

444. Infrared Spectral Variations and the Molecular Mobility of Some Long-chain Monocarboxylic Acids.

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The spectral changes observed with crystalline long-chain monocarboxylic acids as their temperature is varied have been studied. The molecular mobility of the hydrocarbon chains in the C'-form of the odd-membered acids is shown; the approaches to a hexagonal sub-cell of the C'-form of the odd-membered and of the C-form of the even-membered acids are contrasted.

LONG-CHAIN compounds frequently exhibit polymorphism and in many cases readily undergo phase transitions with temperature. X-Ray techniques have been used considerably for phase investigations,¹ and recently infrared spectroscopy has been useful for characterising different phases and providing useful additional information² about the polymorphism of hydrocarbons, esters,² glycerides,³ and acids.⁴ Spectra have been published by von Sydow⁴ characterising the A-, B-, and C-forms of the even-membered monocarboxylic acids and the A'-, B'-, and C'-forms of the odd-membered acids. However, his published spectra of the C'-forms are rather unusual and differ from those published elsewhere.⁵ The present paper clarifies the situation; it also shows, from changes in the spectra with temperature, the considerable molecular flexing or reorientational freedom of the hydrocarbon chains which occurs with this form and the approach to a hexagonal form of the hydrocarbon sub-cells as the temperature nears the melting point.

Experimental.—The acids had been prepared in the Unilever Research Laboratories, Port Sunlight, and were of high purity, as indicated by gas-phase chromatography. The spectra shown in Figs. a and b were obtained from pressed potassium chloride discs. No peculiarities were observed in the spectra obtained in this way in comparison with spectra obtained for Nujol mulls or for films melted between rock-salt, though differences had been found⁵ for spectra obtained by using potassium bromide discs. The spectra were obtained at different temperatures by using a heated cell, at temperatures estimated to be accurate to 0.5°.

Discussion.—The even- and odd-membered monocarboxylic acids each exist in three forms, A, B, C, and A', B', C', respectively. X-Ray single-crystal data have shown that the main types of hydrocarbon chain packing for A- and A'-forms are predominantly triclinic T||; it is common orthorhombic O⊥ for the B-, B'-, C-, and C'-forms.⁶ The C'-form is obtained by crystallisation from the melt, but changes some 10–20° below the solidification point into one or both of the forms A' and B'.

Infrared spectra of the different phases have been obtained, but surprisingly the spectrum said to characterise the C'-form of pentadecanoic acid is in fact qualitatively identical with that given for the acid in the liquid state. This does not seem reasonable for a crystal unless unusual conditions obtain. This spectrum is also very different from those of the C-forms of stearic or myristic acid although an X-ray study implies some similarities in the structure of these phases.⁶ A recent paper,⁵ on the other hand, shows the spectrum of a C'-form possessing a great deal of fine structure and having greater similarity to that obtained with the C-form of (say) myristic acid.⁵

Tridecanoic acid has been shown to occur in two polymorphic modifications, the A'- and the C'-form, A' changing reversibly⁷ to C' at 34°. The spectrum at room temperature

¹ Malkin, "Progress in the Chemistry of Fats and Other Lipids," Pergamon Press, London, Vol. I, 1952.

² Chapman, *Spectrochim. Acta*, 1957, **11**, 609.

³ Chapman, *J.*, 1956, **55**, 2522.

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

⁵ Susi and Smith, *J. Amer. Oil Chemists Soc.*, 1960, **37**, 431.

⁶ von Sydow, *Arkiv Kemi*, 1956, **9**, 231.

⁷ Stenhagen and von Sydow, *Arkiv Kemi*, 1953, **6**, 309.

(Fig. a) corresponds to the A'-form. Outstanding features are the fine structure in the 1380—1180 cm^{-1} region thought to be associated predominantly with in-plane wagging modes, perhaps coupled with carboxyl deformation vibrations.⁸ A band of complex structure associated with the OH out-of-plane deformation mode occurs near 893 cm^{-1} . The main CH_2 rocking vibration gives rise to a strong single band at 716 cm^{-1} . The single band is consistent⁹ with the triclinic T|| packing of the hydrocarbon chains in this form. Heating the acid at 33° causes a considerable change in the spectrum, corresponding to formation of the C'-form. The band associated with the OH out-of-plane deformation mode is shifted by almost 40 cm^{-1} , being now centred near 930 cm^{-1} and having much less fine structure. The bands in the 1380—1180 cm^{-1} region are shifted slightly (see Table 1) and the intensity of a band at 1108 cm^{-1} falls considerably. At this temperature

TABLE I.
Infrared spectra of tridecanoic acid (1500—650 cm^{-1}).

