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Preliminary communication

An example of an unsymmetrically substituted, monofunctionalized anthraquinone-based discotic liquid crystal

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We report here the synthesis and characterization of an unsymmetrically substituted, monofunctionalized anthraquinone-based discotic liquid crystal, namely 5-hydroxy-1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone. Interestingly, this compound, which has only four alkyloxy chains attached to the anthraquinone core, shows a hexagonal columnar phase (Col_h) of much wider temperature range compared with analogues having six alkyloxy chains. Incidentally, among the anthraquinone-based disc-like molecules exhibiting columnar phases known so far, this is the first molecule, which does not possess any C_2-axis of symmetry. Besides its unsymmetrical structure and interesting mesomorphic behaviour, monofunctionalized monomers of this kind, unlike the available C_2-symmetric difunctionalized tetraethers, can serve as potential synthons for obtaining dimers in a unique way. In addition, various anthraquinone-based oligomers, metallomesogens, and side group liquid crystalline polymers can be obtained from these monomers.

Although anthraquinone-based disc-like molecules were found to form columnar phases two decades ago [1], soon after the discovery of discotic liquid crystals [2], only very limited chemical [3–6] and hardly any physical studies have been done on this interesting class of materials. In fact, these yellow materials which form short range ordered columnar phases (Col_h) [4] as well as some three dimensionally ordered phases [5, 6], can serve as good candidates for electrical conductivity and photoconductivity studies†. Anthraquinone-based C_2-symmetric hexaesters, hexaethers, and difunctionalized tetraethers [3–6] have been obtained, and the last of these have been used as precursors for main chain discotic polymers [7]. However, monofunctionalized anthraquinone ethers have not been reported so far in the literature. Monofunctionalized anthraquinone ethers are another important class of compounds because of their use in the synthesis of anthraquinone-based dimers, oligomers and side group liquid crystalline polymers. In triphenylene-based discotic liquid crystals, the unsymmetrical monohydroxy penta-alkyloxytriphenylenes have been synthesized and found to be non-mesomorphic [8]. These monohydroxy pentaethers are the ones which serve as synthons for making various triphenylene-based discotic side group polymers [9], glass-forming liquid crystalline dimers [10], and oligomers such as star-like molecules [11]. Recently, we have described an efficient synthesis of anthraquinone-based mixed chain hexaethers [5], and the synthesis of a series of difunctionalized tetraethers of anthraquinone and of a novel series of anthraquinone-based discotic liquid crystals with bulky substituents [6]. We here describe the synthesis of a novel monofunctionalized unsymmetrical derivative of anthraquinone, which can be used as a synthon for obtaining various anthraquinone-based discotic dimers, oligomers, side group liquid crystalline polymers and metallomesogens.

Synthetic procedures for making hexaethers and difunctionalized tetraethers of rufigallol starting from gallic acid are readily available in the literature [4–6]. Due to the difference in the reactivity of the two different kinds of phenoxyl groups present in the rufigallol, one can easily make any homologue of the tetra- or hexaethers of rufigallol [4–6]. But, while making the hexaethers from the tetraethers, one needs to take great care to convert efficiently and exclusively the latter into the hexaether derivatives. If the hexaethers are contaminated with traces of pentaethers or tetraethers, it is very difficult to

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†Recently we have observed an increase of about seven orders in the electrical conductivity along the column, reaching 10^{-2} S m^{-1}, in the columnar mesophase on doping.

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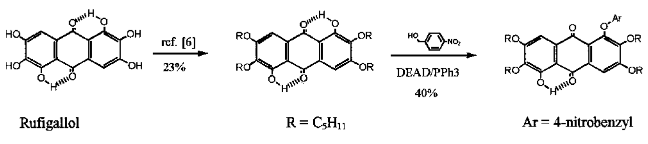
separate them as they all have almost the same R_f value in thin layer chromatography (TLC) in different solvent systems. When we attempted to make pentaethers of rufigallol by heating a mixture of rufigallol tetraether (1 equiv.), bromoalkane (1 equiv.) and potassium carbonate (excess) in DMF, we obtained a mixture of products (tetra-, penta- and hexa-ethers). They were not easily separable by column chromatography; in particular, the desired pentaether could not be obtained without contamination. In order to overcome this purification problem and obtain a penta-alkylated rufigallol, we chose to introduce a polar substituent, namely a 4-nitrobenzyl group at the 1-position of the rufigallol core. Thus, we carried out a monoalkylation reaction (Mitsunobu's conditions) on 1,5-dihydroxy-2,3,6,7-pentapentyloxy-9,10-anthraquinone [6] using 4-nitrobenzyl alcohol, triphenylphosphine and diethyl azodicarboxylate in tetrahydrofuran (THF) at 10°C (see the scheme); we anticipated that the desired monoalkylation product, a pentaether of this sort, unlike those having all alkyl substituents of almost the same polarity, would be easily separable by chromatographic techniques. As anticipated, the penta-alkylated derivative formed in the above reaction was considerably more polar than the starting tetraether in 5% ethyl acetate–hexane (see details that follow) and was easily separable from the unreacted starting materials and by-products by simple column chromatography. The purified pentaether, 5-hydroxy-1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone, was spectroscopically analysed (PMR, ^{13}CMR, IR, and mass) and found to be pure.

