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## Solvation sites in mesophases of discotic liquid crystals

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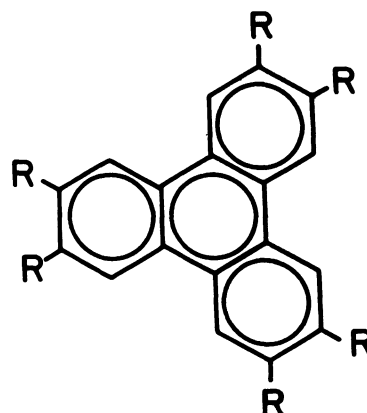
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**Résumé.** — Le splitting quadrupolaire du deutérium,  $\nu_Q$ , de  $C_6D_6$  dissout dans un certain nombre de cristaux liquides discotiques, a été mesuré à des températures où la mésophase est stable. Trois types différents de mésophase furent utilisés. (i)  $D_{ho}$  une phase hexagonale en colonne avec un empilement ordonné des molécules, (ii)  $D_{rd}$  une phase rectangulaire biaxiale avec un empilement désordonné des molécules, (iii) un nématique discotique  $N_D$ . Les trois types de mésophase montrent une dépendance en température de  $\nu_Q$  différente. Dans la phase  $D_{ho}$ , les splittings sont petits et dépendent fortement de la température. Ce comportement est interprété comme un équilibre dynamique rapide entre deux solutions consistant en : (I) des molécules intercalées entre les colonnes discotiques et (II) des molécules dissoutes dans la région aliphatique des chaînes entre les colonnes. Dans la phase  $D_{rd}$ , les splittings sont considérablement plus larges et relativement constants avec la température, indiquant que la solvation dans la phase  $D_{rd}$  se fait principalement dans la région intercalaire. Finalement dans la phase nématique, les splittings sont larges et semblent suivre une dépendance en température de type Maier-Saupe. Ce qui est consistant avec la structure de la phase nématique, où l'on n'espère pas trouver deux sites différents.

**Abstract.** — The deuterium quadrupole splitting,  $\nu_Q$ , of  $C_6D_6$  dissolved in a number of discotic liquid crystals has been measured over the temperature range of the mesophase stability. Three different types of mesophases were used : (i)  $D_{ho}$ , which is a columnar hexatic phase with ordered molecular stacking ; (ii)  $D_{rd}$ , which is a rectangular biaxial columnar phase with disordered molecular stacking ; (iii) a nematic discotic,  $N_D$ . The three types of mesophases exhibit different temperature dependence of  $\nu_Q$  : In the  $D_{ho}$  phase the splittings are relatively small and strongly temperature dependent. This behaviour is interpreted in terms of a fast dynamic equilibrium between two solvation sites consisting of (I) molecules intercalated within the discotic columns, and (II) molecules dissolved in the aliphatic side chain region between the columns. In the  $D_{rd}$  phase the splittings are considerably larger and fairly constant with temperature indicating that solvation in this phase is predominantly in the intercalation site. Finally in the nematic phase the splittings are large and follow a Maier-Saupe type temperature dependence. This is consistent with the structure of the nematic phase where no different sites are expected.

**1. Introduction.** — The new so called discotic liquid crystals [1] have drawn the attention of scientists because of the novel mesomorphic structures that they exhibit and because of their potential use as orienting solvents. The molecules of these mesogens consist of flat (disc-like) aromatic cores to which a number of aliphatic side chains are bonded. The most important group of compounds investigated so far consists of derivatives of triphenylene where R represents side chains. We have recently studied the orienting characteristics of probe molecules dissolved in hexahydroxytriphenylene (THE6,  $R = OC_6H_{13}$ ), using  $^2D$  NMR of deuterated solutes [2]. The mesophase



of this compound belongs to the  $D_{ho}$  class [1c, 3], which is an hexatic columnar phase in which the molecules have a well defined order within the columns (Fig. 1). The behaviour of most aromatic

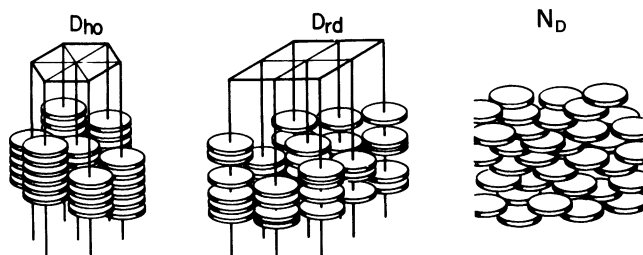


Fig. 1. — Schematic diagrams of the three discotic mesophases discussed in the present work. In the  $D_{ho}$  phase the molecules (rings) are regularly stacked into columns which in turn form an hexagonal array. In the  $D_{rd}$  phase, the molecules are stacked disorderly in the columns and the latter form a rectangular (biaxial) array. In the nematic discotic phase,  $N_D$ , the centre of mass of the molecules is randomly distributed, but their symmetry axes exhibit long range order.

