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Preliminary communication

First rational synthesis of dibenzo[*fg*, *op*]naphthacene discotics

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A novel, versatile and regiospecific synthesis of variable degree substituted dibenzo[*fg*, *op*]-naphthacene (also named dibenzopyrene) is described which involves the preparation of a tetraphenyl using a palladium-catalysed cross-coupling of arylboronic acids followed by photochemical cyclization.

Discotic liquid crystals based on dibenzo[*fg*, *op*]-naphthacene† have been the subject of many recent publications. Bock and Helfrich have demonstrated for the first time the existence of ferroelectricity in the columnar liquid crystals of 1,2,5,6,8,9,12,13-octakis-(S)-(2-heptyloxypropanoyloxy)dibenzopyrene (DBP) [1, 2]. The synthesis of various octaalkoxy-substituted DBP compounds and their photophysical properties have been reported by the Ringsdorf and Markovitsi groups [3, 4]. Mesomorphic properties of five homologues of the 1,2,5,6,8,9,12,13-octaalkoxy-DBPs (see the figure) and their charge transfer complexes with 2,4,7-trinitro-9-fluorenone have been reported by Zamir *et al.* [5]. The electro-optical and electromechanical effects in these materials were also reported very recently [6, 7].

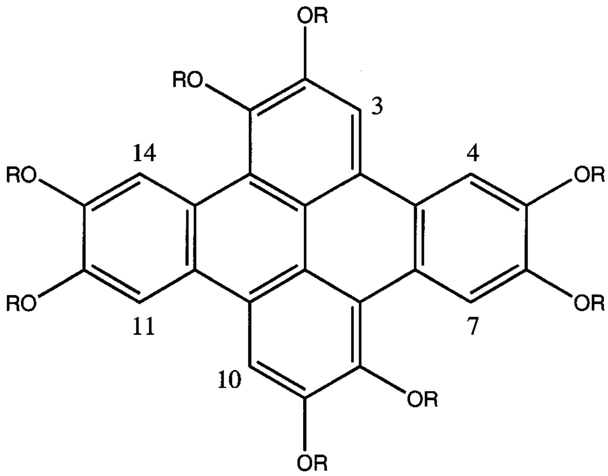

Figure 1. Structure of octaalkoxy—DBP compounds.

In general, the self-assembling of disc-shaped molecules due to favourable π-π interactions between the aromatic cores leads to the formation of discotic liquid crystals [8]. These materials are becoming of increasing interest as self-organizing molecular wires through which charge or excitons can migrate rapidly [9]. Conductivity along the molecular columns was reported to be several orders of magnitude higher than that observed for the organic polymers [10]. Charge carrier mobility in the commonly observed Col$_h$ phase was found [11] to be $1 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ while the mobility in the recently reported columnar plastic phase [12] in some triphenylene derivatives was reported to be $1 \times 10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Extremely high charge carrier mobility, comparable to that of organic single crystals ($1 \times 10^{-1}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$), has been observed in the highly ordered helical phase of hexahexylthiotriphenylene [13]. Because of these properties, the potential applications of these compounds in conducting and photoconducting systems, optical data storage, light emitting diodes, photovoltaic solar cells, gas sensors, and other devices have been envisaged [14].

From the reported charge mobility results, it has been concluded that the degree of order determines charge

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†The naphthacene derivatives have recently been reported as dibenzopyrene derivatives [1–7]. However, we prefer the Chemical Abstracts nomenclature, i.e. dibenzo[*fg*, *op*]-naphthacene (192-51-8).

