point groups in physical and Fourier space under the following condition. The physical space point group has no phase changes which are a function of coordinates. A space group isomorphous with a point group also yields this point group as the index space symmetry. Translations introduced in one space imply, in the other, phase factors which are linear functions of the coordinates.

There is a special type of physical space structure in which the groups possible in the two spaces become identical. Consider the case in which the physical space structure consists of complex point masses located at points which are rational fractions of the repeat distances. The complex density can be written

$$\varrho(\mathbf{r}) = \Sigma_p g(\mathbf{p}) \delta(\mathbf{r}-\mathbf{p}) \tag{47}$$

where $\delta(\mathbf{r}-\mathbf{p})$ is the Dirac delta function and

$$\mathbf{p} = (p_1/n_1, p_2/n_2, p_3/n_3), \text{ with } p_i = 0, 1, 2, \ldots, n_i. \tag{48}$$

Then

$$\begin{aligned} F(\mathbf{K}) &= \int \Sigma_p g(\mathbf{p}) \delta(\mathbf{r}-\mathbf{p}) \exp(-j\mathbf{K}.\mathbf{r}) dV \\ &= \Sigma_p (g(\mathbf{p}) \exp(-j\mathbf{K}.\mathbf{p}) . \end{aligned} \tag{49}$$

In this case Fourier space is periodic with repeat distances (n_1, n_2, n_3). Similarly, with the simple rescaling of coordinates, $x_i' = n_i x_i$, physical space becomes an index space in the sense in which we have defined it. The two spaces are both periodic index spaces of complex functions and must have the same symmetry groups. The Fourier space symmetry group corresponding to a given physical space group is not, of course, identical to that physical space groups, but the sets of possible groups are identical.

Still another interesting limit exists. This is the transition from an index space to a continuous Fourier space. It can be shown, as a generalization of the discussion of equation (1) in section 2, that only the parameters called arbitrary, i.e. those which do not enter into the order equation can be non-zero. This is because the order equation cannot hold otherwise in a continuous space. We know that the non-arbitrary parameters correspond to glide elements which generate infinite periodicity in one or more directions. Thus, the existence of a continuous Fourier space rules out those Fourier space operators which correspond to operators in physical space which generate infinite periodicity.

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The Crystal Structure of the Low-Melting Form of Oleic Acid

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The low-melting form of oleic acid is pseudoorthorhombic with $a = 9{\cdot}51$, $b = 4{\cdot}74$ and $c = 40{\cdot}6$ Å. The space group is $P2_1/a$ and there are four molecules per cell. The molecules are bent at the *cis*-double bond. The two chain parts have the usual planar zig-zag conformation and adopt a side packing $0'$ || not previously found in long-chain compounds. The chain axes of the two parts have equal angles of tilt (56·5°) to the (001) planes but are tilted in opposite directions. The acid dimers are held together by hydrogen bonds (2·64 Å) around centres of symmetry and form a layer structure normal for long-chain compounds.

Introduction

It has long been known (Kirschner, 1912) that oleic acid is dimorphous. Several observations of two melting points have been reported; Lutton (1946) gives the values 13·3° and 16·2°. He investigated the X-ray powder patterns of the two forms and reported the long spacing, $d(001)$, values of 40·5 Å and 42·2 (84·4) Å respectively.

The only single-crystal data given for unsaturated

fatty acids are the cell dimensions of erucic and *cis*-nervonic acids (Craven, 1959). A bent-chain conformation of these acids was postulated because of their similarity to cyclopropane fatty acids.

Experimental

The X-ray photographs were taken in a low-temperature Weissenberg camera similar to that described by Kreuger (1955).

A sample of oleic acid (Mann Research Laboratories) was sealed in a glass capillary and an attempt was made to grow single crystals in the usual way by blowing dry cool air on the capillary. The air was cooled by passing through a copper spiral in solid carbon dioxide. Crystals grew as fine needles which were always parallel to the capillary axis. It proved impossible to select a seed crystal which did not produce a twinned crystal when growing.

It was, therefore, necessary to crystallize oleic acid from different solvents. The best crystals were obtained from acetone at $-14°$. They grew like most long-chain compounds in large very thin plates which were often bent. Cutting with a razor to obtain crystals of comparable width and thickness often led to some deformation.

The crystals are biaxially positive with the acute bisectrix perpendicular to the well developed (001) faces. Crystals for the X-ray work were selected under polarized light and mounted on glass capillaries. These operations were performed at a temperature of $+4°$.

X-ray photographs often revealed imperfections in crystals which appeared good in the polarizing microscope. The selection of crystals suitable for the collection of intensity data proved very tedious.

Rotation and Weissenberg photographs about the *a*- and *b*-axes were taken with Cu $K\alpha$ radiation. The intensity data about the two axes were recorded at $-20°$ for two different crystals. The unit cell is pseudoorthorhombic with

$$a=9{\cdot}51\pm0{\cdot}09,\ b=4{\cdot}74\pm0{\cdot}05,\ c=40{\cdot}6\pm0{\cdot}3\ \text{Å},$$

and contains four molecules. Absent reflexions $h0l$ for h odd and $0k0$ for k odd show that the space group is $P2_1/a$.

Intensities were estimated visually by two observers using a calibrated intensity strip. In all about 500 independent reflexions were used in the analysis. The experimental difficulties mentioned prevented collection of more complete three-dimensional data. The Lorentz and polarization factors were applied but no absorption correction was made.

One of the many crystals investigated from the acetone crystallization was of a different structure. Its cell dimensions were

$$a=9{\cdot}51,\ b=41{\cdot}75,\ c=5{\cdot}39\ \text{Å};\ \beta=122°.$$

The zero level about the *a*-axis shows a similar intensity pattern to that about the *a*-axis of the other crystal form indicating similar structures as seen along the 9·51 Å axis. Unfortunately this one crystal melted before any useful intensity data were recorded and further attempts to find crystals of this form have so far been unsuccessful.

