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Liquid Crystals

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To cite this Article Komolkin, A. V. and Molchanov, Yu. V.(1989) 'Liquid crystal proton N.M.R. spectral analysis by numerical calculation', Liquid Crystals, 4: 2, 117 — 123
To link to this Article: DOI: 10.1080/02678298908029065
URL: http://dx.doi.org/10.1080/02678298908029065

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LIQUID CRYSTALS, 1989, VOL. 4, NO. 2, 117–123

Liquid crystal proton N.M.R. spectral analysis by numerical calculation

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(*Received 7 October 1987; accepted 12 July 1988*)

We offer an approximate method with which to calculate proton N.M.R. spectra generally caused by dipole–dipole interactions. The method consists of subdividing the spin system of the liquid crystal molecule into interacting blocks. The spectrum of each block is calculated exactly. The interaction between spins of different blocks is calculated approximately. The method is compared with the known methods using 4-*n*-pentyl-d_{11}-4′-cyanobiphenyl (5CB-d_{11}) and 4,4′-dimethoxyazoxybenzene (PAA) as examples.

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1. Introduction

Proton N.M.R. spectra of thermotropic liquid crystals, which are partially resolved triplets 20–40 kHz wide, were first recorded as early as 1953 [1]; however the problem of their interpretation is not yet solved. It can be reduced to the analysis of the spectrum for multispin system with dipole–dipole interactions. As intermolecular spin interactions in liquid crystals vanish, the system to be considered is reduced to a single molecule. Early attempts at spectral analysis were based on the two-spin ortho-protons model [2] and the four-spin model for the protons in the benzene rings [3]. It was shown that the outer doublet splitting from the dipolar interactions of the benzene ring, while the central component is a signal from the protons of the flexible aliphatic chain.

Lösche and others [4] suggested a method of constructing the complete spectrum of the mesogenic molecule. The proton N.M.R. spectrum was calculated by neglecting the scalar term of the dipolar spin hamiltonian (NST method)

$$H_{\mathrm{d}}^{\mathrm{NST}} = -\sum_{\substack{i,k \in N \\ i \neq k}} B_{ik} I_{zi} I_{zk}, \tag{1}$$

where

$$B_{ik} = \left\langle \frac{3}{4} \frac{\gamma^2 \hbar}{r_{ik}^3} (3\cos^2 \alpha_{ik} - 1) \right\rangle,$$

α_{ik} is the angle between the internuclear vector $\mathbf{r}_{ik}$ and the magnetic field direction, N is the set of protons in the molecule, the angular brackets denote averaging over intramolecular motion. This approximation allows the proton N.M.R. lineshape of the whole spin system to be expressed analytically.

Analysing the N.M.R. spectra of thermotropic liquid crystal polymers Martins *et al.* [5] suggested the synthesis of the proton spectrum by subdividing the molecule into weakly interacting spin sub-systems (blocks) containing a small number of spins.

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They considered such blocks as non-interacting or independent (subdivision into non-interacting blocks, the SNB method)

$$H_{\mathrm{d}}^{\mathrm{SNB}} = -\sum_{m}^{M} \sum_{\substack{i,k \in N^{[m]} \\ i \neq k}} B_{ik}(I_{zi}I_{zk} - \tfrac{1}{3}\mathbf{I}_i \cdot \mathbf{I}_k), \tag{2}$$

where M is the number of sub-systems, $N^{[m]}$ is the set of protons of the mth-sub-system. The spectrum of the system as a whole is assumed to be the sum of spectra from the blocks, which are computed exactly.

These methods significantly simplify the spin hamiltonian, but their use can lead to substantial distortions in the theoretical spectra. We suggest an approximate method of spectral simulation which takes greater account of the dipole–dipole interactions in the mesogenic molecule.

