187.   *Infrared Spectra and Crystallinity.   Part V.*   Dimethyl and Diethyl Esters of αω-Dicarboxylic Acids.*

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Infrared spectra of liquid and crystalline dimethyl and diethyl alkane-dicarboxylates, $[CH_2]_n(CO_2R)_2$ (where $n = 2$—8, 10, 14) have been measured from 3500 to 670 cm.$^{-1}$.

The spectra of the liquids are blurred but some bands appear which do not occur in the spectra of the crystals.   These are probably due to non-*trans*-configurations of the $[CH_2]_n$ chain.   In the crystalline state, however, bands are sharper and several new bands appear, mostly in the 1000—700 cm.$^{-1}$ region.   These are attributed for the most part to an approximately *trans*-configuration of the $[CH_2]_n$ chain.

PREVIOUS work on polyesters,[1] di-[2] and mono-carboxylic[3] acids, paraffins,[4–6] and alkyl[8] and polymethylene halides[7–11] has established that spectral differences are generally observed between liquid and crystalline states of aliphatic compounds containing a $[CH_2]_n$ chain (where $n \geqslant 2$).

This investigation extends the work on dicarboxylic acids[2] to the dimethyl and diethyl esters.

EXPERIMENTAL

The esters examined were either good-quality commercial materials which were redistilled if the b. p.s differed appreciably from literature values, or were prepared on a semimicro-scale from the appropriate acid and alcohol (fluorosulphuric acid being used as catalyst).   Distillation

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* The Infrared Spectra of Some Monocarboxylic Acids, *J.*, 1957, 1746, is regarded as Part IV.

[1] Davison and Corish, *J.*, 1955, 2428.
[2] Corish and Davison, *ibid.*, p. 2431.
[3] Corish and Chapman, *J.*, 1957, 1746.
[4] Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261.
[5] Sheppard and Simpson, *Quart. Reviews*, 1953, **7**, 19.
[6] Brown, Sheppard, and Simpson, *Phil. Trans.*, 1954, A, **247**, 35.
[7] Brown and Sheppard, *Discuss. Faraday Soc.*, 1950, **9**, 144.
[8] *Idem, Trans. Faraday Soc.*, 1954, **50**, 535.
[9] *Idem, ibid.*, p. 1164.
[10] *Idem, ibid.*, 1952, **48**, 128.
[11] *Idem, Proc. Roy. Soc.*, 1955, A, **231**, 555.

or recrystallisation until constant spectra were obtained yielded products with b. p.s or m. p.s in good agreement with the literature (see Table 4).

Spectroscopic measurements were made with a Grubb-Parsons S.3 spectrometer (with sodium chloride prism) and a D.B.1 double-beam radiation unit.

Spectra of crystals of the esters normally liquid at, or just above, room temperature were obtained in a transmission type " cold cell ",[3] solid carbon dioxide–alcohol being used as refrigerant.

The spectra of esters solid at room temperature were measured by the potassium chloride disc technique; by heating the discs just above the m. p. of the ester in a " hot cell," [1, 2] the spectra of the molten state were obtained. After the diesters had recrystallised, the spectra were re-measured to check that no decomposition had occurred.

DISCUSSION

The previously reported [1-11] spectra of molecules containing a $[CH_2]_n$ chain fall into two main classes: (*a*) Those which have more bands in the liquid-state spectra and fewer in the crystalline-state spectra, *e.g.*, paraffins, alkyl halides, and polymethylene halides; [4-11] only one configuration, the most energetically stable, which is usually *trans*, exists in the solid, and this and other rotational isomers exist in the liquid. (*b*) Those which have more and sharper bands in the crystalline-state spectra and fewer and more blurred bands in the liquid-state spectra, *e.g.*, polyesters,[1] di- [2] and mono- [3] carboxylic acids, and glycols.[12] The *trans*-configuration usually occurs in the solid, and the absence of sharp bands in the liquid is attributed to " non-discrete rotational isomerism." [2]

The general changes in spectra of the diesters on melting are similar to those observed in the polyesters [1] and dicarboxylic acids,[2] *i.e.*, a marked broadening of bands leading to similar spectra for adjacent members of the series. However, unlike the polyesters and dicarboxylic acids, the diesters (especially the lower members) show some additional bands in the liquid which are assigned to discrete non-*trans*-configurations. In this respect the diesters resemble the long-chain paraffins and dihalides.

