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Solute–Solvent Interactions within the Nematic Mesophase

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Abstract—This paper reports the temperature dependence of the orientational order of a spin probe dissolved in the nematic mesophases of four di-*n*-alkoxyazoxybenzenes, determined with the aid of electron resonance spectroscopy. The solute orientational order can provide valuable information concerning the pseudo-potential for the solute in the mesophase and hence the nature of the anisotropic solute–solvent interaction. Techniques for obtaining details of this interaction from our results are discussed in terms of extensions of the Maier–Saupe theory to include a general anisotropic intermolecular potential and to multicomponent mixtures of rod-like molecules. Our analysis suggests that the pseudo-potential for the solute, like that for the solvent, must include interactions in addition to London dispersion forces employed in the Maier–Saupe theory.

The investigations of solute–solvent interactions were extended to an L-shaped spin probe to see if, as has been suggested, its arms are preferentially aligned with respect to the director in a nematic mesophase. No such preferential alignment could be detected.

1. Introduction

The orientational order in the mesophase of a nematic liquid crystal, composed of rod-like molecules, may be defined as

$$S = \overline{(3\cos^2\theta - 1)}/2, \qquad (1)$$

where θ is the angle between the rod-axis and the director.[1] The bar denotes a time or ensemble average. Experimentally[2] S is found to decrease with increasing temperature within the mesophase and to vanish suddenly at the nematic–isotropic transition, T_K. These observations are readily accounted for by the Maier–Saupe theory of the nematic mesophase.[3] This theory attempts to calculate the

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orientational energy or pseudo-potential of a single molecule resulting from its interaction with the field generated by its neighbours. Provided the anisotropic intermolecular interactions are restricted to London dispersion forces the pseudo-potential is found to be

$$U = -AS(3\cos^2\theta - 1)/2V^2. \qquad (2)$$

The parameter A is taken to be independent of temperature and is proportional to the square of the anisotropy in the polarizability. Since the pseudo-potential contains a single parameter the theory predicts that the orientational order should be a universal function of the reduced variable $TV^2/T_K V_K^2$ and hence of the reduced temperature.[4] This prediction is found to be qualitatively correct[2] although it was not known if the small discrepancies between theory and experiment could be attributed to the wide range of techniques employed to determine S. However an electron resonance investigation[4] of eight nematogens has helped to reveal that the discrepancies result from the inherent limitations of the Maier–Saupe theory.

Recently attempts have been made to improve the Maier–Saupe theory by including higher order terms in the intermolecular potential.[5,6] In addition a general statistical theory of solute–solvent interactions within a mesophase has been proposed.[7] These theoretical developments have prompted us to measure the temperature dependence of the orientational order of a spin probe (I) in the mesophases of four di-*n*-alkoxyazoxybenzenes. The results of these measurements are then analysed in depth with the aid of the new theories in order to discover the nature of the information available from such measurements. We have also taken this opportunity to investigate the alignment of an L-shaped spin probe (II) by the mesophase.[8]

2. Experimental

The four nematogens were obtained commercially and used without further purification. Both 4, 4′-dimethoxy- and 4, 4′-diethoxyazoxybenzene were purchased from Sherman Chemicals Limited while 4, 4′-di-*n*-hexyloxyazoxybenzene was bought from Frinton Laboratories and the heptyl compound was purchased from E.

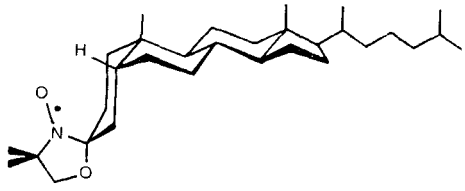
Merck, Darmstadt. Their nematic–isotropic transition points are listed in Table 1 together with the literature values.[2] Although these small differences between the two sets of values are undesirable the presence of trace impurities should not affect our analysis because the orientational order of the probe in the impure mesophase has the same dependence on the *reduced* temperature as in the pure mesophase.[9]

TABLE 1 The Nematic–Isotropic Transition Temperatures

	Transition Temperature T_K/K		
Compound	Literature values[2]	Commercial product	Doped sample
4, 4′-dimethoxyazoxybenzene	408	406.0	405.5
4, 4′-diethoxyazoxybenzene	441	436.7	434.5
4, 4′-di-*n*-hexyloxyazoxybenzene	402	400.0	399.2
4, 4′-di-*n*-heptyloxyazoxybenzene	397	395.0	394.2

