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## Liquid Crystals

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### Non-cylindrical symmetry of the ordering matrix of some spectroscopic probes in a lyotropic mesophase studied by $^2\text{H}$ N.M.R. spectroscopy

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## PRELIMINARY COMMUNICATION

### **Non-cylindrical symmetry of the ordering matrix of some spectroscopic probes in a lyotropic mesophase studied by $^2\text{H}$ N.M.R. spectroscopy**

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Deuterium N.M.R. spectroscopy has been used to investigate the orientational ordering of perdeuteriated naphthalene and two perdeuteriated fluorescent probes (pyrene and perylene) dissolved in a discotic nematic micellar phase of potassium laurate/potassium chloride/decanol/water. The results show that the ordering tensors of these probes are not cylindrically symmetric.

Aromatic hydrocarbons have long been used as fluorescent probes in lyotropic and thermotropic phases and in membranes [1, 2] in order to study liquid-crystalline behaviour by fluorescence depolarization techniques. For perylene, 9,10-dimethylanthracene and 1,6-diphenyl-1,3,5-hexatriene the orientational order of the fluorophores in their ground state, in a lyotropic mesophase, has also been tested by linear dichroism spectroscopy [3]. By using these techniques only one order parameter can generally be determined relative to the direction of the axis of the transition moment [2-4]. To our knowledge, however,  $^2\text{H}$  N.M.R. spectroscopy, a uniquely powerful technique for studying the orientational order of a component in a liquid-crystalline phase [5], has not been used until now for such fluorescent molecular probes in lyotropics, although there has previously been reported a study in lyotropics of the small aromatic hydrocarbons, benzene and naphthalene, by deuterium N.M.R. [6]. This could be partly due to the poor solubility of fluorescent probes in lyotropic phases, coupled with the inherent, low sensitivity of  $^2\text{H}$  N.M.R. Moreover, quite often the peculiar orientational ordering of the solute molecules in lyotropics results in deuterium spectra which are consistent with more than one solution for the ordering tensor.

In this preliminary communication we present a  $^2\text{H}$  N.M.R. study of perdeuteriated pyrene (1), perylene (2) and naphthalene (3), shown in figure 1 with axis labelling, partially oriented in a discotic micellar phase of type II (MD II) [7, 8]. The spectra were recorded on a Varian VXR300 spectrometer. (1) and (3) were synthesized from the corresponding non-deuteriated compounds following [9], while (2) was obtained from a commercial source (MSD, Canada). The composition of the solvent phase was potassium laurate 31.8, potassium chloride 4.2, 1-*n*-decanol 6.3,  $\text{H}_2\text{O}$  57.7 per cent by weight. Long accumulation times (about 100 000 transients) were required

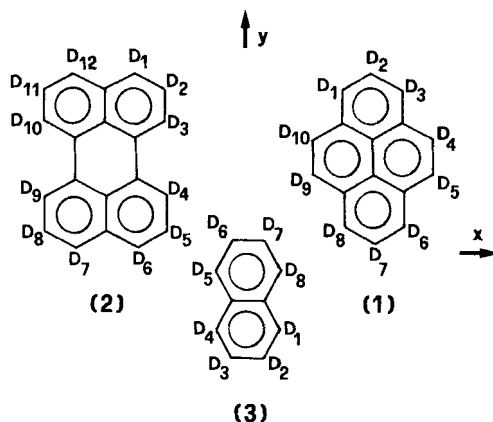


Figure 1. Molecular structure of perdeuterated pyrene (1), perylene (2) and naphthalene (3), including atomic numbering and axis labelling.

