## Liquid Crystals

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# A new, conformationally mobile macrocyclic core for bowl-shaped columnar liquid crystals

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# A new, conformationally mobile macrocyclic core for bowl-shaped columnar liquid crystals

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A new series of bowl-shaped columnar liquid crystals **1**, having a conformationally mobile macrocyclic core, is described. Four compounds of this series **1d–g** display a $D_r$ columnar mesophase. The effect of structural and conformational changes of the core on the mesomorphic nature and properties of this class of mesogens is described.

## 1. Introduction

The design of new liquid crystals has received much attention in recent years. Among others, columnar bowl-shaped compounds, based on the rigid cyclotriveratrylene core, are particularly interesting for their novel supramolecular organization [1,2], as well as the related flexible tetrabenzocyclododecatetraene family [3–5].

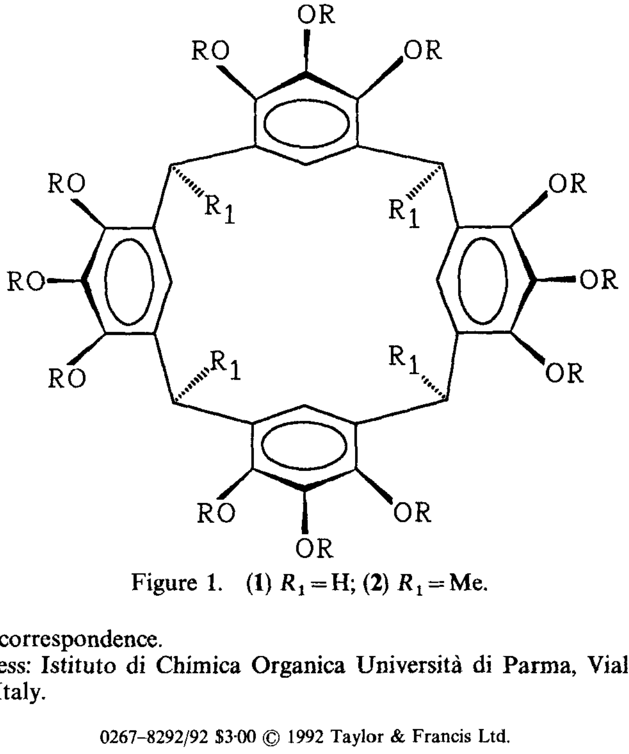

Figure 1. (1) $R_1 = H$; (2) $R_1 = Me$.

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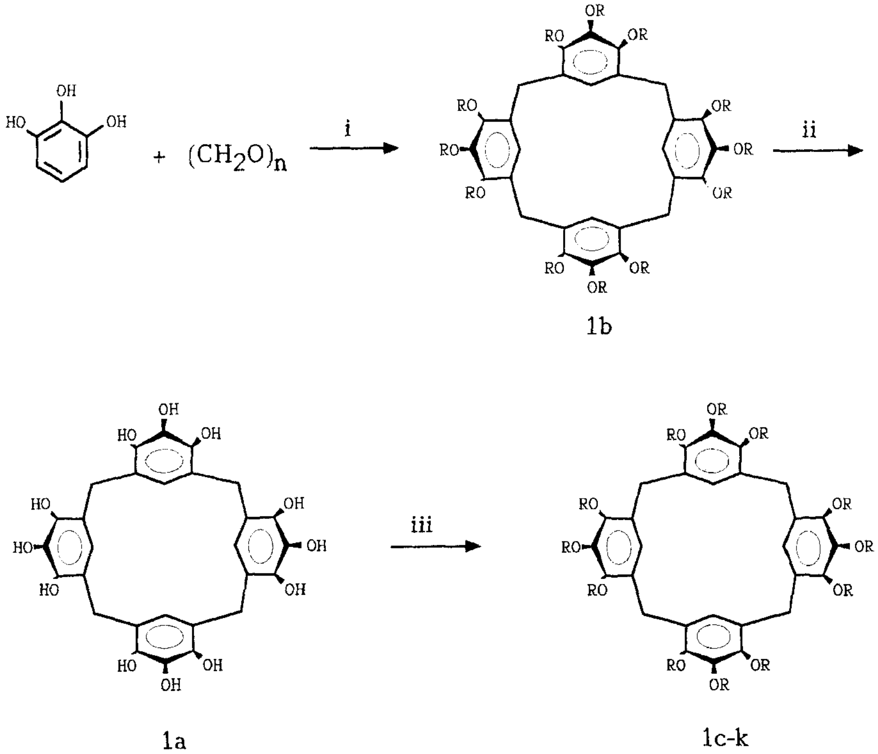
Recently we have introduced a new class of mesogens, consisting of bowl-shaped metacyclophane core symmetrically surrounded by twelve alkyl chains (**2**, figure 1) [6, 7]. Now we report the preparation, physico-chemical characterization and mesomorphic properties of a related class of bowl-shaped columnar liquid crystals (**1**). They have an important additional feature, namely a new, conformationally mobile macrocyclic core, obtained through a fourfold condensation of pyrogallol with paraformaldehyde.