The occurrence of non-discrete rotational isomerism has been attributed [2] to strong intermolecular forces which are comparable to the barriers to free rotation about the C–C bonds. The intermolecular forces in diesters due to interactions of strong permanent dipoles are intermediate in strength between the hydrogen bonding in dicarboxylic acids and the purely van der Waals forces in paraffins, and the observed spectra of the liquid diesters are consistent with a combination of discrete and non-discrete configurations.
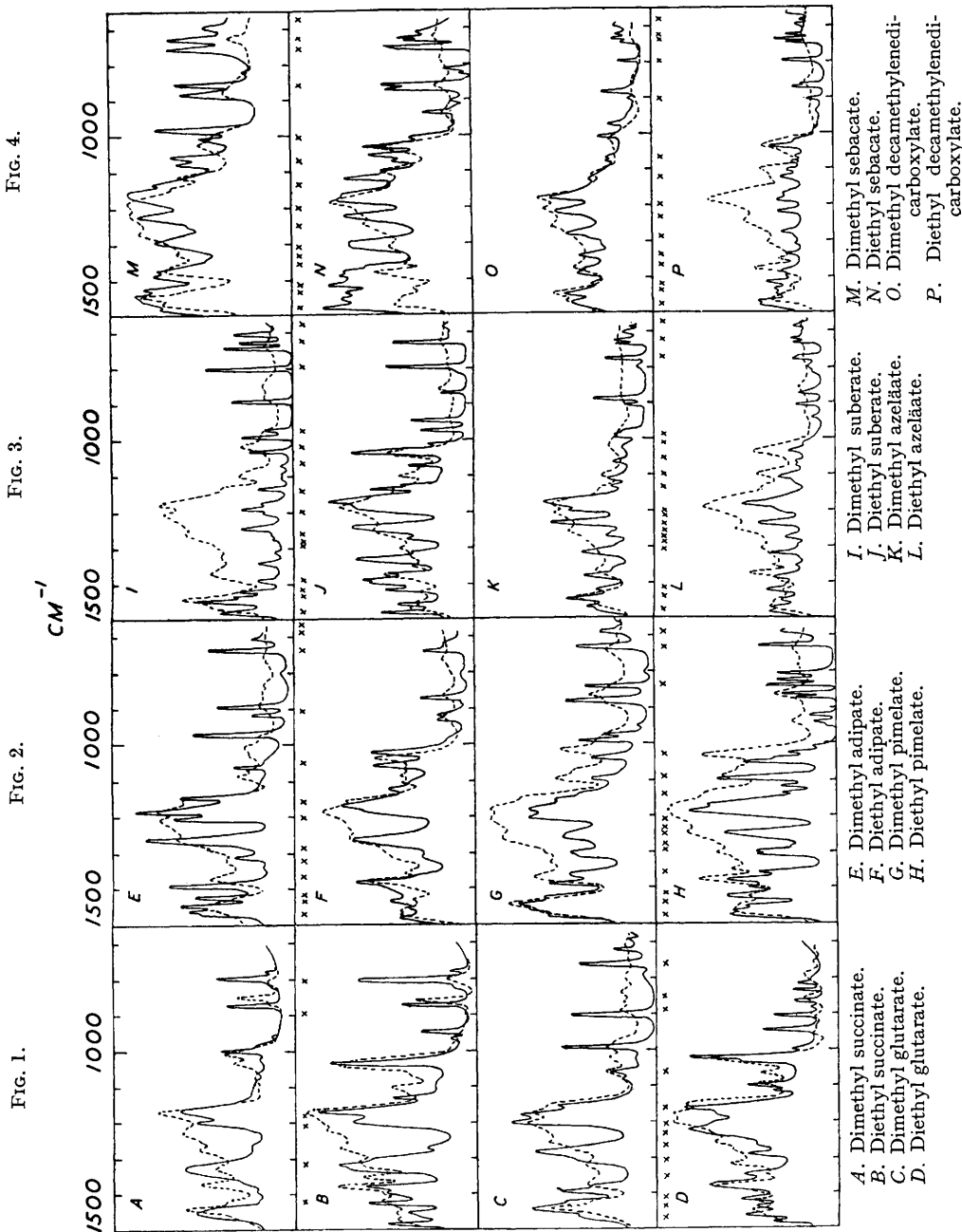
The absorptions which only appear in spectra of liquids are less noticeable in spectra of the higher diesters, in which the number of possible rotational isomers is greater.