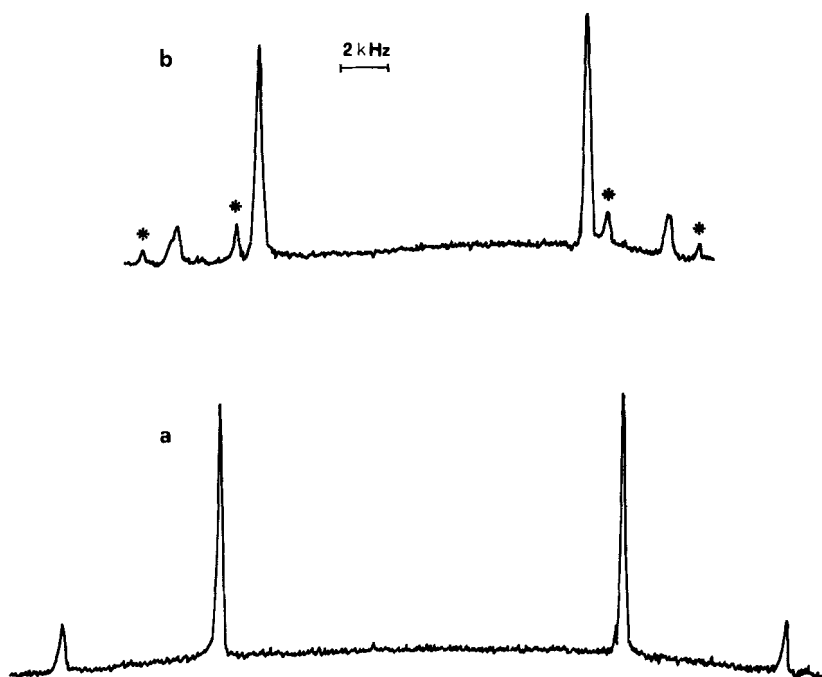


Figure 2.  $^2\text{H}$  N.M.R. spectra of pyrene- $d_{10}$  in the MD II mesophase at 33°C (a) and at 66°C (b). The asterisks indicate the signals due to pyrene- $d_{10}$  in the second oriented phase existing above 63°C.

to detect the weak signals from the probe molecules, which were scarcely soluble in the solvent phase. Deuterium depleted water (Aldrich) was used therefore in order to avoid the presence in the spectra of strong signals from natural abundance  $^2\text{H}$  in water. For each sample, spectra were obtained between 22 and 70°C. Two typical spectra of (1) (saturated solution in the MD II phase at 33°C and 66°C, respectively) are displayed in figure 2. Phase separation is expected at 63°C [8], and this is indeed detected; however, the behaviour of the system above 63°C, as indicated by our

probes, does not agree with the description given in the literature (discotic and isotropic micellar phases coexisting between 63°C and 70°C). In order to clarify the situation, a series of  $^2\text{H}$  N.M.R. spectra was run between 22°C and 73°C on a sample of the same MD II mesophase, but using, as molecular probe,  $\text{D}_2\text{O}$  replacing 20 mole %  $\text{H}_2\text{O}$ . These spectra reveal, at 63°C, the simultaneous formation of small amounts of a second oriented phase (characterized by larger quadrupolar splittings) and of the isotropic micellar phase. On increasing the temperature, the relative amounts of the three phases change: the quantity of the isotropic increases substantially, while the ordered phase with the larger quadrupolar splitting prevails on the other, which disappears at 70°C. Molecular probes (1) and (3) clearly reveal the separation of two oriented phases at 63°C, but not the presence of the isotropic until about 70°C; the lyotropic system containing perylene- $d_{12}$  appears highly perturbed over 63°C, and a second ordered phase cannot be clearly detected. All of this should probably be ascribed to the peculiar partition of the aromatic solutes (which are set inside the lyotropic aggregates) among micelles of different form and size and, at least in the case of perylene- $d_{12}$ , perhaps also to a perturbation of the phases due to the solute.

For each solute at each temperature, the two distinguished quadrupolar splittings obtained from the  $^2\text{H}$  N.M.R. spectrum can be related to the order parameters with respect to the director [5]

$$-2\Delta v_i = (3/2)q \{ -(1/2)S_{zz}(1 - \eta) + (S_{xx} - S_{yy})(l_{\alpha a}^2 - l_{\alpha \beta}^2 + \eta(l_{\alpha b}^2 - l_{\alpha c}^2)/3) \}.$$