2. Algorithm for N.M.R. spectrum computation

The method consists of subdividing the mesogenic molecule into interacting blocks of spins (SIB method) and the spectrum of each block is calculated exactly. The interactions between spins of different spin sub-systems are calculated approximately using the local field mechanism. The spin hamiltonian of the mth-block in this case assumes the form

$$H_{\mathrm{d}}^{[m]} = -\sum_{\substack{i,k \in N^{[m]} \\ i \neq k}} B_{ik}(I_{zi}I_{zk} - \tfrac{1}{3}\mathbf{I}_i \cdot \mathbf{I}_k) - \sum_{i \in N^{[m]}} \sum_{j \in N_{\mathrm{e}}^{[m]}} B_{ij} I_{zi} I_{zj}, \tag{3}$$

where $N_{\mathrm{e}}^{[m]}$ is the set of protons external to the mth-block. The resulting spectrum is a sum of spectra of all sub-systems with normalization taken into consideration. If required, each component of the discrete spectrum obtained is approximated by a lorentzian or gaussian line shape.

Errors in the resulting frequencies and intensities of spectral components are reduced to the discrepancy in calculation of the eigenvalues, E_k, and the eigenvectors, λ_k, of dipolar hamiltonian H_{d} of the spin system. These errors are estimated as

$$\sigma_{\mathrm{E}} = \frac{\|\Delta E_k\|}{\|E_k\|} \leqslant \frac{\|\Delta H_{\mathrm{d}}\|}{\|H_{\mathrm{d}}\|}, \quad \sigma_{\lambda} = \|\Delta \lambda_k\| \leqslant \frac{\|\Delta H_{\mathrm{d}}\|}{\|H_{\mathrm{d}}\|}, \tag{4}$$

where

$$\Delta H_{\mathrm{d}} = H_{\mathrm{d}} - \sum_{m=1}^{M} H_{\mathrm{d}}^{[m]} = \frac{1}{6} \sum_{m=1}^{M} \sum_{i \in N^{[m]}} \sum_{j \in N - N^{[m]}} [f(j, m) B_{ij} I_{zi} I_{zj} + B_{ij}(I_{+i}I_{-j} + I_{-i}I_{+j})]. \tag{5}$$

In this formula the numerical factor before $I_{zi}I_{zj}$ has the value

$$f(j, m) = \left| \frac{+2, j \in N_{\mathrm{e}}^{[m]}}{-4, j \,\overline{\in}\, N_{\mathrm{e}}^{[m]}} \right. . \tag{6}$$

The hamiltonian linear operator norm is determined as $\|H\| = \sup_{\|\varphi\|=1} \|H\varphi\|$. When φ is written in terms of the eigenvectors of the operator I_z

$$\varphi = \sum_{k \in N} (a_k \alpha_k + b_k \beta_k),$$

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its norm is calculated as

$$\|\varphi\| = \Big(\sum_{k\in N} (a_k^2 + b_k^2)\Big)^{1/2}.$$

Let

$$H_{\mathrm{d}}\varphi = \sum_{k\in N} (c_k\alpha_k + d_k\beta_k),$$

then the factors c_k and d_k can be written as

$$c_k = a_k(A_k + Y_k) + b_kX_k, \quad d_k = b_k(A_k - Y_k) + a_kX_k, \quad k \in N, \tag{7}$$

where

$$A_k = -\frac{4}{6}\sum_{\substack{i,j\in N\\ i,j\neq k}} B_{ij}, \quad Y_k = -\frac{4}{6}\sum_{\substack{j\in N\\ j\neq k}} B_{kj}, \quad X_k = \frac{2}{6}\sum_{\substack{j\in N\\ j\neq k}} B_{kj}. \tag{8}$$

It is clear that the maximum of the sum $\Sigma_{k\in N}\,(c_k^2 + d_k^2)$ subject to the condition that

$$\sum_{k\in N} (a_k^2 + b_k^2) = 1$$

is obtained with a certain value of k, i.e.

$$\|H_{\mathrm{d}}\| = \max_{k\in N}\,[\sup_{a_k^2+b_k^2=1} (c_k^2 + d_k^2)]. \tag{9}$$