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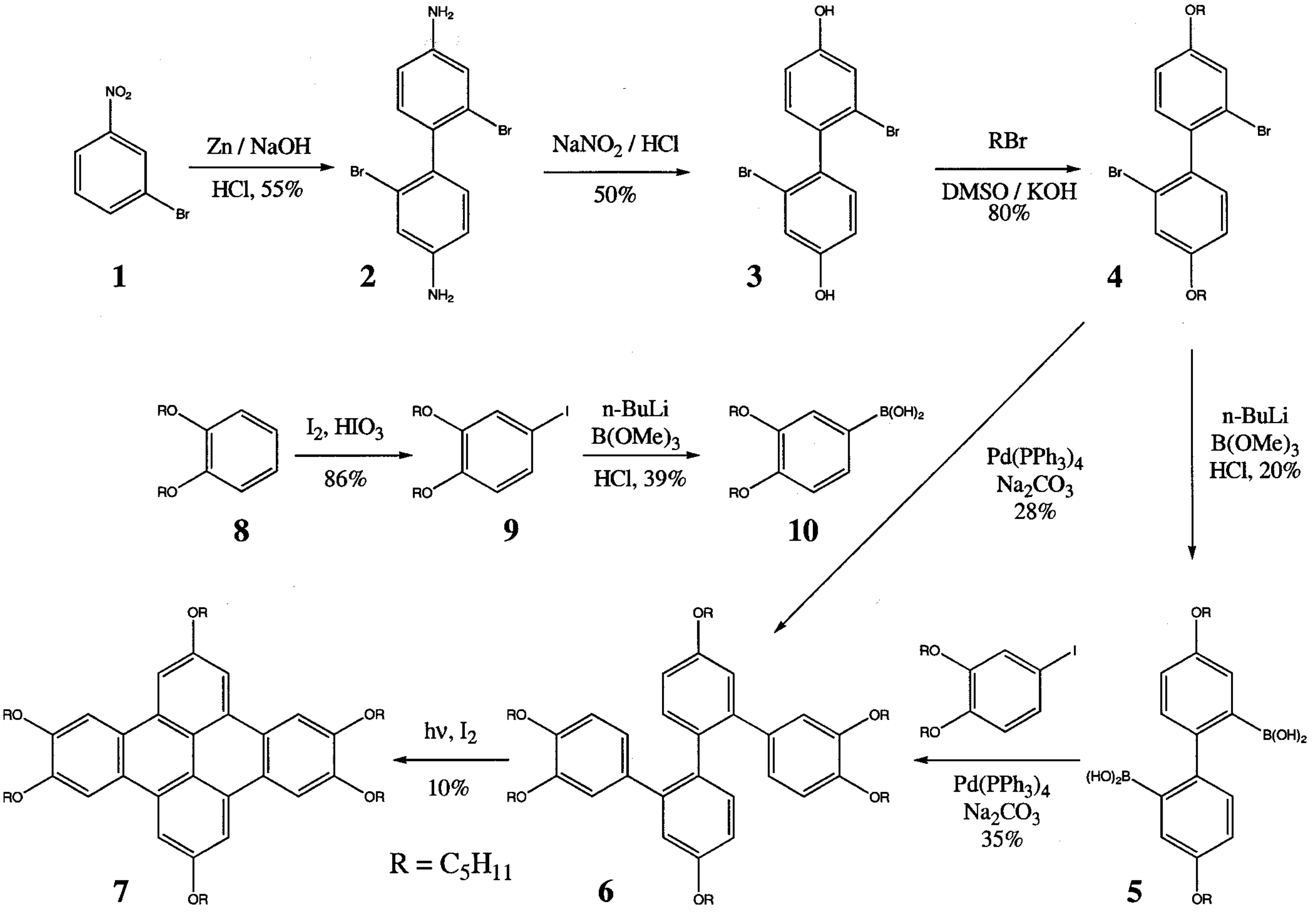
mobility in columnar liquid crystalline materials. It is expected that an increase in the orbital overlap area will lead to higher charge mobility. Van de Craats *et al.* very recently observed a positive effect of increasing the macrocyclic core size on the intracolumnar charge carrier mobility. Hexabenzocoronenes show remarkably high charge carrier mobility ($0.3\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$) in the liquid crystalline phase [15]. The extremely high mobility of graphite ($\sim 3\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$) could be due to the larger aromatic core size.

The question of high photoconductivity in DBP discotic liquid crystals has recently been addressed by the Ringsdorf group [3]. Since the larger core has more delocalized π electrons than triphenylene, a greater degree of π-π interaction and hence higher charge carrier mobility was expected in these derivatives. However, the charge carrier mobility in octasubstituted DBP derivatives was found to be one order of magnitude lower than in the columnar phase of hexaalkoxytriphenylenes [16]. This could be because of a less ordered columnar packing due to steric hindrance caused by the 'way region' alkoxy chains. It is anticipated that removal of the alkoxy chains from the 1 and 8 positions (way region) will give a better core–core interaction and, therefore, higher charge carrier mobility.

Hitherto, the synthesis of any low degree substituted DBP discotic liquid crystal is unknown. All the DBP derivatives so far reported were prepared following the method of Musgrave and Webster [17] which involves the oxidation of 3,3′,4,4′-tetramethoxybiphenyl by chloranil in 70% sulphuric acid to 2,5,6,9,12,13-hexamethoxydibenzo[*fg*, *op*]naphthacene-1,8-quinone and its 1,10-quinone isomer. Reductive acetylation followed by alkylation resulted in the synthesis of octa-substituted DBP liquid crystals. Direct oxidation of tetrapentyloxybiphenyl by chloranil to hexapentyloxy-dibenzo[*fg*, *op*]naphthacene-1,8-quinone and its conversion to octapentyloxy-DBP by the above-mentioned procedure has also been reported by the Ringsdorf group [3]. We have recently reported that $VOCl_3$ can be efficiently utilized under very mild reaction conditions for the preparation of two quinones [18].



Scheme. Synthesis of dibenzo[*fg*, *op*]naphthacene derivatives.

We have now developed a novel, versatile and regiospecific synthesis of variable degree substituted dibenzo[*fg*, *op*]naphthacene derivatives. The synthesis is based on the preparation of tetraphenyl **6** using a palladium-catalysed cross coupling of arylboronic acids followed by photochemical cyclization as shown in the scheme.

