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New columnar liquid crystals Correlation between molecular structure and mesomorphic behaviour

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New columnar liquid crystals

Correlation between molecular structure and mesomorphic behaviour

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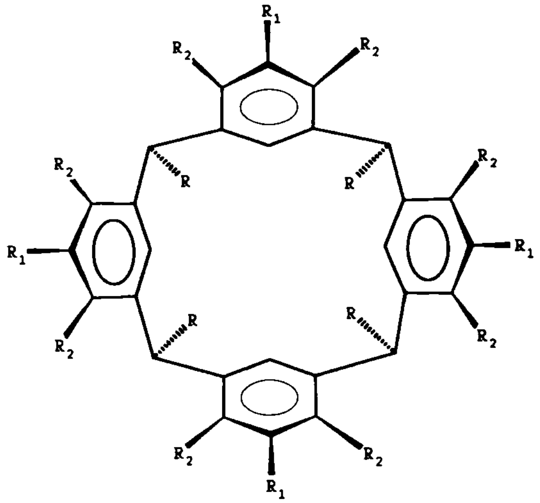
The effect of molecular structural changes on the mesomorphic nature of a new class of macrocyclic columnar liquid crystal is reported. Twenty-six new compounds with general molecular structure I were prepared, characterized and compared.



(I)

Only dodecasubstituted ester derivatives **2d–h** exhibit thermotropic mesophases. The design of mesogens based on these new, unusual macrocyclic cores requires the presence of the following structural elements: twelve aliphatic side chains, esters as bridging units and small R groups on the core.

1. Introduction

Mesomorphic supramolecular ordering in liquid crystals depends mainly on the shape of the individual constituent molecules [1]. For disc-shaped molecules the principal factors influencing the formation of the mesophase are: core dimensions and shape type, number and position of grafted chains, and the nature of the junction between the two parts [2]. Combination of these parameters results in the formation of a columnar arrangement if perfect space filling and optimal coverage of the area in the periphery of the cores is obtained. Most known discostic liquid crystals are

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organized assemblies of molecules composed of flat, rigid aromatic cores surrounded by four to eight flexible chains.

New thermotropic liquid crystals consisting of a cone-shaped cyclotriveratrylene core substituted with six alkyl side chains have been synthesized and characterized [3–10]. They exhibit columnar mesophases, named pyramidic [3], which are different from the discotics. The conic molecules stack on top of each other making the column axis polar and the mesophase potentially ferroelectric [8]. In a recent communication we have described the synthesis and mesogenic properties of a new cyclic molecular architecture consisting of a bowl-shaped metacyclophane core, symmetrically substituted with twelve flexible chains [11]. Here we report the effect of molecular structural changes on the mesomorphic properties of this new class of columnar liquid crystal.

