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K. Krishnan[a]; V. S. K. Balagurusamy[a]
[a] Centre for Liquid Crystal Research, P.O. Box. 1329, Jalahalli, Bangalore-560013, India,

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Preliminary communication

A novel dimeric discotic liquid crystal based on anthraquinone

K. KRISHNAN and V. S. K. BALAGURUSAMY*
Centre for Liquid Crystal Research, P.O. Box. 1329, Jalahalli, Bangalore-560013, India

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A novel dimer based on the disc-like anthraquinone core—bis[1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinon-5-oxy]dodecane, and its corresponding monomer 1-hexyloxy-5-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone, have been synthesized and characterized. X-ray diffraction studies show that this novel dimer exhibits a hexagonal columnar phase ($\mathrm{Col_h}$) with correlation among the molecular cores along the column. The $\mathrm{Col_h}$ phase of the dimer exists over a very wide temperature range, extending from 176°C down to at least − 60°C (the lowest temperature reached in DSC), whereas the monomer exhibits a $\mathrm{Col_h}$ phase at high temperature and a three-dimensionally ordered columnar phase ($\mathrm{Col_x}$) at low temperature.

It is of interest to make dimers and oligomers of molecules with a disc-like core as they, unlike the monomeric materials, usually tend to form glassy columnar phases which would be useful for several applications based on their quasi one-dimensional charge transport. Although a number of dimers with the disc-like core have been reported in the literature, most of them are based on triphenylene and a few on benzene and, to date, there are no reports on anthraquinone-based dimeric materials. Much attention has been paid to the development of triphenylene-based dimers, originally by Ringsdorf *et al.* [1–3], followed by Zimmermann *et al.* [4]. Notably, the latter group carried out a rather detailed study on one such dimer using X-ray diffraction and deuterium NMR, and compared its properties with those of the corresponding monomer. Moreover, they proposed a model for the organization of dimeric discotic molecules in the observed columnar phase ($\mathrm{Col_h}$). Recently, Bushby *et al.* [5, 6] have developed some rational synthetic methodologies for obtaining triphenylene-based dimers and oligomers. More importantly, some of the triphenylene-based dimers they synthesized form a long-lasting glassy phase (existing for months) [6]. Triphenylene-based star-like oligomers [7] and triphenylene-based (nitro)-functionalized oligomers [8] and dimers [9] have also been reported lately. However, no glassy columnar phases have been found in these reported oligomers and dimers.

Recently, we have shown that a number of anthraquinone-based discotic liquid crystals can be obtained easily, starting from gallic acid, by an efficient synthetic method developed by us [10]. We have shown also that unlike earlier reports [11, 12], anthraquinone ethers do exhibit more than one columnar mesophase and some of them are three-dimensionally ordered [10]. We have also shown that the substitution of bulky rigid aromatic cores such as a benzyl group for alkyl chains at the 1,5-positions of anthraquinone hexaethers stabilizes the three-dimensionally-ordered columnar phase ($\mathrm{Col_x}$), whereas it destabilizes the $\mathrm{Col_h}$ phase of the anthraquinone hexaethers [13]. Very recently, we have further demonstrated a new method for obtaining unsymmetrically substituted, mono-functionalized derivatives of anthraquinone, which would be very useful for making dimers, oligomers, and side group liquid crystalline polymers [14]. As a first step, we here demonstrate the use of the unsymmetrically substituted, mono-functionalized derivative for obtaining a novel dimer and its corresponding, but unsymmetrically substituted, monomer.

The starting material for the dimer, 5-hydroxy-1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone, was prepared according to the procedure described in our recent communication [14]. When it was heated with a half equivalent of 1,12-dibromododecane in the presence of potassium carbonate (in excess) and a catalytic amount of tetra-*n*-butylammonium iodide in dimethyl formamide (DMF) at 90°C, for 20 h under a nitrogen atmosphere, the dimer, bis[1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinon-5-oxy]dodecane

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*Author for correspondence; e-mail: uclcr@vsnl.com