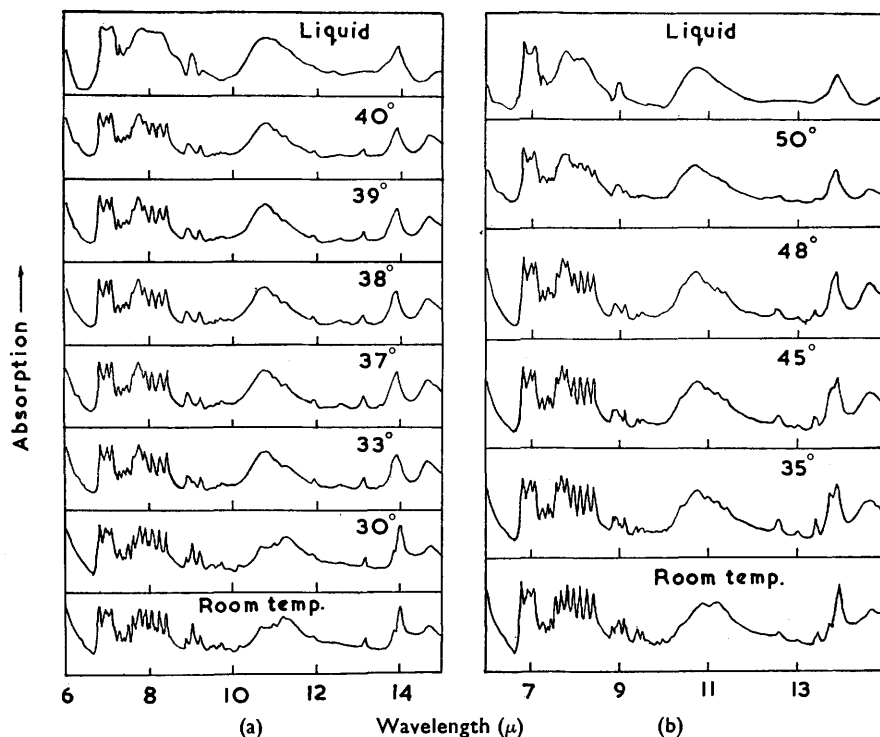
Room temp., A'-form	40°, C'-form	46—47°, liquid	Room temp., A'-form	40°, C'-form	46—47°, liquid	Room temp., A'-form	40°, C'-form	46—47°, liquid
1468s	1468s	1464s	1226w			1030vw		
1438m	1431m		1216s	1217}m		986vw		
1410m	1411m	1412s		1210}m		938w	929s	935s
1373w	1378w	1377w	1189s	1189m	1163(sh)	911m	909m	
1349vw	1352vw		1126w	1125}w	1115m	893s	891m	
1337w	1340w		1108m	1121}w		840w	840w	
1316m	1313m		1088w	1088w	1081w	760w	765w	
1289s	1294s		1062vw	1058vw		723w		
1266s	1268m	1283s	1054vw	1041vw		716s	720s	720s
1252w			1037vw	1031vw		681m	682s	
1240s	1241m	1237s(sh)						

bands occur at 720 and 717 cm^{-1} . On the side of the 720 cm^{-1} band is a shoulder, near 727 cm^{-1} . On further increase in temperature the band at 717 cm^{-1} disappears. At 40° the 727 cm^{-1} band disappears and only a strong single band remains (at 720 cm^{-1}). The bands in the 1380—1180 cm^{-1} region appear to become partly submerged in background absorption as the temperature is brought nearer to the melting point although the positions of the bands remain constant. The spectral changes are shown in Fig. a.

X-Ray studies have shown that pentadecanoic acid undergoes more complicated phase transformations.⁶ The A'-form changes to the B'-form at 45°, and the B'- to the C'-form at 46°. The C'-form is considered to exist between this temperature and the melting point.⁷ At room temperature the spectrum of the acid in the A'-form (Fig. b) shows considerable fine structure. The bands in the 1380—1180 cm^{-1} region are strong and clearly defined. The OH out-of-plane deformation band is at 891 cm^{-1} , with structure superposed. The main CH_2 rocking mode is single, at 716 cm^{-1} , with a weak band at 728 cm^{-1} . A spectral change occurs between room temperature and 35°, corresponding to a change to the B'-modification. Small changes occur in the frequencies of bands in the 1380—1180 cm^{-1} region and a considerable shift occurs in the OH deformation band, namely, from 891 to 929 cm^{-1} . Consistently with the orthorhombic O⊥ packed chains of this modification, the CH_2 rocking mode is associated⁷ with a doublet at 727 and 719 cm^{-1} . At 48° the bands in the 1380—1180 cm^{-1} region begin to become less well defined and the doublet in the 720 cm^{-1} region less well resolved. At 50° these changes are accentuated: a band at 1427 cm^{-1} falls in intensity, the OH deformation band is now at 933 cm^{-1} , and the main band is at 720 cm^{-1} with only a slight inflexion at 725 cm^{-1} . The spectral changes are shown in Fig. b and details given in Table 2.

⁸ Susi, *Analyt. Chem.*, 1959, **31**, 910.

⁹ Chapman, *J.*, 1957, 4489.



Infrared spectral variations with (a) tridecanoic and (b) pentadecanoic acid.

TABLE 2.
Infrared spectra for pentadecanoic acid ($1500-650\text{ cm.}^{-1}$).

