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Mesogens containing the DOBOB group

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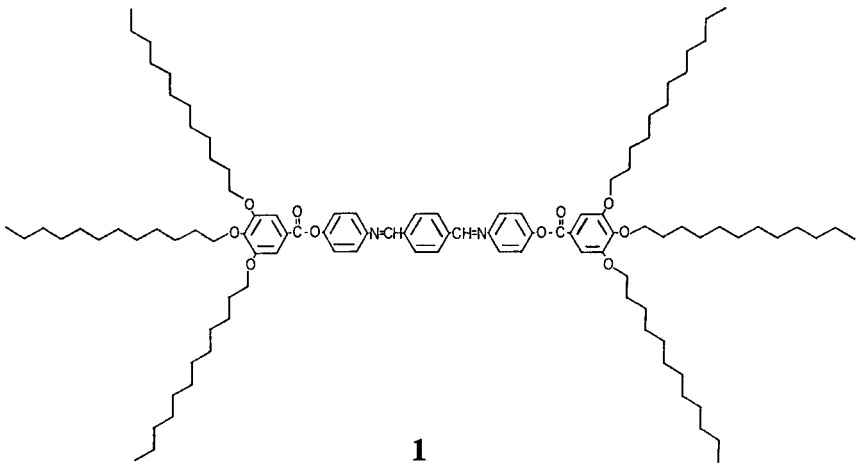
The flat, triangular 3,4,5-tris-(*p*-*n*-dodecyloxybenzyloxy) benzoyloxy group (DOBOB) grafted onto a variety of rod, disc or cone-shaped molecules is shown to yield mesomorphic materials.

1. Introduction

In addition to the classical nematic and smectic thermotropic liquid crystals consisting of rod-like molecules, certain molecules with an overall disc-like shape including flat [1], cone-shaped [2, 3] and macrocyclic [4] compounds have been shown to form mesophases having nematic N_D, columnar or tubular structures. Recently,



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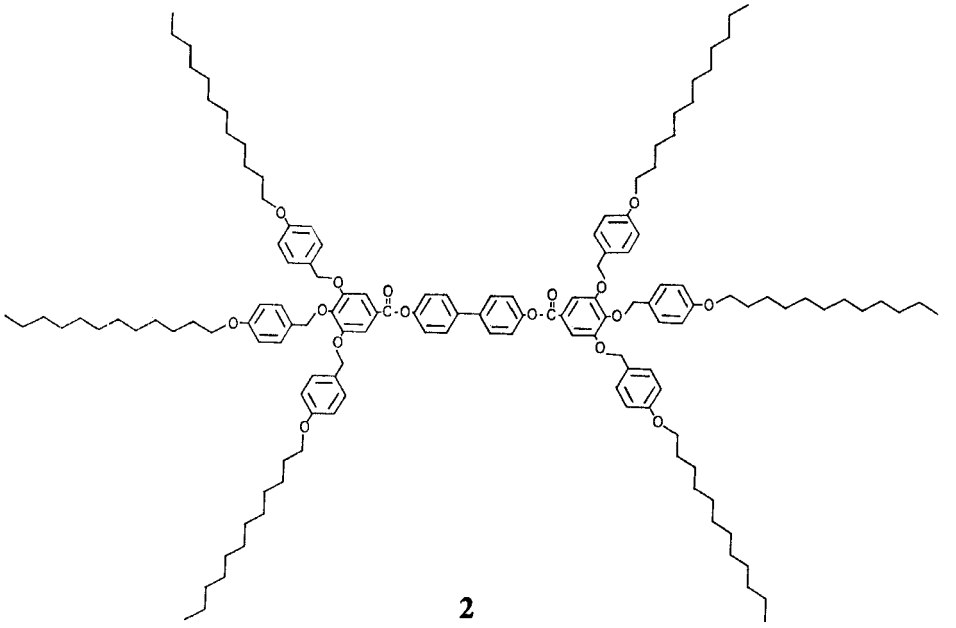
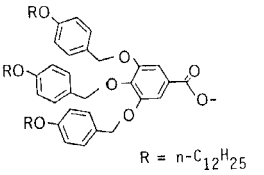
however, a new class of mesogenic molecules has been described [5]. The structural resemblance of **1** and **2** with a six-legged stick-like insect named *phasma* led these molecules which contain a rigid rod-like core ending with two triply-branched groups to be called *phasmids*. Above 81·5°C, compound **1** has a phasmidic mesophase, in which disc-like clusters of three molecules associate to form a hexagonal columnar structure, ϕ_h [6]. Below 81·5°C it forms a lamello-columnar mesophase, ϕ_{ob}, corresponding to a two dimensional oblique lattice. Incidentally, we note that rod-like molecules surrounded by less than six paraffinic chains overall can also exhibit mesomorphic states with a rich polymorphism [7]. We have observed, as have Kok *et al.* [8], that, in order to obtain mesogenic compounds, the use of a large and relatively rigid group for anchoring the paraffinic chains, such as a benzyloxy group, was to be preferred to the direct grafting of the chains onto the core of the molecule. Compound



