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## Liquid Crystals

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### On the transitional properties of rigid oligomers. The orientational order of the monomer 4-*n*-pentyl-4'-cyanobiphenyl and its platinum dichloride linked dimer

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## PRELIMINARY COMMUNICATIONS

### On the transitional properties of rigid oligomers The orientational order of the monomer 4-*n*-pentyl-4'- cyanobiphenyl and its platinum dichloride linked dimer

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We have studied the orientational order of the monomer 4-*n*-pentyl-4'-cyanobiphenyl (5CB) and of the dimer, [PtCl<sub>2</sub>(5CB)<sub>2</sub>], formed by linking two cyanobiphenyl units via a platinum dichloride bridge, dissolved in a common nematic solvent, using deuterium NMR spectroscopy. Analysis of the second rank order parameters, obtained from these experiments, in terms of a molecular field theory yields the anisotropic solute–solvent strength parameter responsible for the solute alignment. In the limit of low solvent order the strength parameters for the monomer and dimer differ significantly, in accord with the differing anisotropies of these two solutes. However, as the solvent order increases, so the relative difference in the strength parameters decreases, tending to zero. A possible explanation for this intriguing behaviour is proposed.

The transitional properties of a liquid crystal oligomer are expected to depend strongly on the number of monomer units which it contains. According to a molecular field theory for rigid, linear oligomers, the nematic–isotropic transition temperature is predicted to be a linear function of the number of monomers in the oligomer [1]. In contrast the entropy of transition should be independent of the length of the oligomer. The number of systems available with which to test these predictions is rather limited. However, the dimers formed by linking two 4-*n*-alkyl- or 4-*n*-alkyloxy-4'-cyanobiphenyls with palladium or platinum dichlorides [2, 3] provide a unique opportunity with which to explore the validity of the theoretical predictions. For example,  $T_{NI}$  for the dimer formed by linking two 4-*n*-pentyl-4'-cyanobiphenyl (5CB) molecules with platinum dichloride is 477 K which is 1.5 times larger than that (308 K) of the monomer [3]. In addition, the entropy change  $\Delta S/R$  at the nematic–isotropic transition for the dimer is 1.0 [4], which is significantly larger than the value of 0.26 found for the monomer. The disagreement between theory and experiment for this

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dimer/monomer system may have a variety of origins which include molecular flexibility and the relatively bulky nature of the linking  $\text{PtCl}_2$  group [1]. In order to explore the problem further we have investigated the orientational order of the dimer  $[\text{PtCl}_2(5\text{CB})_2]$  and the monomer 5CB dissolved in a common nematic solvent. In order to appreciate the object of these experiments it is useful to begin by giving the theoretical background to their analysis.

For the sake of simplicity we shall assume that the molecules, of both the solutes and the solvent, are cylindrically symmetric and rigid. Such assumptions are clearly not strictly valid given the nature of the mesogenic cores and the flexibility of the terminal pentyl chains. However, the approximations are not unreasonable, and indeed the Saupe ordering matrix for pure 5CB has been found to be close to cylindrically symmetric [5]; in addition they have the advantage of facilitating the theoretical development. The potential of mean torque responsible for the orientational order of the solute takes the form [6]

$$U_i(\beta) = -X_i P_2(\cos \beta). \quad (1)$$

Here  $\beta$  is the angle between the assumed symmetry axis of the molecule and the director,  $P_2(\cos \beta)$  is the second Legendre function and the subscript  $i$  denotes the molecular type, namely solvent  $s$ , dimer  $d$  or monomer  $m$ . The parameter  $X_i$  determines the strength of the ordering potential and for infinitely dilute solutions it is predicted to take the form [6]

$$X_i = \bar{u}_2^{is} \bar{P}_2^{(s)}. \quad (2)$$

The anisotropy in the averaged solute-solvent interaction is denoted by  $\bar{u}_2^{is}$  and  $\bar{P}_2^{(s)}$  is the second rank orientational order parameter for the solvent. The order parameter for the solute,  $i$  is related to the potential of mean torque via

$$\bar{P}_2^{(i)} = Z_i^{-1} \int P_2(\cos \beta) \exp \{ (X_i/k_B T) P_2(\cos \beta) \} \sin \beta \, d\beta, \quad (3)$$

where the orientational partition function for the solute is

$$Z_i = \int \exp \{ (X_i/k_B T) P_2(\cos \beta) \} \sin \beta \, d\beta. \quad (4)$$

