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PRELIMINARY COMMUNICATION

Synthesis and characterisation of novel rod–disc oligomers

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Microwave-promoted synthesis of novel rufigallol-based liquid crystalline oligomers, containing six rod-like cyanobiphenyl moieties connected to the rufigallol core via flexible alkyl spacers, is reported. The synthesis of the target compounds was challenging since classical reactions failed to produce these oligomers. Differential scanning calorimetry and polarising optical microscopy analysis revealed the existence of a nematic phase with a shorter spacer and a smectic A (SmA) phase with a longer spacer. The compound with medium alkyl spacer exhibits both nematic and SmA phases at higher temperature and a re-entrant nematic phase at lower temperature.

Keywords: rod–disc oligomer; rufigallol-based oligomer; biaxial nematic

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*), where the unique axes of the molecules are arranged not only in a common direction (known as the director) but also there is a correlation of the molecules in a direction perpendicular to the director. The hunt for this new liquid crystal phase began more than 30 years ago, when it was recognised that the molecules forming liquid crystals deviate from their presumed cylindrical shape (*3*). In fact, the molecules are more lozenge-like, and it is because of this lowering of the molecular symmetry that two nematic phases should be possible. Indeed, the first claimed discovery of a biaxial nematic (*4*) was for a compound formed of spoon-like molecules, and similar claims soon followed for cross-shaped (*5*) and bone-shaped (*6*) molecules. Till now, there have been many claims (*7, 8*) 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. Recently, a biaxial nematic phase was reported in bent-core thermotropic mesogens (*9*).

Theoretical studies and mean field calculations (*10*) have shown that the biaxial nematic phase (N_b) is obtained by changing a shape biaxiality parameter (η) between a rod at one extreme ($\eta=0$) and a disc ($\eta=1$) at the other. The N_b phase exists over ranges such as $0.2 \leqslant \eta \leqslant 0.8$, but is most stable at $\eta=0.4$. Such a structure is then properly intermediate between a rod and a disc, and this led to proposals that the N_b phase might be realised in rod/disc mixtures. 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. This idea was investigated in theoretical approaches to the biaxial nematic phase formed from binary mixtures of rod- and disc-like molecules (*11*). The situation with respect to physical mixtures is not so straightforward because a mixture of rods and disc should (*12*), and indeed does (*13*), separate into two uniaxial nematic phases, one rich in rods and the other rich in discs. However, theoretical work by Sharma *et al.* (*14*) and by Vanakaras *et al.* (*15*) has shown that rod/disc mixtures can lead to N_b phases if the rod and disc are attracted more to one another than to each other.

One way to overcome this problem is to attach rod-like and disc-like units covalently via flexible alkyl spacers, so that they can not phase separate. The reported molecular systems are the interconnection between a rod and a disc and such dimers have recently been the subject of computer simulation study (*16*). For example, Fletcher and Luckhurst synthesised the first rod–disc dimers by joining together the disc-shaped pentakis(4-pentylphenylethynyl)benzene and the rod-shaped 4-cyanobiphenyl moieties through an ether linkage (*17*). Bruce and co-workers (*18*) examined the molecular biaxiality of systems containing a pentyne disc joined to lateral rod-like molecules. Mehl and co-workers (*19*) studied the miscibility of disc- and rod-shaped mesogens in the nematic phase. They also investigated multiple levels of order with nematic and several smectic phases in a material containing disc- and rod-like

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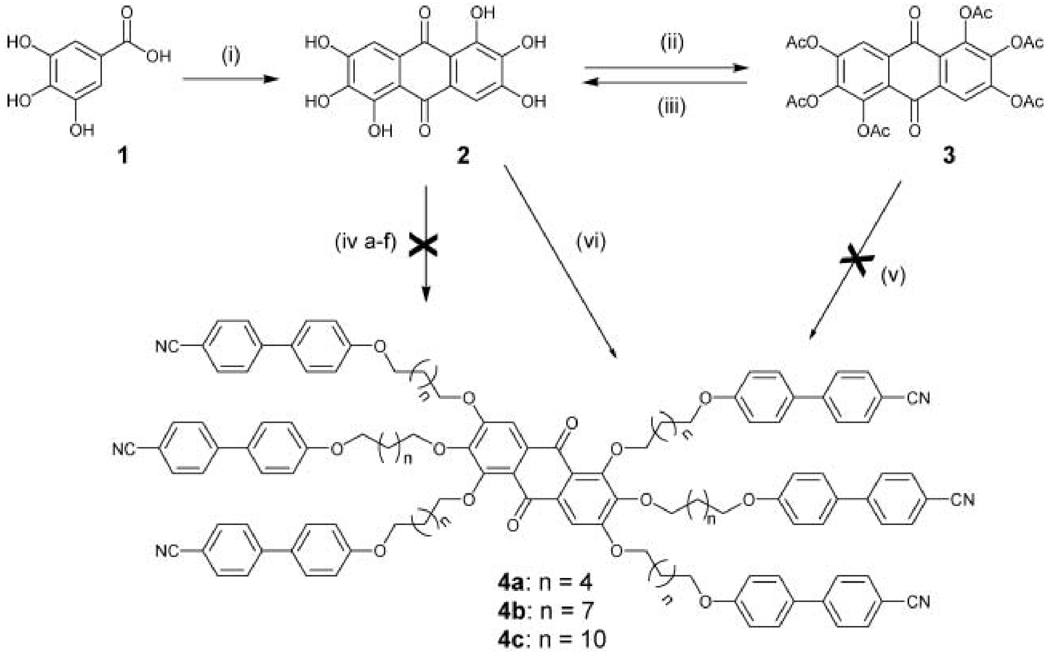
mesogenic units (*20*). Recently, a disc-shaped triphenylene moiety attached with three cyanobiphenyl units has been reported (*21*) to form a thermodynamically stable layered phase.

