Table 1 (*cont.*)

kk	*ll*	F_o	F_c
08	02	5·9	6·4
	03*	0·4	−0·4
	04	3·1	−3·5
	05	5·9	−3·2
	06	6·1	−4·8
	07	4·3	−3·1
	08	2·4	3·0
	09*	1·1	−2·7
09	01	1·8	−1·3
	02	4·3	4·5
	03*	1·1	−2·5
	04*	0·3	−0·3
	05	3·9	1·1
	06	4·1	−2·9
	07*	1·1	−1·3
09	08	3·4	−2·1
10	01	3·8	−4·2
	02	1·6	2·3
	03*	0·8	−0·8
	04	2·9	2·8
	05*	0·3	0·3
10	06*	0·2	0·2
	07	2·5	−2·8
11	02*	1·1	1·8
	03*	1·1	2·0
	04*	1·1	−1·4
	05*	0·4	−0·4

Distances	Length
1–8″	4·177 Å
2–5″	4·844
7–4″	4·386
6–3″	4·230
1–8′	4·644
1–5′	4·576
1–6′	3·659

(Numbering system is shown on Fig. 4).

The present work was carried out under a George Ellery Hale Fellowship in the California Institute of Technology. We wish to testify of our indebtedness to Prof. Dr Linus Pauling whose continued interest in this line of research has been a source of stimulation to us; to Prof. Dr J. Holmes Sturdivant who made available to us the cold room equipment to carry out our experiments at subzero temperatures; to Prof. Dr Eiji Ochiai of the Pharmacological Institute of Tôkyo University who furnished generous samples of 4,4′-*trans*-azopyridine-N-oxide; and to Dr Karst Hoogsteen who repeatedly invested time and effort to give us the benefit of technical advice and assistance.

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The Crystal Structure of *cis* D,L 11-12 Methylene Octadecanoic Acid

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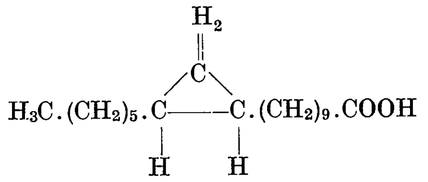
The crystal structure has been determined by two-dimensional Fourier synthesis of the (*h*0*l*) and (0*kl*) diffraction data. In contrast to the 'straight-chain' stereochemistry found in the previously studied C_{19} *trans* cyclopropane acid, this molecule is bent at the *cis* substituted ring so as to have an overall shape somewhat like that of a boomerang.

This compound is believed to be the racemate of the naturally occurring *lactobacillic acid* and is analogous to *dihydrosterculic acid*, in which the *cis* ring is in the 9–10 position.

Introduction

Six *cyclo*propyl fatty acids are at present known; the *cis* and *trans* D,L 9-10, *cis* and *trans* D,L 11-12, methylene octadecanoic acid, which were synthesized by Hofmann *et al.* (1954, 1957); the natural product, *lactobacillic* acid, which was isolated by Hofmann & Lucas (1950) and is believed to be *cis* D or L 11-12, methylene octadecanoic acid from the work of Hofmann, Marco & Jeffrey (1958); the *dihydrosterculic* acid, which is the hydrogenation product of the naturally occurring sterculic acid, $C_{19}H_{34}O_2$, (Nunn, 1952) and was shown by X-ray data to be identical with the *cis* D,L 9-10, methylene octadecanoic acid by Brotherton & Jeffrey (1957); the *dihydromalvalic acid*, which is a hydrogenation product of the naturally occurring malvalic acid, $C_{18}H_{32}O_2$, (Shenstone & Vickery, 1956) and has been shown by crystal structure analysis to be *cis* D,L 8-9 methylene heptadecanoic acid (Craven & Jeffrey, 1959*a*). A dihydrobombacic acid was also reported briefly by Dykstra & Duin (1955) from the bombacic acid of kapok seed oil, which is also believed to be a C_{18} *cyclo*propene acid.

The crystal structure analysis of the *trans* D,L 9-10 methylene octadecanoic acid has been reported by Brotherton, Craven & Jeffrey (1958). This present paper describes an analysis of a racemate in the *cis* C_{19} acid series with the same general objective; to determine the stereochemistry of the long chain molecules in the crystal structure. The 11-12 compound, I, was selected in preference to the closely related 9-10 compound simply because it gave the better crystals for the X-ray intensity measurements.



$$H_3C.(CH_2)_5.\underset{H}{C}\overset{\overset{H_2}{C}}{\text{———}}\underset{H}{C}.(CH_2)_9.COOH$$

(1)

(The carbon atoms are numbered 1 to 18 along the chain from the carboxyl end, the methylene ring carbon is C_{19}.)

