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The elastic behaviour of liquid crystal dimers: an ESR investigation of their induced chiral nematic phases

by D. IONESCU†, G. R. LUCKHURST* and D. S. DE SILVA

Department of Chemistry and Southampton Liquid Crystal Institute,
University of Southampton, Southampton SO17 1BJ, U.K.

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We have attempted to investigate the dependence of the elastic behaviour of liquid crystal dimers on the parity of the spacer linking the two mesogenic groups by using an indirect method. In this the nematic phase formed by the dimers is converted to a chiral nematic by the addition of a chiral dopant. The uniform distribution of the director in the helical structure of the mesosphase is perturbed by the magnetic field of an ESR spectrometer. The extent of the field-induced perturbation is then determined from the appearance of the ESR spectrum of a nitroxide spin probe dissolved in the mesophase. The observed difference in the extent of the field-induced perturbation is analysed in terms of the higher orientational order of the even with respect to the odd dimer. However, the theoretical model fails to account for this difference in behaviour and a possible explanation is discussed.

1. Introduction

Liquid crystal dimers, in which two mesogenic groups are linked by a flexible spacer, have properties that frequently display a dramatic dependence on the parity of the number of groups in the spacer [1]. For example, the entropy change at the nematic–isotropic transition for even dimers can be three times larger than for the neighbouring odd members of the homologous series. This major difference in the transitional entropy implies that there should be a corresponding difference in the second rank orientational order parameter. This proves to be the case for the order parameter of the mesogenic group for the cyanobiphenyl dimers although the difference is not so great, with the order parameter at the nematic–isotropic transition for even dimers being about one and a half times that for odd dimers [2]. For conventional monomeric nematogens the elastic constants are predicted and found to be approximately quadratic in the orientational order parameter [3] and so we might expect the elastic constants for even dimers to be greater than those for odd dimers. Measurements of the elastic constants for two phenyl benzoate dimers have shown that this expectation is correct [4] with the elastic constants for the even dimer being almost twice as large as those for the odd dimer, in keeping with the difference in their orientational order parameters.

To explore the dependence of the elastic behaviour of liquid crystal dimers on the parity of the spacer further we have studied two members of the series of α,ω-bis(4-cyanobiphenyl-4′-yloxy)alkanes. The melting points for the dimers are rather high, typically about 150°C, which complicates the determination of the elastic constants by conventional methods. We have, therefore, adopted an indirect but experimentally convenient route to the elastic behaviour of the dimers. In this method the nematic phase is first converted to a chiral nematic by the addition of a chiral dopant. The pitch of the helical structure of the induced chiral nematic phase is then perturbed by the application of a magnetic field. The change in the pitch produced by the field is determined by, amongst other things, the twist elastic constant of the nematic phase. To study the field-induced distortion of the helical structure we have used ESR spectroscopy which has proved to be a valuable technique for monitoring the director distribution in chiral nematic [5, 6] and other liquid crystal phases [7].

In the following section the theoretical background to the experiments is outlined in order to make clear the relationship between the twist elastic constant and what is measured. The experiments themselves are described in §3 and the analysis of the ESR spectra is given in §4. The results are to be found in §5 where their significance is discussed and our conclusions are in §6.

2. Theoretical background

The application of a field to a chiral nematic with a positive diamagnetic anisotropy, $\Delta\tilde{\chi}$, has two effects.

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* Author for correspondence.

† Permanent address: Department of Physics, 'Politehnica' University of Bucharest, 77206 Bucharest, Romania.

First, the helix axis is aligned orthogonal to the magnetic field and then the pitch of the helix, P, is increased in such a way that more of the director is aligned parallel to the magnetic field than perpendicular. The orientational distribution function, $p(\varphi)$, for the director with respect to the field is predicted to be [8]

$$p(\varphi)=(1-k^2\cos^2\varphi)^{-1/2}\bigg/\int_0^{2\pi}(1-k^2\cos^2\varphi)^{-1/2}\,\mathrm{d}\varphi. \tag{1}$$

The parameter k which determines the distribution function for a particular material and at a given field is

$$k=(P_0B/\pi^2)(\Delta\tilde{\chi}/\mu_0K_2)^{1/2}E(k). \tag{2}$$

Here P_0 is the pitch of the unperturbed helix, B is the magnetic flux density, μ_0 is the magnetic constant, K_2 is the twist elastic constant and $E(k)$ is an elliptic integral of the second kind

$$E(k)=\int_0^{\pi/2}(1-k^2\sin^2\varphi)^{1/2}\,\mathrm{d}\varphi. \tag{3}$$

The parameter k can take values from zero, corresponding to an unperturbed helix, to unity when the helix is unwound and the director is aligned parallel to the magnetic field. In figure 1 we show examples of the distribution function calculated for values of k from 0 to 0·99. The plots of $p(\varphi)$ are shown in the range for φ from 0 to 90° rather than the complete range because of the symmetry of the system. It is apparent that it is not until k is relatively close to unity that $p(\varphi)$ begins to show any significant increase in the probability of finding the director parallel to the magnetic field. As we shall see, the form of the ESR spectrum allows the parameter k to be determined, from which the twist elastic constant can be extracted, provided P_0 and $\Delta\tilde{\chi}$ are known.

The chiral nematic phase is created for the liquid crystal dimers which we have studied by the addition of a chiral dopant. The pitch of the helix in the induced chiral nematic is determined by the mole fraction of the dopant, x, and for the low concentrations used in our experiments

$$P_0=(x\beta_\mathrm{M})^{-1}, \tag{4}$$

where β_M is the helical twisting power [9]. According to theory β_M is also related to the twist elastic constant for the nematic [10], in fact

$$\beta_\mathrm{M}=-RT\mathfrak{I}\varepsilon/2\pi K_2V_\mathrm{m}, \tag{5}$$

where $\mathfrak{I}$ is a chirality order parameter which is determined by the ordering matrix of the dopant and its shape chirality, ε is a scaling parameter which is proportional to the orientational order of the nematic solvent [11] and V_m is its molar volume. Substituting the prediction for the helical twisting power into the expression for the pitch of the unperturbed helix gives the experimental parameter k as

$$k=(2V_\mathrm{m}B/RT\mathfrak{I}\varepsilon x\pi)(\Delta\tilde{\chi}K_2/\mu_0)^{1/2}E(k). \tag{6}$$

Since the quantities needed to extract the twist elastic constant from k are not known for the system which we have studied, it is helpful to consider how the composite quantity represented by k should vary with the orientational order of the liquid crystal dimers. The twist elastic constant is expected to be quadratic in the solvent order parameter, whereas $\Delta\tilde{\chi}$ should be linear as should the chirality order parameter, $\mathfrak{I}$, and the scaling parameter ε. Overall then, $k/E(k)$ is expected to be inversely proportional to the square root of the solvent order parameter; we shall see whether this prediction holds or not in § 5. However, at this stage it should be clear that measurement of k provides a less sensitive probe of the difference in the elastic behaviour of odd and even dimers than for the direct determination of the elastic constants themselves.

