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# An investigation of the mesogenic properties of dibenzoquinoxaline derivatives

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**Abstract**—The syntheses of two new discotic molecules based on the dibenzoquinoxaline core are reported; comparison of their phase behaviors to a known dinitrile compound demonstrates the importance of specific functional groups in stabilizing columnar mesophases.

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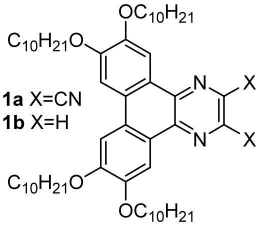
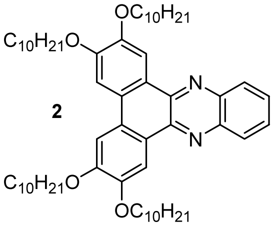
Triphenylene derivatives constitute one of the largest and most important classes of molecules that exhibit columnar liquid crystal phases. Research over the past decade has amply demonstrated the potential that these and related materials have as components in semiconductor devices such as LEDs.[1] A major impediment to the use of triphenylene derivatives in practical applications, however, is the observation that many of these systems exhibit liquid crystallinity over relatively narrow temperature ranges.[2] In this context, the structurally related dibenzoquinoxaline, **1a**, prepared by Ohta and co-workers, is remarkable in that it exists as a $\mathrm{Col_h}$ phase over the range 58–258°C.[3] Although columnar phases of this breadth are not unprecedented, they are generally associated with mesogens possessing much larger aromatic cores.[4–8]



**1a** X=CN
**1b** X=H



**2**

In an effort to probe the remarkable phase stability of this molecule, we have undertaken the synthesis of two analogues, **1b** and **2**. These targets share many distinguishing features of **1a**, including heteroatoms in the core, identical chain lengths and the same symmetry. On the other hand, both molecules lack the strongly electron-withdrawing groups present in Ohta's compound, and all three molecules differ somewhat in size. Thus, it was anticipated that the similarities and differences in the phase behavior of these molecules would provide insight into the relative importance of various factors in providing stable columnar phases.

Our initial synthetic approach to **1b** is outlined in Scheme 1. The tetradecyloxybenzil, **3**, was synthesized in four steps from veratraldehyde according to Wenz's method,[9] and then condensed with ethylene diamine to afford the dihydropyrazine, **4**. This intermediate was readily oxidized by DDQ to afford **5** in 69% yield. Although other oxidants, such as chloranil or ethanolic $FeCl_3$, are also able to carry out this transformation, they do so much less efficiently.

Attempts to oxidatively cyclize this diphenylpyrazine derivative to **1b** using $FeCl_3$ were met with only limited success. Whereas the analogous tetraalkoxy *o*-terphenyl is readily converted to the corresponding triphenylene in the presence of 2–3 equiv. of $FeCl_3$,[10] the reaction of **5** required much more oxidant (up to 20 equiv.) and the addition of catalytic $H_2SO_4$. Under such conditions, the reaction was invariably accompanied by extensive cleavage of the alkyl chains, and we were unable to isolate the desired product from the reaction mixture. It was possible to obtain the desired product directly from the dihydropyrazine precursor, **4**, using $FeCl_3$ and $H_2SO_4$ in dichloromethane, albeit in very low yield. Much better results were achieved, however, with $VOF_3$, which cleanly oxidizes **5** to the dibenzoquinoxaline, **1b**.

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*Keywords*: discotic; liquid crystals; nitriles; columnar phases; structure–property effects.

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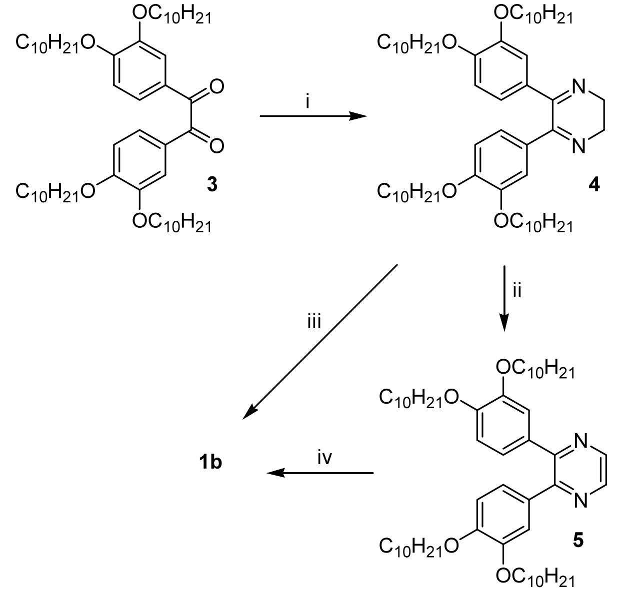
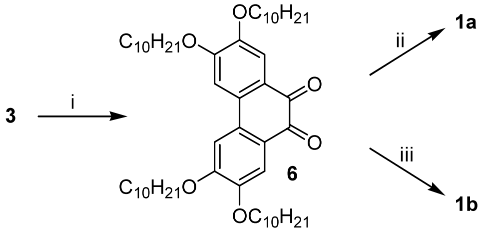