Crystal data

Monoclinic, m.p., 39 °C.

$$a = 8{\cdot}93 \pm 0{\cdot}05,\ b = 5{\cdot}10 \pm 0{\cdot}05,\ c = 88{\cdot}6 \pm 0{\cdot}05\ \text{Å};\ \beta = 98°.$$

$$U = 3994\ \text{Å}^3;\ D_m = 0{\cdot}99\ \text{g.cm.}^{-3};\ Z = 8;\ D_x = 0{\cdot}993\ \text{g.cm.}^{-3};$$

space group, from extinctions $A2/a$ or Aa, from structure analysis $A2/a$. The long spacing, $c \sin \beta$, is twice that reported previously by Brotherton & Jeffrey (1957), when, because of the poor quality of the crystals, the A centering of the lattice was not recognized. A corresponding correction in the indexing of the orders of the long spacings of the powder lines is also required in the earlier paper for consistency with these new data.

Experimental

As was usual in this class of compounds, single crystals suitable for X-ray study were obtained with difficulty as soft thin colorless plates, from acetone and water mixtures. The unit-cell dimensions were measured from Weissenberg photographs, with the exception of the long spacing, $c \sin \beta$, which was obtained from the Bragg angles of the $(00l)$ reflexions using the single crystal orienter of the General Electric XRD-5 diffractometer. The intensity data were obtained photographically from one crystal of relatively exceptional quality with dimensions $0{\cdot}15 \times 0{\cdot}10 \times 0{\cdot}06$ cm. During the exposure the crystal was cooled to about -10 °C., both to preserve the crystal and extend the range of the experimental observations. The $h0l$ reflexions were recorded on multifilm equi-inclination Weissenberg photographs with filtered Cu K radiation. An exposure of 3 days recorded 333 reflexions extending to $\sin \theta/\lambda = 0{\cdot}62$. In the $0kl$ zone, reflexions were recorded up to $\sin \theta/\lambda = 0{\cdot}31$ on precession photographs with Cu K radiation.

The intensities were estimated visually. They extended over a range of 33500 to 1. The usual angle factor corrections were made, but no attempt was made to correct for absorption.

The structure determination

Although the space group is not uniquely determined from the systematic extinctions it was considered likely that the D and L molecules would be related by a crystallographic center of symmetry. It was therefore assumed that the space group was $A2/a$ and no evidence to the contrary was found during the course of the analysis.

The previous work on the *trans* D,L 9-10 compound (Brotherton, Craven & Jeffrey, 1958) had shown how very sensitive the general structure factors are to small changes in the z coordinates in these long-chain compounds. The $00l$ reflections and the projection on the c axis were therefore investigated first. This projection was refined by trial and error methods until after 15 cycles of one-dimensional Fourier synthesis and structure factors the agreement index for the 49 observed $00l$ reflections was $0{\cdot}21$. The final one-dimensional projection synthesis is shown in Fig. 1.

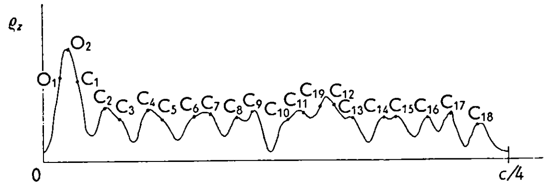


Fig. 1. One-dimensional Fourier synthesis on [c].

The atoms along the chain are well resolved and the position of the *cyclo*propane ring in the 11-12 position is clearly confirmed.

The 020 intensity was observed to be so much stronger than any others in the $0kl$ zone that it was concluded that the chain molecules must lie parallel to the c axis in the $0kl$ projection. It was necessary to consider two possibilities; either with the molecules close to the a glide planes at $y = 0, \frac{1}{2}$, to give a poorly resolved projection, or interleaving these glide planes at $y = \frac{1}{4}, \frac{3}{4}$, to give a good projection. A $(0kl)$ Patterson synthesis supported the second alternative.

By good fortune, the first postulated model for this projection was very close to the final answer and the first synthesis showed resolution of all the atoms except O_2 and C_{19}, which overlapped in adjacent molecules. After five cycles of refinement there were no further sign changes and the agreement index was 0·25. In the absence of higher orders of 0*kl*, further improvement of this projection was not possible. The final Fourier synthesis, Fig. 2(*a*), showed a very symmetrical configuration, with the atoms on either side of the ring related by a non-crystallographic mirror plane through C_{19}.

Despite this good start, the solution of the *h*0*l* projection proved unexpectedly difficult, because it was assumed that, as in most long-chain compounds, the molecule would be as straight as was compatible with the stereochemical requirements of its component parts. In fact a very plausible model of a nearly straight molecule could be made to satisfy the normal stereochemical criteria of the *cis* substituted ring and to fit the 0*kl* projection. All efforts to refine the *h*0*l* projection with a straight chain model were unsuccessful and in particular the C_{15} and C_{16} were not well defined in the Fourier maps. Finally, when the symptoms of the various Fourier maps were recognized and a chain bent at the *cyclo*propane ring was tested, the refinement proceeded without further complications to give a very well-resolved Fourier map.

