

## Accepted Manuscript

Deuteron and proton NMR study of D<sub>2</sub>, *p*-dichlorobenzene and 1,3,5-trichlorobenzene in bimesogenic liquid crystals with two nematic phases

E.E. Burnell, Z. Ahmed, C. Welch, G.H. Mehl, R.Y. Dong

PII: S0009-2614(16)30485-7

DOI: <http://dx.doi.org/10.1016/j.cplett.2016.07.005>

Reference: CPLETT 33999

To appear in: *Chemical Physics Letters*

Received Date: 16 June 2016

Accepted Date: 1 July 2016



Please cite this article as: E.E. Burnell, Z. Ahmed, C. Welch, G.H. Mehl, R.Y. Dong, Deuteron and proton NMR study of D<sub>2</sub>, *p*-dichlorobenzene and 1,3,5-trichlorobenzene in bimesogenic liquid crystals with two nematic phases, *Chemical Physics Letters* (2016), doi: <http://dx.doi.org/10.1016/j.cplett.2016.07.005>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2016. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Deuteron and proton NMR study of D<sub>2</sub>, *p*-dichlorobenzene  
and 1,3,5-trichlorobenzene in bimesogenic liquid crystals  
with two nematic phases

E.E Burnell\*

Department of Chemistry, University of British Columbia,  
2036 Main Mall, Vancouver, B.C., V6T 1Z1, Canada

Z. Ahmed, C. Welch, G.H. Mehl

Department of Chemistry, The University of Hull,  
Hull HU6 7RX, United Kingdom

and

R.Y. Dong<sup>†</sup>

Department of Physics and Astronomy, University of British Columbia,  
6224 Agricultural Road, Vancouver, B.C., V6T 1Z1, Canada

June 28, 2016

---

\*email: [elliott.burnell@ubc.ca](mailto:elliott.burnell@ubc.ca)

<sup>†</sup>email: [rondong@phas.ubc.ca](mailto:rondong@phas.ubc.ca)

## Abstract

The solutes dideuterium, 1,3,5-trichlorobenzene and *p*-dichlorobenzene (pdcB) are co-dissolved in a 61/39 wt% mixture of CBC9CB/5CB, a bimesogenic liquid crystal with two nematic phases. NMR spectra are collected for each solute. The local electric field gradient ( $F_{ZZ}$ ) is obtained from the dideuterium spectrum. A double Maier-Saupe potential (MSMS) is used to rationalize the order parameters of pdcB. The liquid-crystal fields  $G_1$  and  $G_2$  are taken to be due to size and shape interactions and interactions between the solute molecular quadrupole and the mean  $F_{ZZ}$  of the medium. The  $F_{ZZ}$ 's obtained from D<sub>2</sub> and  $G_2$  (from pdcB) are compared and discussed.

## 1 Introduction

There has been much interest recently in bimesogenic liquid crystals that form two nematic phases, a higher temperature “normal” nematic phase and a lower temperature  $N_x$  phase that exhibits local chirality [1,2]. Recently we have studied the solutes *o*-dichlorobenzene (odcb), *m*-dichlorobenzene (mdcb) and *p*-dichlorobenzene (pdcB) in such a bimesogenic LC composed of 39 wt% 5CB and 61 wt%  $\alpha, \omega$ -bis(4-4'-cyanobiphenyl)nonane (CBC9CB) [3]. For the analysis we used a mean-field potential composed of two independent Maier-Saupe (MS) mechanisms [4, 5], the so-called MSMS approach [6] that is reviewed briefly in section 3.2. Each independent MS term involves the interaction of some solute property  $\beta$  with an average LC field  $G$  that the solute experiences in the solvent environment. The crucial assumption is that the average field is the same for all solutes. The solute order parameters were fitted by the MSMS mean potential to better than the 5 % level. In particular in the low temperature  $N_x$  [7] (often called the twist-bend  $N_{tb}$ ) nematic phase, the  $G_1$  (LC average field) value appears to be almost independent of  $T$  whereas the  $G_2$  value has a large variation, even changing sign. The  $G_2$  LC mean field in the mixture, as expected, increases with

decreasing  $T$  in the high temperature region of the N phase [3, 8]. More importantly, it appears to go through a maximum near the mid-point of the N phase. In the pre-transition region as the  $N_x$  phase is approached and in the  $N_x$  phase its value decreases to a more negative value as  $T$  is lowered. The pre-transition region of the N phase is over 10 degrees. Recently there is an interesting report [9] on the order parameter  $S_{zz}$  of the para axis in the difluoroterphenyl group of a dimesogen DTC5C9 that also exhibits large pretransitional behavior (showing a maximum at about 10 degrees above the  $N_{tb}$  phase) in the N phase and decreases continuously deep into the low temperature phase.

The orientational order of rigid solutes dissolved in anisotropic media such as nematic liquid crystals (LCs) depends on their anisotropic intermolecular interactions with the solvent. It is now well-established that at least two ordering mechanisms are involved. One mechanism (mechanism 1 of the MSMS approach) is a short-range interaction that is governed by the size and shape of the solute. The other (mechanism 2 of the MSMS approach) is a longer-range electrostatic interaction: one possibility for this interaction is the molecular electric quadrupole of the solute interacting with the average local electric field gradient ( $F_{ZZ}$ ) of the medium, where  $Z$  is the director axis taken here to lie along the magnetic-field direction. Another possibility is the solute polarizability anisotropy interacting with the mean square electric field of the medium.

Indeed, experiments on molecular  $D_2$  as a solute that is orientationally ordered in nematic liquid crystals indicate the presence of a non-zero  $F_{ZZ}$  at the deuteron nucleus [10]. The orientational orders of the isotopologs of molecular hydrogen are consistent with the interaction of this  $F_{ZZ}$  with the hydrogen molecular quadrupole moment. Mixtures of liquid crystals have been made in which  $D_2$  exhibits zero  $F_{ZZ}$  and essentially zero orientational order [11, 12]. These mixtures are termed magic mixtures (MM). The orientational order of solutes in these mixtures is explained by short-range interactions (mechanism 1 of MSMS) that depend on solute size and shape. Thus  $G_2$  is set

to zero for MM. For other LCs, the  $G_2$  mechanism then accounts for the longer-range interactions that are averaged to zero in the MM. The  $D_2$  results suggest that the second mechanism for solutes in general may well involve the field gradient, and attempts to fit solute orientational order to a combination of short-range and  $F_{ZZ}$  mechanisms fits experiment to about the 10% level [12].