There is an alternative, albeit qualitative, route to the elastic behaviour of the liquid crystal dimers in such experiments involving induced chiral nematic phases. The conversion of a chiral nematic phase to a nematic is usually studied by measuring the threshold magnetic field needed to cause the transition [8]; according to theory this field is given by

$$B_\mathrm{th}=(\pi^2/P_0)(\mu_0K_2/\Delta\tilde{\chi})^{1/2}. \tag{7}$$

However, in our ESR experiments the magnetic field is more or less constant and to control the transition we use the concentration of the chiral dopant. It is possible to predict this threshold concentration by combining equations (4), (5) and (7) to give

$$x_\mathrm{th}=(2BV_\mathrm{m}/RT\mathfrak{I}\varepsilon\pi)(K_2\Delta\tilde{\chi}/\mu_0)^{1/2}. \tag{8}$$

This result is analogous to the expression for k in equation (6) and so use of the same arguments suggests that the threshold concentration of chiral dopant needed to convert the nematic to a chiral nematic state at a given field strength should be smaller for an even than for an odd dimer.

3. Experimental

The liquid crystal dimers studied, i.e. α,ω-bis (4-cyanobiphenyl-4′-yloxy)nonane (BCBO9) (figure 2-I) and α,ω-bis (4-cyanobiphenyl-4′-yloxy)decane (BCBO10) (figure 2-II) were synthesized using a Williamson etherification of 4-hydroxy-4′-cyanobiphenyl with the appropriate dibromoalkane [12]. Their phase behaviour and transition temperatures are: BCBO9: Cr 132°C N 170°C I; BCBO10: Cr 162°C N 183°C I which are in good agreement with literature values. This particular

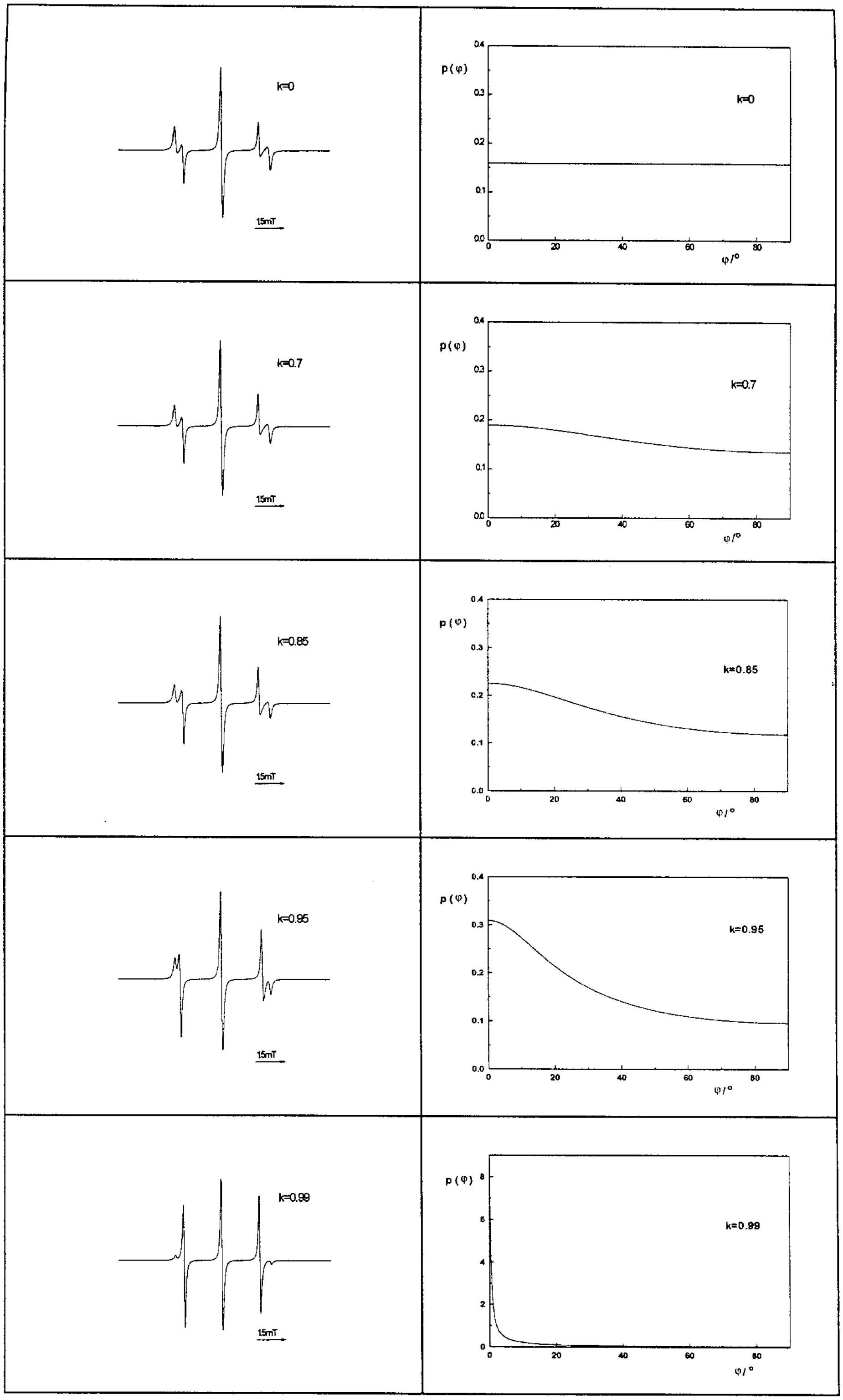

Figure 1. The director distribution function $p(\varphi)$, calculated from equation (1) for different values of k together with the ESR spectra of the spin probe TEMPONE simulated with these distribution funtions, as described in §4.