Reductive dimerization of 3-bromonitrobenzene **1** followed by benzidine rearrangement afforded the 4,4′-diamino-2,2′-dibromobiphenyl **2**. Tetraazotization of **2** followed by alkylation of the phenolic product with 1-bromopentane resulted in 2,2′-dibromo-4,4′-dipentyloxybiphenyl **4**. The tetraphenyl **6** was prepared either by coupling **4** with dipentyloxyboronic acid **10** or by first converting the dibromobiphenyl **4** to diboronic acid **5** and then reacting with dipentyloxyiodobenzene **9**. Photolysis of the tetraphenyl **6** in the presence of an excess of iodine furnished the desired 2,5,6,9,12,13-hexapentyloxydibenzo[*fg*, *op*]naphthacene. The compound was fully characterized from its ^{1}H NMR, ^{13}C NMR, mass and elemental analysis. MS (FAB) *m*/*z* 819.4. ^{1}H NMR (200 MHz, CDCl$_3$) δ 8.18 (s, 4H), 8.09 (s, 4H), 4.32 (m, 12H), 2.0 (m, 12H), 1.55 (m, 24H), 1.0 (m, 18H). ^{13}C NMR (CDCl$_3$) δ 157.0, 149.9, 130.1, 124.7, 107.5, 106.5, 69.5, 68.6, 29.1, 28.4, 22.6 and 14.1. A satisfactory elemental analysis was obtained.

Compound **7** was found to be liquid crystalline and the mesophase behaviour was checked by polarized optical microscopy as well as by differential scanning calorimetry. The crystalline compound **7** melts at 120.5°C (enthalpy 52.1 kJ mol^{-1}) to a liquid crystalline phase which changes to isotropic liquid at 223.1°C (enthalpy 4.0 kJ mol^{-1}). Upon cooling, the Col$_h$ phase appears at 219.9°C, crystallizing at 96.3°C. The assignment of the mesophase as Col$_h$ was based on the similarity of optical textures to that of several well characterized discotic liquid crystals showing the Col$_h$ phase.

The methodology outlined above has given us good control in the modification of the dibenzo[*fg*, *op*]naphthacene discotic core. Whereas the synthesis of octasubstituted dibenzo[*fg*, *op*]naphthacene to give low molar mass discotic liquid crystals is fairly easy, the synthesis of any low degree substituted dibenzo[*fg*, *op*]naphthacene has not previously been achieved. A variety of dibenzo[*fg*, *op*]naphthacene discotics can now be designed and created using the new methodology. These discotic liquid crystals will be excellent candidates for charge migration studies. Efforts are now in progress to optimize the various reaction conditions and to prepare a series of novel dibenzo[*fg*, *op*]naphthacene derivatives.

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References

[1] Bock, H., and Helfrich, W., 1992, *Liq. Cryst.*, **12,** 697.
[2] Bock, H., and Helfrich, W., 1995, *Liq. Cryst.*, **18,** 387.
[3] Henderson, P., Ringsdorf, H., and Schuhmacher, P., 1995, *Liq. Cryst.*, **18,** 191.
[4] Uznanski, P., Marguet, S., Markovitsi, D., Schuhmacher, P., and Ringsdorf, H., 1997, *Mol. Cryst. liq. Cryst.*, **293,** 123.
[5] Zamir, S., Singer, D., Spielberg, N., Wachtel, E. J., Zimmermann, H., Poupko, R., and Luz, Z., 1996, *Liq. Cryst.*, **21,** 39.
[6] Kitzerow, H., and Bock, H., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 117.
[7] Jakli, A., Muller, M., Kruerke, D., and Heppke, G., 1998, *Liq. Cryst.*, **24,** 467.
[8] Chandrasekhar, S., 1993, *Liq. Cryst.*, **14,** 3; Chandrasekhar, S., and Kumar, S., 1997, *Science Spectra*, 66.
[9] Boden, N., Bissell, R., Clements, J., and Movaghar, B., 1996, *Liq. Cryst. Today*, **6,** 1.
[10] Chandrasekhar, S., and Prasad, S. K., 1999, *Contemp. Phys.*, **40,** 237; Balagurusamy, V. S. K., Prasad, S. K., Chandrasekhar, S., Kumar, S., Manickam, M., and Yelamaggad, C. V., 1999, *Pramana-J. Phys.*, **53,** 3.
[11] Adam, D., Closs, F., Frey, T., Funhoff, D., Haarer, D., Ringsdorf, H., Schuhmacher, P., and Siemensmeyer, K., 1993, *Phys. Rev. Lett.*, **70,** 457.
[12] 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.
[13] Adam, D., Schuhmacher, P., Simmerer, J., Häussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., and Haarer, D., 1994, *Nature*, **371,** 141.
[14] Boden, N., and Movaghar, B., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Weinheim: Wiley-VCH), Chap IX; Chandrasekhar, S., *ibid.*, Chap. VIII.
[15] Van de Craats, A. M., Warman, J. M., Fechtenkotter, A., Brand, J. D., Harbison, M. A., and Mullen, K., 1999, *Adv. Mater.*, **11,** 1469.
[16] Personal communication with Ringsdorf group.
[17] Musgrave, O. C., and Webster, C. J., 1969, *Chem. Commun.*, 712; Musgrave, O. C., and Webster, C. J., 1971, *J. chem. Soc. C*, 1393.
[18] Kumar, S., and Varshney, S. K., 2001, *Synthesis*, 305.