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To cite this Article Billard, J. , Luz, Z. , Poupko, R. and Zimmermann, H.(1994) 'The mesophases of octa-alkanoyloxy-9,10-anthraquinone', Liquid Crystals, 16: 2, 333 — 342

To link to this Article: DOI: 10.1080/02678299408029157

URL: http://dx.doi.org/10.1080/02678299408029157

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LIQUID CRYSTALS, 1994, VOL. 16, NO. 2, 333–342

The mesophases of octa-alkanoyloxy-9,10-anthraquinone

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(*Received 23 July 1993; accepted 19 August 1993*)

Nine members of the octa-*n*-alkanoyloxy-9,10-anthraquinone series, ranging from octanoyloxy ($n=8$) to hexadecanoyloxy ($n=16$) (where n is the number of carbon atoms per chain), were prepared and their mesomorphic properties studied by differential scanning calorimetry and optical microscopy. All the compounds studied are mesomorphic with the higher homologues exhibiting two (for $n \geqslant 12$) or even three (for $n \geqslant 14$) columnar mesophases. For $n=8$ to 11, the phase sequence is C–D_B–I, where D_B is an optically biaxial mesophase with a two-dimensional pgg symmetry. For $n=12$, 13, the phase sequence is C–M_3–D_B–I, where M_3 is a highly ordered phase whose structure has not been identified. Finally for $n=14$ to 16, the phase sequence is C–M_3–D_B–D_A–I, where D_A is an hexagonal phase. In all cases, the phases change from high to low order with increasing temperature and all transitions are first order. Compared with the corresponding hexa-substituted naphthoquinones the present series generates larger mesomorphic ranges and the higher homologues exhibit a uniaxial phase which is lacking in the hexa-substituted series. The increase in volume occupied by the aliphatic chains in the octa-substituted series is evidently sufficient to reduce the interaction between the aromatic cores of the different columns to permit the stability of a uniaxial phase.

1. Introduction

Several homologous series derived from 9,10-anthraquinone have been shown to exhibit columnar liquid crystalline mesophases. The best known of these are the members of the rufigallol family, 1,2,3,5,6,7-hexa-substituted-9,10-anthraquinones (**II**) [1–7]. This series provided the first example of discogenic molecules having lower than three-fold symmetry, and the first example of compounds to undergo complete miscibility in the mesomorphic state with mesogenic compounds of different molecular symmetry. In fact mesogens of this series have been used as reference compounds for the identification of the discotic D_B and D_C mesophases, whose structure has been determined by X-ray diffraction [4, 5].

In the present work we extend the study of mesogens derived from 9,10-anthraquinone to the octa-*n*-alkanoyloxy derivatives (**I**). Nine members of the series ranging from octa-*n*-octanoyloxy- to octa-*n*-hexadecanoyloxy-9,10-anthraquinone have been prepared and all are found to be mesomorphic with, depending on the number n of carbons in the side chains, between one and three mesophases. In the following account we describe the preparation of these compounds, their phase sequences, and the identification of their mesophases by polarizing optical microscopy and miscibility studies.

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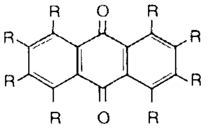
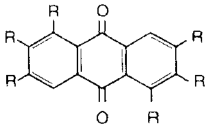
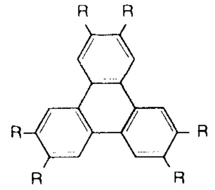