Using c_k and d_k from equation (7) we find

$$\|H_{\mathrm{d}}\| = \max_{k\in N}\left[A_k^2 + Y_k^2 + X_k^2 + P_k\sqrt{\left(\frac{1}{4} - \frac{Q_k^2}{P_k^2 + 4Q_k^2}\right)} + \frac{2Q_k^2}{\sqrt{(P_k^2 + 4Q_k^2)}}\right]^{1/2}, \tag{10}$$

where

$$P_k = |2A_kX_k|, \quad Q_k = 2A_kY_k.$$

The $\Delta H_{\mathrm{d}}\varphi$ coefficients can be written in the same form as equation (7), which also allows us to use equation (10) to calculate $\|\Delta H_{\mathrm{d}}\|$. In this case A_k, Y_k, X_k have the forms

$$\left.\begin{aligned} A_k &= \frac{1}{6}\sum_{m=1}^{M}\sum_{\substack{i\in N^{[m]}\\ i\neq k}}\sum_{\substack{j\in N-N^{[m]}\\ j\neq k}} B_{ij}[2 + f(j, m)],\\ Y_k &= \frac{1}{12}\sum_{\substack{m=1\\ m\neq s(k)}}^{M}\sum_{i\in N^{[m]}} B_{ik}[f(i, s(k)) + f(k, s(i))],\\ X_k &= \frac{2}{6}\sum_{\substack{m=1\\ m\neq s(k)}}^{M}\sum_{i\in N^{[m]}} B_{ik}, \end{aligned}\right\} \tag{11}$$

where $s(j)$ denotes the number of the block which contains the jth proton, i.e. $j \in N^{[s(j)]}$.

It is clear that the norms $\|H_{\mathrm{d}}\|$ and $\|\Delta H_{\mathrm{d}}\|$ depend on the B_{ij} constants and the particular subdivision of the spin system. Thus the analysis of the dipole–dipole interaction matrix for each given case allows the estimation of the eigenvector and eigenvalue errors before the spectra are calculated. In this way the optimum arrangement of blocks and sets of external protons can be obtained. To minimize the incurred errors the system is usually divided into the minimum number of blocks and the most strongly interacting protons are included in them. For each block it is advisable to take into account the maximum possible number of external spins. However the time to calculate a spectrum for an $N^{[m]}$ spin system is estimated to increase as $N^{[m]}!$ and the inclusion of each external spin leads to double this increase.

In all the computations it was assumed that the long molecular axis, which was identified as the axis of the minimum moment of inertia, was parallel to the magnetic field. This corresponds to a perfectly aligned liquid crystal with the order parameters all equal to 1.

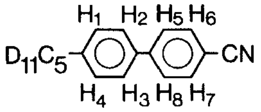
The computational requirements of the SIB-method do not exceed the performance of professional personal computers.

The proposed method allows us (*a*) to analyse the dependence of the spectrum of a separate block on its interaction with the other blocks, and (*b*) to adjust the simulated spectrum to the experiment by spectral variation for each subsystem.

3. Comparison of the NST, SNB, SIB methods

(*a*) *The 8-spin system: 5CB-d_{11}*

A convenient system for testing approximate methods for simulating the proton N.M.R. spectra is the 8-spin biphenyl fragment of partially deuteriated 4-*n*-pentyl-4-cyanobiphenyl



The proton N.M.R. spectrum of such a spin system can be calculated exactly. In the computations it is assumed that the molecule has a rigid geometry with a single parameter determining the structure, the angle between the planes of the benzene rings. (The bond lengths and the bond angles are given their average values.) The best agreement of the exactly calculated spectrum with experiment is observed when the rings rotate by 180° jumps and the dihedral angle between them is equal to 31°, which agrees very well with multiple quantum N.M.R. data [6].