The paramagnetic probes (3-spiro-[2′ N-oxyl-3, 3′dimethyloxazolidine]) 5α-cholestane (I) and (3-spiro-[2′ N-oxyl-3, 3′-dimethyloxazolidine]) 5β-cholestane (II) were prepared using the standard synthetic route.[10] Each nematogen was then doped with spin probe (I) and the nematic–isotropic transition of the binary mixture determined. The results, given in Table 1, show that the addition of the probe depresses the transition by, at most, a few degrees. The alignment of the second spin probe (II) in the mesophase of 4, 4′-dimethoxyazoxybenzene was also investigated. The electron resonance spectrum of each sample was measured as a function of temperature in both the isotropic melt and nematic mesophase using a Varian E-3 spectrometer. The temperature was monitored with the aid of a copper–constantan thermocouple immersed in the sample. In one set of experiments, designed to determine the temperature dependence of the g factor, the klystron microwave frequency was determined with a Hewlett–Packard frequency counter fitted with a 5255 A frequency converter. All of the electron resonance spectra consisted of the three sharp lines expected for such nitroxide radicals. We also measured the polycrystalline spectrum of (I) dissolved in a glass of frozen toluene so as to determine the nitrogen hyperfine tensor.

(I)



(II)

3. Analysis

When the ordering potential or director is parallel to the magnetic field in the electron resonance experiment the coupling constant $\bar{a}$ for any nucleus in a radical dissolved by the mesophase is[11,12]

$$\bar{a} = a + (2/3) \sum_{i,j} A'_{ij} \mathcal{O}_{ij} . \tag{3}$$

In this expression a is the scalar coupling constant, $\mathbf{A}'$ is the anisotropic hyperfine tensor and $\mathcal{O}$ is the ordering matrix which describes the solute alignment.[13] The g factor $\bar{g}$, in the mesophase, is given by an equation analogous to (3):

$$\bar{g} = g + (2/3) \sum_{i,j} g'_{ij} \mathcal{O}_{ij} . \tag{4}$$

If both the g and hyperfine tensors are cylindrically symmetric about the same axis 3 then Eqs. (3) and (4) reduce to

$$\bar{a} = a + A'_{33} \mathcal{O}_{33} ,$$

and (5)

$$\bar{g} = g + g'_{33} \mathcal{O}_{33} .$$

Consequently it is only possible to determine one element of the ordering matrix for such paramagnetic solutes, which include the popular spin probe vanadyl acetylacetonate. Nitroxide radicals do not suffer from this disadvantage for, although the nitrogen hyperfine tensor is cylindrically symmetric, the g tensor deviates considerably

from cylindrical symmetry and for a compound virtually identical to (I) has principal components:[14]

$$g_x = 2.0089,$$
$$g_y = 2.0058, \qquad (6)$$

and $$g_z = 2.0021.$$

The principal coordinate system is shown in Fig. 1.

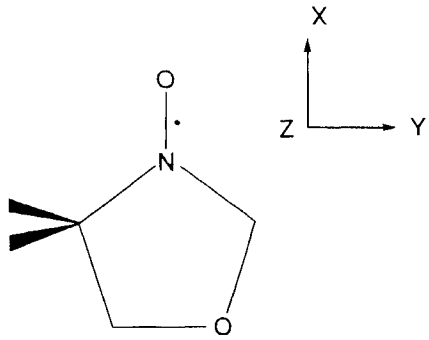


Figure 1. The structure of the oxazolidine ring together with the principal coordinate system for the g and hyperfine tensors.

In the case of the spin probe (I) a molecular model reveals that although the z-axis is likely to be a principal axis of the ordering matrix this is not so for either the x or y-axes. Since the symmetry axis of the nitrogen hyperfine tensor is parallel to the z-axis then the change in the coupling constant on alignment gives the principal component $\mathcal{O}_{33}$ directly. If the other principal axes are labelled 1 and 2 then the g shift is[12]

$$\delta\bar{g} = g'_{11}\mathcal{O}_{11} + (\mathcal{O}_{22} - \mathcal{O}_{33})(g'_{22} - g'_{33})/3. \qquad (7)$$

The components g'_{11} and g'_{22} can be calculated from g_x, g_y and ϕ the angle between axes x and 1. The angle ϕ is estimated to be approximately 20° from an examination of the molecular model. Now if the ordering matrix is cylindrically symmetric about the 1-axis then the ratio of the shifts in the nitrogen coupling constant to that in the g factor is

