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The Crystal Structure of Ethyl Stearate

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Ethyl stearate, $C_{17}H_{35}COOC_2H_5$, is monoclinic with $a=5\cdot59$, $b=7\cdot40$, $c=57\cdot1$ Å; $\beta=118°$. The cell contains 4 molecules and the space group is *Aa*. The molecules form sheets with the molecules tilting towards the end-group planes. The long chains are arranged in the orthorhombic packing $0\perp$. The molecule is bent at the carboxyl group and the OC_2H_5 groups are roughly in an hexagonal packing and seem to be disordered or oscillating.

Introduction

In a series of investigations on esters of long-chain fatty acids the structure of methyl stearate has earlier been reported (Aleby & von Sydow, 1960).

According to X-ray and thermal investigations carried out by Malkin (1931) and Phillips & Mumford (1931), (1932), (1933*a*, *b*) and (1934), ethyl esters exist in two forms, one with the chains tilted 67·5° towards the end group planes (β-form) and another with vertical chains (α-form). The latter crystallizes from melt and is stable only in a small temperature interval just below the melting point. On lowering the temperature a transition occurs to the tilted form obtained on crystallization from solvents. The melting points of the β-form as a function of carbon content lie on two curves, the one for esters of even acids above that for odd. The freezing points of α-forms of ethyl esters lie on one smooth curve (no alternation). This curve cuts the melting-point curves at about ethyl *n*-eicosanoate and ethyl *n*-pentadecanoate respectively. Thus, for the higher esters the α-form is the form stable at the melting point and there is no alternation in the melting points while for the lower esters the β-form is stable at the melting point and alternation occurs. In the intermediate range (ethyl *n*-tetradecanoate-ethyl *n*-eicosanoate) an apparent alternation in the melting points occurs because even esters melt as β-forms and odd as α-forms. The even esters here show monotropic dimorphism while the odd are enantiotropic.

According to Phillips & Mumford (1933*b*) and (1934) some ethyl esters seem to exist in a third (γ-)modification with melting points on a curve below the β-melting-point curve for esters of odd acids.

X-ray data are also reported by Malkin (1933) and Francis & Piper (1939). Thermal investigations have been made by Smith (1931), Meyer & Reid (1933), King & Garner (1934), (1936*a*, *b*). More recently dielectric measurements have been reported by Dryden (1957) and Broadhurst & Fitzgerald (1960) while mechanical resonance dispersion has been studied by Fitzgerald (1960).

Preparation of crystals

Ethyl stearate (ethyl *n*-octadecanoate) with m.p. 33·5–33·8 °C. was crystallized from carbon disulphide, acetone, ethanol and carbon tetrachloride at room temperature (20 °C.) and at −14 °C., and from glacial acetic acid at room temperature. The last mentioned crystallization gave crystals suitable for X-ray work. They were in the form of thin rhombic plates with acute angle 72° 25′. (Several crystals observed had, however, angles around 60°). The crystals were optically biaxial and positive. To reduce absorption errors thin rods were cut from the plates.

X-ray data

Rotation and Weissenberg photographs were taken at room temperature using Cu *K* radiation. The following data were obtained:

Molecular formula: $C_{20}H_{40}O_2$.
Molecular weight: 312·32.
Unit cell: monoclinic.
$a=5\cdot59\pm0\cdot02$, $b=7\cdot40\pm0\cdot02$, $c=57\cdot1\pm0\cdot4$ Å; $\beta=118°\pm30'$.
$d(001)=50\cdot4\pm0\cdot1$ Å (from Guinier powder photograph).
Four molecules per unit cell.
Number of electrons: 704.
Density calculated: $0\cdot995\pm0\cdot008$ g.cm.$^{-3}$.
Density measured: 0·994 g.cm.$^{-3}$.
Absent reflections: *hkl*, when $k+l$ odd, *h*0*l*, when *h* or *l* odd, and 0*k*0, when *k* odd.
Space group: C_s^4–*Aa*.