**Scheme 1.** *Reagents and conditions*: (i) $NH_2CH_2CH_2NH_2$, EtOH, AcOH, 94%; (ii) DDQ, $CH_2Cl_2$, 69%; (iii) $FeCl_3$, $H_2SO_4$, $CH_2Cl_2$, 9%; (iv) $VOF_3$, $BF_3{\cdot}Et_2O$, $CH_2Cl_2$, 88%.

An alternative synthetic route was also pursued in which the benzil derivative, **3**, was first cyclized to the phenanthrene quinone, **6**,[11] which was then condensed with ethylene diamine (Scheme 2). In contrast to the dihydropyrazine, **4**, the condensation product of this reaction spontaneously oxidizes in air to the final aromatic product. Thus, while the two approaches afforded our target in similar overall yields, the latter was preferred as the shorter route. This method has the further advantage that the phenanthrene quinone intermediate, **6**, could also be converted directly to the dibenzophenazine, **2**, via condensation with *o*-phenylene diamine. This method is also useful for the synthesis of **1a**, which we were able to obtain in 58% yield via the condensation of diaminomaleonitrile with **6**.[†]



**Scheme 2.** *Reagents and conditions*: (i) $VOF_3$, $BF_3{\cdot}Et_2O$, $CH_2Cl_2$, 85%; (ii) diaminomaleonitrile, AcOH, 58%; (iii) $NH_2CH_2CH_2NH_2$, EtOH, AcOH, 56%.

The phase behavior of these molecules was investigated using differential scanning calorimetry (DSC) and polarized optical microscopy. Despite the close structural similarities between compounds **1b** and **2b** with the dinitrile derivative, **1a**, neither exhibit mesogenic behavior on either heating or cooling; **1b** and **2** melt directly from crystalline solids to isotropic liquids at 102 and 133°C, respectively. This suggests that the remarkable phase stability of **1a** does not arise from either its lower symmetry or the presence of heteroatoms in its core. Nor does size seem to be a crucial factor, since **1a**'s core is slightly smaller than that of **2**.

The electronic properties of the nitrile groups therefore appear to be specifically responsible for the mesogenic behavior of **1a**. The presence of these electron-withdrawing groups may enhance π–π interactions between the aromatic cores, which would stabilize the columnar phase. Dipole–dipole interactions may also contribute significantly to the phase breadth. Indeed, dipolar interactions between nitriles are well known to stabilize the mesophases formed by calamitic molecules,[12] and a similar effect has recently been observed for bent-rod mesogens.[13,14] Perhaps significantly, one of the only extant nitrile-containing triphenylene derivative also forms an exceptionally stable columnar phase.[15]

The low angle X-ray diffraction pattern of the dinitrile **1a** exhibits reflections that index to the (100) and (110) spacings of a columnar hexagonal phase with an intercolumnar distance of 23.1 Å. This distance is consistent with an arrangement in which adjacent molecules are stacked, on average, in an anti-parallel manner, with the central aromatic rings approximately aligned with one another. This suggests that direct interactions between nitrile groups on neighboring molecules are not responsible for the phase stability, since these would lead to an offset geometry and considerably larger inter-columnar distances. On the other hand, the putative structure is consistent with what one would expect from strong interactions between the molecular dipoles of adjacent molecules.

It should also be noted that the ratio of the distances of the (100) peak to the (110) peak was 1:1.67, which differs slightly from the expected value of 1:1.73 for a two-dimensional hexagonal lattice. This slight deviation may indicate that the molecules are slightly tilted with respect to the columnar axis.[16] XRD studies on aligned samples are needed to obtain further information concerning the arrangement of the molecules in this phase. NMR studies of deuterated analogues would also lend valuable insight into this problem.

We are currently carrying out more extensive investigations of these and other structurally related systems in order to further elucidate the factors that control their phase behavior.

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[†] The sample of **1a** obtained in this manner exhibits a columnar hexatic phase from 72–256°C, as compared to the range of 58–258°C previously reported. Our X-ray diffraction data, however, is in excellent agreement with that reported by Ohta and co-workers. Satisfactory analyses were obtained for this and all other compounds discussed in this paper.

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