probes in this mesophase was quite unexpected; in particular we found that the orientational ordering of the dissolved aromatic molecules was considerably smaller in the discotic mesophase than in the common thermotropic liquid crystals, despite the fact that the orientational order of the discotic solvent is very high [4]. Moreover the elements of the ordering matrix of the solute molecules were strongly temperature dependent and often changed signs within the mesophase region. This too is in contrast with the behaviour of the solvent molecules whose molecular order parameter is nearly independent of temperature [4]. These results were interpreted in terms of a model involving two solvation sites for the  $D_{ho}$  mesophase. It was assumed that the two solvation sites

are (I) solute molecules intercalated within the columnar structures, and (II) solute molecules dissolved in the aliphatic chains between the columns. Under condition of fast dynamic equilibrium between the two sites the observed deuterium quadrupole splitting  $\nu_Q$  is

$$\nu_Q = P_I \nu_Q^I + P_{II} \nu_Q^{II}$$

where  $\nu_Q^i$  is the quadrupole splitting in the  $i$ 's site and  $P_i$  the corresponding fractional population. The temperature dependence of  $\nu_Q$  could then readily be explained by assuming that the orientational order parameter,  $S$ , in the two sites have opposite signs and that the population ratio  $P_{II}/P_I$  is temperature dependent.

The aim of the present paper is to substantiate this model and gain more information on the nature of the solvation sites. To do this we have measured the deuterium quadrupole splitting of benzene- $d_6$  dissolved in a number of different discotic mesophases (Fig. 1). These include (i) four members of a homologous series  $THE_n$  which exhibit the  $D_{ho}$  structure, (ii) a discotic nematic mesophase  $N_D$ , and (iii) a rectangular disordered columnar phase,  $D_{rd}$ .

For experimental details on the sample preparation and NMR measurements see references [2] and [4].

2.  $C_6D_6$  in the  $D_{ho}$  mesophase of  $THE_n$ . — In this set of experiments we determined the temperature dependence of the deuterium quadrupole splitting of  $C_6D_6$  dissolved in the homologous series  $THE_5$ ,  $THE_6$ ,  $THE_7$  and  $THE_8$  (see Table I). The mesophases of all these compounds belong to the  $D_{ho}$  class, though on going from  $THE_5$  to  $THE_8$  there is a gradual lengthening of the aliphatic chains. This corresponds to increasing the probability of the benzene molecules to occupy site II at the expense of site I. In figure 2 are plotted the experimental deuterium quadrupole splitting *versus*  $T_c - T$  (where  $T_c$  is the clearing point of the solution). The full lines in this

Table I. — Details of the discotic solutions used in the present work

Mesogen	— R	Phase	$C_6D_6$ (wt. %)	$T_c$ ( $^{\circ}C$ ) <sup>(a)</sup>	Remarks
1. $THE_5$	$-OC_5H_{11}$	$D_{ho}$	5.9	95	—
2. $THE_6$	$-OC_6H_{13}$	$D_{ho}$	4.9	74	<sup>(b)</sup>
3. $THE_7$	$-OC_7H_{15}$	$D_{ho}$	5.2	73	<sup>(c)</sup>
4. $THE_8$	$-OC_8H_{17}$	$D_{ho}$	4.6	71	—
5. { $THA_8$ $TH_8B$	$-OC(O)C_7H_{15}$ $-OC(O)C_6H_4C_8H_{17}$	$N_D$	5.2	85	<sup>(d)</sup>
6. $THA_8$	$-OC(O)C_7H_{15}$	$D_{rd}$	6.2	117	—

<sup>(a)</sup> Clearing point of the  $C_6D_6$  solution.

<sup>(b)</sup> The solute consisted of a 1 : 2  $C_6D_6$  :  $C_6H_6$  ratio.

<sup>(c)</sup> The solvent consisted of chain perdeuterated  $THE_7$  and contained 7 wt. % ring deuterated  $THE_6$ .

<sup>(d)</sup> The mixture consisted of a 64 : 36 mole ratio of  $THA_8$  :  $TH_8B$ .

