A novel and potential biaxial liquid crystal phase formed by an organo-silicon tetrapode. A deuterium NMR investigation

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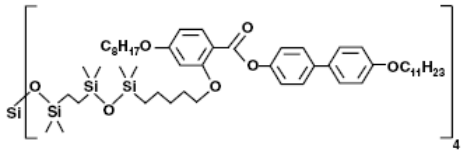
Using polarised FTIR and optical measurements, a thermotropic biaxial nematic phase has been reported for the organo-silicon tetrapode whose molecular structure is shown in the figure together with its transition temperatures [1]. This material can be cooled to -30^{0}C



Isotropic **47^{0}C** Nematic (uniaxial) **37^{0}C** Nematic (biaxial)

before it passes into glass [2]. The phase symmetry was determined from the angular dependence of the intensities of the FTIR spectral lines [1]. In addition, the four orientational order parameters characterising the two nematic phases were determined [1]. Attempts have been made to fit these to molecular field theory predictions but with little success for the phase biaxiality order parameters [3]. Prompted by these results we have used deuterium NMR spectroscopy to investigate the potential biaxial nematic phase using two deuteriated probe molecules: CD_2Cl_2 and p-xylene-d_6 at ~2-3wt% level. The nematic-isotropic transition of the pure sample (46.7-67.8^{0}C (sharp)) is in complete agreement with [1]. The nematic-isotropic transition temperature, due to the presence of these probe molecules, is lowered by only a few degrees. These small probe molecules can execute fast molecular motion and so are able to sample all regions of orientational space for the nematic phase. Magnetically aligned NMR spectra were obtained throughout the nematic phases. Both equilibrium and time-resolved NMR spectra (after a 90^0 sample rotation) were obtained over a wide temperature range extending to -15^{0}C. Our time-resolved NMR measurements have revealed, in contrast to previous work [1, 2, 4], that the entire nematic phase down to -15^{0}C is essentially uniaxial.

However, surprisingly when aligned samples were left overnight in the spectrometer at temperatures between 5 and 0^{0}C a dramatic change in the spectrum was observed the next day: the NMR spectrum now was that characteristic of a **3-D powder** spectrum with a partially-averaged **biaxial** quadrupolar tensor.

The un-aligned biaxial phase persists to 16-19^{0}C before it passes into an aligned uniaxial nematic phase. The biaxiality parameter, η, for the partially-averaged quadrupolar tensor of the probe molecules, measured at low temperatures, is about 0.35 for CD_2Cl_2 and 0.1 for p-xylene-d_6. The structure of this biaxial liquid crystal phase is unknown and requires further investigations; for example, by X-ray diffraction. The puzzling results obtained by this and other studies of the tetrapode will be discussed and possible explanations for the differences observed considered.

References

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