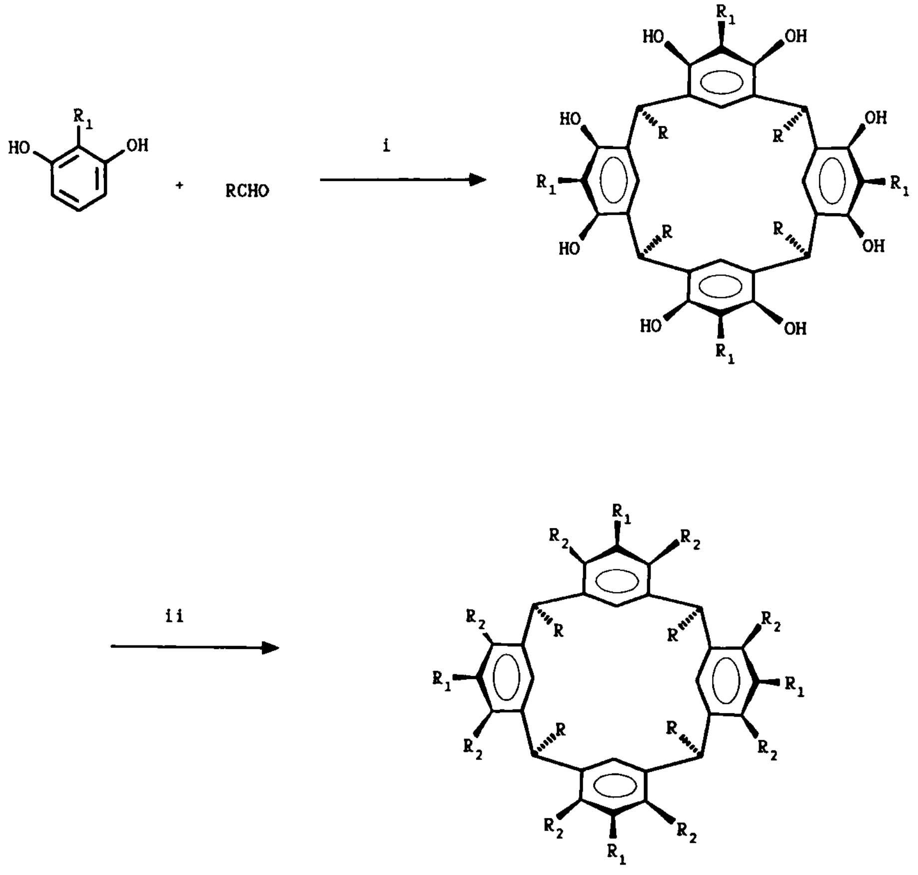
2. Synthesis and characterization

All of the compounds were prepared through the same reaction scheme consisting of two steps (see Scheme 1). The acid-catalysed condensation of resorcinol with acetaldehyde and of pyrogallol with 1,1-diethoxyethane and propionaldehyde provides an easy, high yield entry into macrocyclic precursors **1a–3a** (70–72 per cent). Their condensation with the corresponding acyl chlorides (no solvent used) afforded the ester derivatives **1b–m**, **2b–k** and **3–e** in reasonable yields (24–71 per cent). The spectral (^{1}H-NMR and DCI-MS spectra) and microanalytical data are in agreement with the assigned structure (see tables 1 and 2).

Table 1. Yields, microanalytical and spectral data for compounds **1c–m**.

Compound	Yield per cent	Elemental analysis calculated/found per cent		DCI-MS†
			per cent	
1c	62	75·63	9·97	M$^+$ = 1777
		75·67	10·05	(100%)
1d	60	76·75	10·47	MH$^+$ = 2002
		76·44	10·52	(100%)
1e	61	77·22	10·67	M$^+$ = 2114
		77·03	10·68	(100%)
1f	60	77·65	10·86	M$^+$ = 2225
		77·57	11·01	(20%)
1g	59	78·38	11·18	M$^+$ = 2449
		78·42	11·28	(100%)
1h	62	78·98	11·45	M$^+$ = 2674
		78·80	11·38	(100%)
1i	44	75·38	7·74	M$^-$ = 2289
		75·49	7·85	(100%)
1j	41	77·49	9·05	MH$^+$ = 2851
		77·56	9·05	(100%)
1k	44	78·59	9·77	M$^-$ = 3298
		78·67	9·77	(100%)
1l	47	79·31	7·49	MH$^+$ = 1938
		79·17	7·49	(30%)
1m	51	80·72	9·03	MH$^+$ = 2498
		80·42	8·93	(100%)

