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Sandeep Kumar; M. Manickam

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Preliminary communication

Synthesis of phenanthro[a] phenazine derivatives: a novel ring structure forming discotic liquid crystals

SANDEEP KUMAR* and M. MANICKAM
Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore—560 013, India

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Phenanthro[a] phenazine, a new heterocyclic ring structure of both biological and physical interest, has been prepared by coupling 1,2-phenylenediamine with triphenylene-1,2-diquinone derivatives in high yields. 2,3,6,7,10-Penta-alkoxyphenanthro[a] phenazines are mesogenic over a broad temperature range. These novel unsymmetrical, coloured, polar, heteroaromatic discotic mesogens are potential candidates for the study of conducting, photoconducting, electroluminescence, photorefrective, etc. properties.

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, photovoltaic and optical data storage properties [1, 2]. It has now been recognized that the supramolecular structure of disc-shaped molecules is well suited for one dimensional energy and charge migration [1, 2].

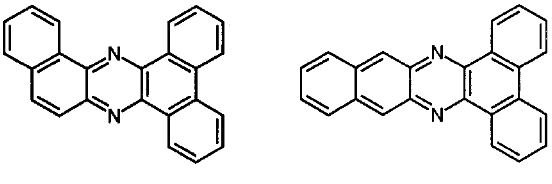
Triphenylene derivatives play important roles in the field of discotic liquid crystals. These thermally and chemically stable materials can easily be prepared and purified. When the electron rich triphenylene discotic LCs are doped with a few % of electron deficient molecules such as aluminum trichloride, they become quasi one dimensional semiconductors [1, 2]. Photoinduced charge carrier mobility (hole mobility) of the order of 10^{-3}, 10^{-2} and $10^{-1}\,cm^2\,V^{-1}\,S^{-1}$ has been reported in the Col_{ho} phase of hexapentyloxytriphenylene, the discotic plastic phase (Col_p) of hexabutyloxytriphenylene and the helical phase of hexahexylthiotriphenylene, respectively [1–3]. The very high charge mobility of these materials makes them suitable to be used as a hole transporting layer in light emitting diodes [4]. One dimensional energy transfer has also been studied extensively in these materials [1, 5].

The charge generating, transporting and photophysical properties of various phenazine derivatives have recently been recognized [6, 7]. Phenazine derivatives are also well known for their antibacterial and insecticidal properties [6]. Numerous dyes based on phenazine derivatives are used in printing industries [6].

We anticipated that the hybridization of phenazine and triphenylene molecules may result in the synthesis of novel materials having interesting material and biological properties. The charge generating, transporting, polar and coloured nature of phenazine derivatives in conjunction with the liquid crystal properties of triphenylene derivatives should yield novel supramolecular systems suitable for molecular electronic devices.

Phenazines condensed with three benzene rings, namely benzonaphthophenazine **1**, tribenzophenazine **2** and their positional isomers are known in the literature. To our knowledge the phenanthrophenzine system **5** (see the scheme) is so far not known. Here we report on the first synthesis of two derivatives of this new heterocyclic ring system.

During the course of our studies on triphenylene based discotic liquid crystals [8], we realized that the ring oxidation in monohydroxypenta-alkoxytriphenylene **3** is extremely facile [9]. Oxidation of 2-hydroxy-3,6,7,10,11-penta-alkoxytriphenylenes (**3a**, **3b**) with well



1 **2**

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

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* Author for correspondence; e-mail: uclcr@giasbg01.vsnl.net.in

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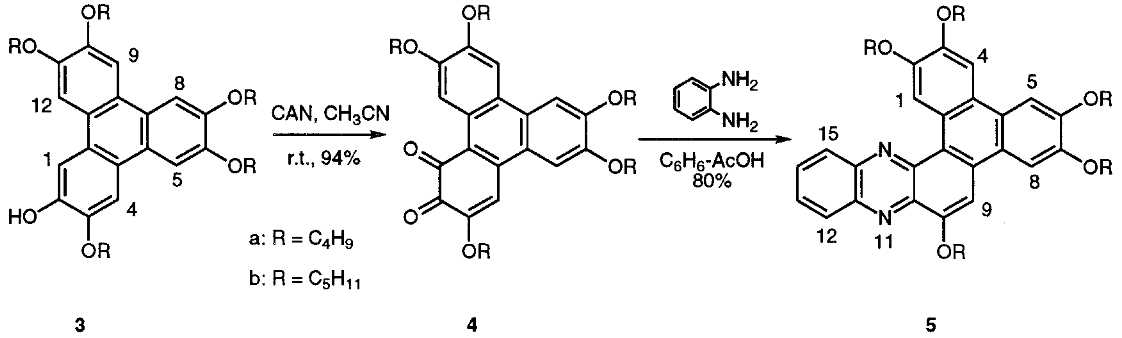

Scheme. Synthesis of phenanthro[a] phenazine derivatives.

known oxidizing agents such as chromium trioxide, ceric ammonium nitrate (CAN) or nitric acid yields black 3,6,7,10,11-penta-alkoxytriphenylene-1,2-diones (**4a** and **4b**) in very high yields (see the scheme). These diquinones condense very readily with 1,2-phenylenediamine to yield novel phenanthro[a] phenazine derivatives. The reaction of 3,6,7,10,11-pentabutyloxytriphenylene-1,2-dione **4a**, or 3,6,7,10,11-pentapentyloxytriphenylene-1,2-dione **4b**, in benzene with equimolar amount of 1,2-phenylenediamine in acetic acid at room temperature for 30 min furnished orange-red 2,3,6,7,10-penta-alkoxyphenanthro[a]-phenazine derivatives **5a** and **5b** in more than 80% yield. The products were characterized by their UV, ^{1}H NMR ^{13}C NMR and mass spectral data. The ^{1}H NMR data of **5a** and **5b** matched that of a phenazine derivative [10] and a triphenylene derivative [9]. Interestingly, all the 24 aromatic carbons and 5 oxy carbons of **5b** appear as distinct signals in the ^{13}C NMR of **5b**.