The intensities of the *h*0*l* and 0*kl*-reflections were estimated visually by two observers using multiple-film technique. They were corrected for Lorentz and polarization factors but not for absorption. The resulting observed structure factors were later brought to an absolute scale by comparison with the calculated structure factors.

Structure determination

From the similarity in the appearance of the Weissenberg zero-layer film rotated around the a-axis it was concluded that the structure as seen in the direction of the a-axis closely resembles that of methyl stearate. The main difference is that the lack of dimerization here causes the unit cell to be only about half as long.

The subcell is of the common orthorhombic type (O ⊥, Bunn, 1939). The average dimensions of the subcell as calculated from the final coordinates are $a_s=5{\cdot}02$, $b_s=7{\cdot}40$, $c_s=2{\cdot}51$ Å, and the angle between a_s and c_s is 89·3°.

The y- and z-coordinates for methyl stearate (Aleby & von Sydow, 1960) were transformed to the actual unit cell and the new carbon atom was given coordinates as if the OC_2H_5 group were a direct continuation of the main chain. Structure factors $0kl$ were calculated with atomic scattering factors taken from Vand *et al.* (1957). They agreed reasonably well with the observed F's and the electron density in the projection along a was calculated. The refinement was made by cycles of structure-factor calculations and difference syntheses. In the later stages hydrogen atoms were included with coordinates from Vainshtein & Pinsker (1950). The difference maps did not admit any good estimation of C–H distances and the calculations were performed for three different distances, 1·05, 1·08 and 1·12 Å, of which the last mentioned gave a slightly better agreement with the observed data than did the shorter distances.

Table 1. *Coordinates and temperature factors of the atoms in ethyl stearate*

	x/a	y/b	z/c	B_{yz}	B_{xz}
C_{18}	0·266	0·210	0·4633	7·6	7·15
C_{17}	0·353	0·312	0·4444	7·5	6·90
C_{16}	0·217	0·205	0·4187	7·3	6·80
C_{15}	0·319	0·295	0·3992	7·1	5·35
C_{14}	0·218	0·196	0·3730	6·9	5·55
C_{13}	0·316	0·293	0·3560	6·6	5·15
C_{12}	0·198	0·201	0·3295	6·4	5·25
C_{11}	0·298	0·282	0·3100	6·2	4·75
C_{10}	0·176	0·205	0·2840	5·8	4·25
C_9	0·291	0·297	0·2660	5·5	4·70
C_8	0·159	0·213	0·2387	5·5	4·75
C_7	0·272	0·297	0·2200	5·5	3·60
C_6	0·143	0·212	0·1922	5·5	4·40
C_5	0·289	0·300	0·1774	5·4	4·15
C_4	0·141	0·207	0·1500	5·4	3·60
C_3	0·248	0·271	0·1320	5·3	3·80
C_2	0·074	0·217	0·1010	4·9	2·65
C_1	0·182	0·233	0·0810	4·7	2·70
C_{01}	−0·293	0·253	0·0420	5·8	3·30
C_{02}	−0·525	0·245	0·0138	5·5	6·20
O_1	−0·015	0·247	0·0555	5·5	5·10
O_2	0·375	0·320	0·0905	5·5	4·00

Individual temperature factors $\exp(-B\sin^2\theta/\lambda^2)$ were used. The final values for B together with the coordinates are given in Table 1. The final value of the reliability index R was 0·13 omitting non-observed reflections. The calculations were performed with the BESK- and FACIT computers.

By studying the reflexions $20\bar{2}$, 200 and 202, x-coordinates were found. Structure factors $h0l$ were calculated using scattering factors from Berghuis *et al.* (1955) and McWeeny (1951) for hydrogen, followed by an electron-density projection along the b-axis. The arrangement with the OC_2H_5 group in the same direction as the main chain gave too short van der Waals contacts and therefore a bend at the carboxyl group was introduced.