$$\delta\bar{a}/\delta\bar{g} = -A'_{33}/2g'_{11}, \qquad (8)$$

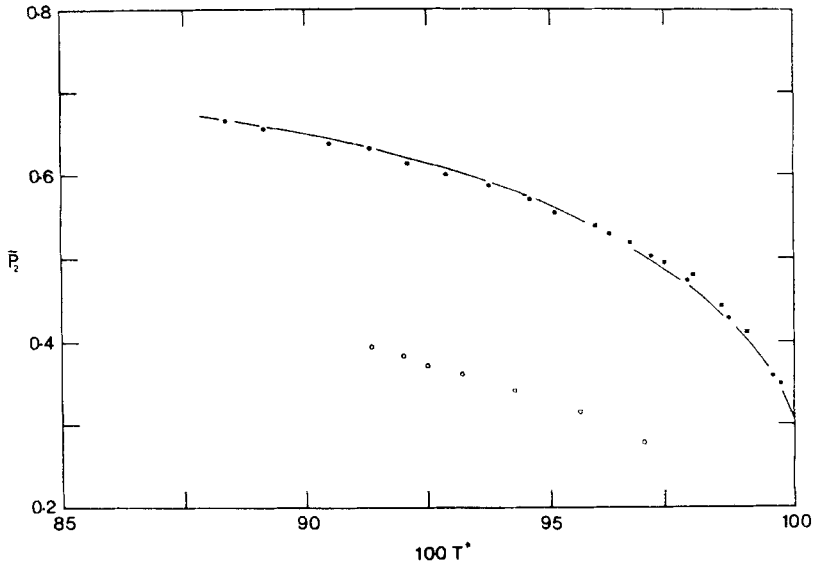


Figure 2. The temperature dependence of the orientational order of the spin probes (I), denoted by ● and ■, and (II) denoted by ○ dissolved in the mesophase of 4, 4′-dimethoxyazoxybenzene.

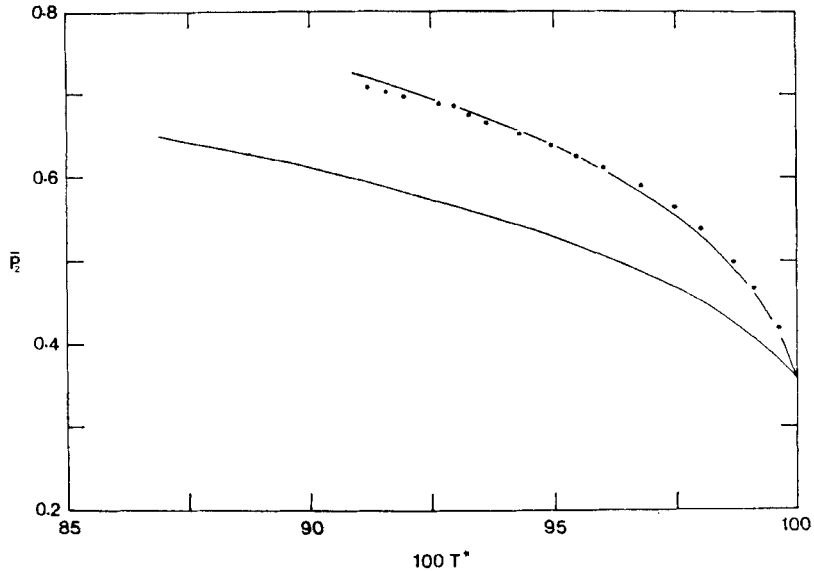


Figure 3. The temperature dependence of the orientational order of the probe (I) dissolved in the mesophase of 4, 4′-diethoxyazoxybenzene.

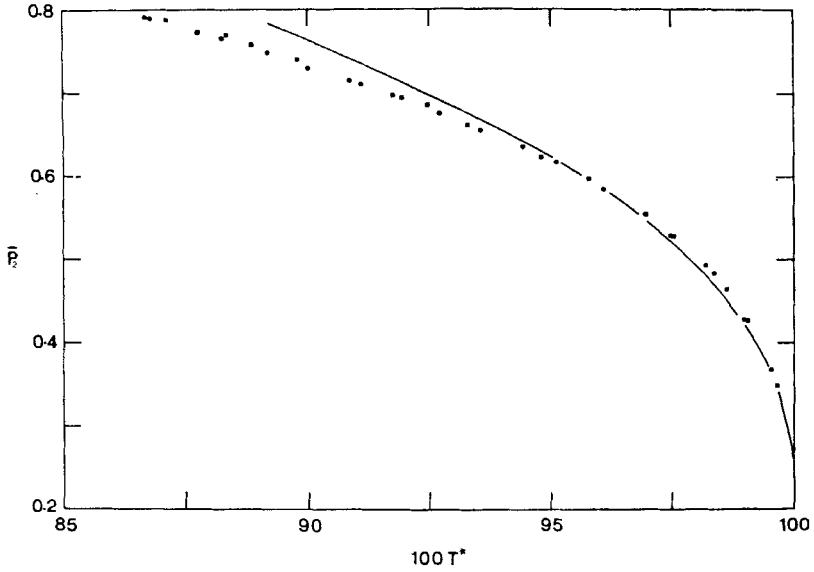


Figure 4. The temperature dependence of the orientational order of (I) dissolved in the mesophase of 4, 4′-di-*n*-hexyloxyazoxybenzene. The different symbols represent the results obtained for different samples.