Selected data for **5b**: *m*/*z* (FAB, −ve) 760.9; (FAB, +ve) 762.2. δ_H ($CDCl_3$) 10.83 (s, 1H), 8.45 (m, 1H), 8.30 (m, 1H), 8.08 (s, 1H), 8.0–7.88 (m, 5H), 4.5 (m, 4H), 4.3 (m, 6H), 2.1 (m, 10H), 1.54 (m, 20H) and 1.0 (m, 15H). δ_C ($CDCl_3$) 151.75, 150.89, 149.49, 148.85, 148.18, 144.78, 141.04, 140.21, 137.48, 130.37, 130.18, 130.03, 129.60, 129.15, 126.79, 125.07, 124.58, 122.79, 118.30, 112.69, 108.21, 106.57, 105.92, 105.19, 69.90, 69.75, 69.53, 69.28, 68.89, 29.15, 29.03, 28.68, 28.54, 28.38, 22.59 and 14.11. λ_{max} (EtOH) 248, 280, 301, 325 (sh), 338 (sh) and 455 nm.

Both the new derivatives were found to be mesogenic. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMFRT polarizing microscope, as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). The heating and cooling rate was 10°C min^{-1}. Pentabutyloxyphenanathrophenazene **5a** melts at 104°C to a highly ordered mesophase. The texture of this mesophase is different from the classical texture of the Col_h phase and resembles well the helical phase of hexahexylthiotriphenylene. However, as texture alone is not sufficient, X-ray investigations are needed for confirmation. This mesophase transform into the Col_h phase at 190°C and finally clears at 231°C. It should be noted that the mesophase of hexabutyloxytriphenylene was recently reported to be more ordered than the Col_h phase and likened to a plastic discotic (Col_p) phase [3]. On the other hand, pentapentyloxyphenanathrophenazene **5b** melts at 98°C to a Col_h phase and clears at 220°C.

In conclusion, phenanthrophenazine, a molecule of both biological and physical interest, has been found to function as the core fragment for a new family of discotic liquid crystals. These unsymmetrical, coloured, polar, heteroaromatic discotic mesogens are potential candidates for conducting, photoconducting, electroluminiscence, photorefrective, etc. studies. The medicinal properties of phenazine derivatives are well documented; there are few volumes of *Chemical Abstracts* that have not reported their biological activities. New substituted and unsubstituted phenanthrophenazine derivatives may also show interesting biological activities. The synthesis of various penta- and hepta-alkoxyphenanthro[a]-phenazines and phenanthro[b] phenazines are currently being investigated in this laboratory.

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References

[1] Chandrasekhar S., 1998, in *Hand Book of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Wiley-VCH), Chap. VIII; Boden, N., and Movaghar, B., 1998, in *Hand Book of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Wiley-VCH), Chap. IX.

[2] Chandrasekhar, S., and Kumar, S., 1997, *Science Spectra*, (8), 66.

[3] Simmerer, J., Glusen, B., Paulus, W., Kettner, A., Schuhmacher, P., Adam, D., Etzbach, K. H., Siemensmeyer, K., Wendorff, J. H., Ringsdorf, H., and Haarer, D., 1996, *Adv. Mater.*, **8**, 815.

[4] Stapff, I. H., Stumpflen, V., Wendorff, J. H., Spohn, D. B., and Mobius, D., 1997, *Liq. Cryst.*, **23**, 613.

[5] Markovitsi, D., Germain, A., Millie, P., Lecuyer, P., Gallos, L. K., Argyrakis, P., Bengs, H., Ringsdorf, H., 1995, *J. phys. Chem.*, **99,** 1005; Marguet, S., Markovitsi, D., Millie, P., Sigal, H., and Kumar, S., 1998, *J. phys. Chem. B*, **102,** 4697 and references therein.

[6] Porter, A. E. A., 1984, in *Comprehensive Heterocyclic Chemistry*, Vol. 3, edited by A. R. Katritzky, C. W. Rees, J. J. Boulton and A. Mckillop (Pergamon Press).

[7] Uchida, M., Izumisawa, J., and Furukawa, K., 1997, Jpn. Kokai Tokkyo Koho JP 09 13 025 [97 13 025], (*CA* 1997, **126,** 192783).

[8] Rego, J. A., Kumar, S., and Ringsdorf, H., 1996, *Chem. Mater.*, **8,** 1402; Rego, J. A., Kumar, S., Dmochowski, I. J., and Ringsdorf, H., 1996, *J. chem. Soc., chem. Commun.*, 1031; Henderson, P., Kumar, S., Rego, J. A., Ringsdorf, H., and Schuhmacher, P., 1995, *J. chem. Soc., chem. Commun.*, 1059; Kumar, S., Schuhmacher, P., Henderson, P., Rego, J., and Ringsdorf, H., 1996, *Mol. Cryst liq. Cryst.*, **288,** 211; Kumar, S., and Manickam, M., 1998, *Mol. Cryst. liq. Cryst.*, **309,** 291; Kumar, S., and Manickam, M., 1997, *Chem. Commun.*, 1615; Kumar, S., and Manickam, M., 1998, *Synthesis*, 1119; Yelamaggad, C. V., Prasad, V., Manickam, M., and Kumar, S., 1998, *Mol. Cryst. liq. Cryst.* (in the press).

[9] Kumar, S., and Manickam, M., 1998, *J. chem. Soc., chem. Commun.*, 1427.

[10] Morita, Y., 1066, *Chem. Pharm. Bull.*, **14,** 419.