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The effect of molecular biaxiality on the bulk properties of some nematic liquid crystals

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The nematic substance 5CB is known from N.M.R. studies to be slightly biaxial, not in the sense that any bulk property measured in a direction at right angles to the director is liable to vary with rotation about the director, but in the sense that there are biaxial terms in the ordering matrix that describes the alignment of individual molecules; $(S_{xx} - S_{yy})$ is non-zero as well as S_{zz}. We show that the biaxial terms should make a significant contribution to the magnetic anisotropy $\Delta\chi^{(m)}$ of 5CB, and that the magnitude and temperature dependence of this bulk property, which we have measured, can be understood if, and only if, they are taken into account. The contribution which they make to the optical birefringence term Σ should, however, be relatively trivial. Although Σ may in principle be affected by local field corrections of a complicated nature, which do not affect $\Delta\chi^{(m)}$, a new theory presented in an Appendix to the paper suggests that these too are likely to be relatively trivial. Hence we believe that Σ is more nearly proportional than is $\Delta\chi^{(m)}$ to the principal order parameter S_{zz}.

The paper includes unpublished data for the magnetic anisotropy and/or the principal refractive indices, n_e and n_o, in a number of other nematics (6CB, 7CB, 8CB, 9CB, 5OCB, 6OCB, 7OCB, 8OCB, 7CCH, MBBA and PAA). Comparison between the temperature dependence of $\Delta\chi^{(m)}$ and of Σ suggests that biaxiality is present in all cyanobiphenyls, on much the same scale as in 5CB, and is not affected by the presence of an oxygen atom between the phenyl core of the molecule and its alkyl tail.

1. Introduction

In a paper [1] devoted to the Frank stiffness constants of nematic 5CB (4-n-pentyl-4′-cyanobiphenyl) we drew attention to the fact that the anisotropy in the magnetic susceptibility per unit mass for this substance, $\Delta\chi^{(m)}$, does not vary with temperature in quite the same way as the quantity Σ $(= (n_e^2 - n_o^2)/(\bar{n}_2 - 1))$ which we use to characterize its optical birefringence. The slight disparity suggested by measurements in our laboratory [2, 3] is confirmed by measurements made elsewhere [4, 5]. The common assumption that nematics are characterized by a single order parameter (variously denoted by $\bar{P}_2$, S, S_2 or S_{zz}), to which both $\Delta\chi(m)$ and Σ are proportional, is therefore not justified for 5CB.

Our principal object in this paper is to point out that $\Delta\chi^{(m)}$, and to a lesser extent Σ, are sensitive to other terms in the Saupe ordering matrix besides S_{zz}. These terms will be defined in §2, where the geometry of the 5CB molecules is described. Here it is sufficient to note that unless the molecules rotate freely about their long (z) axes the quantity $(S_{xx} - S_{yy})$ may be non-zero. Evidence that it is so is in fact available from the N.M.R. work of Emsley *et al.* [6], and we shall show that its magnitude and temperature-dependence are about what are required to explain the disparity which we have noted.

It should be said that at least two alternative explanations could be invoked. In so far as the molecules are flexible they can adopt a variety of conformations, and the probability of each conformation may change as the temperature rises and the alignment relaxes. In principle, the coefficients which relate $\Delta\chi^{(m)}$ and Σ to S_{zz} may be temperature-dependent on this account, and temperature-dependent in slightly different ways. In practice, however, the electric and magnetic polarizabilities of the pentyl chain of 5CB seem to be too nearly isotropic for it to make much difference how this is folded, and we presume that the aromatic core of the molecule, libration apart, is effectively rigid.

The other possibility to deserve mention is that the refractive indices n_e and n_0 are affected by local field corrections which depend, perhaps, not just on the ordering matrix for a single molecule but on correlations between adjacent molecules; such corrections could add to the temperature dependence of Σ, without, of course, affecting $\Delta\chi^{(m)}$. In an Appendix to this paper we outline a hitherto unpublished theory, based upon the continuum theory of nematic disorder [7], which offers a way round the notorious difficulties of the local field problem. This theory implies some variation with temperature of the ratio (Σ/S_{zz}) but a variation that is too slight to be significant.

We conclude from our analysis that of the two bulk properties $\Delta\chi^{(m)}$ and Σ the latter is probably the better guide to the temperature dependence of S_{zz}. This is the reverse of what we believed when that earlier paper [1] was written. We also conclude that a careful comparison between $\Delta\chi^{(m)}$ and Σ may provide evidence for what we call *biaxiality* of the ordering matrix, i.e. non-zero values of $(S_{xx} - S_{yy})$, in nematics other than 5CB which have not yet been the subject of such intensive study by N.M.R. methods. We pursue this point in the final section of the paper, where new data for a number of substances related to 5CB are presented and briefly discussed.

2. The ordering matrix

Saupe's matrix describes the pattern of alignment in nematics by relating the mean director (the significance of *mean* in this context is explained in the Appendix, where director fluctuations are discussed) to xyz axes fixed in a typical molecule. The z axis is chosen to coincide with the long axis of the molecule, which for 5CB may be defined, as in figure 1 (*a*), as the axis which is common to the biphenyl core and the terminal cyano group. Our x and y axes are defined in figure 1 (*b*), which shows the molecule viewed along its z axis with a dihedral angle ϕ between the two phenyl rings. The mean value of this angle—or rather, since it can be plus or minus, of its modulus—is thought to be 31° [6], and no doubt $|\phi|$ varies considerably about its mean due to thermally-excited libration of the rings. It turns out, however, that the magnitude of ϕ does not directly concern us.

