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G. N. Shilstone[ab]; C. Zannoni[a]; C. A. Veracini[c]
[a] Dipartimento di Chimica Fisica ed Inorganica, Universita', Bologna, Italy [b] Department of Chemistry, University of Washington, Seattle, Washington, U. S. A. [c] Dipartimento di Chimica, Universita', Pisa, Italy

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Solute alignment in liquid crystal solvents
The Saupe ordering matrix for perylene and pyrene

by G. N. SHILSTONE† and C. ZANNONI
Dipartimento di Chimica Fisica ed Inorganica, Universita', Viale Risorgimento, 4, 40136 Bologna, Italy
and C. A. VERACINI
Dipartimento di Chimica, Universita', Via Risorgimento, 35, 56100 Pisa, Italy

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The complete second rank ordering matrix for perylene-d_{12} and pyrene-d_{10} in four different thermotropic liquid crystals has been determined over large temperature ranges, by interpreting the quadrupolar splittings observed from the deuterium N.M.R. spectra. The dipolar couplings also observed in the spectra were determined by computer simulation for both probes, allowing the commonly made assumptions of rigidity and planarity of these molecules to be tested. It is found that the perylene results are consistent with a non-rigid and non-planar structure with an average twist angle between the napthtalene units of 11.6°, whereas pyrene is rigid and planar within experimental error. It is also observed that both molecules are highly biaxial in their orientational behaviour and therefore another assumption often made especially in fluorescence measurements, that of disc-like cylindrical symmetry, is invalid. The results are interpreted in terms of a molecular field theory which predicts the variation of $(S_{xx} - S_{yy})$ with S_{zz} by calculating these quantities from the potential of mean torque, $U(\beta, \gamma)$, of rigid solutes, expressed solely in terms of one adjustable parameter, the biaxiality parameter, λ. This parameter is predicted by some theories to be both temperature and solvent independent, but our results show that there is a weak temperature dependence and a stronger solvent dependence.

1. Introduction

An important area of research into liquid-crystalline systems concerns the study of solute molecules. The purpose of these studies is often that of obtaining structural information on the solutes themselves, taking advantage of the wider range of tensor observables available in anisotropic solvents [1]. For example proton N.M.R., also coupled with selective deuteriation has been used to obtain geometric information on solutes in liquid samples (see, e.g., [1, 2]). Another well developed approach is that of employing suitable solutes to test theories of liquid crystals and models of solute–solvent anisotropic potentials. Indeed theories of the nematic state, and particularly molecular field theory [3, 4] can also be applied to solutions and in particular to dilute solutions [5] and be more conveniently put to the test by selecting solutes which conform to the assumptions made in the development of the theory itself. For instance liquid crystal molecules are flexible and lack symmetry, thereby making theoretical treatments of pure systems either intractable or in any case very approximate. In this

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† Present address: Department of Chemistry, University of Washington, Seattle, Washington 98195, U.S.A.

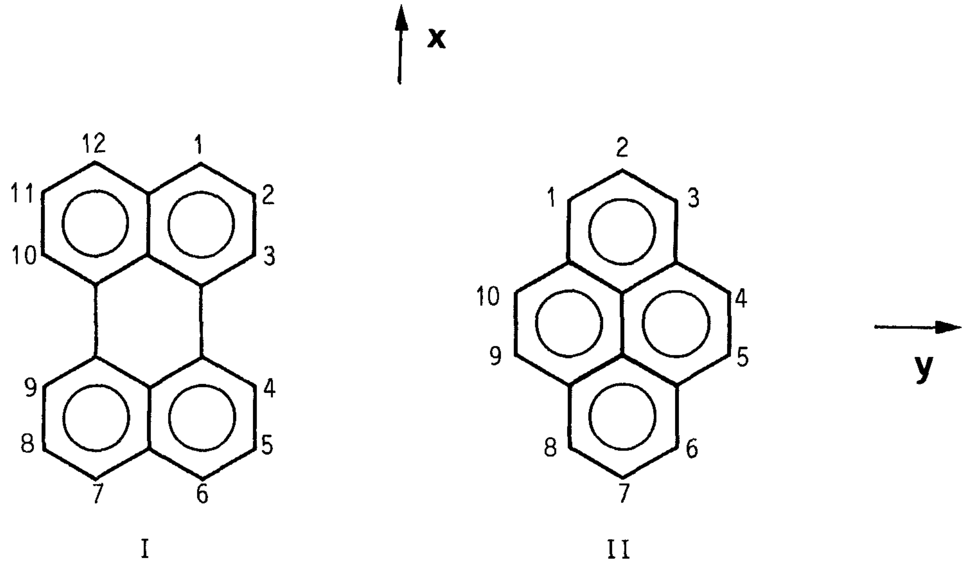


Figure 1. Structures with atomic numbering and labelling of axes for perylene (I) and pyrene (II).

case it might be difficult to assess if a source of disagreement with experiment is due to the theoretical method or to the assumptions that had to be made. On the other hand, probe molecules can be chosen to be rigid and to have a high degree of symmetry, so that the problem is greatly simplified. Another advantage of employing solute molecules is that they can be selected to include (or specifically exclude) various functional groups. In this way their modes of intermolecular interaction can be varied, thus providing the possibility of gaining valuable insights into the mechanisms governing orientational behaviour by comparing the effects of differing local interactions generated by various functional groups [6–10].

