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Influence of steric interactions and random side chain variations on the mesomorphic properties of bowlic mesogens

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Influence of steric interactions and random side chain variations on the mesomorphic properties of bowlic mesogens

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The effect of structural variations on the mesomorphic nature of columnar liquid crystals of general structure I is studied. X-ray crystal structure analyses of compounds **1a** and **2a** reveal the columnar organization of the macrocyclic cores in the solid state. The up and down asymmetry of the cores is resolved in an alternating sequence of up–up and down–down intermolecular contacts. Specific interactions between the *R* substituents are present, which influence the stacking distance between the cores in the down–down intermolecular contacts. Statistical incorporation of different side chains on the same macrocyclic core produces, when the difference in length between the alkyl chains is appropriate, random mixtures having wide mesomorphic ranges. The increase of disorder associated with the statistical side chain distribution on the core and with the structural heterogeneity of each component of the mixture have the effect of depressing mainly the crystal–mesophase transition temperature.

1. Introduction

Structure–property relationships for liquid crystals composed of rod-like molecules have been widely investigated [1]. More recently, several new molecular types of thermotropic mesogens have been discovered [2]. Among these, pyramidic or bowlic mesogens [3–5] are particularly interesting because of the three dimensional shape of the constituent macrocyclic cores [6–8].

We have already investigated the effect of structural changes on the mesomorphic nature of [1_4]-metacyclophanes of general structure I [9]. In particular, the strong influence of the *R* groups on mesophase formation attracted our interest. The influence of methyl groups in exposed positions on the existence of discotic mesophases has already been reported for other mesogens and attributed to steric interactions [10].

Here we report a detailed study of the effect of different *R* substituents on the stacking of the macrocyclic cores in compounds of general structure I, based on single crystal X-ray structure analyses of selected derivatives. Furthermore, we introduce a

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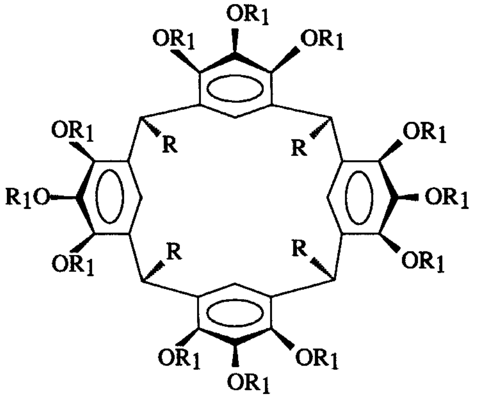


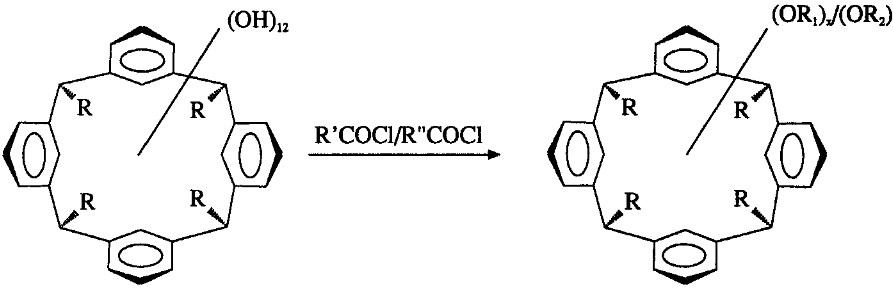
1 R=Me	2 R=Et
a R_1=CO-C_3H_7	a R_1=CO-C_3H_7
b R_1=CO-C_9H_{19}	b R_1=CO-$C_{11}H_{23}$
c R_1=CO-$C_{11}H_{23}$	c R_1=CO-$C_{15}H_{31}$
d R_1=CO-$C_{13}H_{27}$	d R_1=CO-$C_{17}H_{35}$
e R_1=CO-$C_{15}H_{31}$	
f R_1=CO-$C_{17}H_{35}$	

Structure I.

simple method of widening the mesomorphic temperature range in this class of mesogens through the direct, one pot synthesis of random mixtures of dodecasubstituted [1_4]-metacyclophanes [11, 12].

2. Synthesis and characterization

Preparation and characterization of compounds **1a–f** and **2a–d** have already been reported, as well as those of their macrocyclic precursors [9]. In the case of **1a** and **2a**, crystallization from acetonitrile afforded colourless prisms suitable for X-ray structure determinations. The random mixtures **4a–h** were obtained by treating, in each case, the macrocyclic tetramer **3** (R = Me) with the appropriate mixture of acyl chlorides (no solvent used; see scheme 1). Chromatographic purification was employed to eliminate the impurities present in the reaction products (see Experimental section).



