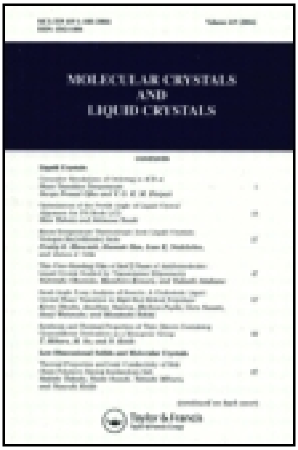

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Synthesis and Mesomorphic Properties of Some Anthraquinone Derivatives: New Difunctionalised Discotic Monomers

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To cite this article: Veena Prasad & D. S. Shankar Rao (2000): Synthesis and Mesomorphic Properties of Some Anthraquinone Derivatives: New Difunctionalised Discotic Monomers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 350:1, 51-65

To link to this article: http://dx.doi.org/10.1080/10587250008025232

Mol. Cryst. Liq. Cryst., Vol. 350, pp. 51-65
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Printed in Malaysia

Synthesis and Mesomorphic Properties of Some Anthraquinone Derivatives: New Difunctionalised Discotic Monomers

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(Received October 15, 1999; In final form November 30, 1999)

Some new 9,10-anthraquinone (rufigallol) derivatives have been prepared and their mesomorphic properties have been studied. The unsymmetrically substituted tetrahydropyranyloxy-ethers (THP-ethers), exhibited columnar mesomorphism at fairly low temperatures and the xray studies carried out for one of the homologues confirmed the hexagonal nature of the mesophase. The deprotected derivatives of these THP-ethers, also form columnar mesophases. All these derivatives are very good candidates for polymerisation studies.

Keywords: anthraquinone; difunctionalised discotic monomers; THP-ethers; columnar phase

INTRODUCTION

9,10-Anthraquinone (rufigallol) derivatives are one of the earliest systems reported to form columnar mesophases [1–3]. These liquid crystalline derivatives are interesting for several reasons: they have a nucleus with only C_2- `symmetry; they can be easily and economically prepared through the acid catalysed self-condensation of gallic acid, their derivatives are coloured and thermally stable. The rufigallol core has six phenolic groups but with unequal reactivity. This allows the selective substitution of four phenolic groups leaving behind the two intramolecularly hydrogen bonded hydroxyl groups and thus, various "mixed tails" discotics can be easily prepared. Moreover, these two functional groups

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* Corresponding Author.

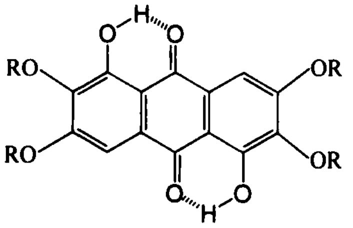
can be utilised to prepare main chain polymers. The quinonide system may behave as an electron acceptor and, therefore, can be doped with electron donors to prepare n-type conductors [4]. First n-type discotic one-dimensional conductor based on tricycloquinazoline core has recently been reported by the Boden and co-workers [5].

Liquid crystalline hexa-esters of rufigallol were reported in 1980 [1] and since then several tetra-, hexa- and octa-substituted derivatives have been synthesised and characterised [2, 6–8]. These derivatives exhibit a number of mesophases, which have been extensively studied by DSC, X-ray and 2H-NMR studies [9, 10]. Formation of highly ordered phases on cooling the normal columnar phase is also reported in many of these derivatives. Similar highly ordered phases exhibited by some of the triphenylene derivatives have recently been characterised as discotic plastic and helical phases. Interestingly the charge carrier mobility in these phases have been found to be one to three orders of magnitude higher than in the normal columnar phase [11, 12].

Despite a substantial work on anthraquinone derivatives, it is only very recently the first thermotropic main-chain discotic liquid crystalline polyethers based on rufigallol have been reported [13]. The important structural features in main chain discotic polymers are the length of the side chains, the length and nature of spacer unit that links the monomer units. With an objective to understand the role of these factors on the mesomorphic properties of the resulting polymers, we have synthesised new difunctionalised monomers, based on rufigallol for polymerisation. During this process we found that many of the intermediates themselves are mesomorphic. In this paper we report the synthesis, characterization and mesomorphic properties of these difunctionalised anthraquinone derivatives III and their intermediates I and II (see Figure 1). Since almost all the members of family II are found to be mesomorphic, we have studied them in greater detail.

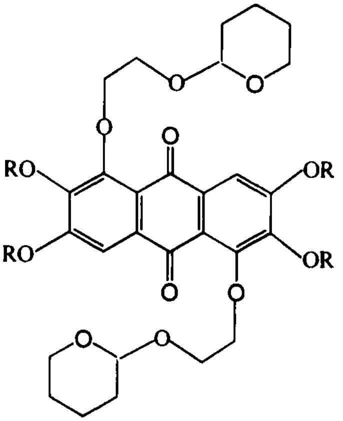
EXPERIMENTAL

Chemicals and solvents (AR quality) were obtained locally and used as such without any purification. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 200MHz Bruker Aveance Series DPX200 NMR spectrometer, using TMS as an internal reference standard. The mass spectra were run on a JEOL JMS 600 spectrometer. The transition temperatures were determined using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMRXP polarising microscope. The enthalpies of transi-