The refinement was made by difference syntheses and in the later stages hydrogen atoms were included at a distance 1·10 Å and 110° angle from the C–C bonds. In the temperature factor $\exp(-B\sin^2\theta/\lambda^2)$ lower values of B had to be used in this projection

Table 2. *Observed and calculated structure factors* ($0kl$)

$0kl$	$\|F_o\|$	$\|F_c\|$	α (rad.)	$0kl$	$\|F_o\|$	$\|F_c\|$	α (rad.)	$0kl$	$\|F_o\|$	$\|F_c\|$	α (rad.)	$0kl$	$\|F_o\|$	$\|F_c\|$	α (rad.)
008	39	43	3·317	0,1,11	6	8	2·652	0,2,26	17	18	5·394	0,3,43	8	6	4·297
0,0,10	17	21	3·991	0,1,15	8	7	0·606	0,2,28	12	15	5·767	0,3,45	15	15	0·637
0,0,12	25	16	1·455	0,1,17	11	10	0·633	0,2,30	7	11	0·246				
0,0,14	34	28	1·813	0,1,19	11	12	0·172	0,2,32	5	7	0·995	040	90	97	0·000
0,0,16	34	26	2·540	0,1,21	33	37	0·048	0,2,34	5	6	5·737	042	20	17	1·351
0,0,18	23	14	3·325	0,1,23	54	53	3·650	0,2,44	21	21	0·472	044	12	15	1·548
0,0,20	21	18	5·468	0,1,25	8	3	4·438	0,2,46	11	6	3·865	046	7	11	2·026
0,0,22	109	113	0·404	0,1,27	5	5	1·229	0,2,48	5	2	1·727	048	6	12	2·487
0,0,24	40	37	2·035	0,1,29	5	5	1·643					0,4,10	5	9	2·836
0,0,26	33	27	2·278	0,1,31	5	4	1·890	031	8	7	0·484	0,4,12	5	10	4·055
0,0,28	25	23	2·531	0,1,45	9	7	3·703	033	7	8	2·208	0,4,14	5	6	4·620
0,0,30	13	13	3·438					035	7	9	1·884	0,4,18	6	8	2·080
0,0,32	9	8	4·656	020	337	344	3·142	037	9	12	4·066	0,4,20	6	3	0·793
0,0,34	9	8	1·992	022	33	34	4·553	039	11	15	5·103	0,4,22	21	21	0·585
1,0,36	7	3	4·292	024	39	36	5·189	0,3,11	10	12	6·203	0,4,24	8	10	2·285
0,0,38	7	5	5·823	026	35	33	5·780	0,3,13	7	5	1·799	0,4,44	9	11	3·609
0,0,40	6	3	2·966	028	26	26	0·067	0,3,15	8	8	3·270				
0,0,42	7	2	2·392	0,2,10	13	11	0·680	0,3,17	11	12	3·793	0,5,21	28	27	0·123
0,0,44	32	31	3·619	0,2,12	5	3	5·718	0,3,19	11	11	3·501	0,5,23	35	39	3·590
0,0,46	15	13	0·982	0,2,14	10	10	5·069	0,3,21	38	36	3·250	0,5,43	7	5	1·129
0,0,48	7	1	4·148	0,2,16	12	11	5·616	0,3,23	57	62	0·478	0,5,45	10	11	3·781
				0,2,18	10	12	6·000	0,3,25	7	5	1·578	060	16	13	3·142
015	7	7	4·544	0,2,20	7	8	2·826	0,3,27	6	6	3·964	062	8	12	4·029
017	10	8	1·513	0,2,22	65	72	3·544	0,3,29	7	8	4·609	0,7,21	15	14	3·322
019	11	13	1·943	0,2,24	24	20	5·275	0,3,31	6	8	5·130	0,7,23	10	16	0·365

Table 3. *Observed and calculated structure factors* ($h0l$)

