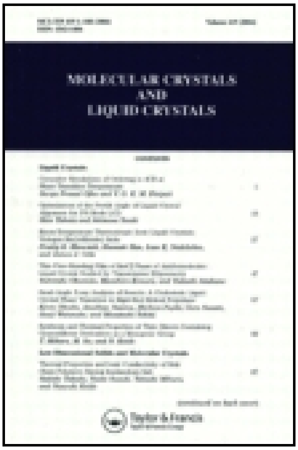

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New Discotic Benzene and Naphthalene Derivatives with Columnar Mesophases

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New Discotic Benzene and Naphthalene Derivatives with Columnar Mesophases†

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The preparation is described of some new discotic liquid crystalline compounds; the hexa-(*p*-alkoxyphenoxymethyl)benzenes, and the 1,2,3,4,5,6,7-hepta- and octa-(*p*-alkoxyphenoxymethyl)naphthalenes. Transition temperatures and latent heats, from DSC-measurements, are presented, and in addition, a preliminary discussion of the structures is given.

INTRODUCTION

Since the discovery of liquid crystalline phases formed by disc-shaped molecules[1] a large number of papers has appeared reporting new compounds and/or new types of phases.[2] Nematic phases can exist in addition to the various types of columnar phases, which are characterized by partial translational ordering of the molecules into a two-dimensional array of flexible columns. A classification of the various types of mesophase has been given by Destrade *et al.*,[3] while the structural aspects have recently been reviewed by Levelut.[4]

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The characteristic feature of discogenic molecules is a flat aromatic (or recently also aliphatic[5]) core to which several (six or more) hydrocarbon chains are attached. In this paper we present new compounds in which the use of benzene as a core is extended to naphthalene and *p*-alkoxyphenoxymethyl groups are used as side chains. Neither the naphthalene core nor the side group chosen have been previously reported as leading to liquid crystalline materials, though alkylthio-substituted naphthalenes have been synthesized.[6] Asymmetrically substituted naphthalenes with seven chains are also described.

RESULTS AND DISCUSSION

The hexa-(*p*-alkoxyphenoxymethyl)benzenes **1** were prepared according to scheme 1. The phase transition temperatures and transition enthalpies are given in Table I. For alkyl chains with n = 5–7, two phase transitions were observed with similar values for ΔH. X-ray

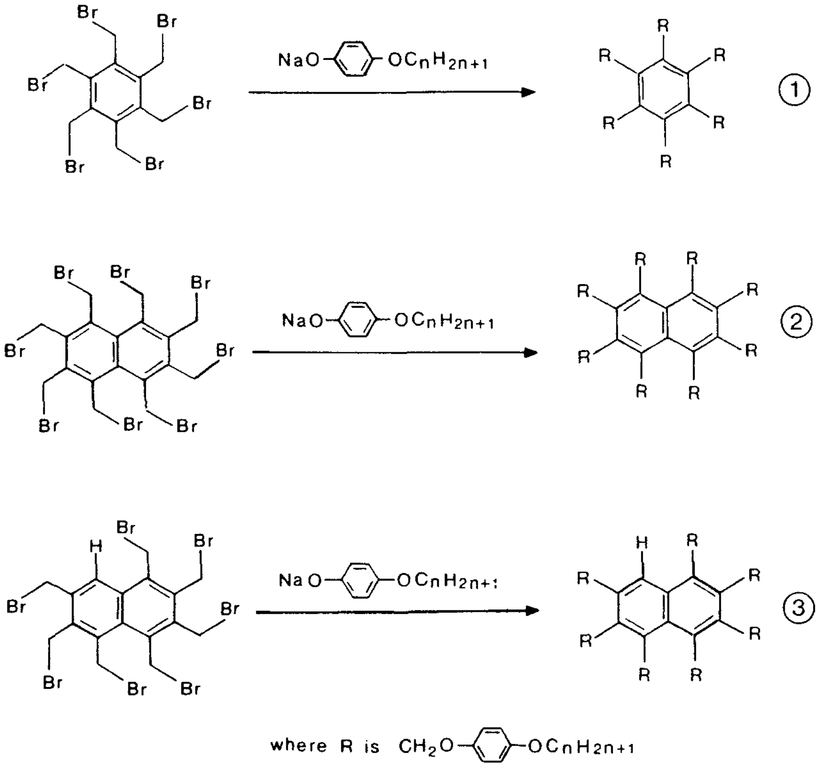

TABLE I

Phase transition temperatures (°C) and transition enthalpies (kcal/mol) of the [6]pizzane[6] series (**1**)

