Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Measurements of the order parameter by proton N.M.R. on *N*-(4-alkoxybenzylidene)4'-toluidines

M. Riccò[a]; G. Guidi[a]; R. De Renzi[a]; C. Vignali[b]
[a] Dipartimento di Fisica, Università di Parma, Parma, Italy [b] Centro Interfacoltà Misure, Università di Parma, Parma, Italy

To cite this Article Riccò, M. , Guidi, G. , De Renzi, R. and Vignali, C.(1988) 'Measurements of the order parameter by proton N.M.R. on *N*-(4-alkoxybenzylidene)4'-toluidines', Liquid Crystals, 3: 6, 705 — 711
To link to this Article: DOI: 10.1080/02678298808086525
URL: http://dx.doi.org/10.1080/02678298808086525

LIQUID CRYSTALS, 1988, VOL. 3, NOS. 6 AND 7, 705–711

Measurements of the order parameter by proton N.M.R. on *N*-(4-alkoxybenzylidene)4′-toluidines

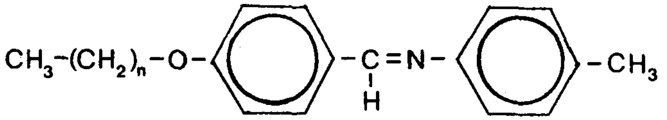
by M. RICCÒ, G. GUIDI and R. DE RENZI
Dipartimento di Fisica, Università di Parma, I-43100 Parma, Italy
and C. VIGNALI
Centro Interfacoltà Misure, Università di Parma, I-43100 Parma, Italy

N-(4-alkoxybenzylidene)4′-toluidines are a family of organic compounds which present a nematic and (depending on the chain length) a smectic mesophase. We have performed proton spin echo measurements on some members of the family in these mesophases. N.M.R. spectra present well-defined structures that can be assigned to one of the two end methyl groups on the basis of phenomenological as well as analytical discussion, despite the large number of protons contributing to the total line shape. The order parameter derived from this analysis is compared with optical data on the same compounds.

1. Introduction

The main problem in an experimental investigation of the static and dynamical parameters of the behaviour of nematogen molecules is that of identifying precisely to which portion of a complex molecular unit the experiment is coupled. N.M.R. often achieves this task by selective deuteration, which allows the singling out of the separate contributions of different groups of atoms from the spectra. In the general case it is virtually impossible to characterize otherwise the features of the broad proton N.M.R. spectrum typical of the liquid-crystalline states.

We have studied a class of molecules, the *N*-(4-alkoxybenzylidene)4′-toluidines, for which part of the spectrum can be unambiguously attributed, so that the behaviour of the nuclei responsible for it can be determined independently. The structure of these toluidines is the following:



(I)

and we have investigated in particular the compounds with $n = 3, 5, 7$ abbreviated respectively as BBT, HBT and OBT.

In §2 of the present paper we discuss some phenomenological support for our partial identification of the proton spectrum. Section 3 describes a simple spin model relevant to our problem and discusses its numerical simulation. The model is based on seven nuclei only, the three methyl protons plus the four protons of the phenyl ring which lies closer to the methyl group. It is argued that their pairwise interaction is the most relevant to the partial spectrum under study. The data are analysed in §4 on the basis of this simple model, and they are compared to other available experimental results on the same compounds.

2. The proton spin echo

Table 1 lists the transition temperatures of the liquid crystals under study. Figure 1 (*a*) shows the Fourier transform of a typical proton N.M.R. spin echo of our compounds in the nematic phase. It presents the characteristic, broad and featureless double peak structure, common to many liquid crystals, but it also shows two additional side groups of lines, symmetric with respect to the centre, with a larger

Table 1. Transition temperature (K). I–N stands for isotropic–nematic, N–C stands for nematic–crystalline, and so on. HBT presents a smectic B phase and OBT a smectic A phase on cooling. The two quoted values refer respectively to IR absorption data [1] and to our N.M.R. data.