A sample of oleic acid crystallized from acetone at $-14°$ was investigated in a powder camera which continuously records the diffraction pattern as a function of temperature (Stenhagen, 1951). The pattern corresponding to the crystal form analyzed here disappeared at $+13{\cdot}0°$, in good agreement with the melting point given by Lutton (1946). As would be expected, no lines due to the high melting form were visible on the X-ray film.

Structure determination

As no sublattice could easily be recognized in the reciprocal lattice, Patterson projections along the two short axes were calculated to give information about the orientation of the carbon chains. The (010) projection (Fig. 1) revealed two possible directions of the chain axes and it was therefore assumed that the molecules were bent at the double bond with the two chain parts in the indicated directions.

The only known chain packing which seemed compatible with the unit cell symmetry was the orthorhombic packing $0\perp$ (Bunn, 1939). The chain plane was accordingly supposed to be inclined about 45° to the shortest axis. The molecules were assumed to be hydrogen bonded to form dimers around centres of symmetry as is usual for long fatty acids.

The trial structure thus obtained was used for the first structure-factor and electron-density calculations. It was clearly indicated, however, that the chain plane was more nearly parallel to the projection direction than the chain arrangement $0\perp$ allows. This was confirmed by further cycles of Fourier refinement.

Several difference syntheses reduced R_{h0l} to 0·11. Later the hydrogen atoms were included in the calculations with coordinates obtained from the difference maps and checked when possible with the data of Vainshtein & Pinsker (1950). After each structure-factor calculation the temperature and scale factors were adjusted from the best least-squares line through the points representing $\ln(F_o/F_c)$ values versus $\sin^2\theta/\lambda^2$.

In the early stages of the analysis, Fourier summations were performed partly with Beevers–Lipson strips (3°) and partly on the Hägg–Laurent machine (1946). Later most calculations were made on the Besk digital computer. The atomic scattering factors were then evaluated from a three-term expression with exponential functions (K. Appel*).

* Available as Technical Note from the Quantum Chemistry Group, University of Uppsala.

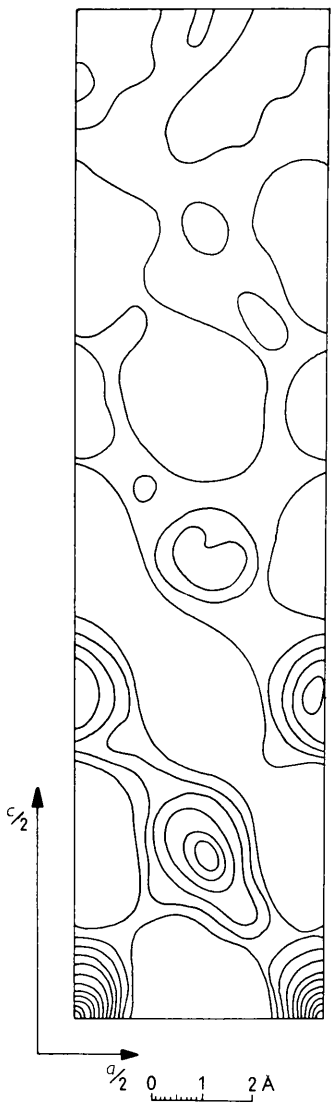


Fig. 1. Patterson projection along the *b*-axis. Contours given at arbitrary but equal levels.

In the (100) projection the Patterson synthesis showed the carbon chains to be parallel to the *c*-axis. With the known *x*- and *z*-coordinates and the usual bond distances and angles it was not difficult to obtain a correct projection. Owing to the heavy overlap (Fig. 3) it was not possible to carry the refinement very far and the three-dimensional data had to be used. An electron-density series was used for the first correction of the coordinates. The hydrogen atoms were included in the structure-factor calculations with positions and isotropic temperature factors as shown in Table 3. The *R*-value at this stage was 0·14 for all observed reflexions. The final refinement was accomplished by anisotropic least-squares treatment with the Rollett program for the Ferranti 'Mercury' computer (Mills & Rollett, 1961). The hydrogen parameters were not refined and there seemed little to be gained by assigning anisotropic temperature factors to the hydrogen atoms. After three cycles, shifts were about one third of the estimated standard deviation and the *R*-value 0·11. This decrease in *R* of 0·03 is not large considering the introduction of 100 new parameters. The least-squares refinement, however, improved distances and angles in the molecule towards the generally accepted values. The weighting scheme used was

$$w = 1/\{1 + [(|F_o| - 8|F_{\min}|)/5|F_{\min}|]^2\} .$$

The scattering factors for carbon and oxygen were those of Berghuis *et al.* (1955) and for hydrogen those of McWeeny (1952).

Results and discussion

The atomic coordinates for carbon and oxygen are given in Table 1, the vibrational parameters in Table 2.

Table 1. *Atomic co-ordinates*

	x/a	*y/b*	*z/c*
C_1	0·8670	0·6757	0·0305
C_2	0·7687	0·7954	0·0557
C_3	0·7086	0·5866	0·0798
C_4	0·6238	0·7578	0·1054
C_5	0·5629	0·5643	0·1324
C_6	0·4872	0·7356	0·1577
C_7	0·4122	0·5505	0·1833
C_8	0·3347	0·7351	0·2093
C_9	0·2569	0·5317	0·2311
C_{10}	0·2562	0·5343	0·2653
C_{11}	0·3370	0·7378	0·2869
C_{12}	0·4225	0·5602	0·3118
C_{13}	0·4909	0·7536	0·3386
C_{14}	0·5695	0·5900	0·3642
C_{15}	0·6468	0·7849	0·3891
C_{16}	0·7178	0·6160	0·4174
C_{17}	0·7970	0·7955	0·4416
C_{18}	0·8736	0·6376	0·4684
O_1	0·8789	0·7881	0·0029
O_2	0·9247	0·4232	0·0358

Table 2. *Allowance made for anisotropic thermal motion with*

$$2^{-10^{-5}\,.\,(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{13}hl+b_{12}hk)}$$