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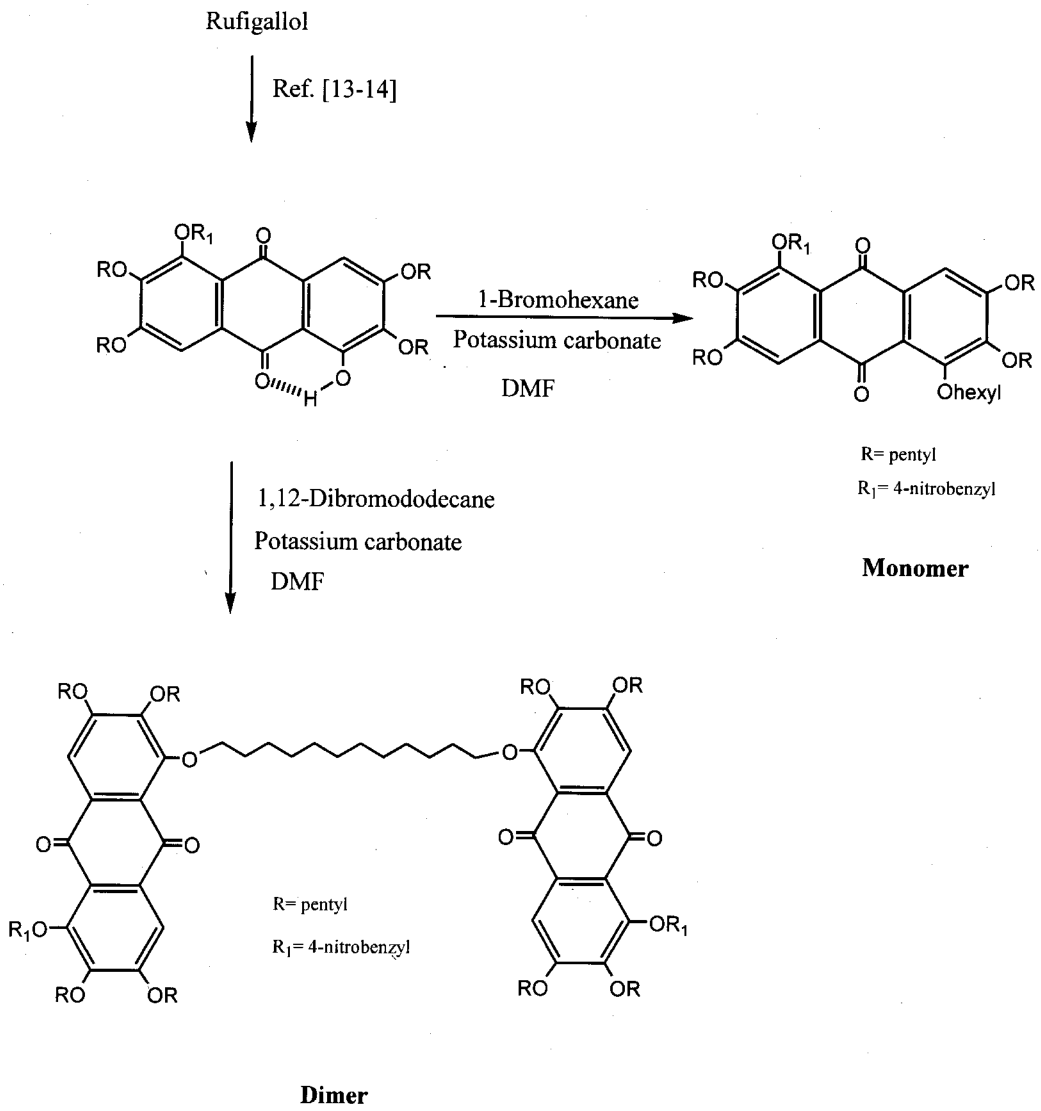
in 35% yield, isolated after column chromatographic purification and then crystallization (ethanol/ethyl acetate); see the scheme.

The IR spectrum of the dimer, unlike that of the starting compound, showed a single carbonyl resonance at 1664 cm^{-1}. The PMR spectrum showed an AB quartet centred at δ 8.06 ppm, two singlet aromatic resonances at δ 7.66 and 7.58 ppm, a singlet resonance at δ 5.21 ppm, and a multiplet at δ 4.0–4.26 ppm, in addition to the other methylene and methyl proton resonances supporting the formation of the dimer. Moreover, there were no resonances at or around δ 12.63 ppm (not even traces), suggesting that there is no unreacted phenolic compound contaminating the purified dimer; further there were no resonances at or around δ 3.5 ppm (not even traces), suggesting the absence of any mono-alkylated bromo compound. The mass spectrum (FAB mode) showed a molecular ion peak at 1603.6, which confirmed the formation and the structure of the dimer unambiguously.