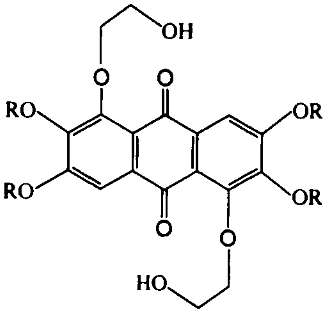
$R = C_nH_{2n+1}$; n = 3, 4,....10

I



$R = C_nH_{2n+1}$; n = 3, 4,....10

II



$R = C_nH_{2n+1}$; n = 4, 6, 8 and 10

III

FIGURE 1 Molecular structures of synthesized difunctionalised anthraquinone derivatives III, and their intermediates I and II tions were determined from thermograms obtained with a differential scanning calorimetry (DSC7 Perkin-Elmer). The precision in the calculation of the enthalpy is estimated to be about 10 J/mol. The heating and cooling rate was 5°C/min. Xray measurements were carried out using a MAC Science image plate set up [14]. The precision in the calculation of wave vector is reckoned to be 3×10^{-3} Å^{-1}.

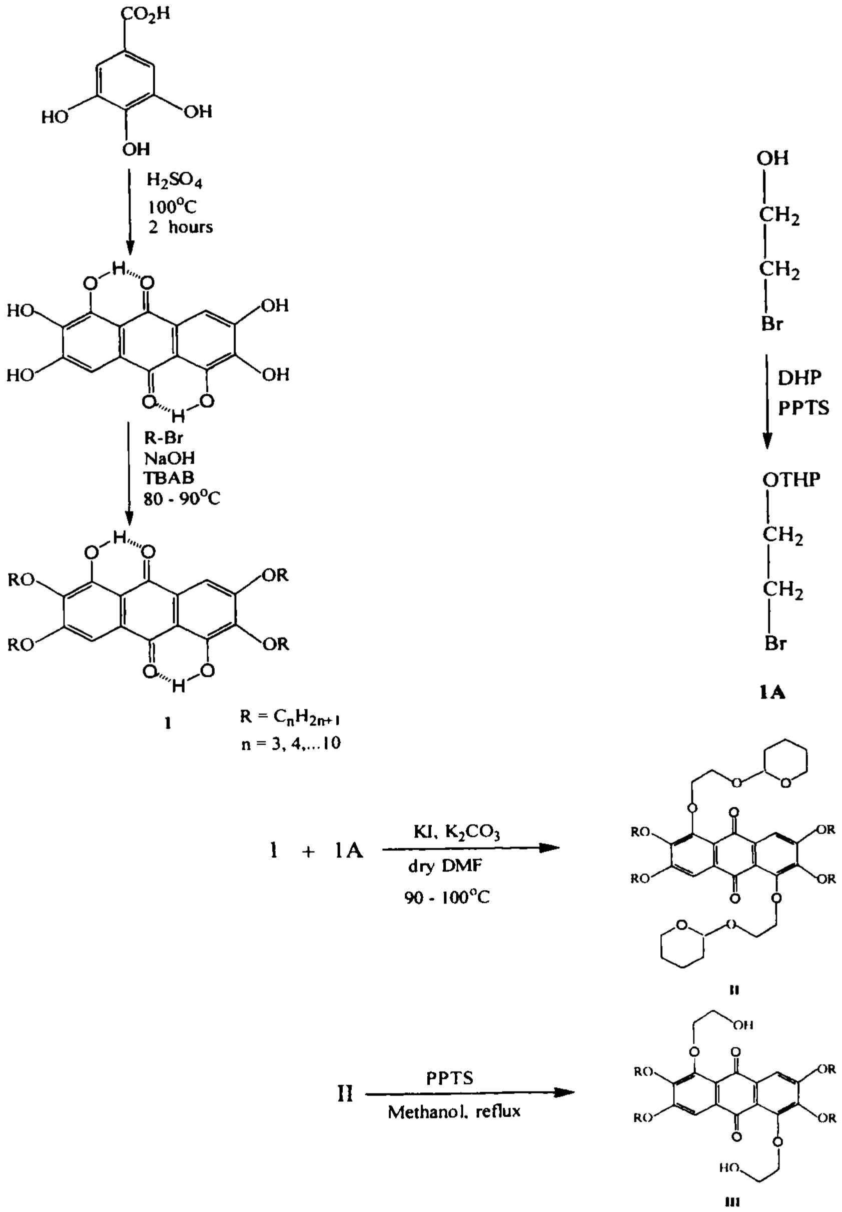
SYNTHESIS

The difunctionalised anthraquinone monomers III, were prepared following the synthetic procedures as outlined in scheme 1. Thus, 1,5-dihydroxy-2,3,6,7-tetraalkyloxy-9,10-anthraquinones I, were prepared starting from gallic acid [8]. The THP-ethers of these compounds, II, were obtained by treating them with 1-bromo-2-tetrahydropyranyloxyethane IA. The deprotection of THP-ethers II, using pyridinium p-toluene sulphonate (PPTS) as a catalyst, yielded the difunctionalised compounds III. All the compounds synthesised were purified either by column chromatography or recrystallisation or sometimes both as per the requirement. The chemical structures as well as the purity of the compounds were checked by TLC, spectral data, and DSC.