The spectra of the liquid and the crystalline diesters (from 1500 to 670 cm.$^{-1}$) are shown in Figs. 1—5, the absorptions of the corresponding crystalline acids [2] (other than the 930 cm.$^{-1}$ δOH absorption) being shown by crosses. It is evident that the spectra of the crystalline esters and acids are very similar, particularly in the region below 1000 cm.$^{-1}$, and this confirms the expected *trans*-configuration of the esters. Diethyl glutarate is an exception as its crystalline-state spectrum differs markedly from those of the corresponding methyl ester and acid. It is probable therefore that diethyl glutarate crystallises in a non-planar configuration.

Two different spectra of both dimethyl and diethyl pimelate were obtained under different conditions and are commented on later. The spectra which are thought to be more representative of an all-*trans*-configuration are shown in Fig. 2.

C–H *Stretching Vibrations* (3050—2800 cm.$^{-1}$).—No pronounced differences occur between spectra of the crystalline and the liquid diesters except that, in the former, the bands are sharper. As a lithium fluoride prism was not used for this region no attempt will be made to report or interpret any small changes.

[12] Corish and Davison, to be published.

FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

CM^{-1}

A. Dimethyl succinate.
B. Diethyl succinate.
C. Dimethyl glutarate.
D. Diethyl glutarate.

E. Dimethyl adipate.
F. Diethyl adipate.
G. Dimethyl pimelate.
H. Diethyl pimelate.

I. Dimethyl suberate.
J. Diethyl suberate.
K. Dimethyl azeläate.
L. Diethyl azeläate.

M. Dimethyl sebacate.
N. Diethyl sebacate.
O. Dimethyl decamethylenedi-
   carboxylate.
P. Diethyl decamethylenedi-
   carboxylate.

In Figs. 1—5: ——— = crystalline, - - - - = molten, and × indicates the corresponding bands for the dicarboxylic acids.

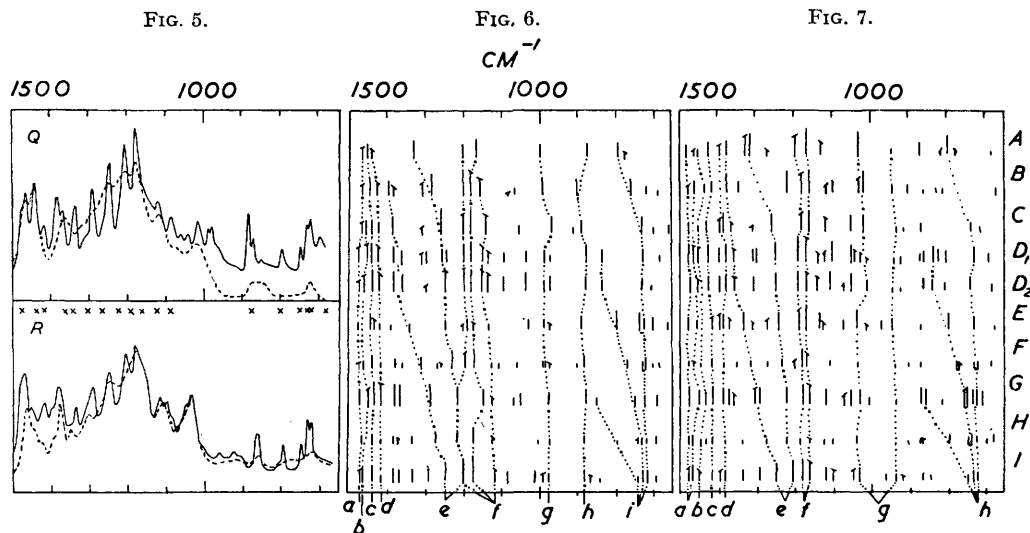Fig. 5.   Fig. 6.   Fig. 7.

$$CM^{-1}$$

FIG. 5.

