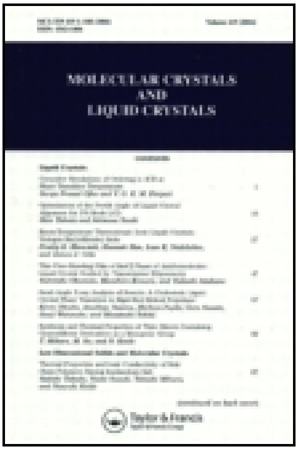

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Discotic Multipodes with Nematic Mesophases

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DISCOTIC MULTIPODES WITH NEMATIC MESOPHASES

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Various core materials have been introduced at the terminal end of a discotic mesogen (based on a pentakis(methylphenylethynyl) phenoxy core), resulting in the formation of liquid crystalline 'monomers' and 'dimers.' The mesomorphic properties of this series of derivatives were investigated as a function of the attached core material. It is shown that the clearing temperatures of the mesogens are dependent on: (i) the fraction of rigid mesogen, (ii) the presence of any linkages between the mesogens and (iii) the presence of any H-bonding interactions. In some materials extra stabilisation of the phase or, indeed, higher ordered mesophases were observed due to the end-group interactions. In addition, we report the investigations to prepare DAB-Am based dendrimers.

Keywords: dendrimer; dimer; discotic; liquid crystals; mesogen; mesomorphic properties

INTRODUCTION

One of the major steps forward in research on discotic liquid crystals [1] was made when well-defined mono-functional materials were obtained [2]. Derivatisation at the terminal end of a single functional spacer of the usually highly symmetric mesogens allowed the preparation of new materials – with new liquid crystalline properties – without the synthesis of new mesogens. Well-known examples include side-chain polymers, wherein the crystallisation process is fully suppressed, resulting in materials with broad

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*Corresponding author. Fax: +44 1482 466411, E-mail: g.h.mehl@hull.ac.uk mesophases, often still at room temperature. Disadvantages of the use of side-chain polymers are their intrinsic high viscosity and the ill-defined chemical structure. Alternatively, multipodes can be used, which are built op from a well-defined core, substituted with a known number of mesogens, giving rise to the formation of dimers, trimers, up to heptamers. In addition, the core can be selected to introduce special chemical properties. Dendrimers can be considered as a special group of multipodes, which show a low viscosity as well as suppression of crystallisation due to a sufficient molecular weight, combining the advantages of multipodes and polymers. Furthermore, interesting properties are expected from dendrimers with substituted discotics, since in the corresponding materials with rod-shaped end-groups remarkable behaviour has been observed as a function of the generation number [3]. As far as we know, no attempts have been made to attach disc-shaped mesogens to dendrimers in order to investigate the role of the dendritic core on the phase behaviour of discotics.

Here, we present the synthesis of mesogen with a pentakis(methylphenylethynyl) phenoxy core and equipped with a carboxylic acid group **1**, see Figure 1.

The carboxylic group at the terminal end of the spacer has been used to introduce various end-groups with different functionalities. By using bi-functional spacers, the corresponding dimers have been obtained. The mesomorphic properties of the monomers and dimers are mutually compared and the phase transitions are explained in terms of the fraction of rigid mesogen and other stabilising effects, occurring from the various end-groups and spacers. In addition, we were interested in coupling this mesogen to a series of dendrimers, which would result in new materials with a fascinating phase behaviour could be obtained, particularly, since the side chain polymers of this mesogen showed both the N_D and the N_{Col} phase [4]. Attempts to synthesise these systems are discussed.

RESULTS AND DISCUSSION

Synthesis of the Mesogens

The synthesis of the mesogen with the carboxylic end-group is outlined in Scheme 1. Pentabromophenol is substituted with a spacer containing a terminal protected carboxylic moiety [5a]. A five-fold palladium catalysed cross-coupling reacting with 4-ethynyltoluene [4a,5b], followed by a deprotection under basic conditions affords the mesogen in reasonable yields. Ester derivatives of **1** were prepared under standard esterification conditions (DCC or DIC, DMAP, *p*TSA). To prepare the dimers a slight excess of mesogen was employed. Amides were prepared from the corresponding pentafluorophenyl esters.

