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Rapid synthesis of new discotic liquid crystals based on diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine containing hexakis(alkoxy) side arms

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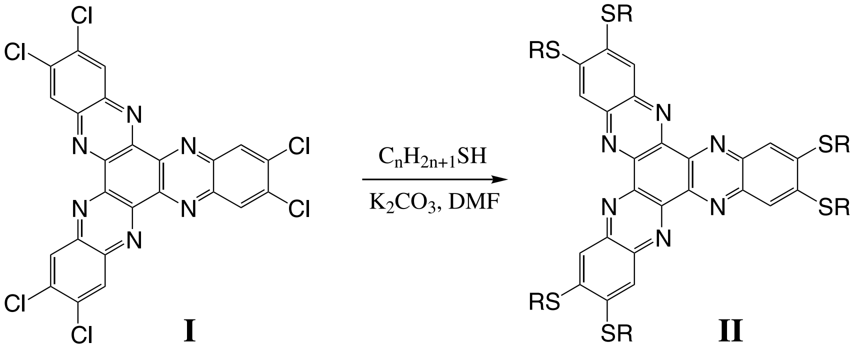
Abstract—The condensation of 1,2-bisalkoxy-4,5-diaminobenzene **2a**–**e** derivatives with freshly prepared hexaketocyclohexane give hexakis(alkoxy)diquinoxalino[2,3-*a*:2′,3′-*c*]phenazines in good yield. DSC and polarization microscopy showed **HATOC6** has both the crystalline (K) to mesophase (M) and the mesophase (M) to isotropic (I) phase transitions. Importantly, the alkoxy substituted compound synthesized showed an M–I transition because of greater stability, whereas the reported alkyl-thiol decomposes after the mesophase. © 2003 Elsevier Science Ltd. All rights reserved.

Hexaazatriphenylenes (**HAT**) are strong electron acceptors that contain three bidentate binding sites and have been studied in the context of supramolecular chemistry[1] and photochemistry.[2] Recently, a **HAT** having three π-deficient pyrazine nuclei at its core was investigated as a potential electron carrier discotic mesogen and was anticipated to possess a low first reduction potential that would facilitate electron injection and high electron mobility.[3] Although acceptor materials with high electron mobility are in demand, examples of acceptor discogens are limited.[4] Reported examples of **HAT** based liquid crystals possess flexible unfused polyphenyl[5] or succinamide-polyphenyl[6] side chains that possess the disadvantage of introducing excessive conformational freedom whereby long-range three-dimensional order may be disrupted. Recently, a fused **HAT** system, hexakis(alkylthio)diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine, was reported to exhibit a number of mesophases (two to five) depending on the chain length but these could not be unambiguously indexed.[7]

It has been reported that the incorporation of oxygen into the side chain of hexakis(alkanoyloxy)benzenes has an effect on both the crystalline to mesophase and the mesophase to isotropic transitions.[8] We now report the successful synthesis of hexakis(alkoxy)diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine (**HATNOCn**) and a preliminary mesophase characterization of these compounds.

The commonly used method for the synthesis of the hexaazatriphenylene (**HAT**) moiety involves the condensation of 1,2-diamino compounds with hexaketo-



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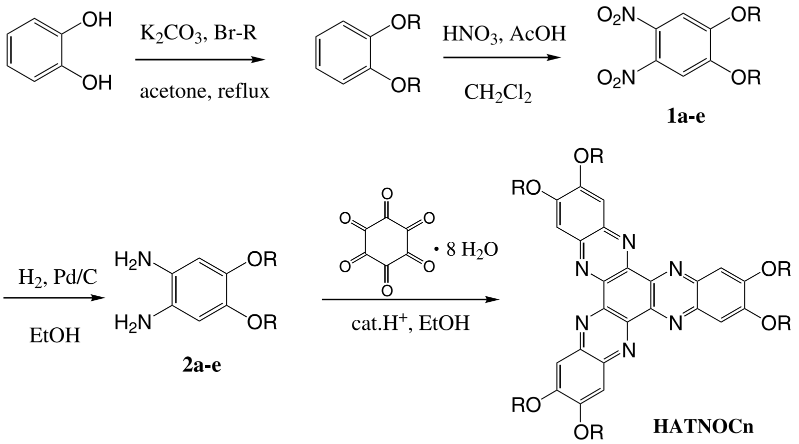