When the agreement index was 0·28, a difference synthesis indicated the need for individual anisotropic temperature factors, progressively increasing from C_{12} to C_{18}. As an approximation, the following isotropic *B* factors were applied; oxygen atoms, 5·0 Å^2; C_1 to C_{12} and C_{19}, 4·3 Å^2; C_{13} to C_{18} 5·5 Å^2. Many peaks which could be associated with reasonable hydrogen atoms positions were also apparent on the difference synthesis and when the hydrogen contributions were included the agreement index dropped to 0·25. Two more refinement cycles with difference syntheses improved the agreement to 0·215.

The experimental intensity data did not justify any attempt to obtain a more precise analysis and the structure refinement was terminated at this stage. The final Fourier projection in the (*h*0*l*) zone is shown in Fig. 2(*b*).

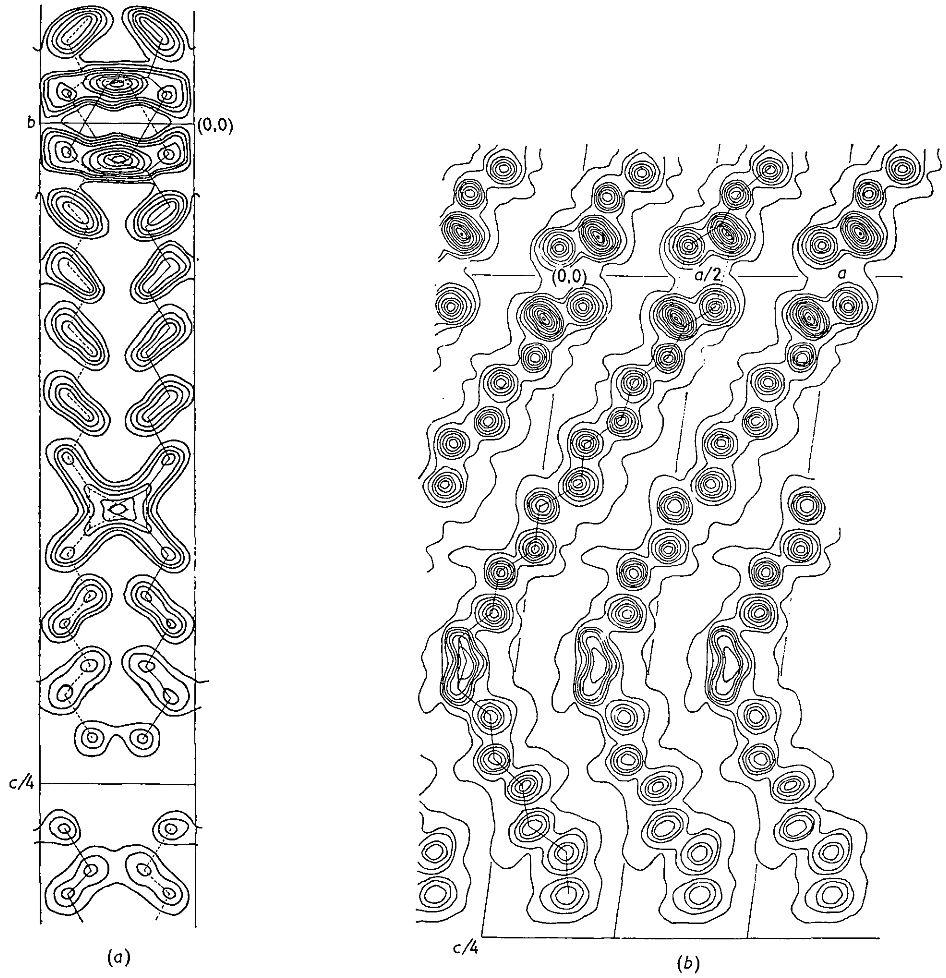
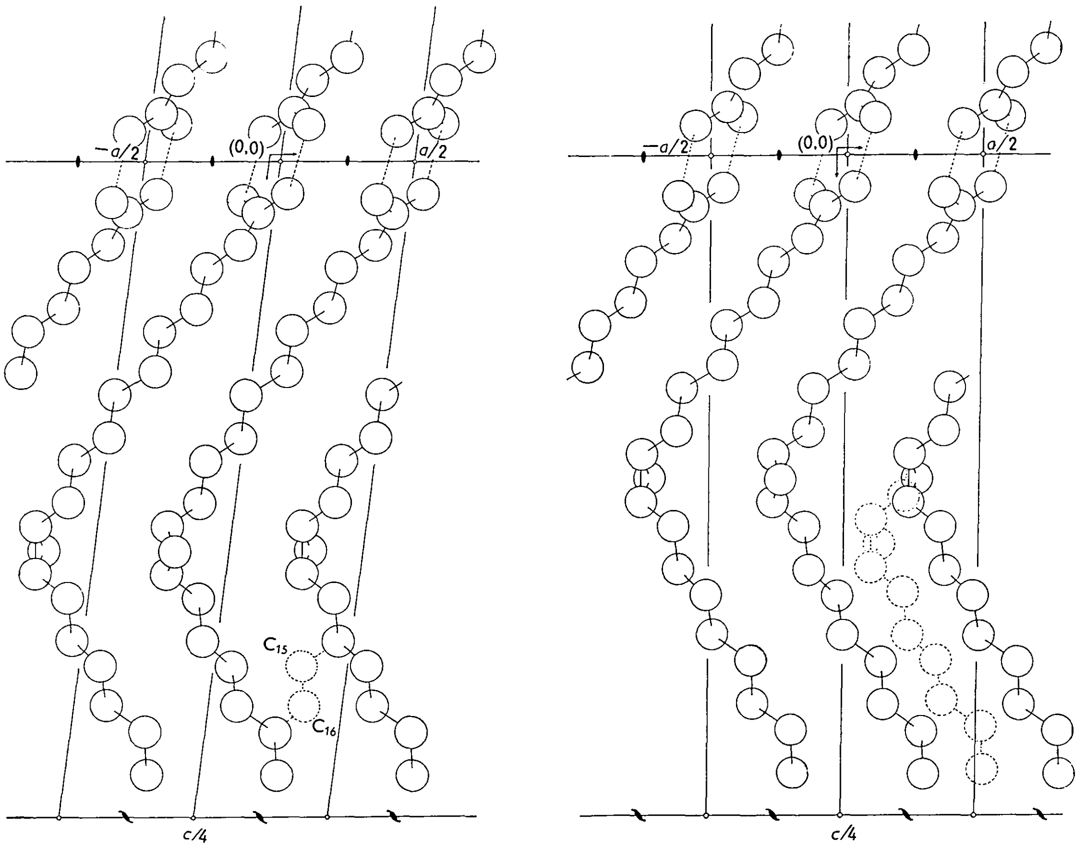


