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Liquid Crystals

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Preliminary Communications. Benzotrisfuran derivatives A new series of disc-like liquid crystals

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To cite this Article Destrade, C. , Tinh, Nguyen Huu , Gasparoux, H. and Mamlok, L.(1987) 'Preliminary Communications. Benzotrisfuran derivatives A new series of disc-like liquid crystals', Liquid Crystals, 2: 2, 229 — 233
To link to this Article: DOI: 10.1080/02678298708086294
URL: http://dx.doi.org/10.1080/02678298708086294

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LIQUID CRYSTALS, 1987, VOL. 2, NO. 2, 229–233

PRELIMINARY COMMUNICATIONS

Benzotrisfuran derivatives
A new series of disc-like liquid crystals

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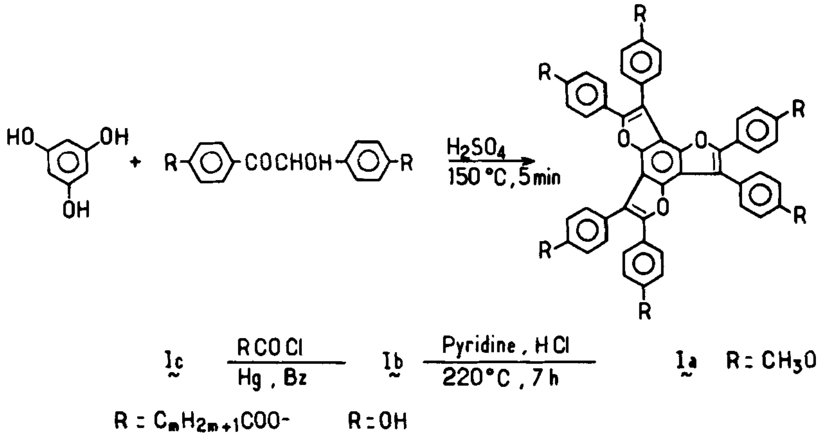
(*Received 28 October 1986; accepted 31 December 1986*)

An homologous series of 2,3,5,6,8,9-hexa-*n*-alkanoyloxyphenylbenzo (1,2*b*; 3,4*b*′; 5,6*b*″)trisfurans has been synthezised. The synthesis and mesomorphic properties are described and compared with those of other disc-like systems. These derivatives exhibit the relatively uncommon hexagonal ordered columnar phase D_{ho}. One hexa-*n*-alkoxybenzoyloxy derivative has also been prepared, it provides a new example of the N_D lenticular nematic phase.

Mesogenic disc-like molecules are currently described as a more or less disc-shaped with a central rigid core either aromatic or alicyclic usually surrounded by at least six lipophilic chains [1]. For example, hexasubstituted benzene [2], triphenylene [3, 4], truxene [5–7], anthraquinone [8], naphthalene [9], cyclohexane [10], and some metallic complexes [11]. These new classes of mesogenic materials can exhibit very viscous and birefringent mesophases corresponding to stacks of molecular discs forming parallel columns in a hexagonal, rectangular or oblique two-dimensional lattice [1, 12]. These mesophases are usually called columnar mesophases; they correspond to a two-dimensionally ordered system. In many cases an hexagonal arrangement has been proved (D_h phase); the order or the disorder of the molecular stacking in the columns can be also taken into account to classify the different columnar mesophases (D_{ho} or D_{hd}). The first case (D_{ho}) corresponds to crystalline order with a coherence length of a few hundred Ångströms which exists along the column; in the second (D_{hd}) there is a genuine liquid-like order in the positional correlations [1]. Another class of mesophase has been observed in some hexabenzoyloxy triphenylenes and several truxene derivatives: a fluid birefringent mesophase with a schlieren texture the structure of which is comparable with the NL or type IIDM mesophase [13] in which the only order is a parallelism between lens-shaped units of soap. This nematic phase built up with lens-shaped or disc-shaped molecules is currently denoted N_D [14]. In addition new investigations have been carried out recently on the relationship between the molecular architecture and the related mesophase and other systems such as cone-like molecules [15], ring molecules [16] or polycatenar molecules (Phasmids [17] and biforked mesogens [18]) have demonstrated the existence of columnar mesophases and consequently open a new field of enquiry. Here we report on a new type of disc-like molecule involving the trisbenzofuran central core which leads to columnar and N_D nematic polymorphism.

The different hexa-*n*-alkanoyloxyphenylbenzotrisfuran derivatives were synthesized following the general scheme:



All the starting materials are commercially available and sufficiently pure for the synthesis of the final products.