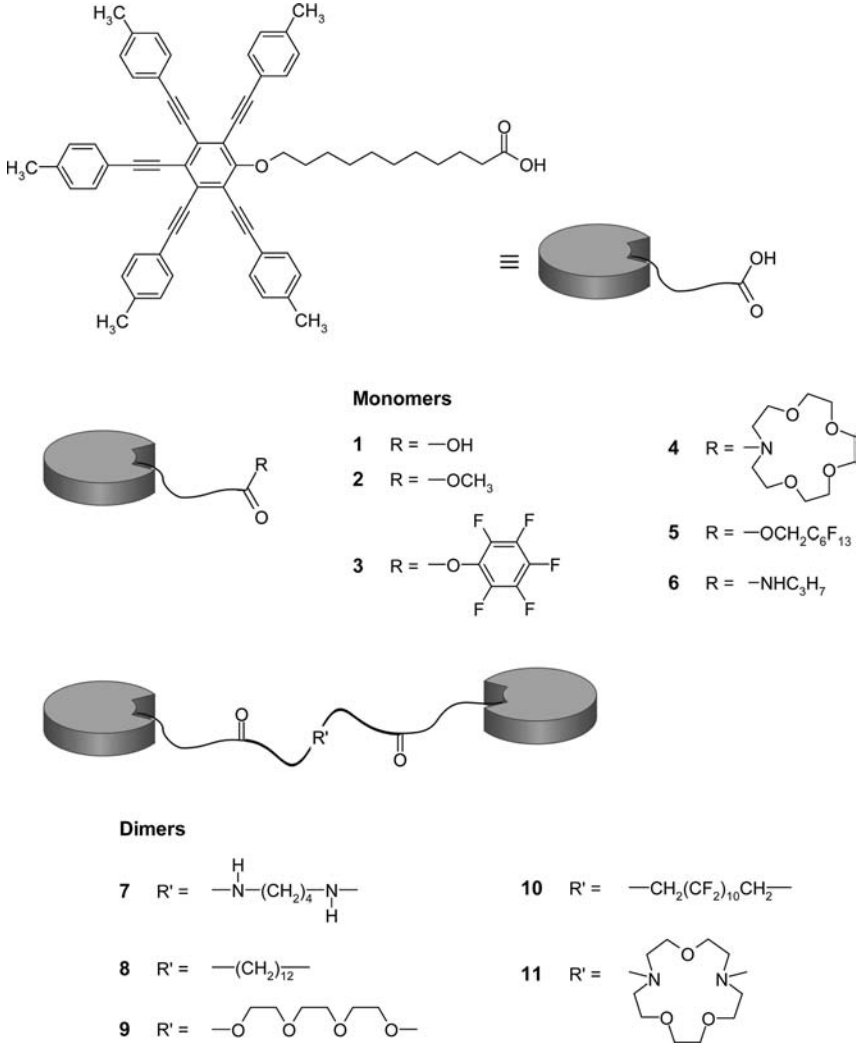
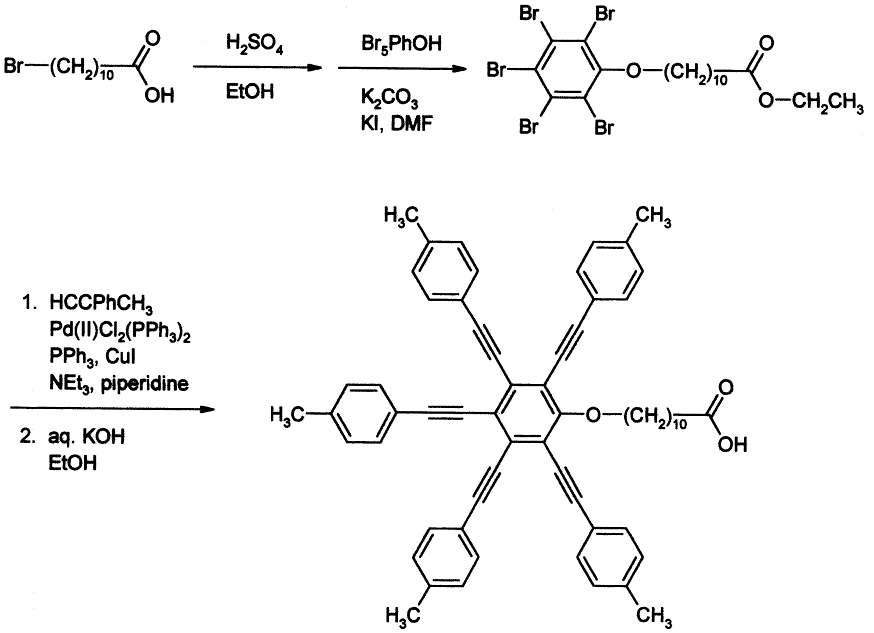