$h0l$	$\|F_o\|$	$\|F_c\|$	α (rad.)	$h0l$	$\|F_o\|$	$\|F_c\|$	α (rad.)	$h0l$	$\|F_o\|$	$\|F_c\|$	α (rad.)	$h0l$	$\|F_o\|$	$\|F_c\|$	α (rad.)
004	55	49	2·626	$2,0,\overline{66}$	7	5	4·811	$2,0,\overline{10}$	25	29	5·723	$4,0,\overline{44}$	15	17	2·269
006	55	50	2·890	$2,0,\overline{58}$	5	5	4·534	$20\overline{8}$	21	26	0·077	$4,0,\overline{42}$	7	8	3·009
008	40	43	3·322	$2,0,\overline{56}$	9	9	4·889	$20\overline{6}$	10	12	5·969	$4,0,\overline{38}$	7	3	4·379
0,0,10	18	21	4·012	$2,0,\overline{54}$	12	12	6·213	$20\overline{4}$	31	32	5·458	$4,0,\overline{36}$	8	6	1·798
0,0,12	25	16	1·474	$2,0,\overline{52}$	12	12	0·960	$20\overline{2}$	96	107	5·572	$4,0,\overline{30}$	14	12	1·439
0,0,14	35	29	1·818	$2,0,\overline{50}$	11	9	1·606	200	87	100	2·889	$4,0,\overline{28}$	21	19	2·137
0,0,16	34	28	2·598	$2,0,\overline{48}$	21	19	2·207	202	21	25	0·578	$4,0,\overline{26}$	18	18	3·072
0,0,18	21	16	3·602	$2,0,\overline{46}$	78	71	2·378	204	26	33	1·226	$4,0,\overline{24}$	69	70	5·139
0,0,20	22	21	5·412	$2,0,\overline{44}$	47	56	5·219	206	23	20	2·116	$4,0,\overline{22}$	21	28	2·715
0,0,22	111	119	0·380	$2,0,\overline{42}$	15	17	5·731	208	14	13	3·104	$4,0,\overline{18}$	9	13	5·985
0,0,24	41	38	2·022	$2,0,\overline{40}$	6	11	0·269	2,0,10	15	6	4·704	$4,0,\overline{16}$	11	12	0·603
0,0,26	33	28	2·269	$2,0,\overline{38}$	7	13	2·405	2,0,12	20	16	0·213	$4,0,\overline{14}$	9	6	1·120
0,0,28	25	23	2·427	$2,0,\overline{36}$	15	18	3·811	2,0,14	17	11	0·402	$4,0,\overline{12}$	8	13	2·427
0,0,30	14	14	3·426	$2,0,\overline{34}$	16	22	5·077	2,0,16	11	16	5·840	$4,0,\overline{10}$	7	14	3·322
0,0,32	9	6	5·162	$2,0,\overline{32}$	15	17	5·567	2,0,18	15	23	6·064	$40\overline{8}$	6	10	3·914
0,0,34	9	10	2·186	$2,0,\overline{30}$	18	11	1·071	2,0,20	38	45	0·232	$40\overline{2}$	14	8	2·665
0,0,36	8	4	4·118	$2,0,\overline{28}$	33	35	1·982	2,0,22	61	57	2·919	400	12	11	5·977
0,0,38	7	6	5·636	$2,0,\overline{26}$	55	60	2·554					4,0,20	22	27	2·538
0,0,40	6	2	2·562	$2,0,\overline{24}$	108	109	2·795	$4,0,\overline{72}$	5	6	5·669	4,0,22	18	13	6·101
0,0,42	7	2	1·944	$2,0,\overline{22}$	94	94	5·287	$4,0,\overline{70}$	5	6	6·005				
0,0,44	33	39	3·667	$2,0,\overline{20}$	38	38	5·453	$4,0,\overline{68}$	14	15	1·496	$6,0,\overline{58}$	6	4	4·846
0,0,46	15	17	0·839	$2,0,\overline{18}$	15	24	6·071	$4,0,\overline{52}$	8	5	5·176	$6,0,\overline{26}$	17	16	5·153
0,0,48	7	2	5·651	$2,0,\overline{16}$	15	8	1·252	$4,0,\overline{50}$	12	10	0·904	$6,0,\overline{24}$	28	27	1·792
				$2,0,\overline{14}$	21	16	2·931	$4,0,\overline{48}$	14	12	1·424	$60\overline{2}$	12	9	1·609
$2,0,\overline{68}$	8	4	2·480	$2,0,\overline{12}$	24	16	4·763	$4,0,\overline{46}$	34	25	5·130				

compared with the yz-projection. The final parameters are shown in Table 1. The final R-value was 0·16. These calculations were made on a Ferranti 'Mercury' computer using programs described by Mills & Rollett (1961). The observed and calculated structure factors are shown in Tables 2 and 3 and the electron-density maps in Figs. 1 and 2.