Since the solute order parameter is, as we shall see, available from experiment, this enables us to determine  $X_d$  and  $X_m$  for the dimer and the monomer as a function of temperature. They both depend on the solvent order parameter which is unknown, but this quantity can be eliminated by taking the ratio  $X_d/X_m$  which is predicted to be

$$X_d/X_m = \bar{u}_2^{ds} / \bar{u}_2^{ms}. \quad (5)$$

Within the molecular field theory, the anisotropic solute-solvent interaction parameter  $\bar{u}_2^{is}$  is predicted to be inversely proportional to the molecular volume of the solvent [7],

$$\bar{u}_2^{is} = \epsilon_{is} / v_s \quad (6)$$

so that the ratio available from experiment is predicted to be

$$X_d/X_m = \epsilon_{ds} / \epsilon_{ms}. \quad (7)$$

We can proceed further by invoking the geometric mean approximation [6] to write the mixed interaction in terms of the pure interaction parameters, for example,

$$\epsilon_{ds} = (\epsilon_{dd} \epsilon_{ss})^{1/2}. \quad (8)$$

This approximation is known to work well at least when predicting the composition dependence of the nematic–isotropic transition temperature for binary mixtures of nematogens [6]. With this approximation, the observed ratio  $X_d/X_m$  is found to depend only on the interaction parameters for the dimer and monomer

$$X_d/X_m = (\epsilon_{dd}/\epsilon_{mm})^{1/2} \quad (9)$$

and so is independent of the common solvent. A similar prediction is made for the biaxiality parameter of the solute–solvent anisotropic interaction for solutes which deviate from cylindrical symmetry, but this parameter is found to be solvent dependent [8], which calls into question the strict validity of the separation contained in equation (8). None the less we shall persist with such a separation since it leads to the further prediction that the pure interaction parameter for a dimer will be four times that for the monomer, so that  $X_d/X_m$  is predicted to be independent of temperature and equal to 2. Strictly  $[\text{PtCl}_2(5\text{CB})_2]$  is not the exact dimer of 5CB, because the platinum dichloride unit linking the two 4-*n*-pentyl-4'-cyanobiphenyl monomers will extend the molecular length and may also broaden the molecule. It is to be expected, therefore, that  $X_d/X_m$  might be larger than 2. Since the nematic–isotropic transition temperatures are also proportional to the interaction parameters [1],

$$T_{\text{NI}}^{(i)} = \epsilon_{ii}/v_i \quad (10)$$

it is also possible to relate the observed ratio  $X_d/X_m$  to the experimental values of  $T_{\text{NI}}^{(i)}$  and of  $v_i$  for the dimer and monomer. Thus