## 2. Synthesis

All of the compounds were prepared through the same reaction scheme, consisting of three steps (scheme). The acid-catalysed condensation of pyrogallol with paraformaldehyde under strictly anhydrous conditions, followed by treatment of the crude product with butyryl chloride, gave pure **1b** in 53 per cent yield. Hydrolysis of **1b** afforded the parent macrocycle **1a** in pure form. Its systematic name (IUPAC nomenclature) is pentacyclo[19.3.1.1$^{3,7}$.1$^{9,13}$,1$^{15,19}$]octacosa-1(25), 3,5,7(28), 9,11,13(27), 15,17,19(26), 21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecaol. Dodeca-acylated compounds **1c–k** were obtained by treatment of **1a** with the appropriate acyl chlorides (see the Experimental section). All of the compounds were



Scheme. (i) (*a*) EtOH, HCl (85°C); (*b*) $C_3H_7COCl$ (100°C). (ii) EtOH, KOH. (iii) Acyl chloride, no solvent (140°C). **1a**, $R = H$; **1b**, $= -CO-C_nH_{2n+1}$, $n = 3$; **1c**, $R = -CO-C_nH_{2n+1}$, $n = 7$; **1d**, $R = -CO-C_nH_{2n+1}$, $n = 8$; **1e**, $R = -CO-C_nH_{2n+1}$, $n = 9$; **1f**, $R = -CO-C_nH_{2n+1}$, $n = 10$; **1g**, $R = -CO-C_nH_{2n+1}$, $n = 11$; **1h**, $R = -CO-C_nH_{2n+1}$, $n = 13$; **1i**, $R = -CO-C_nH_{2n+1}$, $n = 15$; **1j**, $R = -CO-C_2H_4-CH(-CH_3)-C_4H_9$; **1k**, $R = -CO-CH(C_2H_5)-C_4H_9$.

Table 1. Yields, microanalytical and spectral data for compounds **1d–k**.

| | | Elemental analysis calculated/found | | |
|---|---|---|---|---|
| Compound | Yield per cent | C per cent | H per cent | DCI-MS† |
| **1d** | 58 | 73·08<br>73·10 | 9·74<br>10·03 | $MH^+ = 2234$<br>(100%) |
| **1e** | 46 | 73·96<br>73·89 | 10·06<br>10·46 | $MH^+ = 2402$<br>(100%) |
| **1f** | 70 | 74·72<br>74·70 | 10·35<br>10·45 | $M^- = 2569$<br>(100%) |
| **1g** | 64 | 75·39<br>75·44 | 10·59<br>10·44 | $MH^+ = 2738$<br>(100%) |
| **1h** | 53 | 76·51<br>76·27 | 11·01<br>11·20 | $MH^+ = 3075$<br>(100%) |
| **1i** | 50 | 77·41<br>77·41 | 11·34<br>11·56 | $M^- = 3410$<br>(100%) |
| **1j** | 55 | 73·08<br>73·48 | 9·74<br>10·12 | $MH^+ = 2402$<br>(100%) |
| **1k** | 48 | 72·06<br>71·72 | 9·36<br>9·66 | $MH^+ = 2066$<br>(100%) |

† In each case the most abundant molecular ion is reported, considering the $^{13}C$ isotopic abundance.

purified by crystallization from ethanol followed, whenever necessary, by silica gel column chromatography. The spectral ($^1H$ NMR and DCI-MS spectra) and microanalytical data are in agreement with the assigned structures (see Table 1).