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C_1	819	13348	92	184	43	−439
C_2	1539	5099	85	−246	246	−1070
C_3	2176	6966	76	909	137	5159
C_4	1195	5429	73	1029	141	−4417
C_5	972	5923	87	−285	−38	−29
C_6	1524	5109	71	−806	183	2835
C_7	2056	6713	78	−111	244	3271
C_8	1569	9082	48	4	54	2247
C_9	908	7724	120	−61	67	−1377
C_{10}	1160	11418	94	672	83	10149
C_{11}	2275	7938	59	49	−55	2635
C_{12}	2283	11174	114	40	168	−1217
C_{13}	1892	6874	116	−96	156	3657
C_{14}	2770	8700	109	−640	−94	1921
C_{15}	2091	7215	105	−634	285	642
C_{16}	2005	10920	130	23	−143	1705
C_{17}	3175	12766	101	77	73	−1739
C_{18}	2596	14789	138	892	−459	7182
O_1	709	8950	71	776	110	−149
O_2	917	7533	121	309	331	1826

Observed and calculated structure factors are listed in Table 4. The final electron density projections along the short axes are given in Figs. 2 and 3.

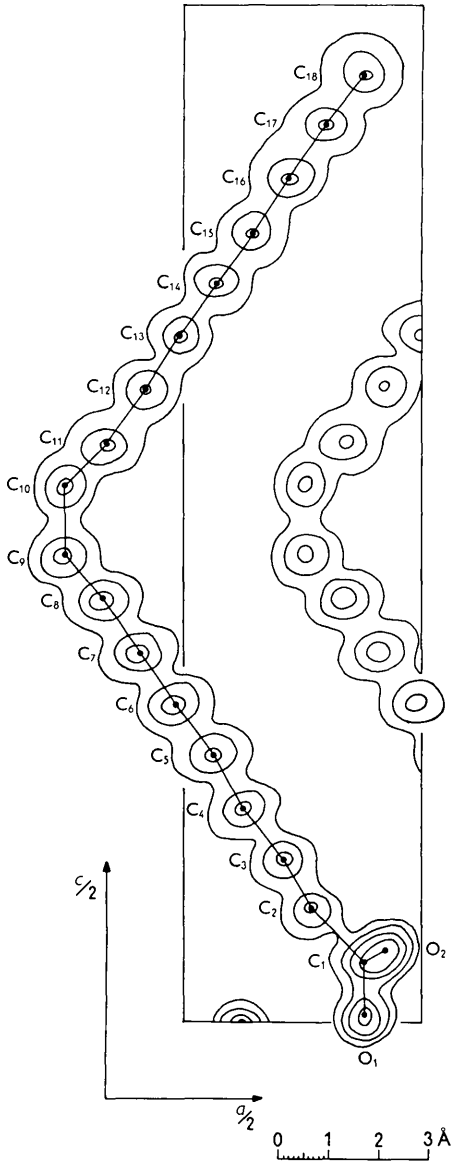


Fig. 2. Electron density projection along the *b*-axis. Contours are at intervals of 2 e.Å^{-2} starting with 2 e.Å^{-2}.

The standard deviations in the coordinates as estimated from the least-squares treatment are rather large owing to the relatively large number of parameters. The average values for carbon atoms are $\sigma(x)=\sigma(z)=0{\cdot}024$ Å, $\sigma(y)=0{\cdot}036$ Å and for oxygen atoms $\sigma(x)=\sigma(z)$ 0·014 Å, $\sigma(y)=0{\cdot}022$ Å. The deviations from these values are small (<0·004 Å).

The bond distances and angles in the molecule are given in Table 5. The average value for a carbon–carbon single bond is 1·53 Å with a maximum deviation of 0·03 Å. The average angle in the chain is 111° with a maximum spread of 5°.

Figs. 4 and 5 illustrate the molecular arrangement. The steric requirements of the *cis*-double bond combined with the demands of a tight side packing of the carbon chains cause the molecule to adopt a bent conformation. A similar shape of long-chain molecule has earlier been found in methyl branched fatty acids (Abrahamsson, 1959, review) and in cyclopropane fatty acids (cf. Craven & Jeffrey, 1959), in which each chain part adopts a fairly efficient side packing. Whereas in branched and cyclopropane acids only the orthorhombic (O ⊥) and triclinic (T ||) chain packings have been found, the chain arrangement in oleic acid represents a new packing for long-chain compounds.

Table 3. *Co-ordinates and temperature factors of the hydrogen atoms*

	x/a	*y/b*	*z/c*	*B*
H_1	0·692	0·925	0·041	2·9
H_2	0·846	0·925	0·068	2·9
H_3	0·629	0·443	0·067	2·9
H_4	0·783	0·443	0·094	2·9
H_5	0·548	0·881	0·092	2·9
H_6	0·702	0·881	0·119	2·9
H_7	0·485	0·411	0·119	2·9
H_8	0·639	0·411	0·145	2·9
H_9	0·411	0·899	0·144	2·9
H_{10}	0·565	0·899	0·171	3·3
H_{11}	0·337	0·396	0·170	3·3
H_{12}	0·490	0·396	0·197	3·3
H_{13}	0·259	0·912	0·196	3·3
H_{14}	0·413	0·912	0·222	3·3
H_{15}	0·258	0·910	0·300	3·3
H_{16}	0·412	0·910	0·273	3·3
H_{17}	0·346	0·421	0·327	3·3
H_{18}	0·500	0·421	0·300	3·3
H_{19}	0·415	0·902	0·351	3·3
H_{20}	0·569	0·902	0·325	3·3
H_{21}	0·489	0·440	0·379	3·3
H_{22}	0·644	0·440	0·352	3·3
H_{23}	0·574	0·909	0·403	3·3
H_{24}	0·728	0·909	0·376	3·3
H_{25}	0·641	0·476	0·430	3·3
H_{26}	0·795	0·476	0·403	3·3
H_{27}	0·727	0·928	0·455	2·9
H_{28}	0·871	0·928	0·428	2·9
H_{29}	0·797	0·497	0·481	2·9
H_{30}	0·951	0·497	0·454	2·9
H_{31}	0·930	0·770	0·486	2·9
H_{32}	0·178	0·392	0·218	2·9
H_{33}	0·175	0·392	0·279	2·9
H_{34}	0·953	0·699	0·012	2·9

The zig-zag planes of both chain parts are nearly parallel with the *b*-axis. C_{12} to C_{18} are within 0·05 Å from the best least-squares plane through these atoms whereas C_{11} is 0·08 Å and C_{10} 0·21 Å off the plane. The chain part C_2 to C_8 is planar within 0·04 Å. C_1 deviates 0·18 Å from the plane and C_9 0·20 Å.