FIGURE 1 Structure of the investigated materials.

Synthesis of the Dimers

Some dimers with varying spacers were synthesised to study the effect of the nature of the core. They were prepared from a straightforward esterification reaction from **1** with the commercially available alcohol-terminated spacers, see Scheme 3. Diisopropyl carbodiimide (DIC) was used as coupling agent, since it is slightly more reactive than the standard



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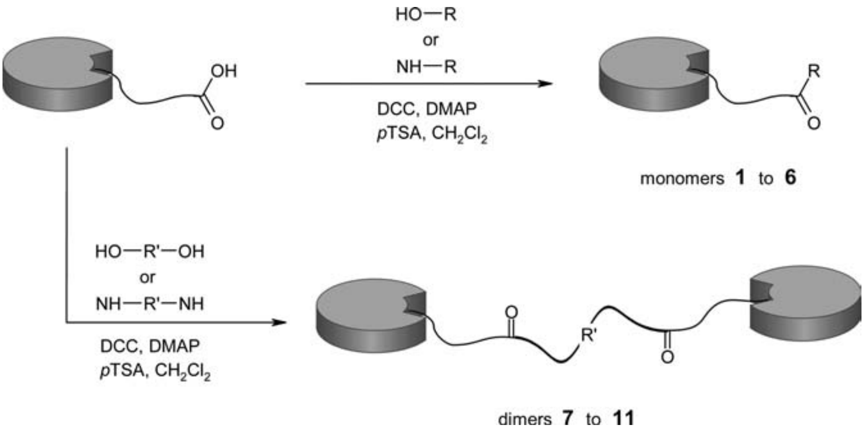
SCHEME 1 Synthesis of the mesogen with a carboxylic acid functional group.

dicyclohexyl carbodiimide (DCC). after the work-up (column chromatography), the mesogen were obtained in rather good yields.

