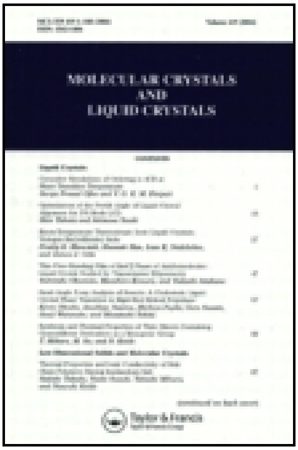

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 27 Oct 2006

To cite this article: Sandeep Kumar & M. Manickam (2000): Synthesis of phenanthro[b] phenazine, a novel heterocyclic ring structure for discotic liquid crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 338:1, 175-179

To link to this article: http://dx.doi.org/10.1080/10587250008024428

Mol. Cryst. Liq. Cryst., Vol. 338, pp. 175-179
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Synthesis of phenanthro[b] phenazine, a novel heterocyclic ring structure for discotic liquid crystals

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(Received March 25, 1999; In final form March 25, 1999)

Phenanthro[b]phenazine, a new heterocyclic ring structure of both biological and physical interests, has been prepared by coupling 1, 2-phenylenediamine with triphenylene-2, 3-quinone derivative. The first derivative of this novel core, 2,3,6,7-tetrapentyloxyphenanthro[b]phenazine, shows a monotropic columnar phase.

Keywords: Phenanthro[b]phenazine; Triphenylene; Phenazine; Discotic liquid crystal; Columnar mesophase

Heterocyclic compounds occur very widely in Nature and are essential to life. An enormous number of natural and synthetic heterocyclic compounds based on various heterocyclic ring structures have found widespread uses in material and biological fields. The charge generating, transporting and photophysical properties of various phenazine derivatives have recently been recognized [1, 2]. They are also well-known for their antibacterial and insecticidal properties [1]. Numerous dyes based on phenazine derivatives are used in printing industries [1].

Phenazines condensed with three benzene rings, such as, tribenzo[a,c,h]phenazine **1**, tribenzo[a,c,i]phenazine **2** and their various positional isomers are known in the literature. To our knowledge, the phenanthro[b]phenazine system **6** (scheme 1) is so far not known. Here we report the first synthesis of this new heterocyclic ring system.

The last few years have witnessed significant advances in the chemistry of various discotic liquid crystals (LCs) because of their pronounced conducting, photoconducting, ferroelectrical and optoelectrical switching, electroluminescence,

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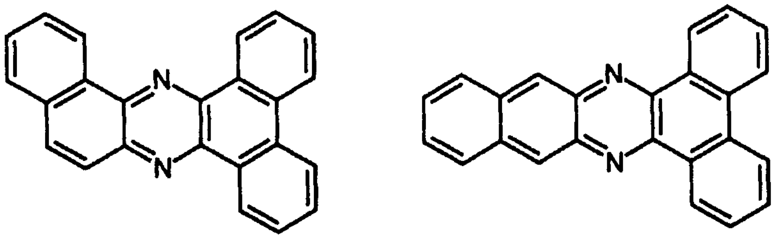


1 **2**

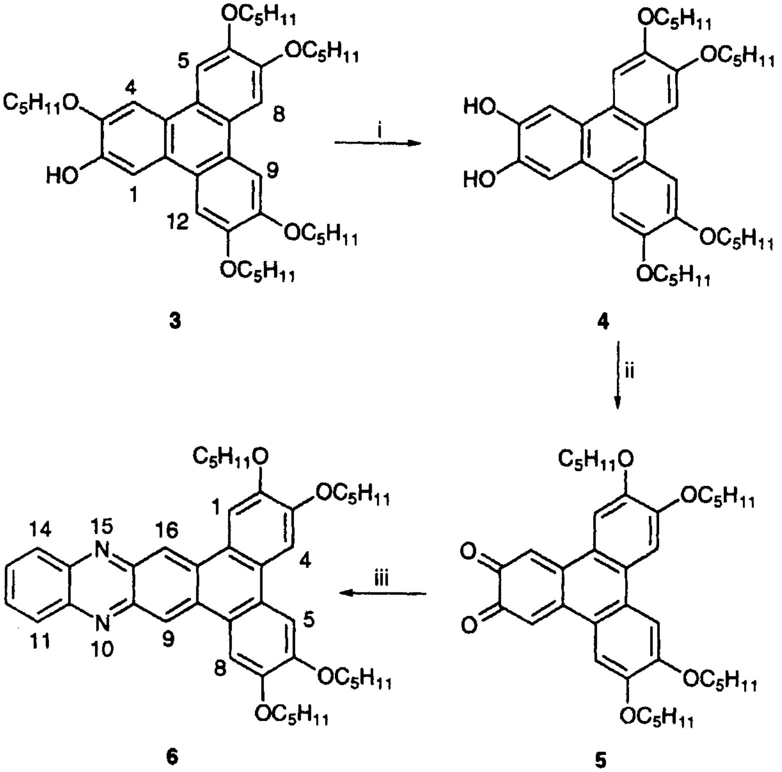
Chemical structure of (1) tribenzo[a,c,h]phenazine and (2) tribenzo[a,c,i]phenazine

photovoltaic and optical data storage properties [3, 4]. It has now been recognized that the supramolecular structure of disc-shaped molecules is well suited for the one-dimensional energy and charge migration [3, 4]. Triphenylene derivatives play important roles in the field of discotic liquid crystals. These thermally and chemically stable materials can easily be prepared and purified. When the electron rich triphenylene discotic LCs were doped with a few percent of electron deficient molecules such as aluminum trichloride, they become quasi-one-dimensional semiconductors [3, 4]. Very high charge carrier mobility (hole mobility) has been reported in various phases of triphenylene based discotic LCs [3–5] and this makes them suitable to be used as hole transporting layer in light emitting diodes [6]. One-dimensional energy transfer has also been studied extensively in these materials [7].