Rufigallol was prepared from gallic acid using a previously reported procedure [15]. The crude product was directly used for further alkylation reactions, unlike purification procedures mentioned for rufigallol before proceeding to further steps [8]. Still the yields of pure alkylated products were reasonably good. The detailed synthesis procedures for one of the homologues with n=6 of these three series are given below:

Compound I

Rufigallol (4.0g, 0.0132 mol), DMSO (350ml) and TBAB (18.76, 0.0582 mol) were taken in a round bottom flask. To this, NaOH in water (2g in 13.0ml) was added, and the mixture was stirred for 15 min. under nitrogen atmosphere. 1-Bromohexane (9.62g, 0.0583 mol) was added to the stirred mixture and the reaction was allowed to proceed at 80–90°C with stirring for 30 hrs. under nitrogen atmosphere. After cooling, the golden yellow needle like crystals of the product was filtered and purified by recrystallisation (EtOH/$CHCl_3$). Yield: 49%; m.p. 107.0°C; ^{1}H NMR ($CDCl_3$) δ: 12.8 (s, 2H, -OH), 7.45 (s, 2H, Ar-H), 4.1–4.3 (m, 8H, OCH_2), 1.4–2.0 (m, 32H, CH_2), 0.98 (m, 12H, CH_3); MS (FAB) m/z: 641 $(MH)^+$.


CO2H
HO
OH
OH
H2SO4
100°C
2 hours
O
H
O
HO
OH
HO
OH
O
H
O
R-Br
NaOH
TBAB
80 - 90°C
O
H
O
RO
OR
RO
OR
O
H
O
1
R = CnH2n+1
n = 3, 4,...10
OH
CH2
CH2
Br
DHP
PPTS
OTHP
CH2
CH2
Br
1A
1 + 1A
KI, K2CO3
dry DMF
90 - 100°C
RO
OR
RO
OR
II
II
PPTS
Methanol, reflux
OH
RO
OR
RO
OR
HO
III

SCHEME 1

Compound IA

This was prepared according to the general procedure described [16]. Thus 2-bromoethanol (5.0g, 0.04 mol) and PPTS (1.0g, 0.004 mol) were taken in a round bottom flask. This was cooled in ice and added 3,4-dihydropyran (DHP) (3.36g, 0.04 mol) through syringe. The reaction mixture was stirred for 6 hours at room temperature. Then it was diluted with ether and washed once with half-saturated brine. The ethereal solution was dried and evaporated. The crude product was chromatographed over silica gel using hexane as an eluent, to get pure compound IA. Yield: 90%; ^{1}H NMR ($CDCl_3$); δ: 4.68 (t, 1H, CH, *J*=3.4 Hz), 3.42–4.08 (m, 6H, CH_2), 1.4–1.9 (m, 6H, CH_2).

Compound II

Compound I (0.64g, 0.001 mol), compound IA (2.1g, 0.01 mol) and K_2CO_3 (1.38 g, 0.01 mol) were taken in dry DMF (50ml). Added catalytic amount of KI and the reaction mixture was stirred at 90–100°C for 30 hours under nitrogen atmosphere. After cooling, the reaction mixture was poured into cold water (50ml). The product was extracted with chloroform (50ml×2), washed with distilled water (100ml×3) and dried (Na_2SO_4). The crude product obtained after removing the solvent was purified by passing through basic alumina using CH_2Cl_2 as an eluent. Finally it was recrystallised using ethanol. Yield: 52%; ^{1}H NMR ($CDCl_3$); δ: 7.57 (s, 2H, Ar-H), 4.73 (m, 2H, CH), 3.88–4.32 (m, 18H, CH_2), 3.54 (m, 2H, CH_2), 1.3–2.0 (m, 44H, CH_2), 0.92 (m, 12H, CH_3); ^{13}C NMR: 181.0, 157.3, 153.5, 146.8, 132.5, 120.3, 107.0, 98.7, 74.1, 73.0, 69.1, 66.7, 61.9, 31.6, 31.5, 30.5, 30.2, 29.0, 25.6, 25.5, 22.6, 19.2, 13.9; MS (FAB) m/z: 919 $(M+Na)^+$.

Compound III

A mixture of compound II (0.448 g, 0.5 mmol) and PPTS (15 mg, 0.06 mmol) in methanol (50ml) was refluxed for 5 hours. On cooling the reaction mixture, the yellow solid separated out. This was filtered and recrystallised from ethanol, to get the pure compound III. Yield: 58%, m.p. 140.0°C, ^{1}H NMR ($CDCl_3$), δ: 7.64 (s, 2H, Ar-H), 4.86 (t, 2H, -OH, *J*=6.0Hz), 4.37 (t, 4H, OCH_2, *J*=4.0Hz), 4.18 (t, 4H, OCH_2, *J*=6.4Hz), 4.06 (t, 4H, OCH_2, *J*=6.6 Hz), 3.8 (m, 4H, CH_2), 1.57–1.92 (m, 8H, OCH_2CH_2), 1.25–1.47 (m, 24H, CH_2), 0.90 (m, 12H, CH_3); MS (FAB) m/z: 751.0 $(M+Na)^+$.