One basic assumption used for the MSMS approach for molecular ordering of solutes in LCs is that all solutes, including molecular hydrogen, sense the same average intermolecular mean field of the medium. Such a simplifying assumption appears to be difficult to avoid even though theory [13] and Monte Carlo simulations of ellipsoids with point quadrupoles [14–16] indicate that the average  $F_{ZZ}$  does depend to some extent on the dimensions of the solutes and their quadrupoles. If the second mechanism is taken to be due to the  $F_{ZZ}$  of the LC mean field, dideuterium dissolved in any LC can then be related to the derived  $G_2$  as demonstrated in Ref. [6]. The temperature variation of  $D_2$ 's  $F_{ZZ}$  has been studied in 4-*n*-pentyl-4'-cyanobiphenyl (5CB) [17]. The  $F_{ZZ}$  of  $D_2$  was found to scale linearly with the nematic order parameter  $S$  [11,12]. Although  $G_2$  has been determined as a function of temperature in smectogens [18], its  $T$  dependence has not been checked by the  $F_{ZZ}$  determination via  $D_2$  measurements in these samples. Even in pure nematogens, such direct verification of the  $T$  dependence of  $G_2$  has not been done.

Above, the interaction between the solute molecular quadrupole and the LC  $F_{ZZ}$  is proposed as a possible candidate for  $G_2$ . As mentioned there,  $G_2$  exhibits unusual behaviour in our recent study of dichlorobenzenes (dcb's), going through a maximum about 10 degrees above the  $N/N_x$  phase transition. It would be interesting to check that this behaviour is actually that of the  $F_{ZZ}$ . Hence, here we propose to check this idea by using the solute  $D_2$  for an independent measure of  $F_{ZZ}$ . If all solutes feel the same LC average  $F_{ZZ}$ , then the  $F_{ZZ}$  from the  $D_2$  experiments should agree quantitatively with the  $G_2$  from the dichlorobenzene experiments. For the present work we choose as solutes dideuterium and pdcB dissolved in the same mixture under pressure to directly

probe the  $G_2$  mechanism and its large variation with temperature. We arbitrarily choose the solute pdcB to relate results back to the earlier data which used pdcB, mdcb and odcB [3, 8].

## 2 Experimental Section

The CBC9CB / 5CB mixture was prepared by the Hull group and optimized to nematic-nematic transitions at low temperatures [19]. This mixture, along with a small amount of both pdcB and 1,3,5-trichlorobenzene (tcb, added as an orientational reference) were placed into a “medium walled Norell valved 5 mm NMR tube for intermediate pressure”. The sample was well mixed using generally established practice for this line of investigation using a vortex stirrer, and attached to a vacuum line. After evacuating, the sample tube was purged several times with  $D_2$  gas, and the valve shut with an over pressure of 10 atm deuterium gas. The tube was heated into the isotropic phase and mixed (shaken, not stirred) to help dissolve the gas. The homogeneity of the sample was confirmed by observing a sharp N to  $N_x$  phase transition.

Spectra were collected using a Bruker 400 MHz NMR spectrometer equipped with an inverse probe. The sample was heated to the isotropic phase and shaken again before placing into the NMR probe which was preheated to over 337 K. It was allowed to equilibrate at 336.6 K. Proton and deuteron spectra were collected separately before reducing the temperature to the next lower value and allowing 10 minutes for thermal equilibrium. 256 and 2624 scans were averaged for the  $^1H$  and the  $^2H$  spectra. An example  $^2H$  spectrum collected in the  $N_x$  phase at 311 K is shown in Fig. 1. Dideuterium is not very soluble, and the gas phase is perhaps responsible for the signal observed in the centre region of the spectrum.

The proton and deuteron NMR spectra were analyzed to give the experimental values of the dipolar couplings in all three solutes ( $D_2$ , pdcB and tcb) as well as the quadrupolar coupling for  $D_2$  (see Table 1. The dipolar couplings were further analysed to give the molecular order parameters