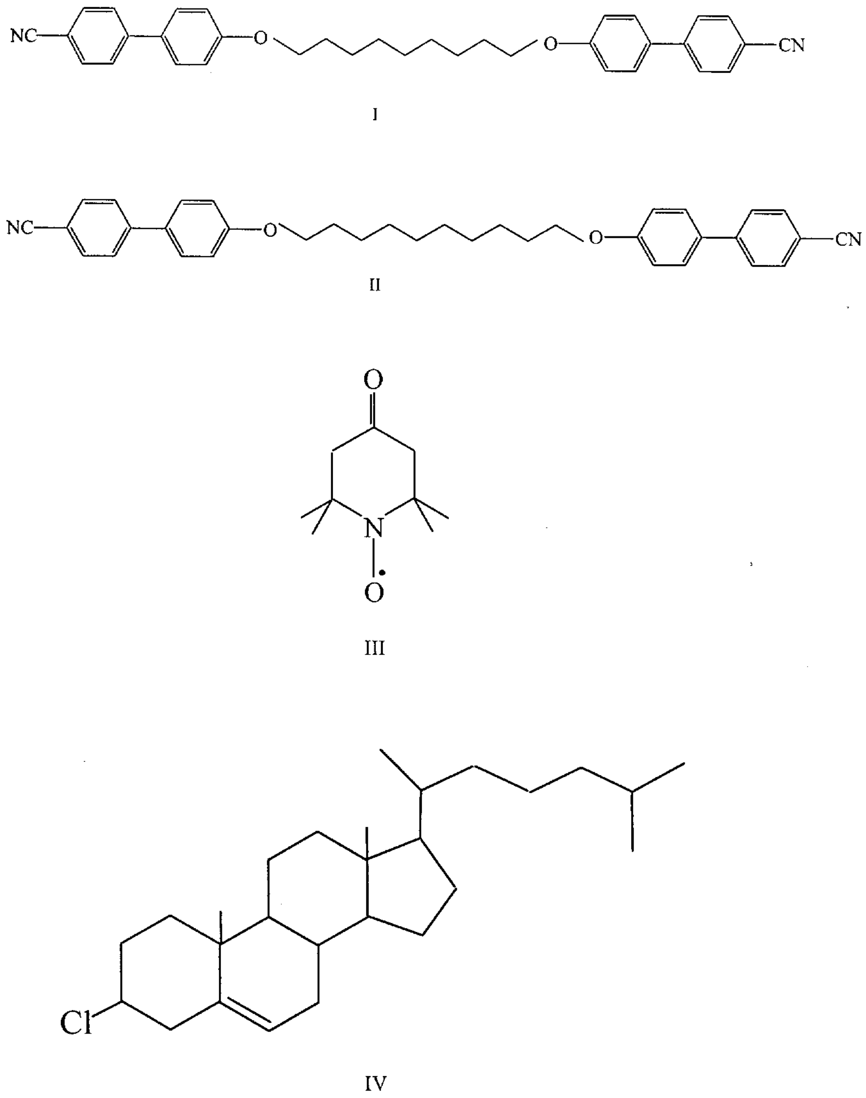

Figure 2. The molecular structures of the liquid crystal dimers (I and II), the spin probe (III) and the chiral dopant (IV) used in this investigation.

pair of dimers was chosen because their nematic–isotropic transition temperatures are amongst the lowest in the series; in addition the spacer lengths are the same as those for the dimers studied by DiLisi *et al.* [4].

The spin probe employed in this ESR investigation was 2,2,6,6-tetramethyl-4-piperidone-*N*-oxide (TEMPONE); it was purchased from Aldrich and used without further purification (figure 2-III). Although at first sight this probe does not seem particularly suitable for liquid crystal studies because of its small shape anisotropy, TEMPONE presents a number of satisfactory features. Thus, it has a relatively rigid molecule, is not chiral and its ESR spectra are well resolved. The ratio of the hyperfine splitting to the linewidth in this case is better than that for the highly anisotropic cholestane nitroxide spin probe and so allows a more sensitive study of the director distribution.

The chiral dopant was cholesteryl chloride; this was purchased from Avocado and also used without further purification (figure 2-IV); it forms only a strongly monotropic liquid crystalline phase and melts at 99°C.

Binary mixtures containing up to 2% by weight of cholesteryl chloride in both BCBO9 and BCBO10 were prepared. The components were dissolved in chloroform and then the solvent was removed under vacuum. A small amount of the solid mixture together with a trace quantity of the probe were introduced into a quartz sample tube and degassed under vacuum. The sample was placed in the microwave cavity of the spectrometer, heated to just within the isotropic phase and the ESR spectra were recorded on cooling as a function of temperature in the mesophase.

The addition of cholesteryl chloride to the nematogens depresses the nematic–isotropic transition and also creates a biphasic region with co-existing isotropic and chiral nematic phases. The phase boundaries were found to approximate to Henry's Law behaviour which is to be expected for this low solute concentration [13]. For the largest concentration of the chiral dopant the width of the biphasic region was observed to be about 7°C while the temperature, T_I, at which the biphasic mixture was converted to the isotropic phase, was approximately 5°C below T_{NI} for the pure material. Similar behaviour was found for both odd and even dimers.

The ESR measurements were made using a Bruker ECS 106 electron spin resonance spectrometer fitted with a Eurotherm B-VT 2000 variable temperature unit.

4. Simulation of the ESR spectra

Before we come to analyse the recorded ESR spectra, we first consider the appearance of the spectrum to be expected for a chiral nematic phase perturbed by a magnetic field [5, 6]. In a uniformly aligned nematic with the director parallel to the magnetic field the ESR spectrum of an organic nitroxide contains three nitrogen hyperfine lines. The hyperfine spacing is the component of the partially averaged hyperfine tensor parallel to the director, $\tilde{A}_{\parallel}$. The position of the central line is determined by the parallel component of the partially averaged g-tensor, $\tilde{g}_{\parallel}$. If the sample can be aligned with the director perpendicular to the magnetic field, then the form of the ESR spectrum is unchanged but the line positions are now determined by the perpendicular components of the tensors, $\tilde{A}_{\perp}$ and $\tilde{g}_{\perp}$, because of the uniaxial symmetry of the nematic phase. When the director adopts a range of orientations with respect to the magnetic field the observed spectrum is a sum of spectra from all orientations, provided the rate of diffusion between different director orientations is slow on the ESR timescale; this is observed to be the case for our systems. To extract information about the director distribution function it is necessary to simulate the ESR powder patterns, usually with some theoretical form for the director distribution. This is achieved in the following way.