	C–N	N–I	I–N	N–S	N–C	S–C
BBT	336·4	342·8	341·5		314·5	
	335	343	346		314	
HBT	327·1	345·2	343·9	325·3		316·5
	327	346	344	324		318
OBT	340·7	349·7	348·8	342·1		334·5
	343	350	350	342		337

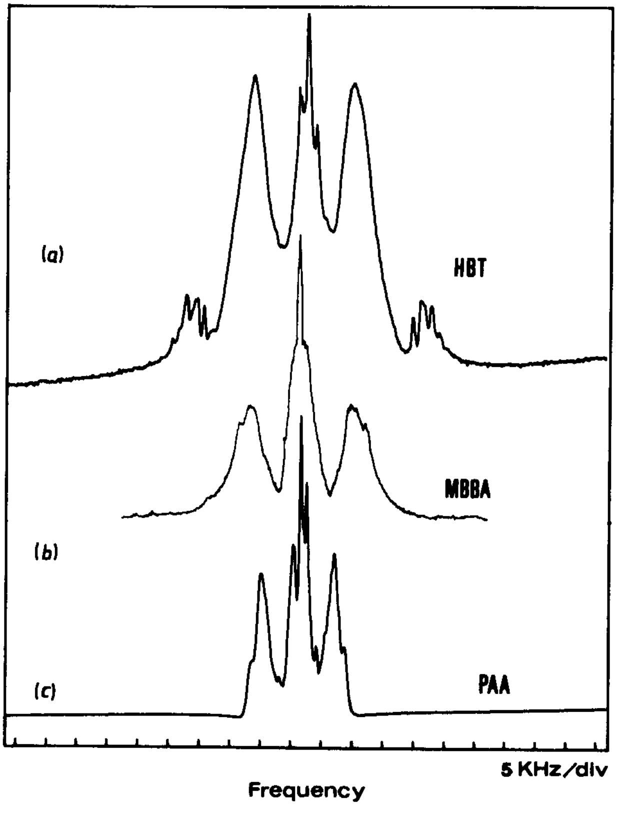


Figure 1. The Fourier transform of the proton spin echo from (*a*) the HBT, (*b*) from MBBA and (*c*) from PAA.

average separation and with a clear finer structure. The quality itself of this portion of the data, as opposed to the absence of features of the central part, suggests the possibility of an unambiguous attribution of its origin. This pattern was already seen in other compounds, like APAPA [2].

The structural characteristic of these toluidines, which they share with all the other compounds displaying similar N.M.R. spectra, is the presence of a methyl group (CH_3^{tol}) directly attached to one of the two phenyl groups of the molecule's rigid part. Therefore this methyl group rotates almost around the axis of the molecule. The other one, instead, like the terminal methyles in most nematogen molecules, rotates at the end of a long chain. As a consequence its axis of rotation is not so well correlated to the direction of the rigid part of the rod-like molecule. We shall presently argue that CH_3^{tol} is different from all other proton groups from the point of view of its dipolar interactions.

A rough analysis of the various protons in the molecule shows that they can be grouped into few categories. First of all come the alyphatic hydrogens, which have other hydrogens in α position. Therefore their main spin–spin interaction tends to be large because of the short distance between the nuclei. However in the nematic mesophase many of these protons rotate on average around an axis which forms with the molecular axis an angle close to the magic angle of 54°. This is, by the way, quite general and particularly true of the methoxyl terminal groups, like in the case of para-azoxyl-anisole (PAA), where no well-resolved side structure is seen in the spectra (figure 1 (*c*)). This consideration is not as stringent, though, in the case of the methylene protons, which tend to contribute to the spectrum over a large range of frequencies. On the other hand the observed dipolar splittings of these latter are reduced, due to the additional internal dynamics of the chain to which they belong, as can be seen by comparison with, for example, MBBA (figure 1 (*c*)). All other proton pairs are in β positions with respect to each other, like the eight phenyl hydrogens, or even further separated. An evaluation of the ratio between the dipolar interaction of the four phenyl pairs and that among the CH_3^{tol} spins gives, for instance, a value of 0·74, when the molecule is perfectly aligned along the magnetic field.