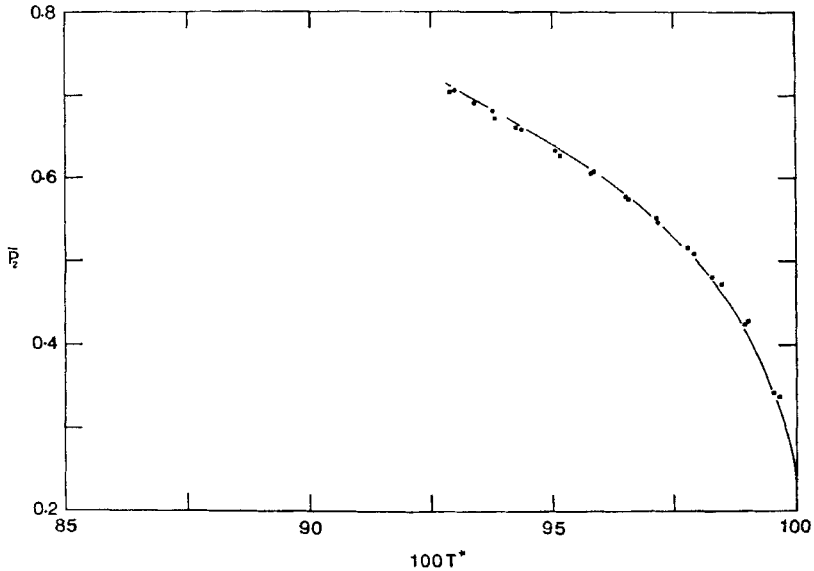


Figure 5. The orientational order of spin probe (I) dissolved in the mesophase of 4, 4′-di-*n*-heptyloxyazoxybenzene. The results found for the two samples used in this investigation are represented by the different symbols.

and therefore independent of temperature. We have measured this ratio for (I) dissolved in the mesophase of 4, 4′-dimethoxyazoxybenzene and find that it is temperature independent. Experimentally the ratio is found to be -3.4×10^4 MHz which should be compared with the theoretical value of -4.5×10^4 MHz. This was calculated using the value of 53.5 MHz determined for A'_{33} from an analysis of the polycrystalline spectrum. In view of the difficulty experienced in measuring $\delta\bar{g}$ precisely and the large experimental uncertainty in the anisotropic g tensor the agreement between theory and experiment is good. We shall therefore assume, in the remainder of this paper, that the ordering matrix for the probe (I) is cylindrically symmetric not only in the mesophase of 4, 4′-dimethoxyazoxybenzene but also in those of the other nematogens. The element of the ordering matrix for the molecular long axis, which we denote by $\bar{P}_2$, can now be obtained from $\mathscr{O}_{33}$ determined from the shift in the nitrogen coupling constant. The results of such determinations of $\bar{P}_2$ for (I) dissolved in the four nematic mesophases are plotted, as a function of the reduced temperature, in Figs 2–5.

4. Interpretation

The solute ordering matrix is readily calculated from its pseudo-potential by taking the appropriate Boltzmann averages. According to a molecular field treatment of a multicomponent system of rod-like molecules the pseudo-potential for molecules of type i is[7]

$$U^{(i)}(\theta) = \sum_{L;j} x_j \bar{u}_L^{(ij)} \bar{P}_L^{(j)} \bar{P}_L^{(i)}(\cos\theta), \tag{9}$$

where x_j is the mole fraction of component j. The coefficients $\bar{u}_L^{(ij)}$ depend on the strength of the anisotropic interaction between two molecules of species i and j:

$$\bar{u}_L^{(ij)} = (1/\rho) \int \sum_n u_{LL:n}(r) n^{(2)}(r)\, \mathrm{d}\mathbf{r}, \tag{10}$$

where ρ is the number density and the pair distribution function $n^{(2)}(r)$ is assumed to be independent of the nature of i and j.[7] The orientational order is defined using the even Legendre polynomials P_L and, for example,

$$\bar{P}_L^{(j)} = \int P_L^{(j)}(\cos\theta) \exp\{-U^{(j)}(\theta)/kT\} \sin\theta\, d\theta / Z_j, \tag{11}$$

where the orientational partition function is

$$Z_j = \int \exp\{-U^{(j)}(\theta)/kT\} \sin\theta \, d\theta \,. \tag{12}$$

At the nematic–isotropic transition the molar orientational Helmholtz function

$$A_m = -(N/2) \sum_{L;i,j} x_i x_j \bar{u}_L^{(ij)} \bar{P}_L^{(i)} \bar{P}_L^{(j)} - RT \sum_i x_i \ln Z_i \,, \tag{13}$$

vanishes and so the transition temperature of the mixture is readily determined as a function of its composition.[7] Saupe has also developed a theory of solute alignment in the nematic mesophase.[15] However his expression for the pseudo-potential is assumed to be independent of both the composition of the mixture and the orientational order of its components. Although the theory has been used to correlate the solute ordering matrices determined in nuclear magnetic resonance experiments,[16] because of its qualitative character, we shall not consider it further.