The ESR experiment records the first derivative of the absorption line shape. This shape may be lorentzian for a pure transition or gaussian if the line is inhomogenously broadened by unresolved proton hyperfine structure. For the spectra which we have recorded we find that the lorentzian line shape provides the best fit. The form for the first derivative of this function is

$$L(B, B_r, T_2^{-1}) = \frac{2T_2^3}{\pi} \frac{(B_r - B)}{[1 + T_2^2(B_r - B)^2]^2} \tag{9}$$

where T_2^{-1} is the width of the absorption line at half its height. In fact, the width of the hyperfine lines of a nitroxide radical tumbling in solution often exhibit a marked dependence on the nuclear quantum number m associated with the transition [14] and has the form

$$T_2^{-1}(m) = A + Bm + Cm^2. \tag{10}$$

However, for a nitroxide dissolved in a liquid crystal, the linewidth is predicted and observed to depend on the orientation of the director with respect to the magnetic field [15]. The theoretical angular dependence of the linewidth coefficients is found to be of the form

$$A = A_0 + A_2 P_2(\cos\varphi) + A_4 P_4(\cos\varphi), \tag{11}$$

where $P_L(\cos\varphi)$ is the L th Legendre polynomial and φ is the angle between the director and the magnetic field. However, this introduces three unknowns for each hyperfine line and so, to reduce the number of adjustable parameters, we have assumed that the linewidth for a director orientation between the two extreme director orientations can be obtained from the interpolation formula

$$T_2^{-1}(\varphi) = T_{\perp}^{-1} + (T_{\parallel}^{-1} - T_{\perp}^{-1})\cos^2\varphi. \tag{12}$$

Here $T_{\parallel}^{-1}$ and $T_{\perp}^{-1}$ are the linewidths observed when the director is aligned parallel and perpendicular to the magnetic field, respectively. The resonance fields, B_r, depend on both components of the partially averaged hyperfine and g-tensors and, for a spin probe containing a single magnetic nucleus of spin I, are given by:

$$B_r(\varphi) = B_0(\varphi) - \frac{h\tilde{K}(\varphi)m}{\tilde{g}(\varphi)\mu_B} - \frac{h^2\tilde{A}_{\perp}^2}{4\tilde{g}(\varphi)^2\mu_B^2 B_0(\varphi)} \frac{\tilde{A}_{\parallel}^2 + \tilde{K}(\varphi)^2}{\tilde{K}(\varphi)^2} \times [I(I+1) - m^2]. \tag{13}$$

In this expression

$$\begin{aligned} B_0(\varphi) &= \frac{h\nu}{\tilde{g}(\varphi)\mu_B}, \\ \tilde{g}(\varphi)^2 &= \tilde{g}_{\perp}^2 + (\tilde{g}_{\parallel}^2 - \tilde{g}_{\perp}^2)\cos^2\varphi, \\ \tilde{K}(\varphi)^2 &= [\tilde{A}_{\perp}^2\tilde{g}_{\perp}^2 + (\tilde{A}_{\parallel}^2\tilde{g}_{\parallel}^2 - \tilde{A}_{\perp}^2\tilde{g}_{\perp}^2)\cos^2\varphi]/\tilde{g}^2(\varphi), \end{aligned} \tag{14}$$

where h is the Planck constant, ν is the microwave frequency and μ_B is the electron Bohr magneton.

The observed spectrum $L(B)$ is then a sum of spectra from all director orientations and so is proportional to

$$L(B) = \int_0^{2\pi} L(B, B_r, T_2^{-1}) p(\varphi)\,d\varphi, \tag{15}$$

where $p(\varphi)$ is the director distribution defined in § 2. To illustrate the changes in the ESR spectrum as the helix is unwound, we have simulated spectra for the same values of k as those used to evaluate the distribution functions shown in figure 1. The magnetic parameters used to simulate the ESR spectra are those which we have determined from the experimental spectra measured for TEMPONE dissolved in the even dimer (BCBO10) at 180°C; they are listed in the table. The simulations show that when k is close to unity (0·99), the ESR spectrum is dominated by three nitrogen hyperfine lines associated with the director parallel to the magnetic field (figure 1). In addition to these strong spectral lines, there are two weak outer features associated with the director perpendicular to the field. Only two of the three hyperfine lines are observed because although $\tilde{A}_{\parallel}$ differs from $\tilde{A}_{\perp}$ the two principal components of the partially averaged g-tensor are almost the same and so the central lines overlap. Although the spectrum contains contributions from other orientations of the director, they are not so apparent as those from its extreme orientations, because it is the first derivative of the absorption spectrum which is observed. As the value of k decreases, so the probability of finding the director perpendicular to the magnetic field grows and so too does the intensity of the perpendicular lines, at the expense of the intensity of the parallel features. This trend continues until, in the limit when k vanishes, there are equal probabilities for finding the director parallel and perpendicular to the field. Accordingly, the heights of the parallel and perpendicular spectral features are almost the same; the slight difference results from the angular dependence of the linewidths. It is important to note that the spectra simulated with $k=0$ and 0·70 are quite similar and so the ESR technique for determining the composite parameter k can only be used with any certainty when this is in the range from about 0·70 to 1·00. In the following section we describe the ESR spectra which we have recorded and how the magnetic parameters necessary for their analysis were determined.