In conclusion it is clear that the largest interaction constant in the total spin hamiltonian of the molecule appears in front of the CH_3^{tol} proton terms. In zeroth order approximation we could neglect all interactions between CH_3^{tol} and the rest of the molecule. This would lead to a spectrum composed of two parts: a typical nematic spectrum like that, say, of PAA, superimposed to the spectrum of a methyl group rotating around its ternary symmetry axis. This last is the well-known three line pattern, with weights 1 : 2 : 1 and splitting equal to three times the interaction frequency constant. The central peak would fall under the PAA-like spectrum, while the two satellites would emerge either side of the latter, due to the large interaction constant. This situation is not too far from what is seen in figure 1 (*a*), although some further interactions must be taken into account to justify the finer structure of the side peaks. Some evidence in favour of such a crude approximation is given by the partial integrals under the spectrum; the ratio of that under the side peaks to the full integral is equal to $(3/2)/n$, where n is the total number of protons, for all three compounds, within experimental errors, as is expected in view of the model.

3. The spin hamiltonian

We assume that the fine side peak structure can be reconstructed by considering the interactions of the three CH_3^{tol} protons with the four protons in the phenyl group.

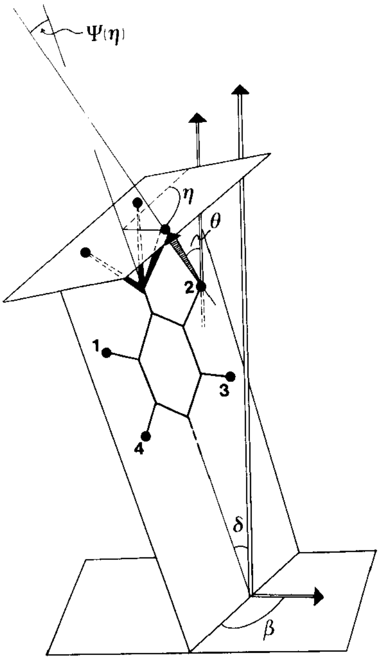


Figure 2. The geometry of the seven hydrogens interacting in the model hamiltonian.

A sketch of the relevant part of the molecule is shown in figure 2. Following, for example, Diehl [3], the resulting effective spin hamiltonian can be written, in units of h, as

$$\begin{aligned}\mathscr{H} &= -\nu_{\mathrm{L}}\left(I_z + \sum_{i=1}^{4} S_z^i\right) - \nu_m(T)\tfrac{1}{2}(I_z^2 - \tfrac{1}{4}(I_+I_- + I_-I_+)) \\ &\quad - \sum_{i=1}^{4} \nu_{m,i}(T)(I_zS_z^i - \tfrac{1}{4}(I_+S_-^i + I_-S_+^i)) \\ &\quad - \sum_{i<j=1}^{4} \nu_{i,j}(T)(S_z^iS_z^j - \tfrac{1}{4}(S_+^iS_-^j + S_-^iS_+^j)), \qquad (1)\end{aligned}$$

where ν_{L} is the proton Larmor frequency, I is the total spin of the three methyl protons ($I = \Sigma_{i=1}^3 I^i$), S^i are the spins of the four phenyl protons and the $\nu(T)$ are given by

$$\nu_m(T) = \nu_m^0\langle 3\cos^2\theta_m - 1\rangle, \qquad (2\mathrm{a})$$

$$\nu_{m,i}(T) = \nu_m^0 r_m^3\left\langle \frac{3\cos^2\theta_{m,i} - 1}{r_{m,i}^3}\right\rangle, \qquad (2\mathrm{b})$$

$$\nu_{i,j}(T) = \nu_m^0\frac{r_m^3}{r_{i,j}^3}\langle 3\cos^2\theta_{i,j} - 1\rangle. \qquad (2\mathrm{c})$$

Here $\langle\ \rangle$ indicates the rotational average, the subscripts m, m, i and i, j refer to intra-methyl proton, to methyl–phenyl proton and to phenyl–phenyl proton quantities respectively, r is the length of the vector joining two protons, θ its azimuthal angle, when the external magnetic field is along z, and the quantity ν_m^0 is defined as $\gamma^2 h/r_m^3 = 20{\cdot}724\,\mathrm{kHz}$ ($\gamma = 4{\cdot}257\,\mathrm{kHz\,gauss}^{-1}$).

