

X-RAY ANALYSIS OF LIQUID CRYSTALS*

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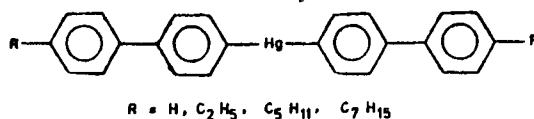
I PROPOSE to review briefly the X-ray work on thermotropic liquid crystals¹ in progress in Bangalore during the last few months. X-ray diffraction has, of course, been a most useful tool in the structural classification of the mesophases. For example, in thermotropic systems (composed of rod-like molecules) it has been possible to identify from the nature of the diffraction pattern, a number of distinct structural types, viz., 'ordinary' and cybotactic nematics²⁻⁴, 'ordinary' and cybotactic cholesterics⁵ and eight different modifications of smectics⁶⁻⁸, and to derive some information on the degree of molecular order in each of them. However, the determination of the detailed positional and orientational distribution functions from the Fourier transform of the intensity of diffraction is a rather more complex problem⁹. The molecule itself is quite large, some 25 Å long and 5 Å broad, and in the liquid crystalline phase there are intramolecular motions (rotations of certain parts, wagging of end chains, etc.) as well as pronounced orientational motions of the molecule as a whole about all three axes. Thus the molecular structure factor corrected for thermal motion is not known with any certainty. Moreover, there are strong correlations between the orientational motions of neighbouring molecules, so much so that a separation of the *intra-* from the *inter-*molecular interference effects becomes a formidable task.

THE HEAVY ATOM METHOD

In principle, the analysis can be simplified by the use of the heavy atom method—as need hardly be explained to an audience of crystallographers. In practice, however, there

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is a serious difficulty, namely, the lack of stable heavy-atom-substituted mesogenic compounds. For example, the first mesogens we examined were some mercury compounds, with the mercury atom located at the centre of the molecule¹⁰ :



From the X-ray point of view, these compounds appeared to be ideally suited to determining the positional distribution function (the Hg-Hg vector); but, in fact, it turned out that these high temperature mesophases are too unstable chemically to be of use in quantitative studies. At present we are investigating some bromine compounds. The diffraction patterns show additional maxima due to the Br-Br distances between neighbouring molecules, which help greatly in the interpretation. For example, from the patterns from nematics, it is at once seen that the molecules form an overlapping or 'imbricated' arrangement, as was indeed anticipated by Bernal and Crowfoot¹¹ forty-four years ago.

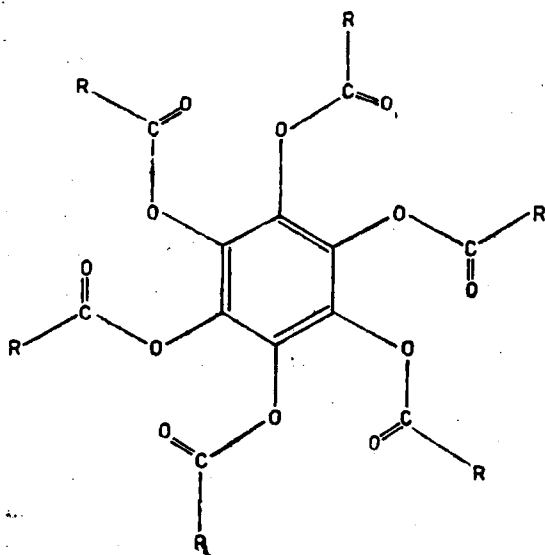
HIGH PRESSURE X-RAY STUDIES

High pressure investigations have been going on in Bangalore for some time now, and a number of new phenomena have been reported¹², e.g., pressure induced mesomorphism in certain compounds¹³⁻¹⁵, suppression of mesophases in certain others¹⁴⁻¹⁵, triple points¹³⁻¹⁵ and tricritical points¹⁴ in single component systems, etc. In order to obtain detailed quantitative information on the structural changes taking place at these pressures we are embarking on a programme of high pressure X-ray study of liquid crystalline

materials. A Van Valkenburg type of X-ray camera has been constructed¹⁶ and some work has begun on the effect of pressure on the layer spacings in smectics A and C. I shall mention just one result: preliminary photographs show that around 1.7 kbars, the layer spacing in the smectic A phase of 4'-n-octyloxy-4-cyanobiphenyl (8 OCB) increases very slightly with increase of pressure, supporting a suggestion put forward by Cladis *et al.*¹⁷ to explain the so-called re-entrant nematic phase, *i.e.*, the reappearance of the nematic phase on cooling the smectic A phase of this compound at these pressures. However, this preliminary X-ray result needs to be confirmed by more careful measurements.

LIQUID CRYSTALS OF DISC-LIKE MOLECULES

Finally, I shall describe some work on an interesting new type of mesophase. Since the discovery by Reinitzer in 1888 of two 'melting' points in cholesteryl benzoate, several thousands of pure compounds have been found to exhibit thermotropic mesomorphism. The single feature common to all of them is the rod-like shape of the molecule. However, recent studies in Bangalore have established for the first time the occurrence of thermotropic mesomorphism in pure compounds consisting of simple disc-like molecules¹⁸. The compounds are



of which four homologues, $R = n-C_8H_{11}$ to $n-C_8H_{17}$ show mesophases. The X-ray pattern from a polydomain sample of the mesophase consists of a diffuse 'liquid-like' outer ring (corresponding to a mean intermolecular spacing of about 5 Å), and relatively sharp inner rings. The Bragg spacings of the first three inner rings are in the ratio $1 : 1/\sqrt{3} : \frac{1}{2}$, characteristic of a hexagonal structure. This is confirmed by the diffraction pattern from a nearly monodomain specimen which directly shows up the hexagonal symmetry. Based on this evidence we have proposed a structure in which the discs are stacked one on top of the other in columns that form a hexagonal array, but the spacing between the discs in each column is irregular (Fig. 1). Thus we have here an entirely new type of liquid crystal in which there is lamellar order in two dimensions and liquid-like disorder in the third. Further experiments are under way to test the validity of this model and to investigate other properties of the mesophase.

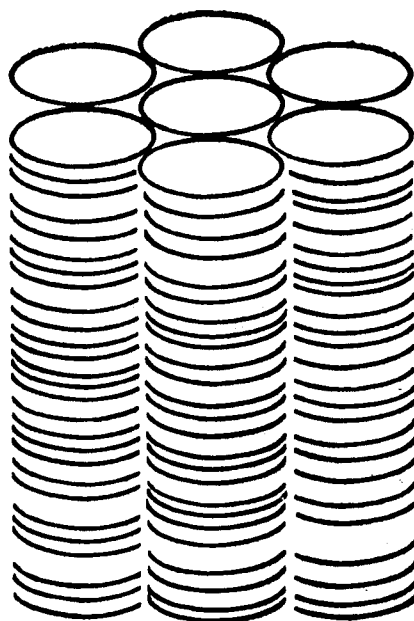


FIG. 1. Schematic representation of the proposed structure of the mesophase of disc-like molecules. The discs are irregularly spaced to form liquid-like columns.

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