Proton NMR Studies and Lineshape Simulations of the Mesophases of Terephthalylidene-Bis-4-n-propylaniline (TBPRA) – Evidence for Conformational Changes

St. Limmer and M. Findeisen

Sektion Physik der Karl-Marx-Universität Leipzig, DDR-7010 Leipzig, Linnéstr. 5

From comparison of simulated and experimental spectra in the nematic, smectic-A, and smectic-C phases of TBPrA it can be concluded that there are conformational changes of the molecule giving obviously rise to a continuous variation of the direction of the long molecular axis with respect to a frame of reference connected with a conformation of the molecule that was derived from the crystal conformation of TBBA.

1. Introduction

The comparison of simulated and experimental proton NMR spectra has been successfully exploited to make assertions concerning the intramolecular mobility and conformation of molecules in mesophases [1–3, 7]. In all cases hitherto reported on, the proton NMR lineshape did not change significantly even when smectic phases were involved [7], i.e. the temperature course of the spectra could be described satisfactorily by a simple scaling of the frequency by a factor $1/S$ (S = common Tsvetkov orientational order parameter) from nematic to smectic-G phase [7]. In this paper we present a substance (terephthalylidene-bis-[4-n-propylaniline], abbreviated by TBPrA) which shows distinct changes of the proton NMR lineshape on running from the nematic down to the smectic-G (and smectic-H) phases (for phase sequence and transition temperatures see Table 1). We shall show that these lineshape changes could be attributed to conformational changes giving rise to alterations in the direction of the long molecular axis with respect to a properly defined molecular frame of reference.

Table 1. Phase transition temperatures (in Kelvin) of TBPrA according to different references.

Reference	T_{IN}	T_{NA}	T_{AC}	T_{CG}	T_{GH}
[4]	528.2	453.6	421.7	415.0	388.8
[5]	533	448.6	431.3	417	383
[6]	533	450	433	419	390

2. Results

2.1. Experimental Proton NMR Spectra

In Fig. 1 typical spectra are displayed for each of the mesophases of TBPrA (except smectic-H). The lineshape seems to change continuously from nematic to smectic-C without distinct sudden "jumps". In the nematic phase the central component consists of three well-resolved lines the two outer ones of which disappear in the smectic-A phase. They shade into a rounded-off "foot" of the central spike whose height decreases with de-
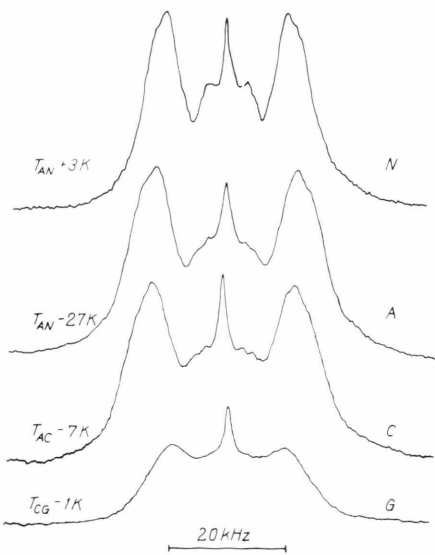

Fig. 1. Temperature course of the proton NMR spectra of TBPrA in different mesophases.

creasing temperature whereas the relative intensity of the central spike grows. At the transition to the G phase the spectrum "collapses", i.e. the splitting of the outer doublet peaks is drastically diminished and the "valleys" between central peak and doublet wings are elevated. In the H phase there remains only one broad structureless line.

2.2. Simulation of the Proton NMR Spectra

For the calculation of the proton NMR spectra as described in detail formerly [1, 2] we have used the co-ordinates from the crystal structure analysis of TBBA by Doucet et al. [8] adding a third proton at the third chain carbon of the TBBA molecule and omitting the terminal methyl group of TBBA. In the crystalline state (and therefore our TBPrA model) the TBBA molecule adopts nearly a "cis" conformation of the three phenyl rings. In Fig. 2 this conformation is displayed with the molecule being projected on two perpendicular planes of the frame of reference relevant for the computation procedure. The direction of the long molecular axis with respect to the chosen molecular geometry (which must be given to compute a spectrum) is defined by the angles Θ (polar angle between chosen long axis and z-axis of the frame), and Φ (azimuthal angle in the $x - y$-plane).

Regarding the molecular conformation used here there is some freedom in defining the direction of the long axis. In Table 2 some couples of Θ- and Φ-values for different conceivable directions of the

long axis with respect to the chosen molecular conformation of Fig. 2 are compiled.