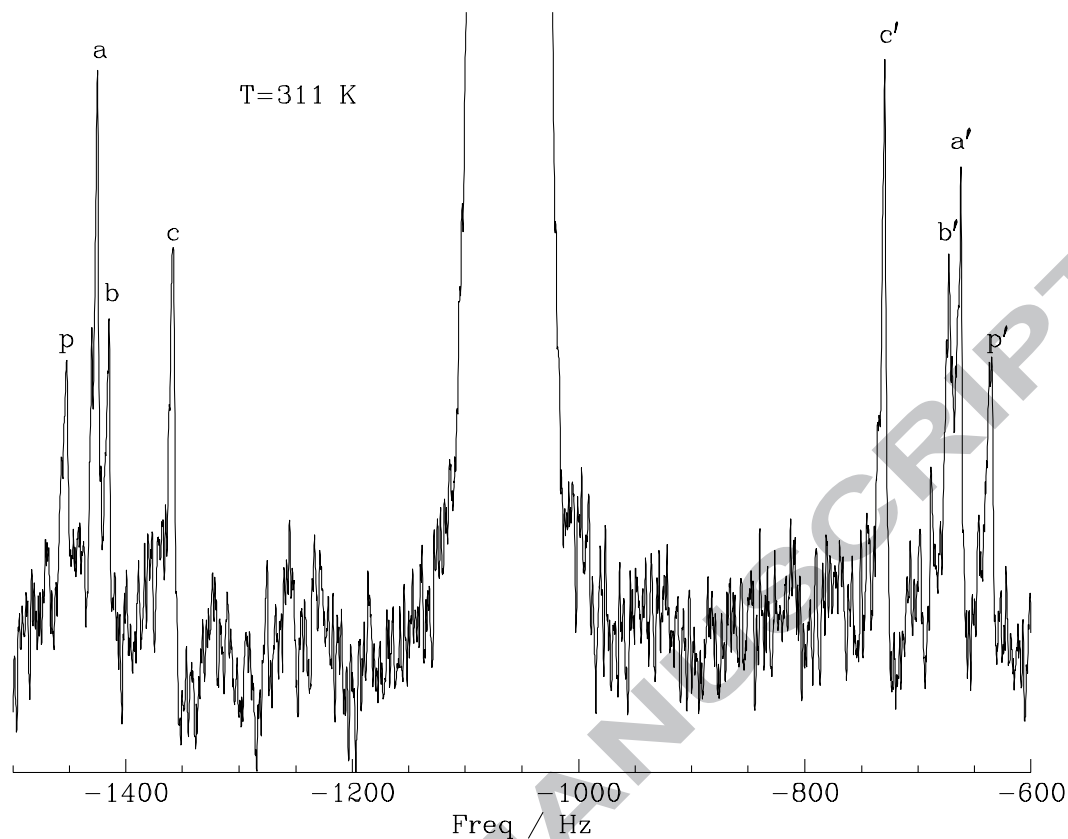


Figure 1:  $^2\text{H}$  NMR spectrum of  $\text{D}_2$  in the  $N_x$  phase of the CBC9CB/5CB mixture (61/39 wt%) at 311 K. The broad central feature is from  $\text{D}_2$  in the gas phase above the solution in the NMR tube. The distance between the peaks p and  $c'$  (or c and  $p'$ ) is  $2B$  (often written  $\Delta\nu_Q$  or  $2\nu_Q$ ), that between p and c (or  $c'$  and  $p'$ ) is  $6D$ , and the small splitting between a and b (or  $b'$  and  $a'$ ) is  $3J$ . The order in which the lines appear in the spectrum can be directly related to the relative signs of  $J$  and  $S_{zz}$ . Peaks p and  $p'$  are from *para*- $\text{D}_2$  ( $I=1$ ) and the other six lines are from *ortho*- $\text{D}_2$  (mixture of  $I=0$  and  $I=2$ ) [12].

of the solutes. In addition, as described below, the dipolar and quadrupolar couplings of  $\text{D}_2$  were used to give values for  $F_{zz}$ .

### 3 Theory

#### 3.1 $F_{ZZ}$ from NMR of $D_2$

There is general agreement that the main mechanism behind the orientational order of the isotopologs of molecular hydrogen involves the anisotropic interaction between the molecular hydrogen quadrupole and the average  $F_{ZZ}$  of the orienting medium felt by the molecule. The  $F_{ZZ}$  at the deuteron nucleus contributes to the quadrupolar splitting  $B(\text{observed})$  obtained from the deuteron spectrum (see Fig. 1 and its caption):

$$\begin{aligned} B(\text{observed}) &= B(\text{intramolecular}) + B(\text{external}) \\ &= \frac{3}{4h} e^2 q Q_D S - \frac{3}{4h} e Q_D F_{ZZ} \end{aligned} \quad (1)$$

where  $Q_D$  is the deuteron nuclear quadrupole moment, and  $eq$  is minus the electric field gradient at the deuteron nucleus that arises from the electronic structure of the  $D_2$  molecule.  $S$  is the  $D_2$  order parameter that is obtained directly from the experimental deuteron-deuteron dipolar coupling  $D$  (assuming no vibration-reorientation interactions) [20]

$$D = -\frac{h\gamma_D^2}{4\pi^2} \left\langle \frac{1}{r_{DD}^3} \right\rangle S \quad (2)$$

where  $r_{DD}$  is the distance between the deuterons. As both  $B(\text{intramolecular})$  and  $D$  are proportional to  $S$ , the ratio of these two quantities is a molecular property that is readily calculated from known data on the  $D_2$  molecule [21]. The variation of the ratio  $(B/D)_{\text{experimental}}$ , as well as its difference from the predicted ratio  $B(\text{intramolecular})/D$ , are clear evidence of the presence of an external contribution ( $F_{ZZ}$ ) to the total electric field gradient ( $F_{ZZ} - eq$ ) at the deuteron nucleus.  $F_{ZZ}$  is readily calculated from Eq. 1.

Assuming that the external  $F_{ZZ}$  felt by the deuteron nucleus is the same as that felt by the



molecule, the order parameter

$$S = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle \quad (3)$$

can be calculated [22,23] by taking a quantum average over the  $J$  and  $m_J$  rigid-rotor states (even  $J$  for *ortho* and odd  $J$  for *para* D<sub>2</sub>) using the Hamiltonian

$$\mathcal{H}_Q = -\frac{1}{2} F_{ZZ} Q_{zz}(\text{mol}) \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \quad (4)$$

where  $z$  is the D–D molecular direction and  $\theta$  is the angle between the  $Z$  and  $z$  axes.

### 3.2 MSMS summary

The order parameters of a collection of rigid solutes in a host of different liquid-crystal solvents are rationalized quite well with an anisotropic intermolecular potential consisting of two second-rank Maier Saupe [4,5] terms. For solutes with sufficient symmetry such that the traceless molecular  $\beta(i)$  tensors (that describe the anisotropic parts of some molecular properties  $i$ ) are diagonal with only two independent components  $\beta_{s,zz}(i)$  and  $b_s(i) = \frac{\beta_{s,xx}(i) - \beta_{s,yy}(i)}{\beta_{s,zz}(i)}$ , the Hamiltonian can be written:

$$\begin{aligned} \mathcal{H}_{N,L_s}(\Omega_s) = & -\frac{3}{4} \sum_{i=1}^{i=2} G_{L,ZZ}(i) \beta_{s,zz}(i) \\ & \times \left[ \left( \frac{3}{2} \cos^2(\theta_s) - \frac{1}{2} \right) + \frac{b_s(i)}{2} \sin^2(\theta_s) \cos(2\phi_s) \right] \end{aligned} \quad (5)$$

where  $\theta_s$  and  $\phi_s$  are polar angles between molecular symmetry axes and  $Z$ . The  $G_{L,ZZ}(i) \equiv G_i$  are liquid-crystal average fields that interact with the solute  $\beta_s(i)$ . This model has been applied to results for the solutes odcb, mdcb and pdcb in the liquid-crystal mixture of Refs. [3,8] and in particular to pdcb in this paper.

This MSMS approach fits experimental results to about the 5% level in all nematogens that have been investigated. There are at least two unknowns for each mechanism in this MSMS intermolecular mean potential. One is the principal component of the assumed axially-symmetric

second-rank LC mean field  $G_i$ . The other is the anisotropic part of some second-rank solute electronic property  $\beta_{s,\gamma\delta}(i)$  that interacts with the LC mean field. The number of independent second-rank tensor  $\beta_{s,\gamma\delta}(i)$  components depends on molecular symmetry and therefore for each mechanism equals the number of independent solute second-rank order parameters. Once the solute  $\beta_{s,\gamma\delta}(i)$  tensor elements have been determined, they can be used for the same solute in different LCs. Here we use values determined in [24]. Thus, the use of a new LC solvent involves only determination of new  $G_i$  values.