Table 4. *Bond lengths and angles in ethyl stearate*

Bond lengths		Interatomic angles	
$C_{18}-C_{17}$	1·57 Å	$C_{18}-C_{17}-C_{16}$	104°
$C_{17}-C_{16}$	1·52	$C_{17}-C_{16}-C_{15}$	106
$C_{16}-C_{15}$	1·61	$C_{16}-C_{15}-C_{14}$	113
$C_{15}-C_{14}$	1·52	$C_{15}-C_{14}-C_{13}$	109
$C_{14}-C_{13}$	1·50	$C_{14}-C_{13}-C_{12}$	108
$C_{13}-C_{12}$	1·50	$C_{13}-C_{12}-C_{11}$	114
$C_{12}-C_{11}$	1·58	$C_{12}-C_{11}-C_{10}$	115
$C_{11}-C_{10}$	1·43	$C_{11}-C_{10}-C_{9}$	111
$C_{10}-C_{9}$	1·60	$C_{10}-C_{9}-C_{8}$	110
$C_{9}-C_{8}$	1·51	$C_{9}-C_{8}-C_{7}$	112
$C_{8}-C_{7}$	1·60	$C_{8}-C_{7}-C_{6}$	113
$C_{7}-C_{6}$	1·54	$C_{7}-C_{6}-C_{5}$	106
$C_{6}-C_{5}$	1·57	$C_{6}-C_{5}-C_{4}$	101
$C_{5}-C_{4}$	1·55	$C_{5}-C_{4}-C_{3}$	111
$C_{4}-C_{3}$	1·49	$C_{4}-C_{3}-C_{2}$	117
$C_{3}-C_{2}$	1·62	$C_{3}-C_{2}-C_{1}$	124
$C_{2}-C_{1}$	1·53	$C_{2}-C_{1}-O_{2}$	108
$C_{1}-O_{2}$	1·15	$O_{2}-C_{1}-O_{1}$	125
$C_{1}-O_{1}$	1·36	$C_{2}-C_{1}-O_{1}$	114
$O_{1}-C_{01}$	1·37	$C_{1}-O_{1}-C_{01}$	138
$C_{01}-C_{02}$	1·52	$O_{1}-C_{01}-C_{02}$	140

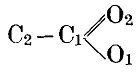
In Table 4 the bond lengths and angles are given. The mean value of the C–C bond lengths in the long chain is 1·54 Å with a maximum deviation of 0·11 Å and the mean value of the angles between these bonds is 110° with a maximum deviation of 9°. The standard deviations were calculated with Cruickshank's formula (Cruickshank, 1949, 1953). The average value for an atom considered as spherically symmetric is $\sigma = 0{\cdot}034$ Å, for a bond $\sigma = 0{\cdot}05$ Å, and for an angle between bonds $\sigma = 3°$.

Discussion

Several unit cells are shown in Figs. 3 and 4 projected along the a- and b-axis respectively. It is seen that the molecules form sheets as in many other long-chain structures. The long chains have an angle of tilt towards the end group planes of 64°. The shortest distance between carbon atoms across the contact planes is 3·66 Å.

The long chains have their planes in {110} which causes the crystals to be bounded by {110} planes thus giving rhombic plates with usual (001)-cleavage. The acute angle calculated from the cell dimensions is 74° 10′ which compares well with the measured value of 74° 25′.