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



Scheme 1. (i) (*a*) EtOH, HCL (0°C); (*b*) heating (85°C). (ii) acyl chloride, no solvent. **(1)** R = CH_3; R_1 = H **(1a)**; **(1b–h)** R_2 = -O-CO-C_nH_{2n+1}, **(1b)** $n = 5$, **(1c)** $n = 9$, **(1d)** $n = 11$, **(1e)** $n = 12$, **(1f)** $n = 13$, **(1g)** $n = 15$, **(1h)** $n = 17$. **(1i–k)** R_2 = -O-CO-C_6H_4-O-C_nH_{2n+1}, **(1i)** $n = 7$, **(1j)** $n = 12$, **(1k)** $n = 16$; **(1l–m)** R_2 = -O-CO-C_6H_4-C_nH_{2n+1}, **(1l)** $n = 5$, **(1m)** $n = 10$. **(2)** R = CH_3; **(2a)** R_1 = -OH; **(2b–i)** $R_1 = R_2$ = -O-CO-C_nH_{2n+1}, **(2b)** $n = 3$, **(2c)** $n = 9$, **(2d)** $n = 11$, **(2e)** $n = 12$, **(2f)** $n = 13$, **(2g)** $n = 15$, **(2h)** $n = 17$, **(2i)** $n = 21$; **(2j)** $R_1 = R_2$ = -O-CO-C_2H_4-CH(-CH_3)C_4H_9; **(2k)** $R_1 = R_2$ = -O-CO-C_6H_4-O-C_nH_{2n+1}, $n = 12$. **(3)** R = C_2H_5; **(3a)** R_1 = -OH; **(3b–e)** $R_1 = R_2$ = -O-CO-C_nH_{2n+1}, **(3b)** $n = 3$, **(3c)** $n = 11$, **(3d)** $n = 15$, **(3e)** $n = 17$.

The thermal properties of the homologous series were studied using differential scanning calorimetry and optical microscopy. Reproducible transition temperatures were obtained for all of the compounds during second and subsequent heating–cooling cycles. The great majority of the compounds reported showed several solid-solid transitions followed by broad melting peaks. Mesophase to crystal transitions occurred with strong supercooling (typically 15–20°C). The interpretation of the thermal behaviour based on DSC measurements was confirmed by optical observations. Thin samples were observed between two untreated cover slips of ordinary glass. The optical textures were observed on cooling from the isotropic liquid with weak supercooling (2–3°C). The transition temperatures of all of the compounds are summarized in tables 3 and 4. Mesomorphic properties were observed for alkanoyloxy derivatives **2d–h**. X-ray diffraction [11], optical microscopy and deuterium NMR studies [12] characterized the mesophase as D_{ho}.

Table 2. Yields, microanalytical and spectral data for compounds **2b–j**.

Compound	Yield per cent	Elemental analysis calculated/found per cent	per cent	DCI-MS†
2b	68	66·28	7·23	MH$^+$ = 1449
		66·20	7·16	(100%)
2c	52	74·22	10·16	M$^+$ = 2457
		74·13	10·45	(100%)
2d	58	75·60	10·67	M$^+$ = 2793
		75·69	10·90	(100%)
2e	58	76·17	10·88	M$^+$ = 2962
		76·17	11·08	(100%)
2f	54	76·67	11·07	M$^+$ = 3130
		76·71	11·26	(10%)
2g	50	77·55	11·39	M$^+$ = 3466
		77·52	11·58	(100%)
2h	53	78·26	11·65	M$^+$ = 3802
		78·30	11·70	(110%)
2i	24	79·37	12·06	M$^-$ − 2R$_1$ = 3831
		79·38	12·24	(10%)
2j	42	74·22	10·16	MH$^+$ = 2458
		74·40	10·23	(100%)

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

Table 3. Transition temperatures (°C) for the alkanoyloxy derivatives **1b–h**, **2b–j** and **3b–e**.

Compound	*n*	K$_1$		K$_2$		C		I
1b	5	●					160, 3	●
1c	9	●					40, 3	●
1d	11	●	23	●			28, 1	●
1e	12	●	20, 5	●			43, 5	●
1f	13	●	28, 9	●			37	●
1g	15	●	40	●			45, 5	●
1h	17	●	49	●			55	●
2b	3	●	98, 5	●			202	●
2c	9	●					76, 8	●
2d†	11	●	60	●			71	●
2e	12	●			46	●	65, 5	●
2f	13	●			31	●	67	●
2g	15	●			48	●	61	●
2h	17	●			58	●	68	●
2i	21	●	79	●			89	●
2j	8‡	●					124	●
3b	3	●					190, 5	●
3c	11	●	40, 5	●			50, 5	●
3d	15	●	40	●			60, 5	●
3e	17	●	49	●			66	●

† Forms the mesophase only on cooling (monotropic).
‡ Branched chains (see Scheme 1).