5. Results and discussion

In figure 3 we show some typical ESR spectra measured for the spin probe TEMPONE dissolved in the two dimers BCBO9 and BCBO10 for different concentrations of the chiral dopant at the same shifted temperature of 13 K. The shifted temperature, $T_{\mathrm{N}}-T$, is defined in terms of T_{N}, the temperature at which the sample is converted from coexisting isotropic and nematic phases to the pure nematic phase, since it is at this temperature that the orientational order first changes with decreasing temperature. For the coexisting nematic phase in the biphasic region above T_{N} the orientational order is essentially independent of temperature [16]. We see that for the lowest concentration of the chiral dopant the spectra contain the expected dominant three hyperfine lines for a nearly uniformly aligned chiral nematic phase with the director parallel to the magnetic field, since $\Delta\tilde{\chi}$ is positive for the dimers. It is clear from the spectra that, even for the lowest concentration of the chiral dopant, the magnetic field of the ESR spectrometer (~0·33 T) is insufficient to unwind the helix of the induced chiral nematic phase completely. We should note that in addition to the nitrogen hyperfine lines there are two carbon-13 satellite lines on either side of the central peak; only one of the satellite lines is observed for each of the outer parallel peaks because the other is overlapped by the perpendicular peaks. The carbon-13 satellites do not contain any information relevant to the director distribution and so in the remainder of the analysis we shall ignore them. As the concentration of the chiral dopant is increased, so the intensity of the perpendicular peaks relative to their parallel counterparts grows as the effect of the magnetic field on the helical distribution of the director decreases. For concentrations of about 2·6 mol % or more, the helical distribution is apparently unperturbed by the field of the spectrometer. The variation in the spectra for concentrations of chiral dopant less than about 2·6 mol % is in good agreement with the simulations (see figure 1), described in the previous section, for increasing values of the parameter k. The increase in k is caused, essentially, by the change in the mole fraction x, since at a constant shifted temperature the other quantities determining k [equation (6)] should be approximately independent of the concentration of the chiral dopant. Although the general trend in the variation of the ESR spectra with increasing concentration of chiral dopant is qualitatively the same for odd and even dimers, there is a quantitative difference. That is, the helical director distribution is less perturbed for the odd than for the even dimer at the same concentration and shifted temperature. This shows that the threshold concentration of the chiral dopant is lower for the odd than for the even dimer, which disagrees with our earlier prediction; we shall return to this point shortly.

Table The magnetic parameters used to simulate the ESR spectra given in figure 1 for the spin probe dissolved in the induced chiral nematic formed by the even dimer BCBO10.

$\tilde{A}_{\parallel}$/mT	$\tilde{A}_{\perp}$/mT	$\tilde{g}_{\parallel}$	$\tilde{g}_{\perp}$	$T_{\parallel}^{-1}$/mT	$T_{\perp}^{-1}$/mT
1·28	1·61	2·0057	2·0054	0·038	0·067

The other feature which is qualitatively apparent from the spectra shown in figure 3 relates to the difference in the parallel and perpendicular components of the partially averaged nitrogen hyperfine tensor

$$\Delta\tilde{A}=\tilde{A}_{\parallel}-\tilde{A}_{\perp}. \qquad (16)$$

This difference is equal to the mean of the high and low field separations between adjacent parallel and

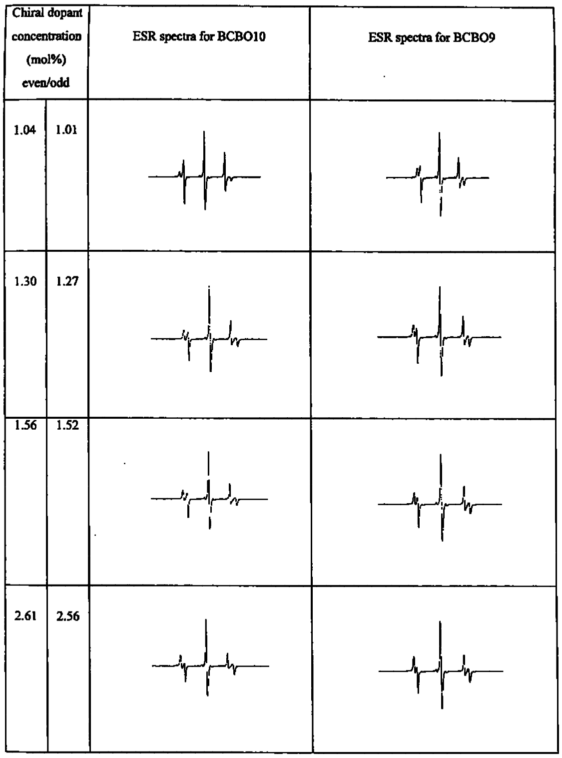

Figure 3. The dependence of the ESR spectrum of TEMPONE dissolved in the odd and even dimers on the concentration of chiral dopant, cholesteryl chloride. The spectra were recorded at the same shifted temperature, T_N-T, of 13 K.

perpendicular spectral features; it is seen to be greater for the even than for the odd dimer and in both cases more or less independent of concentration at the same shifted temperature. Such behaviour is to be expected because $\Delta\tilde{A}$ is proportional to the second rank orientational order parameter, S_{33}, for the symmetry axis-3 of the nitrogen hyperfine tensor which is approximately orthogonal to the CNC plane. In fact

$$\Delta\tilde{A} = (3/2)A'_{33}S_{33}, \qquad (17)$$

where A'_{33} is the anisotropic component of the nitrogen hyperfine tensor along axis-3 and for TEMPONE this is reported to be 1·89 mT [17]. Since the difference is approximately −0·3 mT, this means that the order parameter is only about −0·1. For such low values, S_{33} is expected to be proportional to the solvent order parameter which is normally the same for conventional nematogens at the same shifted temperature [18]. For our solutions where the only difference is in the concentration of the chiral dopant, it is to be expected, therefore, that the solute order parameter should be independent of this concentration at the same shifted temperature, as we have observed.

In order to determine values for the composite parameter, k, and the anisotropic nitrogen hyperfine interaction, $\Delta\tilde{A}$, from which the solute order parameter can be determined, it is first necessary to simulate the ESR spectra. This was achieved by using the theory described in the previous section; the simulated spectra were matched to the experiment by varying $\tilde{A}_\parallel$, $\tilde{A}_\perp$, $\tilde{g}_\parallel$, $\tilde{g}_\perp$, $T_\parallel^{-1}$ and $T_\perp^{-1}$ (for each line) as well as k. Although the number of adjustable parameters is relatively large, good estimates of the majority of them can be obtained directly from the experimental spectrum. In addition, we do not find a particularly strong correlation between the parameters which are determined. We have also found that it was possible to use the same linewidth parameters, $T_\parallel^{-1}$ and $T_\perp^{-1}$, for each of the nitrogen hyperfine lines and that there was a significant difference between these parameters (see the table). It seems likely, therefore, that the origin of the line broadening is unresolved proton hyperfine structure rather than rotational modulation of the magnetic interactions. The quality of the fit between the experimental and simulated spectra was judged visually. As an example of the agreement obtained, we show in figure 4 the observed spectrum for TEMPONE dissolved in BCBO10 doped with 1·30 mol % of cholesteryl chloride at a shifted temperature of 9 K, together with the spectrum simulated using the magnetic parameters given in the table. There is clearly very close agreement between the two; this gives us some confidence in the values of $\Delta\tilde{A}$ and k which we have determined. These are listed in the Appendix for the systems we have studied as a function of the mole fraction of the chiral dopant and the shifted temperature, $T_N - T$. We have not included the results for the highest mole fraction of chiral dopant since for this k is close to the limiting value of zero and cannot be determined with any accuracy. As we have expected, k is closest to unity for the lowest mole fraction of the chiral dopant and the error in k for these solutions is expected to be smallest; we estimate it to be about ±0·02. We shall, therefore, concentrate our discussion on the results for the odd and even dimers with the lowest mole fraction of the chiral dopant. For these and indeed for the other mole fractions, the error in the anisotropy in the partially averaged nitrogen hyperfine interaction, $\Delta\tilde{A}$, is estimated to be ±0·04 mT.