Scheme 1. Synthetic route to **HATNOCn**; a: $R=CH_3$ ($n=1$), b: $R=C_3H_7$ ($n=3$), c: $R=C_4H_9$ ($n=4$), d: $R=C_5H_{11}$ ($n=5$), e: $R=C_6H_{13}$ ($n=6$).

cyclohexane. Furthermore, 2,3,8,9,14,15-hexachlorodiquinoxalino[2,3-*a*:2′,3′-*c*]phenazine, **I**, has been reported to undergo further nucleophilic substitution by an alkyl thiolate to yield the hexakis(alkylthio)diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine, **II**.[7] Similarly, we have synthesized **I** and attempted unsuccessfully nucleophilic displacement of the chloride with alkoxides.

Our synthetic route to the hexakis(alkoxy)diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine discotic liquid crystals, **HATNOCn** involved the condensation of 1,2-bisalkoxy-4,5-diaminobenzenes with hexaketocyclohexane.

Catechol was readily bis alkylated[9] with the appropriate alkyl bromide in high yield, and consecutive dinitration[10] gave 4,5-bisalkoxy-1,2-dinitrobenzenes **1a**–**e** (Scheme 1). The time required for the hydrogenation (H_2, Pd/C; EtOH) of the dinitro- to the diamino-compounds **2a**–**e** was found to be highly dependent on the length of the alkyl chain (6–10 h). The increasing alkyl chain length decreases the solubility of the compounds in ethanol, thus requiring longer reaction times. The diamines obtained in high yield were unstable and had to be used in situ. Condensation of **2a**–**e** with freshly prepared hexaketocyclohexane[11] gave **HATNOC1**, **3**, **4**, **5** and **6** in yields ranging between 50 and 85%. The use of commercially available hexaketocyclohexane gave poor yields of the condensation products. The products were rigorously purified by column chromatography and thin layer preparative plate chromatography on silica gel, followed by washing with hot acetone and finally precipitation from chloroform using ethanol.

The ^1H NMR chemical shifts ($CDCl_3$) of the aromatic protons for **HATNOCn** are around δ 7.85, moving to a higher field as compared to unsubstituted diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine and the hexakis(alkylthio)-**HAT** derivatives. This implies that the alkoxy substituents exhibit a greater electron-donating effect into the discogen. These compounds, **HATNOCn**, showed strong absorption peaks at 308, 341 and 432 nm and also a moderate emission at 459 nm in dilute solution when excited at 308 nm.

Polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) were used to check the thermal behavior of **HATNOC1**, **3**, **4**, **5** and **6**. Only compound **HATNOC6**, having the hexyloxy side chain exhibited an enantiotropic mesophase. The DSC plot showed the crystal to liquid crystal (LC) phase transition and liquid crystal to isotropic phase transition in the heating trace (Table 1). In the POM experiment, the rectangular phase for compound **HATNOC6** was easily recognized by its mosaic textures and displayed a prominent wedge-shaped defect pattern (Fig. 1). The small enthalphies of the LC phase to isotropic transition is indicative of a disordered mesophase (Table 1). Our results indicate that the alkoxy side chain has to reach at least six carbon atoms in length, **HATNOC6**, to attain discotic liquid crystal properties. More importantly, **HATNOC6** is more stable than its reported alkyl-thiol counterpart, decomposing at >300°C. The alkoxy substituted diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine, **HATNOC6**, has been found for the first time to possess both transitions from the crystalline to mesophase and from mesophase to isotropic phase. The mesophase to isotropic transition was totally absent for the reported alkyl-thio derivatives, which decomposed at around 250°C.

The XRD pattern for compound **HATNOC6** at 198°C supported the result from DSC and POM experiments.

Table 1. Phase behavior of **HATNOC6**

Compound	Phase transitions
HATNOC6	$K_1 \underset{92.1\ (-8.81)}{\overset{124.9\ (15.51)}{\rightleftharpoons}} K_2 \underset{179.8\ (-1.37)}{\overset{187.1\ (1.32)}{\rightleftharpoons}} Col_{rd} \underset{226.0\ (-0.52)}{\overset{230.3\ (0.52)}{\rightleftharpoons}} I$

The transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 10°C/min. K, crystalline phase; coloured, disordered rectangular columnar; I, isotropic.