If the mean director lies in the plane OD in figure 1 (*b*), at an angle β to the z axis, then

$$S_{zz} = \langle \tfrac{3}{2}\cos^2\beta - \tfrac{1}{2}\rangle, \tag{1}$$

$$(S_{xx} - S_{yy}) = \langle \tfrac{3}{2}\sin^2\beta\cos^2\gamma\rangle, \tag{2}$$

where angled brackets imply an ensemble average. Now the N.M.R. evidence concerning the magnitude of these quantities comes from proton resonance measurements using specimens in which all the protons except those attached to R2, the ring adjacent to the cyano group, had been replaced by deuterons. These measurements

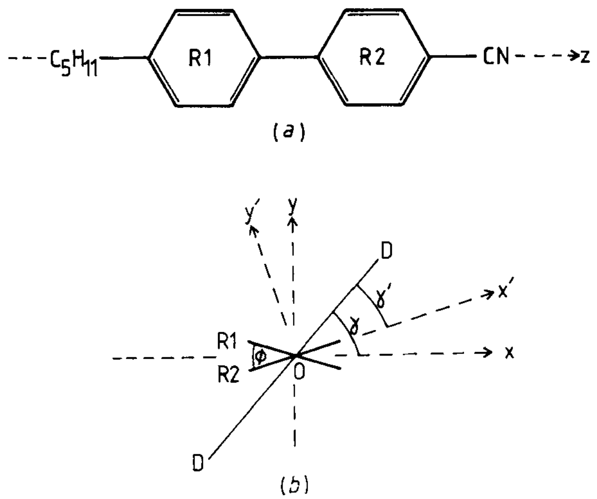

Figure 1. (*a*) Schematic view of the 5CB molecule, defining the *z* axis. (*b*) The biphenyl core of the molecule viewed along its *z* axis. R1 and R2 are its two phenyl rings. OD is the plane containing the mean director.

[6] do not give $(S_{xx} - S_{yy})$ directly, but rather the quantity

$$(S_{x'x'} - S_{y'y'}) = \langle \tfrac{3}{2}\sin^2\beta\cos^2\gamma' \rangle \qquad (3)$$

(see figure 1 (*b*) for details of our notation). If the inter- or intra-molecular forces which are responsible for making this differ from zero were to act wholly on R2 then we would expect

$$(S_{xx} - S_{yy}) = (S_{x'x'} - S_{y'y'})\overline{\cos\phi}.$$

If they were to act wholly on R1 then we would expect

$$(S_{xx} - S_{yy}) = (S_{x'x'} - S_{y'y'})\overline{\cos 2\phi/\cos\phi}.$$

It seems more plausible to suppose, especially in view of results to be discussed in §5, that they act equally on both rings, in which case

$$(S_{xx} - S_{yy}) = (S_{x'x'} - S_{y'y'})/\overline{\cos\phi}. \qquad (4)$$

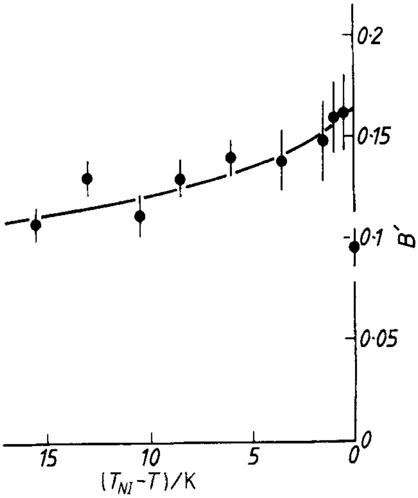

Figure 2. Temperature dependence of the biaxiality ratio for R2 in 5CB, according to Emsley *et al.* [6].

In figure 2 we plot values for what may be called the ***biaxiality ratio*** for R2 in 5CB, $B' = (S_{x'x'} - S_{y'y'})/S_{zz}$, against $(T_{NI} - T)$, where T_{NI} is the nematic–isotropic transition temperature (about 35°C). The values come from data in table 5 of the paper by Emsley *et al.* [6], and the error bars in figure 2 indicate the confidence which these authors have expressed in their data. We imagine the errors to be slightly understated in one or two cases, and in particular mistrust the point at $(T_{NI} - T) = 0$. We have ignored that point in drawing the smooth curve.

3. Molecular polarizabilities

According to Horn and Faber [8], the optical birefringence and the ordering matrix are likely to be related by an equation of the form

$$\Sigma = (C/\bar{\alpha})((\alpha_{zz} - \tfrac{1}{2}(\alpha_{xx} + \alpha_{yy}))S_{zz} + \tfrac{1}{2}(\alpha_{xx} - \alpha_{yy})(S_{xx} - S_{yy})), \qquad (5)$$

where $\alpha_{xx,yy,zz}$ are principal components of the electrical polarizability tensor for a single molecule and $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$; the coefficient C would be unity if the local theory of Vuks [9] were correct and about 1·24 (for 5CB) if the theory of Neugebauer [10] were correct instead. An equivalent result holds exactly for the magnetic anisotropy of a liquid composed of rigid molecules. In terms of the principal components $\chi_{xx,yy,zz}$ of the molar susceptibility tensor for a hypothetical, idealized specimen in which every molecule has the same orientation, it may be written as

$$M\Delta\chi^{(m)} = (\chi_{zz} - \tfrac{1}{2}(\chi_{xx} + \chi_{yy}))S_{zz} + \tfrac{1}{2}(\chi_{xx} - \chi_{yy})(S_{xx} - S_{yy}). \qquad (6)$$

By molar susceptibility we mean M times the mass susceptibility $\chi^{(m)}$ or (M/ϱ) times the true susceptibility χ, where M is the molecular weight and ϱ is the density. The values we quote for $\chi_{xx,yy,zz}$ below are all in unrationalized units of $m^3\,kg^{-1} \times 10^{-9}$.