Table 4. Transition temperatures (°C) for the alkoxy-benzoyloxy derivatives **1i-k** and **2k**, and the alkyl-benzoyloxy derivatives **1l-m**.

Compound	*n*	K_1		K_2	C		I
1i	7	●	63	●		169, 5	●
1j	12	●	46	●		106	●
1k	16	●	43	●		106	●
1l	5	●	149	●		212	●
1m	10	●	64	●		84	●
2k	12	●	18	●		124, 5	●

3. Results and discussion

The present study was undertaken to explore the possibilities of this kind of macrocycles to act as mesogenic cores for columnar liquid crystals. They are especially interesting because of their three dimensional shape which can lead to a novel kind of ferroelectric liquid crystal organization, provided that the molecules organize themselves in a head-to-tail fashion. In order to design and synthesize columnar liquid crystals based on this cyclic molecular architecture the require structure was divided into two subunits, namely the central core and the side chains (see figure 1).

3.1. *Central core*

The acid-catalysed condensation of resorcinol with aldehydes is a remarkably selective reaction: it affords in a single step, using the propert conditions, only one isomeric tetramer out of several theoretically possible [13]. Moreover this reaction is amenable to structural variations in both the reactants, allowing a rational design of the desired central core. In this way three different central cores (**1a**, **2a**, **3a**) were assembled in good yields. The stereochemistry of these tetramers is defined by two criteria: the conformation of the macrocycle and the relative configuration (endo or exo) of the alkyl substituents.

The ^{1}H NMR spectra of compounds **1a–3a** in DMSO-d_6 solution at room temperature are consistent with the presence of a C_{4v} symmetry crown structure, which is the average structure resulting from the rapid interconversion between two equivalent flexible C_{2v} symmetry boat conformers (see figure 2) [14]. All of the ester derivatives synthesized are present in the C_{2v} boat conformation in solution at room temperature (see Experimental Part). The ester moieties freeze the conformational mobility of the macrocycles. The interconversion energy between the two equivalent boat conformers increases with length and bulkiness of the side chains: the ^{1}H NMR coalescence temperature is 60°C for **3c** ($n = 11$), 120°C for **3e** ($n = 17$) and 137°C for **2k** (benzoyloxy derivative with $n = 12$) (see Experimental Part).

The endo configuration of the four R groups is demonstrated by X-ray crystal structure determinations on **1a** [15], **2b** and **3b** [16]. The possibility of a ring inversion conformational process to give the corresponding compounds with four exo R substituents is ruled out by analogy with similar macrocycles [17].

Particularly important for the following discussion is the endo positioning of the R substituents which affects the core stacking in columns. By CPK model examination and X-ray crystal structure analysis [15], the methyl and ethyl feet of macrocycles **1a–3a** form a square framework with a side of approximately 7 Å. They are nearly coplanar and they point in the same direction, i.e. toward another core.

Figure 1. CPK molecular model of compound **2f**: hollow side view of the core.

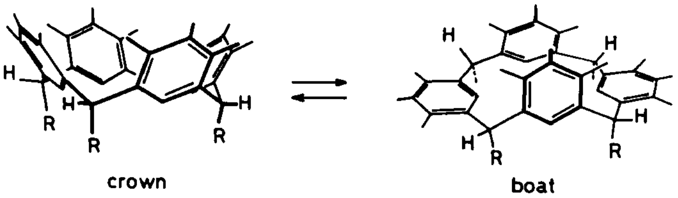


Figure 2. Crown C_{4v} and boat C_{2v} conformers of compounds **1**, **2**, **3**.

DSC and optical microscopy analyses show that only derivatives **2e–h** are mesogens. Comparison of compounds **2d**, **2g** and **2h** ($R=CH_3$) with the corresponding **3c**, **3d** and **3e** ($R=C_2H_5$) evidenced the effect of the **R** groups on the mesophase formation. The presence of R groups bulkier than methyl disturbs the columnar core packing enough to avoid the formation of a mesophase. A small volume variation (ethyl versus methyl substituents) is sufficient to destroy the columnar packing.