Fig. 2. (*a*) Two-dimensional Fourier synthesis down [*a*]. (*b*) Two-dimensional Fourier synthesis down [*b*].



(a) (b)

Fig. 3. (a) Diagram of the molecules of *cis* D,L 11-12 methylene octadecanoic acid corresponding to the Fourier synthesis down [b]. The dotted atoms refer to the distorted straight-chain positions for C_{15} and C_{16}, discussed in the text. (b) Diagram of a postulated structure for *cis* 9-10 methylene octadecanoic acid (dihydrosterculic acid). The dotted atoms refer to the *cis* 11-12 configuration, to illustrate the structural relationship discussed in the text.

Owing to the ambiguity between centers of symmetry, two-fold and screw axes in the *b* axis projection, there were four ways of combining the coordinates from the *a* and *b* axis projections. These were:

x, z	$0, 0$	$0, \frac{1}{4}$
(1)	$\bar{1}$	$\bar{1}, y = \frac{1}{4}$
(2)	2	2_1
(3)	$\bar{1}$	2_1
(4)	2	$\bar{1}, y = \frac{1}{4}$

Since this corresponds to the choice between the face and body-centered monoclinic lattice, it could have been resolved into one pair, (1) and (2) or (3) and (4) from the indexing of *hkl* reflexions, but this was difficult on the Weissenberg photographs because of the long *c* axis. In fact only combination (1) gave rise to intermolecular distances at the ends of the molecules which were consistent with a reasonable hydrogen bonding system and acceptable non-polar methyl group interaction distances. The carboxyl groups then dimerise by hydrogen bonding through centers at $0, 0, 0$; $\frac{1}{2}, 0, 0$; $0, 0, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$; and the terminal methyl groups are related by the screw axes at $0, \frac{1}{4}$; $0, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{4}$; $\frac{1}{2}, \frac{3}{4}$; and the centers at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$.

Table 1. *The atomic coordinates in cis* D,L 11-12 *methylene octadecanoic acid*

Atom	x	y	z
C_1	0·449	0·31	0·0187
C_2	0·408	0·17	0·0322
C_3	0·287	0·34	0·0402
C_4	0·269	0·17	0·0558
C_5	0·148	0·33	0·0643
C_6	0·142	0·17	0·0801
C_7	0·009	0·33	0·0887
C_8	0·002	0·17	0·1051
C_9	0·881	0·33	0·1136
C_{10}	0·877	0·17	0·1291
C_{11}	0·771	0·31	0·1388
C_{12}	0·786	0·31	0·1563
C_{13}	0·918	0·18	0·1655
C_{14}	0·953	0·30	0·1819
C_{15}	0·073	0·17	0·1919
C_{16}	0·126	0·30	0·2076
C_{17}	0·279	0·17	0·2170
C_{18}	0·305	0·30	0·2329
C_{19}	0·806	0·54	0·1479
O_1	0·557	0·15	0·0121
O_2	0·395	0·58	0·0148

The atomic coordinates from the two projections are given in Table 1. The observed and calculated structure factors are given in Table 2. The general orientation of the molecules in the crystal structure is shown in Fig. 3(*a*).

The primary objective of the analysis was to establish the stereochemistry of the molecules rather than the details with respect to the bond lengths and valence angles. Owing to the difficulty in obtaining crystals suitable for good intensity measurements and because of the incomplete refinement of the *a* axis projection, the details of the molecular structure are not very reliable. The C–C bond lengths along the chain vary from 1·40 Å to 1·70 Å with a mean of 1·58 Å; the C–C–C valence angles along the chain lie between 103° and 111° with a mean of 108°. The bond lengths in the *cyclo*propane ring were 1·41, 1·42, 1·54 Å, the latter being C_{11}–C_{12}. However, no significance can be attached to the variations along the chain from the standard values of 1·54 Å for H_2C–CH_2 and the tetrahedral angle for $CH_2.CH_2.CH_2$.