Horn and Faber implied, and we shall confirm, that the term proportional to $(S_{xx} - S_{yy})$ is of little significance in equation (5) because $(\alpha_{xx} - \alpha_{yy})$ is appreciably less than $(\alpha_{zz} - \alpha_{yy})$. The significance of the equivalent term in equation (6) is greater, because the diamagnetism of the phenyl rings in 5CB makes χ_{yy} quite different from χ_{xx} and χ_{zz}. In setting out to estimate values for $\chi_{xx,yy,zz}$ in 5CB we follow a path already trodden by Sherrell and Crellin [3] and by Madhusudana and Pratibha [11]. That is to say, we base our analysis on the susceptibility measurements on crystalline biphenyl at room temperature reported by Krishnan *et al.* [12] and make corrections for the cyano group and the pentyl chain.

The first reliable determination of the structure of crystalline biphenyl seems to have been that of Trotter [13]. His work showed that the unit cell contains two molecules which are oriented with their z axes parallel and their x axes at ±33·2° to the crystallographic b axis. Although the unit cell is monoclinic, the molecular z axes are virtually perpendicular to the ab plane and seem to coincide, as would be expected, with one of the principal axes of the bulk susceptibility tensor. Interpreted in the light of this structural information, the data of Krishnan *et al.* suggest that for biphenyl

$$\chi_{xx} = -63{\cdot}25, \quad \chi_{yy} = -182{\cdot}15, \quad \chi_{zz} = -63{\cdot}4$$

in the units described previously. These figures imply a value for $(\chi_{xx} - \chi_{yy})$ which is not twice as big for biphenyl as it is for benzene but about 2·2 times as big, and London [14] attributed that excess to conjugation between the π electrons in the two rings; but for such conjugation, χ_{yy} would presumably be about -171.

The above estimates are ostensibly for the case $\phi = 0$, since according to Trotter the biphenyl molecules are flat in the crystalline state. Recent X-ray work [15] has shown, however, that they are flat only on average, for there is significant librational motion with a mean square amplitude amounting to 0·032 rad^2 at 300 K. This motion presumably reduces $(\chi_{xx} - \chi_{yy})$, from the value that it would have for a flat molecule, by a factor 0·936 $(= 1 - 2 \times 0{\cdot}032)$, without directly affecting $(\chi_{xx} + \chi_{yy})$. The appropriate value to use for $(\chi_{xx} - \chi_{yy})$ in 5CB would therefore seem to be $(182{\cdot}15\text{–}63{\cdot}25)\overline{\cos\phi}/0{\cdot}936$. There is the additional complication, however, that any increase in the dihedral angle is liable to diminish the conjugation between the two rings and thereby to diminish χ_{yy}. Taking these points into consideration we estimate that for the biphenyl core in 5CB we have

$$(\chi_{xx} - \chi_{yy}) = 122(\pm 5)\overline{\cos\phi}, \quad (\chi_{xx} + \chi_{yy}) = -240(\pm 5), \quad \chi_{zz} = -63{\cdot}4. \tag{7}$$

We do not need to specify $\overline{\cos\phi}$ because this cancels with the same factor in equation (4).

Suppose now that we substitute a cyano group at one end of the twisted biphenyl core to which equation (7) refers and a methyl group at the other, thereby generating a molecule of 4-methyl-4′-cyanobiphenyl or 1CB, what should the molecular susceptibility then become? Flygare [16] has described two procedures whereby such questions may be answered. They tend to give slightly different answers and it is clear that neither is wholly reliable, but we believe their fallibility to be adequately recognized in the errors attached to the following estimates for 1CB:

$$\left.\begin{aligned}(\chi_{xx} - \chi_{yy}) &= 122(\pm 5)\overline{\cos\phi}, \quad (\chi_{xx} + \chi_{yy}) = -279(\pm 6),\\ \chi_{zz} &= -94{\cdot}5(\pm 3), \quad \bar{\chi} = (\chi_{xx} + \chi_{yy} + \chi_{zz})/3 = 124{\cdot}5(\pm 3).\end{aligned}\right\} \tag{8}$$

At this stage we may refer to measurements of the susceptibility in the isotropic liquid phase of various cyanobiphenyl compounds, as reported in table 2 or by Sherrell and Crellin [3], which yield the following values for the quantity $\bar{\chi}$ defined in equations (8): $-213{\cdot}8$, $-202{\cdot}0$, $-191{\cdot}2$, $-179{\cdot}1$ and $-167{\cdot}3$ for 9CB, 8CB, 7CB, 6CB and 5CB respectively. Plotted against the number n of carbon atoms in the alkyl chain these figures give a good straight line, which has a slope of $-11{\cdot}6$. The slopes suggested by Flygare's two procedures and an alternative procedure due to Davies [17] are $-11{\cdot}6$, $-10{\cdot}4$ and $-11{\cdot}4$ respectively. Extrapolated to $n = 1$ the line suggests a value for $\bar{\chi}$ in 1CB of $-121{\cdot}3$, in reasonable agreement with the value suggested in equations (8). We quote these figures partly to substantiate the estimates in equations (8) and partly to add support to Sherrell and Crellin's data. When the paper by Bunning *et al.* [1] was written there was some evidence that Sherrell and Crellin's results were too high, perhaps due to a calibration error, by as much as 7 per cent. In view of the agreement noted here and of fresh evidence which has been summarized elsewhere [18] that no longer seems likely.