n	K		D(?)		I
3	•	154 (8.6)	—		•
4	•	121 (8.0)	—		•
5	•	68 (2.7)	•	97 (5.9)	•
6	•	76 (4.4)	•	83 (4.2)	•
7	•	67 (5.7)	•	71 (3.2)	•
8	•	63 (11.1)	—		•

diffraction patterns of non-oriented samples showed three sharp reflections at small Bragg angles compatible with a rectangular lattice of the columns and disorder within the columns (D_{rd}). Polarization microscopy revealed definite texture changes and a waxy character of the mesophase. However, later X-ray photographs showed that in addition to the three strong reflections of the rectangular lattice there are a large number of very weak reflections. In agreement with the smaller ΔH-values at the low temperature phase transition for the lower homologues this was more pronounced for $n=5$ than for $n=7$. Nevertheless we conclude that in this case probably no mesophase is involved, but a special type of crystal, the nature of which still has to be determined. For $n=6$ and $n=7$ the 1,2,4,5 tetra substituted benzene derivatives were also synthesized. For these compounds only a straightforward melting transition was observed.

Table II gives the results for the corresponding naphthalenes with both 8 and with 7 substituents as depicted in scheme 1. In all cases investigated at least one mesophase has been observed. Compared with the series **1** the transition enthalpies to the isotropic phase are smaller, which is in agreement with the classification as a mesophase. Powder X-ray photographs reveal only one sharp Bragg reflection at small Bragg angles. This classifies this phase unambiguously as D_{hd} (hexagonal lattice of the columns, disordered positions within the columns). As the molecules themselves have only a two-fold axis perpendicular to the naphthalene core, we must conclude that they are randomly oriented around the column axes giving macroscopic hexagonal symmetry. As seen in Table II for some homologues an

TABLE II

Phase transition temperatures (°C) and transition enthalpies (kcal/mole) of the [8]pizzane[10] series (**2**).

n	K_2		K_1		D_{hd}		I
5	—		•	162	•	164	•
				(12.3)		(1.8)	
6	—		•	135	•	167	•
				(11.6)		(2.8)	
7	•	90	•	105	•	167	•
		(3.1)		(9.5)		(2.6)	
8	•	72	•	78	•	167	•
		(4.3)		(5.7)		(2.5)	
9	•	54	•	62	•	165	•
		(7.6)		(9.6)		(2.7)	

additional phase transition is found. Most probably this corresponds to a solid-solid transition, although a highly ordered columnar phase cannot be completely excluded at this stage.

Finally Table III indicates that asymmetric substitution of the naphthalene core with seven chains leads to an increase in the number of mesophases. With decreasing temperature, in addition to the D_{hd} phase a D_{ro} (rectangular lattice of columns, order of the positions within the columns) is also found. For $n = 7$ there is even a third columnar phase which, from the X-ray photographs also seems to be D_{ro}, but with different parameters for the rectangular lattice. This assignment would be in agreement with the small latent heat at the D_3-D_{ro} transition. In Figure 1 the textures of the various phases are shown. The D_{hd} phases of series **2** and **3** show very similar textures.