## 4 Discussion

Fig. 2 presents the order parameters determined from the dipolar couplings of pdcB ( $S_{xx}$ ,  $S_{yy}$  and  $S_{zz}$ ), of tcb ( $S_{zz}$ ) and of  $D_2$  ( $S_{D_2}$ ) in a single graph for comparison. The behaviours of especially the larger order parameters of pdcB ( $S_{xx}$  and  $S_{zz}$ ) are consistent with those observed in the earlier experiments with samples at ambient pressure [3, 8]: the orientational order increases with decreasing temperature in the N phase, and enters a pre-transitional region as it becomes almost constant in the  $N_x$  phase. The decrease of order parameter with increasing temperature observed at higher temperatures in the N phase is the normal, expected behaviour for this phase. One very interesting result is that the  $S_{zz}$  order parameters of both tcb and pdcB are essentially identical. It is also striking that the  $D_2$  order parameter changes almost linearly with temperature: of special note is that this order parameter is definitely **not** constant in the  $N_x$  phase. Thus it appears that pdcB (and tcb) have temperature dependencies of orientational order that are very different from that of  $D_2$ .

A most interesting result is presented in Fig. 3 where the asymmetry of the pdcB order matrix,  $R = \frac{S_{xx} - S_{yy}}{S_{zz}}$ , is plotted in three different ways. The left graph ( $R$  versus  $S_{xx}$ ) emphasizes that  $S_{xx}$  becomes essentially constant in the  $N_x$  phase (and in the pre-transitional region). While the

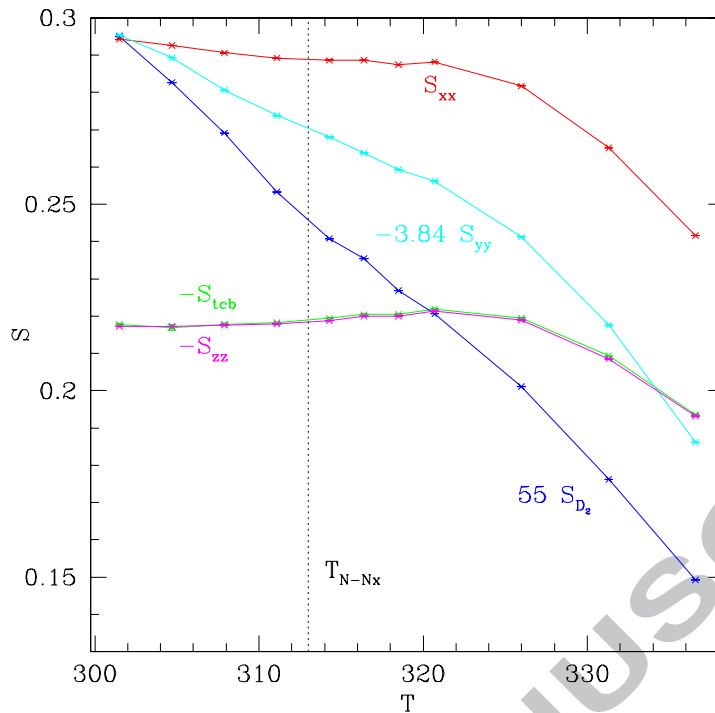


Figure 2: Experimental order parameters as a function of temperature. In order to get all the information into a single graph, some values have been scaled by the amount (or sign) as indicated. The labels  $xx$ ,  $yy$  or  $zz$  are for pdcB where the  $x$  axis lies along the Cl–Cl direction,  $z$  is perpendicular to the benzene ring, and  $y$  is perpendicular to both  $x$  and  $z$ .  $S_{tcb}$  is the order parameter for the  $c_3$  symmetry axis, and  $S_{D_2}$  is for the D–D bond direction.

location of the  $N_x / N$  phase transition is not obvious in this plot, the entry into the pre-translational region is: the change in structure that is associated with the  $N_x$  phase manifests itself about 10 K above the actual phase transition. This result is consistent with that mentioned above for DTC5C9 [9]. In addition, the literature contains several examples where a magnetic field affects a liquid-crystal phase transition in non rod-like mesogens [25–28].

The other two plots present the most interesting result that  $R$  varies linearly with both  $S_{D_2}$  and  $T$ . This result is also consistent with Fig. 2 where we noted above that  $S_{D_2}$  also varies linearly with  $T$ . While the components of the pdcB order tensor behave very differently in the  $N_x$  and

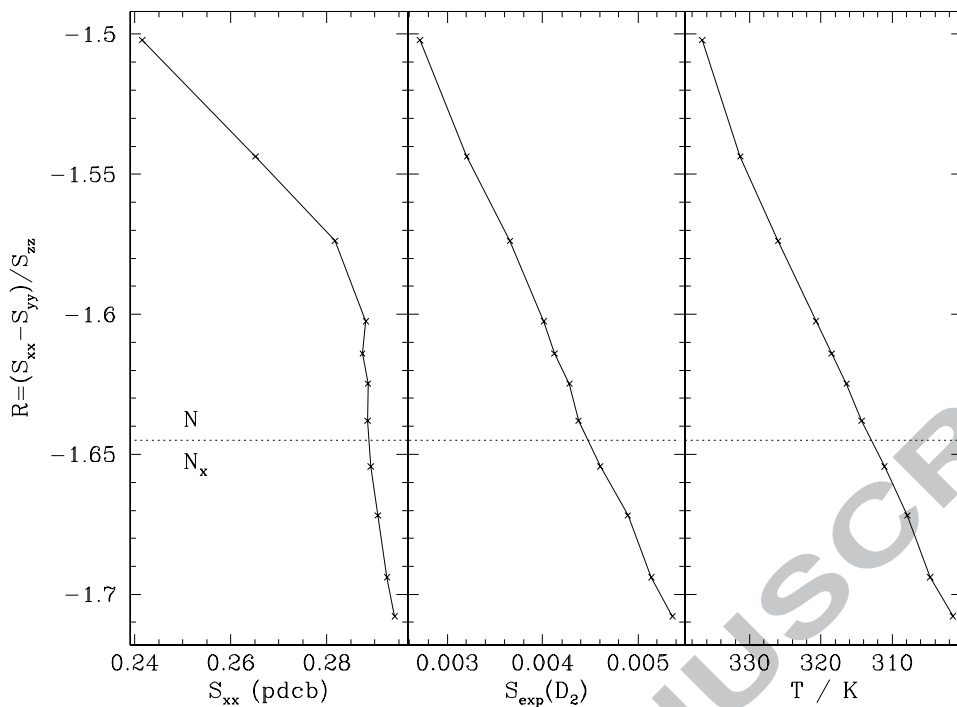


Figure 3: The asymmetry parameter  $R = \frac{S_{xx} - S_{yy}}{S_{zz}}$  in the order matrix for pdcB is examined in several different ways. In the left panel it is plotted *versus* the largest pdcB order parameter  $S_{xx}$ , in the centre *versus* the  $D_2$  order parameter and in the right *versus* temperature.

high-temperature N phases, its asymmetry,  $R$ , varies smoothly and essentially does not see the phase transition. These results may hold a clue to the structure of the  $N_x$  phase.

