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Synthesis of unsymmetrical dibenzoquinoxaline discotic mesogens†

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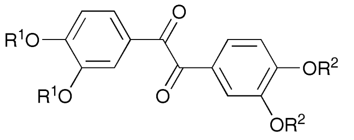
Unsymmetrical dibenzophenazine discotic mesogens were prepared *via* the corresponding tetraalkoxybenzil derivatives. These dibenzophenazines exhibit Col$_{ho}$ phases over extremely broad temperature ranges.

The tendency of many disc-shaped molecules to self-assemble into columnar liquid crystal phases was first recognized in the 1970's. Recently, such discotic mesogens have been targeted as candidates for a variety of device applications including photovoltaics,[1,2] LEDs,[3] xerography[4] and chemical sensing.[5] Understanding the relationship between molecular structure and macroscopic properties is crucial for realizing the full potential of these materials. Molecular symmetry is one factor that is expected to play a decisive role in determining both the stability and the ordering of a columnar mesophase. Although a broad range of discotic mesogens have been examined to date, the vast majority of these have been highly symmetrical molecules. The relatively few reported examples of unsymmetrical discogens have almost invariably been based on the triphenylene core.[6–8] The limited attention received by lower symmetry molecules can be traced to the greater challenges associated with their synthesis.



1a R^1 = $C_{10}H_{21}$, R^2 = CH_3
1b R^1 = $C_{10}H_{21}$, R^2 = C_6H_{13}
1c R^1 = $C_{10}H_{21}$, R^2 = C_8H_{17}
1d R^1 = R^2 = C_6H_{13}
1e R^1 = R^2 = C_8H_{17}
1f R^1 = R^2 = $C_{10}H_{21}$

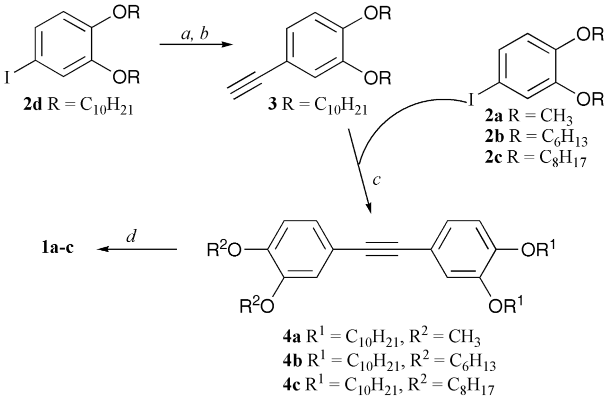
3,3′,4,4′-Tetraalkoxybenzil derivatives (**1**) have been widely exploited as precursors for a variety of mesogens, including triphenylenes,[9] diazatriphenylenes,[10,11] phthalocyanines,[12] metallomesogens[13] and macrodiscotic species.[14] Given their remarkable versatility in this regard, these diones present an inviting entry point into the synthesis of low-symmetry discotic molecules. Symmetrical benzils (R^1 = R^2) can be prepared using a variety of methods, including the benzoin condensation route reported by Wenz.[9] In this manner, we were able to assemble compounds **1d–1f** in four steps from veratraldehyde in average overall yields of 29%. Unfortunately, while the benzoin condensation has been used to cross-couple electronically disparate aldehydes,[15,16] it is not a viable method for the formation of benzil derivatives such as **1a–c**, that have nearly identical functional groups on both rings.

For this reason, we examined a different approach whereby these unsymmetrical benzil derivatives were synthesized in five steps from 1,2-dialkoxybenzenes (Scheme 1). Treatment of 1,2-dialkoxybenzenes with I_2 and HIO_3 in acetic acid affords the iodinated derivatives **2a–d**. Compound **2d** was then converted to the corresponding terminal alkyne **3** by treatment with trimethylsilylacetylene under standard Hagihara–Sonagashira conditions and subsequent removal of the TMS group. Palladium-catalyzed coupling of this alkyne with the appropriate iodobenzene derivatives, **2a–c** affords the unsymmetrical products **4a–c** in excellent overall yields.

A number of literature methods for oxidizing diphenylacetylene to benzil were examined in an effort to convert alkynes **4a–c** to the corresponding 1,2-diones **1a–c**. Attempts to carry out this transformation using $KMnO_4$[17] were only nominally successful, yielding only trace quantities of the desired products. Considerably better results were obtained by employing DMSO as the oxidant in the presence of 5 mol% $PdCl_2$.[18] These electron-rich alkynes are more readily oxidized than diphenylacetylene, and could be converted to the corresponding benzil derivatives at lower temperatures and catalyst loadings. Equally satisfactory results were obtained from the analogous I_2-mediated DMSO oxidation,[19] which affords the diones in near quantitative yields. Since both I_2 and $PdCl_2$ yield almost identical results, the much less expensive I_2 was employed for these conversions. The overall yields obtained for the preparation of the unsymmetrical benzil derivatives from the iodinated precursors using this route ranged from 45–53%; this compares favourably with the yields obtained for the symmetrical derivatives by the benzoin condensation method (*vide supra*).