2

2 was designed along these lines, and forms a hexagonal columnar phase, ϕ_h, in the range 87 to 90°C [9], in spite of its very short biphenyl core. It turns out that in **2** the mesogenic properties should mostly be due to the presence of the large, flat and roughly triangular 3,4,5-tris-(*p*-*n*-dodecyloxybenzyloxy) benzoyloxy units, abbreviated as DOBOB.

DOBOB ≡ 

R = n-$C_{12}H_{25}$

We report here on the mesogenic properties of this group, which actually provides the equivalent of a third of a disc. The DOBOB acid itself (**3**) displays stable columnar mesomorphic properties, doubtless as the dimer. Its methyl ester (m.p. 65·5°C) forms a metastable mesophase. In short, three DOBOB units surrounding a rigid or flexible core allow the formation of columnar mesophases. Two DOBOB units at the ends of a rod give phasmidic mesophases (columnar) and, a single DOBOB group grafted on one end of mesogenic rod-like structures leads either to columnar mesophases or to thermotropic *biaxial* nematics.

The compounds whose properties are discussed here were obtained by reaction of the DOBOB-acid **3** [10] with the appropriate alcohols or phenols, in the presence of dicyclohexylcarbodiimide (stoichiometric) and *p*-dimethylaminopyridine (stoichiometric), in dichloromethane solution. All compounds were purified by thin-layer chromatography and characterized by ^{1}H N.M.R. (200 MHz), I.R. and elemental analyses. Relevant data on the transition temperatures, lattice parameters and core-to-core distances of the hexagonal mesophases are listed in the table.

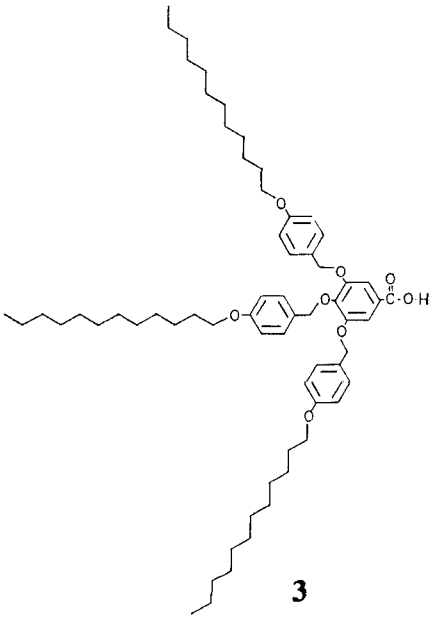
Transition temperatures (°C), *enthalpies* (kJ mol^{-1}), lattice parameters (Å) and core to core distances (Å) of hexagonal mesophases of compounds **1–7** and **9** (*a*).