The monomer, 1-hexyloxy-5-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone, was prepared (see the scheme) by heating a mixture of 5-hydroxy-1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone, bromohexane (12 equiv.), potassium carbonate (16 equiv.) and a catalytic amount of tetra-*n*-butylammonium iodide in DMF at 105°C for 15 h under a nitrogen atmosphere.



Scheme.

The monomer was purified by column chromatography followed by crystallization from chloroform/ethanol and was isolated in 85% yield.

The IR spectral features of the monomer resemble those of the dimer except for changes in the intensities of some of the absorption peaks. The PMR spectral features (chemical shifts as well as shapes of the signals) also resemble those of the dimeric compound. The mass spectrum (FAB mode) showed a molecular ion peak at 803.8, which confirmed the structure of the monomer.

Polarized-light microscopy of the dimer shows, on cooling the isotropic liquid, the appearance of a large number of mainly homeotropic domains with either dark, full or half (L-shaped) crosses, or a set of alternating dark and bright straight bands like the interference pattern from a pair of slits. The appearance of these straight bands has been suggested as resulting from a specific arrangement of the columns of molecules similarly to the formation of π-disclinations [15] which are one of the characteristics of columnar mesophase textures. Further, the texture is very similar to textures observed in other anthraquinone ethers, alkoxytriphenylenes and thiotriphenylene ethers, suggesting that the phase could be a hexagonal columnar phase ($\mathrm{Col_h}$). The texture was preserved till room temperature and remained the same for months.

The monomer, on cooling, shows a similar columnar texture, but in this case some cracks started appearing over the columnar texture when it was cooled below 100°C; the texture was again largely preserved till room temperature. However, a microscope slide preparation of the monomer left for a month at room temperature after a few heating and cooling cycles started forming mosaic domains, as observed in the case of some other anthraquinone ethers [10, 14], suggesting that the monomer exhibits a three-dimensionally ordered columnar phase at low temperature.

Table 1. DSC data for the monomer and dimer. Transition temperatures in °C; enthalpies (in parentheses) in kJ mol^{-1}.

Compound	Runs	$\mathrm{Col_x} \rightleftarrows \mathrm{Col_h}$	$\mathrm{Col_h} \rightleftarrows$ Iso.
Monomer	1st heating	110.0 (13.4)	163.2 (14.0)
	1st cooling	78.2 (− 8.5)	160.0 (− 13.02)
	2nd heating	100.1 (10.8)	162.5 (13.2)
Dimer	1st heating	[147.0 (18.6)][a]	180.4 (29.3)
	1st cooling	—	176.6 (− 27.4)
	2nd heating	[114.7 (6.0)]	180.0 (28.25)

[a] The origin of this transition (including the one that occurs on second heating) is not clear. X-ray investigations carried out at room temperature before and after the latter transition do not reveal any change in the mesophase structure. It may be noted that a similar transition has been observed in a triphenylene dimer by Zimmermann *et al.* [4].

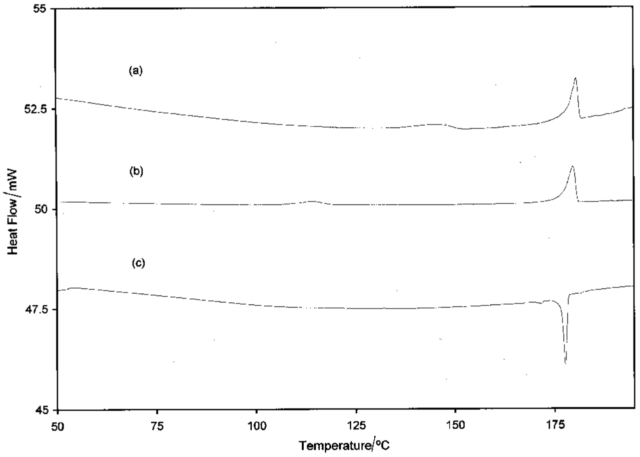


Figure 1. DSC curves of the dimer for first heating (*a*), second heating (*b*), and first cooling (*c*) runs.