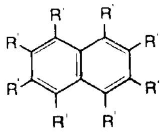
I-n



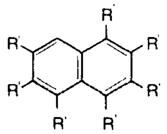
II-n



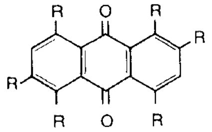
III-n



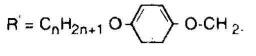
IV-n



V-n



VI-n



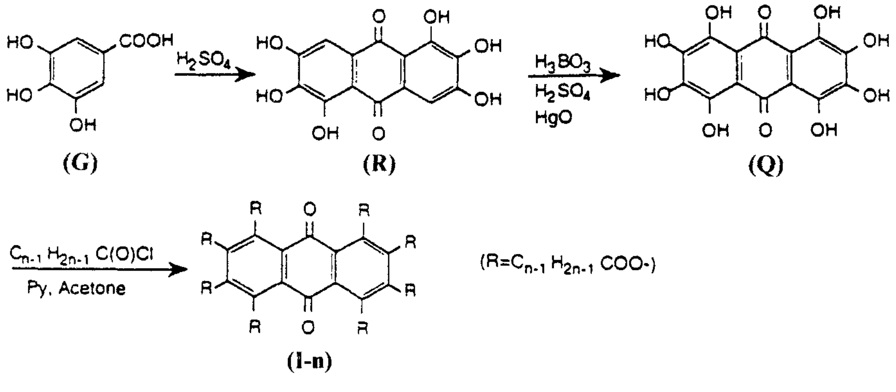
$R' = C_nH_{2n+1}O-C_6H_4-O-CH_2-$

$R = C_{n-1}H_{2n-1}COO-$

2. Experimental

2.1. *Preparation*

The synthesis of the 1,2,3,4,5,6,7,8-octa-alkanoyloxyanthraquinones (**I-n**) starts with the condensation of gallic acid (**G**) (3,4,5-trihydroxybenzoic acid) to rufigallol (**R**) (1,2,3,5,6,7-hexahydroxy-9,10-anthraquinone), followed by oxidation to the corresponding octahydroxyanthraquinone (**Q**). Esterification of the latter with alkanoyl chlorides yields the desired series of compounds. The general scheme is shown below.



Condensation of **G** to **R** was done in concentrated sulphuric acid as described in [8], while the oxidation of **R** to **Q** was performed using a modified, 80-year old procedure due to v. Georgievics [9]. To a solution of **R** (9 g) in concentrated H_2SO_4 (150 ml), crystalline boric acid (12 g) and yellow mercuric oxide (210 mg) were added while stirring for about 10 min. The reaction flask was immersed into an oil bath which was preheated to exactly 250°C with continuous stirring for 45 min. The mixture was then cooled down stepwise, but quickly, using an ice-water bath for the last step. The reaction mixture was poured over ice (600 g) and the solution boiled for 15 min in order to hydrolyse residual boric acid esters. After keeping the mixture overnight in a refrigerator, the precipitated compound **Q** was filtered off, washed with water and dried in air. Purification was effected by dissolving the solid in boiling pyridine (350 ml) and separating the insoluble residue by filtration. The filtrate was mixed first with hot methanol (350 ml) followed by hot water (150 ml) and the mixture allowed to cool. The shining dark red crystals of **Q** which formed (3·5–4 g) were finally filtered off and dried under vacuum at 150°C for 24 hours. ($C_{14}H_8O_{10}$, $m/z = 336$. Elemental analysis: C = 50·26 per cent (calculated 50·04), H = 2·70 per cent (calculated 2·40)).

As an example of the esterification reaction, we give details for the $n = 12$ homologue. Dodecanoyl chloride (3 g) was added dropwise with stirring to a solution of **Q** (0·2 g) in dry pyridine (3 ml) and acetone (100 ml) (over molecular sieves). The mixture was kept for five hours at 40°C, then cooled to room temperature and the solid product isolated by filtration. Repeated crystallization from ethanol, followed by column chromatography (silica, CH_2Cl_2/*n*-hexane 1 : 1) yielded the desired product, **I-12** (620 mg). The lower members of the series were acylated at room temperature and precipitated by pouring the solution into an aqueous *M*-hydrochloric acid–ice mixture. ^1H NMR spectroscopy of the final esters (at 500 MHz) yielded in each case the expected spectra with no observable traces of impurities.