At first we tried to fit the theoretical spectra with only one set of Θ, Φ and mere variation of the *conformational parameters* * S_j [1−3] which approximately describe the degree of reduction of dipolar interactions of the proton spins with their nearest neighbours. However, it turned out after many fruitless attempts that this was impossible. We were unable to fit the spectra of the nematic to the smectic-C phase satisfactorily by a systematic variation of the S_j's of methyl, methylene, and methin protons (S_j of the benzene ring protons was set equal 1 since they are fixed and therefore rigid) although several sets of Θ, Φ within the reasonable limits ($\Theta = 110° \ldots 125°$; $\Phi = 0 \ldots - 25°$) have been employed.

A quite good agreement with experimental spectra could only be attained for all phases if *the direction of the long molecular axis was systematically varied* with the conformational parameters S_j being the same for all phases. The S_j's yielding the best fit were 0.85 for α-methylene protons, 0.80 for β-methylene, 0.38 for methyl protons (all S_j's refer to both chains), 0.31 for methin protons, and 1 for phenyl ring protons. Additionally we had to admit 180°-jumps (π-flips) of the phenyl rings about their para-axes, which is demanded by deuteron [9, 10] and ^{13}C NMR [11] and which seems to be more likely than a free rotation of the rings (at least the outer ones) regarding the hindering potential [12] for this motion. Besides, one has to assume methyl group rotation.

Varying now the direction of the long molecular axis with respect to the molecular frame associated with the molecular conformation of Fig. 2, the temperature course of the proton NMR spectra (cf. Fig. 1) is reflected fairly well, as demonstrated in Figure 3. There the polar angle Θ is varied from 112.5° (representing good fit to the experimental spectra of the nematic phase) to 125° (smectic-C and G phases) with fixed value of Φ (= − 20°) that is of less influence than Θ. With respect to the molecular conformation (crystal conformation of TBBA) the long molecular axis is shifted from a direction inclined by about 8° ÷ 10° against the

Table 2. Sets of Θ, Φ-values for different orientations of the long molecular axis with respect to the molecular conformation of Figure 2.

Axis through	Number of the involved carbon atoms (cf. Fig. 2)	$\Phi/°$	$\Theta/°$
CH$_3$ groups	C23, C26	−16.2	116.8
β-methylene groups	C22, C25	−15.6	115.2
para-axis ring I	C1, C4	−24.7	125.5
para-axis ring II	C8, C11	−16.8	120.0
para-axis ring III	C15, C18	−13.4	119.9
ring I − ring III	C1, C18	−17.8	121.1
principal axis of the moment of inertia tensor		1.6	112.2

* The dipolar interaction between two protons j and k is diminished by a factor $S_j \cdot S_k$ compared to the rigid case (with reference to the applied conformation).
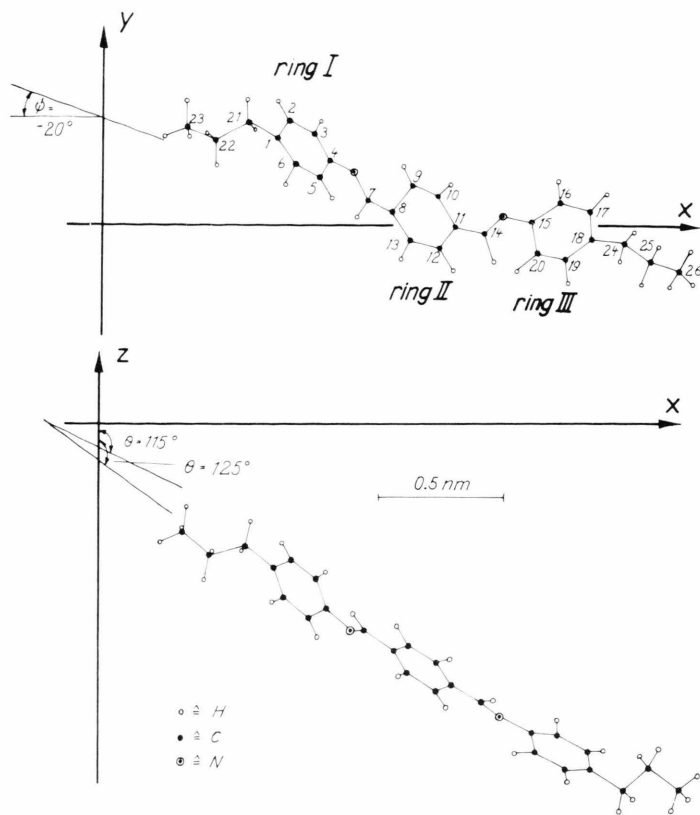
Fig. 2. Sketch of the TBPrA molecule in the frame of reference used in the computation in two planes (derived from the crystal structure analysis of TBBA by Doucet et al. [8]).
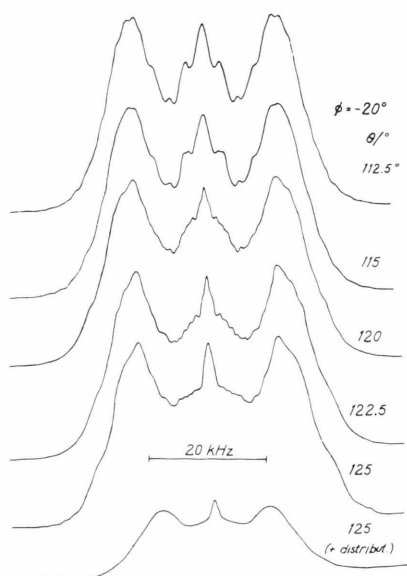