In the molecular systems described above, one, two or three rods have been attached to a single disc-like molecule. We have extended this approach and present here the synthesis and characterisation of three novel molecules in which six rod-like 4-cyanobiphenyl moieties are attached to a central rufigallol core via flexible alkyl spacers. The rufigallol core was chosen because it is an elongated molecule with twofold symmetry. It is known to promote liquid crystalline behaviour in a wide range of molecular architectures and has a very versatile synthetic chemistry (*22*). Its several derivatives are known to display optically biaxial phases (*23*). Therefore, the attachment of cyanobiphenyl groups around the periphery may lead to biaxial nematic phases.

The synthesis of rufigallol-based rod–disc mesogenic oligomers is outlined in Scheme 1. Rufigallol **2** was prepared from gallic acid **1** in 98% H_2SO_4 using microwave heating, as reported by us recently (*24*). Purification of rufigallol was achieved by centrifuging the crude product followed by acetylation of the dried product in acidic conditions. The hexaacetate **3** was obtained in 60% yield. Hydrolysis of the pure hexaacetate **3** furnished pure rufigallol **2**. Liquid crystalline rod–disc oligomers **4** were obtained by reacting pure rufigallol **2** with bromo-terminated alkoxycyanobiphenyl in the presence of caesium carbonate under microwave heating (360 W) for 10 min (30 s × 20). It should be noted that the same reaction conditions under conventional heating, as well as other classical reaction conditions like reflux in DMF, DMSO, acetone, using different reactivities of bases for a period of 24–170 h, did not produce any desired product. Similarly, corresponding hexaacetate **3** under classical thermal conditions failed to produce any product. It is worth mentioning that the use of microwave heating in the synthesis of liquid crystalline materials has attracted a considerable amount of attention recently (*25*). Since the synthetic details for the preparation of rod–disc hexamers for different chain lengths are practically the same, only the procedure for **4a** is described (*26*). Spectral data and elemental analysis of all the compounds were in good agreement with their structures (*27*).

The phase transition temperatures of all the new compounds, together with transition enthalpy values determined by differential scanning calorimetry (DSC) are shown in Table 1. The transition temperatures and associated enthalpy values were determined by DSC at a scanning rate 5°C min^{-1} both on heating and cooling. The textural observations of the



Scheme 1. Synthesis of rufigallol-based rod–disc mesogens. Reagents and conditions: (i) H_2SO_4, MW, 90 s; (ii) Ac_2O, pyridine, reflux, 12 h; (iii) EtOH, 5% aq. NaOH, reflux, 2 h; (iv) a: NaOH, DMSO, RBr, 160°C, 24 h; b: KOH, DMSO, RBr, 160°C, 24 h; c: Cs_2CO_3, DMF, RBr, 160°C, 7 days; d: K_2CO_3, DMF, RBr, 160°C, 3 days; e: Cs_2CO_3, acetone, RBr, 160°C, 3 days; f: K_2CO_3, acetone, RBr, 160°C, 3 days; (v) DMF, Na_2CO_3, RBr, 160°C, 8–48 h; (vi) NMP, Cs_2CO_3, MW (360 W), RBr, 10 min.

Table 1. Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ mol^{-1}, in parentheses) of rufigallol-based rod–disc mesogens.

