

# The Twist-Bend Nematic Phase: NMR Studies

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The twist-bend nematic phase,  $N_{TB}$ , is a generalised version of a chiral nematic phase,  $N^*$ , from which it differs by the tilt of the director with respect to the helix axis. One of the intriguing properties of this new phase is that it is formed, as Dozov predicted<sup>[1]</sup>, by achiral and bent molecules unlike the chiral nematic which requires molecular chirality. The twist-bend nematic was first identified for the odd liquid crystal dimer, CB7CB, in which two cyanobiphenyl groups are linked by a heptane spacer<sup>[2]</sup>. Although flexible the conformationally averaged shape of the dimer is significantly bent<sup>[3]</sup> and so similar to the bent-core systems considered by Dozov<sup>[1]</sup>. One of the key techniques of the many employed in the phase identification was NMR spectroscopy. Subsequently NMR spectroscopy, often combined with theory, has been employed in further studies of the  $N_{TB}$  phase of CB7CB and analogous liquid crystal dimers.

Here we shall be concerned with just some of these investigations which used NMR spectroscopy. In the first study of CB7CB it was shown that the nematic phase is uniaxial from an NMR powder pattern obtained by randomising the director orientation with the aid of surface torques. On passing to the  $N_{TB}$  phase the spectral changes were also consistent with the phase being uniaxial. This result is curious because it appears to conflict with the local symmetry of the twist-bend nematic. However the high symmetry was confirmed by a simple rotation experiment in which the sample was aligned with the helix axis both parallel and perpendicular to the magnetic field. Such NMR results have also been found for the twist-bend nematic phase of CB9CB<sup>[4]</sup>, a homologue of CB7CB. Further NMR experiments have since been performed which allow us to understand such results and pose the interesting question as to what is the director and where is it in the  $N_{TB}$  phase?

One of the defining structural properties of the twist-bend phase is the cone or tilt angle; that is the angle made by the director with the helix axis. This has been estimated from the NMR spectra of a specifically deuterated probe molecule, 8CB-d<sub>2</sub>, dissolved in CB7CB<sup>[5]</sup> and comparison with theoretical predictions of the quadrupolar splittings for the  $N_{TB}$  phase<sup>[6]</sup>. This analysis also allowed the magnitude of the pitch of the helix,  $p$ , for the  $N_{TB}$  phase of CB7CB to be estimated. It is found that  $p$  is extremely small, of the order of a few molecular lengths<sup>[6]</sup>. This remarkable result is in accord with that found using quite different techniques<sup>[7,8]</sup>. Here, two quite different NMR based techniques have been adopted to study the temperature dependence of the cone angle in CB7CB. The results are in good agreement and show the growth of the cone angle with decreasing temperature.

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## References:

- [1] I. Dozov, *Europhys. Lett.*, **56**, 247-253 (2001).
  - [2] M. Cestari, S. Diez-Berart, D. A. Dunmur, A. Ferrarini, M. R. de la Fuente, D. J. B. Jackson, D.O. Lopez, G. R. Luckhurst, M. A. Perez-Jubindo, R. M. Richardson, J. Salud, B. A. Timimi, H. Zimmermann, *Phys. Rev.*, E **84**, 0317049 (2011).
  - [3] G. R. Luckhurst, *Macromol. Symp.* **96**, 1 (1995).
  - [4] A. Hoffmann, A. G. Vanakaras, A. Kohlmeier, G.H. Mehl, D. J. Photinos, arXiv:1401.5445.
  - [5] L. Beguin, J. W. Emsley, M. Lelli, A. Lesage, G. R. Luckhurst, B.A. Timimi, H. Zimmermann, *J. Phys. Chem. B* **116**, 7940 (2012).
  - [6] C.K. Greco, G. R. Luckhurst, A. Ferrarini, *Phys. Chem. Chem. Phys.* **15**, 14961 (2013).
  - [7] C. Meyer, G. R. Luckhurst, I Dozov, *Phys. Rev. Lett.* **111**, 067801 (2013).
- Email
- [8] 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, N. A. Clark, *PNAS*, **110**, 15931 (2013); V. Borsch, Y.-K. Kim, J. Xiang, M. Gao, A. Jáklí, V. P. Panov, J. K. Vij, C. T. Imrie, M. G. Tamba, G. H. Mehl, O. D. Lavrentovich, *Nat. Comm.* **4**, 2635 (2013).