)	2.53 (3)

Table 7. *Bond lengths*

E.s.d.'s are given in parentheses. The mean values quoted are for corresponding bonds in several polyene chain structures as tabulated by Bart & MacGillavry (1968).

	This work	Mean
C(1)—C(2)	1.459 (3) Å	1.461 Å
C(3)—C(4)	1.433 (3)	1.447
C(5)—C(6)	1.444 (3)	1.447
C(7)—C(8)	1.427 (3)	1.436
C(2)—C(3)	1.344 (3)	1.357
C(4)—C(5)	1.340 (3)	1.359
C(6)—C(7)	1.357 (3)	1.356
C(8)—C(8')	1.360 (3)	1.348
C(2)—C(9)	1.485 (3)	1.516
C(6)—C(10)	1.489 (3)	1.504
C(1)—O	1.211 (3)	
C(1)—H(11)	1.07 (2)	
C(3)—H(31)	0.94 (2)	
C(4)—H(41)	1.01 (2)	
C(5)—H(51)	0.96 (2)	
C(7)—H(71)	0.98 (2)	
C(8)—H(81)	1.05 (2)	
C(9)—H(91)	0.95 (3)	
C(9)—H(92)	0.89 (4)	
C(9)—H(93)	0.95 (3)	
C(10)—H(101)	0.94 (2)	
C(10)—H(102)	1.02 (2)	
C(10)—H(103)	0.92 (2)	

Table 8. *Bond angles*

E.s.d.'s are 0.3° for this work. The mean values quoted are for corresponding bonds in several polyene chain structures as tabulated by Bart & MacGillavry (1968).

	This work	Mean
O—C(1)—C(2)	125.6°	—
C(1)—C(2)—C(3)	116.3	117.8°
C(1)—C(2)—C(9)	118.5	118.9
C(9)—C(2)—C(3)	125.2	123.2
C(2)—C(3)—C(4)	127.8	125.6
C(3)—C(4)—C(5)	122.3	122.2
C(4)—C(5)—C(6)	127.4	125.8
C(5)—C(6)—C(7)	117.6	118.1
C(5)—C(6)—C(10)	119.2	119.5
C(10)—C(6)—C(7)	123.2	122.5
C(6)—C(7)—C(8)	128.4	126.9
C(7)—C(8)—C(8')	122.8	123.2

The bond lengths of crocetindialdehyde are given in Table 7 and are also given in Fig. 5 for the heavier atoms. The results of several polyene chain structure determinations have been compiled by Bart & MacGillavry (1968) and their averages have been listed for comparison. Satisfactory agreement with our results can be observed. A common feature of these structures is a decrease in the difference between single and double bonds towards the centre of the molecule, *i.e.* a higher degree of conjugation at the centre. This effect can also be observed in crocetindialdehyde. If one takes the difference δ between alternate single and double bonds from C(1) towards C(8), one obtains: $\delta = 0.115, 0.093, 0.087$ and

0.067 \AA , which is a systematic and significant decrease. The decrease in torsion angles towards the middle of the chain (Table 5) also supports the theory of higher conjugation in this part of the chain. Calculations of zero-order Hückel bond orders for even-membered polyene chains carried out by Binsch & Heilbronner (1968) also show that the differences in bond orders decrease towards the middle of a long chain. There is a significant shortening of the C-C(Me) bonds compared with the normal $C(sp^2)-C(sp^3)$ length of 1.510 \AA given by Sutton (1965). This shortening has also been observed in some of the other polyene chain structures studied, but it is not clear how to account for it.

The bond angles are given in Table 8 and Fig. 4.

