

904. The 720 cm^{-1} Band in the Infrared Spectra of Crystalline Long-chain Compounds.

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A correlation between the appearance of the band associated with the CH_2 rocking mode in the 720 cm^{-1} region of the spectra of crystalline long-chain compounds and the type of packing of the chains is discussed.

RECENTLY it has been suggested¹ that a doublet observed in the 720 cm^{-1} region of the infrared spectrum of some long-chain compounds can be correlated with orthorhombic packing of the hydrocarbon chains, whilst a single band in this region can be correlated with hexagonal or triclinic packed chains. As this correlation may be more usefully and generally extended, it is now considered in greater detail.

Although theory and discussion²⁻⁸ have mainly concerned the appearance of a doublet in the 720 cm^{-1} region of the infrared spectra of Polythene and *n*-paraffins many other long-chain crystals exhibit it. Indeed this doublet has been observed so frequently that Bellamy⁹ states that the band (associated with a CH_2 rocking vibration) can be distinguished from other bands in this region by observing whether it is single in the spectrum of the liquid and double in the crystalline state. However, several long-chain compounds do show only a single band in this region, *e.g.*, the β_L -form of triglycerides.¹⁰

In long-chain crystals the unit cells may contain one, two, or more layers. Chains without any one layer are almost always parallel to one another. They may be either normal or inclined to the basal plane. The arrangement of chains in layers depends essentially on their end groups. If we disregard the end groups a layer of chains can be regarded as composed of repeating units (sub-cells¹¹). For simple structures one sub-cell suffices to describe the arrangement within a layer: for more complicated structures more than one type of sub-cell may be present.

The structures of long-chain crystals so far investigated have been described in terms of two main types of sub-cell.^{12,13} The more important is the orthorhombic sub-cell (Fig. 1) which is common to the structures of $\text{C}_{29}\text{H}_{60}$ hydrocarbon and Polythene (von Sydow¹³). The packing-environment of a hydrocarbon chain in the orthorhombic sub-cell of a long-chain crystal such as the *B* and *C* forms of stearic acid is therefore identical with that which occurs in the orthorhombic paraffin. Since the 720 cm^{-1} doublet in the spectra of the orthorhombic paraffin is attributed to interaction between neighbouring chains, we may expect that similar interaction will occur with other long-chain compounds containing an orthorhombic sub-cell. The doublet is observed in the infrared spectra of many long-chain compounds (Table 1) which have this type of sub-cell.

The correlation is striking, yet it is possible that a long-chain molecule may pack in an orthorhombic manner without causing the appearance of a doublet, *e.g.*, when the dimensions of the sub-cell are larger than normal, or when distortions occur in the cell, since then the interaction between chains may be too small to give a resolvable splitting. (The extent of splitting depends on the nature and magnitude of the forces involved.) However,

¹ Chapman, Sixth International Spectroscopic Colloquium, Amsterdam, 1956.

² Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3.

³ Elliot, Ambrose, and Temple, *J. Chem. Phys.*, 1948, **16**, 877.

⁴ Stein and Sutherland, *ibid.*, 1954, **23**, 1993.

⁵ Stein, *ibid.*, 1955, **23**, 734.

⁶ Keller and Sandemann, *J. Polymer Sci.*, 1955, **15**, 133.

⁷ Krimm, Liang, and Sutherland, *J. Chem. Phys.*, 1956, **25**, 543.

⁸ Tobin, *J. Chem. Phys.*, 1955, **23**, 891.

⁹ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.

¹⁰ Chapman, *J.*, 1956, 2522.

¹¹ Vand, *Acta Cryst.*, 1951, **4**, 104.

¹² Daniel, *Adv. Phys.*, 1953, **2**, 450.

¹³ von Sydow, *Arkiv Kemi*, 1956, **9**, 231.

where two components equal or nearly equal in intensity are observed, it is plausible to predict that the hydrocarbon chains have orthorhombic packing. This packing has been recently predicted for the hydrocarbon chains of the β_L' -form of triglycerides,¹⁴ whose spectra show a doublet at 727 and 719 cm^{-1} .