We begin with the results for $\Delta\tilde{A}$ which we use to determine the solute orientational order parameter, S_{33}, for the 3-axis in the spin probe [see equation (17)]. Since $\Delta\tilde{A}$ is negative for the spin probe dissolved in both liquid crystal dimers it follows that the order parameters are also negative. This shows that the 3-axis tends to be aligned orthogonal to the director, which is to be expected given the disc-like shape of TEMPONE (see figure 2-III).

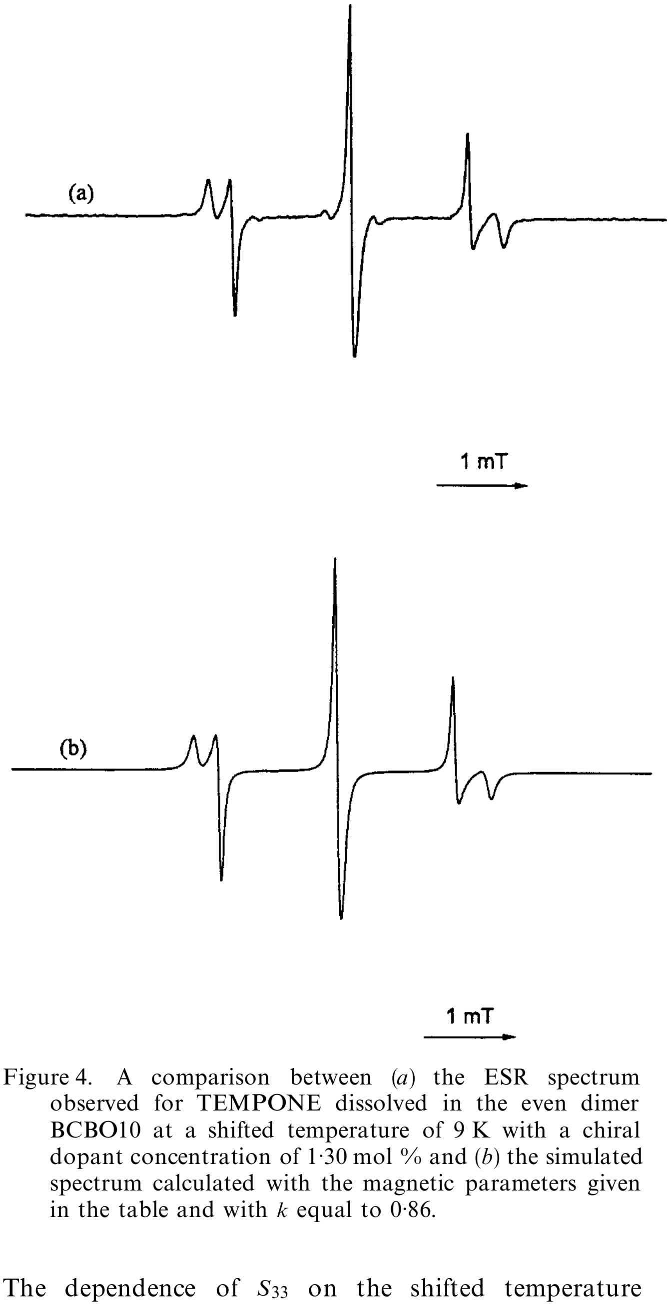

Figure 4. A comparison between (*a*) the ESR spectrum observed for TEMPONE dissolved in the even dimer BCBO10 at a shifted temperature of 9 K with a chiral dopant concentration of 1·30 mol % and (*b*) the simulated spectrum calculated with the magnetic parameters given in the table and with k equal to 0·86.

The dependence of S_{33} on the shifted temperature for both odd and even dimers doped with 1·01 and 1·04 mol % of cholesteryl chloride, respectively, is shown in figure 5; the lines are simply guides to the eye. It is immediately apparent that the solute order parameter for the even dimer is greater than for the odd dimer which is to be anticipated given the larger order parameter found for an even than for an odd dimer [2]. At the smallest shifted temperature of 13 K the ratio of the solute order parameters for the even and odd dimers is 1·23 and this decreases to 1·18 at the largest shifted temperature of 23 K. If we allow for their temperature dependence, these values are consistent with the order parameters of the mesogenic groups measured for the pure dimers, BCBO10 and BCBO9, at the nematic–isotropic transition; here the ratio of the order parameters is found to be 1·51 [2]. This agreement suggests that the molecular field controlling the alignment of the solute originates largely from its anisotropic interaction with the mesogenic groups of the dimers. The temperature dependence of the solute order parameters is found to be essentially the same for the two dimers at least at temperatures removed from the nematic–isotropic transition, in keeping with previous studies of solute ordering in liquid crystal dimers [19]. We find analogous behaviour of the solute order for the other chiral nematic phases with different concentrations of the chiral dopant, at least to within the experimental error (see the Appendix).