It remains to consider whether the contribution made to the molecular susceptibility by the pentyl chain in 5CB is, or is not, isotropic. We have examined this point in considerable detail, using the procedures of Flygare and Davies and various hypotheses about the frequencies with which the many possible configurations of this chain occur—frequencies that may depend not only on temperature but also (see [6]) on the way in which the core of the molecule is oriented with respect to the mean director. Our conclusion is that it should not add significantly to $(\chi_{xx} - \chi_{yy})$ and that its small contribution to $(\chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}))$ should not differ significantly from that of the methyl group in 1CB. Our final predictions for 5CB, with limits of error slightly larger than in equations (8) to reflect uncertainties in this final stage of the argument, are

$$(\chi_{xx} - \chi_{yy}) = 122(\pm 7)\overline{\cos\phi}, \quad (\chi_{zz} - \tfrac{1}{2}(\chi_{xx} + \chi_{yy})) = 45(\pm 7).$$

Thus from equations (4) and (6) we expect

$$\begin{aligned} 10^9 M\Delta\chi^{(m)}/\mathrm{m^3\,kg^{-1}} &= 45(\pm 7)S_{zz} + 61(\pm 4)(S_{x'x'} - S_{y'y'}) \\ &= 45S_{zz}(1 + 1{\cdot}35B'). \end{aligned} \tag{9}$$

As regards the birefringence, we make the plausible assumption that $(\alpha_{xx} - \alpha_{yy})$ is unaffected by the cyano and pentyl groups in 5CB and that its magnitude can therefore be estimated directly from the refractive indices of crystalline biphenyl, using similar arguments to those we have applied in estimating $(\chi_{xx} - \chi_{yy})$. The refractive indices for biphenyl at a wavelength of 546 nm have been reported by Sundararajan [19]. Adjusted slightly in the light of data provided by Horn [2], they suggest that, at a wavelength of 632·8 nm,

$$\Sigma(1 - 0{\cdot}05\Sigma + 0{\cdot}03\Sigma^2) = 0{\cdot}62S_{zz}(1 + 0{\cdot}19B'). \tag{10}$$

The coefficient 0·62 on the right-hand side has been obtained (see figure 4) by fitting this relation to experimental data for Σ in 5CB. From it we have been able to estimate $(\alpha_{zz} - \frac{1}{2}(\alpha_{xx} + \alpha_{yy}))$ by using Horn's values for $\bar{\alpha}$. No assumptions are necessary concerning the coefficient C in equation (5) because, to a first approximation at any rate, this cancels out in equation (10). The terms inside a bracket on the left-hand side of equation (10) represent a rather trivial local field correction, which is discussed in the Appendix.

4. Experimental results for 5CB

Data which may be compared with equations (9) and (10) are shown in table 1. The data for S_{zz} are taken from table 5 of the paper by Emsley *et al.* [6] and those for B' are from the smooth curve drawn through the points in figure 2. The susceptibility data were obtained by one of us (D.A.C.), using the technique described by Sherrell and Crellin [3], with whose results they are in good agreement; arguments for preferring them to the slightly lower values measured by Buka and de Jeu [5] have been outlined in §3. Since the susceptibility measurements were not confined to the temperatures for which Emsley *et al.* measured S_{zz}, the values we quote are not raw data but have been read off from a smooth curve. The same is true of the values quoted for Σ, which derive from results for n_e and n_o listed in table 3. These results were obtained (by J.D.B.) using light from a He–Ne laser (λ = 632·8 nm) and a standard

Table 1. Experimental data for 5CB.

$(T_{NI} - T)$/K	S_{zz}	B'	$10^{11}\Delta\chi^{(m)}/\mathrm{m^3\,kg^{-1}}$	$\Sigma(\lambda = 632{\cdot}8\,\mathrm{nm})$
0	0·388	(0·165)	7·04	0·218
0·5	0·384	0·160	7·97	0·246
1·0	0·414	0·157	8·50	0·265
1·5	0·443	0·153	8·88	0·280
3·5	0·491	0·141	9·87	0·317
6·0	0·524	0·133	10·64	0·346
8·5	0·565	0·125	11·10	0·366
10·5	0·583	0·120	11·40	0·379
13·0	0·599	0·115	11·73	0·393
15·5	0·615	0·111	12·01	0·405

Table 2. Parameters determining magnetic anisotropy (see equation (12)).

Nematogen	$10^9\chi^{(m)}_{\mathrm{iso}}/\mathrm{m}^3\,\mathrm{kg}^{-1}$	$10^9\Delta\chi^{(m)}(0)/\mathrm{m}^3\,\mathrm{kg}^{-1}$	τ/K	n	M
5CB	0·671	0·182	0·35	0·1396	249·4
6CB	0·680	0·164	0·27	0·1429	263·4
7CB	0·689	0·171	0·39	0·1507	277·4
5OCB	0·654	0·172	0·21	0·1829	265·4
6OCB	0·660	0·157	0·17	0·1674	279·4
7OCB	0·662	0·153	0·19	0·1753	293·4
7CCH	0·706	−0·052	0·54	0·1796	289·5
MBBA	0·644	0·217	0·48	0·1875	258·3

Chatelain wedge technique [2]. Relative to their values at some chosen reference temperature both $\Delta\chi^{(m)}$ and Σ should be accurate to within $\pm\frac{1}{2}$ per cent. Systematic (temperature-independent) errors may be present, but they are not likely to exceed ± 3 per cent.