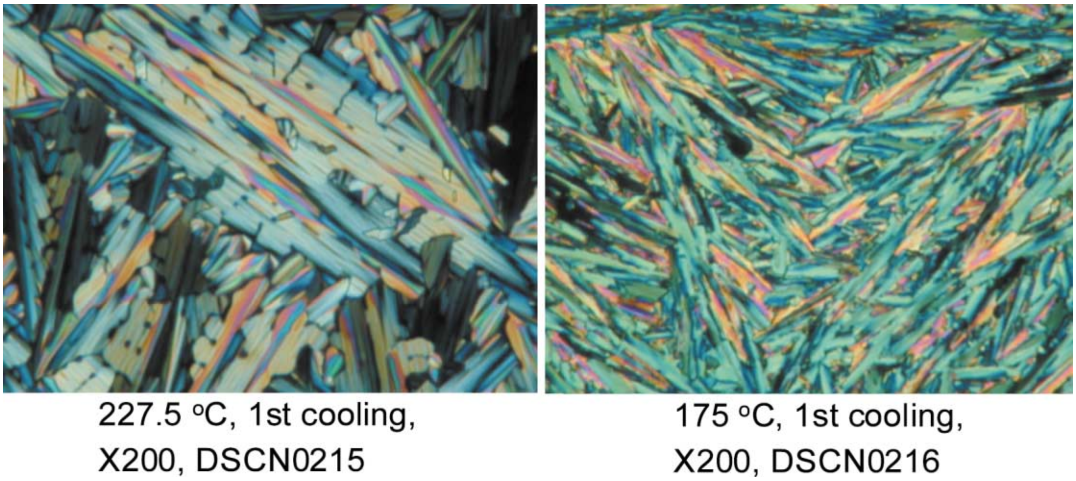

Figure 1. Optical texture for **HATNOC6**.

Broad halos at ~4.6 Å are observed at wide angle for the mesophase indicating a disordered liquid-like organization. In addition, a shoulder at ~3.6 Å corresponding to the average core-to-core correlation as also observed. **HATNOC6** was assigned a rectangular columnar phase based on the two intense low angle peaks indexed to (110) and (200), attributed to an oblique unit cell with the parameters $a = 40.00$ Å and $b = 19.15$ Å.

In summary, we have demonstrated that the heteroatom in the side chains of the disk like mesogen, diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine, affects both the crystalline (K) to mesophase (M) and mesophase (M) to isotropic (I) transition. Both the transition from K–M and M–I was observed for the first time with the alkoxy substituted diquinoxalino[2,3-*a*:2′,3′-*c*]-phenazine, **HATOC6**. Future work will involve the synthesis of longer alkoxy side chains of the same family and the investigation of the charge carrier mobility of this family of compounds.

Experimental

*General procedure for the preparation of **HATNOC1**, **3**, **4**, **5** and **6***: To a solution of the 1,2-diamino-4,5-dialkoxybenzene (15 mM) and hexaketocyclohexane (4 mM) in ethanol (30 mL) was added acetic acid (3 mL). The reaction mixture was refluxed under nitrogen for 24 h. Ethanol was then removed and the residue dissolved in chloroform, followed by washing with $NaHCO_{3(aq)}$ and brine and drying over $MgSO_4$. Removal of the solvent under vacuum gave the crude product which was purified by chromatographic procedures (yield: 50–85%).

HATNOC6: ^{1}H NMR ($CDCl_3$): δ 7.85 (s, 6H), 4.30 (t, 12H), 2.07–1.93 (m, 12H), 1.67–1.35 (m, 36H), 0.95 (t, 18H); m/z (MALDI MS): 985.6 as a single peak. Anal. calcd for $C_{60}H_{84}N_6O_6$: C, 73.14; H, 8.59; N, 8.53. Found: C, 73.42; H, 8.35; N, 8.11%.

Optical investigations were performed on a Nikon E600 POL with a Mettler FP90/FP82HT hot-stage system. Transition temperatures and heats of fusion were determined at scan rates of 10°C/min by differential scanning calorimetry using a Perkin–Elmer Pyris1. X-Ray powder diffraction data were collected on the wiggler beamline BL17A, using a triangular bent Si(111) monochromator and a wavelength of 1.32633 Å. The sample in a 1 mm capillary was mounted on a Huber 5020 diffractometer. An air stream heater was equipped at BL17A beamline.

Acknowledgements

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