A rigorous interpretation of the ordering matrix, determined from experiments employing large solute concentrations is difficult because this high concentration couples the equations for the solute and solvent order. However in an electron resonance experiment the solute concentration is so low that Eq. (9) is effectively decoupled and reduces to

$$U^{(1)}(\theta) = \sum_L \bar{u}_L^{(11)} \bar{P}_L^{(1)} P_L^{(1)} (\cos\theta), \tag{14}$$

and

$$U^{(2)}(\theta) = \sum_L \bar{u}_L^{(12)} \bar{P}_L^{(1)} P_L^{(2)} (\cos\theta) \,, \tag{15}$$

for a binary mixture. In these equations the solvent is denoted by the number (1) and the solute by (2). The solvent order $\bar{P}_L^{(1)}$ is obtained by substituting Eq. (14) into Eq. (11) and is therefore identical to that in the pure mesophase. When calculating the solute order, although $P_2^{(1)}$ for the solvent may be obtained experimentally, values for the higher solvent orders $\bar{P}_L^{(1)}$ must usually be calculated.

The simplest approach is to restrict the summations to those terms with $L = 2$ and this is equivalent to the Maier–Saupe theory of the pure mesophase. For the resulting expressions to be identical with those obtained by Maier and Saupe the interaction coefficients must

be inversely proportional to the square of the molar volume:

$$\bar{u}_2^{(ij)} = u_2^{\circ(ij)} V^{-2}. \tag{16}$$

This is equivalent to assuming that the pair distribution function is proportional to ρ^2 and that the $u_{22;n}(r)$ are determined by London dispersion forces which have an r^{-6} dependence.[17] The solvent order in this theory can be calculated as a function of the single variable α by solving the equation

$$\bar{P}_2^{(1)} = \int P_2^{(1)}(\cos\theta) \exp\{-\alpha \bar{P}_2^{(1)} P_2^{(1)}(\cos\theta)\} \sin\theta \, d\theta / Z_1, \tag{17}$$

where

$$Z_1 = \int \exp\{-\alpha \bar{P}_2^{(1)} P_2^{(1)}(\cos\theta)\} \sin\theta \, d\theta, \tag{18}$$

and the variable α is given by

$$\alpha = u_2^{\circ(11)}/kT V^2. \tag{19}$$

The parameter $u_2^{\circ(11)}$ can be related to experimental quantities because the orientational Helmholtz function vanishes when α takes the value -4.541 and consequently

$$u_2^{\circ(11)} = -4.541 \, kT_K V_K^2, \tag{20}$$

where the subscript K denotes the value at the nematic–isotropic transition. The variable α may therefore be related simply to the reduced temperature T^* and volume V^* by

$$\alpha = -4.541/T^* V^{*2}. \tag{21}$$

Since the reduced volume of the mesophase appears to be a universal function of T^* we can calculate the reduced temperature for a given value of α. The solute order is readily determined from the solvent order by evaluating the integral

$$\bar{P}_2^{(2)} = \int P_2^{(2)}(\cos\theta) \exp\{-\bar{u}_2^{(12)} \bar{P}_2^{(1)} P_2^{(2)}(\cos\theta)/kT\} \sin\theta \, d\theta / Z_2, \tag{22}$$

where

$$Z_2 = \int \exp\{-\bar{u}_2^{(12)} \bar{P}_2^{(1)} \bar{P}_2^{(2)}(\cos\theta)/kT\} \sin\theta \, d\theta. \tag{23}$$

This calculation may also be performed as a function of α by introducing a temperature independent parameter β, defined as the ratio $u_2^{\circ(12)}/u_2^{\circ(11)}$ for then

$$\bar{u}_2^{(12)}/kT = \beta\alpha\,. \tag{24}$$

We have attempted to fit our experimental results by varying this parameter β until the solute order is correctly predicted at the transition point. The results of such a calculation for the spin probe (I) dissolved in the mesophase of 4, 4′-diethoxyazoxybenzene are shown, as the lower curve, in Fig. 3. The theory is clearly in poor agreement with experiment for this particular mesophase and indeed similar discrepancies were found for the other three nematogens.