Figure 1 shows the spectra simulated using (*a*) the NST, (*b*) the SNB and (*c*) the SIB methods as well as the exact spectrum of the 8-spin fragment (*d*). The experimental spectrum is indicated by the fine line. To simplify the comparison of the lineshapes the experimental and model spectra are shown in different frequency scales. It is obvious that their ratio is related to the second rank orientational order parameter. For 5CB-d_{11} at $T_{NI} - T = 1{\cdot}2°C$ we find 0·44 which is in a good agreement with 0·428 obtained by Emsley *et al.* [7].

The eigenvalues and eigenvectors error does not exceed 78 per cent for NST, 14 per cent for SNB and 10 per cent for SIB. The SNB and SIB simulations were performed with a division of the 5CB-d_{11} molecule into two blocks. It is worth noting that the subdivision $[H_1, H_2, H_5, H_6]:[H_3, H_4, H_7, H_8]$ is the optimum for the SNB method. For the SIB method the subdivision $[H_1–H_6]:[H_7, H_8]$ is the best. It can be seen that spectrum (*a*) differs from the spectrum calculated exactly in the maxima frequencies and the width of the components. The SNB simulation gives better agreement. The spectrum calculated with the SIB method is close to the exact one, which agrees within the error estimation.

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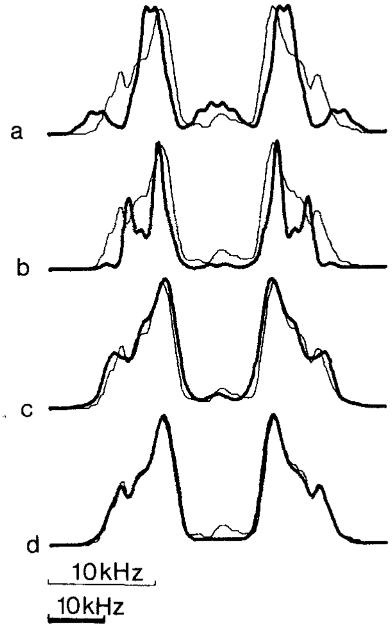
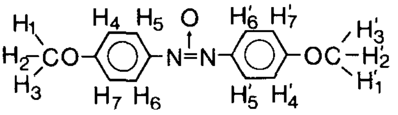


Figure 1. Proton N.M.R. spectra of 5CB-d_{11} obtained by the (*a*) NST, (*b*) SNB, (*c*) SIB methods and (*d*) exact calculations (the dihedral angle was taken to be 31°). The fine line shows the experimental lineshape at $T_{NI} - T = 1{\cdot}2°C$.

(*b*) *The 14-spin system: PAA*

Here we attempt an interpretation of the proton N.M.R. spectrum of a more complex system, for which exact computations are now impossible. Our choice was 4,4′-dimethoxyazoxybenzene (PAA)



since its molecular structure has been well-studied [8–13]. The bond lengths and bond angles were taken from X-ray data [9].

Analysis of the dipole–dipole interaction matrix shows that the PAA molecule divides into two equivalent weakly interacting 7-spin systems. In fitting the model spectrum to experiment we have assumed variations in the dihedral angle β between the planes of the phenyl ring, the bond angle C_{ring}–$\hat{O}$–C_{methyl} and the dihedral angle between the plane of the phenyl ring and that of the methoxy group (it contains the C_{ring}–O–C_{methyl} chain). We also considered the possibility of rotation of the rings and methyl groups as well as the libration of the methoxy groups around O–C_{ring}. The PAA spectrum simulated by the SIB method is very sensitive to variation in the B_{jk} constants.