## 3. Characterization

### 3.1. *DSC and optical microscopy*

The thermal properties of compounds **1b–k** were studied using optical microscopy and differential scanning calorimetry. Optical observations under the polarizing microscope revealed for derivatives **1d–h** the existence of a viscous mesomorphic organization. On cooling from the isotropic phase, mesophases appeared like birefringent spots which slowly grew and transformed into textures typical for highly ordered columnar mesophases (see figure 2). Lack of homeotropic domains on very slow cooling suggested a biaxial symmetry of the columnar organization. Moreover contact preparations performed between these new compounds and the structurally related uniaxial **2** demonstrated their incompatibility. DSC measurements confirmed the optical observations and revealed the relatively high transition enthalpies for the clearing transitions ($\approx 11$–$17\,\mathrm{kJ\,mol^{-1}}$). Reproducible traces were obtained for all the compounds during second and subsequent heating–cooling cycles (see Table 2).

A phase diagram of derivatives **1c–i** is shown in figure 3. Compound **1g** exhibits only a monotropic mesophase on cooling, while for **1h** the monotropic mesophase was observed only with the polarizing microscope by cooling a thin sample.

Figure 2. Photomicrograph of the mesophase of **1e** obtained by heating, viewed between crossed polarizers ($T = 74$°C).

### 3.2. *X-ray diffraction*

X-ray diffraction studies on an unoriented sample of **1e** in the mesomorphic state (70°C) is in accord with a rectangular columnar organization ($D_r$) with lattice parameters $a = 38{\cdot}90$ Å and $b = 24{\cdot}85$ Å. Measurements on aligned samples confirmed the existence of columns parallel to the stretching direction. A quite diffuse diffraction ring, which corresponds to a repeating distance of 7·8 Å along the column axis, showed the irregularity of the molecular stacking in this direction. An isotropic diffraction at 4·4 Å corresponds to the melted paraffinic chains. With these lattice parameters, a specific weight of $1{\cdot}12\,\mathrm{g\,cm^{-3}}$ can be calculated considering two molecules per unit cell. In this case two hypotheses can be assumed: the existence of molecular pairs in the

Table 2. Transition temperatures and enthalpies for **1b–k** (*a*, *d*).

| Compound | Transition (*b*) | *T*/°C | Δ*H*/kJ mol$^{-1}$ | Transition (*c*) | *T*/°C | Δ*H*/kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| **1b** | C–I | 142·0 | 51 | C–I | 245·5 | 67·1 |
| **1c** | C–I | 74 | 65·5 | C–I | 100·5 | 200·8 |
| **1d** | D–I | 63 | 15·6 | C–D | 67 | 44·7 |
|  | C–D | 35 | 69 | D–I | 83 | 19·7 |
| **1e** | D–I | 65 | 16·8 | C–D | 66·5 | 67·3 |
|  | C–D | 33 | 103·2 | D–I | 80·5 | 19·7 |
| **1f** | D–I | 52·5 | 11·3 | C–D | 66·5 | 115·2 (*e*) |
|  | C–D | 31 | 70·5 | D–I | 68·5 |  |
| **1g** (*f*) | D–I | 54 | 11·8 | C–C | 70·4 | 140·5 (*e*) |
|  | C–D | 38 | 102·2 | C–I | 74 |  |
| **1h** (*g*) | C–I | 46 | 188·2 | C–C | 70 | 233 (*e*) |
|  |  |  |  | C–I | 75 |  |
| **1i** | C–I | 63·5 | 262·5 | C–I | 88 | 277 |
| **1j** | C–I | 29·5 | 13·1 | C–I | 42·5 | 25·5 |
| **1k** (*h*) | C–I | −40 | — | C–I | — | — |

(*a*) These results refer to DSC measurements, 10°C min$^{-1}$: (*b*) cooling run, (*c*) second heating run. (*d*) In some cases, one or several solid-solid transitions occur at lower temperatures. (*e*) Sum of both transitions. (*f*) Monotropic mesophase. (*g*) Monotropic mesophase observed only under the polarizing microscope by cooling a thin sample. (*h*) Oil at room temperature. No first order C–I transition is observed; the viscous isotropic phase solidifies at $T_g = -40$°C.