In this paper perylene and pyrene have been chosen for study (see figure 1 for structure and labelling of atoms and axes) because, as fused aromatic hydrocarbons, they may be supposed to be rigid and highly symmetry molecules, behaving therefore in a way which might be predicted by theories developed for such solutes. Their molecular structures are also such that there ought not to be any significant local interactions governing their orientational behaviour, as might be the case if a strongly polar group was present, and therefore our results may be expected to correlate with molecular shape or polarizability [4–12]. One other reason for our particular choice of solutes is that they are important fluorescent probes [13–14]. Indeed such aromatic hydrocarbons have been widely used as reporter molecules in membranes [15–17], in nucleic acids [18] and in polymer systems [19–23] as well as for ordinary isotropic liquids [24–26]. They have also been employed in thermotropic [27, 28] and, more recently, lyotropic liquid crystals [29, 30] in order to study liquid-crystalline behaviour by fluorescence depolarization. The technique of polarized fluorescence spectroscopy as applied to liquid-crystalline systems has been well established recently both theoretically [31] and experimentally [32]. The advantages of this form of spectroscopy include its high sensitivity (probe concentration 10^{-4} M to 10^{-6} M are not unusual), which is especially important in lyotropic phases where the probe molecules may not be very soluble or they may perturb the phases to an unacceptable extent if too much is introduced. Also fluorescence data contain information on both the statics and the dynamics of the probe molecules, and, in principle, second and fourth rank order parameters together with correlation times and diffusion coefficients can be obtained [33]. A relative disadvantage of fluorescence depolarization, apart from, of course, the need for an intrinsic or more often extrinsic chromophore, is that the data analysis is much more complex than, for example in magnetic resonance. Thus a complex non-linear least square fit problem has normally to be solved for deconvoluting experimental time resolved intensities [33]. As in other ill conditioned problems, it is essential in this exercise that all the knowledge that can help in limiting the parameter space is included. For example, it is important that the biaxiality of the probe is taken into account from the start, if this is known to exist to a significant extent. On the other hand, this kind of static second rank information is obtained much more directly from N.M.R. than from fluorescence depolarization, even though higher concentrations have normally to be used in this case. Indeed, over and above the difficulties just mentioned, the fluorescence depolarization technique yields the orientation of the molecule transition moments, i.e. of just one or in a few cases two directions in the fluorophore. A number of approximations and assumptions therefore have normally to be made, including rigidity and usually cylindrical symmetry for the ordering. In particular, perylene and pyrene have normally been thought and assumed to fulfill these conditions. Thus it is important to test, by independent means, whether such assumptions are valid. Perylene and pyrene have been found to deviate from cylindrical symmetry when dissolved in a polymer matrix [20–23] and in a lyotropic liquid crystal [34]. As already hinted, one of the most powerful techniques available, with which we may hope to test both these particular assumptions rigorously and also to test an appropriate molecular field theory predicting the behaviour of solutes in liquid crystals, is deuterium N.M.R. (D.M.R.) spectroscopy. Each deuteron, i, in a molecule has associated with it a quadrupolar interaction tensor, q^i. In DMR this gives a quadrupolar splitting, $\Delta\tilde{\nu}_i$, given by [2]

$$\Delta\tilde{\nu}_i = \tfrac{3}{2}q^i_{zz}S_{zz} + \tfrac{1}{2}(q^i_{xx} - q^i_{yy})(S_{xx} - S_{yy}), \qquad (1)$$

where the axis system is that in which the ordering tensor, S, is diagonal (the principal axis system for S), $(S_{xx} - S_{yy})$ being the biaxiality in that frame. Obviously we would have $(S_{xx} - S_{yy}) = 0$ if pyrene and perylene behaved as true discs. The appropriate axis system is determined by the symmetry of the molecule, if it is C_{2v} or higher, as for our chosen solutes. Note also that since S is defined with respect to the liquid crystal director then for liquid crystals that align perpendicular to the magnetic field all the splittings must be multiplied by -2 when using equation (1). Thus, given just two inequivalent deuterions in a rigid symmetric molecule (or molecular fragment), and knowing the components of the appropriate quadrupolar interaction tensors (from single crystal studies or by using those known for similar molecules), the complete second rank ordering tensor may be determined. Dipolar couplings between deuterons may also be observed and, since such couplings are highly sensitive to internuclear distances, in favourable situations information can be obtained concerning molecular flexibility. We have, therefore, used this technique to investigate the behaviour of perdeuteriated perylene and pyrene dissolved in various thermotropic liquid crystals, and here we present results which show that these molecules do not behave as cylindrically symmetric objects and that perylene is, in fact, non-rigid. The biaxiality of these hydrocarbons has already been demonstrated in stretched polymers [23], but not in a fluid liquid crystal environment. We shall also show that the behaviour of such solutes can only be predicted qualitatively by a relatively simple second rank molecular field approximation, as was previously found for anthracene and naphthalene [7, 9].