All the other compounds of series I, II and III were prepared in a similar way and their spectral data were found to be matching very well with the expected values.

RESULTS AND DISCUSSION

In our present study we have synthesised three different series of compounds, I, II and III. In series I, only one member with n=4 is found to be liquid crystalline [Cr 123.3 (Col 110.5°C) Iso], forming a monotropic columnar mesophase (reported* m.p. 120°C [8]). In contrast, all the THP-ethers of 9,10-anthraquinone, II, except the first homologue IIa, are found to be liquid crystalline and therefore, they have been studied in detail. Their transition temperatures and enthalpies of transitions are given in table I. The compound IIb is monotropic whereas the other homologues are enantiotropic in nature. However in the case of IIb the solvent crystallised and melt crystallised solids have different melting points. The solvent crystallised solid on heating goes directly to isotropic liquid at 103.0°C. On cooling this shows the mesophase at 93.0°C and on further cooling solidifies at around 60°C. When this melt- crystallised solid is reheated it melts at 88.0°C forming the columnar mesophase and on further heating it goes to isotropic liquid at 95.5°C. This type of behaviour is seen atleast in some discotic liquid crystalline systems [17].

TABLE I Transition temperatures (in °C) and enthalpies of transitions (kJ mol^{-1}) enclosed in square brackets, for the compounds of series II. • *the phase exists, – the phase does not exist*

Compound number	*n*	*Cr*		*Col$_h$*		*Iso*
IIa	3	•	126.0	–		•
			[36.80]			
IIb	4	•	103.0	•	(93.0)	•
			[39.05]		[12.70]	
IIc	5	•	79.5	•	101.5	•
			[21.96]		[14.43]	
IId	6	•	83.5	•	91.0	•
			[34.41]		[11.81]	
IIe	7	•	80.5	•	85.5	•
			[38.46]		[10.25]	
IIf	8	•	64.0	•	76.0	•
			[34.48]		[9.99]	
IIg	9	•	58.5	•	70.0	•
			[57.72]		[8.86]	
IIh	10	•	52.0	•	62.5	•
			[56.61]		[7.84]	

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* In literature this compound has been reported as non-mesomorphic.

All these compounds have a fairly low melting as well as isotropic temperature. On cooling from the isotropic liquid, they exhibit the typical "flower" texture of discotic columnar mesophase, which is shown in Figure 2. The mesophase supercools to a large extent (in most cases upto room temperature). The DSC thermogram for the compound IIf is given in Figure 3. As can be seen from this, there are two peaks on first heating: the first peak corresponds to melting and the second peak corresponds to mesophase to isotropic transition. On second heating, we do not see the first peak of melting but observe only the mesophase-isotropic transition peak. On cooling, we see only one peak associated with isotropic-mesophase transition with no other peak seen atleast upto room temperature. However, if the sample is kept for a long time at room temperature, it slowly crystallises.

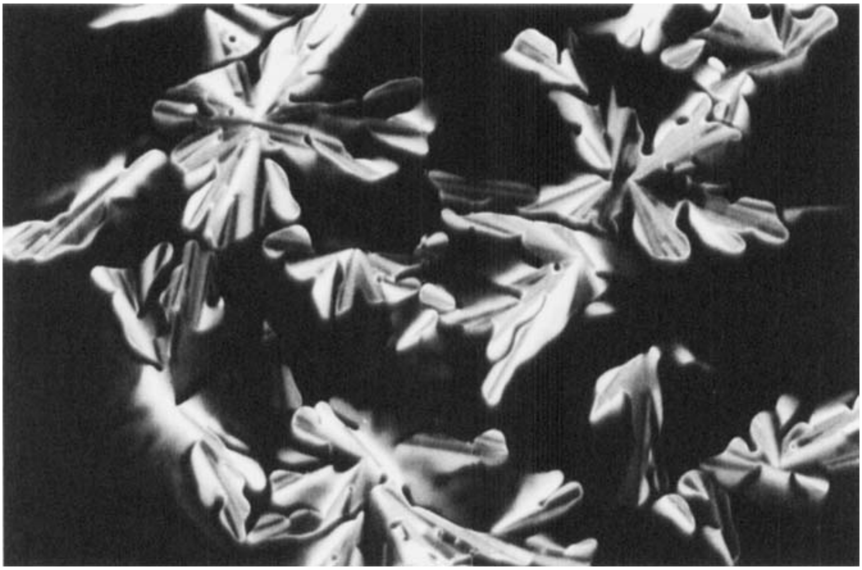

FIGURE 2 Photomicrograph showing the typical texture of discotic columnar phase for a representative compound, IIf at 72°C (See Color Plate III at the back of this issue)

A plot of the different transition temperatures versus the number of carbon atoms (n) in the alkyloxy chains is shown in Figure 4. As usual, the mesophase to isotropic transition temperatures decrease with increasing chain length. It can be seen from the plot that the maximum mesophase range (~22°C) is exhibited by the compound with n=5 (IIc). For this compound the overall length of functionalised chains (at 1 and 5 positions) is almost equal to the length of n-alkyloxy chains. This is in agreement with the observation made [8], wherein the maxi-