The gross discrepancy between theory and experiment may be removed by postulating an alternative form for the volume dependence of the interaction coefficients $\bar{u}_2^{(ij)}$. Since this dependence cannot be predicted with any certainty we shall adopt an empirical approach and assume that

$$\bar{u}_2^{(ij)} = u_2^{\circ(ij)} V^{-\gamma}, \tag{25}$$

where the exponent γ is treated as an adjustable parameter. The temperature dependence of the solute order is now fitted by varying both β and γ. The optimized values of these parameters are given in Table 2 and the theoretical curves calculated from them are shown in Figs. 2–5.

TABLE 2 The Solvent and Solute–Solvent Parameters

Nematogen	β	γ	$\beta^2 T_K^{(1)}/K$
4, 4′-dimethoxyazoxybenzene	0.709	7	204
4, 4′-diethoxyazoxybenzene	0.825	8	296
4, 4′-di-*n*-hexyloxyazoxybenzene	0.612	18	150
4, 4′-di-*n*-heptyloxyazoxybenzene	0.556	25	122

The agreement between theory and experiment is seen to be virtually perfect. However although this success is encouraging we have adjusted two parameters and so must look closely at their values before accepting this modification of the Maier–Saupe theory. The exponent γ appears to be unusually large especially in comparison with the values of three[5] and four[6] used for the pure mesophase. In

addition the mixed parameter $u_2^{\circ(12)}$ has been shown[7] to be given fairly accurately by the geometric mean approximation

$$u_2^{\circ(12)} = (u_2^{\circ(11)} u_2^{\circ(22)})^{1/2}. \tag{26}$$

Since $u_2^{\circ(11)}$ is proportional to the nematic–isotropic transition temperature $T_K^{(1)}$, $\beta^2 T_K^{(1)}$ should be constant and equal to the virtual nematic–isotropic transition point of the spin probe. The calculated values for this temperature are given in Table 2 and it is clear that the quantity $\beta^2 T_K^{(1)}$ is not even approximately constant. We conclude therefore that although this simple extension of the Maier–Saupe theory successfully predicts the temperature dependence of the solute order, the parameters required are unreasonable and we must seek an alternative modification of the theory.

It has been found[6] that to account accurately for the temperature dependence of the orientational order in the pure mesophase it is essential to retain those terms with $L = 2$ and 4 in the pseudo-potential. Presumably we should also keep both terms in the expansion of the pseudo-potential for the solute when attempting to calculate its orientational order. In general such calculations would involve the four arbitrary parameters $\bar{u}_2^{(11)}$, $\bar{u}_4^{(11)}$, $\bar{u}_2^{(12)}$ and $\bar{u}_4^{(12)}$. Since one might reasonably expect to fit virtually any result with four independent parameters we have reduced the number of variables to two in the following way. The orientational order in the nematic mesophases of 4, 4′-dimethoxy- and 4, 4-diethoxyazoxybenzene has been determined by nuclear magnetic resonance[18] and the parameters $\bar{u}_2^{(11)}$ and λ (equivalent to $\bar{u}_4^{(11)}/\bar{u}_2^{(11)}$) determined by fitting the temperature dependence of the orientational order. The optimized values of these parameters, obtained with an exponent γ equal to four, are given in Table 3. These parameters were used to calculate the solvent orders $\bar{P}_2^{(1)}$ and $\bar{P}_4^{(1)}$ which are required in the calculation of the solute pseudo-potential and hence its orientational order. The

TABLE 3 The Interaction Parameters

Compound	$\left(\frac{u^{\circ(11)}}{kT_K}\right)$	$\lambda\left(\frac{u_4^{\circ(11)}}{u_2^{\circ(11)}}\right)$	β	$\lambda\left(\frac{u_4^{\circ(12)}}{u_2^{\circ(12)}}\right)$	$\left(\frac{\beta^2 T_K^{(1)}}{K}\right)$
4, 4′-dimethoxyazoxybenzene	−4.59	−0.187	0.831	0.141	280
4, 4′-diethoxyazoxybenzene	−4.54	0.116	0.737	0.535	236