Space filling molecular models of the disc-like molecules described here show that the substituents on the central benzene or naphthalene ring fill the space surrounding the center very efficiently. One could consider the central ring and the surrounding benzene rings with linkage groups as one central disc-like unit to which the alkoxy chains

TABLE III

Phase transition temperatures (°C) and transition enthalpies (kcal/mole) of the [7]pizzane[10] series (**3**).

n	K		D_3		D_{ro}		D_{hd}		I
6	•	65	—		•	147	•	184	•
		(2.9)				(9.5)		(1.7)	
7	•	79	•	92	•	138	•	182	•
		(5.8)		(1.1)		(9.4)		(1.6)	

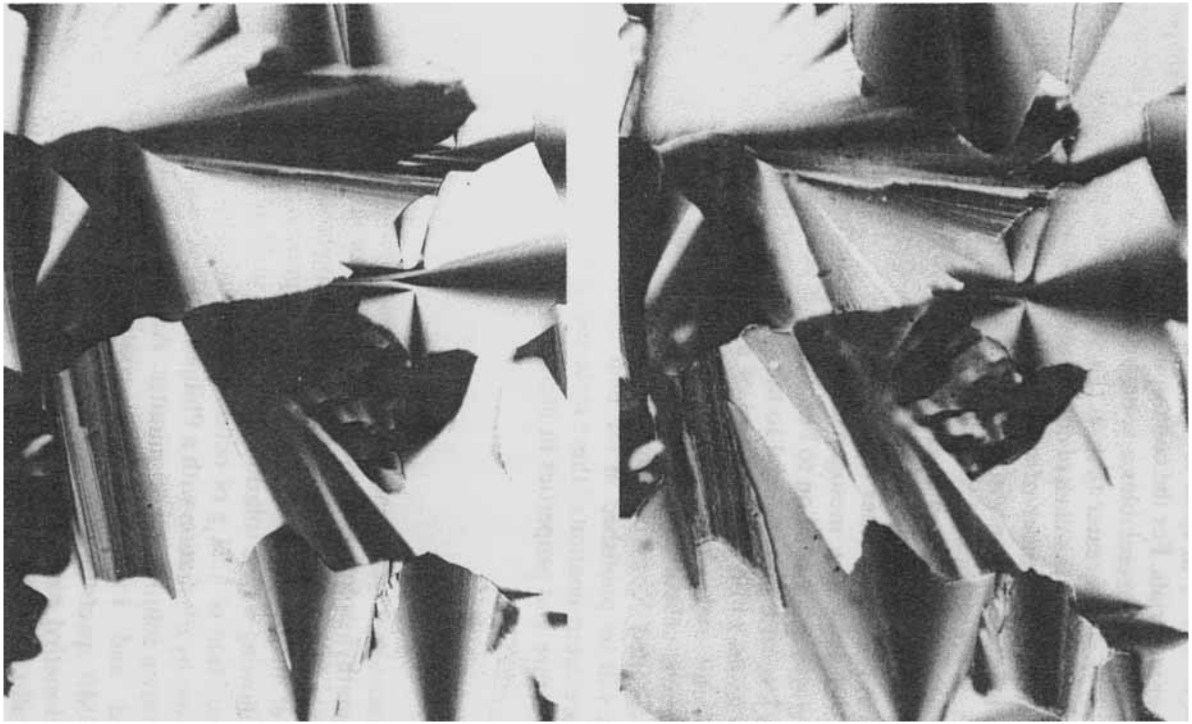

FIGURE 1 Textures, between crossed polars, of the D_{hd} phase at 180°C (a) and the D_{ro} phase at 110°C (b) of [7]pizzane[10] ($n=7$).

are attached. In agreement with this idea of optimal packing, no mesophases were observed if the linkage group was extended to —CH_2—O—CO—, in spite of the relatively low melting points of these latter materials. For the compounds of Table I the overall shape of the central part resembles a pancake or pizza, with the thickness at the rim slightly greater than at the center. We propose a trivial name "pizzane" for this class of compounds, indicating with the prefix [6], [7] or [8] the number of substituents, and with the suffix [6] or [10] the number of atoms in the central ring. Thus the benzene derivatives **1** are indicated as [6]pizzane[6] compounds, while the naphthalene series **2** and **3** are [8]pizzane[10] and [7]pizzane[10], respectively. This type of nomenclature has proved to be very convenient in the crown ether field.

