330. *The Infrared Spectra of Some Monocarboxylic Acids.*

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Infrared spectra in the region 3500—670 cm.$^{-1}$ have been obtained for the simple normal monocarboxylic acids including dodecanoic acid and acids of shorter chain length in the liquid and the crystalline state. Characterisation of these acids by means of their crystalline spectra has been made possible, and information on the dimeric form and also on the shape of the $[CH_2]_n$ chain has been deduced.

THE infrared spectra of the crystalline forms of the longer-chain monocarboxylic acids (C_{14}—C_{21}) have been discussed by Sinclair *et al.*[1] and Jones *et al.*,[2] who pointed out the existence of characteristic groups of bands in the 1180—1350 cm.$^{-1}$ region which could be used as a means of identifying individual acids. In the present paper the infrared spectra of the lower members of the monocarboxylic acid series in the liquid and the crystalline state are presented and discussed. Such characterisation in the region 1180—1350 cm.$^{-1}$ has been extended, and supplemented by the finding of series of bands in the 900—720 cm.$^{-1}$ region.

EXPERIMENTAL

The acids examined had either been prepared in the Unilever or the Dunlop Research laboratories, *e.g.*, dodecanoic (m. p. 43·95°), decanoic (m. p. 30·6°), and octanoic (m. p. 16·4°), or were distilled fractions of good-quality commercial acids, *e.g.*, acetic (b. p. 118°), propionic (b. p. 141°), butyric (b. p. 163°), valeric (b. p. 186°), hexanoic (b. p. 202°), heptanoic (b. p. 211°), and nonanoic (b. p. 253°).

The spectra of acids crystalline at room temperature were obtained in the normal manner between rock-salt plates. The spectra of such acids in the liquid state were obtained by means of a heated cell.

For crystalline-state spectra the acids normally liquid at room temperature were obtained as capillaries by using a transmission-type low-temperature cell with solid carbon dioxide–alcohol and liquid nitrogen as refrigerants. The spectrometer was a Grubb-Parsons S.3. double-beam instrument.

The spectra are shown in Figs. 1 and 2.

DISCUSSION

Spectral changes occurring on transition from the liquid to the crystalline state may be due to the effect of the imposed symmetry of the unit cell, to rotational isomerism, or to changes in hydrogen bonding. With respect to changes due to the symmetry of the unit cell, it is important to take polymorphism into account.

Even-membered fatty acids occur in three modifications, A, B, and C, giving different long spacings decreasing in that order. The fused even-membered acids, *e.g.*, dodecanoic, always crystallise in the C form.[3] This form has been shown to be of monoclinic symmetry with orthorhombic packing of the hydrocarbon chains. In dodecanoic acid the chains are considered to be bent and not strictly in the orthorhombic sub-cell.

The polymorphism of the odd-membered acids is more complex,[3] but the C′ form is always the first to separate from the molten acid and changes some 10—20° below the solidifying point into one or both of the forms A′ and B′. The A′-form is triclinic with the hydrocarbon chains packed roughly in the triclinic manner.[4] The chains are thought to be probably helically twisted in *n*-pentadecanoic and lower acids, but less twisted for the

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[1] Sinclair, McKay, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2570.

[2] Jones, McKay, and Sinclair, *ibid.*, p. 2575.

[3] Malkin, " Progress in the Chemistry of Fats and Other Lipids," Pergamon Press, London, 1952, Vol I, p. 10.

[4] von Sydow, *Acta Chem. Scand.*, 1955, **9**, 1119.

higher members. Form B′ has a symmetry similar to that of form A′, but the hydrocarbon chains are orthorhombically packed and deformed near the carboxyl groups;[4] there is unfortunately no information available for the lower members. It seems probable that the form from the melt for the odd-acids here examined will be the A′-form since this is the only form observed with tridecanoic acid.[4] Evidence about this for the lower members is not, however, available.

FIG. 1.

