

Oligomeric rod–disc nematic liquid crystals

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Six new oligomeric nematic liquid crystals are reported consisting of a triphenylene-based core attached to which are six 4-cyanobiphenyl units via flexible alkyl spacers.

One of the most active areas of research in liquid crystal science in recent years has been the search for the elusive biaxial nematic phase.^{1,2} In the uniaxial nematic phase, the molecules are arranged such that there are no positional correlations between their centres of mass but the unique axes of the molecules are arranged about a common direction known as the director. By comparison in the biaxial nematic phase there is also a correlation of the molecules in a direction perpendicular to the director. The existence of the biaxial nematic phase was predicted over 30 years ago by Freiser³ and there have been many claims for its discovery in low molar mass thermotropic liquid crystals, although experimental difficulties in unambiguously identifying the symmetry of these phases raise questions concerning these assignments.^{4,5}

Theoretical studies have shown that mixtures of rods and discs can exhibit the biaxial nematic phase.^{6,7} In such a mixture the optimum packing arrangement has the long axes of the rods arranged perpendicularly to the short axes of the discs and hence, the system has two directors. In these simulations an attractive interaction is required between the rods and discs to prevent phase separation into two uniaxial nematic phases and in real systems phase separation does indeed occur. To overcome this difficulty a number of authors have attached rod-like and disc-like units via flexible alkyl spacers.^{8–15} In these molecular systems a single rod and disc have been interconnected and such dimers have recently been the subject of a computer simulation study,¹⁶ or one, two or three rods have been attached to a single disc. We have extended this approach and report here the synthesis and characterisation of a series of molecules in which six rod-like 4-cyanobiphenyl moieties

are attached to a central triphenylene core via flexible alkyl spacers (Fig. 1).† The triphenylene core was chosen because it is known to promote liquid crystalline behaviour in a wide range of molecular architectures and has a very versatile synthetic chemistry.^{17,18} The acronym used to refer to these compounds is TP(*n*CB)₆ where *n* refers to the number of methylene units linking the triphenylene and 4-cyanobiphenyl units.

The thermal behaviour of the TP(*n*CB)₆ series was determined using optical polarizing microscopy and differential scanning calorimetry and the transition temperatures and associated entropy changes, expressed as the dimensionless quantity $\Delta S/R$, are listed in Table 1. A classical schlieren texture indicative of a nematic mesophase but consisting of a 3–4 fold excess of $\pm \frac{1}{2}$ over integer disclinations was observed for all members of the TP(*n*CB)₆ series when viewed under a polarizing optical microscope (Fig. 2); this was observed on both heating and cooling each homologue with the exception of TP(5CB)₆ for which the nematic phase was observed only on cooling the isotropic melt.

On cooling the nematic phase for each member, crystallisation was not observed and instead vitrification occurred. On reheating, each member exhibited a glass transition and a nematic–isotropic transition, except for TP(5CB)₆ which underwent cold crystallisation and a subsequent crystal–isotropic transition at 171 °C. The glass transition temperatures initially decrease on increasing the spacer length but appear to reach a limiting value, after which T_g is no longer sensitive to changes in spacer length.

On increasing the length of the flexible spacers, the nematic–isotropic transition temperature falls sharply by 58 °C on passing from TP(5CB)₆ to TP(6CB)₆, decreases by 14 °C going to TP(7CB)₆ while further increasing the spacer length increases the transition temperature. The entropy change associated with the nematic–isotropic transition reveals a similar dependence on the length of the flexible spacers although a more marked relative increase is observed for the higher homologues. These values of the entropy change are particularly high for a nematic–isotropic

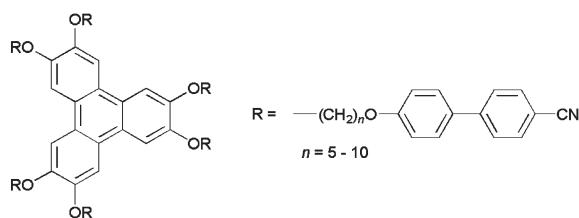


Fig. 1 Structure of the TP(*n*CB)₆ series.

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Table 1 Transitional properties of the TP(*n*CB)₆ series extracted from a second heating DSC trace^a

<i>n</i>	T _g /°C	T _{NI} /°C	$\Delta S_{NI}/R$
5	50	[167] ^b	2.08
6	49	109	1.38
7	33	95	1.23
8	30	116	2.25
9	31	115	3.04
10	32	123	4.05

^a T_g glass transition temperature; T_{NI} nematic–isotropic transition temperature; $\Delta S_{NI}/R$ scaled nematic–isotropic entropy; [] denotes a monotropic transition. ^b Undergoes cold crystallisation on heating. All measurements were made at a heating rate of 10 °C min^{−1}.