Differential scanning calorimetry (Perkin Elmer, DSC 7) (see table 1) of a solution-crystallized sample of the dimer, run at a rate of 5°C min starting from around room temperature, shows (figure 1), during the first heating run, an endothermic transition at 147°C (enthalpy 18.6 kJ mol^{-1}), and transition to the isotropic liquid at 180.4°C (enthalpy 29.3 kJ mol^{-1}). However, during the first cooling run only one transition, namely I–$\mathrm{Col_h}$ at 176.6°C (enthalpy − 27.4 kJ mol^{-1}), is shown till room temperature. Separate DSC cooling runs down to − 60°C showed no additional transitions, including any glass transition. The second heating run showed a small endothermic transition at 114.7°C (enthalpy 6.0 kJ mol^{-1}) and a transition to the isotropic state at 180°C (enthalpy 28.25 kJ mol^{-1}). The second cooling thermogram was just like the first; it is unclear why the cooling runs do not show a transition corresponding to the one seen at 114.7°C on the second heating run. It may be noted that a similar behaviour was observed by Zimmermann *et al.* [4]. The DSC thermogram (figure 2) of a solution-

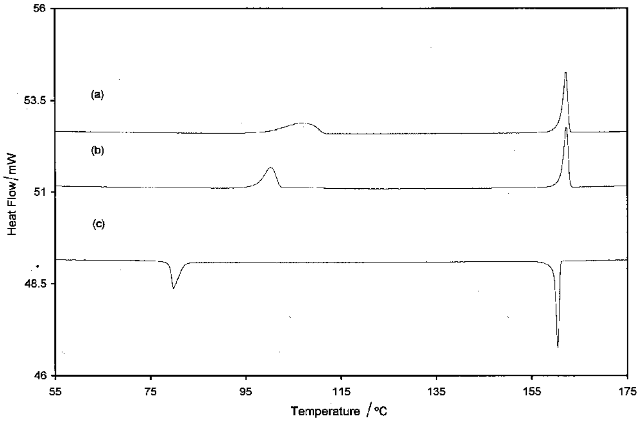


Figure 2. DSC curves of the monomer for first heating (*a*), second heating (*b*), and first cooling (*c*) runs.

Table 2. X-ray diffraction data for the dimer at room temperature.

d-Spacings of observed peaks/Å							
Intercolumnar, for index indicated				Diffuse, wide angle		2D Hexagonal lattice constant/Å	Correlation length/Å
(1 0)	(1 1)	(2 1)	(3 0)	Alkyl chain	Core-core		
16.1	9.51	6.30	5.53	4.12	3.46	18.60[a]	32.3[b]

[a] Calculated from the (1 0) peak *d*-spacing.
[b] Please see the footnote to the discussion in the text.

crystallized sample of the monomer, run at a rate of 5°C per minute, starting from around room temperature, shows, during the first heating run, two endothermic transitions. The first is at 110°C (enthalpy $13.4\,\mathrm{kJ\,mol^{-1}}$) and could mark the change of a three-dimensionally ordered columnar phase to a hexagonal columnar phase; the other is at 163.2°C (enthalpy $14.0\,\mathrm{kJ\,mol^{-1}}$) and represents the hexagonal columnar phase to isotropic liquid transition as suggested by microscopy. The first cooling thermogram showed an I–$\mathrm{Col_h}$ transition at 160°C (enthalpy $-13.02\,\mathrm{kJ\,mol^{-1}}$) and a $\mathrm{Col_h}$–$\mathrm{Col_x}$ transition at 78.2°C (enthalpy, $-8.5\,\mathrm{kJ\,mol^{-1}}$). No further transitions occurred down to room temperature; again, cooling runs going down to -60°C showed no additional transitions, including any glass transition. The second heating thermogram showed the $\mathrm{Col_x}$–$\mathrm{Col_h}$ transition at 100.1°C (enthalpy, $10.8\,\mathrm{kJ\,mol^{-1}}$) and a $\mathrm{Col_h}$–I transition at 162.5°C (enthalpy $13.2\,\mathrm{kJ\,mol^{-1}}$).