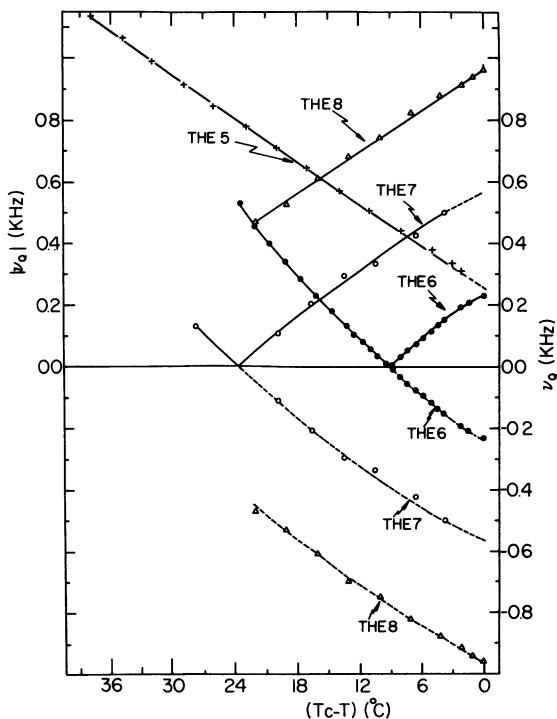


Fig. 2. — The temperature dependence of the deuterium quadrupole splitting of  $C_6D_6$  dissolved in THE5, THE6, THE7 and THE8. The composition of the solutions and the definitions of the mesogens are given in table I. The full lines correspond to the measured magnitudes of  $v_Q$  (left scale), while the dashed curves correspond to their algebraic values (right scale) under the assumption that  $v_Q$  becomes continuously more negative with increasing temperature.

figure refer to the measured magnitude of  $v_Q$ , (left scale). Note that in THE5,  $|v_Q|$  decreases with temperature, in THE8 it increases, while in THE6 and THE7 there is a discontinuous change in the temperature dependence of  $|v_Q|$ : it first decreases and then increases again. The results are replotted in figure 2 (dashed curve) on the assumption that the algebraic value of  $v_Q$  becomes continuously more negative with increasing temperature. This is the trend expected on the basis of the model [2] in which upon increasing temperature the population of site I (the intercalation site) where  $S > 0$ , gradually shifts to the aliphatic region (site II) where  $S < 0$ . It may be seen that these four lines are very nearly parallel to each other and that at a given value of  $T_c - T$  with each additional methylene group,  $v_Q$  becomes more negative by approximately the same amount. We thus find that increasing the chain length has the same effect on  $v_Q$ , as increasing temperature. This observation supports the two-site model discussed above, and the conclusion that with increase in temperature the solute population of the aliphatic site (II) increases.

3.  $C_6D_6$  in a nematic  $N_D$  mesophase. — The effect of two solvation sites on  $v_Q$  is particularly pronounced in the  $D_{ho}$  phase because its structure exhibits well defined aromatic and aliphatic regions. For the

discotic nematic phase  $N_D$ , no such regions exist (Fig. 1) and accordingly we expect the temperature dependence of  $v_Q$  in the  $N_D$  phase to be more similar to that of the conventional thermotropic liquid crystals. To check on this point we have measured the quadrupole splitting of  $C_6D_6$  dissolved in a discotic nematic solvent (see Table I) [5]. The  $v_Q$  values (Fig. 3) are indeed considerably larger than those observed for the  $D_{ho}$  mesophase and their temperature dependence is very much like the Maier-Saupe behaviour. This comparison between  $N_D$  and  $D_{ho}$  further support the two-site model for the latter phase. It should however be emphasized that on the molecular level multiple site interaction between the solute and solvent molecules can occur also in the  $N_D$  phase. Such effects have been observed in certain normal thermotropic liquid crystals, but the effect was much less pronounced than that observed for the  $D_{ho}$  phase.

4.  $C_6D_6$  in a disordered columnar phase. — The tendency of the solute molecules to shift to the aliphatic sites with increasing temperature is presumably driven by the larger entropy of this site, as compared to the intercalation site within the columns. This is particularly true for the  $D_{ho}$  phase in which the solvent molecules are stacked in a regular ordered way within the columns (hence the subscript « o » for « ordered »). We therefore expect that in mesophases with disordered columns the tendency to shift the equilibrium from the intercalation site to the aliphatic site would be less pronounced than in the phases of ordered columns. To check this hypothesis we measured the temperature dependence of the quadrupole splitting of  $C_6D_6$ , dissolved in the discotic mesophase of THA8 (see Table I) [1c, 6]. This mesophase belongs to the

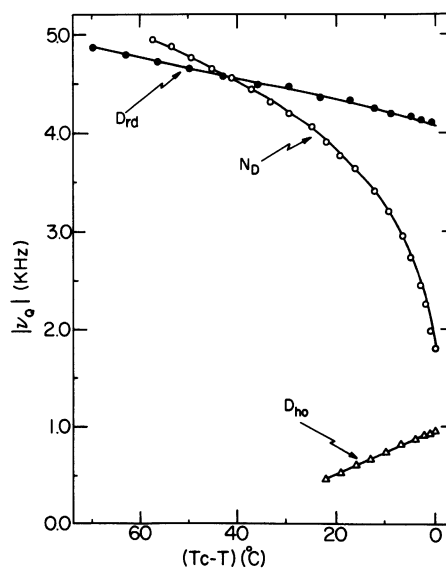


Fig. 3. — The measured magnitude of the quadrupole splittings of  $C_6D_6$  dissolved in nematic ( $N_D$ ) rectangular ( $D_{rd}$ ) and hexagonal ( $D_{ho}$ ) discotic phases. The results correspond respectively to solutions 5, 6 and 4 of table I.