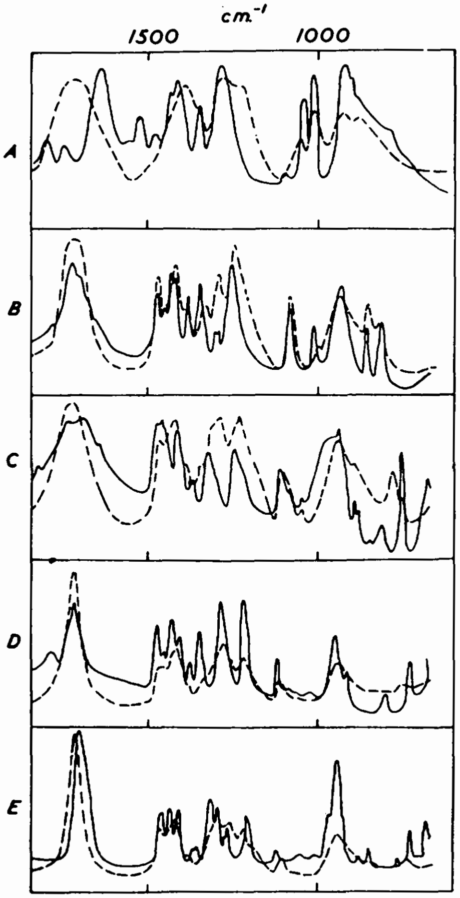
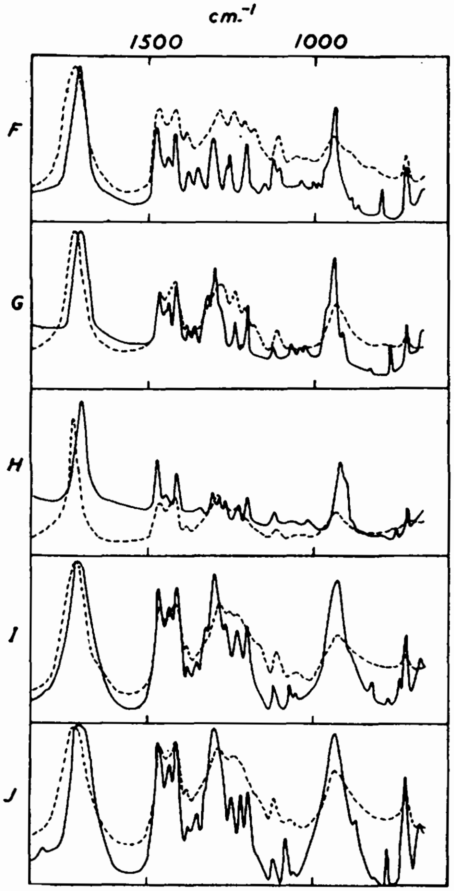


FIG. 2.



--- *Liquid.* —— *Solid.*

Acids : *A*, *acetic*; *B*, *propionic*; *C*, *butyric*; *D*, *valeric*; *E*, *hexanoic*; *F*, *heptanoic*; *G*, *octanoic*; *H*, *nonanoic*; *I*, *decanoic*; *J*, *dodecanoic*.

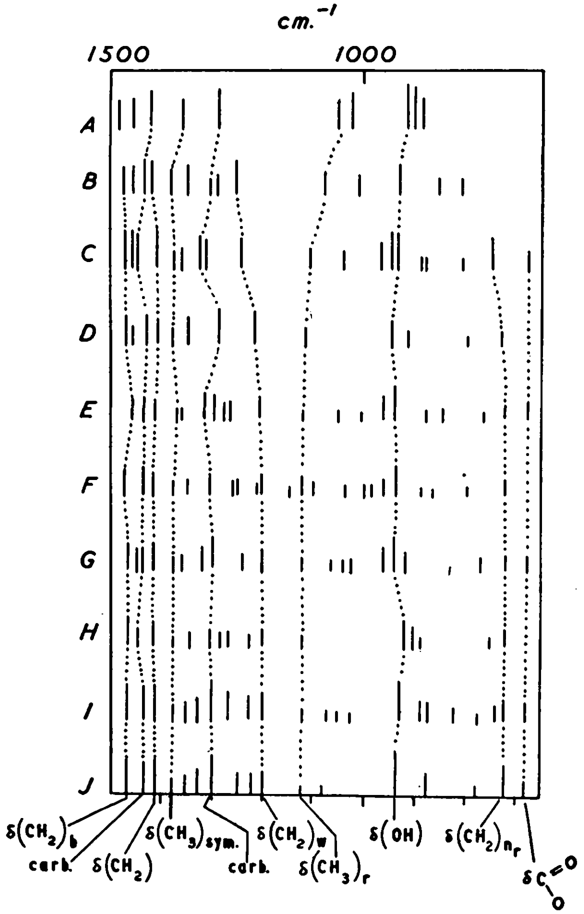
Therefore, when the spectra of the even and odd acids are compared, effects due to the different crystal structures may occur.