The axes of the two chain parts form an angle of 113°. The coordinates of the carbon atoms are roughly such as are required by the presence of a mirror plane through the double bond parallel to (001). The two chain parts thus have equal angles of tilt (56·5°) to

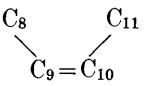
Table 4. *Observed and calculated structure factors*

The three columns in each group contain values of l, $|F_o|$ and F_c.
Each group is headed by the common values of h and k for that group printed after an *

*	0	0				-15	10.1	10.3	-40	11.0	-11.1	*	3	1				-16	11.7	-9.9
	5	40.0	40.0			-14	8.8	11.0	-39	28.9	-26.8		-32	14.9	10.0			-8	12.3	-14.0
	6	11.7	12.8			-13	52.0	-51.3	-27	13.6	5.2		-31	19.5	16.4			-7	12.7	-14.4
	7	8.2	28.4			-12	39.3	35.1	-26	9.1	-7.6		-29	20.1	-19.2			-6	12.7	-17.3
	8	22.1	-22.3			-11	27.3	-25.0	-25	7.8	-5.3		-22	16.9	-13.9			-4	26.0	-24.8
	9	14.9	12.6			-10	66.9	-60.9	-24	7.8	-4.9		-21	18.5	-18.4			-3	14.0	-16.7
	10	6.2	0			-8	46.1	-45.3	-22	16.2	-12.3		-20	15.9	-10.8			-1	26.7	-26.4
	11	13.3	12.5			-7	45.5	-46.7	-21	31.5	-28.6		-18	17.5	-15.7			0	8.1	-9.5
	12	34.4	-30.5			-6	65.0	-61.2	-20	8.4	-5.9		-17	20.5	-20.7			1	8.1	2.4
	14	8.8	8.1			-5	33.1	-31.2	-19	19.2	-15.9		-14	22.1	-20.8			2	17.2	11.9
	16	24.0	-19.5			-4	38.3	-35.6	-17	29.6	24.1		-13	39.3	-34.0			4	9.7	-6.1
	18	12.7	10.7			-3	38.0	-38.6	-16	9.1	-3.7		-12	25.7	-21.8			5	15.3	-12.1
	19	17.2	12.8			-2	51.0	-49.8	-15	18.5	-19.4		-10	22.1	17.2			6	11.4	13.2
	20	8.4	-5.4			-1	23.1	-24.1	-13	7.8	10.8		-9	91.6	81.3			10	12.7	12.7
	21	15.3	13.0			0	20.8	-21.6	-12	5.2	-3.7		-8	36.7	30.5			12	11.7	22.0
	22	20.8	19.0			1	33.8	-29.1	-11	16.9	-13.0		-6	38.0	33.5			13	13.6	-8.4
	23	22.1	20.0			2	56.9	-47.1	-7	24.4	-20.9		-5	37.0	32.6			14	11.0	13.2
	24	10.1	8.9			5	11.4	-14.1	-6	7.1	8.0		-4	15.9	12.5			16	20.8	-24.1
	25	17.5	14.7			6	22.4	-20.6	-5	18.5	-16.0		1	34.8	-29.4			17	13.6	17.3
	26	24.0	19.0			9	31.5	-35.1	-3	74.7	-79.1		2	16.6	-14.4			18	29.6	-31.7
	27	21.1	17.3			10	51.0	-53.9	-2	6.5	8.5		4	16.6	-14.4			20	14.0	-14.6
	28	15.6	15.7			11	30.2	-32.3	-1	162.1	-156.9		5	43.2	-40.7			21	12.7	-15.4
	29	15.6	14.8			12	28.9	26.2	1	162.1	156.9		7	15.6	12.7	*	2	2		
	30	16.9	14.1			13	40.3	39.7	2	6.5	-8.5		9	91.9	-90.9			-25	23.4	23.1
	31	11.7	11.2			14	24.4	22.7	3	74.7	79.1		10	15.6	-16.8			-16	32.2	33.6
	32	10.7	10.2			15	9.4	-9.3	5	18.5	16.0		11	15.6	-7.6			-15	28.3	27.0
	34	12.7	9.6			16	6.5	-5.3	6	7.1	-8.0		12	37.7	-34.5			-13	48.4	-40.9
	36	10.4	8.3			17	9.4	-8.9	7	24.4	20.9		13	36.4	33.9			-12	48.1	-43.2
	38	34.4	11.0			19	17.2	-15.4	11	16.9	13.0		17	18.8	18.9			-11	17.9	-17.2
	39	19.5	13.7			20	10.1	-10.6	12	5.2	3.7		21	15.6	15.2			-8	22.1	-17.4
	40	21.0	-15.5			21	22.4	-24.6	13	7.8	-10.8	*	4	1				-5	14.9	16.9
	42	11.0	-5.7			22	7.1	-6.1	15	18.5	19.4		-30	14.0	12.6			-2	20.8	19.3