The validity of equation (9) is tested in figure 3 where we plot the ratio of $M\Delta\chi^{(m)}$ to both S_{zz} and $S_{zz}(1 + 1{\cdot}35B'))$ against temperature. It is clear that inclusion of the biaxiality correction factor $(1 + 1{\cdot}35B')$ removes the temperature dependence which is apparent in the upper curve in this figure. The lower points lie within $\pm\frac{1}{2}$ per cent of a horizontal line, except for two which seem to be affected by random errors in S_{zz} (cf. figure 4, where the same errors show up). This line corresponds to

$$10^9 M\Delta\chi^{(m)}/\mathrm{m}^3\,\mathrm{kg}^{-1} = 42{\cdot}4S_{zz}(1 + 1{\cdot}35B') \qquad (11)$$

and the distinction between 42·4 and 45 is within the limits of error. Thus the analysis presented in §3 seems to give a good description of the magnetic anisotropy.

A similar test of equation (10) is presented in figure 4. Here we plot three ratios against temperature: Σ/S_{zz}, $\Sigma/S_{zz}(1 + 0{\cdot}19B')$ and $\Sigma(1 - 0{\cdot}05\Sigma + 0{\cdot}03\Sigma^2)/S_{zz}(1 + 0{\cdot}19B')$. Evidently the biaxiality correction and the proposed local field correction

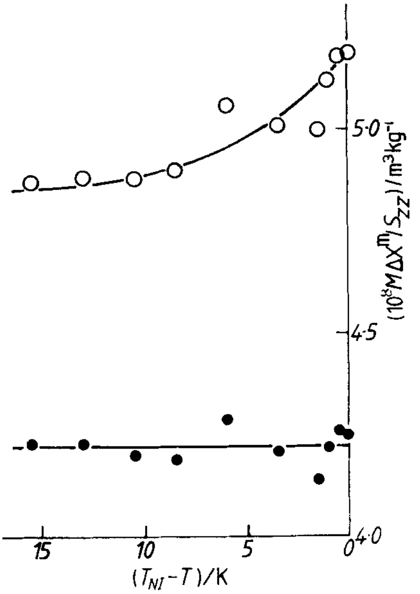

Figure 3. The ratio between magnetic susceptibility and order parameter versus temperature for 5CB: open circles, without biaxiality correction; full circles, with biaxiality correction.

Table 3. Refractive indices at $\lambda = 632{\cdot}8$ nm.

$(T_{NI} - T)$/K	5CB		6CB		7CB		8CB		9CB	
	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
0·1	1·6518	1·5474	1·6353	1·5489	1·6300	1·5331	1·6213	1·5320	1·6265	1·5163
0·2	1·6543	1·5461	1·6378	1·5479	1·6322	1·5321	1·6240	1·5310	1·6289	1·5153
0·5	1·6598	1·5438	1·6433	1·5456	1·6380	1·5299	1·6296	1·5284	1·6338	1·5130
1·0	1·6652	1·5408	1·6499	1·5425	1·6445	1·5271	1·6360	1·5254	1·6395	1·5103
1·5	1·6698	1·5384	1·6549	1·5407	1·6492	1·5252	1·6407	1·5237	1·6439	1·5087
2·0	1·6735	1·5367	1·6590	1·5395	1·6531	1·5239	1·6443	1·5223		
3·0	1·6803	1·5348	1·6652	1·5375	1·6591	1·5220	1·6502	1·5202		
4·0	1·6854	1·5333	1·6700	1·5360	1·6638	1·5210	1·6550	1·5186		
5·0	1·6899	1·5321	1·6739	1·5348	1·6676	1·5200	1·6591	1·5171		
6·0	1·6938	1·5311	1·6770	1·5339	1·6707	1·5191	1·6629	1·5160		
8·0	1·7002	1·5294	1·6835	1·5323	1·6761	1·5178				
10·0	1·7057	1·5281	1·6889	1·5311	1·6810	1·5169				
12·0	1·7103	1·5271	1·6933	1·5301	1·6855	1·5164				
14·0	1·7148	1·5267	1·6971	1·5294	1·6894	1·5158				
16·0	1·7191	1·5263	1·7011	1·5289	1·6929	1·5150				
18·0	1·7236	1·5262			1·6962	1·5142				
20·0					1·6997	1·5142				
22·0					1·7030	1·5142				

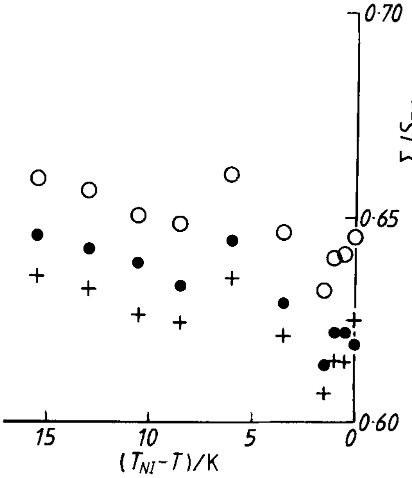

Figure 4. The ratio between birefringence and order parameter versus temperature for 5CB; open circles, without biaxiality correction; full circles, with biaxiality correction; crosses, with additional local field correction.

both alter the magnitude of the ratio, by about $1\frac{1}{2}$ per cent in each case, but since we are unable to predict its magnitude with anything like that accuracy we cannot use this to check that they are present in the data. It is also evident that the temperature-dependence of both correction factors is too slight to show up directly. In fact all three sets of points in figure 4 seem to lie on lines which slope slightly, by rather more than would be expected from the $\pm 1\frac{1}{2}$ per cent random error in Σ and from the random errors in S_{zz} suggested by the lower set of points in figure 3. Thus the validity of equation (10) is at best unproved; the treatment of the local field problem suggested in the Appendix may not be fully adequate.