Ia-Hexamethoxyphenylbenzotrisfuran. 35ml of sulphuric acid (73 per cent) was added at room temperature to an intimate mixture of phloroglucinol **1** (3 g; 0·0195 mol) and of *p,p′*-dimethoxybenzoin **2** (15 g; 0·055 mol) [19]. The mixture was heated at 150°C for 5 min, cooled and poured on to crushed ice, filtered and washed with water. 15·5 g of crude solid was obtained and triturated with hot ethyl acetate and a few per cent of methylene chloride, filtered off and washed with ethyl acetate to give 5·5 g (35 per cent yield) of the required hexamethoxyphenylbenzotrisfuran as a white solid, $T_f > 260°C$.

Ib-Hexahydroxyphenylbenzotrisfuran. A mixture of 3 g of Ia and 50 g of pyridine hydrochloride was heated at 220–230°C for 7 hours under a nitrogen atmosphere. The mixture was cooled and poured on to crushed ice (10 g), concentrated hydrochloride acid (10 ml) and water (20 ml); the precipitate was filtered off and dried carefully under a vacuum.

Ic-Hexa-*n*-alkanoyloxyphenylbenzotrisfuran. A mixture of Ib (0·28 g; 0·00037 mol) magnesium (0·1 g; 0·0041 mol) benzene (2·5 ml) and 0·35 g of (for instance) heptanoyl chloride was refluxed for 7 hours, cooled, dissolved in chloroform and filtered [20]. The organic solution was washed with water, dried over sodium sulphate and the solvent removed under reduced pressure. The crude product was recrystallized from 150 ml of absolute ethanol and 10 ml of benzene and finally purified by chromatography (twice) on silica gel with a benzene (90 per cent) ether (10 per cent) mixture and finally recrystallized from absolute ethanol (100 ml) and benzene (10 ml) to yield a colourless solid.

Elemental analysis

C_5HATF	C	H	O
Calculated:	75·3	6·7	17·9
Found :	75·2	6·7	17·8
C_6HATF			
Calculated:	75·9	7·2	16·9
Found :	75·9	7·3	16·9

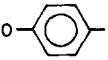
C_7HATF			
Calculated:	76·5	7·6	15·9
Found :	76·5	7·6	15·8

The identification of the mesophases was carried out through the observation of their optical textures using a polarizing microscope and for some by X-ray diffraction. The heats of transition were determined by differential scanning calorimetry (Dupont 990). The transition temperatures and types of mesophase are given in the table.

Transition temperatures (°C) of hexa-*n*-alkanoyloxyphenylbenzotrisfurane. The corresponding heats of transition are given between brackets (kJ mol^{-1}).

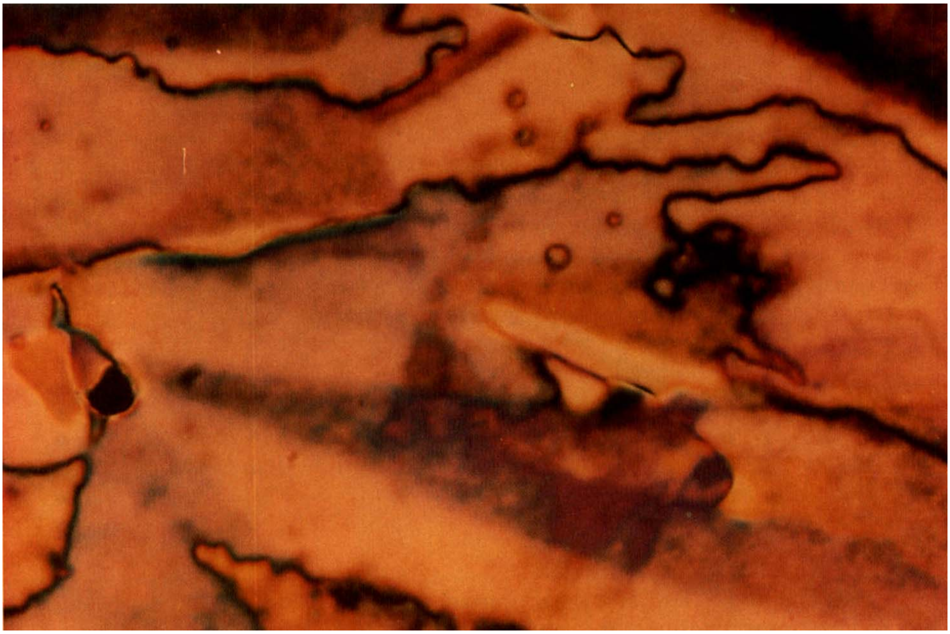
R	C		D_{ho}		I
C_5H_{11}	●	186 (25·24)	●	244 (0)	●
C_6H_{13}	●	134 (52·66)	●	177 (0·33)	●
C_7H_{15}	●	134 (48·9)	[●	100] (0·439)	●
C_8H_{17}	●	107	[●	95]	●
C_9H_{19}	●	97	—		●
$C_{14}H_{29}$	●	86	—		●

C, crystalline phase; D_{ho}, hexagonal ordered columnar phase; I, isotropic phase; [ ], indicates monotropic transition; ●, the phase exists; —, the phase does not exist.