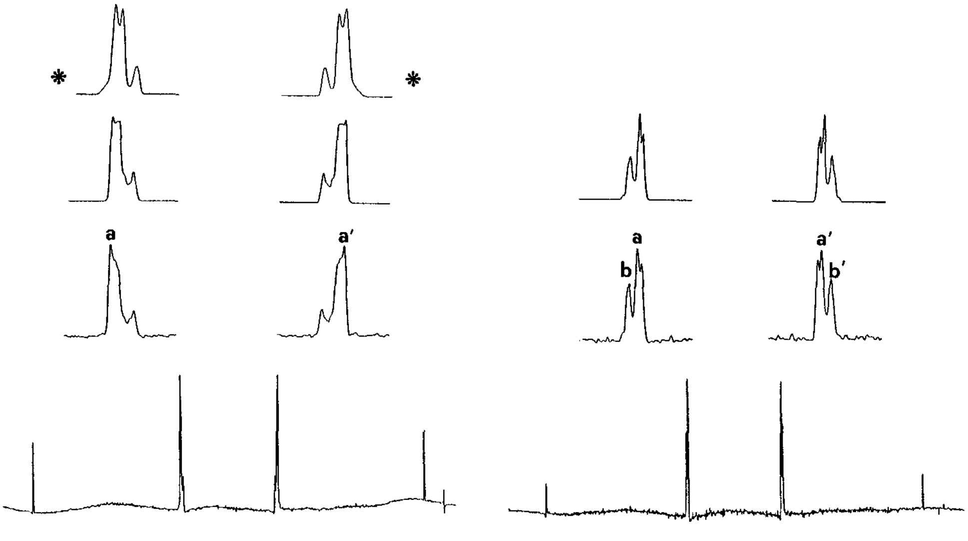
2. Experimental and spectral analysis

Four different thermotropic liquid crystal solvents were employed in this study: E 63, a cyanobiphenyl based mixture (nematic); I 52, 4-ethyl, 2-fluoro, 4′-(2-(4-trans-pentylcyclohexyl)ethyl)biphenyl (nematic); ZLI 1167, an alkylcyanobicyclohexyl based eutectic mixture (nematic and smectic A) and ZLI 2585, a di-alkyl, axial-cyano, bicyclohexane (nematic). ZLI 1167 was purchased from E. Merck (Darmstadt), the others were supplied by BDH Limited (Poole). Both E63 and I52 align so that the director is parallel to the magnetic field, whereas the ZLI liquid crystals align with the director perpendicular to the field. Perdeuteriated perylene was obtained from Merck, Sharp & Dohme (Canada) while perdeuteriated pyrene was synthesized following [35]. Solutions of these two probes with concentrations between 0.5 and 1.0 per cent w/w were prepared in the four liquid crystals and the deuteron N.M.R. spectra were recorded over wide temperature ranges (generally from T_{NI} to room temperature) in 10 mm o.d. glass tubes at 46 MHz on a Bruker CXP300 spectrometer. A typical spectrum for each of the probes dissolved in I52 is shown in figure 2 (bottom traces); the shapes of the spectra do not change significantly with temperature or solvent.

The outer pair of lines in each spectrum is assigned unambiguously to deuterons 1,6,7,12 in perylene and deuterons 2,7 in pyrene on the basis of their relative intensity. The inner lines, originating from the remaining deuterons, are shown on an expanded scale as the middle traces in figure 2. These show extensive structure which arises from two sources; firstly there are relatively small dipolar couplings between the deuterons, and secondly the deuterons giving rise to these lines are not necessarily all equivalent and so could have different quadrupolar splittings. The simulation of systems of more than five or six deuterons is too time consuming at present. However, some insight can be obtained recalling that the dipolar coupling between two deuterons, *i* and *j*, is given by [2]

$$\tilde{D}_{ij} = -\gamma_{\mathrm{D}}^2 h S_{r_{ij}}/4\pi^2 r_{ij}^3, \tag{2}$$

where r_{ij} is the distance between the two nuclei, $S_{r_{ij}}$ is the order parameter of the internuclear vector and γ_{D} is the gyromagnetic ratio for the deuteron. Using this expression, the geometries obtained from X-ray studies of single crystals of perylene [36] and pyrene [37] and the order parameters calculated from the quadrupolar splittings using equation (1), all of the dipolar couplings may be estimated and it is found that those between groups 2,3,4,5 and 8,9,10,11 in perylene and 1,8,9,10 and 3,4,5,6 in pyrene should be negligible. Moreover the couplings between these groups and deuterons 1,6,7,12 in perylene and 2,7 in pyrene, although calculated to be somewhat larger, might also be neglected since no dipolar structure is observed on the outer lines of the spectra. Thus, it should be possible to simulate the structure exhibited by the inner lines as arising from effectively isolated four deuteron systems, namely the symmetric groups 2,3,4,5 and 8,9,10,11 in perylene, and 1,8,9,10 and 3,4,5,6 in pyrene. This indeed is found to be the case and the successful simulations are displayed as the top traces in figure 2 for both perylene and pyrene. This was accomplished by using the calculated values of the dipolar couplings and iteratively varying the quadrupolar couplings for each of the two symmetrically equivalent groups of two deuterons and also for perylene the largest dipolar coupling until



(*a*) (*b*)

Figure 2. Bottom: 46 MHz deuterium N.M.R. spectra of perylene at 320 K (*a*) and pyrene at 322 K (*b*) in I52 using a spectral width of 125 kHz. The splitting of the outer pair of lines in each spectrum gives $\Delta\tilde{\nu}_1$ for perylene and $\Delta\tilde{\nu}_2$ for pyrene. Middle: expansion of the inner group of lines exhibited in each spectrum. The points marked *a*, *a'* for perylene give the splitting $\Delta\tilde{\nu}_2$ and those marked *a*, *a'* and *b*, *b'* for pyrene give the splitting $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_4$, respectively (see text). Top: computer simulation of the inner bands for each spectrum using the parameters given in table 1. For perylene the simulation at the very top (*) is the best calculated using parameters consistent with a planar structure.

approximate agreement was obtained, fine tuned by subsequent small changes in the other parameters. The final parameters are given in table 1.

The success of the simulations shows that our initial assumptions concerning the couplings are valid and allows us to conclude that the relative signs of the quadrupolar couplings $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_2$ for both molecules are such that all the quadrupolar couplings are positive, assuming, reasonably, that the order parameter along the out of plane axis is negative. The simulations also show that the quadrupolar splitting $\Delta\tilde{\nu}_2$ for perylene is given by the separation of peaks *a* and *a'* to within 1 percent and for pyrene $\Delta\tilde{\nu}_1$ is given by the separation of peaks *a* and *a'* to within 0·5 percent and $\Delta\tilde{\nu}_4$ by *b* and *b'* to within 1 per cent, all of the estimates from peak positions being slight overestimates (see table 1). Note that there are no obvious spectral peaks from which $\Delta\tilde{\nu}_3$ for perylene can be estimated accurately without resorting to a simulation. Fortunately to obtain the order parameters S_{zz} and $(S_{xx} - S_{yy})$ from equation (1) it is only necessary to determine one quadrupolar coupling from the inner lines together with that given by the outer lines in the spectrum, and this can be done by inspection for all of the temperatures and solvents with good precision without having to simulate the lineshapes each time. The order parameters were determined by transforming equation (1) so that q_{zz} and $(q_{xx} - q_{yy})$ in the ordering matrix frame are related to the components of the quadrupolar interaction tensor in its principal axis frame (*abc*). This frame is, to a good approximation, such that *a* lies along the C–D bond and *c* is normal to the molecular plane in common with other aromatic hydrocarbons [38]. Now for each deuteron *i*, taking note that *c* is parallel to *z*,