3.2. *Side chains*

The formation of the mesophase is influenced by type, number and length of the alkyl chains attached to the core. Two classes of derivatives were prepared, both having an ester linkage. (Alkoxy derivatives have also been prepared but none of them were mesogenic.)

(*a*) *Alkanoyloxy derivatives*

Alkanoyloxy derivatives **1b–h**, **2b–j** and **3b–e** were prepared following the straightforward procedure outlined in Scheme I. Comparison of the related series **1c–h** and **2c–h** clearly demonstrates that eight substituents are not sufficient to generate mesomorphic behaviour in this system. Only the presence of twelve alkyl chains enables the molecule to cover homogeneously the peripheral space surrounding the centre core. This is the first reported class of columnar liquid crystals having twelve aliphatic chains. (Preliminary results from our laboratory indicate that eleven chains can suffice.)

The effect of the chain length on the mesomorphic behaviour can be studied in the **2b–i** series. A columnar arrangement is obtained for $12 \leqslant n \leqslant 17$, while when $n = 11$ it is observed only on cooling (i.e. a monotropic mesophase). The crystal–mesophase transition temperatures decrease with increasing chain length, reaching a minimum for $n = 13$ (**2f**); then they increase (see figure 3). A similar, but less pronounced effect, is observed for the clearing point temperatures, where the minimum is observed at $n = 15$ (**2g**). Compared with other columnar liquid crystals this new class of compounds needs longer alkyl chains to form mesogenic properties. The dimensions and thickness of the core require the presence of such numerous and long paraffinic chains to respect the relative partial densities of the two parts [2]. However the mesophase formation is prevented when the side chains are too long, as observed in the case of **2i** ($n = 21$).

Introduction of branch points on the side chains as in **2j** does not induce the formation of the mesophase, as reported in the literature for other columnar liquid crystals [18].

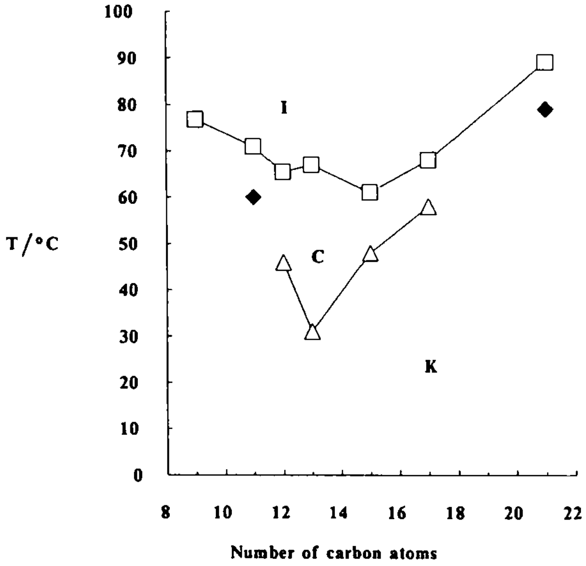


Figure 3. Phase diagram of derivatives **2c–i** based on DSC measurements. Solid–solid transitions (◆); solid–columnar mesophase transition (△); solid–isotropic liquid and columnar mesophase–isotropic liquid transitions (□).

(*b*) *Alkylbenzoyloxy and alkoxybenzoyloxy derivatives*

Derivatives **1i–m** and **2k** were prepared as shown in Scheme 1. None of them proved to be liquid-crystalline. In this case the alkyl chains are linked to the central core through benzoyloxy groups. The bulky phenyl rings are not coplanar due to steric hindrance. Their non-planar arrangement inhibits mesophase formation by preventing the columnar stacking of the cores. The length of the alkyl chains attached to the phenyl rings has no influence on the thermal behaviour of the compounds studied. In this case the presence of benzoyloxy groups does not generate any nematic discotic mesophase, as reported for triphenylene derivatives [19].

