

example of the enantiomeric CD bands for jellies of D- and L-12HOA. Little linear dichroism was observed when jellies were examined by the procedure of Tunis-Schneider and Maestre³. Therefore we ascribed the observed CD to the preferential reflection of circularly polarised light of one sense by the jellies. The same optical phenomenon¹ has been observed for cholesteric liquid crystals and explained by assuming a supramolecular helical structure with the twist determined by the chirality of the constituent molecules.

Enantiomeric induced CD (ICD) could also be observed for some achiral molecules dissolved in jellies of chiral 12HOA. Figure 2 shows the ICD bands (superimposed on the CD curve of the jelly) and electronic spectra between 330 and 395 nm for anthracene dissolved in a jelly of D-12HOA. Interestingly, the ICD bands show a single sign and follow closely the electronic spectral bands; such ICD characteristics have been obtained for lyotropic cholesteric mesophases of poly- γ -benzyl-L(or D)-glutamate (PBG)⁴ and other polypeptides, and more recently for those of *N*-acylamino acids⁵.

In view of these CD and ICD results, it is possible that a supramolecular helical structure exists in jellies of 12HOA. Then the 350 nm CD band maximum would correspond to the 'pitch band' and the observed ICD would be caused by the dissymmetrical field of the helical structure, although it is weak compared with the effect in cholesteric systems⁴. This proposed helical structure is associated with the jelly structure in which hydrogen bonding is involved⁶, because melting of the jelly by heating resulted in the loss of all the optical properties mentioned above.

We found that all the optical phenomena described here manifested themselves more clearly in thin semi-transparent solid films (about 50 μm) obtained by drying jellies of chiral 12HOA on quartz supports. When the films were dried, the CD increased in intensity and the peak was shifted to the shorter wavelength side. These results indicate that the original supramolecular helical structure in jellies is fully retained in such solid films. Similar behaviour has been found with the cholesteric mesophase of polypeptides⁷.

Microscopy with a controlled hot stage showed that, when such solid films were heated, the mesomorphic texture became obscure at about 348 K, and then needle-like microcrystals formed: CD was no longer observed. Finally the microcrystals melted at 353 K (melting point of chiral 12HOA).

X-ray diffraction patterns for these solid films obtained by drying were similar to those for the crystalline powder, although slightly more broad. A long spacing of 46.7 \AA was obtained and interpreted as the distance between double plane layers of amphiphilic molecules of 12HOA. This suggests that the mesophase structure retained in these solid films, and possibly also the structure of the mesophase itself, is not nematic, as has been shown for the cholesteric mesophase of PBG, but smectic. In the layer structure with a twisting, the molecular long axes would have to be tilted relative to the layer planes. The length of the crystallographic *c* axis of octadecanoic acid which is an analogue of 12HOA, that is, the extended length of the bimolecule, has been reported to be 49.38 \AA for the B form⁸ and 50.7 \AA for the C form⁹. These values are greater than 46.7 \AA . This result supports the tilt possibility. It was impossible, however, to prepare orientated samples of jellies and solid films which exhibited regularly-spaced retardation lines or iridescent colours like those observed for the cholesteric mesophase of polypeptides. It seems reasonable to consider that the twisted mesophase structure exists locally as small domains which disperse with randomly-orientated helical axes within jellies or solid films. This would explain the small size of the observed CD band compared with the effect in cholesteric mesophases.

Electron microscopy has shown that both chiral 12HOA (ref. 2) and PBG (ref. 9) formed by precipitation from certain solvents produce helically twisted fibrils with handedness determined by the chirality of the molecule. Because biologically important molecules are essentially chiral, it may be biologically significant that some chiral molecules form helically

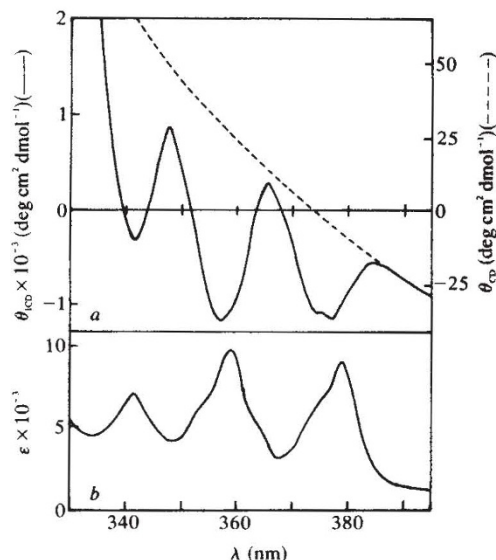


Fig. 2 a, ICD spectral bands (—) for anthracene (8.8 mmol l^{-1}) superimposed on the CD curve (-----) of the jelly (D-12HOA- CCl_4). b, Electronic spectra of anthracene. Enantiomeric ICD bands were obtained for a jelly of the L acid. On addition of anthracene, the CD maximum of the jelly itself was shifted to the longer wavelength side ($\sim 450 \text{ nm}$).

organised systems in different stages, as has been shown for 12HOA and polypeptides.

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Erratum

In the letter 'Maximum density of random placing of membrane particles' by L. Finegold and J. T. Donnell, *Nature* **278**, 443-445, the bottom line of the legend to Table 1 should be included in the table under 'Circular particles'.

Corrigendum

In the letter 'Deficient production of tyramine and octopamine in cases of depression' by M. Sandler *et al.*, *Nature* **278**, 357-358, the units of the third column of Table 2 should read nmol instead of μmol .