The successful assembly of the unsymmetrical benzils **1a–c** affords access to a broad array of potential mesogens. As part of this preliminary investigation, we examined a series of dicyanodibenzoquinoxaline derivatives, **6a–c**. The symmetrical analog, **6f**, has been shown to possess a remarkably broad mesophase range;[10] this is a common feature of polar discotic mesogens[20,21] that makes these molecules attractive candidates for device applications. Oxidative cyclization of the benzil derivatives **1a–c** to the phenanthrene-9,10-diones, **5a–c**, followed by condensation with diaminomaleonitrile yields the desired products **6a–c** (Scheme 2). For comparison, the symmetrical analogues **6d** and **6e** were also prepared.

The phase behavior for each of these compounds was examined using polarized optical microscopy (POM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC); these results are summarized in Table 1. With the exception of the non-mesogenic dimethoxy derivative, **6a**, all members of this series are liquid crystalline over broad temperature ranges. These liquid crystals exhibit the characteristic dendritic textures of columnar



Scheme 1 *Reagents and conditions:* (a) TMS–acetylene, $PdCl_2(PPh_3)_2$, CuI, (*i*-Pr)$_2$NH, THF; (b) K_2CO_3, MeOH–THF; c) $Pd(PPh_3)_4$, CuI, (*i*-Pr)$_2$NH, THF; (d) I_2, DMSO, 145 °C.

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† Electronic supplementary information (ESI) available: full synthetic and analytical details, POM images. See http://www.rsc.org/suppdata/cc/b4/b400998c/

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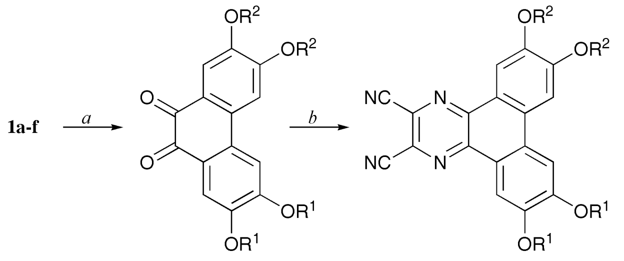

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5f $R^1 = R^2 = C_{10}H_{21}$

6a $R^1 = C_{10}H_{21}$, $R^2 = CH_3$
6b $R^1 = C_{10}H_{21}$, $R^2 = C_6H_{13}$
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6e $R^1 = R^2 = C_8H_{17}$
6f $R^1 = R^2 = C_{10}H_{21}$

Scheme 2 *Reagents and conditions:* (a) VOF_3, $BF_3{\cdot}Et_2O$, CH_2Cl_2; (b) diaminomaleonitrile, AcOH, reflux.

Table 1 Phase behaviour of compounds **6a–f**. Transition temperatures and enthalpies were determined by DSC (scan rate = 5 °C min^{-1}). Intercolumnar spacings, *a*, were determined by XRD

Compound	Phase	T_t/°C [ΔH/J g^{-1}] →			Phase
6a	Cr	264.1 [4.8] →			I
6b	Cr	37.8[56.0] →	Col$_{ho}$ *a* = 22.1Å	215.6 [1.2] →	I
6c	Cr	56.2 [62.2] →	Col$_{ho}$ *a* = 23.3 Å	231.2 [1.0] →	I
6d	Cr	72.4 [75.3] →	Col$_{ho}$ *a* = 20.2 Å	256.1 [6.6] →	I
6e	Cr	85.7 [38.2] →	Col$_{ho}$ *a* = 21.5 Å	252.1[2.3] →	I
6f	Cr	71.6 [10.5] →	Col$_{ho}$ *a* = 22.7 Å	254.2 [0.7] →	I

hexagonal phases when viewed by POM. The XRD patterns of these mesophases exhibit peaks that index to the (100) and (110) spacings of a two-dimensional hexagonal lattice, and a broad peak at approximately 3.5 Å, which corresponds to the π–π stacking distance. On the basis of these observations, the liquid crystals were identified as ordered columnar hexagonal phases (Col$_{ho}$).

Breaking the symmetry in this class of mesogens has a dramatic effect on their observed phase ranges. While the symmetrical derivatives **6d–f** exhibit columnar phases over similar temperature ranges, both the T_m and T_c of the unsymmetrical mesogens **6b** and **6c** are appreciably lowered. This results in phase ranges that are of similar breadth to those of the parent compounds, but that are shifted downwards by 20–40 °C. This effect becomes more pronounced as the disparity between the chain lengths, R^1 and R^2, increases. This depression of the phase transitions is consistent with a lower efficiency of packing of the columnar structures formed by unsymmetrical derivatives. A similar effect has been observed with triphenylene derivatives.[6–8]

The intercolumnar distances obtained from the XRD data also point to a lower density of packing in the case of low symmetry analogues. While the *a* spacing for the symmetrical derivatives **6d–f** increases uniformly with increasing chain length, the unsymmetrical derivatives show larger intercolumnar distances than would be expected based on this trend. In particular, we note that the intercolumnar distance of **6c** is somewhat larger than that of **6f**, despite the former being the smaller molecule. Likewise, while the average chain lengths of **6b** and **6e** are the same, the former exhibits an appreciably larger intercolumnar spacing.

In conclusion, we have developed a convenient synthesis of unsymmetrical discotic mesogens. Our preliminary studies indicate that reducing the symmetry of the mesogen provides a practical method for shifting the phase transitions to lower temperatures, and as such is complementary to other strategies[22] developed for creating room temperature columnar phases. Although these early studies have focused on derivatives that contain only two different functional groups, this approach could be adapted to the assembly of analogues in which all four alkyl chains differ. Further investigations are under way to examine such compounds and other mesogenic derivatives of compounds **1a–f**.

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