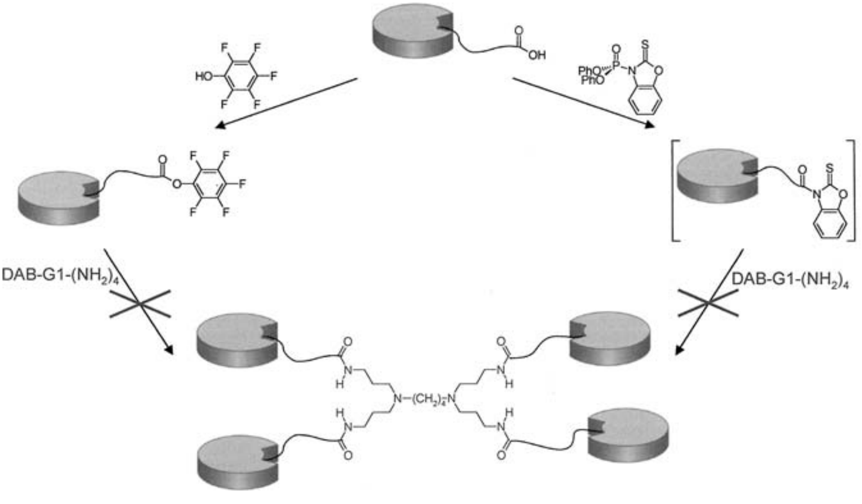
Attempted Synthesis of the Dendrimers

To attach the mesogens to the dendritic cores, the pentafluorophenyl ester was stirred with commercially available polypropylenimine (DAB-Am) dendrimers of the first and second generation (see Scheme 2), according to literature procedures [6a]. Although stirring was continued for 3 to 10 days, it has been impossible to isolate a fraction with solely four (first generation) amide groups. Instead GPC experiments indicated an inseparable mixture of components with an average degree of substitution of about three mesogens. Another approach employed the use of a diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate activator [6b], prepared from 2-benzoxazolethiol and phosphorochloridate. The activated ester was formed *in-situ* by reacting **1** with an excess of activator. Surprisingly, subsequent addition of the dendrimer did not result in fully substituted dendrimers either.



SCHEME 2 Synthesis of the monomers **1-6** and dimers **7-11**.

We believe that the lack of complete substitution is likely to be caused by the limited solubility of the intermediate products in the reaction mixture. This might be due to the combination of the amide groups forming hydrogen bonds and the strong aromatic character of the mesogens that is lacking multiple flexible tails. Therefore, future research will focus on



SCHEME 3 Schematic representation of the attempted substitution of the mesogen to the first generation (DAP-Am-4) dendrimer.

the use of mesogens with flexible tails laterally attached to the mesogen as well as other methods to attach the mesogens to the dendritic core.

Liquid Crystalline Properties

The liquid crystalline properties of the mesogens were investigated by differential scanning calorimetry (DSC), optical polarising microscopy (OPM) and X-ray diffraction (XRD). All materials exhibit the nematic discotic phase at high temperatures, easily characterised by their characteristic optical textures. Their phase behaviour is summarised in Tables 1 and 2.

Rigid Mesogen Fraction

Various factors that are responsible for diversity in the phase behaviour can be enumerated: (*i*) the dilution the fraction rigid mesogen (*ii*) the reduction of the mobility of the mesogens by a chemical linkage and (*iii*) the introduction of specific stabilising intermolecular interactions, such as hydrogen bonding.

It has been shown that, for a series of side chain polymers with methyl-substituted mesogens attached, the clearing temperature T_{NI} shows a virtually linear dependence with the rigid mesogen fraction [M] [7]. We have calculated the rigid mesogen fraction for all derivatives of **1** (see Tables 1 and 2) and drawn them in a master phase diagram, see Figure 2. Mutual comparison of the materials gives insight into the various interactions between the mesogens and/or the end-groups or spacers.

The phase diagram clearly shows the strong dependence of the clearing temperature with the rigid mesogen fraction. In addition, the stabilising effects of hydrogen bonding as well as chemically linking the mesogens

TABLE 1 Liquid Crystalline Properties of the Mesogens

	Endgroup –R	Phase behaviour[a]					[M]/%-wt[b]
1	–OH	Cr	187	N	244	I	78.2
2	$-OCH_3$	Cr	167	N	201	I	76.7
3	$-OPhF_5$	Cr	150	N	196	I	65.4
4	–(aza-5-crown-15)–	Cr	151			I	62.4
5	$-CH_2C_6F_{13}$	Cr	165	N	176	I	56.2
6	$-NH(CH_2)_2CH_3$	Cr	168	N	189	I	74.6
7	$-[NHCH_2CH_2]_2-$	Cr	202	N	230	I	75.9

[a] Transition temperatures in [°C], K = crystalline, N = nematic, I = isotropic.
[b] [M] is the mesogen weight fraction.