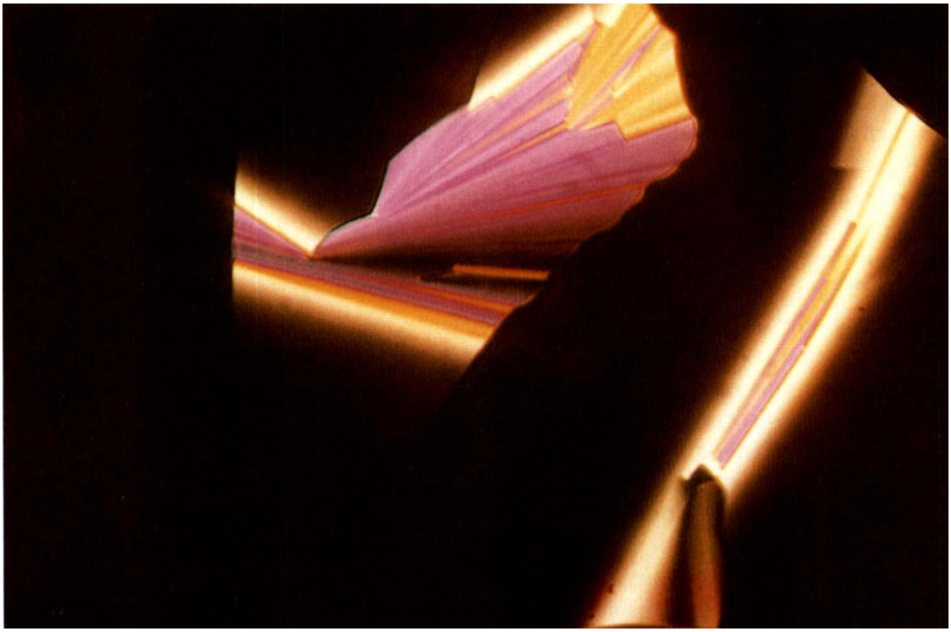
Hexa-*n*-alkoxybenzoyloxyphenyltrisbenzofuran (HBTF). Only one sample has been prepared in this series (*R* = $C_8H_{17}O$––COO–). At 203°C the crystalline phase melts to give a fluid birefringent mesophase, the texture of which is in every way similar to that of the common nematic phase; marbled or threaded textures (cf. figure (*a*)) with strong thermal fluctuations give evidence of a N_D nematic phase. This material decomposes rather quickly and so is not suitable for physical investigations.

Hexa-*n*-alkanoyloxyphenyltrisbenzofuran (HATF). In contrast these compounds are chemically stable and show mesomorphic properties at lower temperature (cf. the table). On slow cooling from the isotropic phase, the mesophase grows from small homeotropic hexagons which develop into digitated stars which then merge into a mosaic of domains with some linear birefringent defects (cf. figure (*b*)) [22]. This behaviour reveals the existence of a hexagonal columnar phase D_h; this identification was confirmed by X-ray diffraction [17, 23]. Moreover the diffraction pattern obtained with a magnetically oriented sample shows, when the X-ray beam is perpendicular to the column axis, localized crescent-shaped arcs corresponding to crystalline order along the columns with a coherence length of a few tens of Ångströms [21]; this phase is a D_{ho} ordered hexagonal columnar phase.

Within the hexa-*n*-alkanoyloxyphenyltrisbenzofuran series only four members are mesogenic (cf. the table); two show enantiotropic mesophases. This behaviour is really different from that observed with the triphenylene or truxene series, for example, where mesophases were observed for aliphatic substituents from C_5H_{11} to at least $C_{12}H_{25}$. Therefore the phenyltrisbenzofuran core seems to be less favourable than larger central rigid cores. Despite this fact an interesting behaviour can be underlined: with hexaalkoxytriphenylenes the coherence length of the crystalline order along a column decreases strongly when the chain length increases from the C_5H_{11} derivative, correlating with the decreasing heat of the isotropic–D_{ho} transition following probably the relative importance of core to core interactions (stabilizing the mesophase) and chain to chain ones (destabilizing the mesophase). With HATF compounds it is just



(*a*)



(*b*)

Optical textures of: (*a*) C_8HBTF, at 220°C in the N_D phase, (*b*) C_6HATF, at 172°C in the D_{ho} phase.

the opposite, both the heat of transition isotropic–D_{ho} and the coherence length increases with the chain length.

These new materials extend the range of disc-like mesogens, furthermore these materials are easily available from a chemical preparative point of view. Their manifestation of the interesting D_{ho} columnar phases opens the way to interesting structural investigations.

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