4. Conclusions

A new class of columnar liquid crystal, based on a flexible macrocyclic core, have been designed and synthesized. These compounds become mesogens when the following requirements are fulfilled:

small R groups (maximum R=CH_3) to allow an optimal core stacking;
twelves alkyl side chains having 12 to 17 carbon atoms each to cover homogeneously the periphery of the core;
esters as bridging units, without bulky substituents cloe to the macrocyclic core.

These experimental observations can be rationalized by assuming that a columnar mesophase is formed when the energy required to unstack the cores is higher than that necessary to melt the side chains [18]. In the context of this simple model it appears that these new macrocyclic derivatives stack on to each other less efficiently than flat rigid aromatic molecules having comparable dimensions and ring size such as the porphyrins [20].

5. Experimental part

ACS grade reagents were used without further purification. Both column chromatography and flash chromatography were performed by using silica gel 60 (Merck, 400–230 mesh ASTM). Analytical TLC was conduced 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 ($\delta_{\mathrm{TMS}} = 0$) 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 (values 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.

Tetramer **1a** was obtained following a published procedure [15].

1b. A stirred mixture of 0·544 g (1 mmol) of **1a** and 5·6 ml (40 mmol) of hexanoyl chloride was heated at 140°C for 10 hours. The excess acyl chloride was removed by vacuum distillation (1×10^{-2} mm Hg) to give a waxy residue which was dissolved in dichloromethane. The organic phase was extracted with 0·2 N sodium hydroxide, washed with water to neutrality and dried over sodium sulphate. After filtration and evaporation of the solvent the residue was purified by column chromatography with chloroform as eluant. 0·91 g (68 per cent) of pure **1b** as white crystals were obtained.

^{1}H NMR ($CDCl_3$, boat conformation): δ 0·91 [t, 24 H, $(CH_2)_n$–CH_3]; 1·34 [bs, 32 H, $(CH_2)_2$]; 1·46 (d, 12 H, J = 7·2 Hz, CH–CH_3); 1·54 (m, 8 H, CO–CH_2–$CH_{2'}$); 1·69 (m, 8 H, CO–CH_2–$CH_{2'}$); 2·28 (m, 8 H, CO–CH_2); 2·60 (m, 8 H, CO–$CH_{2'}$); 4·22 (q, 4 H, J = 7·2 Hz, CH); 5·97 (s, 2 H, Ar–H_s); 6·78 (s, 2 H, Ar–H_b); 6·93 (s, 2 H, Ar–$H_{b'}$); 7·39 (s, 2 H, Ar–$H_{a'}$).

MS (DCI^+): MH^+ = 1329 (100 per cent). $C_{80}H_{112}O_{16}$. Calculated C 72·26, H 8·49. Found C 72·25, H 8·43.

Compounds **1c–h** were obtained following this procedure, using in each case the corresponding acyl chloride (see table 1).

2a. To a solution, stirred under argon, of 12·61 g (100 mmol) of 1,2,3-trihydroxybenzene in 50 ml of ethanol and 10 ml of hydrochloric acid 37 per cent 14·22 ml (100 mmol) of 1,1-diethoxyethane were added dropwise at 0°C. After addition was complete the solution was stirred at room temperature for 48 hours, then heated to 85°C for 6 hours. The final orange solution was poured into water and the precipitate formed was filtered and washed to neutrality with water. The solid was crystallized from ethanol yielding, after careful drying (1×10^{-3} mm Hg/25°C), 11·0 g (72 per cent) of pale pink crystals melting at 315–320°C (dec.). The product is light and oxygen sensitive so it must be stored in the dark under an argon atmosphere.

^{1}H NMR (DMSO-d_6, crown conformation): δ1·55 (d, 12 h, J = 7·5 Hz, CH_3); 4·56 (*q*, 4 H, J = 7·5 Hz, CH); 6·79 (s, 4 H, Ar–H); 8·02 (bs, 4 H, OH_a); 8·22 (s, 8 H, OH_b).

MS (DCI^+): MH^+ = 609 (100 per cent). $C_{32}H_{32}O_{12}$. Calculated C 63·15, H 5·30. Found C 63·01, H 5·43.