Compound	K		Hex		I	Lattice parameter	Core to core distances
1	(*b*)		●	92	●	46	≈4·6
				5·9			
2	●	87	●	90	●	45·7	≈4·6
3	●	64·5	●	136	●	42·9	≈4·6
		73·2		*10·9*			
4			●	150–159	●	42·1	3·9
				31·4			
5	(*c*)		Hex_1	40		79·2	3·9
			Hex_2	153–158	●	43·5	3·9
				35·6			
6			●	148–150	●	35·25	4·6
				53·1			
7	●	64	●	84	●	53·4	≈4·6
				1·42			
9	●	56	(●	34·5)	●	42·9	≈4·6
		103·8		*4·6*			

(*a*) K, crystal; Hex, mesophase with an hexagonal 2D lattice; I, isotropic liquid. Transition temperatures and *enthalpies* were determined by using a Perkin–Elmer DSC-2 microcalorimeter.

(*b*) Crystal–crystal transition at 28°C (ΔH = 3·76 kJ mol^{-1}); crystal–ϕ_{ob} transition at 70°C (ΔH = 65·3 kJ mol^{-1}); ϕ_{ob}–ϕ_h transition at 81·5°C (ΔH = 0·25 kJ mol^{-1}).

(*c*) Two hexagonal columnar phases exist.



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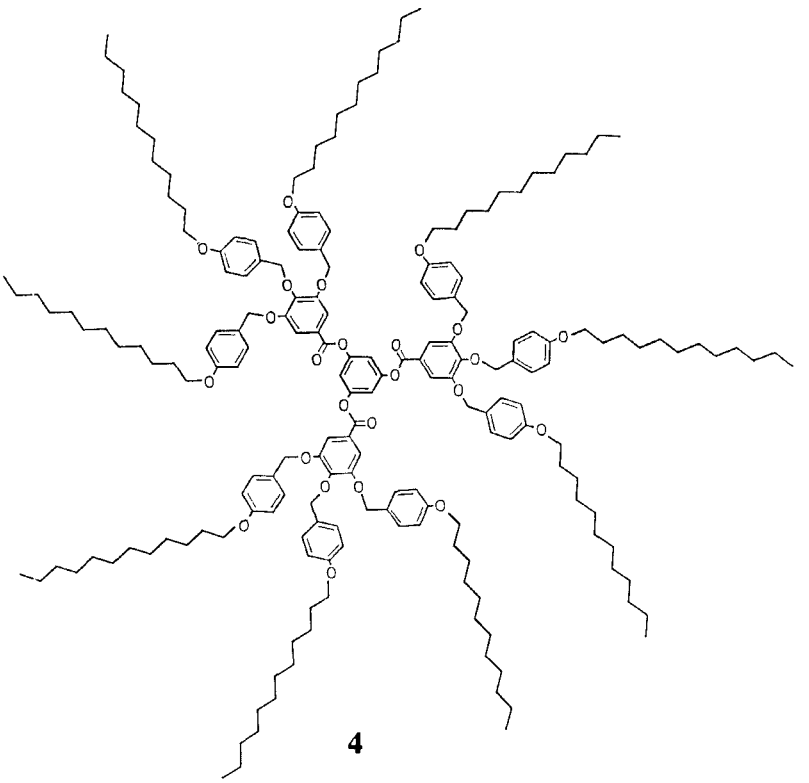
2. Discussion

Three DOBOB groups grafted in 1,3,5-positions on a benzene ring lead to the room-temperature mesogen **4** which displays a hexagonal phase existing up to 150°C. In an analogous compound with shorter paraffinic chains ($C_{10}H_{21}$ instead of $C_{12}H_{25}O$–C_6H_4–CH_2 in **4**) Latterman observed only a metastable columnar phase below 29°C [11]. The tris-DOBOB derivative **5** of tris-(hydroxymethyl) nitromethane forms two columnar mesophases, one existing below 40°C and the other in the range 40° to 158°C, both hexagonal, whereas the corresponding tris-DOBOB derivative **6** of 2,7,12-cyclotriphenolene, a cone-shaped molecule [13], forms a single hexagonal mesophase at room temperature, and which is stable up to 145–150°C.