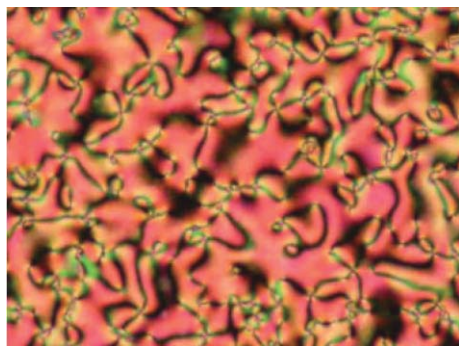


Fig. 2 Schlieren texture of the nematic phase of TP(10CB)₆ (120 °C).

transition but it may be argued that they should be scaled by the number of interacting mesogenic units per molecule.¹⁹ This would give values more comparable to those seen for conventional low molar mass liquid crystals. For conventional oligomeric liquid crystals consisting of molecules containing rod-like units interconnected *via* flexible alkyl spacers varying the length and parity of the flexible spacers normally gives rise to pronounced alternations in both the transition temperatures and associated entropy changes.^{20–22} Such behaviour is most commonly interpreted in terms of the change in the average molecular shape on varying the length of the spacer while the observed behaviour of the TP(*n*CB)₆ series implies such pronounced shape changes do not occur for these oligomers.

The nematic phase exhibited by TP(10CB)₆ was studied using X-ray diffraction† and a typical diffraction pattern obtained for a magnetically aligned nematic sample is shown in Fig. 3. The pattern is characteristic of a discotic nematic phase. The sharp small angle peak indicates the presence of local columnar-like orientational fluctuations within the nematic phase and corresponds to a spacing or intercolumnar distance of about 32 Å. The calculated disc diameter is *ca.* 56 Å assuming the alkyl chains are in extended all *trans* conformations. This implies that the side chains are essentially fully interdigitated. The simple diffraction pattern also suggests that all the aromatic rings, including the core triphenylene disc and the 4-cyanobiphenyl units in the tails, lie in

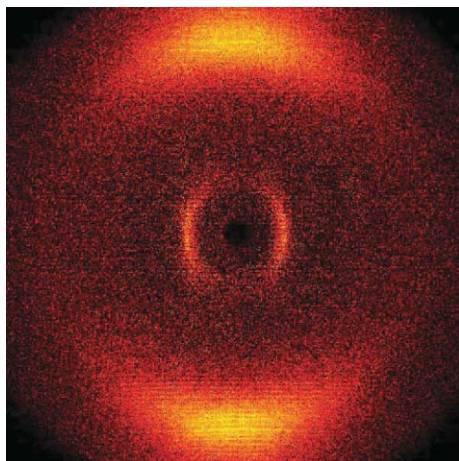


Fig. 3 X-ray diffraction pattern of an aligned nematic phase of TP(10CB)₆ (90 °C); the magnetic field direction is along the equator.

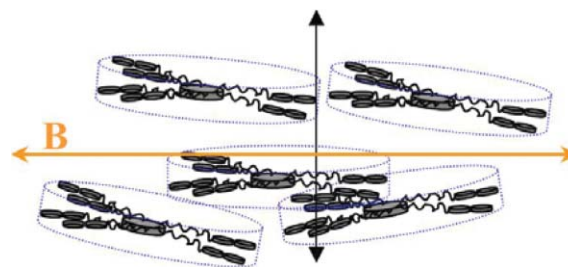


Fig. 4 Schematic representation of the local molecular arrangement in the nematic phase.

the same plane forming a large discotic entity (Fig. 4). Thus the aligned N_D diffraction pattern suggests that the overall molecular geometry in the nematic phase is disc-like, and even the presence of the six 4-cyanobiphenyl groups in the tails has not given rise to a more rod-like geometry.

As the temperature is increased in the discotic nematic phase, a remarkable shift to smaller angles is observed in the interdisc spacing. This indicates that the interdisc spacing increases, which we believe is caused by the thermal motion and increasing disorder of the calamitic 4-cyanobiphenyl tails. This shift is not normally observed in columnar discotic phases. To keep the overall density constant, the intercolumnar distance has to compensate for this change by shifting to higher angles, *i.e.* smaller distances (Fig. 5 and 6). Thus, on increasing temperature the discs are becoming thicker due to the increased fluctuations of the 4-cyanobiphenyl moieties and therefore, less wide. We should note that the apparent peak at about 27° in the X-ray diffraction profiles (Fig. 5) is in fact an artefact. If one draws a baseline at 10–12° 2-theta, this coincides with the level at about 24–25°. The “shoulder” at 27° is due to the integration procedure because at wide angles some parts of the signal are outside the detector grid (see Fig. 3).

The combination of rod–disc-like moieties in the TP(*n*CB)₆ series has not sufficiently perturbed the average molecular shape to yield calamitic mesophases. The average molecular shape is disc-like for these homologues. It is noteworthy, however, that these compounds show the widest temperature range discotic nematic phases yet to be reported in the literature and columnar mesophases are not observed. This indicates that although the rod-like units in the tail have not significantly changed the overall shape, their thermal and orientational fluctuations inhibit the molecular packing required to observe columnar mesophases.