Figs. 1 and 2 show differences between the crystalline-state spectra of the even- and the odd-membered acids which may be due to this effect. Except acetic acid (which probably has a different crystalline form), all the even-membered acids show a band near 680 cm.$^{-1}$, and the odd-membered acids show an " analogous " band at a lower frequency. Further, the band near 1300 cm.$^{-1}$ (assigned to a dimeric carboxyl vibration) appears to alternate somewhat in frequency as we change from an odd- to an even-membered acid.

The type of effect imposed by the symmetry of the unit cell in the monocarboxylic acids is perhaps illustrated by the spectrum of the B-form of stearic acid. It is of interest that, under certain conditions, decanoic acid also exhibits two C=O bands (see Appendix).

Comparison between spectra for the liquid and the crystalline state of the acids shows that the region between 700 and 1350 cm.$^{-1}$ becomes much less defined for the liquid state. (This is presumably due to an increase in the number of possible rotational isomers in the liquid state, but it may also be that the thermal agitation in the liquid tends to make the twisting and the wagging modes of the additional CH_2 groups less well defined.)

FIG. 3.



Acids : A, acetic ; B, propionic ; C, butyric ; D, valeric ; E, hexanoic ; F, heptanoic ; G, octanoic ; H, nonanoic ; I, decanoic ; J, dodecanoic.

It should be noted that *X*-ray investigation of these monocarboxylic acids in the liquid and the crystalline state [5] led to the conclusion that the molecules are not arranged in the same way in the two states.

In general, crystallisation results in only small shifts in the C=O frequencies, except with acetic acid (see Table 1). No odd–even alternation of the carbonyl frequency as reported by Sinclair *et al.*[1] was observed. Slight shifts and additional bands in the 2500 – 3000 cm.$^{-1}$ ν-OH region (OH stretching) also result from crystallisation. These shifts are

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[5] Morrow, *Phys. Rev.*, 1928, **31**, 10.

possibly due to perturbation effects of the crystalline field or to small changes in hydrogen-bond distances. The additional bands in the 3000 cm.$^{-1}$ region may arise from combination of the OH stretching frequency with lattice vibrations or with low frequencies associated with the dimeric ring;[6] *e.g.*, in the spectrum of hexanoic acid these bands are at approximately constant frequency intervals of *ca.* 60 cm.$^{-1}$. An alternative explanation for the extra peaks may be in terms of summation bands due to appropriate combinations of fundamental vibrations of the coupled carboxyl groups of the dimeric molecules.[7]

TABLE 1.

	νC=O (cm.$^{-1}$)				νC=O (cm.$^{-1}$)		
Acid	liquid	crystalline	ν (cm.$^{-1}$)	Acid	liquid	crystalline	ν (cm.$^{-1}$)
Acetic	1715	1654	−61	Heptanoic ...	1724	1710	−14
Propionic ...	1725	1730, 1710 (sh)	+ 5?	Octanoic ...	1722	1702	−20
Butyric	1729	1740, 1705	+11?	Nonanoic ...	1726	1700	−26
Valeric	1722	1722	0	Decanoic ...	1716	1705	−11
Hexanoic ...	1721	1710	−11	Dodecanoic	1720	1705	−15

The band at 935 cm.$^{-1}$ increases in intensity on crystallisation whilst bands at 1435 and 1300 cm.$^{-1}$ become more intense and sharper. The band at 1435 cm.$^{-1}$ is almost absent in most of the liquid spectra.

X-Ray measurements on crystalline dodecanoic[8] and stearic acid[9] show that both exist in a dimeric form. Infrared measurements permit the deduction that most of the liquid acids also exist in the dimeric form. Hadži and Sheppard[10] have shown that, under these conditions, the dimeric carboxyl group gives rise to absorption bands at 1420 ± 20, 1300 ± 15, and 935 ± 15 cm.$^{-1}$. The first two bands correspond to closely coupled OH deformation and C–O stretching vibrations occurring in the plane of the $(CO_2H)_2$ dimeric ring; the third band is caused by the out-of-plane OH deformation vibration. As bands in these regions occur for all the liquid and solid monocarboxylic acids examined in the present investigation, it seems very probable that these acids also exist in the dimeric form in both the liquid and the solid state; however, formic acid exists as a polymer in both states.[11]

The bands in the solid-state spectra have been assigned to particular vibrations (although this is somewhat tentative in part, Fig. 3). Bands have been assigned to dimeric carboxyl vibrations following the asignments by Hadži and Sheppard.[10]