In order to evaluate the orientational average a few crude assumptions will be made. First of all we shall neglect the effects of the molecule's biaxiality. The averaged value of equation (2 b) can then be evaluated by integrating over the configurations and orientations of the molecule, weighted with their distribution probability $\mathscr{P}(\delta, \beta, \eta)$, where δ is the angle between the molecular axis and the nematic director, β and η are the angles that the phenyl plane and the CH_3^{tol} respectively form rotating around the molecular axis (figure 2). Assuming further that the CH_3^{tol} reorientations and those of the phenyl group are not correlated both among themselves and to the molecular axis fluctuations, we can factorize $\mathscr{P}$ as $P(\delta)F(\beta)G(\eta)$. Therefore

$$\left\langle \frac{3\cos^2\theta_{m,i} - 1}{r_{m,i}^3} \right\rangle = \int d\eta \frac{G(\eta)}{r^3(\eta)} \int d\delta d\beta P(\delta)F(\beta)(3\cos^2\theta(\delta, \beta, \eta) - 1). \quad (3)$$

The innermost integral is the order parameter [3] of a hypothetical rigid molecule in which $\mathbf{r}(\eta)$, the vector joining the two protons, forms an angle $\psi(\eta)$ with the molecular axis. As a consequence:

$$\left\langle \frac{3\cos^2\theta_{m,i} - 1}{r_{m,i}^3} \right\rangle = \left\langle \frac{3\cos^2\delta - 1}{2} \right\rangle \int d\eta G(\eta) \frac{3\cos^2\psi(\eta) - 1}{r^3(\eta)}. \quad (4)$$

We have assumed G as a uniform distribution; therefore the residual integral does not depend on temperature and it can be evaluated numerically.

The average quantities in equations (2 a) and (2 b) are also known, within the same approximations [3], to be proportional to the order parameter of the molecular axis $S(T) = (1/2)\langle 3\cos^2\delta - 1\rangle$. In particular for CH_3^{tol}

$$\nu_m(T) = \nu_m^0 S(T)\left(3\cos^2\frac{\pi}{2} - 1\right) = -\nu_m^0 S(T). \quad (5)$$

The interaction constants are listed in table 2; they are obtained from scaling by $|\nu_m(T)|$ all the quantities appearing in equation (1).

Table 2. The interaction constants appearing in equation (1), in units of $\nu_m^0 S(T)$ (ν_m^0 = 20·724 kHz). m indicates the protons in the CH_3^{tol} group; for the other indices refer to figure 2.

Protons	m	$(m, 1)$ $(m, 2)$	$(m, 3)$ $(m, 4)$	(1, 2) (3, 4)	(1, 3) (2, 4)	(1, 4) (2, 3)
$\nu(T)$	−1	0·150	0·062	−0·070	−0·012	0·742

The table shows that ν_m is the largest interaction and that $\nu_{m,1}$ and $\nu_{m,4}$ are both much smaller. In first approximation, therefore, the methyl and the phenyl groups are decoupled and their mutual interaction is a small perturbation. We obtained the proton N.M.R. transitions from the hamiltonian of equation (1) by numerical simulation. A finite resolution function was convoluted with the spectrum resulting from the full matrix diagonalization. Figure 3 shows the result of the simulation under a typical experimental spectrum. As was expected, the perturbation introduced by all the couplings of table 2 gives two side multiplets, besides a complicated central structure around $\nu = \nu_L$ and two intermediate groups originating from the phenyl protons. Only the first are of interest, of course, because the rest of the spectrum is experimentally indistinguishable from the many other proton contributions which add up in the same frequency region. The agreement between the simulated side