Discussion of the structure

This analysis has determined the general stereochemistry of the *cis* D,L 11-12 methylene octadecanoic acid molecules in the crystal. The outstanding feature of this stereochemistry is the boomerang-like shape of the long-chain molecule with the bend at the *cis* substituted *cyclo*propane ring (see Fig. 3). This is in direct contrast to the general straight-chain geometry of the *trans* C_{19} *cyclo*propyl acid previously studied, (Brotherton, Craven & Jeffrey, 1958).

As in the case of the *trans* acid, the stereochemistry along the chain can be described with respect to the sections in which the atoms, excluding the hydrogens, are coplanar.

(i) The carboxylic acid group, C_1, $O_1.O_2$ lies in a plane inclined at 70° to (010).

(ii) The plane of the carbon chain then twists through about 20° from C_1 to C_5, after which the carbon atoms are approximately coplanar to C_{11}. Thus, $C_1.C_2.C_3$ is inclined at 70°, $C_2.C_3.C_4$ at 55°, and $C_5 \cdots C_{11}$ at 50° to (010). A similar effect was observed in the crystal structure of the 9-10 *trans* acid (Brotherton, Craven & Jeffrey, 1958). It undoubtedly arises from the necessity for the long-chain molecules to accommodate themselves to the stereochemical demands of the hydrogen bonds at one end and the packing of the *cyclo*propane ring configurations near the middle of the chains.

(iii) The *cyclo*propane ring, $C_{11}.C_{12}.C_{19}$, makes an angle of 103° with (010).

(iv) The chain beyond the ring, $C_{12} \cdots C_{18}$, is approximately coplanar and is inclined again at 50° to (010), in the same sense as $C_5 \cdots C_{11}$. The angle between the chain axes of C_1–C_{11} and C_{12}–C_{18} is 118°.

A notable feature of the stereochemistry is the non-crystallographic mirror-plane symmetry parallel to the *b* axis and passing through C_{19}, which relates the carbon atoms extending on either side of the ring. Superficially this would appear to be contrary to expectation, since the orientation of the methylene groups at the C_{10} and C_{13} positions does not appear to be close to that of minimum steric repulsion, in that there is a short and a long $H \cdots H$ separation, rather than equal distances, cf. Fig. 4. The 'short' non-bonded $H \cdots H$ distance of 2·1 Å shown in Fig. 4 was deduced from the carbon atom positions assuming tetrahedral C–C–H angles and is subject to the error of this approximation in addition to the uncertainty of the analysis.

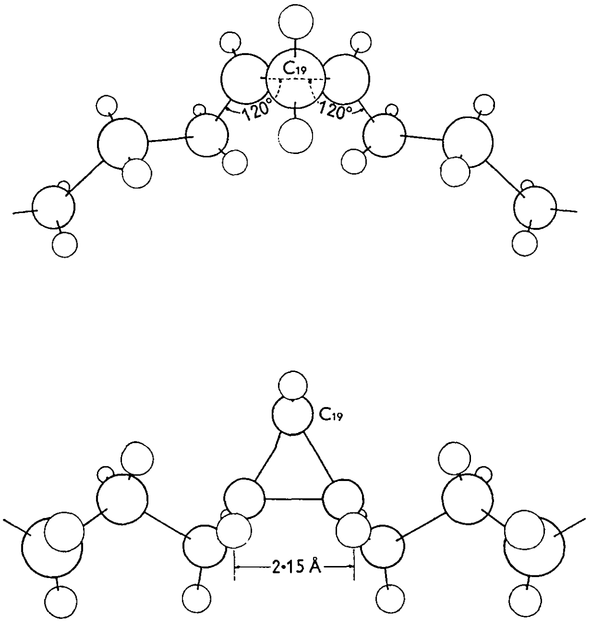


Fig. 4. Views of the *cis* 11-12 methylene octadecanoic acid molecule in the vicinity of the *cyclo*propane ring, to illustrate the hydrogen interactions of the methylene groups adjacent to the ring.

The $C_{19}C_{11}C_{10}$ and $C_{19}C_{12}C_{13}$ angles (126°, 121°) are observed greater than those along the polymethylene chain, but it is unknown whether this is a characteristic of the *cyclo*propane ring stereochemistry or a consequence of strain bond-bending from the methylene group interactions.

The molecules are hydrogen-bonded into dimers through the centers of symmetry. The O–$H \cdots O$ distance is 2·70 Å. At the non-polar ends of the molecules the closest distances between terminal methyl groups are 4·1, 4·3, 4·6 Å and 5·2.