The bands at *ca.* 1435, 1300 ± 15, and 935 ± 15 cm.$^{-1}$ and a band near 680 cm.$^{-1}$ are thus assigned to dimeric carboxyl vibrations, the last being assigned to a $\delta\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}}$ angle deformation mode; a band occurring at *ca.* 1420 cm.$^{-1}$ is associated with a CH_2 group immediately adjacent to a carbonyl group,[12] and the remaining bands in the 1500—700 cm.$^{-1}$ region are tentatively assigned by analogy with similar classifications in hydrocarbons[13] and alkyl bromides.[14]

Two constant sets of bands at 1460 and 1380 cm.$^{-1}$ arise from CH_2 and CH_3 symmetric bending deformation modes respectively, and a variable set of bands at *ca.* 1450 cm.$^{-1}$ is probably due to CH_3 asymmetric bending modes. These are well-known frequencies and occur in the spectra of all paraffinic compounds. In alkyl bromides[14] a regular array of bands has been traced to its origin near 1250 cm.$^{-1}$ in the spectrum of the first member

[6] Davies and Evans, *J. Chem. Phys.*, 1952, **20**, 342.

[7] Bratoz, Hadži, and Sheppard, *Bull. sci. Conseil Acad. R.P.F., Yougoslavie*, 1953, **1**, 71.

[8] Vand, Morley, and Lomer, *Acta Cryst.*, 1951, **4**, 324.

[9] von Sydow, *ibid.*, 1955, **8**, 557.

[10] Hadži and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247.

[11] Chapman, *J.*, 1956, 225.

[12] Francis, *J. Chem. Phys.*, 1951, **19**, 942.

[13] (*a*) Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261; (*b*) *Phil. Trans. Roy. Soc.*, 1954, *A*, **247**, 35.

[14] Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 535.

of the series and shown to originate from CH_2 wagging vibrations. In the higher members frequencies split out from this origin towards higher and lower frequencies within the range 1200—1380 cm.$^{-1}$. In the monocarboxylic acids a similar distribution of frequencies occurs in this region. The origin of this distribution might be expected to occur in the spectrum of propionic acid and it is possible to trace a series of bands back to a band near 1250 cm.$^{-1}$ in this spectrum (see Fig. 3). Previously this band has been tentatively assigned to a dimeric carboxyl vibration [10] but the present assignment to a CH_2 wagging or twisting mode seems better, particularly since a band persists in this position even in the deuterated molecule. Whilst the analogy with the spectra of the alkyl bromides suggests that this distribution also arises from CH_2 wagging modes, this conclusion is not certain since no detailed assignment of dimeric propionic acid is yet available to show that the band at 1250 cm.$^{-1}$ arises from an in-plane vibration. Jones *et al.*[2] assign the distribution generally to CH_2 wagging and twisting modes.

A band at 1080 cm.$^{-1}$ in the spectrum of crystalline propionic acid is assigned to a methyl rocking mode. It may in fact correspond to both in-plane modes. The out-of-plane CH_3 rocking modes may give rise [14] to a band near 890 cm.$^{-1}$ but this region is covered by part of the absorption due to the (δOH) mode near 930 cm.$^{-1}$ and no significant series can be picked out. Series of bands in the 900—720 cm.$^{-1}$ region are attributed to CH_2 rocking modes. The most characteristic series of bands in the 720—810 cm.$^{-1}$ region is listed in Table 2 which also shows the corresponding CH_2 rocking frequencies for normal paraffins [13a] in the crystalline state and for the dicarboxylic acids.[15] Comparison of these data confirms our assignments. It also suggests that the acids which are liquid at room temperature crystallise predominantly in the same *trans*-zig-zag configuration as do the acids which are normally solid at room temperature.

TABLE 2. *Frequencies (cm.$^{-1}$) assigned to $\delta[CH_2]_n$ rocking vibrations.*

n	Monocarboxylic acids, $H\cdot[CH_2]_n\cdot CO_2H$	Dicarboxylic acids, $HO_2C\cdot[CH_2]_n\cdot CO_2H$	Paraffins, $H\cdot[CH_2]_n\cdot H$
2	807	804	822
3	750	754	748
4	731	733	732
5	727	731	728
6	724	725	726
7	723	726	723
8	723	722	722
9	721	—	720
11	721	—	720

APPENDIX

Possible New Polymorphic Forms of Decanoic Acid.—When the spectrum of decanoic acid is obtained at different temperatures, marked changes are observed (Fig. 4). The frequencies (cm.$^{-1}$) of some of the main bands at different temperatures are shown in Table 3.