We are currently attempting to prepare the corresponding octa-ethers of anthraquinone using the octahydroxy- and octa-alkanoyloxy-derivatives as starting materials. However due to formation of chelates between the carbonyl and neighbouring hydroxy groups, the reactivity of the peri-hydroxy-anthraquinones is very low [10]. Preliminary results show discotic phases for $n > 3$, but the compounds are subject to degradation even during chromatographic separation.

2.2. *Differential scanning calorimetry (DSC)*

Transition temperatures and transition enthalpies were determined using a Mettler TA 3000 differential scanning calorimeter. All results are reported for increase in temperature (1 to 10°C min^{-1}).

2.3. *Optical microscopy (OM)*

Polarizing optical microscopy observations were made using Leitz, Panphot or Zeiss, Universal microscopes equipped with Mettler FP 52 heating stages. The samples were placed between two untreated cover slips of ordinary glass. Binary phase diagrams at atmospheric pressure were constructed by observation of contact preparations [11] and the solubilities of the solids were calculated by the Le Chatelier–Schröder equation [12].

3. Results and discussion

3.1. *The phase diagrams and optical microscopy of the mesophases*

Transition temperatures and enthalpies, as determined by DSC and OM, are summarized in table 1 for the nine compounds of the **I-n** series. In the crystalline form, they are pale yellow and stable over the temperature and time range of the measurements. The melting of the solids is difficult to observe by texture changes under the microscope, but could readily be detected by the effect on the domain boundaries brought about by pressing the cover slip with a fine steel needle [13]. The clearing temperatures are sharp and readily detected by the complete extinction of the viewing field. Slow cooling (1 or 0·2°C min^{-1}) of the isotropic liquid gives, just below the clearing temperature, birefringent domains with digitized (finger-like) contours [14]. Some defects with rectilinear axes can be observed. The optical sign is negative as is common for discotic mesophases. When the transformation of the liquid to the mesophase is complete, two different types of texture are observed depending on the

Table 1. Transition temperatures (°C) and (in parentheses) molar enthalpy changes (kJ mol^{-1}) for the octa-alkanoyloxy-9,10-anthraquinones studied in the present work.†

n	C		M_3		M_2		M_1		I
8	●	85·5 (902)			●			150·1 (22·6)	●
9	●	86·5 (85·4)			●			148·0 (21·6)	●
10	●	98·7 (146·2)			●			147·2 (19·9)	●
11	●	102·0 (149·5)			●			143·4 (19·6)	●
12	●	101·0	● (164·2)	104·6	●			140·1 (18·3)	●
13	●	99·2	● (163·8)	104·5	●			138·0 (16·7)	●
14	●	104 (61·6)	●	110·1) (188)	●	134·6 (~0)	●	135·9 (14)	●
15	●	102·5 (50·5)	●	109·5 (198)	●	121·9 (~0)	●	132·3 (13)	●
16	●	107·3 (57·7)	●	113·0 (236·7)	●	121·2 (~0)	●	131·1 (13)	●

† The number n is the number of carbon atoms in each of the eight side chains. The symbol C stands for crystalline phases, M_3, M_2 and M_1 for mesophases, and I for liquids. The temperatures and molar enthalpy changes were obtained by DSC measurements, except for the M_2–M_1 transitions which were only detected by optical microscopy. For **I-12** and **I-13**, the enthalpies of the C–M_3 and M_3–M_2 transitions could not be resolved and the combined values are given.

compound. For the six lower members in the series ($n = 8$ to 13), striated (see, for example, figure 1) or marbled areas with low birefringence appear, but they do not include domains which are completely extinct at all orientations of the microscope stage. This suggests that the mesophases (M_2) of these compounds are optically biaxial.