X-ray diffraction (XRD) studies (table 2) were carried out on the dimer (unoriented) at 125°C, and at room temperature (before heating to 125°C as well as after cooling from 125°C) with an X-ray imaging plate set-up (MAC-SCIENCE, Japan) with mirror–mirror optics. All three diffraction patterns show the presence of sharp low angle reflections (one very strong and three weak rings) and a broad diffuse peak in the wide angle region arising from the liquid-like alkyl chains. In addition, they show a relatively narrow diffuse ring in the wide angle region that would correspond to the existence of short range correlation among the molecular cores along the columns due to the overlap of the π-electron clouds. In the XRD pattern recorded at room temperature after heating the sample to 125°C and cooling, the sharp low angle rings observed correspond to the *d*-spacings 16.1, 9.51, 6.30 and 5.53 Å. These values are consistent with those expected for a 2D hexagonal lattice with the cell dimension 18.6 Å (also the column diameter), with the indices (1 0), (1 1), (2 1) and (3 0), respectively. The diffuse nature of the wide angle peak observed due to the correlation between the molecular cores along the columns shows that the correlation is only short range. It turns out that the correlation exists over about 10 near-neighbour distances (32.3 Å)† with an average separation of 3.46 Å between the neighbours. Hence the molecules are arranged in columns with only liquid-like order, and the columns are in turn organized in a 2D hexagonal lattice. These features are the same as those expected from a $\mathrm{Col_h}$ phase. The diffraction pattern recorded at 125°C shows features expected from a $\mathrm{Col_h}$ phase except that the correlation length among the molecular cores is 23.3 Å (7 near neighbour distances) with an average separation of 3.60 Å between neighbours.

The monomer X-ray diffraction pattern recorded at 120°C shows features that would be expected from a $\mathrm{Col_h}$ phase. Whereas the pattern recorded at 60°C (after cooling from 120°C) shows the appearance of a sharp doublet in the wide angle region, a diffuse peak appears in the high temperature $\mathrm{Col_h}$ phase. In the low angle

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†It may be pointed out that the correlation length of the molecular cores along the column has been calculated elsewhere [4] using the equation that relates the diffraction peak widths of small crystals with their size [16], which is also very similar to Scherrer's formula, differing only in the value of a coefficient. The correlation length calculated in that manner for the columnar phases discussed here yields for the dimeric system 182.4 Å (53 near neighbour distances) as against 32.3 Å (10 near neighbour distances) calculated here from the reciprocal of the HWHM of the Lorentzian fitting the peak profile. For the alkyl chain peak, the Scherrer-like equation yields a correlation length of 21.5 Å (5 near neighbour distances) which is quite large for the liquid-like order of the alkyl chains, whereas the Lorentzian fit gives 3.8 Å which is just about one nearest neighbour. It may be noted that the correlation length for the alkyl chains calculated from the HWHM of the peak profile, which is well described by a Lorentzian for the hexagonal columnar phase of a truxene-based system, also is 4.4 Å which is just about one nearest neighbour [17]. The correlation length calculated by us from the Scherrer-like equation for pure alkane liquids (in this case octadecane) from the diffraction data obtained by Richardson *et al.* [18] gives 24.9 Å (6 near neighbour distances) which is quite large for a liquid. The correlation length calculated from the HWHM, however, yields a value of 4.41 Å, which is just about one near neighbour distance. Hence it is clear that the application of a Scherrer-like equation for calculating the correlation length from a liquid-like peak gives about a six times larger value than that obtained from the Lorentzian peak profile fit.

region, only one very strong ring appears in the region where the (1 0) ring occurs in the $\mathrm{Col_h}$ phase, suggesting that this phase could be a hexagonal columnar rather than a rectangular columnar phase, but with long range order among the molecules along the column, making it a three-dimensionally ordered phase. In addition, there are many sharp rings observed in the pattern in the intermediate region (more than would be expected from a 2D hexagonal lattice), which is to be expected from a three-dimensionally ordered system.

In summary, the novel dimer, bis[1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinon-5-oxy]dodecane reported here exhibits a very wide temperature range (at least 236°C) hexagonal columnar phase with short range correlation among the molecular cores along the column ($\mathrm{Col_h}$) without undergoing any glass transition. The corresponding monomer, 1-hexyloxy-5-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone exhibits two columnar phases: the high temperature one is hexagonal columnar ($\mathrm{Col_h}$) whereas the low temperature one is three-dimensionally ordered. Unlike the triphenylene-based dimer and monomer reported by Zimmermann *et al.* [4], the anthraquinone-based dimer reported here exhibits a hexagonal columnar phase, stabilized over a wide temperature range (at least 236°C) compared with the corresponding monomer. This suggests that it may be possible to obtain systems forming glassy columnar phases by varying the length of the alkyl chain linking the two molecules. Work on this aspect is currently in progress in this laboratory.

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