TABLE 3.

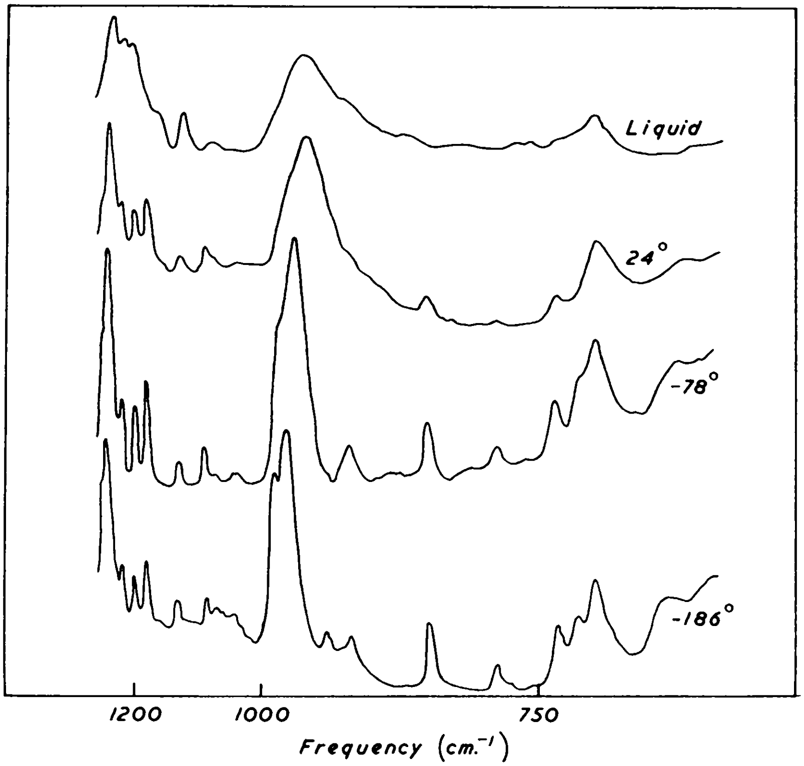
	$\nu C{=}O$	δ(OH)	$\delta C{<}^{O}_{O}$	δCH_2 rocking
Liquid	1714	937	—	720
Crystalline, 24°............................	1698	935	678	720
Crystalline, −78°..........................	1700	946, 964 (sh)	687	729, 721
Crystalline, −186°	1700, 1692	957, 975 (sh)	690, 668	729, 721

The broad band assigned to the out-of-plane OH bending vibration shifts and narrows as the temperature is lowered. (This may be due to depopulation of dimeric ring vibrations of higher energy.) Further, between 24° and −78° the band at 720 cm.$^{-1}$ (assigned to a CH_2

[15] Corish and Davison, *J.*, 1955, 2431.

rocking mode) splits into two components (at 721 and 729 cm.$^{-1}$). The latter behaviour is analogous to the change observed [16] when long-chain hydrocarbons, esters, and alcohols change from a hexagonal form with rotating chains to a more stable form (probably with orthorhombic packed chains). This prompts the suggestion that a similar type of polymorphic change occurs for decanoic acid. (It would be of interest to study this phenomenon with nuclear magnetic resonance spectroscopy to see whether there is rotation of the chains, and also by *X*-rays to see whether a phase change has occurred.) It might, however, be argued that contraction of the lattice might also produce this change since it increases the opportunity for interaction between adjacent methylene chains (cf. Stein [17]).

FIG. 4. *Spectrum of decanoic acid at various temperatures.*



Below −78°, further gradual shifts in the frequencies of the bands occur, in particular of the band assigned to the δOH out-of-plane vibration (see Table 3). At −186°, the absorption near 1700 cm.$^{-1}$ consists of two peaks. This is of interest since von Sydow reports that the absorption near 1700 cm.$^{-1}$ in the B-form of stearic acid consists of two close peaks despite the fact that crystals in this form do not contain two different C=O bonds. Since there are four molecules per unit cell in this crystal, coupling of the vibrations can occur, giving rise to a number of components of the fundamental vibrations. This might suggest a further polymorphic transition below −78° in decanoic acid, but this seems improbable. It may be that hydrogen bonding of the carboxyl groups of the dimer is sensitive to the lattice contraction.

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[16] Chapman, Sixth Internat. Spectroscopic Symp., Amsterdam, 1956.
[17] Stein, *J. Chem. Phys.*, 1955, **23**, 734.