$$X_d/X_m = (v_d T_{\text{NI}}^{(d)}/v_m T_{\text{NI}}^{(m)})^{1/2} \quad (11)$$

In order to test these predictions, we have determined the second rank order parameters for 5CB and the platinum linked dimer  $[\text{PtCl}_2(5\text{CB})_2]$  using deuterium NMR spectroscopy. The monomer had been deuteriated in the first methylene group of the pentyl chain for a previous study [9] and this sample was used in the present investigation. It was employed to prepare a specifically deuteriated sample of the dimer using the melt synthesis described by Bruce *et al.* [10]. The nematic solvent used to investigate the orientational order of both monomer and dimer was 1-(4-*trans*-propylcyclohexyl)-2-(2'-fluoro-4'-*n*-pentylbiphenyl-4-yl)ethane (I35) supplied by Merck Ltd (Poole, U.K.); its transition temperatures are  $T_{\text{CN}} = 305$  K and  $T_{\text{NI}} = 380$  K. This particular solvent was chosen because it is relatively inert and so should inhibit the decomposition of the dimer. In addition, it has a wide nematic range, in excess of 60 K, over which measurements can be made. The concentration of the solute was about 2.5 per cent by weight for both monomer and dimer. The addition of the solute changes the nematic–isotropic transition temperature of the solvent; in the case of the dimer,  $T_{\text{NI}}$  was increased by 2 K, while for the monomer, it was depressed by 4 K. Such changes are in accord with the larger anisotropy of the dimer with respect to the solvent, while the monomer has a smaller relative anisotropy. The deuterium NMR spectra were measured with a Bruker MSL 200 spectrometer at 30.7 MHz as a function of temperature, from the isotropic phase to just above the freezing point of the solution. The NMR spectra in the nematic phase consisted of a doublet whose splitting increased dramatically with decreasing temperature. In addition the splitting found for the dimer was significantly greater than that of the monomer, as expected. This difference in quadrupolar splittings was greatest at the nematic–isotropic transition and decreased with decreasing temperature as the orientational order of both solutes approaches the limiting value of 1.

If we persist with our assumption that the monomer and dimer can be taken to be rigid and cylindrically symmetric, then the second rank order parameter,  $P_2^{(i)}$ , for solute  $i$  can be extracted from the quadrupolar splitting,  $\Delta\bar{\nu}_i$ , via

$$\Delta\bar{\nu}_i = (3/2)q_{CD}\bar{P}_2^{(i)}P_2(\cos\theta). \quad (12)$$

To obtain this expression, the quadrupolar tensor is assumed to be cylindrically symmetric about the C-D bond, which is a good approximation for aliphatic deuterons. The angle between the C-D bond and the effective symmetry axis of the ordering matrix is denoted by  $\theta$ . We assume that this symmetry axis deviates by about  $10^\circ$  from the *para*-axis of the cyanobiphenyl groups for both monomer and dimer. This small deviation allows, in an approximate way, for the influence of the pentyl chain on the location of the effective molecular symmetry axis. The angle between this and the C-D bond was calculated using the bond angles  $\widehat{C\hat{C}D}$  of  $107.5^\circ$  and  $\widehat{D\hat{C}D}$  of  $113.6^\circ$