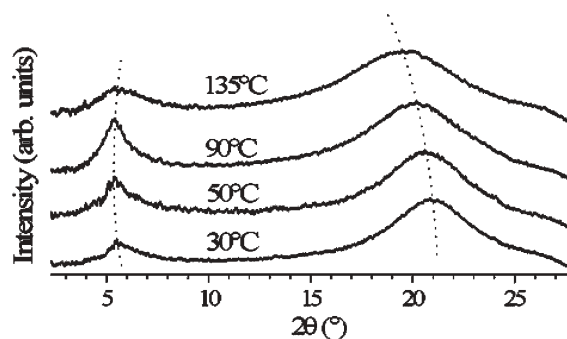


Fig. 5 X-ray diffraction profiles for TP(10CB)₆.

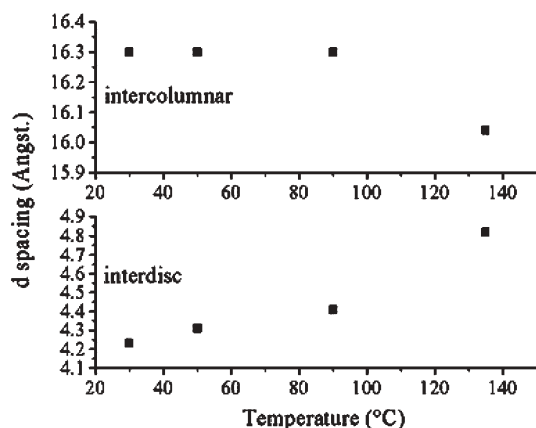


Fig. 6 Intercolumnar and interdisc spacings for TP(10CB)₆ (120 °C).

These also affect the interdisc spacing in the nematic phase which increases on increasing temperature as well as prevent the crystallisation of the nematic phases and instead stable glassy nematic phases are seen. To our knowledge only two compounds with similar molecular structures have been reported in the literature.^{23,24} Shimizu *et al.*²³ reported a compound containing a triphenylene core attached to which were six azobenzene-based mesogens. In this system the length of the terminal chains on each rod-like mesogen considerably exceeded that of the spacer connecting the rod and disc. Consequently, the interdigitation we observed here between the discs was not possible and only a columnar phase was seen. Rahman *et al.*²⁴ described the properties of a triphenylene-based compound containing six nitroazobenzene units attached *via* hexamethylene spacers. This compound exhibited a nematic phase and the authors considered that the triphenylene moiety acted only as a linking unit connecting the rod-like groups rather than as a disc-like unit which would promote columnar phase formation. By comparison, we have shown that the molecules are indeed disc-like in shape and a discotic nematic phase is formed. Thus, the triphenylene core effectively controls the overall molecular shape and hence the transitional behaviour. It is interesting to note that for other types of structure containing a comparable number of cyanobiphenyl units attached to a central unit, for example, substituted siloxysilanes²⁵ or functionalised fullerenes,²⁶ conventional smectic A phases are seen. This behaviour has been interpreted in terms of the formation of rod-like structures by these supermolecules,²⁷ indicating that the central units in these structures do not control the average molecular shape in the same way as the core triphenylene group in the compounds reported here.

Notes and references

† First, 1,2-di-(ω -bromoalkoxy)benzene was prepared from the reaction of catechol and a large excess of the appropriate α,ω -dibromoalkane (5–10 fold) with potassium carbonate in refluxing acetone overnight. The product was trimerised using ferric chloride in dichloromethane to give hexakis(ω -bromoalkoxy)triphenylene in around 20% yield, which was reacted with 4-hydroxy-4'-biphenylcarbonitrile in the presence of potassium carbonate in refluxing acetone to give the expected product.

TP(10CB)₆: ¹H-NMR (in CDCl₃): 7.82 (s, 6H, ArH from triphenylene), 7.62 (dd, 24H, ArH from biphenyl, J = 8.8 Hz), 7.48 (d, 12H, ArH from biphenyl, J = 8.8 Hz), 6.94 (d, 12H, ArH from biphenyl, J = 8.8 Hz), 4.21 (t, 12H, ArOCH₂, J = 6.4 Hz), 3.96 (t, 12H, ArOCH₂, J = 6.4 Hz), 1.93 (m, 12H, CH₂), 1.78 (m, 12H, CH₂), 1.70–1.25 (m, 72H, CH₂).

‡ The samples were analysed with an X-ray diffractometer D8-Discover from Bruker-nonius with a GADDS 2-D detector. A high strength magnetic field of about 4 T is applied using NdFeB permanent magnets with focussing polecaps. The temperature of the sample in a standard glass 0.7 mm X-ray capillary is controlled using a small graphite tube heating element which is mounted between the polecaps of the magnet (10 mK stability, 20–350 °C range, >100 K min⁻¹ heating and cooling rate).

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