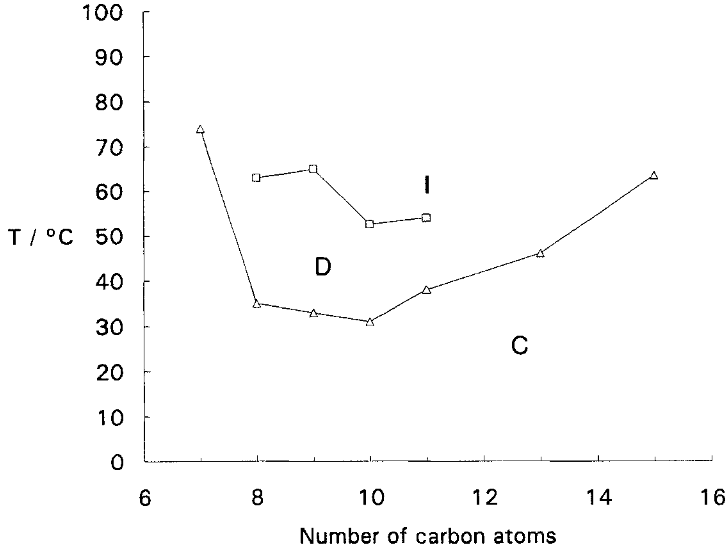


Figure 3. Phase diagram of **1c–i** based on DSC measurements (cooling cycle). Squares: D–I transitions; triangles: C–I or C–D transitions. I, isotropic liquid; D, columnar mesophase; C, crystal.

columns with a 38·90 × 24·85 Å$^2$ section or two different types of columns with a half section and a molecular distance of 7·8 Å. The first model seems more probable if we consider that the structurally similar **2** forms stable pairs in the crystalline state [8]. However, to interpret the recorded diffraction intensities, a zig-zag stacking of the cores along the column axis must be assumed giving a chevron organization on projection onto the *ab* plane.

## 4. Results and discussion

With respect to **2** already reported this series requires shorter alkyl chains to generate the mesophase. This experimental evidence can be interpreted by assuming a correlation between the thickness of the core and the length of the side chains, in order to assure a perfect space filling of the overall molecule [9]. In our case the macrocyclic core of **1** is 0·8 Å thinner than that of **2** [10], and so to be a mesogen alkanoyloxy side chains with 9–12 carbon atoms instead of the 12–18 necessary for **2** are needed.

The branched side chain derivatives **1j–k** do not form liquid crystals. In both cases the melting point was depressed with respect to that of the corresponding straight chain compounds (compare **1k** with **1c** and **1j** with **1d**, Table 2). Such an effect is especially evident in **1k**, where the ethyl groups are close to the core. The introduction of branch points in the side chains destabilizes the columnar organization through steric interference of the alkyl substituents with efficient stacking of the cores [11].

The high conformational mobility of **1a** was demonstrated by deuterium NMR measurements: the macrocyclic ring inversion process was frozen only at −90°C in acetone-$d_6$, with **1a** locked in the crown conformation [12, 13]. The conformational mobility of the core in derivatives **1b–i** is only slightly decreased by the presence of twelve bulky acyl groups (**1b** mobility was frozen out at −70°C in acetone-$d_6$). The length of the alkyl chains does not affect significantly the energy required for the ring inversion process. The same process in **2** is prevented by the presence of four methyl substituents in the endo position on the macrocyclic core [12].

## 5. Conclusions

Substitution of $R_1 = CH_3$ (**2**) with $R_1 = H$ (**1**) on the macrocyclic core in bowl-shaped mesogens has several interesting consequences for the structure of the mesogens and the nature of the mesophase formed. A correlation between the thickness of the core and the length of the side chains is established, which shows the high sensitivity of this system towards the thickness of the macrocyclic moiety [7]. The mesophase structure also changes from uniaxial $D_{ho}$ (**2**) to biaxial $D_r$ (**1**) with a chevron organization in the *ab* plane. Finally, removal of the bulky methyl groups provides a new, conformationally mobile macrocyclic core. Analogous to **2**, the central core of **1** in its crown conformation has a net electric dipole moment oriented along the $C_{4v}$ symmetry axis. In this case however, the presence of a fast ring inversion conformational process overcomes the constraint of antiferroelectric couplings of the molecules within the columns, observed for **2** [8]. In this way these mesogens should be able to align their dipoles freely under the influence of an electric field.

$^2$H NMR studies are under way on deuteriated derivatives of **1e** to establish the preferred core conformation in the mesophase.