TABLE 2 Liquid Crystalline Properties of the Dimers

	Spacer –R′–	Phase behaviour[a]					[M]/%-wt[b]
8	$-O(CH_2)_{12}O-$	Cr	159	N	180	I	71.2
9	$-OCH_2CH_2(OCH_2CH_2)_2O-$	Cr	167	N	197	I	71.5
10	$-OCH_2(CF_2)_{10}CH_2O-$	Cr	166	N	196	I	59.7
11	–(diaza-5-crown-15)–	Cr	158	N	172	I	70.6

[a] Transition temperatures in [°C], K = crystalline, N = nematic (discotic), I = isotropic.
[b] [M] is the mesogen weight fraction.

can be observed [8]. Interestingly, while the clearing temperature shows a nearly linear dependence with [M] the melting temperature is for all materials rather constant (apart from the materials with strong H-bonding, the T_m's are between 150 and 170°C). This explains why materials with a too low rigid mesogen fraction (such as the mono-crownether **4**) show no

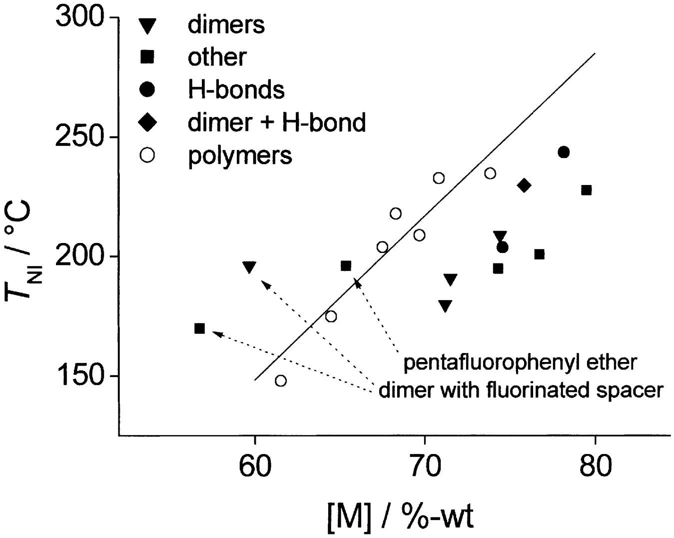


FIGURE 2 Clearing temperature T_{NI} of the studied mesogens as a function of the rigid mesogen fraction [M]. The solid symbols the mesogens discussed in this contribution: dimers (triangles); strong H-bonding groups (solid circles); strong H-bonding dimers (diamond) and other (squares). Note that some compounds based on the same mesogen with an undecanol spacer, have been added to the diagram [4]. The open symbols represent a series of side chain polymers bearing the same mesogen [4]. The solid line represents the nearly linear dependence of the clearing temperature of the polymers with the rigid mesogen fraction [M]: $T_{NI} = 695{\cdot}[M]^{0.98}$, obtained after fitting the phase diagram [7].

mesophase behaviour. The corresponding dimer with an increased [M] by attaching two mesogens per crown ether unit, shows again the nematic phase. It was anticipated that by the introduction of metal ions in the crown ethers, the mesophase could be stabilised. However, we observed a destabilisation of the nematic phase and a slight stabilisation of the crystalline phase, resulting in a loss of the liquid crystalline properties: **11**:Na^+Tf^- complexe (1:1):K 161 I. No mesophase could be induced by complexing **4** with one equivalent of Na^+Tf^-: **4**:Na^+Tf^- complexe (1:1):K 135 I.

Two materials show anomalous behaviour, indicating a strong stabilising effect. For the pentafluorophenyl ester **3** stabilising quadrupolar interactions are believed to increase the clearing temperature [9]. The largest deviation, observed for the dimer with the fluorinated spacer **8**, is most probably due to microphase separation.

It is stressed that only after constructing the phase diagram, shown in Figure 2, we realised that nematic mesophase was stabilised because of specific interactions, in particular the nanophase separation process in the fluoroalkyl-substituted materials. Note that these materials (**5** and **10**) have similar mesophases and phase transitions to all other materials and are therefore not easily selected as the odd ones out. With Figure 2 so clearly indicating mesophase stabilisation, we performed X-ray diffraction to look for any higher extent in order.