5. Experimental results for other nematics

Our unpublished measurements of $\Delta\chi^{(m)}$ extend to several other nematics besides 5CB, namely: 6CB and 7CB (cyanobiphenyls, with n-hexyl or n-heptyl chains in place of the n-pentyl chain in 5CB); 5OCB, 6OCB and 7OCB (oxycyanobiphenyls, distinguished from 5CB etc. by the inclusion of an oxygen atom between the alkyl chain and the phenyl ring R1); 7CCH (a cyanocyclohexyl compound, distinguished from 7CB by having two cyclohexyl rings instead of phenyl rings); and MBBA (4-methoxybenzylidene-4′-n-butylaniline). For each of these substances the results may be fitted by the equation

$$\Delta\chi^{(m)} = \Delta\chi^{(m)}(0)(1 - T/(T_{\mathrm{NI}} + \tau))^{n}, \qquad (12)$$

which proves to be at least as accurate as, and more convenient than, the polynomial expression used by Sherrell and Crellin [3]. Appropriate values for the parameters $\Delta\chi^{(m)}(0)$, τ and n are listed in table 2, together with values for the temperature-independent mass susceptibility in the isotropic phase, from which $\bar{\chi}$ may be deduced if required using the molecular weights given in the final column.

Our refractive index measurements cover all of these compounds except 7CCH and MBBA, and also 8CB, 9CB and 8OCB and PAA (p-azoxyanisole). For the last of these, values for $\Delta\chi^{(m)}$ are available from the work of de Jeu *et al.* [20]. The results have not been fitted by an analytic expression, so we record them in tabular form;

Table 4. Refractive indices at λ = 632·8 nm.

$(T_{NI} - T)$/K	5OCB		6OCB		7OCB		8OCB		PAA	
	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
0·1	1·6220	1·5480	1·6135	1·5390	1·5975	1·5370	1·5927	1·5280	1·7410	1·5811
0·2	1·6270	1·5469	1·6180	1·5370	1·6030	1·5352	1·5980	1·5262	1·7446	1·5803
0·5	1·6365	1·5438	1·6255	1·5333	1·6120	1·5311	1·6047	1·5230	1·7449	1·5780
1·0	1·6450	1·5406	1·6338	1·5301	1·6221	1·5273	1·6108	1·5195	1·7560	1·5753
1·5	1·6504	1·5382	1·6391	1·5280	1·6283	1·5246	1·6152	1·5171	1·7605	1·5732
2·0	1·6550	1·5362	1·6432	1·5261	1·6335	1·5221	1·6187	1·5152	1·7649	1·5718
3·0	1·6620	1·5330	1·6502	1·5247	1·6408	1·5192	1·6234	1·5130	1·7719	1·5690
4·0	1·6681	1·5311	1·6559	1·5218	1·6459	1·5173	1·6271	1·5113	1·7779	1·5669
5·0	1·6728	1·5299	1·6607	1·5202	1·6501	1·5160	1·6304	1·5100	1·7830	1·5652
6·0	1·6771	1·5289	1·6648	1·5190	1·6539	1·5150	1·6337	1·5089	1·7877	1·5639
8·0	1·6848	1·5267	1·6721	1·5168	1·6602	1·5137	1·6388	1·5073	1·7958	1·5617
10·0	1·6910	1·5251	1·6782	1·5151	1·6658	1·5123	1·6429	1·5061	1·8029	1·5599
12·0	1·6963	1·5239	1·6837	1·5140	1·6703	1·5111	1·6466	1·5052	1·8092	1·5583
14·0	1·7011	1·5230	1·6885	1·5131	1·6745	1·5104	1·6498	1·5043	1·8150	1·5572
16·0	1·7055	1·5224	1·6931	1·5126	1·6783	1·5100	1·6527	1·5035	1·8203	1·5562
20·0	1·7131	1·5219	1·7005	1·5115	1·6851	1·5095	1·6589	1·5021	1·8299	1·5550
24·0	1·7200	1·5211	1·7072	1·5110	1·6910	1·5091	1·6641	1·5008	1·8387	1·5539
28·0	1·7268	1·5209	1·7141	1·5108	1·6967	1·5090	1·6688	1·4993	1·8469	1·5531
32·0	1·7331	1·5208	1·7209	1·5108	1·7021	1·5088			1·8540	1·5527
36·0	1·7394	1·5207	1·7273	1·5108	1·7075	1·5087			1·8609	1·5518
40·0									1·8677	1·5510

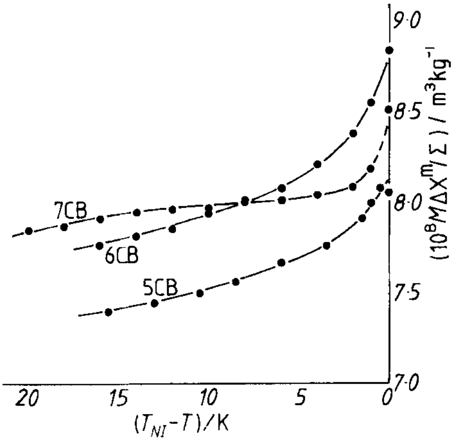

Figure 5. Temperature dependence of $M\Delta\chi^{(m)}/\Sigma$ for three cyanobiphenyls.

table 3 gives values for n_e and n_o (from which Σ may readily be calculated) for the alkyl-cyanobiphenyls at $\lambda = 632{\cdot}8$ nm, and table 4 gives similar values for the alkoxy compounds and for PAA. The data could contain systematic errors as large as $\pm 0{\cdot}001$, but Σ is primarily determined by $(n_e - n_o)$ and this should be reliable to within $\pm 0{\cdot}0003$; where there is overlap with the results of previous workers [2, 4] there is agreement within these limits. During our studies of 8CB, 9CB and 8OCB we observed the well-known transition into the smectic state, but in tables 3 and 4 we confine ourselves to ranges of temperature where the materials were nematic.