Q. Dimethyl thapsate (tetradecamethylenedicarboxylate).
R. Diethyl thapsate (tetradecamethylenedicarboxylate).

FIG. 6.   *Dimethyl esters.*

A. Succinate.
B. Glutarate.
C. Adipate.
D. Pimelate $\begin{cases} D1, \text{ tttt confign.} \\ D2, \text{ tttg confign.} \end{cases}$
E. Suberate.
F. Azeläate.
G. Sebacate.
H. Decamethylenedicarboxylate.
I. Thapsate.

a. $\delta(CH_2)$ Bending vibrations.
b. $\delta_a(CH_3O)$ Vibrations.
c. $\delta_s(CH_3O)$ Vibrations.
d. $\delta(CH_2 \cdot CO)$ Vibrations.
e. $\delta(CH_2)$ Wagging vibrations.
f. $\nu C{-}O$ and $\nu C{-}O{-}C$ Vibrations.
g. $\delta(CH_3)$ Rocking vibrations.
h. $\delta(CH_3)$ Rocking vibrations or CO_2CH_3 vibrations.
i. $\delta(CH_2)$ Rocking vibrations.

FIG. 7.   *Diethyl esters.*

A. Succinate.
B. Glutarate.
C. Adipate.
D. Pimelate $\begin{cases} D1, \text{ tttt confign.} \\ D2, \text{ tttg confign.} \end{cases}$
E. Suberate.
F. Azeläate.
G. Sebacate.
H. Decamethylenedicarboxylate.
I. Thapsate.

a. $\delta(CH_2)$ Bending vibrations.
b. $\delta_a(CH_3)$ Vibrations.
c. $\delta(CH_2CO)$ Vibrations.
d. $\delta_s(CH_3)$ Vibrations.
e. $\delta(CH_2)$ Wagging vibrations.
f. $\nu C{-}O$ and $\nu C{-}O{-}C$ Vibrations.
g. Ethyl vibrations.
h. $\delta(CH_2)$ Rocking vibrations.

C=O *Stretching Vibrations* (1800—1700 cm.$^{-1}$).—Small frequency shifts of the C=O stretching absorptions occur on going from the liquid to the crystalline state. These are listed in Table 1; malonic and oxalic diesters are also included (for liquid only), and show a splitting of the carbonyl absorptions. However, for $n \geqslant 2$ both the diacids and diesters show single carbonyl bands, indicating only weak coupling across two or more carbon atoms. This is in contrast with the strong coupling across oxygen which results in a split of *ca.* 25 cm.$^{-1}$ for diacyl peroxides [13] and *ca.* 60 cm.$^{-1}$ for acid anhydrides [14] (cf. 30 cm.$^{-1}$ for malonic acid [25]).

There are no consistent differences in ν(C=O) between the crystalline and liquid states, unlike the di- and mono-carboxylic acids in which ν(C=O) was greater in the liquid owing

[13] Davison, *J.,* 1951, 2456.
[14] Randall, Fowler, Fuson, and Dangl, " Infra-red Determination of Organic Structures," Van Nostrand, New York, 1949, 20.

to a reduction in hydrogen bonding. In the dimethyl esters, however, the even members (except $n = 2$) in both crystalline and liquid states have C=O frequencies which are higher than those in the odd members. This is similar to the even–odd alternation discussed by Sinclair *et al.*[15] for monocarboxylic acids with chains longer than $[CH_2]_{11}$ in which the acids with an even $H \cdot [CH_2]_n$ chain have maxima at 1705 cm.$^{-1}$ and the acids with an odd $H \cdot [CH_2]_n$ chain have maxima at 1698—1701 cm.^{1}.