Compounds **2b–j** were obtained following the same procedure as for **1b–h**, using in each case the corresponding acyl chloride (see table 2).

2k. A stirred mixture of 0·304 g (0·5 mmol) of **2a** and 3·00 g (9·23 mmol) of 4-dodecyloxybenzoyl chloride [21] was heated to 180°C for 6 hours. The crude product was dissolved in dichloromethane; the organic phase was extracted with 0·2 N sodium hydroxyde, washed with water to neutrality and dried over sodium sulphate. After filtration and evaporation of the solvent the residue was purified by repeated column chromatography on silica gel with dichloromethane/acetone (9:1) and dichloromethane/ethylether (49:1) mixtures as eluants yielding 0·900 g (44 per cent yield) of **2k** as white crystals. ^{1}H NMR ($C_2D_2Cl_4$, 137°C, crown conformation): δ 0·91 [t, 36 H, $(CH_2)_n$-CH_3]; 1·31 [bs, 216 H, $(CH_2)_9$]; 1·72 (d, 12 H, J = 7·1 Hz, CH-CH_3); 1·81 (m, 24 H, O-CH_2-CH_2); 3·86 (t, 8 H, O-$CH_{2'}$); 4·00 (t, 16 H, O-CH_2); 4·69 (q, 4 H, J = 7·1 Hz, CH); 6·48 (d, 8 H, J = 8·2 Hz, Ph-H_{a2}); 6·79 (d, 16 H, J = 9·0 Hz Ph-H_{a1}); 7·20 (s, 4 H, Ar-H); 7·56 (d, 8 H, J = 8·2 Hz, Ph-H_{b2}); 7·79 (d, 16 H, J = 9·0 Hz, Ph-H_{b1}).

MS (DCI^-): M^- = 4066 (100 per cent, 2 × ^{13}C). $C_{260}H_{368}O_{36}$. Calculated C 76·73, H 9·11. Found C 76·73, H 9·21.

Compounds **1i–m** were obtained following the same procedure as for **2k**, reacting in each case the corresponding acyl chloride with tetramer **1a** (see table 3).

3a. To a solution, stirred under argon, of 6·30 g (50 mmol) of 1,2,3-trihydroxybenzene in 25 ml of ethanol and 5 ml of hydrochloric acid 37 per cent 3·60 ml (50 mmol) of propionaldehyde were added dropwise at 0°C in 1 hour. The solution was stirred at room temperature for 24 hours, then heated to 85°C for 6 hours. Upon cooling a white precipitate was formed, which was filtered and washed to neutrality with water. The solid was crystallized from ethanol yielding, after careful drying (1×10^{-5} mm Hg/25°C), 6·00 g (72 per cent) of white crystals (m.p. > 320°C, dec.).

^{1}NMR (DMSO-d_6, crown conformation): δ 0·84 (t, 12 h, CH_3); 2·20 (m, 8 H, CH_2); 4·05 (q, 4 H, CH); 6·89 (s, 4 H, Ar-H); 8·02 (bs, 4 H, OH_a); 8·60 (s, 8 H, OH_b).

MS (DCI^+): MH^+ = 665 (100 per cent). $C_{36}H_{40}O_{12}$. Calculated C 65·05, H 6·06. Found C 65·24, H 6·33.

Compounds **3b–e** were obtained following the same procedure as for **1b–h**, using in each case the corresponding acyl chloride.

3b was obtained in 54 per cent yield after double crystallization from ethanol.

^{1}H NMR ($CDCl_3$, boat conformation): δ 0·92 (t, 12 H, CH-CH_2-CH_3]; 1·00 [bs, 36 H, $(CH_2)_n$-CH_3]; 1·68 (bs, 24 H, CO-CH_2-CH_2); 1·88 (bs, 8 H, CH-CH_2); 2·40 (bs, 24 H, CO-CH_2); 4·01 (t, 4 H, CH); 6·11 (bs, 2 H, Ar-H); 7·24 (bs, 2 H, Ar-H′).