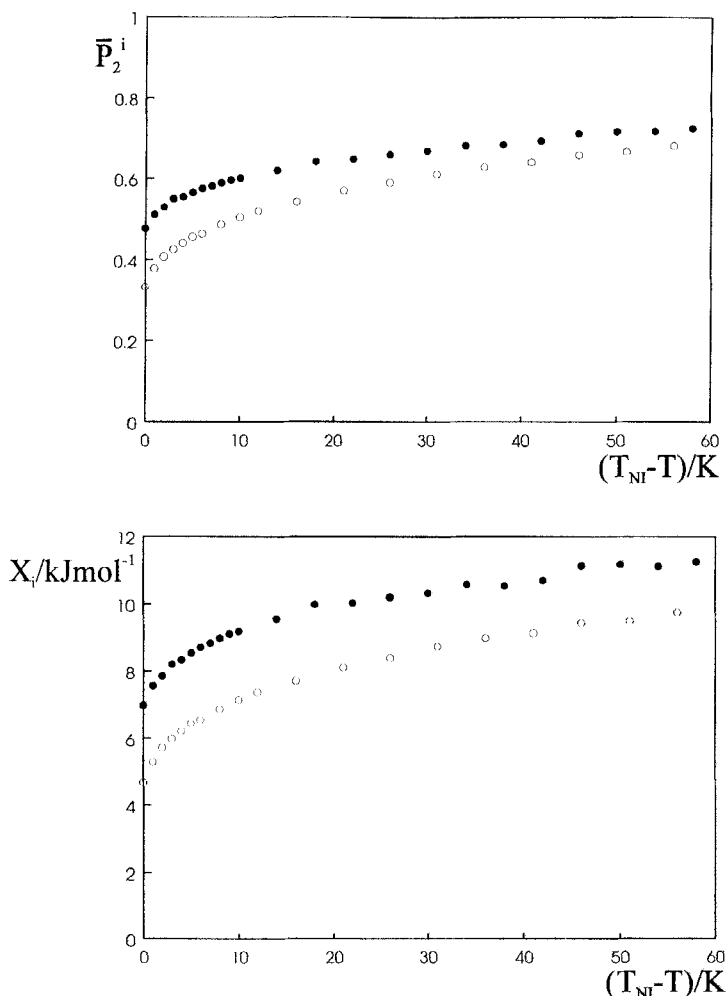


Figure 1. The dependence on the shifted temperature  $(T_{NI}-T)$  of (a) the order parameter  $\bar{P}_2^{(i)}$  for the effective molecular symmetry axis and (b) the strength parameter  $X_i$  in the potential of mean torque for the monomer ( $\circ$ ) and the dimer ( $\bullet$ ).

[11], and found to be  $102.3^\circ$ . Using this value and a quadrupolar coupling constant  $q_{CD}$  of 168 kHz, the quadrupolar splittings were converted to the order parameters  $\bar{P}_2^{(i)}$  for the effective symmetry axis of the monomer and the dimer. These results are shown as a function of the shifted temperature ( $T_{NI} - T$ ) in figure 1 (a) for both the monomer and the dimer. At the nematic–isotropic transition, the order parameter for the monomer 5CB is found to be 0.33 which is close to that for the pure nematogen [5]. The order parameter then increases rapidly with decreasing temperature and is still growing relatively rapidly even at the lowest shifted temperature at which measurements were made. The behaviour of the monomer contrasts with that for the  $[\text{PtCl}_2(5\text{CB})_2]$  dimer; its order parameter at the transition is 0.48, which is significantly larger than that for the monomer, as we had expected. The order parameter then grows quite rapidly with decreasing temperature. However, the rate of growth soon slows, so that at the lowest shifted temperature which we were able to study, the difference in the order parameters for the monomer and dimer had decreased to just 0.04. Given the large difference in the shape anisotropy between the monomer and the dimer, such a small difference in  $\bar{P}_2$  at the same shifted temperature is somewhat surprising. Of course, for pure nematogens the order parameter must tend to a limiting value of 1 at low temperatures and so a progressive reduction of the difference in the order parameters is to be expected. This should not be the case, however, for solutes in a common nematic solvent, where the limiting value of the solute order parameter at low temperatures is expected to be determined by the anisotropy in the solute–solvent interaction.

The order parameter itself is not directly proportional to the solute–solvent interaction and so to explore the significance of the results for the monomer and dimer further, we have extracted the molecular field strength parameters, via equation (3), from the order parameters. The dependence of  $X_m$  and  $X_d$  on the shifted temperature is shown in figure 1 (b). At the nematic–isotropic transition the strength parameter for the dimer is  $7.0 \text{ kJ mol}^{-1}$  which is significantly greater than the value for the monomer of  $4.7 \text{ kJ mol}^{-1}$ ; this difference between  $X_d$  and  $X_m$  is essentially independent of temperature. However, the relative difference in the strength parameters does decrease from a value of about 40 per cent at the transition to just 17 per cent at the lowest shifted temperature for which results are available. This behaviour of the molecular field strength parameters does indeed reflect that of the order parameters and is equally surprising given the apparent large difference in the anisotropies of the monomer and dimer. As we have seen, theory predicts that the ratio  $X_d/X_m$  should be a constant; the value of this can be calculated from the nematic–isotropic transition temperatures of the monomer and dimer via equation (11) and gives 1.76 assuming that the ratio of the molar volumes is 2. To test this prediction we have plotted in figure 2  $X_d$  versus  $X_m$ . It is apparent that whereas  $X_d$  is almost linear in  $X_m$ , the best straight line does not pass through the origin, so that the ratio  $X_d/X_m$  is not a constant. Since both  $X_d$  and  $X_m$  must vanish simultaneously, we have put the best curve through the data, consistent with this constraint. The slope of this curve at the origin is approximately 1.9, which is in good agreement with the theoretical prediction. However, as the temperature is lowered and the solvent order grows, so the slope of the curve decreases until at the lowest temperature for which we have measurements, it has fallen to 1.2. Our results show, therefore, that the anisotropic strength parameters for the monomer and dimer are not directly proportional to each other as predicted by the molecular field theory. Perhaps of greater significance is the observation that the anisotropy in the solute–solvent interactions for the dimer and the monomer in a common nematic solvent become similar as the orientational order of the solvent grows.