Here  $q$  and  $\eta$  are the coupling constant and asymmetry parameter of the quadrupolar interaction tensor (assumed to be the same for all deuterons in a molecule); the subscript or superscript  $i$  defines the deuteron giving rise to the observed quadrupolar coupling and  $l_{\alpha\beta}^i$  is a direction cosine between the molecular axis,  $\alpha$ , and the quadrupolar interaction tensor principal axis,  $\beta$ , for the  $i$ th deuteron. The  $\beta$  axes are such that  $a$  is along the C-D bond and  $c$  is parallel with  $z$ . The factor of  $-2$  is needed since the director is orthogonal to the magnetic field in MD II type mesophases. Therefore, knowing or assuming the molecular geometries of (1) [10], (2) [11], and (3) [12] (the C-D bonds are assumed to bisect the appropriate C-C-C angle) and the values of  $q$  and  $\eta$  (for (3) we use the values 177 kHz and 0.055 respectively [13] and for (1) and (2) we assumed average values of 180 kHz and 0.06 respectively of those found for anthracene [14] and naphthalene [13]), the principal ( $S_{zz}$ ) and biaxial ( $S_{xx} - S_{yy}$ ) order parameters for (1), (2) and (3) can be obtained as a function of temperature. The signs of  $\Delta v_i$  are, however, unknown and, as already mentioned, various solutions are possible on the basis of the  $^2\text{H}$  spectra alone. The problem can be solved for naphthalene- $d_8$ , since the complete ordering tensor for the non-deuteriated molecule in the same MD II phase has already been determined from the proton N.M.R. spectrum [15]. Note that, although not specifically mentioned in [15], it has been shown that the absolute signs of the dipolar couplings can be obtained if the spectrum is sufficiently sensitive to a known isotropic  $J$  coupling [16]. Thus, the short axis is ordered perpendicular to the director for naphthalene, and, given only that the same is true for perylene and pyrene, the assignment is also unambiguous for (1) and (2) since in alternative cases  $S_{zz}$  would not be the most negative order parameter ( $-0.5$  indicating complete perpendicular alignment). Thus, we assign the  $z$  direction to be the one of maximum ordering, i.e. perpendicular to the molecular plane with  $S_{zz} < 0$ ; otherwise the values of  $S_{xx}$  and  $S_{yy}$  which we might expect from the molecular shapes to be similar, with the assignment of the long axis to the  $y$  direction resulting in a

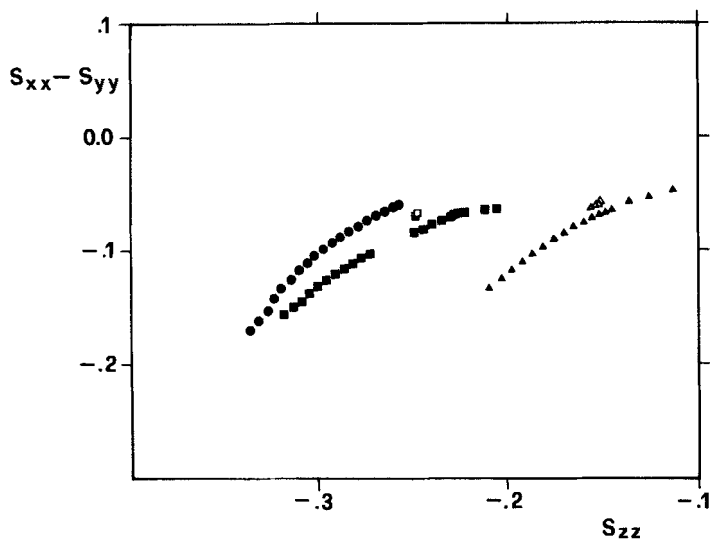


Figure 3.  $S_{xx} - S_{yy}$  versus  $S_{zz}$  for perylene- $d_{12}$  (●), pyrene- $d_{10}$  (■ or □) and naphthalene- $d_8$  (▲ or △) in the MD II mesophase. Empty symbols are relative to the solutes in the second oriented phase existing above 63°C.

negative biaxiality ( $S_{xx} - S_{yy}$ ). This assignment is reasonable in any case since intuitively we should expect the long axis to align with the laurate chains and also it has been found that exactly the same assignment applies for all three probes in thermotropic liquid crystals [17]. In figure 3 the plot of ( $S_{xx} - S_{yy}$ ) versus  $S_{zz}$  is shown.

The biaxiality values in this lyotropic mesophase, even if much lower than those observed for the same molecules in thermotropic liquid crystals [17], are significant and the assumption of cylindrical symmetry for their ordering tensors would be by no means adequate. Thus, we conclude that far more care is required in the analysis and interpretation of fluorescence depolarization data of probes without at least an effective three-fold symmetry axis, than has usually been the case hitherto. The reduction of  $S_{zz}$  and ( $S_{xx} - S_{yy}$ ) with increasing temperature is, however, regular and these biaxiality plots are similar to those usually obtained in thermotropic solvents [18–20].