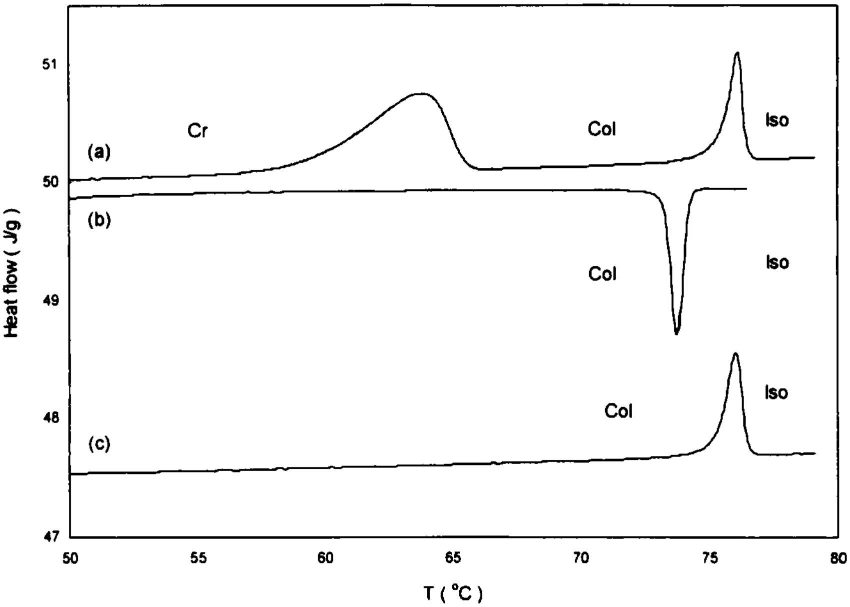

FIGURE 3 DSC thermograms for the compound IIf. The heating/cooling rate was 5°C/min. The curve (a) represents the first heating scan which shows two peaks, the low temperature one corresponding to the melting and the high temperature peak for the columnar (col) to isotropic transition. Cooling scan upto 50°C (b) doesn't show crystallisation peak This is also reflected in the second heating scan (c) where no melting peak is observed

mum mesophase range was found for the compound with all the 6-alkyloxy chains of the same length (R68, in the notation of Ref. 8). One can also see that the mesophase range reaches a minimum (~5°C) for the compound with n=7. The mesophase range increases for the compound with n=8 and for n=9 and 10, it remains almost the same. All these observations are in accordance with the reported results [8].

The plots of melting entropy (ΔS_m) and isotropisation entropy (ΔS_i), versus n are shown in Figure 5. The compound with n=5 has the minimum ΔS_m and from there onwards upto n=7 it gradually increases. ΔS_m shows a sudden jump, from n=8 to n=9 but hardly varies between n=9 and n=10. The value of ΔS_i reaches a maximum for the compound with n=5, for which the mesophase range has also been found to be maximum. There is a gradual decrease in ΔS_i value from n=6 onwards upto n=10. All these results are again in agreement with the observations made previously [8].

In both the symmetrically and unsymmetrically substituted derivatives of anthraquinone reported so far, the flexible part consists of normal aliphatic

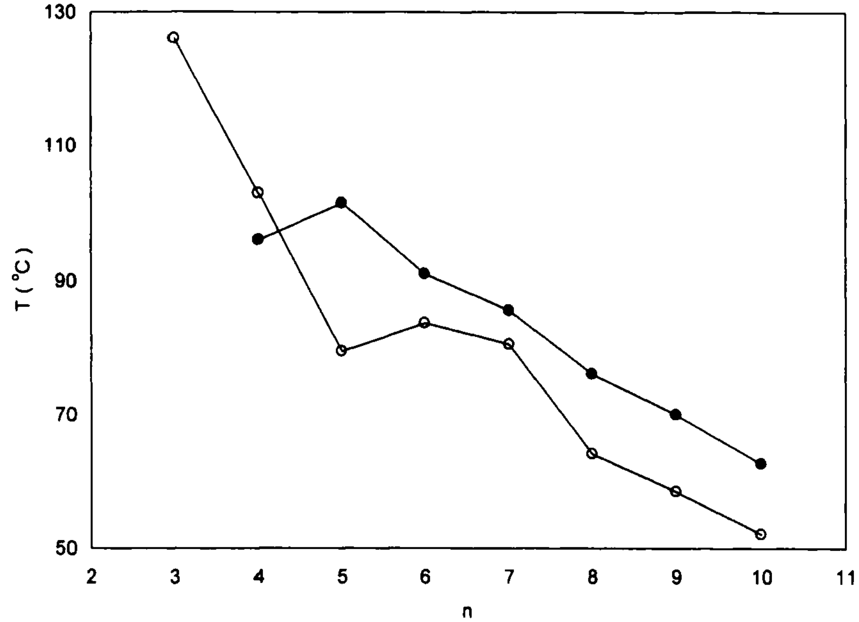

FIGURE 4 Plot showing the width of the columnar phase as a function of chain length for series II. Here open circles represent the melting point and the filled circles the clearing point. The solid line is meant to be a guide to the eye

chains bound to the central core by ether or ester linkages. To understand the structure-property relationship of 9,10-anthraquinone derivatives, we have, earlier carried out substitution of slightly bulkier pendant groups viz., benzyl groups on this core at 1 and 5 positions [18]. These materials are also found to be liquid crystalline forming a columnar mesophase. The transition temperatures of these benzyl ethers are higher than the transition temperatures of THP-ethers II. This could be attributed to the enhanced π-π electronic interactions between the molecules in benzyl ethers due to the additional benzene rings. When we compare the mesophase range of these THP-ethers II, with the symmetrically substituted [6] and unsymmetrically substituted [8] hexa-n-alkyloxy ethers, the mesophase range is lower for the present system II.