$$\Delta\tilde{\nu}_i = \tfrac{3}{4} q^i_{aa}\{S_{zz}(\eta^i - 1) + (S_{xx} - S_{yy})[l^{i2}_{xa} - l^{i2}_{ya} + \tfrac{1}{3}\eta^i(l^{i2}_{xb} - l^{i2}_{yb})]\}, \qquad (3)$$

Table 1. Chemical shifts, δ_i, dipolar coupling constants, $\tilde{D}_{ij}$, and quadrupolar splittings, $\Delta\tilde{\nu}_i$, used in the simulation of the inner bands of the spectra of perylene and pyrene dissolved in I52 at 320 and 322 K respectively.

(*a*) Perylene. The figures in brackets refer to the simulation assuming a planar structure, the dipolar couplings being varied slightly to give a better fit than is possible with a strictly regular structure (in which, for example, $\tilde{D}_{34} = -193$ Hz).

	Hz
$\delta_{2,5} - \delta_{3,4}$†	0
$\tilde{D}_{23} = \tilde{D}_{45}$	−70 (−71)
$\tilde{D}_{24} = \tilde{D}_{35}$	−14 (−15)
$\tilde{D}_{25}$	−3 (−3)
$\tilde{D}_{34}$	−121 (−188)
$\Delta\tilde{\nu}_2 = \Delta\tilde{\nu}_5$	26960 (26540)
$\Delta\tilde{\nu}_3 = \Delta\tilde{\nu}_4$	26320 (26450)

(*b*) Pyrene.

	Hz
$\delta_{3,6} - \delta_{4,5}$†	4
$\tilde{D}_{34} = \tilde{D}_{56}$	−48
$\tilde{D}_{35} = \tilde{D}_{46}$	−9
$\tilde{D}_{36}$	−3.5
$\tilde{D}_{45}$	−81
$\Delta\tilde{\nu}_3 = \Delta\tilde{\nu}_6$	25630
$\Delta\tilde{\nu}_4 = \Delta\tilde{\nu}_5$	26180

† Taken from the isotropic spectrum.

where η^i, the asymmetry parameter, is $(q^i_{bb} - q^i_{cc})/q^i_{aa}$ and l^i are direction cosines between the *xyz* and *abc* molecular frames of reference. The quadrupolar coupling constants, q^i_{aa}, and the attendant asymmetry parameters are not known for perylene and pyrene. However, it is known that for aromatic deuterons all values of these parameters which have been determined so far lie within a narrow range both for different molecules and for different positions in the same molecule. Therefore it is reasonable to assume that a unique value for q^i_{aa} and for η^i is a good approximation for all positions for both perylene and pyrene, and that these values will be an average of values found for suitable, fused aromatic hydrocarbons. The only such hydrocarbons for which values have been determined are anthracene [38] ($q_{aa} = 181$ kHz, $\eta = 0.064$) and naphthalene [7, 39] ($q_{aa} = 177$ kHz, $\eta = 0.055$), and so we have employed the values $q_{aa} = 180$ kHz and $\eta = 0.06$. We shall see later on that these values are consistent with the dipolar couplings calculated both for pyrene and perylene. It has been found, however, that in anthracene [9] q_{aa} (and also possibly η) does vary with position in the molecule by about 4–5 kHz and so the error in using a value of 180 kHz is estimated to be about 5 kHz. The error in η is not easy to determine, but the smallness of this parameter means that our results will not be affected much by this error. It is interesting to note that the simulations of the spectra for perylene and pyrene also show that it is highly likely that the quadrupolar interaction tensor differs in both molecules with different positions in each molecule by the same order of magnitude as is found in anthracene. Indeed the difference in quadrupolar splittings given by the inner spectral lines cannot easily be explained solely by the geometrical factors involved. These geometrical terms (see equation (3)) have been calculated from X-ray structural determinations of single crystals of perylene [36] and pyrene [37], with the extra assumption that the C–D bonds bisect the corresponding C–C–C angle. Thus in perylene the bonds C–D_1 and C–D_2 are taken to make angles of 2·0° and 58·0° respectively with the x axis and in pyrene C–D_1 is taken to make an angle of 59·0° whereas C–D_2 must, by symmetry, be parallel to x.

3. Results and discussion

3.1. (i) *Analysis of dipolar couplings*

The most striking feature shown by the computer simulation of the spectra of perylene and pyrene is that, whereas all the dipolar couplings in pyrene agree with the molecular structure given by X-ray, showing that this molecule is indeed rigid and planar in solution, for perylene this is not the case. The largest dipolar coupling, $\tilde{D}_{3,4} = \tilde{D}_{9,10}$, is found to be very much smaller than it would be if the molecule, dissolved in a liquid crystal, had the same structure as that determined by X-ray diffraction for a single crystal. In order to show this clearly the asterisked trace at the very top of figure 2 is the best computer simulation of the inner bandshapes achieved for perylene, while keeping the dipolar couplings fixed within reasonable limits calculated for the planar structure obtained from X-ray, the parameters being given in table 1. It can be seen that the simulation does not represent the experimental bands very well, whereas the simulation obtained by relaxing the planar structure does accurately reproduce them, showing that the largest dipolar coupling is actually almost 40 per cent less than that calculated assuming a regular planar structure (see table 1).