X-ray Diffraction

The dimers with the alkyl and glycol spacers (**8** and **9**) show the expected diffraction patterns of the nematic (discotic) phase: two (weakly aligned) diffuse reflections of the disc-dimensions and one (non-aligned) diffuse reflection of the alkyl tails, see Figure 3 and Table 3. The pattern of the dimer with the fluorinated spacer **10** looks quit different. The sample is better aligned and shows in the small angle area an extra reflection of at 34 Å.

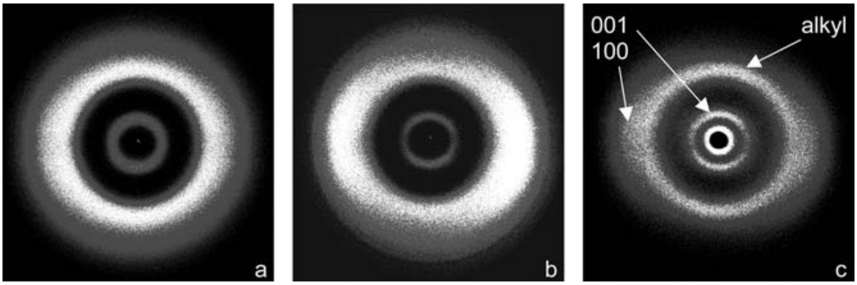


FIGURE 3 Two-dimensional X-ray diffraction pattern of the dimers: (a) dimer **8**, alkyl spacer; (b) dimer **9**, glycol spacer and (c) dimer **10**, fluorinated spacer.

TABLE 3 Results of the X-ray Diffraction Measurements of the Dimers **8–10**

Dimer	$T/°C$	Phase	$d_{100}/Å$	$d_{001}/Å$	$d_{\mathrm{alkyl}}/Å$
8	175	N	15.7	4.2	5.3
9	175	N	15.4	4.2	5.2
10[a]	175	N	14.2	4.0	5.2

[a] The fluorinated dimer **10** shows an extra reflection at $d = 34.2$ Å.

Although the assignment of this extra reflection is at present not completely clear, it clearly indicates an increased order, even stronger pointed out by the high correlation length of this reflection: $\xi = 255$ Å [10]. This is in good agreement with the stabilisation of the nematic phase, observed in the phase diagram in Figure 3. Similarly, the corresponding 'monomer' 5 showed a sharper small angle reflection at similar angels. these interesting materials are currently under detailed investigation.

CONCLUSIONS

We have synthesised a disc-shaped and carboxylic acid-functionalised mesogen. Several attempts to attach the mesogen to commercially available DAB-Am dendrimers did not afford the desired products, presumably due to the limited solubility of the intermediate products. The mesogen has been attached to a series of end-groups, of which some were bi-functional, resulting in dimeric species. All members of this series of mesogens display the nematic discotic phase at high temperatures. The clearing temperatures of the individual materials could be well understood by taking into account: (*i*) their fraction of rigid mesogen, (*ii*) the presence of any linkages between the mesogens and (*iii*) the presence of any non-covalent interactions. We would like to stress the large value of constructing a phase diagram as shown in Figure 2 in comparing a series of derivatives in order to easily select 'exceptional' materials. Special cases of stabilisation of the nematic phase were observed for **3** (caused by quadrupolar interactions) and **5** and **10** (caused by microphase segregation). Detailed investigation of the latter is still in progress.

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(b) The rigid mesogen fraction is defined as the weight fraction of the rigid (aromatic) part of the mesogen. In this specific mesogens, the peripheral methyl groups are included in the rigid part of the molecule.

[8] Note that the clearing temperatures of the polymer samples are all slightly higher because of the far-reaching degree of linking the mesogens.

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[10] The correlation length of a reflection is determined from the width (at half maximum) from the radially integrated diffraction pattern with the Scherrer equation. It is a measure for the extent of positional order in the material. Typical values, measured for these mesogens in the N_D phase are: $\xi_{100} = 50\,\text{Å}$, $\xi_{001} = 12\,\text{Å}$ and $\xi_{\text{alkyl}} = 10\,\text{Å}$.