*	2	0				23	16.6	-17.1	16	9.1	3.7		-29	15.3	18.7			2	22.7	21.2
	-43	8.8	-11.2			24	7.8	-4.2	17	29.6	-24.1		-27	16.2	-17.3			3	16.2	17.0
	-40	9.4	-8.1			25	33.1	-34.0	19	19.2	15.9		-26	15.3	-15.7			6	21.4	-22.2
	-39	10.1	-11.9			27	21.4	19.2	20	8.4	5.9		-14	25.5	24.7			9	20.5	-17.2
	-36	16.5	-8.7			28	39.0	-41.6	21	31.5	25.6		-12	19.8	-20.9			12	15.6	-39.4
	-35	29.5	-28.0			31	10.1	-7.4	22	16.2	12.3		-11	60.1	60.5			13	19.8	20
	-34	28.3	-26.1			32	10.1	-11.0	24	7.8	4.9		-8	17.9	-10.3			15	39.6	-37.9
	-32	19.5	19.0	*	6	0			25	7.8	5.3		-7	23.1	-15.8			25	23.4	-19.9
	-31	18.8	17.4			-25	14.3	12.8	26	9.1	7.6		-4	17.9	16.9			26	18.8	-28.3
	-27	12.3	11.0			-24	14.9	15.1	27	13.6	-5.2		0	21.4	20.4	*	0	3		
	-25	10.1	6.3			-23	18.2	-16.7	39	26.9	26.8		4	22.4	19.5			-23	13.6	-13.8
	-24	14.9	13.3			-22	40.9	-37.1	40	11.0	11.1		7	19.5	12.6			-22	9.1	6.9
	-23	11.7	9.2			-21	25.3	-21.3	42	5.8	5.2		11	57.8	-61.9			-21	43.2	34.3
	-21	13.6	10.2			-20	10.7	12.3	*	1	1		12	47.7	-49.9			-20	5.8	-7.5
	-20	13.6	14.6			-19	7.8	-8.8	-24	17.5	-19.0		13	25.3	-28.3			-19	5.8	4.5
	-18	11.7	-14.0			-18	30.8	33.2	-23	24.4	22.9		25	13.0	11.1			-18	13.0	-14.3
	-16	7.1	-4.8			-17	15.9	16.2	-22	11.4	10.7		26	16.2	-20.3			-17	42.6	-37.8
	-15	19.5	-20.5			-16	11.4	-11.5	-21	16.9	17.1	*	5	1				-11	11.7	10.7
	-14	37.4	-36.5			-15	27.9	31.9	-20	12.3	-11.4		-16	16.6	-20.9			-10	7.1	9.1
	-13	14.9	-13.4			-14	16.2	15.9	-19	22.7	-25.0		-13	15.6	-19.6			-9	12.3	11.3
	-12	20.8	-17.2			-13	12.6	15.7	-17	28.9	32.1		-5	18.2	-13.4			-7	14.9	12.5
	-11	39.0	-39.4			-11	15.3	17.2	-16	43.5	51.2		-3	32.8	31.1			-6	11.0	9.6
	-10	36.1	-35.5			-10	15.3	16.9	-15	42.2	45.3		3	24.0	-18.7			-4	9.1	11.8
	-8	6.5	-5.2			-9	8.8	8.4	-14	25.3	25.5		6	25.3	-26.0			-3	7.8	7.2
	-7	137.7	-134.0			-8	7.1	1.6	-13	14.3	15.6		8	14.6	-15.8			-2	7.1	8.0
	-6	136.4	131.3			-6	8.8	9.0	-12	1.0	15.3		10	15.9	-17.4			2	7.1	-6.6
	-5	85.1	-92.2			-5	7.1	2.0	-11	24.4	23.5		16	14.9	19.7			3	7.8	-7.2
	-4	70.8	-69.6			-4	17.2	-18.3	-10	22.1	22.3	*	0	2				4	9.1	-11.8
	-3	70.8	69.5			-3	8.4	-5.1	-9	12.7	7.6		-38	8.4	-10.6			6	11.0	-9.6
	-2	20.1	-16.8			-2	8.4	-6.8	-7	17.5	14.7		-36	9.1	-9.0			7	14.9	-12.5
	-1	20.1	-16.6			-1	17.2	-22.7	-6	22.4	18.5		-26	10.4	11.4			8	12.3	-11.3
	0	36.1	-33.1			0	23.1	-25.5	-5	10.7	-14.4		-24	9.1	-11.1			10	7.1	-9.1
	1	59.8	54.6			1	15.3	-14.5	-4	36.4	-39.9		-23	7.1	4.7			11	11.7	-10.7
	2	7.0	-6.0			2	8.4	-6.7	-3	63.7	64.2		-22	36.0	36.8			17	42.6	37.8
	3	49.7	-48.5			3	11.7	-13.0	-2	40.9	41.1		-21	20.5	-19.0			18	13.0	14.3
	4	75.7	-70.6			4	15.3	-12.0	-1	31.8	-38.3		-20	38.7	-35.6			19	5.8	-4.5
	5	80.6	-77.3			5	10.1	5.7	0	34.6	35.2		-19	19.8	-18.7			20	5.8	7.5
	6	159.5	155.2			10	12.3	10.0	1	21.1	21.5		-18	61.1	-52.2			21	43.2	-34.3
	7	160.2	160.0			14	14.9	14.6	2	49.1	-50.6		-16	17.9	18.8			22	9.1	-6.9