Room temp., A'-form	35°, B'-form	50°, C'-form	60°, liquid	Room temp., A'-form	35°, B'-form	50°, C'-form	60°, liquid
1468s	1469s	1464s	1466s	1108w			
	1462s			1094w	1095w	1095w	
1438m	1428s	1427m	1415s	1063w	1064w	1064vw	
1397m	1410s	1406s		1048w	1048w	1048vw	
1369w	1376w	1376w	1377w	1032vw			
1348w	1351w	1350vw		1012vw	961m(sh)		
1335w	1339w	1340vw		1002vw			
1317m	1319m	1317m		917m	929s	933s	934s
1295s	1300s	1289s	1282s	891s	908m(sh)	796w	
1276s	1278s	1252m	1230m(sh)	793w	891m	746w	
1254s	1233s	1231m		745w	874m		
1230s	1229s			741m	796m		
1207s	1210 _l s	1207m	1170m(sh)	728w	766w		
	1205 _l s				741w		
1188s	1188s	1188m			727s	725(sh)	
1127w	1126w	1120w	1115m	716s	719s	720s	720s
1117w	1119w			668m	684m	683m	

Heptadecanoic acid was also examined in a similar manner. X-Ray studies have shown that crystallisation at room temperature from solution or the melt always gives the B'-form. At 54–56° this changes to the C'-form. Points of significance are as follows.

(a) Spectra of the same phases of the different acids are very similar. The A'-forms of tridecanoic and pentadecanoic acids have the OH out-of-plane deformation band at 893 and 891 cm.^{-1} , respectively (this is consistent with Susi and Smith's conclusions⁵ but

differs from earlier observations⁴), whilst the main CH_2 rocking mode gives rise to a doublet at 727 and 719 cm^{-1} . For the C'-form the OH deformation band is near 932 cm^{-1} and the CH_2 rocking mode gives a strong single band at 720 cm^{-1} at the higher temperatures; there is an additional shoulder, near 726 cm^{-1} , at lower temperatures. Heptadecanoic acid, on melting and resolidifying at room temperature, shows the main OH deformation band at 938 cm^{-1} , although the spectrum of the B'-form obtained by dispersion in Nujol shows this band at 928 cm^{-1} . This may be an orientation effect. When the material is warmed above 54–56°, where the C'-form exists,⁷ the band shifts to 932 cm^{-1} , consistently with the spectra of the other C'-phases examined.

(b) The variation for the C'-forms in the appearance of the bands in the 1380–1180 cm^{-1} region must be related to the flexing and molecular mobility of the hydrocarbon chains which occur with this form.^{6,10} X-Ray evidence suggests that the thermal motion is larger at the methyl end of the molecule than at the carboxyl end. The spectra are analogous to those observed with other long-chain compounds such as 1-monoglycerides,³ and with ethyl esters² in the hexagonal (α -)form. It is in contrast to the anhydrous sodium soaps where all the fine detail in the 1380–1180 cm^{-1} region disappears some 100° below the melting point owing to formation of the liquid crystalline phase.¹¹ With the odd acids some structure remains in this region at temperatures very close to the melting point, in contrast with an earlier observation;⁴ our finding implies that in this form the individual CH_2 groups do not move completely freely with respect to each other, as may happen in the liquid state. The variation in the appearance of the band in the 720 cm^{-1} region as the temperature approaches the melting point is analogous to that observed² with long-chain compounds when they change from an orthorhombic O \perp packed form to a hexagonal sub-cell. There are no measurements of the variation of the sub-cell dimensions for tri-, penta-, and hepta-decanoic acid. The value⁶ (1.62) of the $b : a$ ratio of undecanoic acid (C-11) at 23° (m. p. 28°) can be compared with that (1.73) associated with the hexagonal sub-cell. It seems probable that a close approach to the hexagonal sub-cell occurs with the acids examined.

(c) A similar examination of stearic acid in its C-form shows only a very slight shift and fall in intensity in the higher-frequency component of the 720 cm^{-1} doublet. The changes are considerably less marked than for the odd-membered acids. The sub-cell dimensions of this acid have been determined;¹² the $b : a$ ratio, extrapolated to 70° (m. p. 69.7°), is here only 1.54. Spectroscopic examination of the shorter even-membered acids, e.g., myristic and lauric, close to their melting points shows behaviour more analogous to that observed with the odd-membered acids, for both the 1380–1180 and the 720 cm^{-1} region. An earlier investigation¹³ revealed that decanoic acid exhibited similar behaviour (doublet 729, 719 cm^{-1} at –78°; single band 720 cm^{-1} at 24°; m. p. 30.6°), suggesting that a hexagonal type of sub-cell is more nearly approached with this acid. Nuclear magnetic resonance measurements show that molecular motion occurs with the C-form of the even-membered acids some 10° below their melting points.¹⁴

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¹⁰ Komatsu, *J. Phys. Soc. Japan*, 1956, **11**, 755.

¹¹ Chapman, *J.*, 1958, 784.

¹² Degerman and von Sydow, *Acta Chem. Scand.*, 1959, **13**, 984.

¹³ Corish and Chapman, *J.*, 1957, 1746

¹⁴ Grant, personal communication, 1960.