There has been much controversy in the past over the structure of perylene, not only as an isolated molecule but even in the crystal state. This is partly due to the fact that X-ray diffraction is not very accurate in locating protons. Secondly, there exist crystal packing forces which in some cases are known to be so strong as to distort C–H bond angles e.g. in anthracene [40], so that the structure determined in the crystalline phase can only be transferred to fluid phases in so far as it refers to rigid (undistorted) parts of the molecule. Thirdly, perylene in particular is an unusual molecule in that it contains one of the longest sp^2–sp^2 carbon bonds (the peri bonds) and one of the shortest H–H non-bonded interactions (the 3–4 and 9–10 interactions) known. To relieve the non-bonded interactions requires a distortion of the 3,4,9 and 10 C–H bonds if molecular planarity and rigidity are to be preserved. The X-ray evidence suggests that this must indeed take place in the crystal phase. However, there have been theoretical arguments indicating that the energy of the isolated molecule does not increase much, if at all, when the naphthalene units (connected via the peri bonds) are twisted with respect to each other about the molecular long axis [41], suggesting that one naphthalene can easily librate with respect to the other one. Recently there has appeared direct experimental evidence that perylene exhibits low frequency vibrational (the so-called butterfly and accordion) motions [42]. However, these motions are about axes parallel to the medium length axis with angular changes which are still probably small enough to allow the continued use of the approximation of rigidity and planarity. In fact the observed deuteron dipolar couplings are not consistent with large amplitude motions of this type. The only possible torsional motion which could significantly reduce the 3,4 and 9,10 dipolar couplings is that suggested by theoretical considerations, i.e. the twisting of the naphthalene units in opposite directions about the long molecular axis, represented schematically in figure 3.

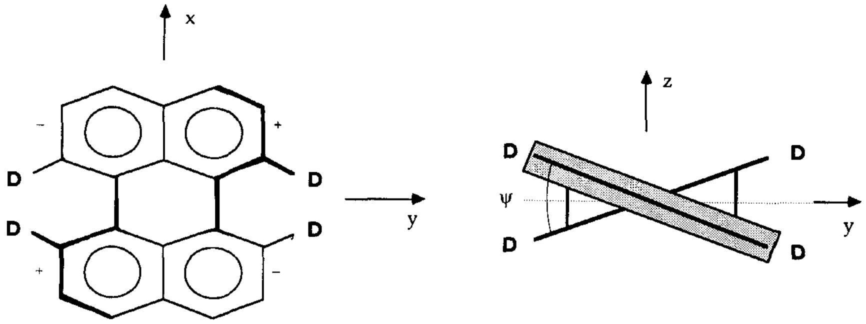


Figure 3. Schematic representation of the large amplitude torsional motion with labelling of the molecular symmetry axes. The x axis is the long axis and the twist angle between the naphthalenes is denoted by ψ (see table 2).

Table 2. Variation of the major dipolar coupling and molecular order parameters for perylene in I52 at 320 K with the twist angle, ψ.

ψ	0°	10°	20°	30°	11·6°
$\tilde{D}_{34}$/Hz	−193	−136	−44	+8	−121†
S_{xx}	0·399	0·399	0·399	0·399	0·399
$(S_{yy} - S_{zz})$	0·393	0·399	0·419	0·453	0·401

† Measured value of $\tilde{D}_{34}$, corresponding also to an internuclear distance of 1·91 Å (1·80 Å for a planar molecule) and order parameter of 0·296 (making an angle of 21·1° with the x axis in the xz plane). The peri bonds make an angle of 9·8° with the x axis at this twist angle. Note that the normal closest approach of non-bonded aromatic hydrogens is 2·0 Å [45].

Note that since all of the other dipolar couplings, and the quadrupolar couplings too, remain consistent with regular naphthalene units the reduction of the 3,4 and 9,10 couplings cannot simply be a result of a distortion in the C–H bond angles, as theory would predict if the molecule were planar. Therefore not only is the molecule quite non-rigid, exhibiting a relatively large amplitude torsional motion to produce the observed couplings, but also the molecule should not be considered simply as a vibrating planar molecule. Indeed the couplings are consistent with a twisted structure, although other conformational distributions, e.g. a flat distribution centred at 0° cannot be ruled out. The situation is reminiscent of that in a biphenyl molecule in which the highest probability for the dihedral angle between the phenyl rings is given at between 30° and 40°, the planar structure actually having a very low probability [43].

In table 2 we show how the major dipolar coupling, $\tilde{D}_{3,4} = \tilde{D}_{9,10}$, varies with the dihedral angle, ψ (see figure 3), given the observed quadrupolar couplings, which define the orientational order, and in this case neglecting the quadrupolar asymmetry parameter and the angle which the C–D bond makes with the x axis (both small), and assuming a one conformer model. The calculation of $\tilde{D}_{3,4}$ using equation (2) is fairly straightforward since for any one given conformer the principal ordering axes can be located by symmetry (see figure 3), requiring therefore only the two order parameters given by the quadrupolar couplings (see equation (3)) to describe completely the ordering. The dipolar coupling can then be determined given fixed bond lengths and within the naphthalene units fixed bond angles all taken from the X-ray analysis. As can be seen in table 2, $\tilde{D}_{3,4}$ is very sensitive to ψ, allowing a fairly accurate prediction of the average twist angle in perylene of 11·6°, despite the relatively large error in measuring $\bar{D}_{3,4}$. Of course a similar result might be obtained by simply twisting the appropriate C–D bonds out of plane. The N.M.R. data do not support such a model, but in this case the data are not accurate enough to rule out entirely a contribution from this source. It should be pointed out that the N.M.R. data in isolation are consistent with a rigid molecule twisted at an angle of 11·6° as shown in figure 3. However the additional theoretical evidence showing little energy difference between conformers with such dihedral angles allows us to predict a relatively wide angular distribution consistent with a torsional motion in which the twist angle of maximum probability is about 11·6°.