The main motivation for this work is the interesting behaviour observed for the  $G_1$  and  $G_2$  *versus*  $T$  plots reported earlier [3, 8] and displayed in Fig. 4 for the pdcB results of the present work (which is in complete agreement with the older data). The value of  $G_1$  is essentially constant in the  $N_x$  phase and in the pre-transitional region, whereas  $G_2$  exhibits a very different behaviour in the different regions, and even changes sign. As discussed in the Introduction, in the MSMS potential mechanism 1 is taken to be associated with size and shape interactions which are solute dependent and mechanism 2 could be associated with interactions of the molecular quadrupole with the average electric-field gradient felt by the solute. If the latter is correct, then experiments

using  $D_2$  as solute should yield  $F_{ZZ}$  values that are consistent with the  $G_2$  values obtained for pdcB (right panel of Fig. 4).

In order to get an estimate of  $F_{ZZ}(\text{pdcB})$  from the pdcB  $G_2$  values, we recognize that what we measure is products such as  $G_2\beta_{\text{pdcB},zz}(2)$ . The  $G_2$  values reported in Fig. 4 are based on  $\beta$  values determined in Ref. [24] ( $\beta_{\text{pdcB},zz}(2) = -0.236$  and  $\beta_{\text{pdcB},yy}(2) = 0.229$ ). If the molecular property of interest is the molecular quadrupole, then  $F_{ZZ}(\text{pdcB})Q_{\text{pdcB},zz} = \frac{3}{2}G_2\beta_{\text{pdcB},zz}(2)$ .

For the estimate of  $F_{ZZ}$  from  $G_2$  values, we choose to use use  $Q_{\text{pdcB},zz} = -3.327 \times 10^{-26}$  esu (from GAUSSIAN 03 as reported in [6]) to calculate  $F_{ZZ}(\text{pdcB})$  using the ratio of  $Q_{\text{pdcB},zz}/\beta_{\text{pdcB},zz}(2) = 14.1 \times 10^{-26}$ . One reason for choosing the  $zz$  component is that  $S_{zz}$  is equal for tcb and pdcB, and  $Q_{zz}(\text{tcb}) = -1.834 \times 10^{-26}$  esu, being less negative than the pdcB value. Note that a less negative (smaller absolute value)  $Q$  leads to a larger  $F_{ZZ}$ .

Next, we need the  $F_{ZZ}$  values from the  $D_2$  experimental results. We present in Fig. 5 the experimental  $B/D$  ratio and the expected  $B(\text{intramolecular})/D$  ratio. Eq. 1 then allows the determination of the  $F_{ZZ}$  felt by  $D_2$ .

We compare the values of  $F_{ZZ}$  determined from the pdcB and the  $D_2$  experiments in the left panel of Fig. 6. We also show values calculated from the  $G_2$  values determined for odcb, mdcb and pdcB in a different sample with higher solute concentration [3]. Examination of Figure 3 of [3] shows that  $G_i$  values for the different solutes (odcb, mdcb and pdcB) show similar trends, with similar  $G_1$  values but with a large shift with solute in  $G_2$  values. We display in Fig. 6 three  $F_{ZZ}$  curves calculated from the data of Ref. [3], one for each solute odcb, mdcb and pdcB. When we use odcb, the  $F_{ZZ}$  values agree quite well with the  $D_2$  ones at higher temperature in the N phase. In the pre-transition region and in the  $N_x$  phase the variations with  $T$  have opposite slopes. The values for mdcb and pdcB show similar general trends, but give smaller (even negative)  $F_{ZZ}$  values.

If  $G_2$  of pdcB is indeed the  $F_{ZZ}$ , and if all solutes experience identical average fields, then

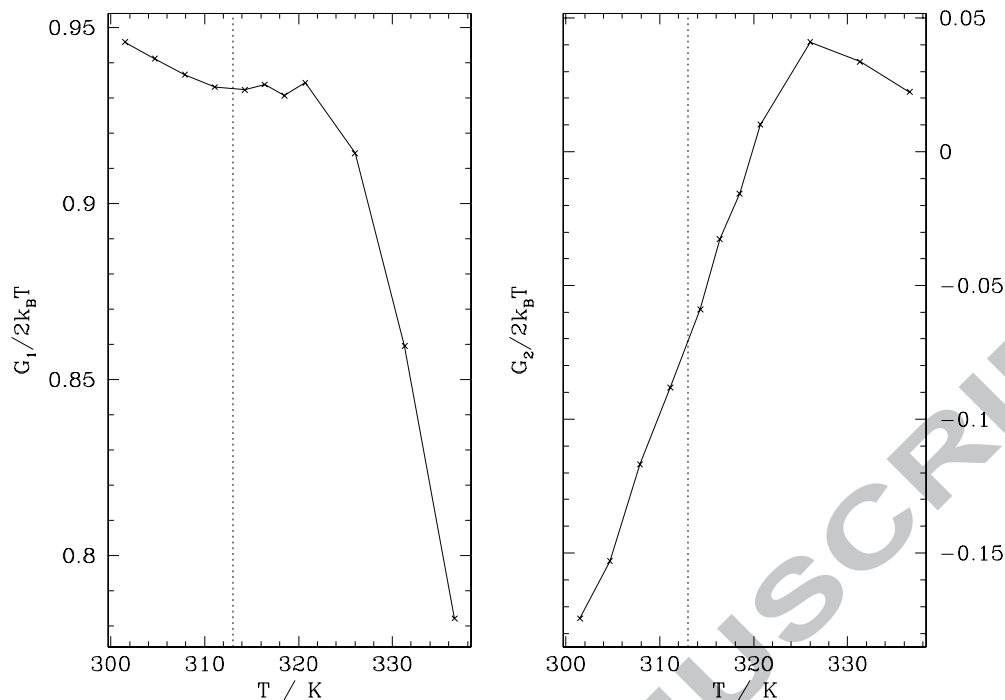


Figure 4: Temperature dependence of  $G_1/2k_B T$  and  $G_2/2k_B T$  values obtained by fitting the MSMS potential to the pdcB order parameters determined in the present study using the pdcB molecular  $\beta$  parameters from reference [24].

the two values should be the same. The large spread in  $G_2$  (and hence  $F_{ZZ}$ ) values for the dichlorobenzenes makes quantitative comparison difficult. However, at higher  $T$  in the N phase, similar  $T$  dependence is observed, and in one case (odcb) the  $F_{ZZ}$  values agree with those from  $D_2$ . However, at lower temperatures and in the  $N_x$  phase, the curves diverge. Thus  $D_2$  and dcb's behave very differently in the  $N_x$  phase. Assuming that the  $F_{ZZ}$  experienced by the dcb's has a similar temperature behavior to that of  $D_2$ , then the fit to MSMS theory suggests at low temperatures an additional mean field that vanishes at *ca* 10 degrees above the  $N/N_x$  phase transition. The explanation of this mean field must have something to do with the structure of this fascinating  $N_x$  phase which shows local chirality.