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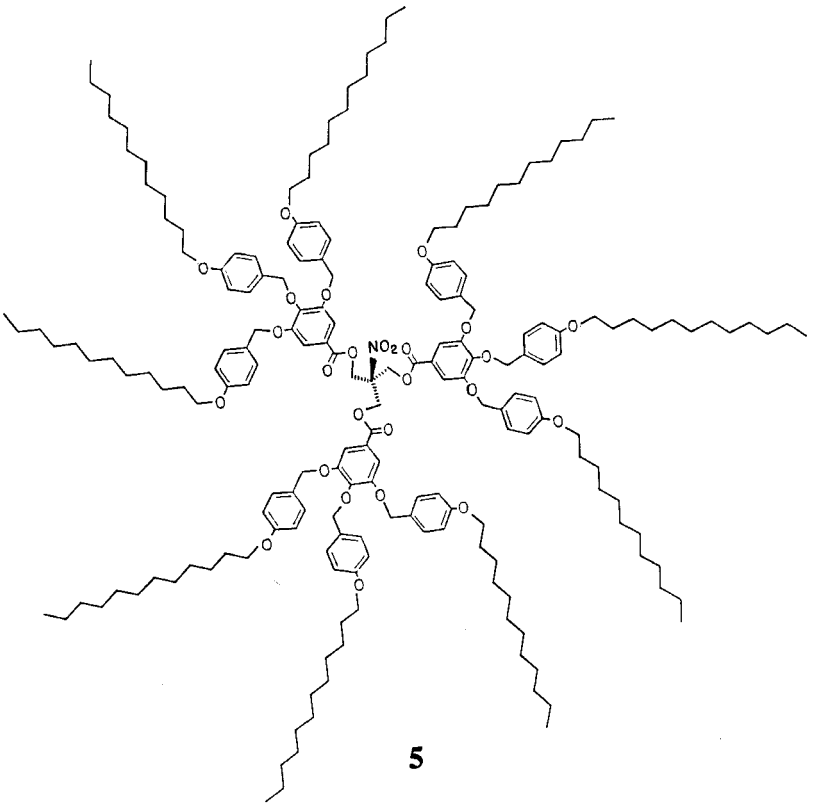
We have investigated the structure of the hexagonal columnar mesophases of **4**–**6** by X-ray diffraction. In **4** and **5** the driving force for the formation of the columnar mesophases should be ascribed solely to the three DOBOB groups, which make the molecules disc-shaped. This is especially true for **5**, in which the flexible tetrahedral unit, which holds the DOBOB groups together, does not convey any mesogenic properties by itself. The existence of a maximum intensity corresponding to core–core interferences is evidenced on X-ray patterns of aligned samples of **4** and **5**. In the columns the mean distance between two molecules can, therefore, be estimated to be *c.* 3·9 Å; the specific gravity of *c.* 0·85–1·09 g cm^{-3} indicates that the three DOBOB groups efficiently fill the space by themselves.

The structure of the low temperature columnar mesophase of **5** is particularly unusual. The hexagonal lattice contains four columns arranged in a P31m or P3m1 symmetry space group. Such an array has rarely been observed (there are just three



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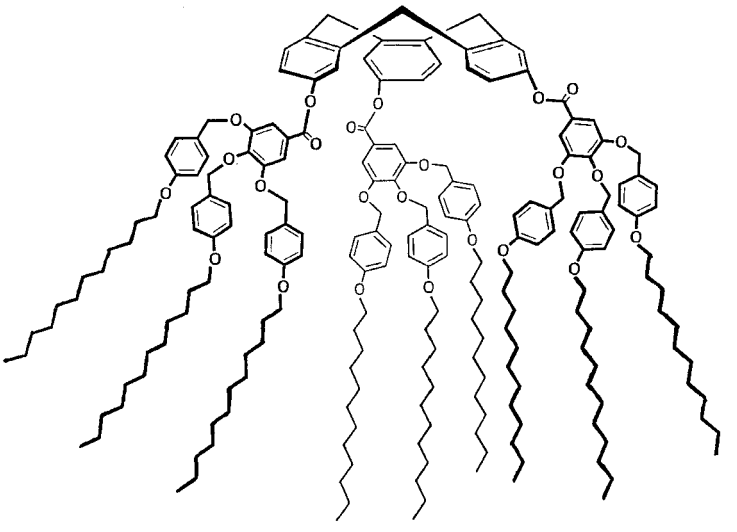
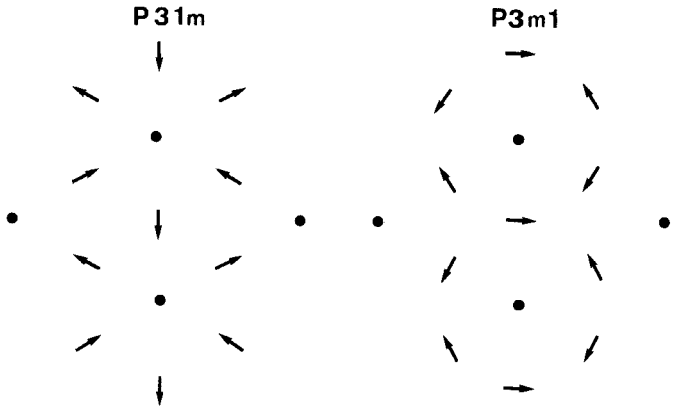