Compound	Heating scan	Cooling scan
4a	Cr 183 (126) I	I 126 (7) N 148 (88) Cr
4b	Cr 94 (81) SmA 116^{a} N 125 (7) I	I 124 (7) N 110^{a} SmA 79^{a} N
4c	Cr$_1$ 85 (27) Cr$_2$ 115 (49) Cr 143 (141) I	I 130 (24) SmA 82 (49) Cr

[a] From POM; Cr=crystalline phase; SmA=smectic A phase; N=nematic phase; I=isotropic phase.

mesophase were carried out using polarising optical microscopy (POM) together with a heating stage and a central processor.

The first compound of the series, **4a**, exhibited only a monotropic nematic phase. It melted at 183°C to the isotropic phase. However, on cooling the nematic phase appeared at 176°C and then crystallised at 148°C. Under the microscope it displayed a typical schlieren texture of a nematic phase, as shown in Figure 1(a). Compound **4b** on heating melted at about 94°C to a smectic A (SmA) phase, which transformed to a nematic phase at 116°C and finally cleared at 125°C. However, the transition from SmA to nematic phase was not discernable by DSC. On cooling, it showed an isotropic (I) to nematic (N) transition at 124°C. Although its DSC traces showed

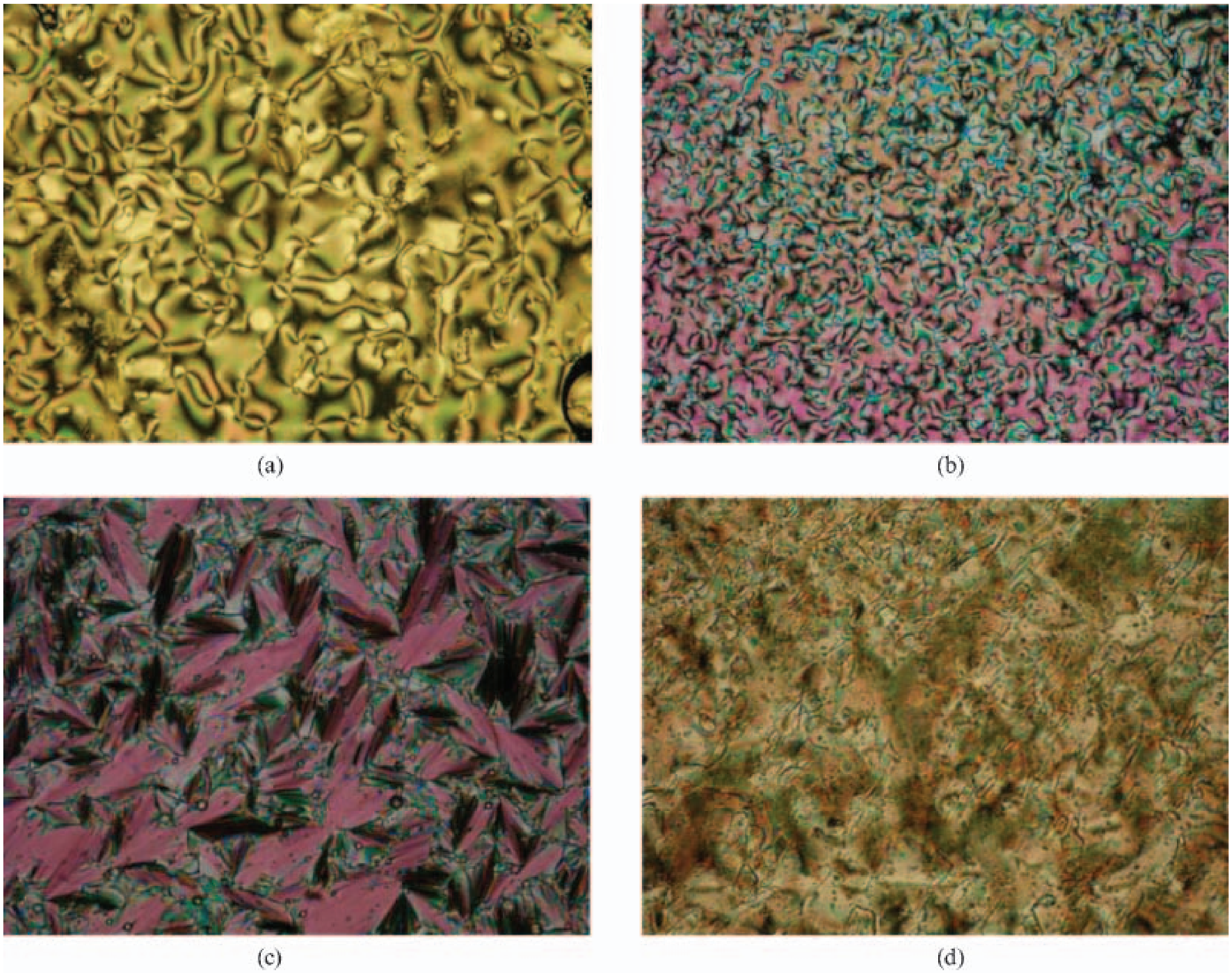


Figure 1. (a) Optical photomicrograph of the nematic (N) phase of compound **4a** obtained with a polarising microscope on cooling from the isotropic liquid at 170°C; (b) texture obtained on cooling the isotropic liquid of compound **4b** at 120°C; (c) focal-conic fan textures of SmA phase obtained on slow cooling the isotropic liquid of **4b** at 100°C; (d) photomicrograph of re-entrant N phase obtained on cooling the isotropic liquid of compound **4b** at 70°C (crossed polarisers, magnification × 200 for all photomicrographs).

one single I–N transition, POM revealed two other second-order transitions. The appearance of a SmA phase at 110°C and a re-entrant nematic phase at 79°C can be clearly seen by POM. The photomicrographs of the nematic, SmA and re-entrant nematic phases are shown in Figures 1(b)–1(d). X-ray studies confirmed that the higher temperature nematic as a classical uniaxial nematic phase. The X-ray diffraction pattern of the lower temperature nematic was slightly different than the higher temperature nematic. Detailed X-ray studies to characterise these mesophases are in progress and will be reported in due course. Compound **4c**, having a longer spacer, exhibited only a monotropic SmA phase. On heating, it melted at 143°C to the isotropic phase. Before melting it displayed two crystal to crystal transitions at about 85°C and 115°C. On cooling, the SmA phase appeared at 130°C and then crystallised at about 82°C.