We anticipated that the hybridization of a phenazine and triphenylene molecules may result in the synthesis of novel materials having interesting material and biological properties. The charge generating, transporting, polar and colored nature of phenazine derivatives in conjunction with the liquid crystal properties of triphenylene derivatives will yield novel supramolecular systems suitable for molecular electronic devices. Additionally, the hitherto unknown heterocyclic phenanthro[b]phenazine ring system may also show interesting biological properties.

Synthesis of phenanthro[b]phenazine is shown in Scheme 1. The 2,3-dihydroxy-6,7,10,11-tetrapentyloxytriphenylene **4** was prepared from 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene [8] **3** by cleaving the pentyloxy group at 3-position with BBr_3 at low temperature. It was found to be identical with the compound prepared by Ringsdorf group by cleaving the methoxy group of 2-hydroxy-3-methoxy-6,7,10,11-tetrapentyloxytriphenylene with butyllithium and boron tribromide [9]. Compound **4** was easily oxidized with ceric ammonium nitrate (CAN) to 6,7,10,11-tetrapentyloxytriphenylene-1,2-diones **5**.

Reaction of this *o*-quinone **5** in benzene with equimolar amount of 1, 2-phenylenediamine in acetic acid at room temperature for 2 hrs furnished orange-red 2,3,6,7-tetrapentyloxyphenanthro[b]phenazine **6** in about 80% yield. Product was characterized from its ^{1}H, ^{13}C NMR and mass spectral data.



SCHEME 1 *Reagents and conditions*: i, BBr_3, CH_2Cl_2, −60°C, 30%; ii, CAN, MeCN, room temp., 30min, 90%; iii, 1,2-phenylenediamine, benzene-AcOH, room temp., 2hr, 80%

The new phenazine derivative **6** was found to be mesogenic. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMFRT polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). It shows crystal to isotropic transition at 193.6°C on heating but on cooling it comes to a highly ordered mesophase at 175.7°C. Its texture (Figure 1) resembles very well with that of ordered columnar mesophase of hexalkoxytriphenylenes. However, x-ray studies must be done to confirm this. This monotropic mesophase has a high crystallization tendency and starts to crystallize in the mesophase and completely crystallizes at

171.5°C. Compound **6** has a C_2 symmetry and is not symmetrically shaped as usually required for discotic liquid crystals. However, it may organize itself in an antiparallel alignment with the neighbor molecules to form the supramolecular structure of the columnar phase.

In conclusion, we reported the synthesis of phenanthro[b]phenazine, a new heterocyclic ring structure and a molecule of both biological and physical interests. It has been found to function as the core fragment for a new family of discotic liquid crystals. These unsymmetrical, colored, polar, heteroaromatic discotic mesogens are potential candidates for the conducting, photoconducting, electroluminiscence, photorefrective, etc., studies. Medicinal properties of phenazine derivatives are well documented. New substituted and unsubstituted phenanthrophenazine derivatives may also show interesting biological activities.

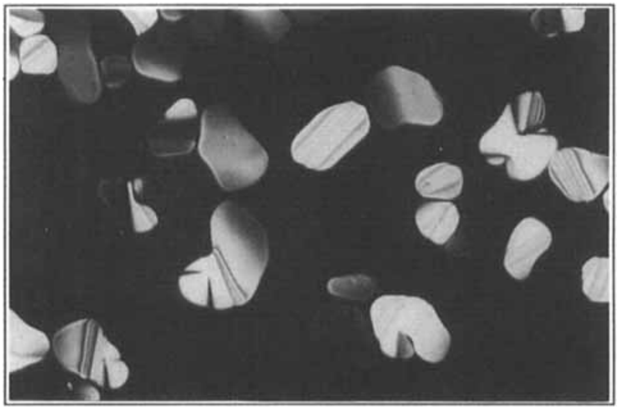


FIGURE 1 Optical texture of the compound **6** at 174°C (See Color Plate XVI at the back of this issue)

Selected data for **6**:

MS: m/z (FAB) 675 (100% M+H)

^{1}H NMR ($CDCl_3$) δ 9.27 (s, 2H), 8.27 (m, 2H), 8.21 (s, 2H), 7.88 (m, 2H), 7.75 (s, 2H), 4.27 (t, *J*= 6.5, 8H), 1.97 (m, 8H), 1.56 (m, 6H) and 1.0 (m, 12H)

^{13}C NMR ($CDCl_3$) δ 150.77, 149.41, 143.93, 141.24, 133.18, 130.18, 129.57, 125.03, 122.69, 121.58, 107.99, 107.54, 69.72, 69.28, 29.07, 28.32, 22.56 and 14.09

Acknowledgements

We are very grateful to Professor S. Chandrasekhar for helpful discussions. The authors also gratefully acknowledge the technical assistance of Mr. Sanjay K. Varshney.

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