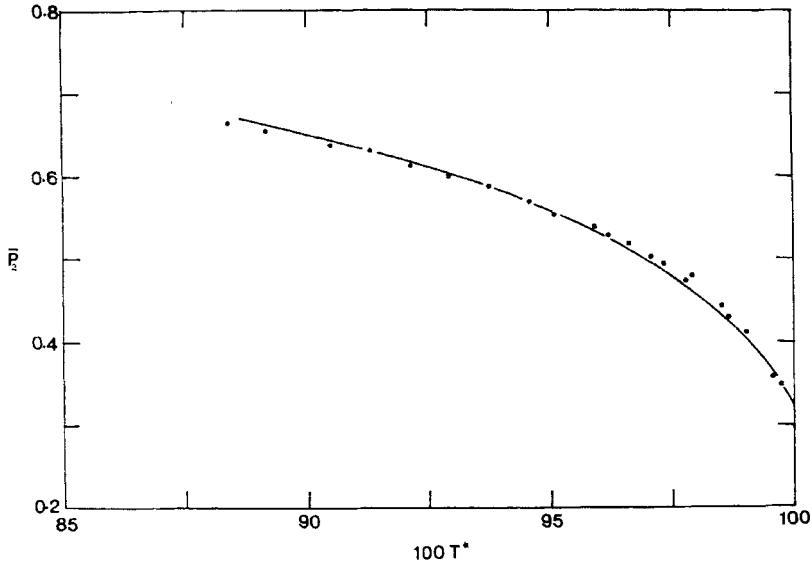


Figure 6. A comparison of the theoretical and experimental orientational order of (I) dissolved in the mesophase of 4, 4′-dimethoxyazoxybenzene.

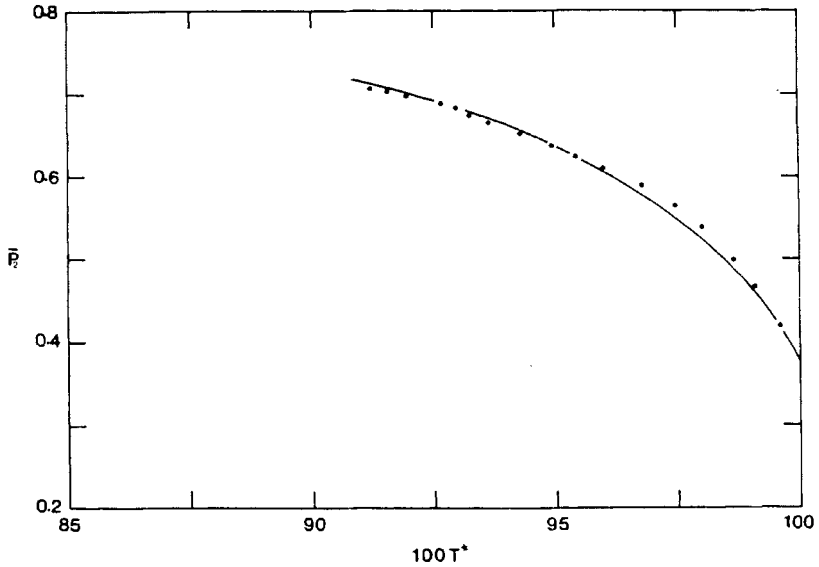


Figure 7. The predicted temperature dependence of the orientational order of the spin probe (I) dissolved in the mesophase of 4, 4′-diethoxyazoxybenzene together with the experimental order.

difference between experiment and theory was then minimized by adjusting the solvent–solute parameters β and λ where β is given by Eq. (24) and λ is the ratio $\bar{u}_4^{(12)}/\bar{u}_2^{(12)}$. The curves, calculated with the parameters listed in Table 3, are shown in Figs. 6 and 7. The agreement between theory and experiment for these two solvents is most encouraging. In this modification of the Maier–Saupe theory the ratio of the interaction parameter $u_2^{\circ(11)}$ to the nematic–isotropic transition temperature is no longer constant but varies with λ.[6] However, as we can see from the ratios given in Table 3, the extent of this variation is rather small and so the quantity $\beta^2 T_K^{(1)}$ should be approximately constant. The two values for $\beta^2 T_K^{(1)}$ given in Table 3 are indeed similar and so lend some support to the theory. Since only a few values of λ have been determined even for the pure mesophase it is difficult to know how the solute–solvent λ should vary. However these values of λ do parallel those found for the pure solvent.

In view of the reasonable results found for the solute–solvent interaction parameters it would appear that the solute pseudopotential, like that for the solvent should be extended to include those terms with L equal to four. However it will only be possible to predict the temperature dependence of the solute order if that of the solvent is already known. When this information is absent an unambiguous analysis is difficult because of the large number of arbitrary parameters in the theory.

5. The Alignment of L-shaped Solutes

In 1969 Havach *et al.* reported an electron resonance investigation of the alignment of four nitroxide radicals dissolved in the nematic mesophase of 4-*n*-hexyloxy-4′-ethoxyazobenzene.[8] Although one of these radicals gave an electron resonance spectrum containing the expected three nitrogen hyperfine lines the others gave spectra containing two or even three sets of three lines. This unusual behaviour was interpreted in the following fashion. The spin probes were non-rigid but, it was argued, could adopt a stable L-shaped conformation. If each arm of the L was oriented parallel to the director and if exchange between these configurations was slow on the electron resonance time scale then the observed spectrum might consist of sets of hyperfine lines.[8] Such behaviour is of considerable impor-

tance in understanding solute–solvent interactions. Since certain of the effects noted by Havach *et al.* were not reproducible we have studied the alignment of the L-shaped spin probe (II) dissolved in the mesophase of 4, 4-dimethoxyazoxybenzene.