At the carboxyl group there is a twist so that the OC_2H_5 group lies in a plane approximately parallel to the ac-plane. This is shown in Fig. 5 where the unit cell is seen along the c-axis (which is pointing down from the plane of paper). The lines of intersection with the a^*b-plane are shown for the best least-squares planes through the main chain, the group



$$C_2-C_1\begin{smallmatrix}\nearrow O_2\\ \searrow O_1\end{smallmatrix}$$

and the group $C_1-O_1-C_{01}-C_{02}$. The centres of gravity for the different groups of atoms are also shown. The first and the third of these planes are very nearly parallel to the c-axis while the angle between the normal to the carboxyl group plane and the positive direction of the c-axis is 82°. The angles of tilt between the intersection lines shown and the *b*-axis are 42° for the chain plane and 71° for the carboxyl group (compared with 44° and 63° respectively in methyl stearate). For the alcohol chain the angle is 92°.

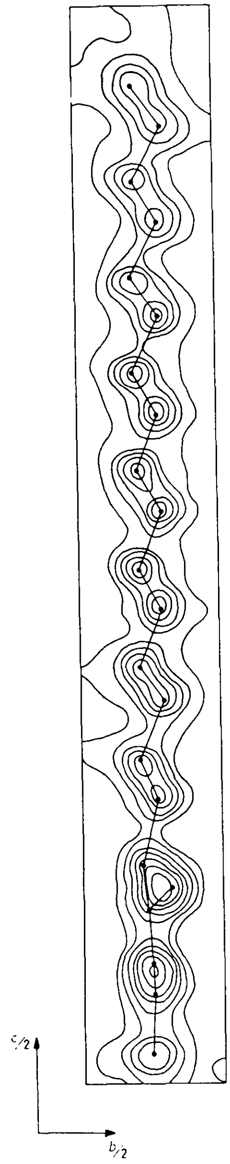


Fig. 1.

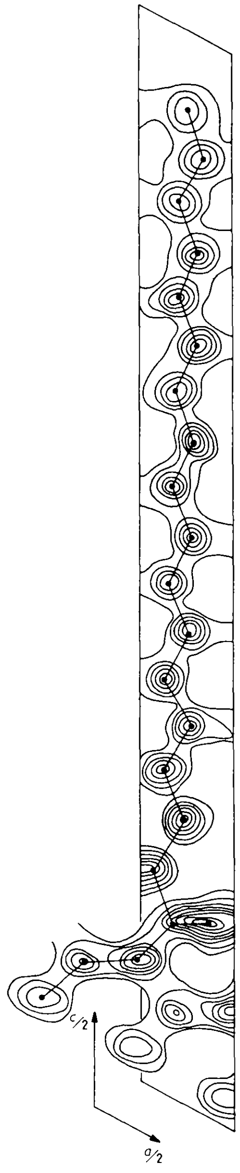


Fig. 2.

Fig. 1. Electron-density projection of ethyl stearate along the *a*-axis. Contours given at intervals of 1 e.Å^{-2} starting with 1 e.Å^{-2}.

Fig. 2. Electron-density projection of ethyl stearate along the *b*-axis. Contours given at intervals of 1 e.Å^{-2} starting with 2 e.Å^{-2}.

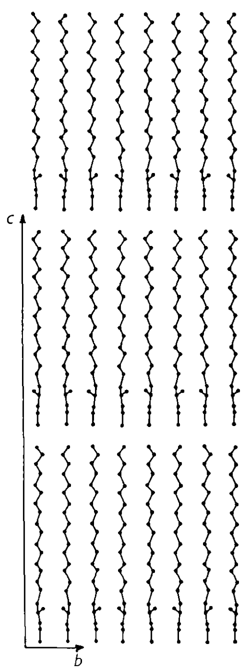


Fig. 3.

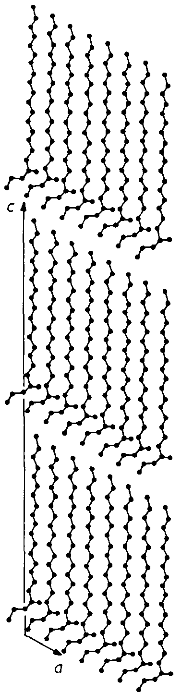
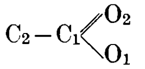


Fig. 4.

Fig. 3. Schematic view of ethyl stearate seen along the *a*-axis.