For the three higher members of the series ($n = 14$ to 16), cooling the isotropic liquid results in domains with non-uniform extinctions and curved boundaries (figure 2). Sometimes, completely extinct areas are observed which remain dark at all orientations of the microscope stage. These areas must be identified as normally oriented domains and their presence indicates that the mesophases (M_1) obtained for the higher homologues by cooling the normal liquid are optically uniaxial. On further cooling of M_1, a temperature is reached at which a clear transition to a second phase, M_2, is observed suggesting that the phases are optically biaxial. The transition is reflected in the appearance of striations perpendicular to the major axes of the domains and a splitting of the originally dark domains into many birefringent areas with uniform extinction (figure 3). On further cooling, there is also a gradual formation of a general mosaic-like texture, as observed earlier with the M_2 phase of the lower homologues. As in the latter, no completely extinct areas are observed, suggesting that the phases are optically biaxial. The transformation between M_2 and M_1 is completely reversible; heating M_2 results in the disappearance of the striations and the formation of the textures observed earlier in M_1. Supercooling of M_1 is often observed. For example for **I-16**, the M_1–M_2 transition occurs at 118·2°C on cooling, but at 121·2°C on heating. The transitions are therefore first order, but apparently with very low transition enthalpy, as they are not detected by DSC. The results in table 1 for these transitions are

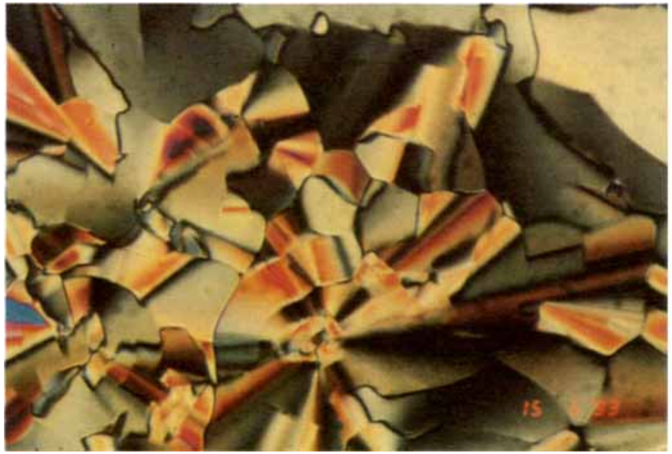


Figure 1.

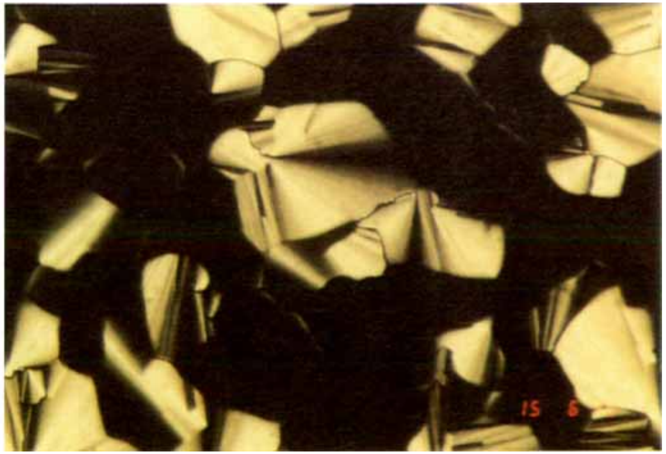


Figure 2.

Figure 3.

Figure 1. Polarizing optical microscopic texture for the D_B phase in **I-13** at 130°C.

Figure 2. Polarizing optical microscopic texture for the D_A phase of **I-16** at 128°C.

Figure 3. Polarizing optical microscopic texture for the D_B phase of **I-16** at 116°C.

