New Bowl-shaped Columnar Liquid Crystals

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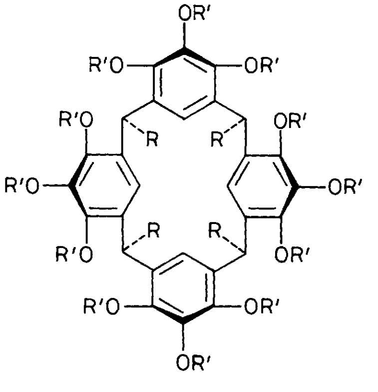
A series of bowl-shaped dodeca-alkanoyloxy macrocyclic derivatives (**1**) is described; four compounds of this series (**1c—g**) display a D_{ho} columnar mesophase.

The existence of potentially ferroelectric, bowl-shaped columnar liquid crystals has been theoretically established since 1982[1] and experimentally proved a few years later.[2] The specific physico-chemical properties of the resulting mesophases are of interest because of their potential applications in the field of optoelectronics.[3]

We report the preparation, physico-chemical characterization, and mesomorphic properties of a new class of columnar liquid crystals, consisting of a bowl-shaped metacyclophane core symmetrically surrounded by twelve flexible alkyl chains.

The acid-catalysed condensation of pyrogallol with 1,1-diethoxyethane in ethanol (25 °C, 48 h, then reflux for 6 h)



(1)

R = Me

a; R' = H
b; R' = COC_nH_{2n+1}, $n = 9$
c; R' = COC_nH_{2n+1}, $n = 11$
d; R' = COC_nH_{2n+1}, $n = 12$
e; R' = COC_nH_{2n+1}, $n = 13$
f; R' = COC_nH_{2n+1}, $n = 15$
g; R' = COC_nH_{2n+1}, $n = 17$
h; R' = COC_nH_{2n+1}, $n = 21$
i; R' = $COC_6H_4OC_nH_{2n+1}$, $n = 12$

Figure 1

provides an easy, high yield (72%) entry into the macrocyclic precursor (**1a**). The precursor (**1a**) in solution is present exclusively in its crown conformation† with all four methyl groups in *endo* configuration,‡ as shown in Figure 1. The possibility of a ring inversion conformational process to give the corresponding compound with four *exo*-methyl substituents is ruled out by analogy with macrocycles of the same kind having eight OH substituents.[5] Compound (**1a**) is therefore the precursor of bowl-shaped mesogenic compounds.

Dodeca-acylated compounds (**1b**—**i**) are obtained by treatment of (**1a**) with the appropriate acyl chlorides (140 °C, 10 h; yields 44—58%). All compounds are purified either by silica gel column chromatography (dichloromethane/hexane as eluant) or by crystallization from dichloromethane/ethyl ether.§

The thermal properties of compounds (**1b**—**i**) are studied by polarized microscopy, differential scanning calorimetry (DSC), and *X*-ray diffraction. The transition temperatures and enthalpy changes are summarized in Table 1. The mesomorphic behaviour is observed only for alkanoyloxy derivatives (**1c**—**g**). Compound (**1c**) presents only a monotropic mesophase on cooling, while (**1h**) forms a re-entrant solid from the isotropic phase upon heating. The benzoyloxy analogue (**1i**) shows no liquid crystal phase. Steric hindrance¶ seems to inhibit the planar distribution of the phenyl groups around the central core, destabilizing the core stacking.

Table 1. Transition temperatures (°C) and enthalpies in parentheses (kJ mol^{-1}) for (**1b**—**i**).[a]

Compound	K$_1$[b,c]	K$_2$[b]	C	I
(**1b**)				76.8(12.6)
(**1c**)[d]	59–I–62[d]			71(≈8.1)
(**1d**)			46(187)	65.5(10.5)
(**1e**)			31(70.5)	67(12.5)
(**1f**)			48(78.0)	61(10.0)
(**1g**)			58(87.0)	68(13.0)
(**1h**)[d]	76–I–82[d]			89(30.5)
(**1i**)				24(51.9)

[a] These results refer to DSC measurements on the second heating run, 10 °C min^{-1}. [b] Nature of K$_1$ and K$_2$ for different compounds are not correlated. [c] In some cases, one or several solid–solid transitions occur at lower temperatures. [d] A K$_1$–I–K$_2$–I sequence is observed, *i.e.* on first clearing the material immediately crystallizes into a K$_2$ phase which clears again on further heating.

The optical textures observed on slow cooling from the isotropic liquid present mosaic and fan-shaped forms with a tendency to homeotropy,|| typical of columnar hexagonal mesophases. Moreover, it is possible to obtain fibre samples with the fibre axis parallel to the stretching direction by shearing the mesophase between two untreated cover slips of ordinary glass. Compounds (**1c**—**g**) are totally co-miscible in the mesomorphic and liquid states and therefore they have the same type of mesophase.