In figures 5 and 6 we plot the ratio $\Delta\chi^{(m)}/\Sigma$ against $(T_{NI} - T)$, for all those substances for which we have data for both the magnetic anisotropy and the birefringence. Some temperature-dependence of the ratio is apparent in all cases, except perhaps that of PAA for which the scatter is relatively large. In each case the ratio rises as T_{NI} is approached, but there seem to be two slightly different patterns of behaviour, one of them followed by 5CB, 6CB and 6OCB and the other by 5OCB, 7CB and

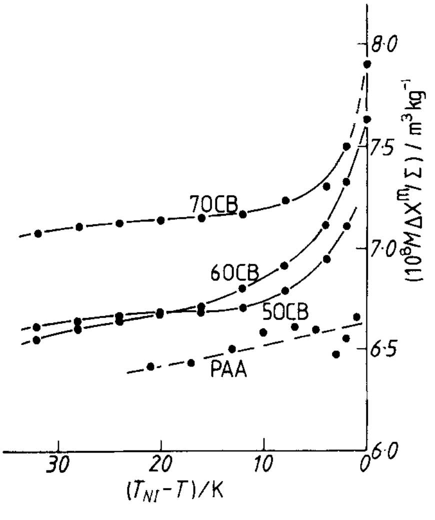

Figure 6. Temperature dependence of $M\Delta\chi^{(m)}/\Sigma$ for three oxycyanobiphenyls and for PAA.

7OCB. In so far as we can attribute the temperature-dependence in the case of 5CB to the biaxiality correction to $\Delta\chi^{(m)}$, it seems fair to conclude that biaxiality is present in all the other cyano-compounds, and present in much the same degree. The similarity of behaviour between 6CB and 6OCB on the one hand, and between 7CB and 7OCB on the other, to some extent masked in figures 5 and 6 by a difference in the choice of temperature scales, is particularly striking. Some models would suggest that biaxiality is imposed on the biphenyl core of the nematic molecule by preferential alignment, parallel to the mean director, of the alkyl chain. If these models were correct, however, the biaxiality of the core would depend upon the degree of steric hindrance to rotation about the bond or bonds linking the chain to the core, in which case it would surely be less marked in the alkoxycyanobiphenyls than in the alkylcyanobiphenyls. The curves for 6CB, 6OCB, 7CB and 7OCB in figures 5 and 6 seem to us to be inconsistent with such models, which is why we have preferred to assume, in deriving equation (4), that the biaxiality is due to intermolecular forces which act on the core itself.

Needless to say, these conclusions must remain tentative until the other cyanobiphenyls have been subjected to examination by N.M.R. methods with the care that Emsley *et al.* have devoted to 5CB.

Appendix

The philosophy of the continuum model of nematic disorder suggested by Faber [7] is that the molecules would all be perfectly aligned were it not that a spectrum of distortion modes, involving either splay and bend of the director field or twist and bend, are thermally excited. The amplitude ψ of each mode is calculated in terms of its wavevector q and the Frank stiffness constants K_1, K_2 and K_3 with the aid of the equipartition principle, and S_2 ($\equiv S_{zz}$) is evaluated from the equation

$$\ln(1/S_2) = \tfrac{3}{2}X = \tfrac{3}{2}\sum_q \langle\psi^2\rangle. \qquad (A\,1)$$

The spectrum is cut off at a wavevector q_c sufficient to enclose $2N$ discrete modes, this being the number required to describe all the orientational degrees of freedom in a specimen composed of N molecules. Although in many respects over-simplified, the model seems to provide an adequate description of many observable properties of nematics, except perhaps in the neighbourhood of T_{NI}. One property it does *not* describe, however, is the type of ordering associated with a non-zero value for $(S_{xx} - S_{yy})$, and throughout this Appendix we shall ignore this particular aspect of nematics such as 5CB. We can therefore use a different set of x, y, z axes from the set defined by figure 1. Our axes are now fixed relative to the specimen container rather than fixed in one molecule. The local director fluctuates symmetrically about the z axis, which therefore coincides with what we have referred to as the *mean* director in the main text.

Consider the effect of exciting a single distortion mode in a homogeneous uniaxial medium whose ordinary and extraordinary relative permittivities are ε_o and ε_e respectively. To simplify the discussion let us choose q to lie in the z direction too. In that case excitation tilts the director locally through a small angle $\psi(z) \propto \cos qz$, and we may distinguish two possible polarizations, for one of which the tilt is about the x axis and for the other about the y axis. For the first of these polarizations, excitation evidently makes no difference to the dielectric response of the medium to a field applied along the x direction: if the mean relative permittivity after excitation is denoted by ε'_o we have

$$\varepsilon'_o = \varepsilon_o. \tag{A 2}$$

For the second polarization, however, the response to a field in the x direction is described by

$$\begin{aligned}\varepsilon'_o &= \langle \varepsilon_o \cos^2\psi + \varepsilon_e \sin^2\psi - (\varepsilon_e - \varepsilon_o)^2 \sin^2\psi \cos^2\psi/(\varepsilon_e \cos^2\psi + \varepsilon_o \sin^2\psi)\rangle,\\ &\simeq \varepsilon_o + (\varepsilon_o/\varepsilon_e)\Delta\varepsilon\langle\psi^2\rangle, \end{aligned}\tag{A 3}$$

where

$$\Delta\varepsilon = (\varepsilon_e - \varepsilon_o). \tag{A 4}$$

(In the first line of equation (A 3) the origin of the first two terms is transparent enough. The complicated third term allows for the periodic variation in the z component of the electric dipole moment per unit volume, which generates a periodic space charge and hence a periodic field in the z direction, and which thereby contributes to the x component of the dipole moment per unit volume.) Averaging over both polarizations we obtain

$$\varepsilon'_o = \varepsilon_o + \tfrac{1}{2}(\varepsilon_o/\varepsilon_e)\Delta\varepsilon\langle\psi^2\rangle. \tag{A 5}$$