TABLE 1. *Frequency of carbonyl absorptions,* $\nu(C \dot{:} O)$ *(cm.$^{-1}$).*

		Dimethyl esters			Diethyl esters		
n		cryst.	liquid	$\delta\nu$	cryst.	liquid	$\delta\nu$
0	Oxalate	—	—	—	—	1754, 1774	—
1	Malonate	—	1750, 1768	—	—	1750, 1764	—
2	Succinate	1742	1751	+9	1743	1753	+10
3	Glutarate	1740	1749	+9	1730	1741	+11
4	Adipate	1754	1752	−2	1738	1749	+11
5	Pimelate *	I II	1749	+9	I II	1739	+ 1
		1740 (1741)			1738 (1744)		
6	Suberate	1751	1749	−2	1743	1741	− 2
7	Azeläate	1745	1743	−2	1750	1745	− 5
8	Sebacate	1750	1755	+5	1740	1747	+ 7
10	Decamethylenedicarboxylate	1753	1753	0	1745	1733	−12
14	Thapsate	1750	1755	+5	1750	1743	− 7
	Even ($n \geqslant 4$) =	1750—1754	1749—1755	—	1738—1750	1733—1753	—
	Odd ($n \geqslant 3$) =	1740—1745	1743—1749	—	1730—1750	1739—1745	—

* I = tttt Configuration, II = tttg configuration; see p. 932.

C–H *Bending Vibrations* (1500—1300 cm.$^{-1}$).—In the dicarboxylic acids,[2] there are three distinct bands in the 1500—1400 cm.$^{-1}$ region at 1475, 1435, and 1415 cm.$^{-1}$ which are assigned respectively to a normal CH_2 bending vibration, a dimeric carboxyl vibration, and a CH_2 bending mode, adjacent to a C=O group. In the diesters we expect the bands at *ca.* 1475 and *ca.* 1415 cm.$^{-1}$ to persist, together with absorptions arising from the methyl and ethyl groups.

The dimethyl esters all show a medium absorption at 1435—1445 cm.$^{-1}$ in both crystalline and amorphous phases, which is assigned[16] to the symmetrical bending mode of a methyl group attached to an oxygen atom, $\delta_s(CH_3O)$. The weaker $\delta_a(CH_3O)$ at *ca.* 1460 cm.$^{-1}$ is not resolved in most cases owing to overlapping $\delta(CH_2)$ bending and $\delta_s(CH_3O)$ vibrations. However, a shoulder at *ca.* 1462 cm.$^{-1}$ in the spectrum of dimethyl succinate is probably due to this mode.

The diethyl esters show a more complex series of bands in this region. Absorptions at *ca.* 1480 and *ca.* 1420 cm.$^{-1}$ are assigned respectively to a normal CH_2 bending vibration and a bending mode of CH_2 adjacent to a carbonyl group as for the dimethyl esters. The band at *ca.* 1480 cm.$^{-1}$ is split in the longer-chain diethyl esters. This is attributed to CH_2 groups in two different environments, in the terminal ethyl groups and in the polymethylene chain. Bands at *ca.* 1380 cm.$^{-1}$ ($n = 5$—14) are attributed to $\delta_s(CH_3)$ and a variable series of absorptions at *ca.* 1450 cm.$^{-1}$ is assigned to $\delta_a(CH_3)$. These two sets of absorptions are common to all paraffin-type compounds.[5] In the shorter-chain esters ($n = 2$—4), the $\delta_s(CH_3)$ is shifted from 1380 cm.$^{-1}$ and appears[17,18] at *ca.* 1395 cm.$^{-1}$ owing probably to interaction with wagging vibrations of the polymethylene chain. Two series of CH_2 wagging vibrations can be traced in the diethyl esters with origins at 1378 and 1321 cm.$^{-1}$ in diethyl succinate (cf. alkyl bromides[8] and monocarboxylic acids[3]). Bands at 1376 and 1337 cm.$^{-1}$ in the spectrum of liquid diethyl malonate may also form part of this distribution.

Two similar series of CH_2 wagging vibrations can be traced in the spectra of the dimethyl

[15] Sinclair, McKay, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2570.
[16] Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1465.
[17] Nolin and Jones, *Canad. J. Chem.*, 1956, **34**, 1382.
[18] *Idem, ibid.*, p. 1392.

esters with origins at 1315 cm.$^{-1}$ in the spectrum of dimethyl succinate and 1395 cm.$^{-1}$ in that of dimethyl glutarate.

The frequencies of bands in these series are listed in Table 2. The assignments in this Table are strengthened by the fact that, for the most part, corresponding bands appear in the spectra of the dicarboxylic acids (see crosses in Figs. 1—5). In the longer-chain diesters, more especially the dimethyl esters, the lower-frequency series overlaps the ν(C–O) vibrations.

TABLE 2.   δCH$_2$ *Wagging frequencies* (*crystalline state*) (cm.$^{-1}$).