$D_{rd}$  class (Fig. 1) which is characterized by disordered molecular stacking within the column and a rectangular arrangement of the columns (hence the subscripts « d » and « r »). The results for  $\nu_Q$  are plotted in figure 3. As may be seen the splittings are much larger than in the  $D_{ho}$  phase and they are almost independent of temperature even very close to the clearing point. (Very recently we found similar results for  $\nu_Q$  of benzene dissolved in the  $D_{hd}$  phase of hexadecanoyloxytriphenylene.) This behaviour is similar to that observed [4] for the aromatic core in the columnar  $D_{ho}$  mesophase of THE6, and suggests that the benzene molecules in disordered phases are predominantly intercalated in the columnar site (I) and dissolve only very little in the side chain region. In this mesophase the stabilization energy due to interaction appears to be the dominant factor determining the equilibrium distribution of the solute even at high temperature. Apparently the intercalation does not significantly disturb the columnar structure which is disordered anyhow and there is less gain in entropy on shifting to the aliphatic region.

Before concluding we wish to emphasize a specific feature of the  $C_6D_6$  spectra in the  $D_{rd}$  phase. In figure 4 are shown examples of  $C_6D_6$  spectra in the three types of solvents used. It may be seen that while for the  $D_{ho}$  and  $N_D$  solutions the doublet components are sharp, those for  $D_{rd}$  are broad and exhibit typical spectra of two-dimensional domain

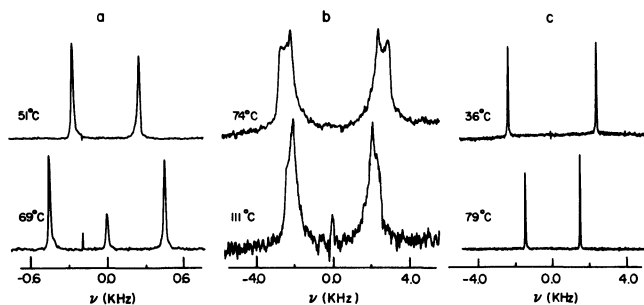


Fig. 4. — Examples of the deuterium NMR spectra for the same solutions used to obtain the results shown in figure 3. Traces a, b, and c, correspond respectively to  $D_{ho}$ ,  $D_{rd}$  and  $N_D$ . Note the « biaxial » spectrum of the  $D_{rd}$  solution. The quadrupole splitting for this solution was taken as the splitting of the inner peaks of the spectrum.

distribution. This effect results from the biaxiality of the  $D_{rd}$  phase and can be explained as follows : The principal optical axis of a discotic domain (the director) aligns in a magnetic field perpendicular to the field direction [4]. Thus in the samples studied in the present work which were prepared by slow cooling in the magnetic field there is a distribution of domains whose major axes all lie perpendicular to the magnetic field. The observed spectra therefore correspond to a configuration in which the magnetic field is perpendicular to the major axes of the discotic domains. For uniaxial systems this results in sharp NMR peaks since all perpendicular directions are equivalent. For biaxial phases like  $D_{rd}$  this is not so and consequently one observes a distribution of resonances which depends on the biaxiality of the phase. We are currently investigating the spectra of this and other biaxial liquid crystals and will report these results in a forthcoming publication.

**5. Conclusions.** — In summary the following characteristics concerning the solvation sites in discotic mesophases have been demonstrated :

In columnar phases there is an equilibrium between molecules intercalated within the columns (site I) and molecules dissolved in the aliphatic chains (site II). The equilibrium population ratio  $P_{II}/P_I$  increases with temperature and within a homologous series it increases with the chain length.

In disordered columnar phases the preferred solvation site corresponds to the intercalation site and the ratio  $P_{II}/P_I$  is almost independent of temperature. This site is stabilized by the interaction between the solute molecules and the aromatic core of the mesogen molecules, and there is no significant gain in entropic free energy on going to site II. In ordered columnar phases both sites are populated and the ratio  $P_{II}/P_I$  is strongly temperature dependent.

In the nematic discotic phase the two sites defined in connection with the columnar phases do not exist, and the behaviour of the solute molecules is similar to that in the normal thermotropic liquid crystals.

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