## 6. Experimental

Acs grade reagents were used without further purification. Column chromatography was performed by using silica gel 60 (Merck, 70–230 mesh ASTM). Analytical TLC was conducted on precoated silica gel 60 plates. NMR spectra were recorded on Bruker AM 300 and AM 200 spectrometers. Chemical shifts are given in parts per million ($\delta_{TMS} = 0$) using as an internal reference the solvent peak referred to TMS. Mass spectra were recorded on a Finnigam MAT 8400 spectrometer, using the DCI technique (the values are corrected for mass defect). Elemental analyses were performed by the microanalytical laboratory of the Donegani Institute. All products were identified through their elemental analysis, NMR and DCI-MS spectra. Transition temperatures and enthalpies were measured using a Perkin–Elmer DSC 7 thermal analyser. Optical textures were observed with a Leitz–Panphot polarizing microscope, equipped with a Mettler FP 82 hot stage. Powder diffraction patterns were recorded on a Siemens D 500 TH–TH diffractometer with Ni-filtered radiation (Cu–$K_\alpha$ = 1·5418 Å).

**1b.** 1,2,3-trihydroxybenzene (10·00 g, 79·3 mmol) and paraformaldehyde (2·60 g) were dissolved under argon in dry ethanol (80 ml), previously saturated with anhydrous hydrochloric acid. The solution was stirred at 60°C for 24 h, then heated to 85°C for 6 h. The final solution was poured into diethylether (600 ml). The precipitate formed was filtered under argon, then washed with diethylether. The solid (7·0 g) after drying under vacuum ($1 \times 10^{-3}$ mm Hg/25°C), was treated with butyryl chloride (70 ml) at 100°C for 24 h. The excess acyl chloride was removed by vacuum distillation (20 mm Hg) to give a residue, which was dissolved in dichloromethane. The organic phase was extracted with sodium hydroxide (0·2 N), washed with water to neutrality and dried over sodium sulphate. The residue was crystallized twice from acetonitrile/ethanol to give pure **1b** (14·60 g, 53 per cent). $^1$H NMR ($CDCl_3$): $\delta$ 0·95 (m, 36 H, $CH_3$); 1·65 (m, 24 H, CO–$CH_2$–$\underline{CH}_2$); 2·40 (m, 24 H, CO–$CH_2$); 3·62 (s, 8 H, Ar–$CH_2$–Ar); 6·57 (s, 4 H, Ar–H). MS ($\underline{DCI}^+$): $MH^+ = 1393$ (100 per cent). $C_{76}H_{96}O_{24}$. Calculated C 65·50, H 6·94. Found C 65·48, H 7·34.

Tetramer **1a** was obtained in pure form by hydrolysis of **1b**, following a published procedure [14]. $^1$H NMR (acetone-$d_6$): $\delta$ 3·71 (s, 8 H, Ar–$CH_2$–Ar); 6·60 (bs, 12 H, OH); 6·57 (s, 4 H, Ar–H). MS ($DCI^+$): $MH^+ = 553$ (100 per cent). $C_{28}H_{24}O_{12}$. Calculated C 60·87, H 4·38. Found C 60·48, H 4·74.

**1c.** A stirred mixture of **1a** (0·552 g, 1 mmol) and octanoyl chloride (6·8 ml, 40 mmol) was heated at 140°C for 12 h. The excess acyl chloride was removed by vacuum distillation ($1 \times 10^{-2}$ mm Hg) to give a waxy residue which was dissolved in dichloromethane. The organic phase was extracted with sodium hydroxyde (0·2 N), washed with water to neutrality and dried over sodium sulphate. After evaporation of the solvent the residue was purified by repeated crystallization from ethanol, followed by column chromatography with dichloromethane as eluant. Pure **1c** (1·24 g, 60 per cent) as white crystals was obtained. $^1$H NMR ($CDCl_3$): $\delta$ 0·88 [t, 36 H, $(CH_2)_n$–$\underline{CH}_3$]; 1·29 [bs, 96 H, $(CH_2)_4$]; 1·61 (m, 24 H, CO–$CH_2$–$\underline{CH}_2$); 2·43 (t, 24 H, CO–$CH_2$); 3·61 (s, 8 H, Ar–$CH_2$–Ar); 6·53 (s, 4 H, Ar–H). MS ($\underline{DCI}^-$): $M^- = 2065$ (100 per cent, $1 \times {}^{13}C$). $C_{124}H_{192}O_{24}$. Calculated C 72·06, H 9·36. Found C 72·01, H 9·60. Compounds **1d–k** were obtained following this procedure, using in each case the corresponding acyl chloride (Table 1).

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