We turn now to the temperature dependence of $k/E(k)$; this is shown for both odd and even dimers with the lowest concentration of the chiral dopant in figure 6. At the same shifted temperature, the ratio $k/E(k)$ is larger for the even than for the odd dimers. This difference is small, no more than about 10%, but as we can see from the results given in the Appendix, it is also found for the other systems with higher concentrations of the chiral dopant. However, according to the theory described in §2 the ratio $k/E(k)$ should be inversely proportional to the square root of the order parameter and so it should be larger for the odd than for the even dimers. The difference is predicted to be small with a ratio of $k/E(k)$ for odd to even of about 1·2 whereas experiment gives a value which is less than unity and approximately 0·9. It is not clear why the model fails to predict this ratio correctly. What evidence that is available certainly suggests that the anisotropy in the diamagnetic susceptibility, $\Delta\tilde{\chi}$, is linear in the solvent order parameter, while the twist elastic constant, K_2, is quadratic in this. The other assumption concerns the helical twisting power which is taken to be independent of the orientational order of the solvent. This certainly appears to be a reasonable assumption for the chiral dopant used in this study, for direct measurements of β_M for this and analogous chiral dopants show the helical twisting power to be more or less temperature independent [20] as expected from equation (5). A possible explanation is that the proportionality constants relating the various quantities to the orientational order parameters are not the same for odd and even dimers. This is not expected to be the case for $\Delta\tilde{\chi}$ and K_2 but it is conceivable that the chiral order parameter, $\mathfrak{J}$, and the scaling parameter, ε, [see equation (5)] are related to the order parameter by different proportionality constants for the odd and even dimers. However, further studies of the helical twisting power of a given chiral dopant in liquid crystal dimers with spacers of different parity are required to see if this is the case. In contrast to the behaviour of the ratio $k/E(k)$ at a given shifted

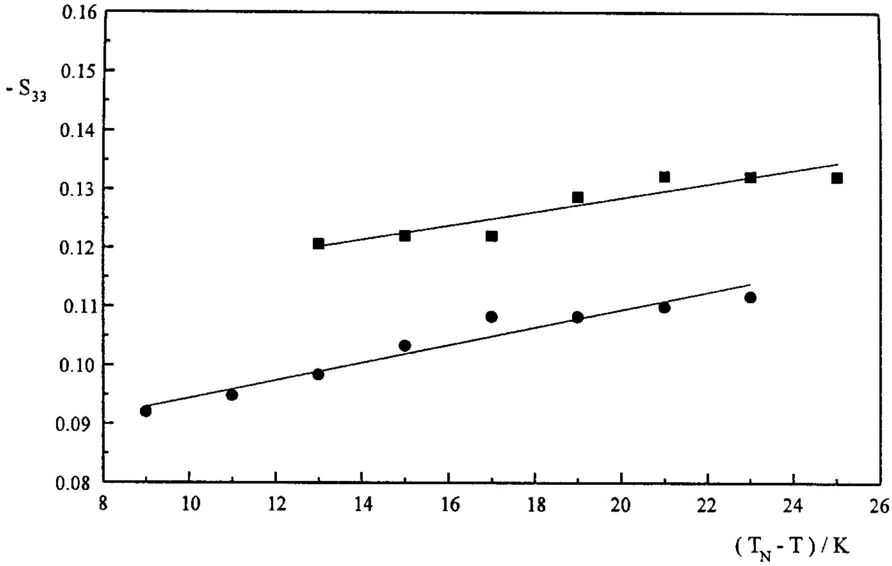

Figure 5. The dependence of the solute order parameter, S_{33}, on the shifted temperature, T_N-T, for the odd (●) and even (■) dimers containing 1·01 and 1·04 mol % of the chiral dopant.

temperature, the temperature dependence of this is in qualitative agreement with theory. Since the orientational order grows with decreasing temperature, $k/E(k)$ is predicted to decrease with decreasing temperature—as we find (see figure 6). Over the temperature range studied, the ratio $k/E(k)$ varies linearly with the shifted temperature and the slope is found to be independent of the concentration of the chiral dopant, to within the experimental error (see the Appendix). To make a quantitative comparison of experiment with theory we have calculated $|S_{33}|^{1/2}k/E(k)$ which for a given concentration of the chiral dopant is predicted to be independent of temperature. Since the temperature dependence of the solvent order parameter has not been measured for these dimers, we have used the solute order parameter as a surrogate for this. The results for the scaled quantity $|S_{33}|^{1/2}k/E(k)$ are listed in the Appendix for the three concentrations of the chiral dopant in the odd and even dimers. It is apparent that although the scaling has reduced the temperature variation, a small dependence remains. To remove this temperature variation completely it would be necessary to invoke some higher power of the order parameter with which to scale $k/E(k)$, but there does not appear to be any theoretical justification for this. Alternatively it may simply be that the solute order parameter cannot be determined with sufficient accuracy, although we should note that similar behaviour is exhibited by all of the systems which we have studied.

We now consider the dependence of the ratio $k/E(k)$ on the concentration of the chiral dopant used to induce the chiral nematic phase. For the low concentrations employed in our experiments the theory outlined in §2 predicts that $k/E(k)$ should be inversely proportional to the mole fraction, x, of the dopant. To test this prediction we have calculated $xk/E(k)$ with the results listed in the Appendix for three concentrations. Comparison of these at the same shifted temperature for either the odd or the even dimer reveals that much of the concentration dependence has been removed, especially when allowance is made for the uncertainty in k. However, the largest discrepancy is for the smallest mole fraction of the chiral dopant where the measurement of k is expected to be the most reliable. In addition the same behaviour is found for both odd and even dimers which suggests that the experimental error may not account for the failure of the theory to account for the our results.

6. Conclusions

The order parameter determined for the spin probe dissolved in the induced chiral nematic phase is found to be greater in the even dimer than in the odd, which is in keeping with the higher orientational order of the even dimer. The key quantity we have determined is k which is related primarily to the anisotropy in the diamagnetic susceptibility, the helical twisting power and the twist elastic constant. The ratio, $k/E(k)$, for both dimers is observed to decrease with decreasing temperature as predicted by theory although the rate of change appears to be larger than the theoretical value. Of perhaps more significance is that $k/E(k)$ is greater for the even than the odd liquid crystal dimer which contrasts with the theoretical prediction based on apparently