TABLE I. *Compounds showing the doublet near 727 and 719 cm^{-1} in the spectrum of their stable crystalline form and their hydrocarbon-chain packing.*

Monocarboxylic Acids.— C_{18} (B form), O*; C_{18} (C form) O*; C_{20} , CH; C_{18} , CH; C_{14} , CH; C_{15} (B' form), O*; C_{17} (B' form), CH; C_{19} (B' form), CH; C_{21} (B' form), CH.
Others.—Octadecyl alcohol, O†; octadecyl palmitate, O†; hexadecanedicarboxylic acid, O†; long-chain methyl esters (*e.g.*, methyl stearate), probably O‡; long-chain ethyl esters (*e.g.*, ethyl stearate), probably O‡.

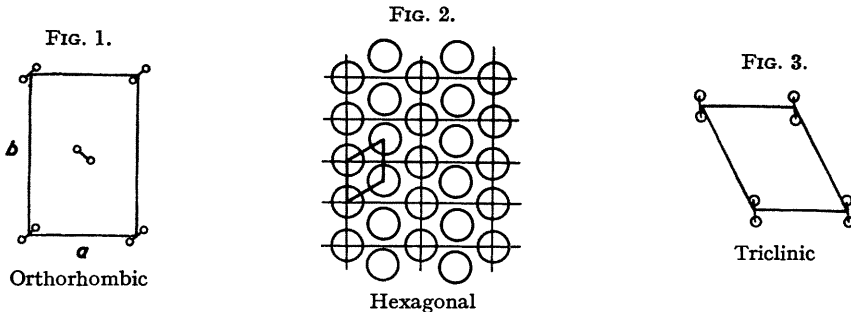
O, Orthorhombic; CH, crystallographically homologous.

The main X-ray short spacings ‡ of long-chain methyl and ethyl esters are at *ca.* 3.7 and 4.2 Å whilst those of hydrocarbons in the orthorhombic form are at *ca.* 3.8 and 4.2 Å.

* von Sydow, ref. 13. † Schoon, *Z. phys. Chem.*, 1938, B, **39**, 385. ‡ Malkin, "Progress in the Chemistry of Fats and other Lipids," Pergamon Press, London, 1952, Vol. 1, p. 14.

An important variant on the orthorhombic sub-cell is obtained when the angle θ between the diagonals is 60° , *i.e.*, the basal figure is a regular hexagon (Fig. 2). This hexagonal form, corresponding to the best packing of cylindrical rods, was discovered by Muller¹⁵ who noted that there was only a single strong short-spacing at 4.12 Å in the X-ray powder photograph of certain long-chain hydrocarbons. He postulated that, in this form of sub-cell, rotation of the hydrocarbon chain occurs about its long axis; this has been confirmed.¹⁸ Other long-chain compounds also exhibit this hexagonal form, *e.g.*, long-chain ethyl esters,¹⁷ 1-monoglycerides¹⁷ and triglycerides.¹⁷ The spectra^{1,4} of the hexagonal form of all these molecules show a strong single band at 720 cm^{-1} .

The reason for the appearance of only a single band at 720 cm^{-1} can be understood if we note that the chains in this sub-cell are in a more symmetrical environment than in the orthorhombic sub-cell. The chains in the hexagonal sub-cell will tend to equivalence so that there will be effectively only one chain per primitive sub-cell and hence only one



component of each fundamental vibration will be allowed (*cf.* Tobin⁸). Furthermore, apart from symmetry considerations, the interchain distance in the hexagonal form is practically the same as in the liquid (where, it is suggested, the chains pack in a square array). For hexatriacontane the distances are 4.86 Å in the liquid and 4.85 Å in the hexagonal form, to be compared with the smaller interchain distance¹⁸ in the orthorhombic sub-cell of 4.47 Å. Although the chains in the hexagonal form may rotate in an analogous fashion to a closed set of gear wheels,¹⁶ the average interaction due to the large interchain

¹⁴ Chapman, *J.*, 1957, 2715.