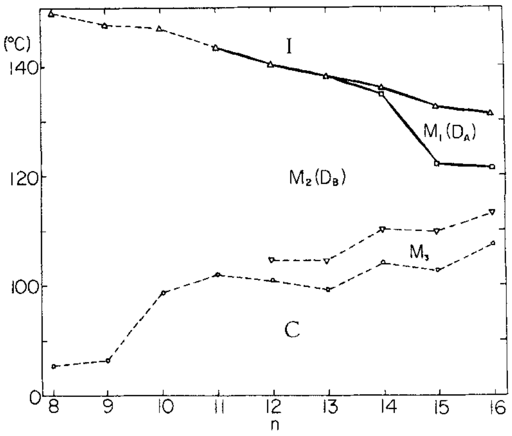


Figure 4. Isobaric phase diagrams of binary mixtures of neighbouring homologues of the **I-n** series. Continuous lines are from experimentally studied binary phase diagrams. The dashed lines connect similar transitions for neighbouring homologues. The letter I stands for liquid, M for mesophase and C for solid. n = number of carbons in the chain of the alkanoyloxy group.

from the optical microscopic studies and the $\Delta H \sim 0$ entries indicate that the enthalpies are below the detection level of our differential scanning calorimeter.

The five higher homologues of the series with $n = 12$ to 16 exhibit another low temperature phase which we label M_3. The M_3–M_2 transitions are readily detected by DSC, but difficult to observe by optical microscopy due to the high viscosity of the mesophases in the temperature range of this transition. When crystals (grown by very slow cooling through the ranges of the mesophases: fine birefringent needles) are reheated and observed under very strong illumination (high vapour pressure mercury lamp), the melting to M_3 can be detected by the expansion of the needles. The M_3–M_2 transition is then reflected in a sudden appearance of distinct striations.

The neighbouring homologues in this series are totally miscible in the liquid and mesomorphic states. Miscibility diagrams for the high temperature phases of the $n = 11$ to 16 homologues are summarized in figure 4, where the melting temperatures and the M_3–M_2 transitions are also indicated. The binary phase diagram of the homologues **I-13** and **I-14** confirms the equivalence of the M_2 mesophase for the lower members of the series with the second phase of the higher homologues.

Summing up all the phase diagram results, the nine homologues of series **I-n** studied in the present work, **I-8** to **I-16**, are all mesomorphic and exhibit the optically biaxial M_2 mesophase. The three higher members (**I-14** to **I-16**) exhibit an optically uniaxial mesophase, M_1 above M_2, while the homologues **I-12** to **I-16** exhibit in addition a low temperature, highly viscous mesophase M_3.

3.2. *Identification of the M_2 and M_1 mesophases*

To identify the mesophases M_2 and M_1 with known discotic structures, we studied binary phase diagrams of **I-14** (which exhibits both phases) with reference compounds having the same side chains. As reference compound, we used hexa-*n*-tetradecanoyloxytriphenylene (**III-14**), which has the phase sequence [15]

$$C \xrightarrow[(113{\cdot}7)]{86{\cdot}5} D_1 \xrightarrow[(\sim 0)]{96} D_2 \xrightarrow[(1{\cdot}05)]{111} I.$$

(An earlier report [16] gives. $M_1 \xrightarrow{55{\cdot}5} M_2 \xrightarrow{106} I$ for this compound, but the above sequence is consistent with our observations.) The identification of the discotic mesophases in this reference compound is based on those of the **III-12** homologue. This compound has the phase sequence [16, 17]

$$C \xrightarrow[(59{\cdot}4)]{80} D_0 \xrightarrow[(\sim 0)]{93} D_B \xrightarrow[(0{\cdot}15)]{111} D_A \xrightarrow[(2{\cdot}41)]{122{\cdot}3} I,$$

where D_B and D_A have, respectively, two-dimensional pgg and hexagonal structures [18, 19]. These structures were established by optical microscopy [4] and X-ray studies [20]. The binary phase diagram of **III-14** and **III-12** is shown in figure 5 where the complete miscibility of the two high temperature mesophases is established.