In a typical experiment, diethyl azodicarboxylate (0.47 ml, 3 mmol, 1.5 equiv.) was added dropwise over a period of 10 min to a cold (10°C), stirred solution of 1,5-dihydroxy-2,3,6,7-tetrapentyloxy-9,10-anthraquinone (1.17 g, 2 mmol), 4-nitrobenzyl alcohol (460 mg, 3 mmol, 1.5 equiv.), and triphenylphosphine (787 mg, 3 mmol, 1.5 equiv.) in dry THF (18 ml) under a nitrogen atmosphere; the mixture was stirred at 10°C for an hour, then warmed to room temperature, and held there for 15 h. The THF was removed and the resulting residue purified by column chromatography (silica gel, 250–400 mesh) using 5% ethyl acetate in hexane as eluent; this was followed by 'recrystallization' (see later discussion) from ethanol–ethyl acetate to give 5-hydroxy-1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone, (576 mg, 40%). In TLC (5% ethyl acetate in hexane), the R_f-value of the starting material is 0.53 and that of product is 0.3.



Scheme.

The PMR spectrum of the new pentaether (figure 1), showed a resonance at δ 12.63 ppm, integrating for one proton corresponding to the intramolecularly hydrogen bonded phenoxyl proton, two aromatic proton resonances as singlets at δ 7.70 and 7.37 ppm, integrating for one proton each corresponding to the aromatic protons of the anthaquinone, two doublets (AB quartet) at δ 8.30 and 7.85 ppm, integrating for two protons each corresponding to the aromatic protons of the 4-nitrobenzyl group, a singlet resonance at δ 5.20 ppm, integrating for two protons corresponding to the benzyloxy protons and a multiplet at δ 4.25–4.00 ppm, integrating for eight protons corresponding to the four aryloxy methylene resonances, in addition to the other methylene- and methyl-proton resonances. The IR spectrum showed, as expected, two different quinone carbonyl resonances at 1660 and 1633 cm^{-1} due to the unsymmetrical nature of the molecule. The ^{13}CMR spectrum of this compound, unlike those of symmetrical tetra- or hexa-ethers, exhibited two carbonyl resonances at δ 186.6 and 180.6 ppm, sixteen aromatic carbon resonances at δ 158.5, 157.4, 156.6, 153.3, 147.9, 147.6, 144.9, 140.2, 130.8, 130.5, 128.5 (2C), 123.6 (2C), 121.1, 111.3, 107.4, and 104.9 ppm (of which twelve are due to the aromatic carbons of the unsymmetrically substituted anthraquinone core and the other four to the 1,4-disubstituted phenyl group), and four aryloxy methylene resonances at δ 74.4, 73.9, 73.6, and 69.4 (2C) ppm, in addition to the other methylene- and methyl-carbon resonances (δ 30.0, 28.8, 28.1, 22.4, and 14.0 ppm). Finally, the mass spectrum showed the expected molecular ion peak [M$^+$, 719.6]. These spectral features confirmed the structure of the unsymmetrical pentaether unambiguously.

Polarizing optical microscopy of this pentaether shows, on cooling from the isotropic liquid, the appearance of a large number of domains (varying from dark to highly birefringent) and some π-disclination-like regions (figure 2). The texture is very similar to those observed

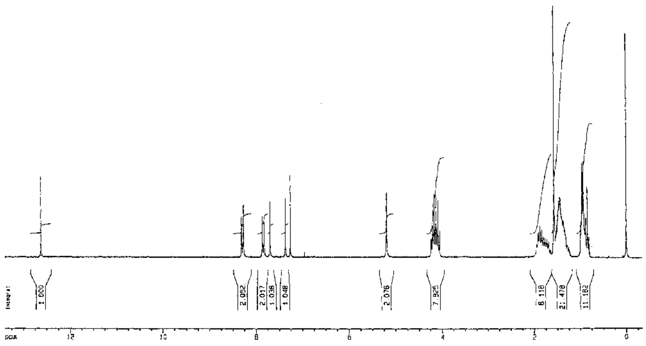


Figure 1. PMR (200 MHz, CDCl$_3$) spectrum of 5-hydroxy-1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone.