In series III, we have synthesised four derivatives with n=4, 6, 8 and 10. The transition temperatures and enthalpies of transitions for these compounds are given in Table II. Among these the compounds with n=4 and n=6 are non-mesomorphic. The compound with n=8 shows a texture (shown in Figure 6) which resembles the texture of a highly ordered "discotic plastic" type of mesophase[19] and the "coverslip test" confirms this observation. The compound with n=10 showed two different mesophases [Cr 82.0°C Col_{x1} 107.7°C Col_{x2} 122.5°C Iso]. Col_{x1} is a highly ordered phase and the microscopic texture of Col_{x2} appeared like a columnar mesophase. It should be noted that all these difunctionalised liquid crystalline monomers can be used for polymerisation. Such difunctionalised monomers have been already found to be very valuable precursors for the preparation of liquid crystalline main-chain polymers and networks in the case of triphenylene based discotic liquid crystals [20]. In fact, we have carried out the polymerisation reactions, the details of synthesis and characterisation of which will be reported soon.

TABLE II Transition temperatures (in °C) and enthalpies of transitions (kJ mol^{-1}) enclosed in square brackets, for the compounds of series III. • *the phase exists, – the phase does not exist*

n	*Cr*		*Col_{x1}*		*Col_{x2}*		*Iso*
4	•	162.0	-		-		•
		[34.40]					
6	•	140.0	-		-		•
		[26.27]					
8	•	72.5	•	130.5	-		•
		[56.76]		[20.26]			
10	•	82.0	•	107.7	•	122.5	•
		[89.30]		[1.33]		[12.38]	

X-RAY STUDIES

As all the homologues of series II showed very similar texture under the microscope which is characteristic of columnar phase, xray diffraction experiments have been done on one representative compound, viz., with n=8 (II f).

The diffraction patterns were recorded at three different temperatures in the columnar phase, namely, 70°C, 60°C and 40°C with the isotropic temperature being 76°C. The pattern obtained at 70°C (similar ones are obtained at lower temperatures), along with a one-dimensional intensity vs. 2θ scan extracted from the pattern are shown in Figure 7. In the small angle region, four sharp peaks are seen at all temperatures. Taken in the ascending order of the diffraction angle, the d-spacing of the first reflection (lowest angle and highest intensity) to the other three is in the ratio of $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$. These values correspond to what is expected from a 2-dimensional hexagonal lattice. In the wide angle region there are two diffuse peaks: a broad one at $2\theta \sim 20°$ and another fairly sharp, at higher

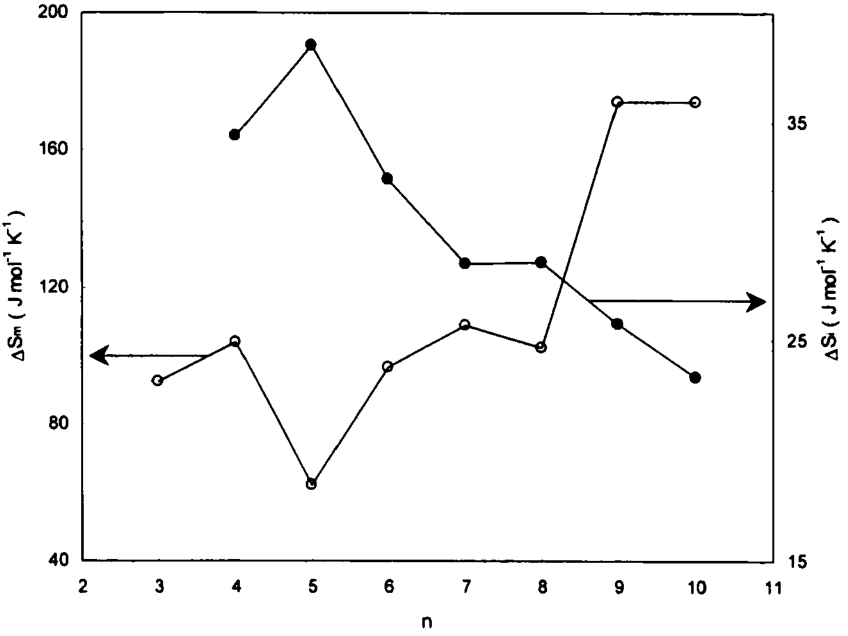

FIGURE 5 Plot of entropy ΔS vs. chain length for series II. Open circles are for melting (ΔS_m) and filled circles are for the clearing point (ΔS_i). The solid line is only a guide to the eye

angles. The broad peak with a d-spacing of ~ 4.6Å is due to the liquid-like packing of the aliphatic chains. The sharper peak, which is well separated from the broader one, corresponds to a spacing of 3.6Å. All these features fit into the well known model for the **col$_h$** phase, in which the disc-like molecule stack one on top of another to form columns and the columns in turn are arranged in a two-dimensional hexagonal lattice. Within a column, the chains have only liquid-like correlations while the molecular cores have a better positional order, albeit short ranged and with an inter-core separation of 3.6Å