The best agreement experimental and model spectra was obtained when β was 30°, the angle C_{ring}–$\hat{O}$–C_{methyl} was 120°, the methoxy groups were in a trans conformation in the planes of the rings to which they were attached, the rings rotated by 180° jumps and the methyl groups rotated by 120° jumps. These data are quite reasonable and correspond to the results of other works [8, 10, 11]. The error in the eigenvalue and

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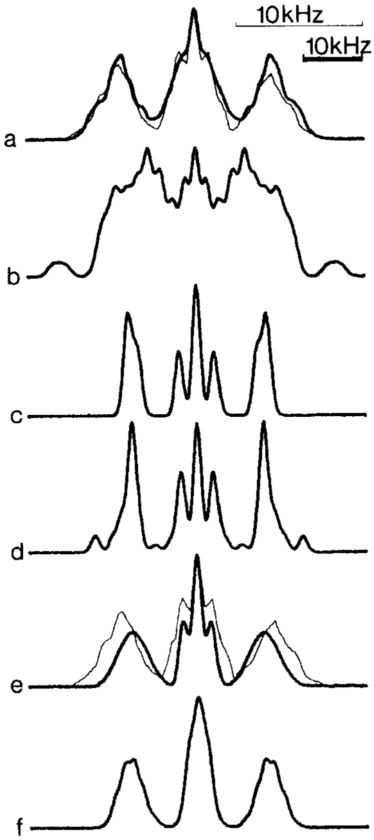

Figure 2. Proton N.M.R. spectra of PAA obtained by the (*a*) SIB, (*b*) NST, (*c*) SNB ($[H_1-H_3]:[H_4-H_7]$), (*d*) SNB ($[H_1-H_5]:[H_6, H_7]$) (the angle β was set equal to 30°, the methoxy groups are taken to be in the planes of the phenyl rings); (*e*) NST and (*f*) SIB (the conformational order parameters for the methoxy protons are set equal to 0·3) methods. The fine line shows the experimental lineshape at $T_{NI} - T = 15°C$.

eigenvector calculations is not more than 4 per cent. The value of the second rank order parameter from the ratio of the spectral scales is 0·52 ($T_{NI} - T = 15°C$), which is equal to the value obtained previously [12].

In the NST computation the error introduced by the omission of the scalar term from the spin hamiltonian reaches 87 per cent. The spectrum obtained (see figure 2 (*b*)) is markedly distorted.

In [5] the SNB calculations were restricted to a maximum subsystem of 6 spins. This restriction was caused by the use of tabulated data for the proton N.M.R. spectra of the simplest spin systems with dipole–dipole interactions. Under these conditions reasonable subdivision into independent subsystems cannot be assumed possible. The dipolar constants for the ortho-protons in the benzene rings are approximately equal to 24 kHz, to −2·5 kHz for the methoxy protons and the dipolar interaction of the latter with the nearest protons of the rings is about 8 kHz. The subdivision into the small subsystems $[H_1-H_3]:[H_4-H_7]$ or $[H_1-H_5]:[H_6, H_7]$ for the PAA molecule leads to a considerable increase in the errors to 63 and 39 per cent, respectively. Spectra for both the first (see figure 2(*c*)) and the second (see figure 2(*d*)) subdivisions differ significantly from experiment.

We must note that the NST and SNB simulations can, in principle, provide good agreement with experiment. Limmer *et al.* [13] obtained a simulated spectrum for PAA similar to the experimental one (see figure 2(*e*)) by using the NST approximation. This was achieved by introducing a conformational order parameter $S_{\mathrm{methyl}}(=0{\cdot}3)$ which describes the averaging of the dipolar interactions of the methoxy protons as a result of intramolecular motion. According to our estimate this calculation error reaches 87 per cent. The proton N.M.R. spectrum constructed by the SIB method for the same molecular structure (see figure 2(*f*)) is markedly different from the experimental one; here the error is reduced to 5 per cent.

4. Conclusions

The method proposed for the simulation of proton N.M.R. spectra by subdividing the interacting spin subsystems allows us to calculate the spectra of liquid crystals whose molecules contain between 20 to 40 protons. The method provides higher precision than the NST and SNB calculations. At the same time the computations remain within the capacity of professional personal computers. The method can be used to study the molecular structure of mesogens. To increase the reliability and to speed up the calculations, it is expedient to distinguish, initially in some appropriate way, a set of possible molecule conformers. For instance, this could be done by using numerical presimulation of liquid crystal spectra. This work is in progress now.

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