Fig. 3. Theoretical spectra of TBPrA calculated with $S_j = 1$, 0.85, 0.80, 0.38, and 0.31 for phenyl, α-methylene, β-methylene, methyl, and methin protons, respectively, for varying direction of the long molecular axis (Θ varies as indicated in the drawing, $\Phi = -20°$ fixed).

average para-axes direction ($\Theta = 112.5°$) to a position nearly parallel to the para-axes of the phenyl rings ($\Theta = 125°$).

The spectra of the smectic-G phase could be computed using those of the smectic-C phase under the assumption of a specific azimuthal distribution of the tilt directions of the individual domains, which will be described in detail elsewhere [13].

3. Discussion

The values of the conformational parameters S_j indicate a reduction of the dipolar interaction between the chain protons by motional processes whose nature is not quite clear. The terminal methyl group possesses obviously a fairly high mobility besides its rotation about its C_3 symmetry axis, in agreement with the results of Doucet et al. [8] for the methyl group of TBBA in the crystal as well as with the deuteron NMR data of Deloche et al. [14]. The small value of the conformational parameter $S_j = 0.31$ for the methin protons could be inter-

preted as follows: The most important interactions of the methin protons are those with the inner protons of the neighbouring aniline rings. Therefore any S_j ascribed to the methin proton will reflect chiefly the degree of reduction of the dipolar inter- action with the inner aniline ring protons (because of the π-flip motion). In the conformation of Fig. 2 the dihedral angles between the azomethin groups and ring I and ring III are 21.6° and 36.5°, respectively $S_j = 0.31$ for the methin protons thus means to a first approximation that these interactions are reduced by a factor 0.31 in our case. This can be achieved both in a dynamic manner (by some kind of motion decoupling the interaction between methins and phenyl protons, which is not quite easy to conceive since e.g. simple free rotation of the rings about their para-axes wouldn't suffice as calculations show [15]), and a more "static" one. The alternative static reduction implies an addi- tional twist of the azomethin against the aniline ring planes with respect to the underlying molecular conformation (Figure 2). In our case this means a dihedral angle of about 40° between ring I and the neighbouring azomethin group, and slightly more than about 50° for ring III and the other azomethin group [15], i.e. additional rotations of ca. 15° ÷ 20° in comparison with the crystalline state. That does not seem unreasonable in view of the results obtained by Averyanov et al. [16] for MBBA (the dihedral angle between the aniline ring and the azomethin group in the nematic phase changes from about 38° ca. 25 K below the clearpoint to about 51° close to the clearpoint).

One could be tempted to discuss the S_j's of the chain protons in the same way; there, however, the most important interaction is that between the protons of a certain methylene proton pair. More- over, the potentially strong interaction of the α-methylene protons with the neighbouring ring protons is already strongly decoupled statically since the chain planes are nearly perpendicular to the ring planes. So the S_j's < 1 must originate from motional averaging processes.

As to the alteration of the long molecular axis, it is to be noted that it refers to a particular starting conformation (here derived from the crystal con- formation of a closely related molecule) which very probably differs from the actual average con- formation in the mesophases. As, however, line- shape simulations of other three-ring compounds

proved, the computed spectra are still very similar if only the ring arrangement is changed from "all- trans" to "cis" (which is conceivable since the most important contributions to the lineshape-deter- mining dipolar interactions are not influenced by such a conformational change).

From the comparison of computed and experi- mental spectra one could conclude a variation of the long axis direction which should probably be due to conformational changes (e.g., isomerizations of the aromatic part, or of the aliphatic chains).

In the nematic phase this average conformation should be characterized by an angle ($\approx 8° \dots 12°$) between the long axis and the average direction defined by the para-axes of the three rings, whereas the long axis gets more and more parallel to the para-axes with decreasing temperature (till the end of the C phase).

In a way the above statements differ from the results of Charvolin and Deloche [9] and Luz et al. [10] for TBBA, who concluded from the ratio of the deuterium quadrupole splittings of phenyl and methin deuterons that the angle between the long and para-axes increases with decreasing temper- ature. For the tenth homologue of the same series (TBDA) Benattar et al. [17] have observed a nearly constant value of that ratio with a tendency to increase with growing temperature in the C phase (their plot ends before reaching the A phase).