	Dimethyl	Diethyl	Dimethyl	Diethyl
$n = 1$	—	1376 *	1346 *	1337 *
$n = 2$	—	1378	1315	mean = 1321 (1327, 1315)
$n = 3$	1395	— †	mean = 1293 (1304 sh, 1282)	— †
$n = 4$	1390	1367	1262	1260
$n = 5$	I mean = 1374 (1385, 1363)	I 1359	I mean = 1252 (1258, 1247 sh)	I 1249
$n = 6$	1340	1330	1246	1240
$n = 7$	1315	1319	1233	1235
$n = 8$	1290	mean = 1300 (1305, 1294)	1220 ‡	1222
$n = 10$	1275	1275	1215 ‡	1220
$n = 14$	1249	1250	1205 ‡	1205

* Liquid.   I = tttt Configuration (see below).
† Not *trans*.   ‡ Overlap C–O vibrations.

Absorptions below 1300 *cm.*$^{-1}$.—Bands at *ca.* 1170—1180 and *ca.* 1200 cm.$^{-1}$ in the spectra of the dimethyl esters and at *ca.* 1180—1190 and 1165—1170 cm.$^{-1}$ in those of the diethyl esters are assigned to ν(C–O) and ν(C–O–C) vibrations.[15, 20] In the longer-chain diesters ($n = 8$—14), these absorptions overlap the δCH$_2$ wagging distribution, resulting in slightly anomalous frequencies.

Comparison of the crystalline-state spectra of the diesters with those of the corresponding dicarboxylic acids supports the assignment of bands at *ca.* 950 and 1030 cm.$^{-1}$ in the spectra of the diethyl esters to absorptions characteristic of ethyl groups. The dimethyl esters have absorptions at 880 and 990 cm.$^{-1}$ which are attributed to methyl absorptions, the latter to a methyl rocking mode [17, 19] and the former possibly to a methoxycarbonyl vibration.[17, 19] These assignments are confirmed by a comparison of the spectra of some simple esters, *viz.*, methyl and ethyl formate, methyl and ethyl acetate, methyl and ethyl benzoate, etc.[20]

δ[CH$_2$]$_n$ *Rocking Vibrations.*—In the crystalline-state spectra of both the dimethyl and the diethyl esters, three series of absorptions in the 900—700 cm.$^{-1}$ region can be traced which are very similar to those observed in the di- and mono-carboxylic acids of corresponding chain lengths. These are assigned to δ[CH$_2$]$_n$ rocking modes of the *trans*-zigzag chain. Diethyl glutarate is an exception, and this is taken as evidence for this ester's having a non-*trans*-configuration in the crystalline state.

Crystalline dimethyl and diethyl pimelate exhibit two different spectra depending upon the conditions of crystallisation. These differences may be due to two polymorphic modifications of which those with the lower δ[CH$_2$]$_n$ frequency, *i.e.*, 731 cm.$^{-1}$ for the dimethyl ester and 728 cm.$^{-1}$ for the diethyl ester, are taken as having the planar *trans*-configuration. The higher frequencies, *i.e.*, 734 and 737 cm.$^{-1}$ for the dimethyl and the diethyl esters respectively, probably correspond to a slightly twisted planar tttt configuration or to a tttg isomer (t = *trans*, g = *gauche* [11]); any other isomer would have its main rocking mode at a higher frequency than that observed. A similar metastable polymorph was reported for glutaric acid.[2]

[19] Günthard, *Helv. Chim. Acta*, 1953, **36**, 1149.
[20] Thompson and Torkington, *J.*, 1945, 640.

The lowest series of $[CH_2]_n$ rocking absorptions for the diesters are listed in Table 3, together with those for the corresponding dicarboxylic acids,[2] polyesters,[1] and hydrocarbons.[5, 6]

TABLE 3. $\delta[CH_2]_n$ *Rocking frequencies for* $X \cdot [CH_2]_n \cdot X$ *type molecules.*

(cm.$^{-1}$)