¹⁵ Muller, *Proc. Roy. Soc.*, 1932, A, **138**, 5.

¹⁶ Andrew, *J. Chem. Phys.*, 1950, **18**, 607.

¹⁷ Malkin (a) *Trans. Faraday Soc.*, 1933, **29**, 977; (b) "Progress in the Chemistry of Fats and other Lipids," Pergamon Press, London, 1954, Vol. 2.

¹⁸ Vand, *Acta Cryst.*, 1953, **6**, 797.

distance must be considerably less than in the orthorhombic sub-cell, so that even if two components were allowed their separation would be negligible (cf. Stein ⁵). (The large sub-cell also probably explains why the band is at 720 cm.⁻¹ in the unperturbed position.)

The second main type of sub-cell is the triclinic cell (Fig. 3) which occurs in the β_L -form of trilaurin.¹⁹ In this sub-cell all the planes of zig-zag are parallel to one another, whilst making an angle ϕ with the a -axis. In this sub-cell the environment of any hydrocarbon chain is different from that occurring in the orthorhombic sub-cell so that we might expect that a doublet at 720 cm.⁻¹ will not be observed with this type of packing. Further, whilst there are two chains in the orthorhombic sub-cell, and hence two components of each fundamental vibration are possible, in the triclinic sub-cell there is only one chain and hence only one component of each fundamental vibration is possible (cf. Tobin ⁸).

Some compounds which have triclinic packed hydrocarbon chains are given in Table 2. The shift in the band from the unperturbed position at 720 cm.⁻¹ to 717 cm.⁻¹ probably arises because of a change in the internal potential energy function of the molecule due to the equilibrium field of the crystal, which in turn is due to the van der Waals forces

TABLE 2. *Compounds showing a strong single band in the 720 cm.⁻¹ region of the spectrum of their stable crystalline form, and their hydrocarbon-chain packing.*

Octadecane, T *; silver stearate, T †; trilaurin (β_L form), T ‡; tristearin (β_L form), CH; tripalmitin (β_L form), CH; 1-palmitodistearin (β_L form), CH; 1-stearodipalmitin (β_L form), CH; stearo-oleostearin (β_L form), CH; myristic acid (A form), T §; pentadecanoic acid (A' form), T §. T, triclinic; CH, crystallographically homologous.

* Muller and Lonsdale, *Acta Cryst.*, 1948, **1**, 129. † Vand, Aitken, and Campbell, *ibid.*, 1949, **2**, 398. ‡ Ref. 19. § Ref. 13.

operative in the sub-cell. A decrease in the frequency of a band is quite commonly observed when a change from the liquid to the crystal phase occurs.

The orthorhombic and triclinic sub-cells are by far the most important known. Indeed, von Sydow states that these are the only two types present in covalent normal-chain compounds.¹⁴

In general, we can conclude that for these two types of sub-cell, particularly for the orthorhombic type, there appears to be a good correlation between the appearance and position of the band in the 720 cm.⁻¹ region and the type of sub-cell. This may prove useful in predicting the type of hydrocarbon-chain packing in long-chain crystals before their more definitive X -ray analysis of single crystals.

Finally, there is a third and unusual (and so far unique) type of sub-cell discovered by Vand, Lomer, and Lang²⁰ in the crystal structure of the A -form of potassium hexanoate. This differs from other sub-cells in that the chain axes (as distinct from zig-zag planes) are not all parallel. They cross one another within the same layer so that the zig-zags of neighbouring chains fit one another. The spectrum of potassium hexanoate in this form shows only a single band at 717 cm.⁻¹, with a weaker additional band at 737 cm.⁻¹.

We thank Dr. N. Sheppard for an interesting discussion, and the directors of Unilever Limited for permission to publish this work.

UNILEVER LIMITED, PORT SUNLIGHT, CHESHIRE.

[Received, April 29th, 1957.]

¹⁹ Vand and Bell, *Acta Cryst.*, 1951, **4**, 465.

²⁰ Vand, Lomer, and Lang, *ibid.*, 1949, **2**, 214.