6

reported examples) [3, 12] and only for the low temperature mesophase of non-centrosymmetrical molecules. The four columns are non-equivalent, one having 3/m or 3 (chiral columns) symmetry whereas the three remaining ones have 2/m (or 2) symmetry. If each column bears an intrinsic dipole with a component perpendicular to its axis, the dipoles cannot be completely ordered due to frustration occurring in



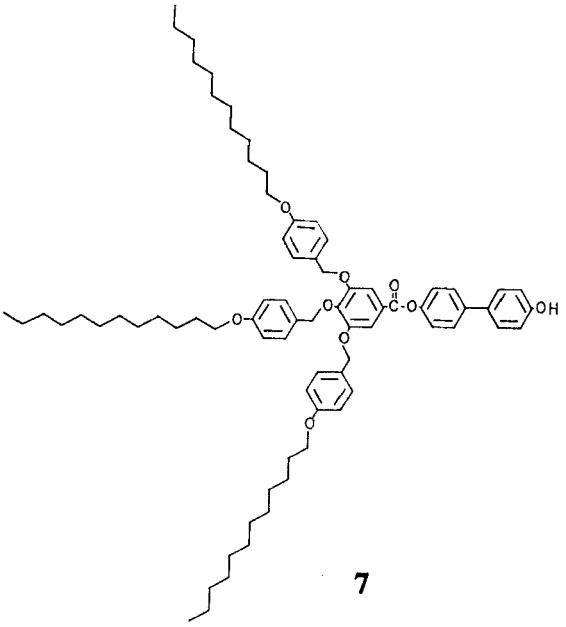
Partially ordered array of dipoles on a triangular lattice (the dots represent orientationally disordered sites).

a triangular lattice (see the figure). The superlattice P31m (or P312) and P3m1 (or P321) corresponds to the case in which three quarters of the columns are ordered while the last one remains orientationally disordered around the lattice C3 axis.

In **6**, the tight embedding of the cone-shaped cores into one another certainly provides an additional stabilization to the columns in making the molecular displacements perpendicular to the column axes more difficult. Here the core-to-core distance is 4·6 Å, a value slightly smaller than in the crystal structure of the parent molecule cyclotriveratrylene (4·87 Å), which also stacks in columns. There is a further modulation along the column axis with a periodicity of 43 Å corresponding to *c.* 9 molecules, suggesting a helical structure resembling that of the low-temperature mesophase of a hexabenzoate of cyclotricatechylene [11]. In the mesophase columns, inversion of the cones takes place over a (high) barrier of *c.* 125 kJ mol^{-1}, i.e., 12 kJ mol^{-1} higher than in the isotropic solution [13], and the possibility that ferroelectric materials could be designed by using such mesophases has been contemplated [13].

