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Tuning the mesomorphic properties of liquid-crystalline dibenzotetraaza[14]annulenes — discotic nematic phases of tetraalkoxy-substituted derivatives

Jarosław Grolik, Łukasz Dudek, Julita Eilmes*

Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

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ABSTRACT

A homologous series of five tetrasubstituted dibenzotetraaza[14]annulene-based discotic mesogens was prepared and studied using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). A nematic phase was identified for the product bearing two peripheral isobutoxy and two dode-cyloxy substituents.

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The majority of interest in discotic liquid crystals is due to the unique physical properties exhibited by their columnar mesophases. For example, the one-dimensional charge and energy transport abilities of these materials make them interesting candidates for practical applications in a variety of devices, such as one-dimensional conductors, photoconductors, field effect transistors, and sensors.¹

In recent years, the potential of discotic nematic liquid crystals has been recognized in the field of liquid crystal display (LCD) technology. Due to their more suitable viewing angle characteristics, it has been shown that discotic nematic liquid crystals can be employed instead of the commonly used calamitic nematics.² Alternatively, these discotic nematics can be used in compensation films to improve the viewing angle performance and contrast ratio of conventional twisted angle nematic liquid crystal displays (TNLCD), which are made of calamitic materials.³

However, in contrast to rod-shaped molecules that form calamitic nematic liquid crystals, discotic mesogens rarely exhibit nematic phases. Moreover, nematic mesophases formed by discotic molecules are often characterized by high-temperature phase transitions and narrow mesophase temperature ranges, and therefore are of limited application.

Significant effort has been applied to the search for methods that would allow rational influence of the self-assembly processes

and to control the thermal behavior of the mesomorphic molecular aggregates. A number of papers have been published which show that formation of the nematic assembly, rather than columnar stacking of the discotic molecules, can be achieved effectively by reducing π - π inter-core interactions through careful synthetic control of the size, shape, and flexibility of discotic units.⁴ The number of peripheral side chains, their structures, and their attachment positions to the central core have also been suggested to be important factors in the successful design of discotic nematics.^{2b,4,5}

Although remarkable progress has been achieved in recent years in the design of nematic discogens, few of the known discotic systems display a discotic nematic phase. Among these phases are materials that have been successfully prepared through appropriate structural modifications of typical disc-like cores, such as benzene,^{5,6} triphenylene,^{4,7} naphthalene,⁸ and truxene.⁹ For example, the first room temperature discotic nematic liquid crystals exhibiting wide viewing angle characteristics were prepared based on carefully designed substituted alkynylbenzenes.^{2b} In addition, due to reduced inter-core interactions, peripherally substituted triphenylene dimers appeared to display a nematic mesophase over a wide temperature range.⁴ It has also been found that modification of discotic molecules with appropriate rod-like counterparts results in materials with a stable nematic phase.¹⁰

We recently developed a new discotic liquid crystal based on the dibenzotetraaza[14]annulene (DBTAA) macrocycle bearing two *meso* 2-hydroxybenzoyl substituents and four 3,7-dimethyloctoxy groups attached to *o*-phenylene moieties (Fig. 1).¹¹ The



^{*} Corresponding author. Tel.: +48 12 6632294; fax: +48 12 6340515. *E-mail address:* jeilmes@chemia.uj.edu.pl (J. Eilmes).

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Figure 1. Liquid crystalline dibenzotetraaza[14]annulenes.^{11,12}

optically pure analogues of these materials were also synthesized, and a lamello-columnar mesomorphism with helical organization of the mesophase was assigned to them based on POM, DSC, and small-angle X-ray diffractometry (SA-XRD) supported by molecular dynamics simulations.¹²

In this paper, we describe new DBTAA-based discotics in which four promesogenic 3,7-dimethyloctoxy side chains have been replaced by two isobutoxy and two unbranched *n*-alkoxy groups of varying lengths. A series of five products was prepared (Scheme 1) and the temperature behavior of the compounds was tested using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). We report the first example of a discotic nematic phase in the liquid crystalline derivatives of DBTAA.

The synthetic procedure that we employed was analogous to that described earlier and is based on the condensation of *o*-phenylenediamine with 3-formylchromone to yield *meso*-bis(2-hydroxybenzoyl)dibenzotetraaza[14]annulene.¹³ In the case of the unsymmetrically substituted *o*-phenylenediamines **13–17**, however, the synthesis led to equimolar mixtures of isomers A and B of products **18–22** (Scheme 1). The preparation started with the



Figure 2. Optical textures observed under polarized light microscopy (crossed polarizers): (a) **18** at 180 °C (annealing on heating), magnification $50\times$; (b) **19** at 170 °C (annealing on heating), magnification $20\times$.



Scheme 1. Reagents and conditions: (i) 3,4-dihydro-2*H*-pyran, PPTS, CH₂Cl₂, rt, 3 h, (89%); (ii) 1-bromo-2-methylpropane, K₂CO₃, DMF, 80 °C, 4 h; EtOH, PPTS, 55 °C, 2 h, (67%); (iii) alkyl bromides, K₂CO₃, DMF, 80 °C, 4 h, (81–87%); (iv) CH₂Cl₂/HNO₃, H₂SO₄, rt, 1.5 h, (75–85%); (v) MeOH, 10% Pd/C, NaBH₄; 65 °C, 30 min (vi) MeOH, reflux, 1 h, (66–86%).