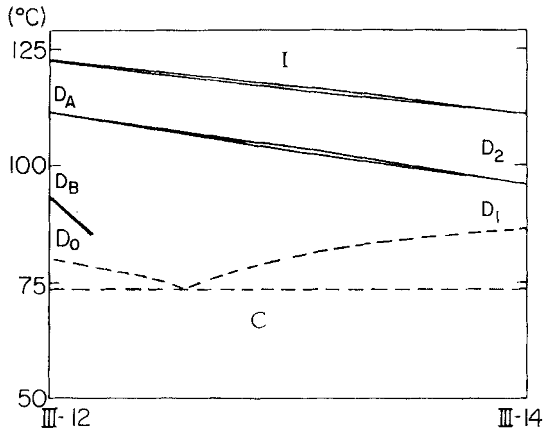


Figure 5. Isobaric binary phase diagram for **III-12** (left) and **III-14** (right), showing the total miscibility of D_A and D_B for both compounds. The continuous lines indicate transitions observed by optical microscopy, while the dashed lines are calculated solubility curves for the solids.

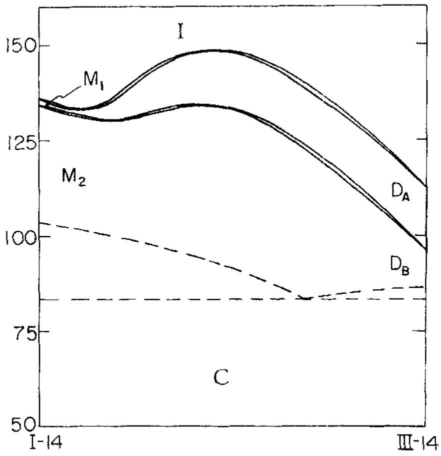


Figure 6. Isobaric binary phase diagram for **I-14** (left) and **III-14** (right) showing the complete miscibility of M_1 with D_A and M_2 with D_B. The continuous lines indicate transitions observed by optical microscopy, while the dashed lines are calculated solubility curves for the solids.

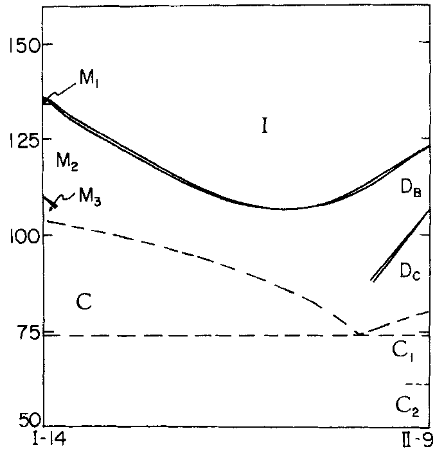


Figure 7. Isobaric binary phase diagram for **I-14** (left) and **II-9** (right) showing the complete miscibility of M_2 with D_B. The continuous lines indicate transitions observed by optical microscopy, while the dashed lines are calculated solubility curves for the solids.

The binary phase diagram of **I-14** and **III-14** is shown in figure 6. Although it exhibits minima and maxima, the complete miscibility of M_1 and D_A, and M_2 and D_B is clearly demonstrated. The identification of M_2 as D_B is further established by the binary phase diagram of **I-14** with **II-9** (see figure 7) [2].

4. Summary and conclusions

The mesomorphic properties of nine members of the series **I-n** (with $n = 8$ to 16) were studied. All compounds are mesomorphic exhibiting a D_B phase, but the higher members are polymorphic with one or two additional phases. In general, the melting points increase regularly with the length of the side chains, while the clearing temperatures decrease in that order, thus reducing the stability range of the mesomorphic state. For the homologues with long side chains, the D_B phase is gradually replaced by a uniaxial D_A phase at the high temperature end of the mesophase, and by a highly ordered M_3 phase at the low temperature end. It is therefore likely that for even higher homologues, only the M_3 and D_A phases will be stable.