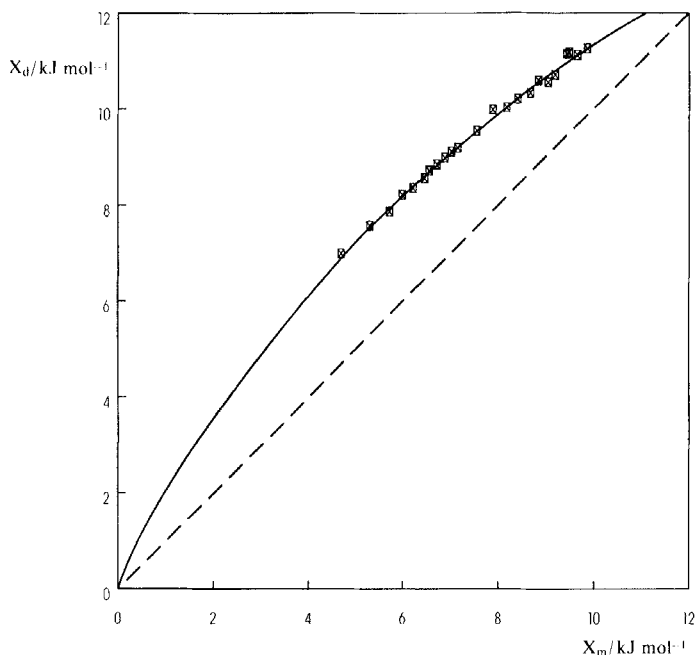


Figure 2. The dependence of the molecular field strength parameter  $X_d$  for the dimer on that for the monomer  $X_m$ .

The theoretical model against which we had intended to test our results assumes that the molecules of both solutes are rigid and cylindrically symmetric. Strictly they are neither, but as the temperature is lowered and the solvent order increases, so we should expect the pentyl chains to become more rigid and the effect of molecular biaxiality to become less important. It is unlikely, therefore, that these effects can account for the unusual tendency of the monomer and dimer to be ordered to the same extent in the high order limit. We find this result puzzling and within the framework of the molecular field theory extremely difficult to rationalize. However, a model used to extract the singlet orientational distribution function from X-ray diffraction patterns of nematics [12] might offer an explanation. In the model, it is assumed that the basic unit responsible for the X-ray diffraction is a small cluster of perfectly aligned molecules with the symmetry axis of the cluster distributed with respect to the director. This is supported, in part, by computer simulation studies of realistic model potentials which reveal high, but not perfect angular correlations between nearest neighbours in the nematic phase [13]. According to this model in an extreme situation the orientational order of a solute would be determined not by the anisotropic solute-solvent interactions, but by the anisotropic interactions between clusters of molecules. Since these clusters are largely composed of solvent molecules the difference in the molecular anisotropy for the two solutes should play a smaller role in determining the difference in the orientational order of the solutes. In other words, it would be the anisotropic interactions of the cluster and not individual molecules which would control the solute order. According to the computer simulations, the angular correlations between nearest neighbours are smallest near the nematic-isotropic phase transition and then grow with decreasing temperature [13]. It would be expected, therefore, that the cluster is less effective at determining the orientational order at high rather than low shifted temperatures. This is in accord with the behaviour which we

have observed, where the difference in the ordering of the dimer and monomer is greatest near the nematic-isotropic phase transition and then decreases with decreasing temperature. Clearly it is important to test this interpretation further and to check the generality of our results by studies of the orientational ordering of analogous solute pairs. Such investigations are in progress.

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