In the right panel of Fig. 6 we compare the experimental order parameters obtained directly from the experimental deuteron-deuteron dipolar coupling  $D$  using Eq. 2 with those calculated

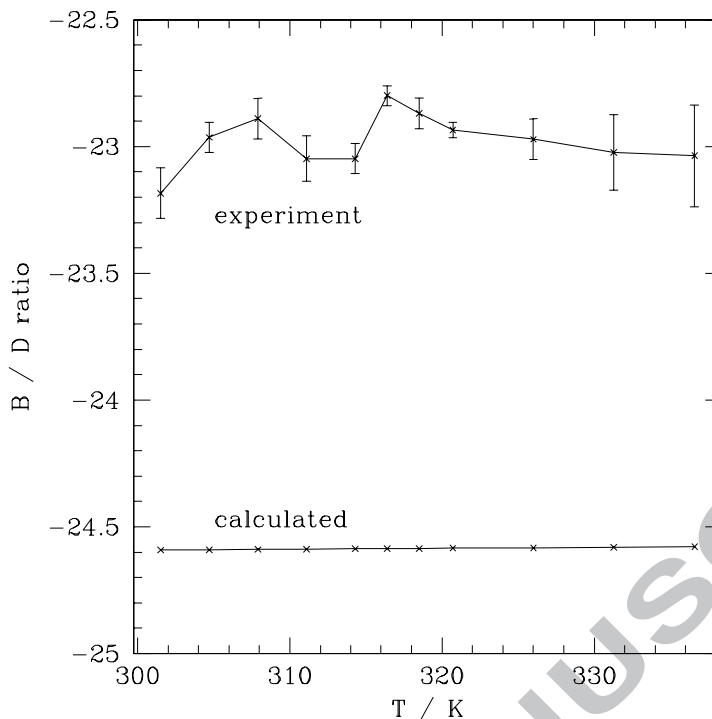


Figure 5: The  $B/D$  ratio from the  $D_2$  spectra (experimental) and calculated from  $D_2$  molecular properties (calculated).

(using Eqs. 3 and 4) from the  $F_{ZZ}$  values (in the left panel) obtained from the  $D_2$  spectra. The values obtained (labeled “ $S$  calculated from  $F_{ZZ}$ ”) agree quite well with the experimental ones from the  $D$ . In both nematic phases, the orientational order of  $D_2$  is the result of interaction between the average  $F_{ZZ}$  felt by the molecule and its molecular quadrupole  $Q_{zz}$ (mol).

## 5 Conclusion

The MSMS potential is quite successful in rationalizing the orientational order parameters of odcb, mdcb and pdcb at all temperatures in the N and  $N_x$  phases. While the  $G_2$  values obtained differ among solutes, the same general trend is obtained for all solutes, *i.e.*  $G_2$  increases with lowering  $T$  in the N phase, goes through a maximum and decreases in the pre-transitional region and in the  $N_x$  phase. The values of  $F_{ZZ}$  obtained from  $G_2$  also vary with solute, and for odcb agree

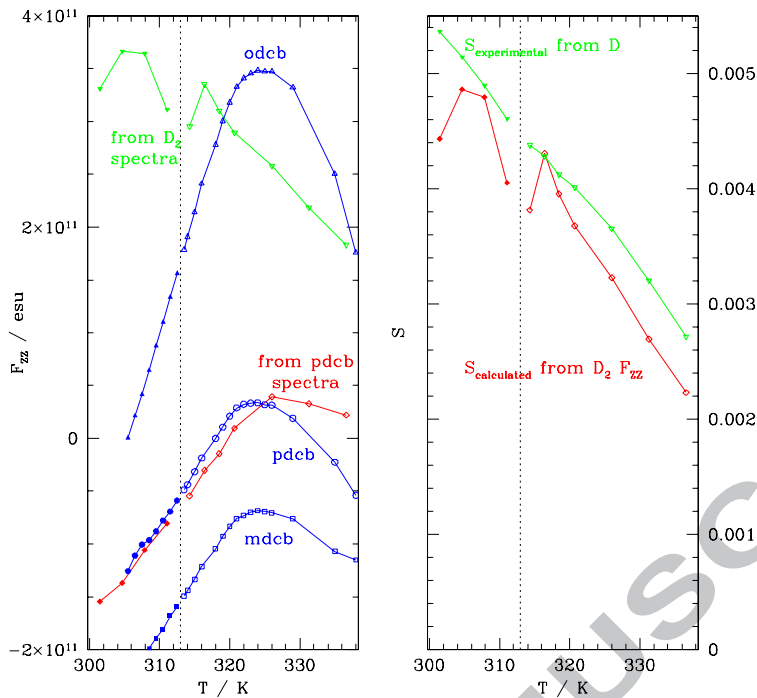


Figure 6: Left panel: the temperature dependence of the different  $F_{ZZ}$  values determined from the dichlorobenzene and  $D_2$  results. In the case of  $D_2$  (upside-down green triangles), the  $F_{ZZ}$  is determined from the difference in the ratio of the experimental  $B$  and  $D$  values from those that apply to the free molecule in the gas phase. In the case of odcB, mdcB and pdcB, the  $F_{ZZ}$  is assumed to be the  $G_2$  of the MSMS two-potential model. Two curves are shown for pdcB: the red curve (diamonds) is from the experimental results of this paper, and the blue curves (circles for pdcB, triangles for odcB and squares for mdcB) are from the data of Ref. [3]. The  $N/N_x$  phase transition is indicated by the dotted line. The blue points have been shifted 2K to higher  $T$  to account for the shift in the transition temperature caused by different solute concentrations in the different samples. Right panel:  $D_2$  order parameters: experimental values from the dipolar coupling, Eq. 2 (upside-down green triangles) and calculated using Eqs. 3 and 4 (red diamonds).



with those obtained from the  $D_2$  spectra in the high- $T$  region of the N phase. The interesting result is that  $F_{ZZ}$  from  $D_2$  increases monotonically while those from the dcb spectra go through a maximum, and then steadily decrease at lower  $T$  into the  $N_x$  phase. This difference between the temperature dependence of the orientational order of  $D_2$  and the dichlorobenzenes may be indicative of the structure of the  $N_x$  phase. One possibility is that the different solutes may be experiencing different average fields. While the different dcb's suggest differing values for  $F_{ZZ}$ , suggesting that using a single solute for the MSMS approach has large inherent error, the values obtained (especially for odcB at high  $T$  in the N phase) suggest that the second MS mechanism may be related to the interaction of the mean electric field gradient with the molecular quadrupole.