With regard to the transition enthalpies, those of the clearing points are relatively small and decrease with increasing chain length, while those for the melting (or melting plus the $M_3 \rightarrow D_B$ transition) increase steeply with the molecular weight. Particularly noteworthy is the large $M_3 \rightarrow D_B$ transition enthalpy, where this can be measured separately from the melting process. This indicates that M_3 is a highly ordered mesophase. Its structure is however not yet known.

It is interesting to compare the phase sequences of the **I-n** compounds with those of the corresponding hexa-alkanoyloxy-9,10-anthraquinones (series **II-n**). These compounds also exhibit discotic mesophases, although they have a smaller number of side chains. A compilation of the transition temperatures and enthalpies for the latter materials is given in table 2. In general, on going from **I-n** to **II-n**, there is a slight increase in the melting temperature, the clearing temperature decreases and the mesophase range also decreases. Both series exhibit the D_B phase; however, unlike

Table 2. Compilation of previously measured transition temperatures (°C) and (in parentheses) molar enthalpy changes (kJ mol^{-1}) for hexa-alkanoyloxy-9,10-anthraquinones (series **II-n**)†.

n	C		D_C		D_B		I	Reference
4	●					215·5 (47·5)	●	[3]
5	●					169·5 (42·1)	●	[3]
6	●					152·2 (42·2)	●	[3]
7	●	98 (24·6)	●	107·9 ($\sim$3)	●	127 (16·2)	●	[2]
	●	111·8 (35·3)			●	133·8 (16·8)	●	[3]
	●	104·4			●	132·5	●	[5]
8	●	107·5 (47·2)	●	99‡ ($\sim$0)	●	127·5 (13·8)	●	[1]
	●	110·1 (45·8)			●	132·7 (15·1)	●	[3]
	●	106			●	126·2	●	[5]
9	●	80 (33·4)	●	106 (0·08)	●	123 (12·5)	●	[2]
	●	90·5 (40·4)	●	82·9‡ ($\sim$2)	●	128·2 (11·9)	●	[3]
10	●	106 (55·7)			●	127·8 (12·5)	●	[2]
	●	108·8 (56·4)			●	128·1 (12·2)	●	[3]
11	●	91·6 (59·1)			●	125·7 (11·3)	●	[3]
12	●	98·5 (123·5)			●	123·6 (10·8)	●	[3]
	●	90·8			●	106·2	●	[5]
13	●	95·4 (129·2)			●	120·2 (10·1)	●	[3]
14	●	102·5 (175·3)			●	117·2 (8·6)	●	[3]

† See table 1 for explanation (explain references).
‡ Monotropic transitions.

series **II-n**, in series **I-n**, there are compounds which possess a uniaxial D_A phase (and there is no D_C mesophase). Apparently the core, because of its elongated shape, promotes biaxial symmetry, but for sufficiently long side chains, the effect of the aliphatic units overshadows the interaction between aromatic cores in neighbouring columns and a more symmetric uniaxial phase is stabilized. A similar effect can be noted in the two series (**IV-n**) and the corresponding hepta-derivatives (**V-n**) studied by Kok *et al.* [21].

The series of octa-alkanoyloxy-9,10-anthraquinones has extended the range of discogenic compounds having large centre cores, but lower than three-fold symmetry. It is gratifying to note that despite this variance in structure, the mesophases of this series can be classified in terms of previously characterized reference mesophases whose structures have been determined by X-ray diffraction.

We finally mention that in another attempt to extend the range of poly-substituted anthraquinone mesogens, two esters of the series of 1,2,4,5,6,8-hexa-alkanoyloxyanthraquinones (**VI-n**) with $n = 9$ and 13 were prepared and found to be mesomorphic.

We thank Professor Nguyen Huu Tinh for the loan of the discogens used as reference compounds. This work was partly supported by a grant from G.I.F., the German–Israeli Foundation for Scientific Research and Development.

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