For (1) and (3), the order parameters could be determined at various temperatures in both the oriented phases coexisting between 63°C and 70°C (see figure 2). If the phase with the smaller quadrupolar splittings is considered, no discontinuity in the variation of the order parameters is found at 63°C. As far as the other phase is concerned,  $S_{zz}$  is higher and ( $S_{xx} - S_{yy}$ ) relatively smaller than in the first one; moreover, such values are almost stationary with increasing temperature. The interpretation of these observations is complicated (e.g. with respect to thermotropic systems) by the multicomponent nature of the lyotropic phase. However, two possible causes for the jumps in order parameters between the two phases, which we intend to investigate in the future, are the edge effect in the micellar (lower ordered) phase and the orientational distribution of the micelles themselves, both of which would reduce the order parameters in a micellar phase with respect to a coexisting lamellar phase.

Further work on this subject is in progress, consisting of a  $^2\text{H}$  N.M.R. study of the same aromatic probes in various thermotropic phases and in a cylindrical micellar phase (potassium laurate, potassium chloride, water), with the final aim of explaining

the different orientational ordering (in particular the biaxiality values) on the basis of the different solvent structure. In addition, the orientational order will be investigated by fluorescence depolarization spectroscopy for the solutes in the MD II phase, for which such data are not reported in the literature.

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### References

- [1] BEDDARD, G. S., and WEST, M. A. (editors), 1981, *Fluorescent Probes* (Academic Press).
- [2] ZANNONI, C., ARCIONI, A., and CAVATORTA, P., 1983, *Chem. Phys. Lipids*, **32**, 179.
- [3] JOHANSSON, L. B.-A., 1985, *Chem. Phys. Lett.*, **118**, 516.
- [4] JOHANSSON, L. B.-A., and LINDBLOM, G., 1987, *Liq. Crystals*, **1**, 53.
- [5] EMSLEY, J. W., and LINDON, J. C., 1975, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon Press).
- [6] JOHANSSON, L. B.-A., DAVIDSSON, A., LINDBLOM, G., and NORDEN, B., 1978, *J. phys. Chem.*, **82**, 2604.
- [7] LONG, R. C., JR., 1973, *J. magn. Reson.*, **12**, 216.
- [8] LONG, R. C., JR., and GOLDSTEIN, J. H., 1974, *Liquid Crystals and Ordered Fluids*, Vol. 2, edited by J. F. Johnson and R. S. Porter (Plenum Press), p. 147.
- [9] GARNETT, J. L., LONG, M. A., VINING, R. F. W., and MOLE, T., 1972, *J. Am. chem. Soc.*, **94**, 5913.
- [10] CAMERMAN, A., and TROTTER, I., 1965, *Acta crystallogr.*, **18**, 636.
- [11] CAMERMAN, A., and TROTTER, I., 1964, *Proc. R. Soc. A*, **279**, 129.
- [12] PAWLEY, G. S., and YEATS, E. A., 1969, *Acta crystallogr. B*, **25**, 2009.
- [13] BARNES, R. G., and BLOOM, J. W., 1972, *J. chem. Phys.*, **57**, 3082.
- [14] ELLIS, D. M., and BJORKSTAN, J. L., 1967, *J. chem. Phys.*, **46**, 4460.
- [15] BECHTOLD, W., LONG, R. C., JR., and GOLDSTEIN, J. H., 1980, *J. magn. Reson.*, **40**, 361.
- [16] LONG, R. C., JR., and GOLDSTEIN, J. H., 1972, *Molec. Crystals liq. Crystals*, **23**, 137.
- [17] SHILSTONE, G. N., and VERACINI, C. A., and ZANNONI, C. (results to be published).
- [18] EMSLEY, J. W. (editor), 1985, *NMR of Liquid Crystals* (NATO ASI Series C) (Reidel), p. 379.
- [19] CATALANO, D., FORTE, C., VERACINI, C. A., and ZANNONI, C., 1983, *Israel J. Chem.*, **23**, 283.
- [20] CATALANO, D., FORTE, C., VERACINI, C. A., EMSLEY, J. W., and SHILSTONE, G. N., 1987, *Liq. Crystals*, **2**, 357.