The boomerang configuration of the molecule is very closely related to that for a distorted straight-chain. If C_{15} and C_{16} are translated by $a/4$ the other possible

Table 2. *Observed and calculated structure factors*

($h0l$)

l	F_c	F_o
	($00l$)	
2	118	—
4	-30	—
6	117	—
8	-23	—
10	25	37
12	-34	21
14	67	81
16	-71	67
18	-14	13
20	-24	23
22	-36	18
24	-89	84
26	-19	25
28	-52	44
30	-84	84
32	-58	56
34	-43	45
36	-47	57
38	5	19
40	-191	186
42	-100	116
44	-69	78
46	-9	18
48	24	32
50	-21	24
52	10	4
54	17	22
56	31	19
58	-5	10
60	32	30
62	18	20
64	20	15
66	12	13
68	28	28
70	3	10
72	24	27
74	5	10
76	10	14
78	42	40
80	-20	21
82	-15	18
84	-22	20
86	-1	6
88	16	21
90	1	6
92	1	6
94	11	10
96	5	10
98	-5	5
	($20l$)	
0	-6	12
2	224	178
4	-19	13
6	2	27
8	219	227
10	484	434
12	148	142
14	-69	81
16	-73	82
18	-14	4
20	-52	57
22	-54	55
24	-9	12
26	-64	66
28	-30	32
30	-35	21
32	-35	32
34	-60	54
36	-20	10
38	-41	36
40	-34	23
42	-47	37
44	-12	6
46	-15	10
48	3	9
50	-80	76
52	-88	98
54	-32	36
56	62	74
58	16	16
60	0	5
62	62	68
64	-20	31
66	49	46
68	9	5
70	5	9
72	28	25
74	4	10
76	8	5
78	7	5
80	9	5
82	0	5
84	7	5
86	3	5
88	2	5
90	2	5
92	-3	5
94	-7	8
96	-1	5
98	8	9
100	-2	4
102	-8	14
104	-13	16
$\overline{2}$	-24	2
$\overline{4}$	59	40
$\overline{6}$	152	156
$\overline{8}$	-182	172
$\overline{10}$	93	77
$\overline{12}$	112	111
$\overline{14}$	-264	208
$\overline{16}$	179	127
$\overline{18}$	-83	51
$\overline{20}$	-43	68
$\overline{22}$	-10	8
$\overline{24}$	-17	18
$\overline{26}$	-39	51
$\overline{28}$	-57	52
$\overline{30}$	3	10
$\overline{32}$	-17	25
$\overline{34}$	-49	45
$\overline{36}$	1	23
$\overline{38}$	-6	3
$\overline{40}$	-11	15
$\overline{42}$	-5	13
$\overline{44}$	22	10
$\overline{46}$	-7	11
$\overline{48}$	26	24
$\overline{50}$	1	7
$\overline{52}$	-13	4
$\overline{54}$	66	54
$\overline{56}$	-42	40
$\overline{58}$	32	25
$\overline{60}$	18	37
$\overline{62}$	-11	12
$\overline{64}$	-3	5
$\overline{66}$	37	42
$\overline{68}$	42	44
$\overline{70}$	-29	18
$\overline{72}$	-56	62
$\overline{74}$	-54	50
$\overline{76}$	-5	5
$\overline{78}$	5	13
$\overline{80}$	-5	5
$\overline{82}$	-6	5
$\overline{84}$	18	15
$\overline{86}$	0	5
$\overline{88}$	2	9
$\overline{90}$	2	5
$\overline{92}$	9	10
$\overline{94}$	8	8
$\overline{96}$	-5	8
$\overline{98}$	8	8
$\overline{100}$	4	7
$\overline{102}$	-4	4
$\overline{104}$	6	7
$\overline{106}$	4	5
$\overline{108}$	-13	16
	($40l$)	
0	-8	17
2	-42	28
4	13	16
6	-16	6
8	15	3
10	-84	83
12	82	74
14	-8	3
16	-63	92
18	77	80
20	95	98
22	13	21
24	-46	49
26	-32	50
28	-43	43
30	-24	28
32	-1	6
34	-22	18
36	0	8
38	4	7
40	9	13
42	-11	14
44	7	13
46	33	37
48	-49	53
50	59	66
52	-16	12
54	-20	25
56	50	66
58	-4	5
60	-32	29
62	-48	63
64	4	5
66	30	38
68	36	44
70	8	10
72	13	12
74	9	10
76	3	5
78	-2	9
80	0	5
82	-2	6
84	-7	11
86	-4	7
88	0	4
90	-9	11
92	-1	6
94	5	6
96	-8	10
$\overline{2}$	9	3
$\overline{4}$	-59	38
$\overline{6}$	-9	25
$\overline{8}$	-24	14
$\overline{10}$	+13	22
$\overline{12}$	-53	49
$\overline{14}$	-24	34
$\overline{16}$	-62	65
$\overline{18}$	-36	39
$\overline{20}$	59	83
$\overline{22}$	175	152
$\overline{24}$	-27	25
$\overline{26}$	8	4
$\overline{28}$	86	82
$\overline{30}$	-9	13
$\overline{32}$	44	36
$\overline{34}$	17	24
$\overline{36}$	45	24
$\overline{38}$	22	23
$\overline{40}$	6	13
$\overline{42}$	29	27
$\overline{44}$	20	21
$\overline{46}$	5	4
$\overline{48}$	22	15
$\overline{50}$	5	27
$\overline{52}$	4	4
$\overline{54}$	-5	5
$\overline{56}$	48	52
$\overline{58}$	52	61
$\overline{60}$	-18	27
$\overline{62}$	-118	131
$\overline{64}$	-50	50
$\overline{66}$	-18	16
$\overline{68}$	-45	43
$\overline{70}$	-1	5
$\overline{72}$	-33	28
$\overline{74}$	3	5
$\overline{76}$	-5	11
$\overline{78}$	-8	7
$\overline{80}$	-7	15
$\overline{82}$	5	7
$\overline{84}$	9	13
$\overline{86}$	-6	5
$\overline{88}$	7	8
$\overline{90}$	8	5
$\overline{92}$	1	8
$\overline{94}$	6	4
$\overline{96}$	8	7
$\overline{98}$	-4	7
$\overline{100}$	-2	5
$\overline{102}$	14	16
$\overline{104}$	17	24
$\overline{106}$	7	8
	($60l$)	
0	-34	47
2	17	21
4	-54	39
6	-27	22
8	-2	11
10	-15	16
12	-40	30
14	10	4
16	-9	4