Let us now turn to molecules with a single DOBOB unit attached to one end of a rod structure. Compound **7** is an example of this category [7]. It forms a hexagonal columnar mesophase in the range 64 to 84°C. On increasing the length of the rod part of the molecule, nematic properties are obtained, e.g., in compounds **8 a, b** [9, 14, 15]. However, due to the presence in the mesophase of two directors, one parallel to the main molecular axis, the other perpendicular to this axis, *biaxial* nematic properties are obtained, as revealed by conoscopic observations and X-ray diffraction measurements [14–16]. Not unexpectedly, compound **9**, in which the rod-like core is shorter, only forms a hexagonal columnar mesophase.

Information on the packing of the molecules in the hexagonal mesophases can be obtained by combining X-ray data (lattice parameters and core-to-core distance) with the molecular weight of the compound and the specific gravity of the phase (17). We then arrive at the idea that, in phasmids, the basic unit of a column is not a single molecule (as in ordinary disk-like mesogens) but is a cluster of several molecules forming a flat disc. For instance, the hexagonal columnar phase of **1** is made of clusters of three molecules, stacked on one another at a distance of 4·6 Å along the column axis. A cluster is thus surrounded by 18 aliphatic chains. In **2**, which contains two DOBOB ends, the clusters are made of only two molecules (6), and they are therefore surrounded by 12 chains. The structure of the DOBOB acid mesophase is



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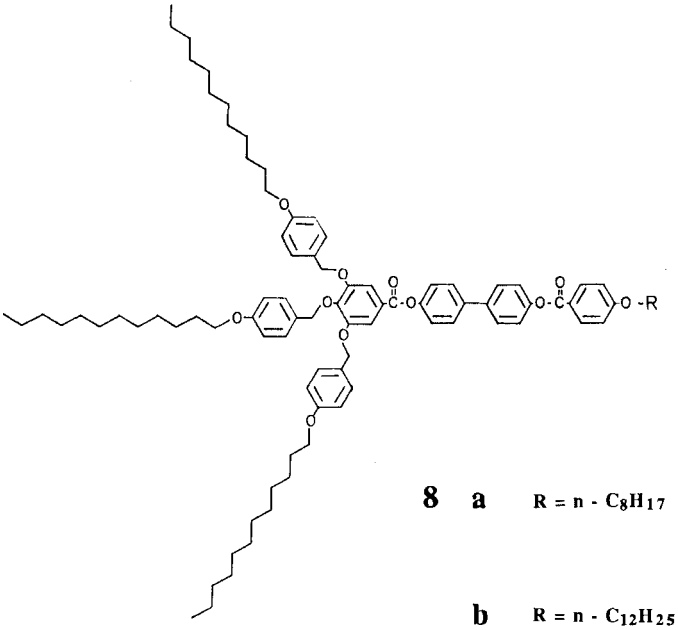
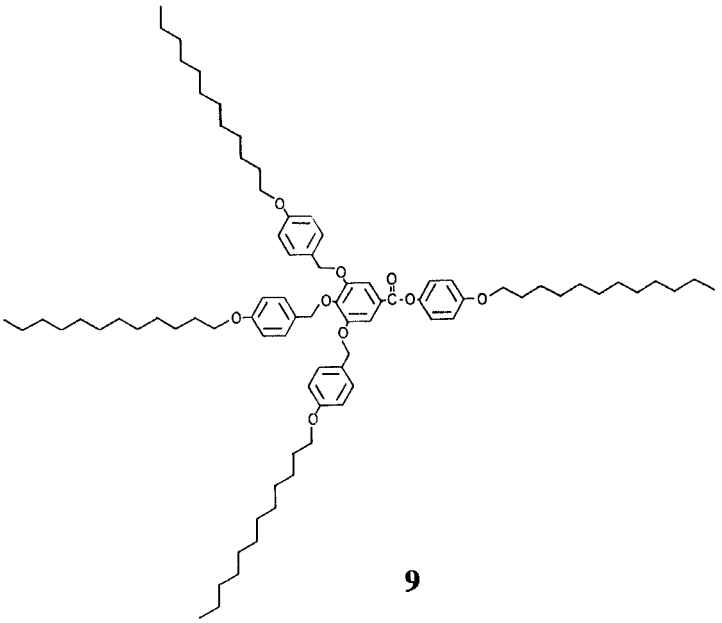


8 **a** R = n - C_8H_{17} K (93 N) 97.5 I
0.63 *83.7*

b R = n - $C_{12}H_{25}$ K (86 N) 86 I
0.54 *95.4*

quite similar; the clusters contain four molecules (presumably as two carboxylic acid dimers), which gives 12 chains overall. Finally, in the mesophase of **7** and **9** (containing a single DOBOB group) the clustering number is estimated to be about six and four, respectively, and the number of aliphatic chains surrounding the disc is then 18 (as in phasmid **1**) and 16.