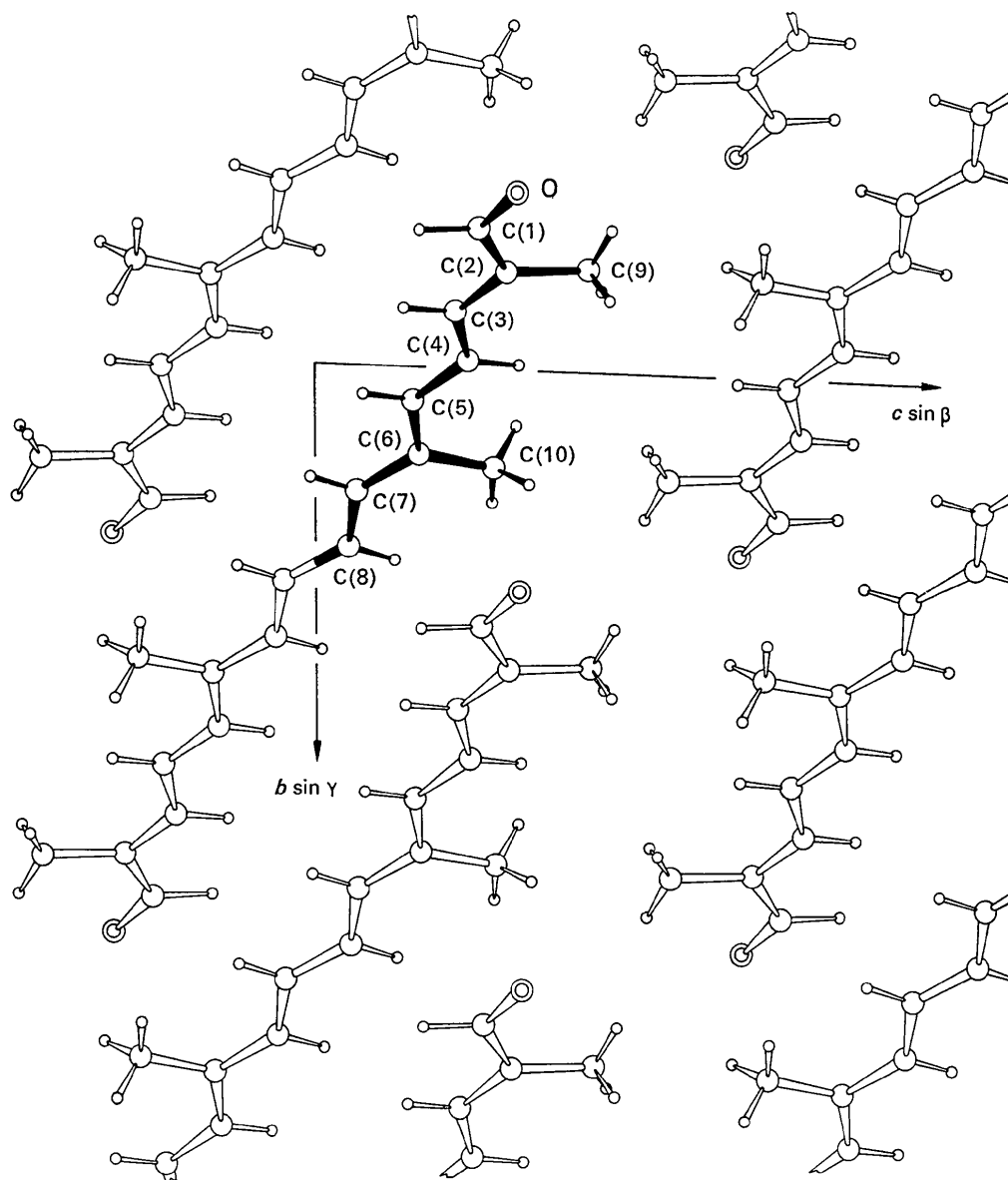


Fig. 2. Molecular packing in crocetindialdehyde. Projection down the a axis.

There is close agreement with the mean values tabulated by Bart & MacGillavry. It is probable that the bond angles and lengths are governed mostly by intramolecular forces since there are such small deviations from the mean values for similar structures. Differences in molecular packing do not seem to have any appreciable influence on bond lengths or angles. This is in agreement with the observations of Hirschfeld &

Schmidt (1957). But a slight bending of a planar molecule out of the molecular plane will not influence the bond lengths or angles very much, so it is still possible that the deviations from planarity are partly due to intermolecular forces.

The molecules pack in layers nearly parallel to the (577) plane. Within a layer the chains are stacked end to end with the aldehyde and terminal methyl groups

Table 9. *Intermolecular distances*

Distances are included within a limit 0.2 Å greater than the sum of the van der Waals radii of the participants.

$$R_C = 1.80 \text{ \AA}, R_O = 1.36 \text{ \AA}, R_H = 1.17 \text{ \AA}.$$

Symmetry operations:

$$\begin{array}{ll} 1: x+1, y, z & 10: -x+1, -y, -z \\ 2: x+1, y-1, z & 11: -x+1, -y-1, -z+1 \\ 3: x, y+1, z & 13: -x, -y, -z+1 \end{array}$$

		Sym. op.			Sym. op.
C(1)—C(4)	3.49 Å	1	C(3)—H(103)	3.04 Å	1
C(3)—C(10)	3.68	1	C(1)—H(81)	3.03	2
C(1)—C(3)	3.80	1	H(102)—C(1)	3.09	3
C(4)—C(10)	3.70	1	H(11)—C(7)	3.08	10
C(6)—C(1)	3.70	3	C(1)—H(71)	3.16	10
C(10)—C(1)	3.56	3	H(92)—C(10)	3.16	13
C(7)—C(1)	3.72	3			
C(8)—C(1)	3.63	3	H(102)—O(1)	2.73	3
C(8)—C(3)	3.76	3	H(91)—O(1)	2.67	11
C(10)—C(9)	3.75	13	H(71)—H(11)	2.17	10