In conclusion, the combination of rod- and disc-like moieties in the rufigallol–cyanobiphenyl series has sufficiently perturbed the average molecular shape to yield calamitic mesophases. The average molecular shape is not disc-like in these homologues. It indicates that rod-like units in the tail have significantly changed the overall shape so that their thermal and orientational fluctuations inhibit the molecular packing required to observe the columnar mesophase. To our knowledge only three compounds have been reported where six rod-like moieties have been attached to a discotic core. Shimizu *et al.* (*28*) reported a compound containing a triphenylene core to which six azobenzene-based mesogens were attached. 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. Rahman *et al.* (*29*) 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 a disc-like unit that would promote columnar phase formation. Imrie *et al.* (*30*) recently reported oligomeric discotic nematic liquid crystals consisting of a triphenylene core to which six cyanibiphenyl units were attached via flexible alkyl spacers. By comparison, we have shown that the molecules are indeed rod-like in shape although they are derived from well known rufigallol discotic core. This behaviour has been interpreted in terms of the formation of rod-like structures by these supermolecules (*31*) indicating that the central units in these structures do not control the average molecular shape. Similar behaviour has been observed with comparable number of cyanobiphenyl units attached to a central unit for example substituted siloxysilanes (*32*) or functionalised fullerenes (*33*). The two nematic phases observed in compound **4b** are very interesting, particularly the re-entrant nematic phase that occurs at lower temperatures. Detailed X-ray studies to characterise these mesophases are in progress.

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(26) Synthesis of **4a**: in a typical reaction, **2** (100 mg, 0.32 mmol), 4′-[(6-bromohexyl)oxy]-1,1′-biphenyl-4-carbonitrile (1.4 g, 3.9 mol), Cs_2CO_3 (1.3 g, 3.9 mol) were mixed in a small glass vial and loosely covered with a rubber septum. The mixture was heated in an unmodified household microwave oven at 360 W for 10 min (30 s × 20). The vial was taken out and water (10 ml) was added. Then the mixture was extracted with dichloromethane (3 × 10 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The residue was then passed through a small column chromatography using 1:1 dichloromethane/petroleum ether as an eluent to afford **4a** (300 × mg, 46%).

(27) Selected data for compound **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): 7.69 (d, J=8.2 Hz, 12H), 7.65 (d, J=8.2 Hz, 12H), 7.59(s, 2H), 7.45 (d, J=8.6 Hz, 12H), 6.95 (d, J=8.6 Hz, 12H), 3.95–4.25 (m, 24H), 1.4–2.1 (m, 48H). IR (KBr, all the derivatives **4a–4c** showed similar spectra, v_{max}/cm^{-1}): 2939, 2221, 1660, 1602, 1568, 1494, 1315, 1290, 1178, 1128,997, 821. UV–visible ($CHCl_3$, all the derivatives **4a–4c** showed similar spectra): λ_{max} 300 nm. Elemental analysis: calculated for $C_{128}H_{122}N_6O_{14}$, C 78.10, H 6.25, N 4.24%; found, C 77.99, H 6.01, N 4.15%.

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