Table 2 also shows the variation of the molecular order parameters, as measured by the deuterium quadrupolar splittings, with ψ. The S_{xx} order parameter remains constant since the quadrupolar coupling of the C–D bond in the x direction is unaffected by the motion. S_{zz} and S_{yy} elements are, on the other hand, affected, but only by a small amount, for dihedral angles up to about 10°, and for the particular twist angle measured in this system $(S_{yy} - S_{zz})$ is just 2 per cent higher than that for a planar molecule. This means that for the analysis of the quadrupolar data it would be a reasonable approximation to calculate molecular order parameters as if perylene were rigid and planar, thus giving slight underestimates of $(S_{yy} - S_{zz})$. This approximation is necessary in our case because most of the spectra, especially those in the ZLI liquid crystals, do not exhibit inner bands sufficiently well resolved to allow successful simulations to determine twist angles, which may change especially with solvent. Also our data are too limited to determine the effect of non-rigidity and so the application of a 2 per cent correction, which in any case is within experimental error, would not be meaningful. It must be noted that for other techniques this approximation may be invalid; e.g. even for N.M.R. if the largest dipolar coupling is considered in isolation the major order parameter may be underestimated by up to 40 per cent. Another important technique often used to study perylene is fluorescence depolarization spectroscopy, and here such large amplitude motions might well affect absorption and emission transition moments. Thus it should be considered essential to test such assumptions rigorously for perylene whatever technique is used.

(ii) *Analysis of molecular orientation*

The appropriate quadrupolar splittings measured from each spectrum of perylene and pyrene in the four liquid crystals and the order parameters calculated therefrom (using equation (3) and the approximation of planarity for perylene) are contained in eight tables comprising ten pages, which have been deposited with the British Library Lending Division; copies of this Supplementary Publication may be obtained from the British Library by using the procedure described at the end of this issue and quoting the number SUP 16514.

The systematic errors arising from the non-planarity of perylene and the use of a single average value of the quadrupolar coupling constant and asymmetry parameter have already been discussed. These errors however will not significantly affect the precision with which order parameters can be compared at different temperatures and between different solvents. The random errors in measuring the quadrupolar splittings give rise to errors of about 1 per cent in S_{xx} and 2 per cent in $(S_{yy} - S_{zz})$. The temperature dependencies of the order parameters is similar to that which has already been observed for naphthalene [7], a fused aromatic hydrocarbon with similar biaxial

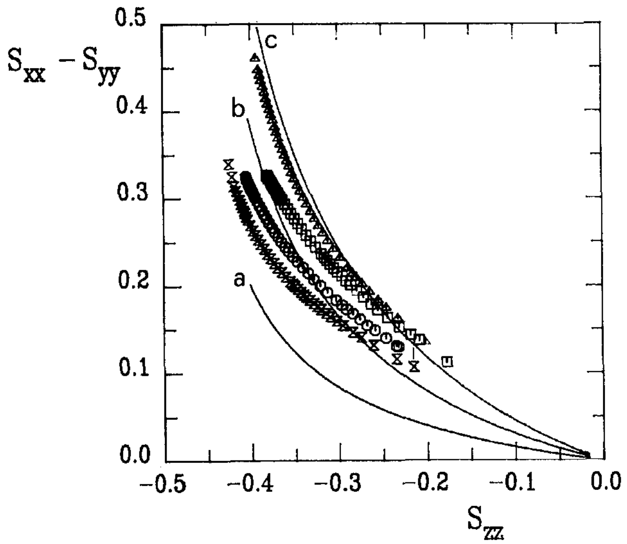


Figure 4. Plots of $(S_{xx} - S_{yy})$ against S_{zz} for perylene in the four liquid crystals: E 63 (circle), I 52 (triangle), ZLI 1167 (hour-glass), ZLI 2585 (square). The solid lines are theoretical predictions for the values of the molecular biaxiality parameter $\lambda = -0{\cdot}05$ (*a*), $-0{\cdot}10$ (*b*), $-0{\cdot}15$ (*c*).

order parameters. Thus in all solvents the longest axis order parameter (S_{xx}) increases with decreasing temperature, while the biaxiality with respect to this axis levels off more quickly and in two cases reaches a maximum, such an observation has been made in the cases of anthracene [9] and naphthalene [7]. Of more interest however is the variation of $(S_{xx} - S_{yy})$ with S_{zz} and this is shown in figure 4 for perylene and figure 5 for pyrene. The first thing to notice is that neither perylene nor pyrene behave as effective discs and they exhibit different ordering matrices in the different solvents. Note that ZLI 1167 has a smectic phase below 305 K and the points at lowest S_{zz} for this solvent (hour-glass symbols) for both probes refer to this phase. However, only a small effect can be observed and this issue will not be discussed in any detail. We only note that the S_A – N transition is practically second order and a small pretransitional increase of S_{xx} is observed near the transition. This kind of plot is sensitive to changes in conditions (here solvent), showing up clearly differences in behaviour in a way independent on the changes in transition temperature going from one system to the other. It is also much more straightforward to describe the variation of the order parameters with respect to each other by molecular field theory, making the interpretation of a comparison between theory and experiment simpler. The molecular field theory for biaxial particles applicable to the work in this paper has been around for some years now [4, 5]. The potential of mean torque, $U(\beta, \gamma)$, which describes the interaction of a rigid solute molecule with a molecular field of rod-like particles (the liquid crystal solvent, existing as a uniaxial nematic) is assumed to be second rank in nature, given by

$$-U(\beta, \gamma)/kT = aP_2(\cos\beta) + \sqrt{\tfrac{3}{8}}\, b \sin^2\beta \cos(2\gamma), \tag{4}$$

where

$$a = -[u_{200} S^{\text{solv}}_{zz} + 2u_{220}(S^{\text{solv}}_{xx} - S^{\text{solv}}_{yy})/\sqrt{6}]/kT, \tag{5a}$$

$$b = -2[u_{202} S^{\text{solv}}_{zz} + 2u_{222}(S^{\text{solv}}_{xx} - S^{\text{solv}}_{yy})/\sqrt{6}]/kT. \tag{5b}$$