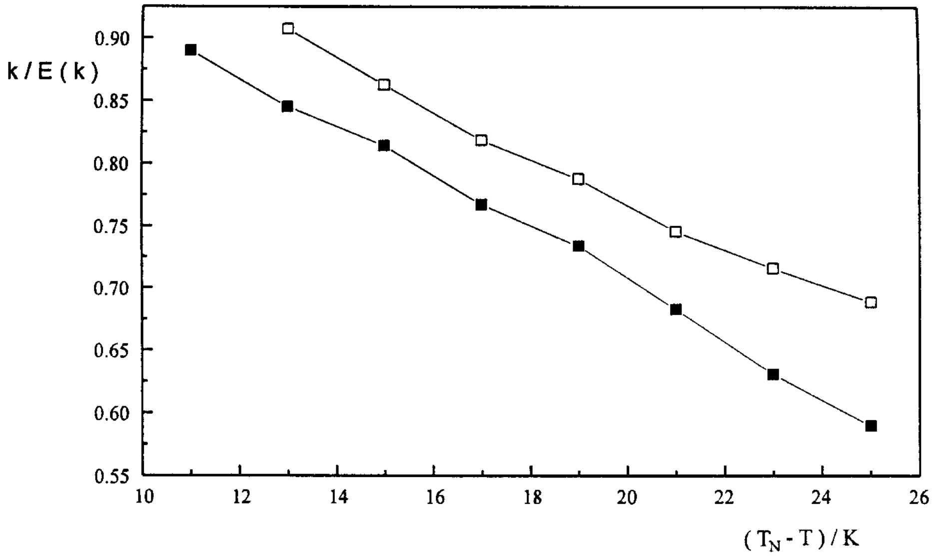

Figure 6. The dependence of $k/E(k)$, on the shifted temperature, (T_N-T), for the chiral nematic phases formed by the odd (■) and even (□) liquid crystal dimers with the lowest concentration of chiral dopant, i.e. 1·01 and 1·04 mol %, respectively.

reasonable assumptions concerning the dependence of $\Delta\tilde{\chi}$, β_M and K_2 on the orientational order of the dimers. This disagreement suggests that the proportionality constant for β_M and the orientational order may differ for the odd and even dimers

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Appendix

Here we give the results for the parameters, $\Delta\tilde{A}$ and k, extracted from the ESR spectra for the spin probe dissolved in the chiral nematic phase produced by the addition of the chiral dopant to the nematic phase of the odd and even liquid crystal dimers. The results are listed as a function of the mole fraction, x, of the chiral dopant and the shifted temperature, $T_N - T$.

BCBO10 $x = 0{\cdot}0104$ $T_N = 485$ K

$(T_N - T)$/ K	$-\Delta\tilde{A}$/ mT	$-S_{33}$	k	$k/E(k)$	$10^2xk/E(k)$	$\|S_{33}\|^{1/2}k/E(k)$
13·0	0·342	0·121	0·97	0·91	0·94	0·315
15·0	0·346	0·122	0·95	0·86	0·89	0·301
17·0	0·346	0·122	0·93	0·82	0·85	0·286
19·0	0·365	0·128	0·91	0·78	0·82	0·283
21·0	0·375	0·132	0·89	0·75	0·77	0·271
23·0	0·375	0·132	0·87	0·72	0·74	0·260
25·0	0·375	0·132	0·85	0·69	0·72	0·251

BCBO9 $x = 0{\cdot}0101$ $T_N = 444$ K

$(T_N - T)$/ K	$-\Delta\tilde{A}$/ mT	$-S_{33}$	k	$k/E(k)$	$10^2xk/E(k)$	$\|S_{33}\|^{1/2}k/E(k)$
9·0	0·261	0·092	0·97	0·89	0·89	0·270
11·0	0·269	0·095	0·95	0·84	0·85	0·260
13·0	0·279	0·098	0·93	0·81	0·82	0·255
15·0	0·293	0·103	0·90	0·77	0·77	0·247
17·0	0·307	0·108	0·87	0·73	0·74	0·242
19·0	0·307	0·108	0·84	0·68	0·69	0·225
21·0	0·312	0·110	0·80	0·63	0·64	0·209
23·0	0·317	1·112	0·77	0·59	0·59	0·197

BCBO10 $x = 0{\cdot}0130$ $T_N = 456$ K

$(T_N - T)$/ K	$-\Delta\tilde{A}$/ mT	$-S_{33}$	k	$k/E(k)$	$10^2xk/E(k)$	$\|S_{33}\|^{1/2}k/E(k)$
9·0	0·332	0·117	0·86	0·71	0·92	0·243
11·0	0·338	0·119	0·84	0·68	0·88	0·236
13·0	0·342	0·121	0·80	0·63	0·82	0·219
15·0	0·347	0·122	0·76	0·58	0·76	0·204
17·0	0·357	0·126	0·72	0·54	0·69	0·190
19·0	0·372	0·131	0·68	0·49	0·64	0·179

BCBO9 $x = 0{\cdot}0127$ $T_N = 442$ K

$(T_N - T)$/ K	$-\Delta\tilde{A}$/ mT	$-S_{33}$	k	$k/E(k)$	$10^2xk/E(k)$	$\|S_{33}\|^{1/2}k/E(k)$
9·0	0·251	0·089	0·82	0·65	0·82	0·192
11·0	0·271	0·096	0·76	0·58	0·74	0·180
13·0	0·271	0·096	0·74	0·56	0·71	0·173
15·0	0·280	0·099	0·65	0·47	0·59	0·148
17·0	0·306	0·108	0·65	0·47	0·59	0·153
19·0	0·306	0·108	0·62	0·44	0·56	0·145

BCBO10 $x = 0{\cdot}0156$ $T_N = 455$ K

$(T_N - T)$/ K	$-\Delta\tilde{A}$/ mT	$-S_{33}$	k	k/ $E(k)$	10^2xk/ $E(k)$	$\|S_{33}\|^{1/2}k$/ $E(k)$
7·0	0·325	0·115	0·74	0·56	0·87	0·188
9·0	0·340	0·120	0·73	0·55	0·87	0·192
11·0	0·360	0·127	0·73	0·54	0·85	0·194
13·0	0·360	0·127	0·73	0·54	0·85	0·193
15·0	0·360	0·127	0·71	0·52	0·82	0·185
17·0	0·370	0·131	0·67	0·48	0·76	0·175
19·0	0·370	0·131	0·63	0·45	0·69	0·161

BCBO9 $x = 0{\cdot}0152$ $T_N = 440$ K

$(T_N - T)$/ K	$-\Delta\tilde{A}$/ mT	$-S_{33}$	k	k/ $E(k)$	10^2xk/ $E(k)$	$S_{33}^{1/2}\|k$/ $E(k)$
9·0	0·255	0·089	0·69	0·51	0·77	0·152
11·0	0·245	0·086	0·68	0·49	0·75	0·145
13·0	0·256	0·093	0·66	0·48	0·73	0·146
15·0	0·280	0·098	0·64	0·46	0·69	0·144
17·0	0·280	0·098	0·60	0·42	0·64	0·132
19·0	0·280	0·098	0·53	0·36	0·55	0·114

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