			X = CO$_2$Me		X = CO$_2$Et		
n	X = H	X = CO$_2$H	Cryst.	Liquid	Cryst.	Liquid	Polyesters
2	822	804	797 sh, 778	805	819 sh, 800, 777 sh	804	800—810
3	748	754	760, 720	751	815 †	754	—
4	732	733	735	750	735	733	733—740
5	728	731	731 (734 *)	741	728 (737 *)	731	—
6	726	725	728	732	730	725	—
7	723	726	724	726	723	726	—
8	722	722	730	724	724	722	720—725
9	721	—	—	—	—	—	—
10	720	723	720	722	723	723	—
11	720	—	—	—	—	—	—
12	722	—	—	—	—	—	—
13	723	—	—	—	—	—	—
14	722	727, 721	731, 720	720	730, 720	721	—
15	—	—	—	—	—	—	—
16	—	727, 720	—	—	—	—	—

* Slightly twisted *trans*-chain or tttg.   † Non-*trans*-configuration, probably tg.

TABLE 4. *Physical constants of esters.*

	Literature		Observed	
	B. p./mm.	M. p.	B. p./mm.	M. p.
Dimethyl succinate	195·2°/760	19°	200°/760 145°/150	—
Diethyl ,,	217·7°/760	−21°	212°/760	—
Dimethyl glutarate	222°/760 84·5°/6	—	217°/760 105°/20	—
Diethyl ,,	240°/760 103—104°/7	−24·1°	230°/760 115°/20	—
Dimethyl adipate	242°/760 112°/10	8° 0° *	235°/760 120°/20	—
Diethyl ,,	245°/760	—	238°/760	—
Dimethyl pimelate	257°/760 130—135°/17	—	255°/760 139°/23	—
Diethyl ,,	252—255°/748	—	282°/760 152°/15	—
Dimethyl suberate	268°/760 174—175°/13—20	−3·1°	270°/760 146—149°/20	—
Diethyl ,,	282°/763	5·9°	284°/760 160—163°/20	—
Dimethyl azeläate	281°/760 140—141°/9	—	281°/760 158—162°/22	—
Diethyl ,,	291°/760 148°/7·5	—	291°/760 155—165°/16	—
Dimethyl sebacate	293°/754 175°/20	26·4° (38°)	288°/763	—
Diethyl ,,	306°/773 158—159°/7·5	1·25° —	312°/760 179—181°/17	—
Dimethyl decamethylenedicarboxylate ...	167—169°/9	31°	—	26·7°
Diethyl ,, ,, ...	347°/760 204—205°/5	— *ca.* 16°	339°/760 210—212°/25	—
Dimethyl thapsate	—	51—52°	—	40°
Diethyl ,,	—	39°	—	30°

* Freezing point.

In the liquid-state spectra, however, the *trans*-$\delta[CH_2]_n$ rocking absorptions are still present, although weaker. In the longer-chain esters, only one band at *ca.* 722 cm.$^{-1}$ is present in the liquid-state instead of at least two in the crystalline-state spectra. As the splitting of the 722 cm.$^{-1}$ band in long-chain compounds is attributed to coupling of $\delta[CH_2]_n$

rocking vibrations between adjacent molecules in the orthorhombic unit cell,[21,22] the diesters may crystallise with this symmetry also. In particular, the crystalline diesters cannot have the hexagonal packing suggested for the fatty acids just below their melting points,[3,21,23] nor a triclinic unit cell.[24]

In the liquid-state spectra of the shorter-chain esters, several bands appear in the 1000—700 cm.[-1] region which are not present in the crystalline-state spectra. These are thought to arise from the presence of discrete rotational isomers in the liquid state, *e.g.*, dimethyl and diethyl glutarate can exist as tt, gt, and gg types.[11] As the chain is increased in length, the number of possible rotational isomers increases markedly, and in the longer-chain esters, a dynamic mixture of a large number of rotational isomers would give a spectrum which was indistinguishable from the product of non-discrete rotational isomerism.

[21] (*a*) Stein and Sutherland, *J. Chem. Phys.,* 1954, **22**, 1993; (*b*) Stein, *ibid.,* 1955, **23**, 734.
[22] Chapman, *Nature,* 1955, **176**, 216.
[23] Malkin, " Progress in the Chemistry of Fats and Other Lipids," Pergamon Press Ltd., London, 1952, **1**, 8.
[24] Chapman, Colloquium Spectroscopicum Internationale VI, Amsterdam, May, 1956.
[25] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954, 145.