Fig. 4. Schematic view of ethyl stearate seen along the *b*-axis.

The atoms in the chain all lie within 0·08 Å from the plane except C_3 and C_2 which tend to the more vertical arrangement of the carboxyl group. The carboxyl group is not precisely planar; the sum of the bond angles is 347°. The maximum deviation from the least squares plane through



$$C_2-C_1\begin{matrix}\diagup O_2\\ \diagdown O_1\end{matrix}$$

is 0·21 Å. Because of the overlap between C_2, C_1 and O_2 in both projections the error in the coordinates might here be greater than indicated by the average standard deviations. The alcohol group C_1–O_1–C_{01}–C_{02} is planar within 0·04 Å.

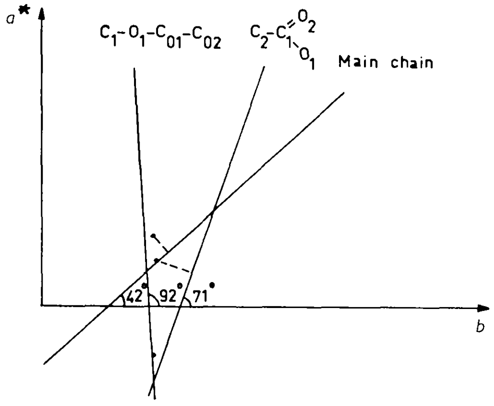


Fig. 5. Least-squares planes through different parts of the molecule.

Malkin (1933) has discussed the arrangement of the polar region in various types of esters and suggests that in ethyl esters the terminating C–C bond is perpendicular to the end-group contact plane while the terminating bond in the main chain tilts towards the end-group planes. It was supposed that the alcohol chain was a direct continuation of the main chain and then, without knowing the structure the perpendicular arrangement seemed probable. Malkin's suggestion was put forward to explain the alternation in the increments of the long spacing in a series of methyl-, ethyl-, propyl-, butyl- and amyl-esters of the same acid. The bent form now found does not have the terminating bond in the alcohol chain quite perpendicular to the end group plane, but nevertheless it fits Malkin's view.

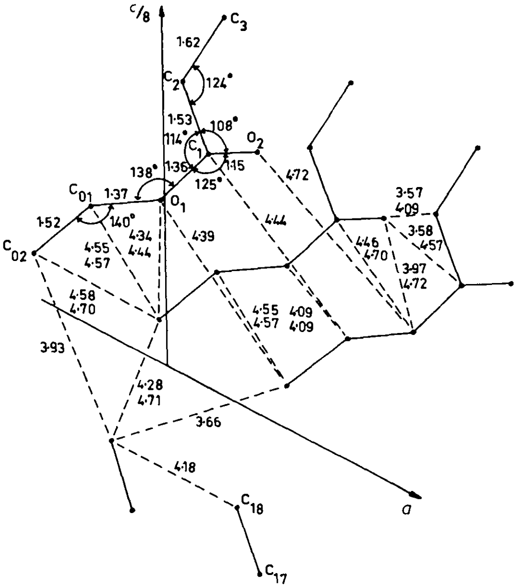


Fig. 6. Detail of the ester group region.

In Fig. 6 a schematic view of the ester group region is shown with bond lengths and angles and some contact distances. (Where two distances are given together they refer to atoms displaced one *b*-axis from each other). Here it is obvious that the angles at O_1 and C_{01} are greater than normal. A state of disorder or an appreciable oscillation of the alcohol chain might well give an effect of that kind in the *xz*-projection. The high values of the temperature factor for these atoms (Table 1) also support this view. Because of the short length of this part of the molecule and the different kinds of bonds involved it is difficult to speak of any chain packing in the usual way but schematically the chain axes form an hexagonal arrangement with the dimension $a = 3{\cdot}7$ Å instead of the value 4·3 Å corresponding to an hexagonal close-packing of rotating hydrocarbon chains. This small dimension is quite reasonable since there are no hydrogens on one of the atoms (O_1) and at the same time C_{02} is in contact with a neighbouring chain only on one side and in the other direction projects into the end group contact layer.

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