	8	59.8	55.8			15	16.6	-15.8	3	78.9	-91.4		-15	14.3	-10.9			23	13.6	13.8
	9	18.2	20.5			16	29.6	-32.1	4	53.3	-60.0		-14	23.1	-19.0	*	1	3		
	11	31.8	28.4			17	34.8	-34.6	6	16.2	19.5		-13	13.0	-8.7			-14	12.0	-11.4
	12	10.7	11.5			21	28.9	27.5	9	8.1	7.2		-11	17.9	-16.8			-13	15.3	-14.9
	13	4.8	2.0			22	33.1	-30.7	10	20.5	18.1		-10	24.4	-23.8			3	14.3	-15.2
	14	30.2	-26.2			24	9.4	11.2	11	9.7	6.2		-9	16.9	-16.2			16	11.4	-8.4
	15	5.2	-3.6			26	8.4	-10.0	12	12.0	15.7		-7	17.5	-15.9			19	14.9	-15.5
	16	7.8	-3.	*	8	0			13	13.0	13.8		-6	23.1	-21.5			21	15.9	-15.3
	17	14.9	-13.6			-26	11.4	11.3	14	33.5	37.7		-5	16.2	-10.9			25	16.2	-14.6
	18	23.1	-18.7			-25	12.3	-14.3	15	27.3	-28.7		-3	16.9	-16.4	*	2	3		
	19	13.6	-11.8			-23	11.7	11.3	16	48.1	52.7		-2	27.0	-30.2			-14	25.0	25.8
	21	9.4	-6.9			-22	8.4	-8.0	19	28.9	32.3		-1	11.7	-12.0			-13	15.9	14.4
	22	8.8	-8.5			-21	8.4	7.5	21	12.7	12.5		0	19.2	-21.4			-5	16.8	16.4
	23	10.1	-12.2			-19	15.3	13.4	22	16.9	18.3		1	11.7	-12.0			-4	17.5	16.0
	26	7.8	5.8			-18	18.8	15.6	*	2	1		2	27.0	-30.2			-3	17.5	17.5
	28	11.4	11.5			-17	10.1	9.8	-15	39.3	-37.4		3	16.9	-16.4			-2	14.6	14.3
	29	8.4	5.4			-16	10.1	7.4	-14	48.4	-51.1		5	16.2	-10.9			-1	21.1	19.2
	30	19.5	17.7			-15	14.3	12.0	-13	46.8	-49.6		6	23.1	-21.5			0	18.5	16.4
	31	13.6	-13.3			-12	14.3	17.3	-9	46.4	-48.5		7	17.5	-15.9			10	12.3	-7.7
	32	18.8	15.2			-9	10.1	13.0	-8	58.0	56.7		9	16.9	-16.2			11	12.3	8.9
	33	18.8	17.2			-8	18.2	21.1	-7	43 /	-44.4		10	24.4	-23.8			13	19.5	-18.2
	34	15.9	-16.1			-7	10.1	8.5	-6	30.5	-29.3		11	17.9	-16.8			14	21.7	20.0
	35	17.9	18.1			-5	10.1	13.6	-5	63.7	65.4		13	13.0	-8.7			15	16.2	-12.0
	64	8.8	13.8			-4	12.3	17.5	-4	80.6	-90.9		14	23.1	-19.0			23	15.9	17.5
	45	8.8	10.5			0	13.4	17.7	-3	15.9	10.9		15	14.3	-10.9			24	21.7	25.7
*	4	0				4	10.7	11.4	0	51.7	-50.3		16	17.9	18.8			25	18.5	13.8
	-33	13.0	-10.4			8	10.7	9.2	1	19.2	-16.3		18	61.1	-52.2	*	0	4		
	-32	13.6	-9.9			12	13.0	16.8	3	41.3	-37.6		19	19.8	-18.7			-40	12.3	11.9
	-30	11.4	-9.0			15.	24.4	8.3	4	90.6	-100.7		20	38.7	-35.6			-18	22.4	13.0
	-29	39.6	-37.6			18	11.7	12.0	5	93.9	-106.2		21	20.5	-19.0			-2	11.0	-8.5
	-28	53.9	-59.3			20	8.8	11.6	6	61.7	-65.9		22	38.0	36.8			0	11.0	14.6
	-27	26.0	-26.4			23	14.3	-19.6	7	24.4	-20.8		23	7.1	4.7			2	11.0	-8.5
	-26	13.6	8.5			24	10.7	-14.0	11	42.8	-42.5		24	9.1	-11.1			18	22.4	13.0
	-25	22.4	18.4			26	10.7	14.9	13	14.0	11.8		26	10.4	11.4			20	12.3	11.5
	-22	10.7	7.6	*	10	0			14	38.0	-40.2		36	9.1	-9.0	*	1	4		
	-21	12.3	7.0			9	18.3	15.5	17	15.9	-18.7		38	8.4	-11.6			-21	12.7	11.6
	-19	10.1	11.2	*	0	1			32	18.5	-20.0	*	1	2				-14	13.6	6.9
	-18	11.5	10.9			-42	5.8	-5.2					-23	13.6	-15.2			1	12.0	9.7
													-20	13.0	-14.6	*	0	5		
													-17	12.0	-13.7			1	15.6	11.9