The coefficients u_{Lmn} are average solute–solvent interaction terms and the solvent orientational ordering is described by a single second rank ordering matrix $\mathbf{S}^{\text{solv}}$. The significance of this is of course limited when the solvent is a mixture, and in these cases it should be interpreted mainly as a means of quantifying the anisotropic field acting on the solute molecule of interest. The solute ordering is related to $U(\beta, \gamma)$ by a Boltzmann average

$$S_{zz} = \frac{1}{Z}\int d\beta \sin\beta d\gamma P_2(\cos\beta)\exp[-U(\beta, \gamma)/kT], \quad (6a)$$

$$S_{xx} - S_{yy} = \frac{3}{2Z}\int d\beta \sin\beta d\gamma \sin^2\beta \cos 2\gamma \exp[-U(\beta, \gamma)/kT]. \quad (6b)$$

where

$$Z = \int d\beta \sin\beta d\gamma \exp[-U(\beta, \gamma)/kT]. \quad (7)$$

The solute order parameters can therefore be predicted by inputting into equations (6) and (7) a potential of mean torque (equation (4)) given by appropriate choices of the parameters a and b. It is convenient to define a biaxiality parameter, $\lambda = b/2a$, and unique order parameter curves are obtained by fixing λ and varying a. In general λ will depend on the solute–solvent coefficients u_{2mn} and on the solvent order parameters and be, in general, temperature dependent. However, two important special cases should be considered. First if the solvent biaxial order parameter, $(S_{xx}^{\text{solv}} - S_{yy}^{\text{solv}})$, is negligible, λ is a constant for that solute–solvent couple. Indeed putting $(S_{xx}^{\text{solv}} - S_{yy}^{\text{solv}}) = 0$ and combining equations (5) and (6) gives

$$\lambda = u_{202}/u_{200}. \quad (8)$$

Secondly there will be not only temperature independence but also no solvent dependence in λ if the solute–solvent interactions can be decomposed into a product of averaged single particle second rank properties with elements $\bar{X}^{2,n}$, $\bar{X}^{2,m}_{\text{solv}}$ for the solute and solvent respectively, so that, e.g.,

$$u_{2mn} \propto \bar{X}^{2,m}_{\text{solv}}\bar{X}^{2,n}. \quad (9)$$

Substituting into equation (8) it is found that λ then depends only on $\bar{X}^{2,n}$, i.e. solute properties, whatever the solvent biaxiality. This special case is obtained for example when dispersion interactions dominate.

The experimental data do not agree very well with either of the cases as can be seen by comparing the theoretical curves plotted in figures 4 and 5. In particular a solvent dependence is apparent, since the various curves, although similar, are not coincident, so the assumption of separable interactions does not strictly hold. Moreover the experimental points for one solvent are not quite represented by a unique λ curve. A possible source of deviation is a certain amount of solvent biaxiality [44] (cf. equations (5)). Another factor which may contribute to this deviation is the truncation of the potential to second rank terms [5]. The solvent dependence is more serious and suggests that the anisotropic interactions cannot be represented by a single averaged second rank property even for these simple molecules. One possibility is that there might be two (or more) competing anisotropic interactions present or the interaction is site specific. The former possibility has already been investigated to some extend by Burnell, De Lange and co-workers [8, 10, 11], who have found that the orientational ordering of a number of relatively small solutes could be well described using a

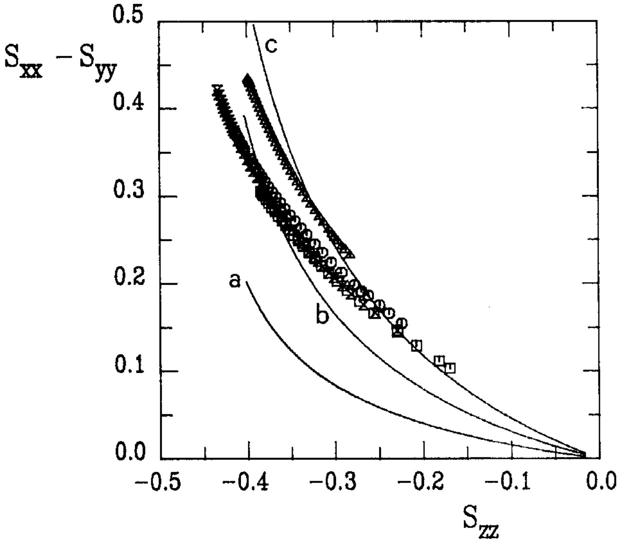


Figure 5. Plots of (S_{xx} − S_{yy}) against S_{zz} for pyrene in the four liquid crystals: E 63 (circle), I 2 (triangle), ZLI 1167 (hour-glass), ZLI 2585 (square). The solid lines are theoretical predictions for the values of the molecular biaxiality parameter $\lambda = -0{\cdot}05$ (*a*), $-0{\cdot}10$ (*b*), $-0{\cdot}15$ (*c*).