Table 2 (*cont.*)

l	F_c	F_o	l	F_c	F_o	l	F_c	F_o	l	F_c	F_o
18	−36	30	$\overline{10}$	35	60	$\overline{86}$	13	12	54	−4	7
20	−5	6	$\overline{12}$	82	68	$\overline{88}$	3	12	56	5	5
22	6	13	$\overline{14}$	2	11	$\overline{90}$	4	4			
24	−7	11	$\overline{16}$	−3	15	$\overline{92}$	2	11	$\overline{2}$	45	46
26	−13	24	$\overline{18}$	41	40	$\overline{94}$	8	13	$\overline{4}$	−9	16
28	14	17	$\overline{20}$	28	38	$\overline{96}$	3	8	$\overline{6}$	−22	35
30	19	24	$\overline{22}$	17	4	$\overline{98}$	2	8	$\overline{8}$	18	23
32	−22	15	$\overline{24}$	10	21	$\overline{100}$	9	11	$\overline{10}$	24	15
34	24	18	$\overline{26}$	53	45				$\overline{12}$	−37	36
36	−22	36	$\overline{28}$	22	16		(80*l*)		$\overline{14}$	20	17
38	−9	15	$\overline{30}$	5	5	0	9	30	$\overline{16}$	10	12
40	29	26	$\overline{32}$	34	46	2	−28	22	$\overline{18}$	−4	18
42	−19	24	$\overline{34}$	29	19	4	−46	51	$\overline{20}$	10	11
44	17	12	$\overline{36}$	−5	7	6	−46	40	$\overline{22}$	−8	5
46	18	7	$\overline{38}$	37	44	8	−13	16	$\overline{24}$	18	9
48	12	7	$\overline{40}$	13	19	10	3	8	$\overline{26}$	−12	5
50	5	5	$\overline{42}$	8	8	12	4	11	$\overline{28}$	9	5
52	21	10	$\overline{44}$	18	29	14	−9	13	$\overline{30}$	9	16
54	6	7	$\overline{46}$	47	52	16	0	11	$\overline{32}$	6	5
56	7	7	$\overline{48}$	54	52	18	14	24	$\overline{34}$	11	9
58	5	5	$\overline{50}$	−12	17	20	−8	7	$\overline{36}$	25	37
60	17	11	$\overline{52}$	−60	68	22	0	8	$\overline{38}$	35	35
62	3	5	$\overline{54}$	−32	40	24	16	18	$\overline{40}$	1	7
64	−6	7	$\overline{56}$	−18	14	26	−17	11	$\overline{42}$	−18	22
66	12	8	$\overline{58}$	−21	26	28	4	5	$\overline{44}$	1	5
68	7	9	$\overline{60}$	−29	33	30	1	5	$\overline{46}$	−3	5
70	−14	17	$\overline{62}$	−20	18	32	−7	5	$\overline{48}$	−9	8
72	−29	37	$\overline{64}$	−1	17	34	−7	5	$\overline{50}$	−13	8
74	3	4	$\overline{66}$	−21	24	36	1	5	$\overline{52}$	0	5
76	17	20	$\overline{68}$	−10	16	38	7	5	$\overline{54}$	−3	9
78	13	15	$\overline{70}$	−9	5	40	−5	17	$\overline{56}$	−7	10
80	1	4	$\overline{72}$	−9	21	42	−8	8	$\overline{58}$	0	5
82	2	4	$\overline{74}$	−7	5	44	−6	9	$\overline{60}$	−10	6
			$\overline{76}$	11	5	46	12	8	$\overline{62}$	−4	8
$\overline{2}$	−44	48	$\overline{78}$	−16	23	48	11	6	$\overline{64}$	−3	6
$\overline{4}$	−18	23	$\overline{80}$	9	6	50	5	4	$\overline{66}$	3	4
$\overline{6}$	−105	103	$\overline{82}$	5	8	52	7	4	$\overline{68}$	−6	6
$\overline{8}$	−12	29	$\overline{84}$	−12	18				$\overline{70}$	3	6