Figure 3. Optical textures of **22** observed under polarized light microscopy (crossed polarizers, magnification $20 \times$): (a) at 153 °C (cooling 5 °C/min); (b) at 162 °C (heating 5 °C/min); (c) at 136 °C (cooling 5 °C/min).

protection of one OH group of catechol using 3,4-dihydro-2*H*-pyran and alkylation of the other OH group with 1-bromo-2-methylpropane. In the next step, the phenolic OH was deprotected and was subsequently alkylated with the appropriate alkyl bromide $CH_3(CH_2)_nBr$ (n = 3,5,7,9, and 11) to yield the dialkylated catechols **3–7**. The dinitro derivatives **8–12** were synthesized according to the general procedure reported earlier,¹⁴ and were subsequently reduced using NaBH₄/methanol in the presence of 10% Pd/C. Next, diamines **13–17** were condensed with 3-formylchromone to give the final products **18–22** in reasonable yields of 66–86%. The new products **3–12** and **18–22** were fully characterized by IR, ¹H, and ¹³C NMR spectroscopy, mass spectra, and elemental analyses. Detailed procedures, analytical and spectroscopic characterization of the new compounds are given in the Supplementary data.



Figure 4. (a) Optical texture of **22** observed under polarized light microscopy, at 159.7 °C (crossed polarizers, magnification $20 \times$, cooling 1 °C/min).

Table 1			
Phase transition	temperatures	of compounds	18-22 (DSC data)

Compound	Heating (°C)	Cooling (°C)
18	Cr 184 Col	Col 135 Cr
19	Cr 152 Col	Col 99 Cr
20	Cr 155 Col	Col 73 Cr
21	Cr 149 Col 166 Col	Col 114 Col 92 Cr
22	Cr 157 N 168 I	I 161 N 136 Col 109 Col 85 Cr

Cr- crystal; Col- discotic columnar phase; N- nematic phase; I- isotropic phase.

The thermal behavior of products 18-22 was studied using DSC and POM, and the results were analyzed as a function of the length of the *n*-alkoxy substituent attached *ortho* to the isobutoxy group. The photographs were taken during heating and on slow cooling from the isotropic liquid (in the case of compound **22**), or from the temperature close to decomposition (compounds **18–21**). All samples were found to exhibit liquid crystalline textures under polarized light microscopy. The textures of compounds 18-21 were typical of discotic columnar phases,¹⁵ and representative examples of pseudo focal conic textures are shown in Figure 2a and b. The product with the longest aliphatic side chain (22, n = 11) displayed well-defined schlieren textures typical of discotic nematic mesophases upon both heating and cooling (Fig. 3c and d). In addition, droplets, recognized as highly characteristic of nematic discotic phases¹⁶ were observed in a slightly thicker sample of **22**, immediately below the clearing point (Fig. 4f). The texture shown in Figure 3c contains four-brush defects ($|s| = \pm 1$), whereas that in Figure 3d reveals almost exclusively two-brush disclinations of strength $|s| = \pm \frac{1}{2}$. According to a test of biaxiality of the nematics, as formulated by Chandrasekhar, textures that exhibit only two brush defects, such as that shown in Figure 3d, usually correspond to the biaxial nematic phase N_b¹⁷. Interestingly, the dimensions of the DBTAA macrocyclic core were in good agreement with those reported as optimal for biaxial nematics.¹⁸ According to theoretical predictions, optimal molecular dimensions for the broadest temperature range of the nematic phases corresponded to a lengthto-breadth-to-width ratio (L:B:W) of approximately 5:3:1. Assuming that the average width of the molecules ranges from 3.35 to 3.5 Å,¹² using the above criterion gives 16.75–17.50 Å and 10.05– 10.50 Å for the length and breadth, respectively. These values appear to be in good agreement with the DBTAA core dimensions.¹

It is worth noting that compound **22** shows fairly good thermal stability below the isotropization temperature. On heating, this compound melts at 157 °C to a nematic phase represented by texture (d) (Fig. 3) and clears at approximately 168 °C without

decomposition. In contrast, products **18–21** partially decompose before becoming isotropic liquids, as judged from the results of TLC tests performed on the corresponding samples. On cooling from the isotropic liquid, the nematic phase of **22** appears at 161 °C and crystallizes at 85 °C. At 136 °C, a fan-like texture of the discotic columnar phase was identified using polarizing optical microscopy (Fig. 3e). The phase-transition temperatures of products **18–22**, as determined by means of differential scanning calorimetry, are given in Table 1, and the corresponding DSC traces are collected in the Supplementary data.

In conclusion, by incorporating two isobutoxy and two dodecyloxy substituents into the mesogenic DBTAA core, we have prepared a liquid crystalline material **22** showing a typical discotic nematic phase.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012. 07.053.

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