MS (DCI^+): MH^+ = 1505 (100 per cent). $C_{84}H_{112}O_{24}$. Calculated C 67·00, H 7·49. Found C 66·98, H 7·63.

3c was obtained in 59 per cent yield after purification by column chromatography with dichloromethane/hexane (4:1) as eluant.

^{1}H NMR ($CDCl_3$, 60°C, crown conformation): δ 0·90 [m, 48 H, $(CH_2)_n$-CH_3 + CH-CH_2-CH_3]; 1·32 [bs, 192 H, $(CH_2)_8$]; 1·61 (m, 24 H, CO-CH_2-CH_2); 1·90 (m, 8 H, CH-CH_2); 2·45 (m, 24 H, CO-CH_2); 4·02 (t, 4 H, CH); 6·77 (bs, 4 H, Ar-H).

^{1}H NMR ($CDCl_3$, boat conformation): δ 0·87 [t, 48 H, $(CH_2)_n$-CH_3 + CH-CH_2-CH_3]; 1·25 [bs, 192 H, $(CH_2)_8$]; 1·61 (bm, 24 H, CO-CH_2-CH_2); 1·80 (bm, 8 H, CH-CH_2); 2·36 (bm, 24 H, CO-CH_2); 3·99 (t, 4 H, CH); 6·07 (bs, 2 H, Ar-H); 7·24 (bs, 2 H, Ar-H′).

MS (DCI^+): MH^+ = 2850 (100 per cent, 1 × ^{13}C). $C_{180}H_{304}O_{24}$. Calculated C 75·79, H 10·74. Found C 75·57, H 10·90.

3d was obtained in 44 per cent yield after crystallization from ethanol followed by purification by column chromatography with dichloromethane/hexane (4:1) as eluant.

^{1}H NMR ($CDCl_3$, boat conformation): δ 0·87 [t, 48 H, $(CH_2)_n$-CH_3 + CH-CH_2-CH_3]; 1·25 [bs, 288 H, $(CH_2)_{12}$]; 1·60 (bm, 32 H, CO-CH_2-CH_2 + CH-CH_2); 2·35 (bm, 24 H, CO-CH_2); 3·98 (t, 4 H, CH); 6·06 (bs, 2 H, Ar-H); 7·24 (bs, 2 H, Ar-H′).

MS (DCI$^+$): M$^+$ = 3522 (20 per cent, 2 × ^{13}C). $C_{228}H_{400}O_{24}$. Calculated C 77·67, H 11·43. Found C 77·65, H 11·43.

3e was obtained in 54 per cent yield after purification by column chromatography with dichloromethane/hexane (4 : 1) as eluant.

^{1}H NMR ($C_2D_2Cl_4$, 120°C, crown conformation): δ 0·96 [m, 48 H, $(CH_2)_n$-CH_3 + CH-CH_2-CH_3]; 1·36 [bs, 336 H, $(CH_2)_{14}$]; 1·71 (m, 24 H, CO-CH_2-CH_2); 1·96 (m, 8 H, CH-CH_2); 2·41 (t, 8 H, CO-CH_{2a}); 2·49 (m, 16 H, CO-CH_{2b}); 4·12 (t, 4 H, CH); 6·77 (bs, 4 H, Ar–H).

^{1}H NMR ($CDCl_3$, boat conformation): δ 0·89 [t, 48 H, $(CH_2)_n$-CH_3 + CH-CH_2-CH_3]; 1·25 [bs, 336 H, $(CH_2)_{14}$]; 1·59 (bm, 32 H, CO-CH_2-CH_2 + CH-CH_2); 2·35 (bm, 24 H, CO-CH_2); 3·98 (t, 4 H, CH); 6·07 (bs, 2 H, Ar–H); 7·25 (bs, 2 H, Ar–H′).

MS (DCI$^-$): M$^-$ = 3858 (20 per cent, 2 × ^{13}C). $C_{252}H_{448}O_{24}$. Calculated C 78·36, H 11·69. Found C 78·24, H 11·96.

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