In conclusion, new mesogenic disclike materials have been presented showing, in addition to benzene, it is possible to use naphthalene as a central unit. Crucial to the occurrence of columnar mesophases seems to be the existence of a "super-disc," consisting of a central unit and a quasi-macrocarbycyclic ring of benzene rings. Asymmetric substitution is also possible in the naphthalene case. More detailed X-ray investigations of the various observed mesophases will be published in the near future. In addition, an X-ray structure determination of these molecules is needed in order to relate the structure and properties in more detail.

EXPERIMENTAL

Hexabromomethylbenzene,[7] octamethylnaphthalene[8] and 1,2,3,4,5,6,7 heptamethylnaphthalene[8] were prepared according to literature procedures. The bromination of octamethylnaphthalene described by Hart *et al.*[9] (Br_2, solvent CS_2, room temperature) was modified in the following way: a solution of 9.12 g Br_2 in 50 ml of CCl_4 was added to a solution of 1.71 g of octamethylnaphthalene in 50 ml of CCl_4, followed by irradiation with a Philips 300 W UV lamp of the resulting red brown solution for 30 minutes. An additional 1.8 g of Br_2 were added and irradiation was continued for 45 minutes. A ^{1}H-NMR spectrum of a sample of the solution showed the absence of ^{1}H-methyl resonances. After evaporation of the solvent and recrystallization of the residue from chloroform 4.70 g of octabromomethylnaphthalene were isolated (76% yield). In a similar way 1,2,3,4,5,6,7 heptamethylnaphthalene yielded 67% of 1,2,3,4,5,6,7 bromomethylnaphthalene.

The *p*-alkoxyphenols, n = 5, 6 and 7, were purchased from Janssen Pharmaceutica. The other *p*-alkoxyphenols were synthesized as previously described for *p*-hexyloxyphenol.[10] The ethers **1**, **2**, and **3** were prepared as follows: to 30 ml of absolute ethanol was added 6 mmol of sodium. After the sodium had dissolved, 6 mmol of the *p*-alkoxyphenol was added and the solvent evaporated. Thereafter 70 ml of DMF was added followed by 1 mmol of the bromide. The magnetically stirred mixture was heated for 2 hours at 80°C. After evaporation of the solvent under vacuum, water and ether was added. The organic layer was extracted twice with water, dried over $MgSO_4$ and the ether evaporated. The residue was recrystallized twice from petroleum ether 40–60/absolute ethanol, isopropanol/ether or isopropanol and the ethers were isolated in 20–63% yield.

All structures were confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy, *e.g.* for [6]pizzane[6] (n = 7): ^{1}H-NMR ($CDCl_3$, TMS, Jeol C60): 0.65-2.00 (m, 78H), 3.90 (t, 12H, J = 6Hz), 5.20 (br s, 12H), 6.90 (s, 24H); ^{13}C-NMR: 13.9 (q, CH_3), 22.5, 25.9, 28.9, 29.2, 31.7, (t, all CH_2), 64.3, 68.4 (t, both CH_2O), 115.2, 115.6 (d, both arom. CH), 137.8, 152.5, 153.6 (s, all arom. C); and for [8]pizzane[10] (n = 7): ^{1}H-NMR 0.65-2.08 (m, 104 H), 3.80, 3.88 (2t, 16H, J = 6Hz), 5.42 (br s, 16H), 6.65 (s, 16H), 6.85 (s, 16H); ^{13}C-NMR: 14.0 (q, CH_3), 22.5, 25.9, 29.0, 29.1, 29.3, 29.4, 31.7 (t, all CH_2), 64.8, 65.3, 68.4, (t, all CH_2O), 114.9, 115.2, 116.0 (d, all arom. CH), 133.4, 136.4, 137.7, 151.7, 152.7, 153.3, 153.6 (s, all arom. C).

Transition temperatures and heats were determined by differentional scanning calorimetry using a Perkin-Elmer DSC-II. The transition temperatures were checked with a polarizing microscope (Leitz orthoplan-pol) equipped with a heating stage (Mettler FP52). X-ray photographs were made from unoriented samples in Lindemann glass tubes ($\phi = 0.3$ mm) with a Guinier-Simon camera (Enraf-Nonius) using $CuK_{\alpha 1}$ radiation.

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