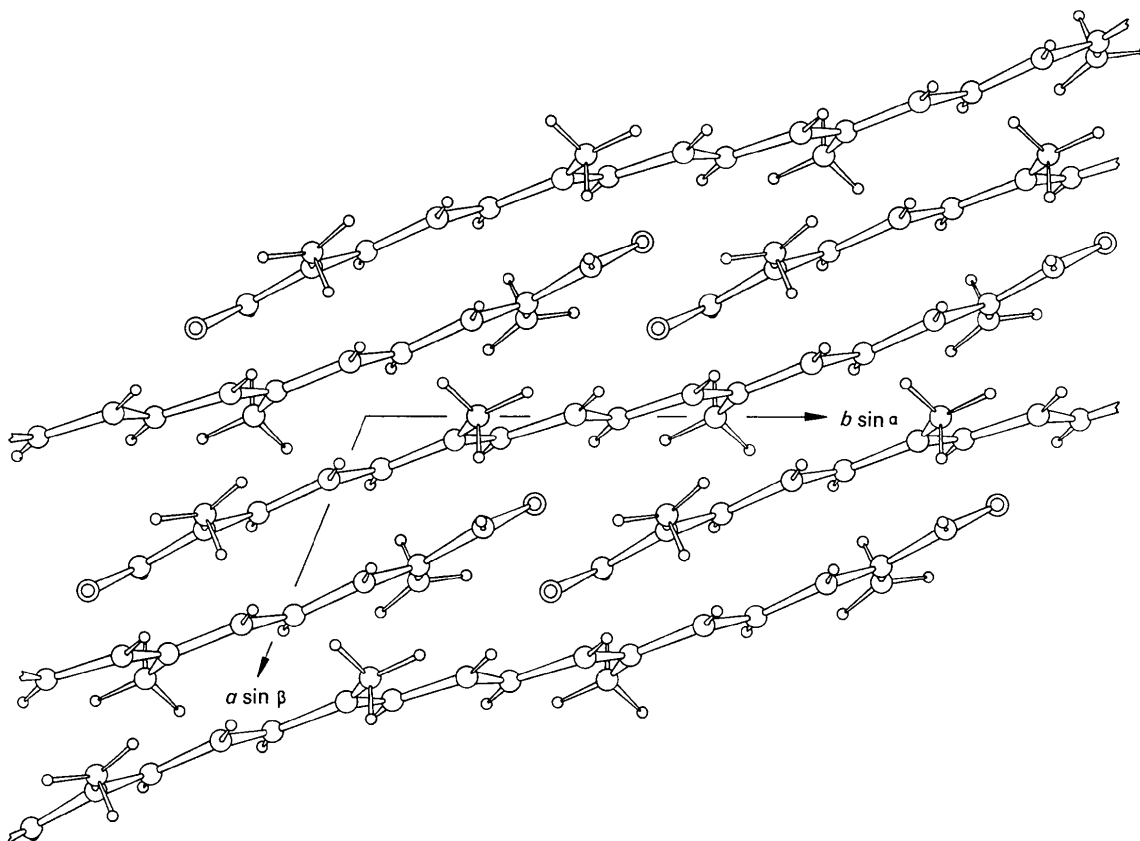


Fig. 3. Molecular packing in crocetin dialdehyde. Projection down the *c* axis.

situated around a centre of symmetry. The other methyl groups in a chain are accommodated in the space between chain ends in neighbouring layers (Fig 4). In this way all methyl and aldehyde groups are given space between chain ends and the chains themselves may adopt relatively tight side-packing. The molecular packing is probably mainly determined by the packing of methyl and aldehyde groups. This theory is substantiated by the list of shortest intermolecular distances given in Table 9. Most of the shorter contact distances can be found around the methyl and aldehyde groups, but none are shorter than the normal range of van der Waals contacts.

The *XRAY67* program system supplied by Stewart (1967) has been used on an UNIVAC 1108 computer for the structure determination (*PHASE*), least-squares refinement (*ORFLS*), Fourier calculations (*FOURR*) and calculations of best planes (*LSQPL*). The author's ALGOL programs *SCALER*, *SIGMA2*

and *SYMBOL* were also used on the 1108 computer for part of the structure determination.

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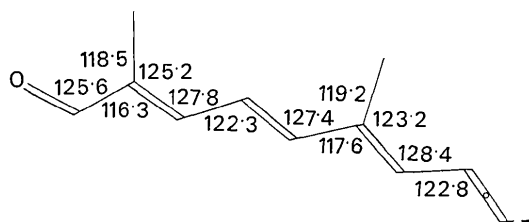


Fig. 4. Bond angles ($^{\circ}$).

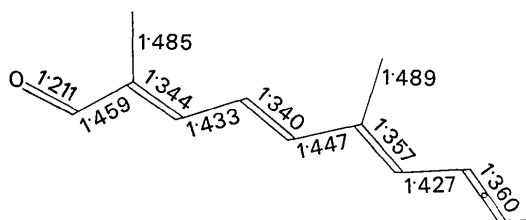


Fig. 5. Bond distances (\AA).