The ratio of the above-discussed quadrupolar splittings of about 2.6 ÷ 2.8 in the nematic and smectic-C phases of TBBA [9, 10] and about 2.7 ÷ 2.75 for the C phase of TBDA [17] can well be explained on the basis of benzene ring flips assuming bond angles of about 58° ÷ 59° for the phenyl deuterons and about 65° ÷ 66° for the methin deuterons, in good agreement with X-ray structure analysis of TBBA [8] and other azomethin com- pounds [18]. The small but significant difference in the bond angles of phenyl and methin deuterons is hence the main reason for the quite different quadrupolar splittings (assuming the same coupling constants for both bonds, cf. [9, 10], even if the long molecular axis is parallel to the para-axes.

If both phenyl rings and azomethin groups would reorient independently about the para-axes and the $C_{ar}-N$ bond, resp., the splitting ratios would be independent of the angle α between long axis and para-axis for "free" rotations, and weakly depen- dent on α for independent π-flips [15]. In the latter

case, as in the case with only the phenyl rings reorienting, the ratio would become greater with increasing α.

It could be checked by deuteron and ^{13}C NMR experiments if the before-discussed picture of changes of the long axis direction with respect to a molecule-fixed frame (that should be due to conformational changes of the molecule) is indeed superior to the ideas discussed in the literature [9, 10].

A similar, even more striking lineshape variation with temperature has been observed for: [2-chloro-1,4-bis-(4-octyloxy-benzoyloxy)-benzene] [19]. Within the (fairly wide) nematic phase the spectrum drastically changes. Preliminary simulations of the proton NMR lineshape again suggest an interpretation by simply varying the long axis direction with respect to a molecular frame of reference. It might be that three-ring compounds could perform conformational changes easier than "normal" two-ring mesogens because there is an increased conformational variability (greater number of conformers). Perhaps the conformational changes here are simply better reflected.

In how far the transverse ordering about the long molecular axis can produce similar lineshape changes has still to be checked. Considering, however, the probable geometry of the molecule (with substantial deviations from planar structure owing to distinct rotations of the different molecular parts such as phenyl rings, azomethin groups and chains against each other) there does not seem to exist a preferred axis of the molecular frame of reference perpendicular to the long axis which could make anisotropic fluctuations of the long molecular axis about the two perpendicular molecular axes physically more plausible.

[1] H. Schmiedel, B. Hillner, S. Grande, A. Lösche, and St. Limmer, J. Magn. Reson. **40**, 369 (1980).
[2] St. Limmer, H. Schmiedel, B. Hillner, A. Lösche, and S. Grande, J. Physique **41**, 869 (1980).
[3] St. Limmer, M. Findeisen, H. Schmiedel, and B. Hillner, J. Physique **42**, 1665 (1981).
[4] S. Diele, H. Hartung, P. Ebeling, D. Vetters, H. Krüger, and D. Demus, Proc. 3rd Liqu. Cryst. Confer. Social. Countries, Budapest 1979.
[5] S. Kumar, Phys. Rev. **A 23**, 3207 (1981).
[6] Y. Kamiishi, S. Kobayashi, and S. Iwayanagi, Mol. Cryst. Liqu. Cryst. **67**, 125 (1981).
[7] St. Limmer and M. Findeisen, submitted for publication.
[8] J. Doucet, J.-P. Mornon, R. Chevalier, and A. Lifshitz, Acta Cryst. **33**, 1701 (1977).
[9] J. Charvolin and B. Deloche, J. Physique **37**, C3-69 (1976).

[10] Z. Luz, R. C. Hewitt, and S. Meiboom, J. Chem. Phys. **61**, 1758 (1974).
[11] J. Schulz, Thesis, Sektion Physik der Karl-Marx-Universität Leipzig.
[12] H. Perrin and J. Bergès, J. Physique-Lett. **43**, L-531 (1982).
[13] St. Limmer and M. Findeisen, to be published.
[14] B. Deloche, J. Charvolin, L. Liébert, and L. Strzelecki, J. Physique-Coll. C1 **36**, C1-21 (1975).
[15] St. Limmer, unpublished results.
[16] E. M. Aver'yanov, Fiz. Tverd. Tela **24**, 2839 (1982).
[17] J. J. Benattar, F. Moussa, and M. Lambert, J. Chim. Physique **80**, 99 (1983).
[18] cf., e.g., I. Bar and J. Bernstein, Acta Cryst. **B 33**, 1738 (1977).
[19] H. K. Singh, St. Limmer, M. Findeisen, and S. Grande, to be published.