the end-group contact planes but are tilted in opposite directions. A non-crystallographic mirror plane is also present in *cis*-DL-11,12-methyleneoctadecanoic acid (Craven & Jeffrey, 1959*a*) through the cyclopropane ring at which a similar bend as in oleic acid is found.

The bonds C_8–C_7 and C_{11}–C_{12} are rotated 47° (mean value) out of the plane of the double-bonded group



which is planar within 0·01 Å. In *cis*-1,4-polybutadiene (Natta & Corradini, 1956) and *cis*-1,4-polyisoprene (Nyburg, 1954) the corresponding rotations

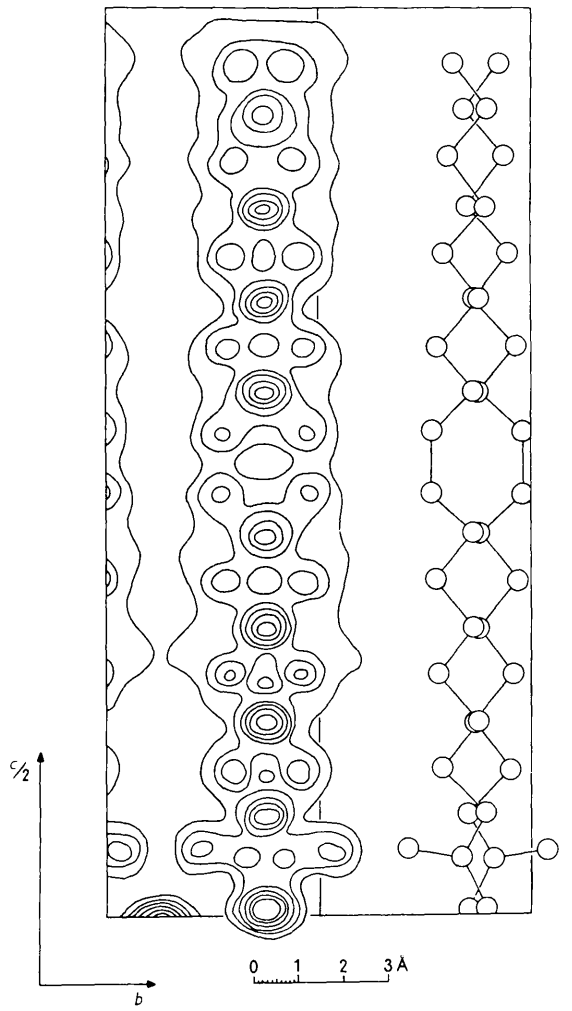


Fig. 3. Electron density projection along the *a*-axis. Contours given at intervals of 2 e.Å^{-2} starting with 2 e.Å^{-2}.

Table 5. *Bond lengths and angles in the oleic acid molecule*

O_1–C_1	1·25 Å	O_1–C_1–O_2	119°
O_2–C_1	1·33	O_1–C_1–C_2	121
C_1–C_2	1·50	O_2–C_1–C_2	119
C_2–C_3	1·51	C_1–C_2–C_3	116
C_3–C_4	1·55	C_2–C_3–C_4	110
C_4–C_5	1·54	C_3–C_4–C_5	111
C_5–C_6	1·50	C_4–C_5–C_6	110
C_6–C_7	1·54	C_5–C_6–C_7	112
C_7–C_8	1·56	C_6–C_7–C_8	111
C_8–C_9	1·50	C_7–C_8–C_9	106
C_9–C_{10}	1·39	C_8–C_9–C_{10}	126
C_{10}–C_{11}	1·51	C_9–C_{10}–C_{11}	126
C_{11}–C_{12}	1·55	C_{10}–C_{11}–C_{12}	107
C_{12}–C_{13}	1·56	C_{11}–C_{12}–C_{13}	111
C_{13}–C_{14}	1·50	C_{12}–C_{13}–C_{14}	113
C_{14}–C_{15}	1·55	C_{13}–C_{14}–C_{15}	112
C_{15}–C_{16}	1·55	C_{14}–C_{15}–C_{16}	112
C_{16}–C_{17}	1·50	C_{15}–C_{16}–C_{17}	114
C_{17}–C_{18}	1·51	C_{16}–C_{17}–C_{18}	116

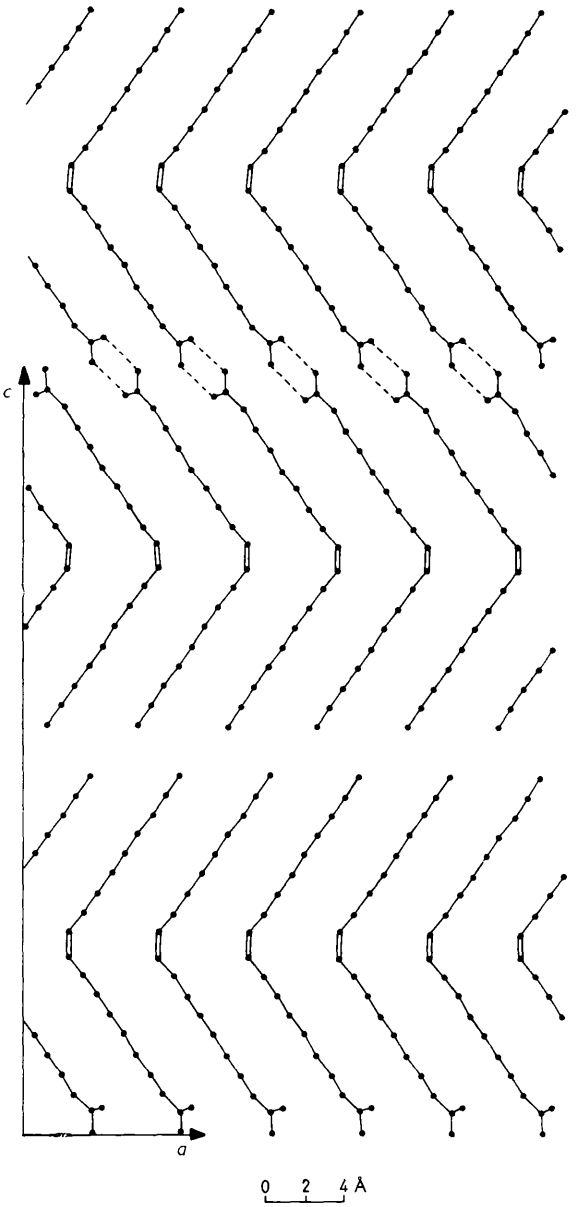


Fig. 4. Molecular arrangement of oleic acid as seen along the *b*-axis.

from the plane of the double-bonded group are 48° and 45° respectively. In these structures the two bonds have opposite and parallel directions on the two sides of the plane whereas in oleic acid they extend from the same side of the plane.

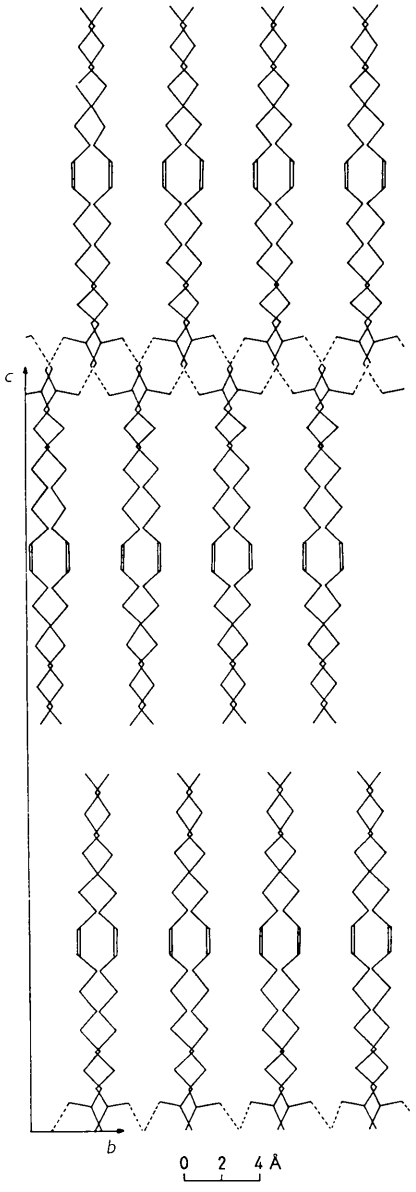


Fig. 5. Molecular arrangement of oleic acid as seen along the a-axis.