Now if this probe was oriented with either arm parallel to the director then the plane of the oxazolidine ring would also be parallel to the preferred molecular orientation. Consequently the observed nitrogen hyperfine spacing should be the same for both configurations because of the cylindrical symmetry of the nitrogen hyperfine tensor. However since the g tensor is not cylindrically symmetric the g factors for the two configurations will not be identical and so the centres of the two spectra could be separated by as much as 9 gauss. In fact we observe only three lines in the spectrum and must conclude that this L-shaped solute is not preferentially oriented about either arm. Our result casts further doubt therefore on the interpretation of the electron resonance spectra obtained by Havach *et al.*

The orientational order for this second probe dissolved in the mesophase is shown, as open circles, in Fig. 2. The order was determined from the hyperfine shift using Eq. (5) but plotted as twice this value so as to accommodate the results in the figure. As we can see the orientational order determined in this way is less than that measured for the first probe in the same mesophase. This does not necessarily mean that the L-shaped probe is less oriented than radical (I) for in (II), unlike (I), the symmetry axis of the hyperfine tensor is not a principal axis of the ordering matrix. The quantity which is calculated from the hyperfine shift can be related to the principal components of $\mathcal{O}$ and if the ordering matrix is cylindrically symmetric this relationship is particularly simple:[19]

$$\mathcal{O}_{33} = \frac{(3\cos^2\psi - 1)}{2}\bar{P}_2 . \tag{27}$$

In this expression $\bar{P}_2$ is the orientational order of the rod-like molecule and ψ is the angle between the symmetry axes of the hyperfine tensor and the ordering matrix. To estimate ψ we make the bold assumption that, at the same reduced temperature, the orientational order for both spin probes is the same. With this assumption and the results shown in Fig. 2 we find that ψ is virtually independent of temperature

and about 67°. This value is consistent with a molecular model of the probe and so suggests that both probes are oriented to about the same extent by the mesophase.

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REFERENCES

1. Zwetkoff, V., *Acta Physicochim.* (*U.S.S.R.*)**16**, 132 (1942).
2. See e. g. Saupe, A., *Angew. Chem. Int. ed.* **7**, 97 (1968).
3. Maier, W. and Saupe, A., *Z. Naturforsch* **13a**, 564 (1958). **14a**, 882 (1959); **15a**, 287 (1960).
4. Chen, D. H., James, P. G. and Luckhurst, G. R., *Mol. Cryst. and Liq. Cryst.* **8**, 71 (1969).
5. Chandrasekhar, S. and Madhusudana, N. V., *Acta Cryst.* **27**, 303 (1971).
6. Humphries, R. L., James, P. G. and Luckhurst, G. R., *J. C. S. Faraday II*, **68**, 1031 (1972).
7. Humphries, R. L., James, P. G. and Luckhurst, G. R., *Symp. Faraday Soc.* **5**, 107 (1971).
8. Havach, G., Ferruti, P., Gill, D. and Klein, M. P., *J. Amer. Chem. Soc.* **91**, 7526 (1969).
9. Chen, D. H. and Luckhurst, G. R., *Trans. Faraday Soc.* **65**, 656 (1969).
10. Keana, J. F. W., Keana, S. B. and Beetham, D., *J. Amer. Chem. Soc.* **89**, 3055 (1967).
11. Luckhurst, G. R., *Mol. Cryst.* **2**, 363 (1967).
12. Falle, H. R. and Luckhurst, G. R., *J. Magn. Resonance* **3**, 161 (1970).
13. Saupe, A., *Z. Naturforsch.* **19a**, 161 (1964).
14. Hubbell, W. L. and McConnell, H. M., *J. Amer. Chem. Soc.* **93**, 314 (1971).
15. Saupe, A., *Mol. Cryst.* **1**, 527 (1966).
16. Nehring, J. and Saupe, A., *Mol. Cryst. and Liq. Cryst.* **8**, 403 (1969); Robertson, J. C., Yim, C. T. and Gilson, D. F. R., *Can. J. Chem.* **49**, 2345 (1971).
17. Pople, J. A., *Proc. Roy. Soc. A.* **221**, 498 (1954).
18. Rowell, J. C., Phillips, W. D., Melby, L. R. and Panar, M., *J. Chem. Phys.* **23**, 878 (1965).
19. Luckhurst, G. R. and Sundholm, F., *Acta. Chem. Scand.* **24**, 3759 (1970).