semi-empirical model incorporating steric forces and a quadrupolar interaction. We also notice that the detailed solvent dependence is different between perylene and pyrene. It is possible that the non-rigidity of the perylene molecule compared to pyrene contributes to this different behaviour. We now turn to considering the extent of biaxial ordering for these molecules. The shape of the molecules would intuitively suggest that they should behave more like discs than like rods; in fact so disc-like that in the past it has been usual to assume that they behave as if there was cylindrical symmetry about the out of plane axis [15]. Our results show, however, that in rod-like liquid crystal phases the biaxial order parameter is not negligible compared to the order parameter of the would be disc axes (as can be seen in figures 4 and 5), showing that orientationally these molecules behave somewhere between discs and rods. We see from figures 4 and 5 that the λ values are of the order of $-0{\cdot}1$. The theory predicts that there is a maximum value for the magnitude of the biaxiality parameter, λ, corresponding to the solute being half-way between a disc and a rod, that is at $\lambda = 1/\sqrt{6} \approx 0{\cdot}408$. Thus the observed orientational behaviour is actually consistent with only a small molecular biaxiality, defined to be negative for deviations from disc-like cylindrical symmetry, and therefore still seemingly consistent with the molecular shapes. We have already seen that a solute biaxiality alone is not sufficient to explain the results in figures 4 and 5. However, it is still interesting to calculate a shape biaxiality for the two solutes, partly to see how different it is from what is obtained in the various solvents and partly to gauge the similarity of the two solutes from this standpoint. Although there is no rigorous way of associating molecular shape to the coefficients in the potential, various estimates of the shape biaxiality can be put forward. In one of the simplest approaches we can define a molecular shape tensor, F [12] whose principal components F_{aa} along the symmetry axis, are obtained from the length of the molecule along that direction. If the biaxiality is determined by an anisotropic interaction which can be related to these shape parameters through proportionality constants, then we have

$$\lambda = \frac{1}{\sqrt{6}}(F_{xx} - F_{yy})/(F_{zz} - f), \tag{10}$$

where f is one third of the trace of F. The appropriate molecular dimensions can be determined from the X-ray structure and the aromatic carbon and hydrogen van der Waals radii, taken to be 1·77 and 1·0 respectively [45]. The values determined for the corresponding λ values are $-0{\cdot}24$ for perylene and $-0{\cdot}23$ for pyrene. We notice that this estimates the correct sign for λ but also that it gives essentially the same λ for both perylene and pyrene, as we might expect from the fact that the two molecules have a similar length to breadth ratio. Our experimental data show that this is not the case since the two solutes have, in general, a different biaxiality. A different ordering of the two solutes was also found by Michl *et al.* [19] in stretched polymers. Perhaps unexpectedly the magnitude of λ predicted in this manner is also much larger than that shown by our experimental results. Another estimate of molecular shape biaxiality can be obtained by calculating as in [6] a shape tensor analogous to the inertia tensor, but where masses are replaced by van der Waals spheres. This calculation leads to different λ values for perylene and pyrene giving even larger biaxialities namely $-0{\cdot}33$ and $-0{\cdot}28$, respectively.

There is another point to note from figures 4 and 5. It is that it can be misleading to associate a definite shape, rod-like or disc-like, say, to a molecule, based on just the ordering matrix at a certain temperature or in a particular solvent. The behaviour of such a molecule would not be represented by a point, but rather by a curve in an ordering triangle [23]. In our representation we see that a molecular field curve corresponding to a well-defined shape (λ value) actually crosses the diagonal, thus exploring combinations of order parameters that we would call disc-like or rod-like. Intuitively such a situation may be rationalized in the following way. The near disc axis tries to reach its limiting order parameter of $-0{\cdot}5$. At complete order or zero temperature even a slight preference between the two other axes decides which one is going to be more aligned and this takes up the value of one. The third order parameter, corresponding to the other axis has to be $-0{\cdot}5$ at complete order to preserve the uniaxiality of the phase. Thus as long as the phase remains uniaxial, the biaxiality curve is expected to be very flat in a plot like that in figures 4 and 5 and then to go to 1·5. Thus both our theoretical predictions and the experimental results show that a near disc-like solute will appear to behave more and more like a rod as a liquid crystal solvent composed of rod-like molecules approaches perfect order.

4. Conclusions

We have explored the validity of the commonly made assumptions of planarity and rigidity of the probe molecules perylene and pyrene in thermotropic mesophases and find that for perylene these assumptions are invalid. Thus for this particular probe molecule the analysis of spectral data should be handled with these factors specifically taken into account. We have shown that deuterium quadrapolar resonance can, to a good approximation, still be interpreted to give the complete second rank molecular ordering tensor and we find that these probes behave orientationally with a non-negligible biaxiality, contrary again to the commonly held assumption of disc-like cylindrical symmetry. Therefore we conclude that spectroscopic data for these probes must be interpreted in terms of a biaxial as well as a major order parameter to give meaningful results.

The N.M.R. results have been interpreted in terms of a molecular field theory, which predicts qualitatively the orientational behaviour very well. There exist small systematic deviations with temperature, which could probably be rationalized in many ways, such as the effect of a small solvent biaxiality or the inclusion of fourth rank terms in the potential of mean torque. However, the experimental data are not sufficient to distinguish between the various possibilities. There also exists a larger solvent dependence, which is different to that observed for similar hydrocarbons, namely anthracene and naphthalene. The large solvent dependence shows that there are likely to be at least two dominant anisotropic interactions governing solute alignment, but no further conclusion could be reached without more detailed studies. Such studies are now being undertaken, including the correlation of molecular quadrupole moments for different solutes with ordering characteristics, and the simultaneous measurement of solvent order parameters together with those of the solute by N.M.R.

We also conclude that although the ordering characteristics of such probe molecules as ours are correlated with molecular shape, e.g. here the biaxiality calculated from the shape is non-zero and has the correct sign, the biaxiality is overestimated if a shape parameter based on the van der Waals molecular dimensions is considered.

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