If the field is applied along the z direction, it follows from the continuity of the electric induction D that the mean relative permeability after excitation is

$$\begin{aligned}\varepsilon'_e &= \langle(\varepsilon_e \cos^2\psi + \varepsilon_o \sin^2\psi)^{-1}\rangle^{-1},\\ &\simeq \varepsilon_e - \Delta\varepsilon\langle\psi^2\rangle. \end{aligned}\tag{A 6}$$

Equations (A 5) and (A 6) now need to be generalized to the case where q makes an angle Θ, say, with the director, and the results averaged over Θ. The calculation is straightforward but too lengthy to describe in detail here. The results may be summarized in the equations

$$\frac{d\varepsilon_o}{dX} = \tfrac{1}{2}\Delta\varepsilon\langle\varepsilon_o/(\varepsilon_o + \Delta\varepsilon\cos^2\Theta)\rangle, \tag{A 7}$$

$$\frac{d\varepsilon_e}{dX} = -\tfrac{1}{2}\Delta\varepsilon\langle 1 + \varepsilon_e/(\varepsilon_e - \Delta\varepsilon\sin^2\Theta)\rangle. \tag{A 8}$$

To evaluate the averages it is convenient to expand the relevant functions of Θ in powers of the quantity

$$p = 3\Delta\varepsilon/(\varepsilon_e + 2\varepsilon_o) = \Delta\varepsilon/\bar{\varepsilon}. \tag{A 9}$$

At optical frequencies, where ε_e can be identified with n_e^2 while ε_o can be identified with n_o^2, the quantity thus defined is typically about 0·2, and it can be shown that on this account the expansion can safely be terminated after the term in p^2. (If it were desired to use the present theory to discuss the dielectric constants of nematics at low frequencies, greater care would be needed.) Thus we may rewrite (A 7) as

$$\frac{d\varepsilon_o}{dX} = \tfrac{1}{2}\Delta\varepsilon(1 - p(1 + \tfrac{1}{3}p)\,\langle\cos^2\Theta\rangle + p^2\langle\cos^4\Theta\rangle). \tag{A 10}$$

If the three Frank constants for 5CB were equal to one another, the averages here would be isotropic ones, leading to

$$\frac{d\varepsilon_o}{dX} = \tfrac{1}{2}\Delta\varepsilon(1 - \tfrac{1}{3}p + \tfrac{4}{45}p^2). \tag{A 11}$$

In fact, however,

$$4K_1 \simeq 8K_2 \simeq 3K_3 \tag{A 12}$$

in the middle of the temperature range of interest to us, and $\langle\psi^2\rangle$ is therefore greater for a mode that involves a large degree of twist deformation than for one that involves mainly bend. As a result the appropriate averages over Θ are not isotropic. We have worked out the appropriate weighting functions for the conditions described by (A 12), using formulae for $\langle\psi^2\rangle$ to be found in the work of Faber [7], and obtain

$$\frac{d\varepsilon_o}{dX} = \tfrac{1}{2}\Delta\varepsilon(1 - 0{\cdot}27p + 0{\cdot}06p^2). \tag{A 13}$$

The difference between (A 13) and (A 11) turns out to be rather trivial in practice, so that errors in our weighting procedure at temperatures where (A 12) is not exactly obeyed should be of little account. By a similar procedure we obtain

$$\frac{d\varepsilon_e}{dX} = -\Delta\varepsilon(1 + 0{\cdot}27p + 0{\cdot}03p^2). \tag{A 14}$$

Combining (A 14) and (A 13), and making use of (A 1) we then have

$$\begin{aligned}\frac{d\ln p}{d\ln S_2} &= -\frac{2}{3}\frac{1}{\Delta\varepsilon}\frac{d(\Delta\varepsilon)}{dX} - \frac{p}{\Delta\varepsilon}\frac{d\bar{\varepsilon}}{dX},\\ &= (1 + 0{\cdot}09p - 0{\cdot}08p^2),\end{aligned}$$

from which it follows that (to order p^3)

$$p(1 - 0{\cdot}09p + 0{\cdot}05p^2) \propto S_2. \tag{A 15}$$

Now the quantity Σ is related to p by

$$\bar{\varepsilon}p = (\bar{\varepsilon} - 1)\Sigma, \tag{A 16}$$

and from (A 13) and (A 14) it may be estimated that (to order p^2)

$$\bar{\varepsilon} \propto (1 + 0{\cdot}06p^2). \tag{A 17}$$

In 5CB the constant of proportionality on the right of (A 17) is close to 2·50 at $\lambda = 632{\cdot}8$ nm. Using this value and substituting (A 16) into (A 15) we obtain our final result

$$S_2/\Sigma \propto (1 - 0{\cdot}05\Sigma + 0{\cdot}03\Sigma^2). \tag{A 18}$$

In principle the constants of proportionality in both (A 17) and (A 18) depend upon density and may therefore be affected by thermal expansion. We have convinced ourselves, however, that over the temperature range of interest thermal expansion should in practice be negligible.

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