TABLE III d spacing values at different temperatures for compound IIf

Temperature (°C)	*Xray spacing numbers (Å)*			*Core-core correlation length (Å)*
	$d_{intercolumnar}$	$d_{core\text{-}core}$	$d_{alkyl\text{-}chain}$	
70	21.44	3.62	4.64	95
60	21.5	3.59	4.62	115
40	21.54	3.54	4.58	125

Table III gives the values for the different spacings at the three temperatures, 70°C, 60°C and 40°C. Notice that intercolumnar distance or the disc diameter hardly changes with temperature. In contrast, the inter-core separation decreases from 3.62 Å at 70°C to 3.54 Å at 40°C. Using the full width at half maximum of the inter-core peak and the Scherer expression[21], the correlation length of the molecular cores within the column, has been calculated. Its value is 95 Å at 70°C and shows ~30% increase on lowering the temperature from 70°C to 40°C.

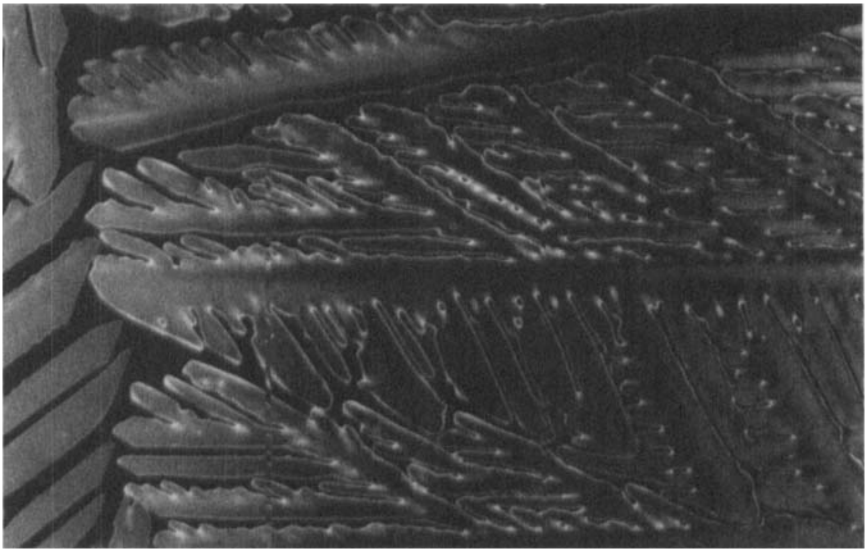

FIGURE 6 Photomicrograph of the texture at 126.5°C for compound III with n=8. The texture is similar to that for a highly ordered "discotic plastic" type of mesophase [19] (See Color Plate IV at the back of this issue)

CONCLUSIONS

In an attempt to extend the range of poly-substituted anthraquinone mesogens, we have prepared several new anthraquinone derivatives. Among these the THP-ethers exhibited hexagonal columnar mesophases at fairly low temperatures. The higher homologues of compound with hydroxy-functionalised chains are also liquid crystalline. All these hydroxy – functionalised derivatives can be used as precursor molecules for obtaining a variety of oligomers, polymers, copolymers and networks via their acrylates, methacrylates, etc. Various polyesters have been prepared simply by condensing these double hydroxy-functionalized anthraquinones with different diacid dichlorides. Synthesis and