Several interesting results come out of this study. First, the hydrogens behave quite differently from the dcb's in the  $N_x$  phase (and in the pre-transition region). Second, the  $S_{zz}$  order parameters of tcb and pdcb are equal throughout the N and  $N_x$  phases. Third, the asymmetry on the order matrix of pdcb ( $R$ ) changes monotonically throughout the temperature region investigated, and correlates with  $S_{D_2}$ . Fourth, the orientational order of  $D_2$  in both N and  $N_x$  phases is explained by the interaction between the molecular quadrupole and the average  $F_{ZZ}$  that the molecule feels. Fifth, the orientational order of the dcb's is dominated by size and shape interactions, with a second mechanism also being important. While this second mechanism may involve  $F_{ZZ}$ , it is interesting that its  $T$  dependence in the  $N_x$  phase and the pre-transition region is opposite that observed for  $D_2$ . These results may indicate that the larger solutes (such as pdcb) and hydrogen tend to gather at different regions of the liquid-crystal molecules, especially in the  $N_x$  phase. Alternatively, maybe the  $G_2$  mechanism involves more than the field gradient for the dcb's. While the size and shape ( $G_1$ ) mechanism remains constant and behaves similarly for the dcb solutes, the longer-range interactions ( $G_2$ ) are sensitive to the pre-transition and the  $N_x$  phase structure. It is clear that these results present a challenging question as to the effect of the  $N_x$  phase structure on

the partitioning of the different solutes. It is also clear that molecular dideuterium is an interesting probe for the investigation of liquid crystals, including the different nematic and smectic phases that are possible.

## 6 Acknowledgment

We thank C.A. deLange for stimulating discussions. ZA, CW and GHM acknowledge funding through the EPSRC projects EP/M015726 and EP/J004480.

## References

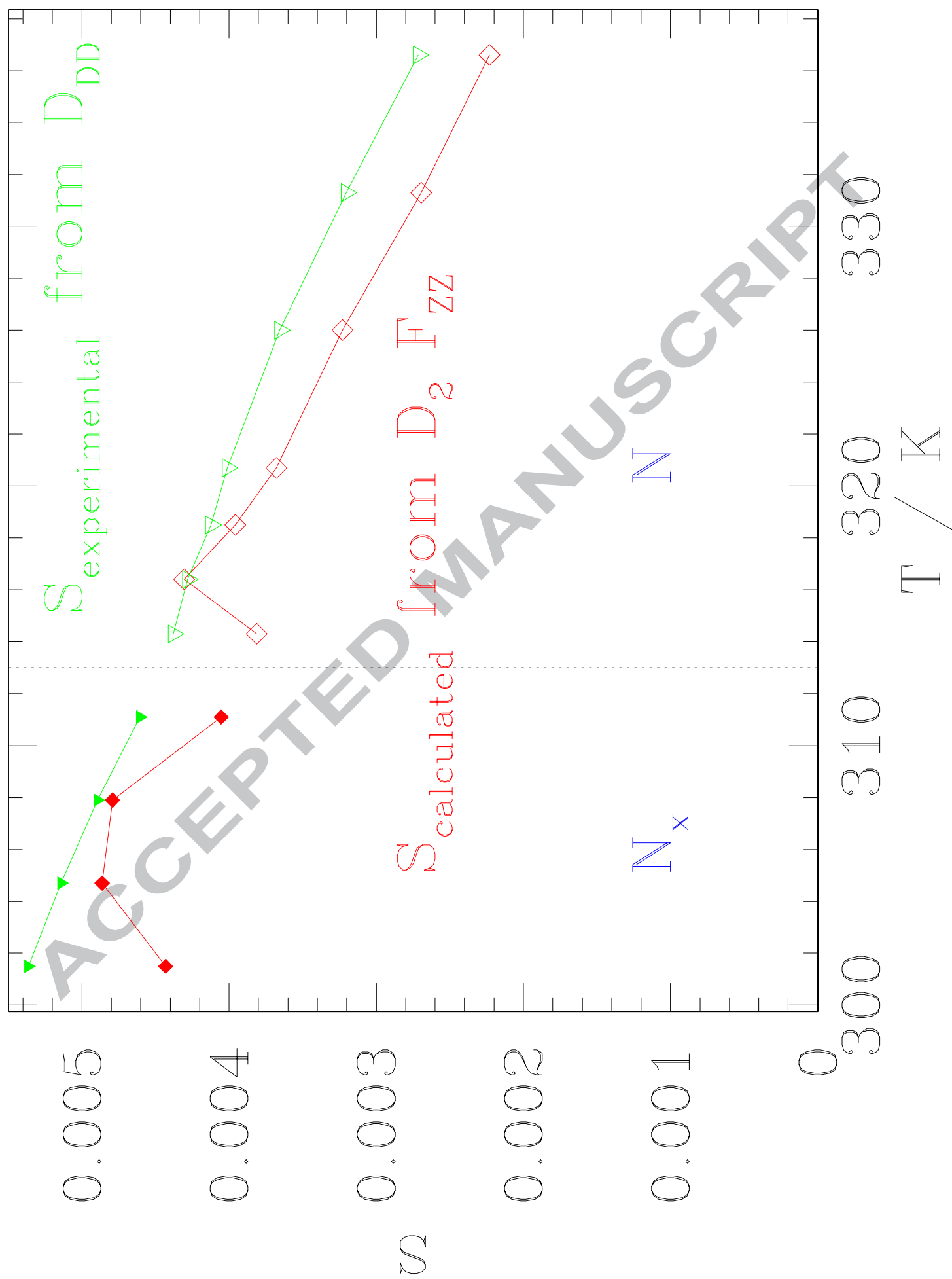
- [1] L. Beguin, J.W. Emsley, M. Lelli, A. Lesage, G.R. Luckhurst, B.A. Timimi, and H. Zimmermann, *J. Phys. Chem. B.* **116**, 7940 (2012).
- [2] D. Chen, J.H. Porada, J.B. Hooper, A. Klitnick, Y. Shen, M.R. Tuchband, E. Korblova, D. Bedrov, D.M. Walba, M.A. Glaser, J.E. MacLennan, and N.A. Clark, *PNAS.* **110**, 15931 (2013).
- [3] R.Y. Dong, A. Kohlmeier, M.G. Tamba, G.H. Mehl, and E.E. Burnell, *Chem. Phys. Lett.* **552**, 44 (2012).
- [4] W. Maier and A. Saupe, *Z. Naturforsch. A.* **14**, 882 (1959).
- [5] W. Maier and A. Saupe, *Z. Naturforsch. A.* **15**, 287 (1960).
- [6] E.E. Burnell, L. C. ter Beck, and Z Sun, *J. Chem. Phys.* **128**, 164901 (2008).
- [7] A.G. Vanakaras and D.J. Photinos, *Soft Matter.* **12**, 2208 (2016).