(0*kl*)

	(01*l*)		39	30	37	28	12	4	15	−15	8
1	−48	43	41	30	45	30	−23	20	17	0	9
3	8	20	43	−53	41	32	−5	15	19	−10	5
5	−8	29	45	−52	39	34	5	12	21	9	3
7	−65	56				36	−12	27	23	−14	6
9	11	14		(02*l*)		38	−46	45	25	7	3
11	32	4	0	−234	172	40	56	57	27	3	14
13	−50	47	2	12	28	42	22	39	29	10	6
15	7	19	4	12	33	44	−20	12	31	−21	28
17	46	34	6	14	21	46	6	3	33	28	40
19	7	8	8	36	34				35	12	21
21	−27	33	10	−15	10		(03*l*)		37	−51	35
23	66	50	12	23	21	1	−16	28	39	−13	21
25	26	31	14	15	20	3	−10	16	41	−43	30
27	−13	19	16	6	5	5	−14	14	43	83	55
29	22	25	18	−10	7	7	−13	17	45	75	61
31	78	84	20	30	15	9	−9	11	47	2	21
33	−23	24	22	−1	4	11	−14	10	49	20	21
35	−3	11	24	−10	12	13	1	7	51	32	31
37	101	99	26	5	6						

configuration is obtained; see Fig. 3(*a*). It was this ambiguity which led to the difficulties in solving the phase problem for the *b* axis projection referred to previously.

Comparing these two configurations in the crystal lattice, the intermolecular interactions are the same, the intramolecular interactions differ only in having a longer C_{12}–C_{15} distance for the boomerang molecule, 3·9 Å versus 3·3 Å.

A closely related crystal structure is expected for the *cis* D,L 9-10 methylene octadecanoic acid, i.e. dihydrosterculic acid. In the earlier work by Brotherton & Jeffrey (1957) the similarity in the diffraction data in the 9-10 and 11-12 compounds in the *cis* and *trans* series, respectively, was discussed in terms of a structural isomorphism. In the *trans* compounds, the straight-chain arrangement of the molecules is such that the packing will be little affected by the position of the ring, provided it is near the center and in an odd-even position (e.g. Fig. 1, Brotherton & Jeffrey, 1957). In the *cis* molecules, a change in ring position from 11-12 to 9-10 will shift one half of the chain by about $a/4$ with respect to the other half, as shown in Fig. 3(*b*). The general orientation of the two halves will be unchanged, however, and this could account for the similarity in unit-cell dimensions and powder line side-spacings which have been observed.

A similar contrast in overall configuration between the *cis* and *trans* compounds, found in these C_{19} *cyclo*propyl acids, might be expected in the *cis* and *trans* unsaturated fatty acids, with the double bond near the center of a chain of comparable length (e.g. oleic acid, $C_{18}H_{34}O_2$; *cis* and *trans* vaccenic acids, $C_{18}H_{34}O_2$; erucic acid, $C_{22}H_{42}O_2$; nervonic acid, $C_{24}H_{46}O_2$). The *trans* unsaturated acids, like the *trans* *cyclo*propyl compounds, can readily adopt a straight-chain shape which is very close to that of a normal saturated long chain acid (see Brotherton, Craven & Jeffrey, 1958). The *cis* unsaturated acids can adopt either the distorted straight-chain or the boomerang shape. Carter & Malkin (1947) discussed the stereochemical differences between *cis* and *trans* unsaturated acids and showed by means of powder photographs that the crystal structures of erucic and brassidic acids, *cis* and *trans* $CH_3(CH_2)_7.CH{:}CH.(CH_2)_{11}COOH$, respectively, are quite different. Rideal (1945) found that erucic acid on water formed a more 'open' monomolecular surface film than brassidic and, in relating this to the ease of permanganate oxidation in the surface film of the *cis* structure as compared with the *trans*, he postulated a bent *cis* and a straight *trans* configurations rather similar to those described in this paper.

A similarity in the single crystal data for erucic and *cis* nervonic acids with that of the *cis cyclo*propyl fatty acids has been found by Craven & Jeffrey (1956*b*).

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A General Least-Squares Program for the Refinement of Anisotropic Thermal Parameters

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A program is described for the refinement of anisotropic thermal parameters and atomic coordinates on the IBM 704 computer. The program covers all space groups of the triclinic, monoclinic, orthorhombic and tetragonal systems. A set of general structure factor expressions has been derived, one expression covering all space groups in a single system. A modified diagonal approximation is used.

1. Introduction

The art of measuring X-ray intensities has improved greatly in the last few years, and the data published in the reports of structure analyses are becoming increasingly exact. Concurrently, large high-speed electronic computers have been developed which are