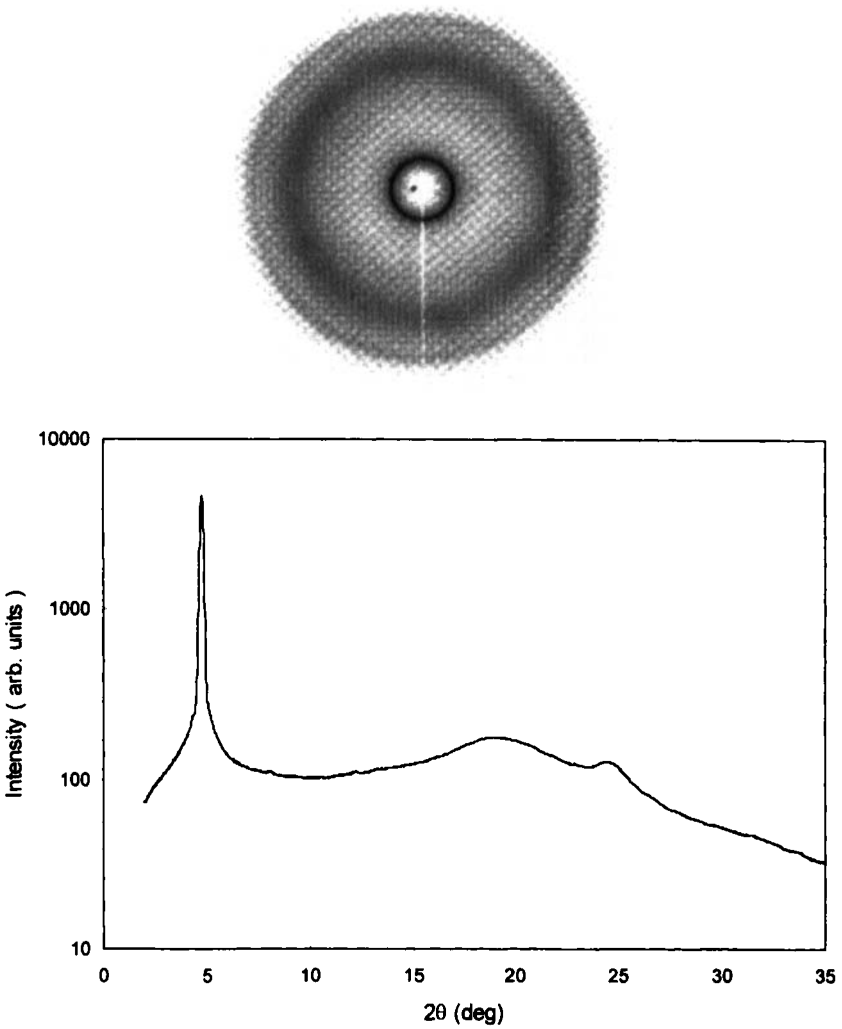

FIGURE 7 (a) X-ray diffraction pattern obtained at 70°C for compound IIf. Notice a sharp inner ring at low angles and two well separated diffuse rings at wide angles. (b) χ-averaged one-dimensional intensity vs. 2θ profile derived from (a). The first diffuse peak at 2θ~20° is from the aliphatic chains and the sharper second peak at higher angles corresponds to the packing of the molecular cores with an inter-core distance of 3.62 Å within the column

characterisation of these polyesters and other polymers will be published in due course.

Acknowledgements

We are very much grateful to Prof. S. Chandrasekhar for his keen interest in this project. We are also grateful to Drs. Sandeep Kumar and S. Krishna Prasad for their valuable discussions and suggestions during the course of this work.

References

[1] A. Queguiner, A. Zann, J.C. Dubois and J. Billard, *Proc. Intern. Conf. on Liquid Crystals, Bangalore*, Heyden and Son, London (edited by S. Chandrasekhar), p35 (1980).

[2] J. Billard, J.C. Dubois, C. Vaucher, A.M. Levelut, *Mol. Cryst. Liq. Cryst.*, **66**, 115 (1981).

[3] C. Carfagna, A. Roviello and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, **122**, 151 (1985).

[4] V. Khodorkovsky and J.Y. Becker in *Organic Conductors* (Chapter 3), edited by Jean Pierre Farger, Marcel Dekker, Inc., 270 Madison Avenue, New York, New York, 10016.

[5] N. Boden, R.C. Borner, R.J. Bushby, J. Clements, *J. Am. Chem. Soc.*, **116**, 10807 (1994).

[6] C. Carfagna, P. Ianelli, A. Roviello and A. Sirigu, *Liq. Cryst.*, **2**, 611 (1987).

[7] J. Billard, Z. Luz, R. Poupko and H. Zimmermann, *Liq. Cryst.*, **16**, 333 (1994).

[8] K.S. Raja and S. Ramakrishnan and V.A. Raghunathan, *Chem. Mater.*, **9**, 1630 (1997).

[9] M. Werth, J. Leisen, C. Boeffel, R.Y. Dong and H.W. Spiess, *J. Phys.*, **3**, 53 (1993).

[10] H. Hollander, J. Hommels, K.O. Prins, H.W. Spiess and M. Werth, *J. Phys.*, **6**, 1727 (1996).

[11] D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K.H. Etzbach, H. Ringsdorf and D. Haarer, *Nature*, **371**, 141 (1994).

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

[13] K.S. Raja, V.A. Raghunathan and S. Ramakrishnan, *Macromolecules*, **31**, 3807 (1998).

[14] S. Kumar, D.S. Shankar Rao and S. Krishna Prasad, *J. Mater. Chem.*, **9**, 2751 (1999).

[15] J.Grimshaw, R.D.Haworth, J. Grimshaw, R.D. Haworth, *J. Chem. Soc.*, 4225 (1956).

[16] Vogel's Text Book of Practical Organic Chemistry (Fifth Edition, Longman 1989), p552.

[17] S. Kumar (personal communication).

[18] Veena Prasad, K. Krishnan and V.S.K. Balagurusamy, *Liq. Cryst.*, (submitted).

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

[20] S. Kumar, P. Schuhmacher, P. Henderson, J. Rego, H. Ringsdorf, *Mol. Cryst. Liq. Cryst.*, **288**, 211 (1996) and the references therein.

[21] See e.g., "Xray Diffraction Procedures", H.P. klug and L.E. Alexander, John Wiley & Sons, New York 1954, chapter 9.