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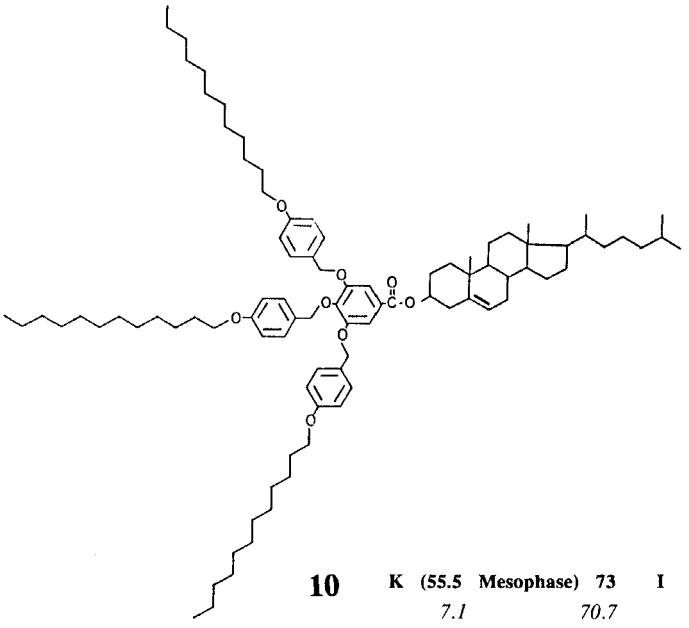
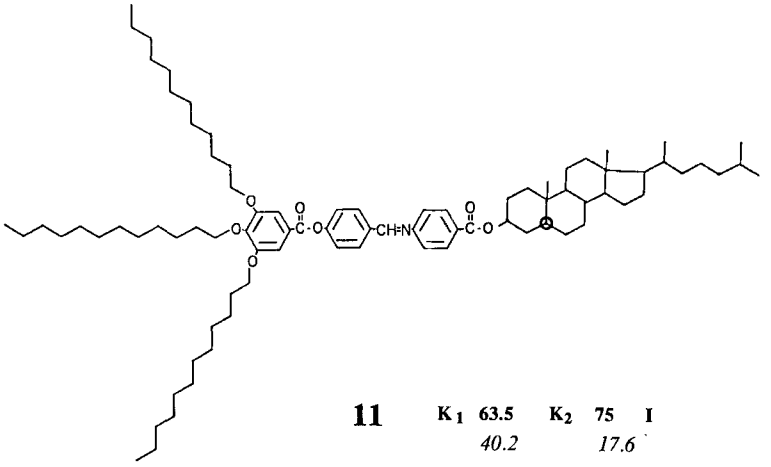


10 K (55.5 Mesophase) 73 I
7.1 *70.7*

Attempts to obtain mesophases by combining DOBOB with chiral steroids were only partially successful. Esterification of cholesterol itself with the DOBOB-acid **3** led to **10**, which forms a metastable mesophase, too unstable to be studied by X-rays (optical observations suggest a columnar ordering). Compound **11** in which the steroid is separated from the DOBOB group by a rod-like spacer only showed crystalline phases.



11 K_1 63.5 K_2 75 I
40.2 *17.6*

In conclusion, all of these features point to the DOBOB group as a potential *columnarogenic* unit. When three DOBOB moieties are grafted onto a rigid or flexible core, the molecules stack on one another in columns, as in D_h phases. With only two or one DOBOB group(s) attached to both or one end(s) of a rod structure, the hexagonal phase consists of stacks of clusters made of two to six molecules.

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