Careful DSC and optical microscopy measurements evidence the metastable nature of some of the mesophases studied. For homologues (**1c**—**d**), upon cooling from the isotropic phase, the mesophase rapidly crystallizes in a more stable and higher melting solid form†† [≈1 s for (**1c**) at 52 °C and 15 min for (**1d**) at 59 °C]. Mesophase stability over time readily increases with chain length: compounds (**1f**) and (**1g**) present stable phases (>8 h at 57 and 65 °C, respectively). We attribute these differences in the thermal behaviour of compounds (**1b**—**h**) to the increased viscosity of the longer chain compounds. The interpretation of the thermal behaviour based on DSC measurements is confirmed by optical observations. A phase diagram of the (**1b**—**h**) series is represented in Figure 2.

X-Ray diffraction studies (λ Cu-K_α radiation) on compound (**1f**) confirm the symmetry properties of the mesophase. The diffraction pattern of the mesophase obtained on a non-aligned sample shows a sharp inner ring corresponding to a lattice spacing of 31.25 Å and two diffuse rings corresponding to scattering angles of $2\theta = 7.9$ and 19.1°. Further information on the molecular organization in the mesophase is obtained by aligning the samples *in situ* and stretching them along the walls of a Lindemann glass tube. The column axis is parallel to the stretching direction. Two sharp spots are present in the

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† The C_{4v} symmetry of the crown conformer of (**1a**) is reflected in its ^{1}H NMR spectrum. For a discussion on the possible conformations of this class of macrocycles see ref. 4.

‡ The *endo* configuration of the four methyl groups is demonstrated by a 25% NOE enhancement observed on the four aromatic hydrogens close to the irradiated methyl groups of the acetylated derivative of (**1a**).

§ All new compounds gave satisfactory analytical and spectral data.

¶ Confirmed by Corey–Pauling–Koltun (CPK) model examination.

|| This fact strongly suggests a uniaxial organization with columns perpendicular to the molecule plane, which is also confirmed by deuterium NMR studies.[6]

†† Upon cooling from the isotropic phase, the DSC traces show one exothermic peak representing the mesophase formation, immediately followed by crystallization in the more stable crystal.

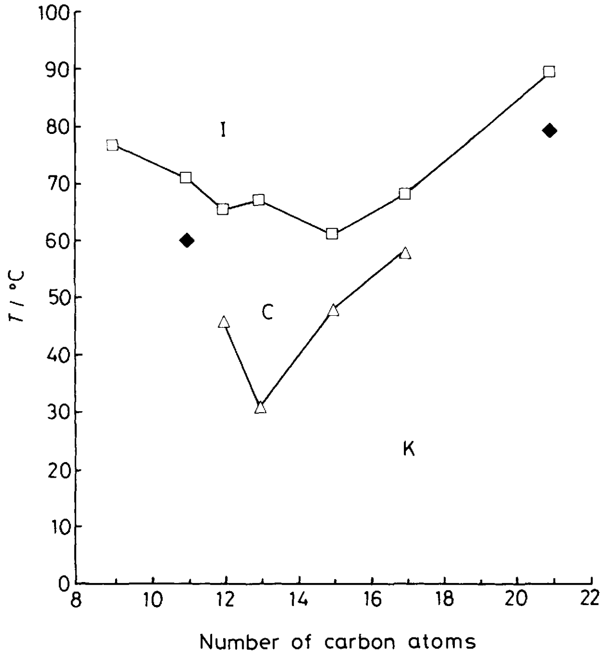

Figure 2. Phase diagram of (**1b**—**h**) based on DSC measurements. ◆ = solid–solid transitions; △ = solid–columnar mesophase transitions; □ = solid–isotropic liquid and columnar mesophase–isotropic liquid transitions. I = isotropic liquid, C = columnar mesophase, K = crystal.

equatorial plane with lattice spacings proportional to 1 and $1/\sqrt{3}$, this last one of very weak intensity. Therefore the 2D network of parallel columns is hexagonal with a lattice constant $a = 36.1$ Å. The outer diffuse ring ($2\theta = 19.1°$) is still isotropic with aligned samples: it corresponds to the diffuse scattering of the aliphatic chains in a very disordered state.

A rather sharp diffuse line, corresponding to the inner diffuse ring present on powder pattern, is visible in the meridian direction. It derives from the diffraction of a periodic linear modulation along the column axis, with a period of 11.2 Å. The correction length is at least seven times this period. The 11.2 Å value corresponds to roughly twice the thickness of a rigid core. This modulation can be interpreted either by an antiferroelectric pairing of the molecules within the columns or by an alternatively short and long spacing along the column axes.[7]

Since the central core is bowl-shaped, compounds (**1b**—**i**) have a net electric dipole moment directed along their C_4 symmetry axes. The orientation of both molecular and columnar dipoles can give a ferroelectric or antiferroelectric mesophase. With the data presently available on this new class of liquid crystals this problem remains open: single crystal *X*-ray analyses and dielectric measurements are in progress to address it.[8] Efforts are underway to study the electric properties of orientated mesophases under the influence of an electric field.

We thank Prof. A. Collet and Prof. J. Malthête (Ecole Normal Supérieure de Lyon) for helpful discussions.

Received, 25th September 1989; Com. 9/04109E

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