Though, as Fig. 5 shows, the chain axes of chain parts with parallel chain planes are not all parallel, the carbon chain arrangement is most clearly illustrated by introducing the subcell concept. The idealized subcell for the low melting form of oleic acid is shown in Fig. 6. It is orthorhombic with four CH_2-groups and shows the symmetry $P2_122$. The dimensions are: $a_s=7{\cdot}93$, $b_s=4{\cdot}74$ and $c_s=2{\cdot}53$ Å. The coordinates of the carbon atoms in the two independent CH_2 groups are $(\frac{1}{4}, -0{\cdot}015, \frac{1}{2})$ and $(\frac{1}{4}, 0{\cdot}171, 0)$. The y-coordinate represents an average value for the structure.

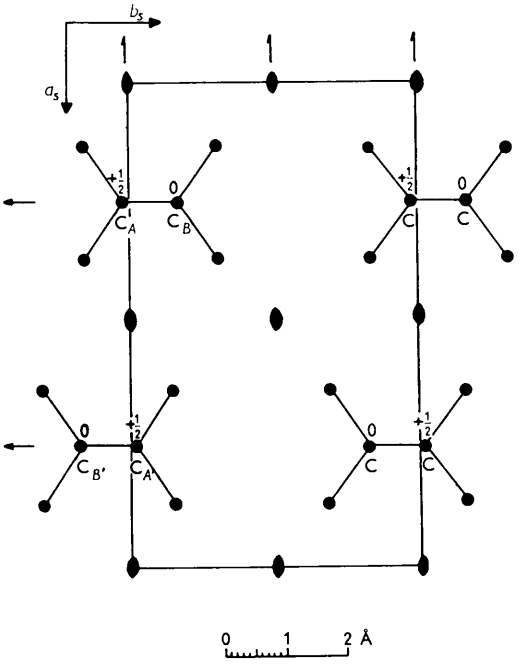


Fig. 6. Idealized subcell 0′ || of oleic acid.

All chain planes are parallel as in the orthorhombic packing O || (von Sydow, 1958). O′ || of oleic acid has the planes of chains repeated along b_s coinciding, whereas two adjacent chains in O || are about 1 Å displaced when seen in the corresponding direction parallel to the zig-zag planes.

The volume per CH_2-group of O′ || is 23·8 Å^3 which is surprisingly low (cf. Abrahamsson, 1959) considering the short parts along which the chains can interact. The b_s axis coincides with the b axis of the main cell.

The chain arrangement is very similar to that found in the β-form of odd short dicarboxylic acids (pimelic acid, MacGillavry *et al.*, 1948). Lutton (1946) points out that the side spacings of azelaic acid showed resemblance to those of the low-melting form of oleic acid. This is now explained by the similar chain packing of the two acids. Azelaic acid has been shown to be isostructural with pimelic acid (Banerjee *et al.*, 1961).

In the structure of oleic acid the shortest interchain distances are C_A–$C_{A'}=3{\cdot}97$ Å, C_B–$C_{B'}=4{\cdot}28$ Å and C_A–$C_{B'}=4{\cdot}23$ Å (Fig. 6). With the coordinates given for pimelic acid we have calculated the corresponding average distances to be 4·12, 4·29 and 4·33 Å.

The molecules are as usual linked together to form dimers. Hydrogen-bonded oxygens are 2·64 Å apart.

Another two oxygen contacts under 4 Å are found (3·32 and 3·35 Å). The angle C–OH···O is 116°. The carboxyl group and C_2 are planar within 0·05 Å. The planes of two hydrogen bonded groups do not coincide but are displaced by 0·35 Å. The carboxyl group plane is twisted 26° from the plane of the adjoining carbon chain.

The tilt (56·5°) of the end part of the chain to the methyl group contact planes is similar to that of most straight long-chain compounds. The layer structure therefore shows usual methyl group packing distances, the closest approaches being 3·75 and 4·21 Å.

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A Procedure for Parameter Refinement in Simple Structures*

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A procedure for the refinement of atomic position parameters in suitable simple structures is described. The method has been applied to the refinement of published position parameters of the oxygen atom in yttrium iron garnet. The new values are:

$$x = -0{\cdot}0269 \pm 0{\cdot}0001,\ y = 0{\cdot}0581 \pm 0{\cdot}0003,\ z = 0{\cdot}1495 \pm 0{\cdot}0001.$$

In the investigation of the structures of simple crystals in which certain atoms occupy special positions, the primary objective is often limited to the precise determination of a small number of atomic position coordinates. In recent years problems of this sort have usually been dealt with by least squares techniques. It is well known that, even in simple cases where the number of observations far exceeds the number of variable parameters, many serious errors may affect the accuracy of the least squares results. These include errors resulting from uncertainties in our knowledge of atomic scattering factors, inadequate corrections for dispersion factors, errors due to absorption, and errors in the determination of scale and temperature factors. Geller (1961) has analyzed parameter interactions in least squares structure refinements; such interactions may be very strong in just those simple structures under consideration.

In this paper we describe a simple technique for coordinate refinement which, though limited to a relatively small number of structure types, does make it possible to avoid most of the errors listed above in cases where it can be applied. In this procedure, calculations are based not on structure factors but on the *ratios* of intensities of selected pairs of reflections. In cubic crystals the members of each of these

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