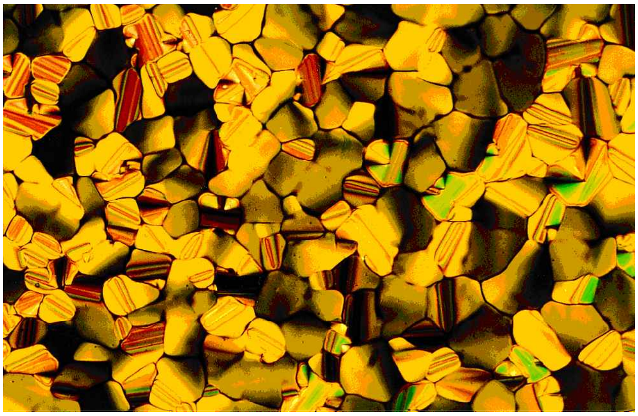


Figure 2. Texture observed by polarizing optical microscopy for the title compound at 160°C, obtained after cooling from the isotropic phase.

for anthraquinone hexaethers [5, 6], alkoxytriphenylenes and thioalkoxytriphenylenes suggesting that it could be a hexagonal columnar phase ($\mathrm{Col_h}$). On cooling from the columnar phase, the texture is almost preserved even across the other lower temperature transition (cf. discussion on the DSC thermograms) with only the formation of some cracks in the texture, and there is no sign of crystallization.

Here it is noted that the solvent 'crystallised' material has been examined by X-ray diffraction at room temperature. This shows the presence of a columnar phase with liquid-like alkyl chains and correlation between the cores along the columns. The columns are not arranged hexagonally as in the $\mathrm{Col_h}$ phase, and the two dimensional phase could be rectangular. This phase, and that referred to below in the discussion of the DSC results as the M1 phase, appear to be the same. The material apparently therefore exists as a columnar mesophase at room temperature.

Differential scanning calorimetry (Perkin Elmer, DSC 7) of a solution-'crystallized' sample of the pentaether, run at a rate of 5° $\mathrm{min^{-1}}$, during the first heating run and started from room temperature, shows two endothermic transitions: the first one at 71.9°C (enthalpy, 8.52 kJ $\mathrm{mol^{-1}}$) is presumably from the room temperature mesophase (M_1) which is yet to be fully characterized to the hexagonal columnar phase ($\mathrm{Col_h}$) [5, 6]; the second transition at 171.6°C (enthalpy, 6.95 kJ $\mathrm{mol^{-1}}$) is from the hexagonal columnar phase ($\mathrm{Col_h}$) to the isotropic liquid (I). During the first cooling run, the $\mathrm{I \rightarrow Col_h}$ transition occurs at 170.3°C (enthalpy, 6.9 kJ $\mathrm{mol^{-1}}$) and, $\mathrm{Col_h \rightarrow M_1}$ at 51.6°C (enthalpy 5.9 kJ $\mathrm{mol^{-1}}$). The second heating thermogram is similar to that of the first heating run; it shows the $\mathrm{M_1 \rightarrow Col_h}$ at 71.0°C (enthalpy, 7.9 kJ $\mathrm{mol^{-1}}$) and the $\mathrm{Col_h \rightarrow I}$ at 171.3°C (enthalpy, 6.8 kJ $\mathrm{mol^{-1}}$). This unsymmetrical compound therefore shows a much wider hexagonal columnar phase range (99.7°, obtained from the first heating run) when compared with that of C_2-symmetric derivatives, 1,2,3,5,6,7-hexapentyloxy-9,10-anthraquinone (*c.* 42°) [4 (*a*)] and 1,5-dibenzyloxy-2,3,6,7-tetrapentyloxy-9,10-anthraquinone (monotropic). The behaviour of this monohydroxy compound is also quite different from that of monohydroxy penta-alkoxytriphenylenes, which are generally non-mesomorphic. The columnar mesophase range for this unsymmetrical derivative is the widest for any of the monomeric anthraquinone ethers exhibiting hexagonal columnar phases ($\mathrm{Col_h}$) reported thus far [4–6].

Preliminary X-ray diffraction studies carried out on the $\mathrm{Col_h}$ phase at 120°C show the appearance of one strong and one very weak low angle peaks, and one broad diffuse peak and a relatively narrow diffuse peak in the wide angle regions. The positions of the low angle peaks show that the columns are arranged in a two-dimensional hexagonal lattice. The broad diffuse peak corresponds to the alkyl chains and the relatively narrow diffuse peak corresponds to that arising from the short range correlation among the molecular cores along the column. Further, the separation between the molecular cores along the column is very close to that measured by us in the case of hexaethers of anthraquinone [5]. All the above observations are in conformity with the usual features of a $\mathrm{Col_h}$ phase.

In summary, the unsymmetrically substituted, monofunctionalized anthraquinone-based discotic mesogen 5-hydroxy-1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone reported here shows a hexagonal columnar phase ($\mathrm{Col_h}$) of much wider temperature range when compared with similar C_2-symmetric analogues having six alkyloxy chains attached to the anthraquinone core. This compound can serve as a potential synthon for making several discotic materials, especially dimers, oligomers, and polymers, which may exhibit some interesting properties such as, the formation of liquid crystalline glass phases. Moreover, since a benzyl group can be easily removed by hydrogenolysis, one can also make use of this compound for preparing other unsymmetrical penta- and hexa-ethers. The synthesis of the homologous series of this derivative and novel dimers, together with results from their X-ray diffraction studies are currently being undertaken.

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