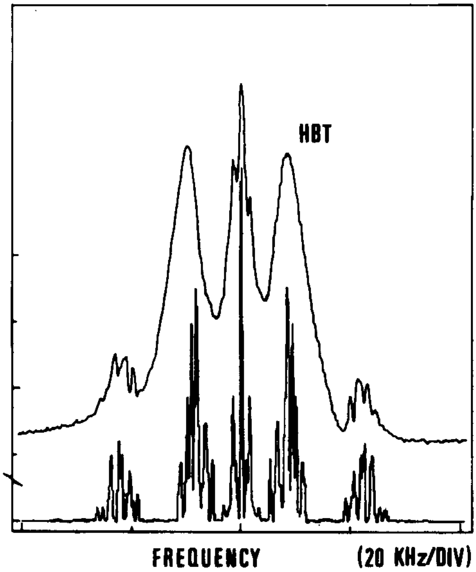


Figure 3. Comparison between an experimental spectrum and the simulation. Only the outer multiplets in the simulated plot are relevant.

multiplets and the experimental ones is remarkable and indicates that our crude approximations on the orientational dynamics are sufficient for the purpose of this work. From numerical integration the centre of each side multiplet corresponds to the frequency $\nu = \nu_L \pm (3/2)\nu_m(T)$ which coincides approximately with the position of the central largest peak in the multiplet.

4. The order parameter

Figure 4 shows the behaviour of the order parameter of HBT versus temperature, as obtained from equation (5), after a small correction which takes into account the angle $\phi \simeq 8°$ [4] between the CH_3^{tol} ternary axis and the molecular axis. Similar

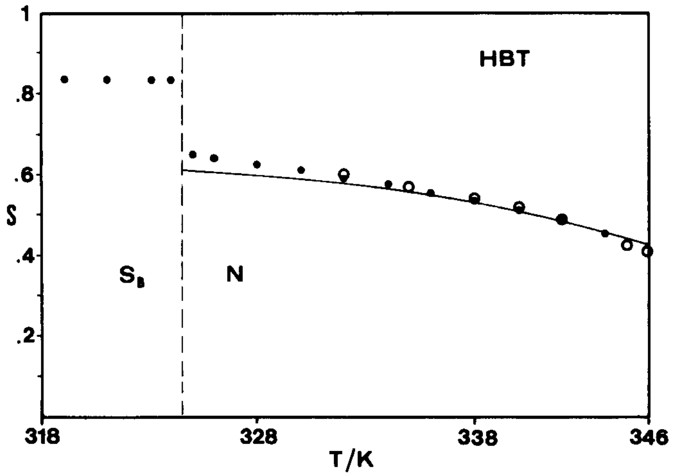


Figure 4. The order parameter of HBT from equation (5). Solid circles refer to cooling, open circles to heating. The solid line is the Maier–Saupe curve.

behaviour was observed for OBT. They both agree quite well with the Maier–Saupe predictions up to the nematic–isotropic transition. The experimental points from BBT, instead, lie systematically above the theoretical curve (by nearly 0·1).

On the other hand I.R. absorption data [1], obtained from a line assigned to a vibrational mode of the phenyl rings, agree with the Maier–Saupe curve also in the case of BBT at lower temperatures, but they always tend to fall more rapidly on approaching the transition to the isotropic phase.

We shall merely note that deviations from the Maier–Saupe predictions are as expected in view of the molecules' biaxiality, which was neglected in our simple model, and, close to T_C, also to the inadequacy of the mean-field theory approximation.

The convincing assignment of the methyl side peaks will hopefully allow future extensions of the study to dynamical aspects of the order in these liquid crystals. Applications of this tool can also be envisaged in order to explore the Freedericks transition.

We wish to thank Professor N. Kirov, who kindly lent us the three samples.

References

[1] Dosov, I., Kirov, N., and Penchev, I., 1988, *J. molec. Liq.* (in the press).
[2] Visintainer, J. J., Bock, E., Dong, R. Y., and Tomchuk, E., 1975, *Can. J. Phys.*, **53**, 1483.
[3] Diehl, P., 1985, *N.M.R. of Liquid Crystals*, edited by J. W. Emsley (Reidel).
[4] Luz, Z., Hewitt, R. C., and Meiboom, S., 1975, *J. chem. Phys.*, **61**, 1758.