- [8] E.E. Burnell, R.Y. Dong, A. Kohlmeier, M.G. Tamba, C. Welch, and G.H. Mehl, *Mol. Cryst. Liq. Cryst.* **610**, 100 (2015).
- [9] J.W. Emsley, M. Lelli, H. Joy, M.-G. Tamba, and G.H. Mehl, *PCCP.* **18**, 9419 (2016).
- [10] G.N. Patey, E.E. Burnell, J.G. Snijders, and C.A. de Lange, *Chem. Phys. Letters.* **99**, 271 (1983).
- [11] P.B. Barker, A.J. van der Est, E.E. Burnell, G.N. Patey, C.A. de Lange, and J.G. Snijders, *Chem. Phys. Letters.* **107**, 426 (1984).
- [12] E. E. Burnell and C. A. de Lange, *Chem. Rev. (Washington, D.C.).* **98**, 2359 (1998).
- [13] J.W. Emsley, G.R. Luckhurst, and H.S. Sachdev, *Mol. Phys.* **67**, 151 (1989).
- [14] J.M. Polson and E.E. Burnell, *Phys. Rev. E.* **55**, 4321 (1997).
- [15] E.E. Burnell, R. Berardi, R.T. Syvitski, and C. Zannoni, *Chem. Phys. Lett.* **331**, 455 (2000).
- [16] J.S.J. Lee, R.O. Sokolovskii, R. Berardi, C. Zannoni, and E.E. Burnell, *Chem Phys. Lett.* **454**, 56 (2008).
- [17] A. Weaver, A.J. van der Est, J.C.T. Rendell, G.L. Hoatson, G.S. Bates, and E.E. Burnell, *Liquid Crystals.* **2**, 633 (1987).
- [18] E.E. Burnell, R.Y. Dong, A.C.J. Weber, X. Yang, and A. Yethiraji, *Can. J. Chem.* **89**, 900 (2011).
- [19] C.S.P. Tripathi, P. Losada-Perez, J. Leys, A. Kohlmeier, M.-G. Tamba, G. H. Mehl, and C. Glorieux, *Phys. Rev. E.* **84**, 041707 (2011).
- [20] E.E. Burnell and C.A. de Lange, *eMagRes*, DOI 10.1002/9780470034590.emrstm1477. **5**, 901-912 (2016).

- [21] E.E. Burnell, C.A. de Lange, and J.G. Snijders, *Phys. Rev.* **A25**, 2339 (1982).
- [22] J.G. Snijders, C.A. de Lange, and E.E. Burnell, *Israel J. Chem.* **23**, 269 (1983).
- [23] E.E. Burnell, C.A. de Lange, A.L. Segre, D. Capitani, G. Angelini, G. Lilla, and J.B.S. Barnhoorn, *Phys. Rev. E.* **55**, 496 (1997).
- [24] A.C.J. Weber, X. Yang, R.Y. Dong, and E.E. Burnell, *J. Chem. Phys.* **132**, 034503 (2010).
- [25] T. Ostapenko, D.B. Wiant, S.N. Sprunt, A. Jákli, and J.T. Gleeson, *Phys. Rev. Lett.* **101**, 247801 (2008).
- [26] O. Francoscangeli, F. Vita, F. Fauth, and E.T. Samulski, *Phys. Rev. Lett.* **107**, 207801 (2011).
- [27] P.K. Challa, V. Borshch, O. Parri, C.T. Imrie, S.N. Sprunt, J.T. Gleeson, O.D. Lavrentovich, and A. Jákli, *Phys. Rev. E.* **89**, 060501 (2014).
- [28] S.M. Salili, M.G. Tamba, S.N. Sprunt, C. Welch, G.H. Mehl, A. Jákli, and J.T. Gleeson, *Phys. Rev. Lett.* **116**, 217801 (2016).

Table 1: Experimental couplings in Hz for  $D_2$ , tcb and pdcB. Numbers are accurate to about 0.1 Hz

	$D_2$		tcb	pdcB			
	$T$	$B$	$D_{tcb}$	$D_{ortho}$	$D_{meta}$	$D_{para}$	
	336.6	425.5	-18.5	143.3	-1888.1	-25.0	74.5
	331.3	501.9	-21.8	155.0	-2072.4	-24.4	86.7
	326.0	571.7	-24.9	162.6	-2202.5	-23.8	96.0
	320.7	626.4	-27.3	164.4	-2252.1	-22.5	102.0
	318.5	641.9	-28.1	163.3	-2246.5	-21.7	103.2
	316.4	664.8	-29.2	163.2	-2256.6	-21.1	105.1
	314.3	687.0	-29.8	162.5	-2255.9	-20.3	106.7
	311.1	723.0	-31.4	161.7	-2260.0	-19.1	108.9
	307.9	762.9	-33.3	161.3	-2271.4	-17.9	111.5
	304.7	804.0	-35.0	160.7	-2286.0	-17.7	115.3
	301.5	847.1	-36.5	161.2	-2299.2	-15.7	117.2



Highlights of “Deuteron and proton NMR study of D<sub>2</sub> and *p*-dichlorobenzene in bimesogenic liquid crystals with two nematic phases”

by

E.E Burnell, Z. Ahmed, C. Welch, G.H. Mehl and R.Y. Dong

There is much current interest in liquid crystals that form two nematic phases. The precise nature of the lower-temperature N<sub>x</sub> phase is undergoing much discussion in the current literature. In a previous NMR study we analyzed the orientational order of three dichlorobenzene solutes in terms of a double Maier-Saupe mean field model. The study opened the possibility that the mean liquid-crystal electric field gradient (efg) went through a maximum about 10 degrees above the N / N<sub>x</sub> phase transition. In this paper we investigate this possibility via a more direct measure of the efg using molecular dideuterium. In the N<sub>x</sub> phase and the pre-transition region in the N phase we find the interesting result that the two estimates of the efg (one from the dichlorobenzenes and the other from D<sub>2</sub>) have opposite temperature dependencies. We postulate that this result is related to the structure of the N<sub>x</sub> phase, and are convinced that it will be of interest to others working on the same problem.