3 4a-h x + y = 12

Scheme 1.

The random mixtures were characterized by desorption chemical ionization mass spectrometry (DCI-MS). Our previous experience with this kind of multi-armed macrocycle showed that DCI-MS is the technique of choice for characterization. The following features make DCI-MS particularly attractive for multicomponent mixture analyses: negligible fragmentation, no thermal degradation and high sensitivity [13].

The molecular weight distribution of mixtures **4a–h**, obtained by DCI-MS, is comparable to the statistical figure based on the assumption of equal reactivity of two equimolar reactants (see figure 1).

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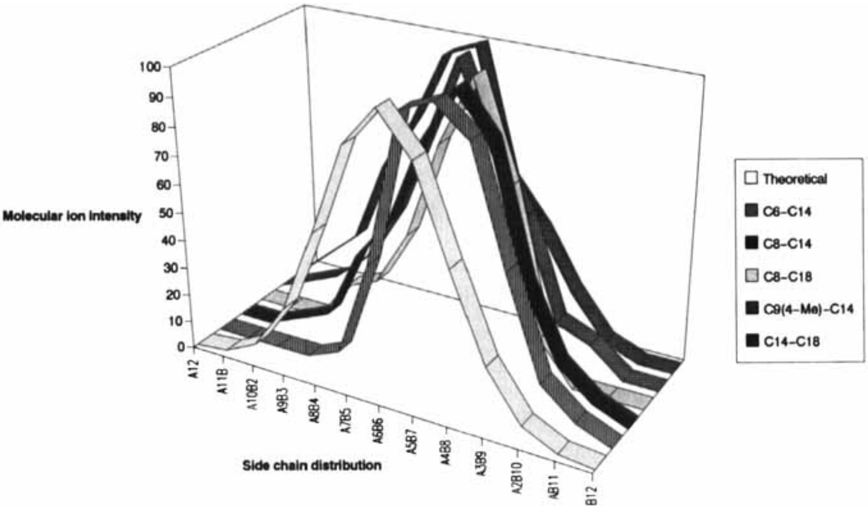

Figure 1. Observed *versus* theoretical side chain distribution for random mixtures **4a**, **4b**, **4c**, **4e**, **4g** (1 : 1 acyl chloride molar ratio). Values derived from the molecular weight distributions, obtained by DCI–MS.

Table 1. Transition temperatures† (°C) for random side chain mixtures **4a–h**, compared with those of the pure compounds **1d–f**.

Mixture	R_1	R_2	R_3	Acyl chloride molar ratio	C		Col.‡		I
1d	—	C_{14}	—		●	29·5	●	67	●
4a	C_6	C_{14}	—	1/1	●			42·5	●
4b	C_8	C_{14}	—	1/1	●	−10	●	40	●
4c	C_9(4-Me)	C_{14}	—	1/1	●			−15	●
1e	—	C_{16}	—		●	48	●	61	●
4d	C_6(2-Et)	C_{16}	—	1/3	●	33	●	55	●
1f	—	C_{18}	—		●	58	●	68	●
4e	C_8	C_{18}	—	1/1	●	−20	●	40·5	●
4f	C_{12}	C_{18}	—	2/3	●	36	●	51·5	●
4g	C_{14}	C_{18}	—	1/1	●	41	●	64	●
4h	C_{14}	C_{16}	C_{18}	1/1/1	●	40·5	●	65·5	●

† Second heating run, 10°C min^{-1}.
‡ Columnar mesophase.

The thermal properties of the random mixtures were studied using differential scanning calorimetry (DSC) and optical microscopy (OM). Reproducible transition temperatures were obtained for all the mixtures during second and subsequent heating–cooling cycles (see table 1).

The large majority of the reported mixtures **4a–h** showed broad melting peaks, and mesophase to crystal transitions occurred with strong supercooling.

OM observations confirmed the interpretation of the thermal behaviour based on DSC measurements. The columnar hexagonal type of phase for mixtures **4a–h** was confirmed by miscibility studies with known columnar, hexagonal bowlic mesogens **1d–f**.

Table 2. Transition temperatures† (°C) for mixtures of pure compounds, compared with those of the pure compounds **1e–f**.

Components	R_1	R_2	R_3	Component molar ratio	C		Col.‡		I
1b–1f	C_{10}	C_{18}	—	1/1	●			55	●
1c–1f	C_{12}	C_{18}	—	1/1	●	52	●	55	●
1d–1f	C_{14}	C_{18}	—	1/1	●	50·5	●	63·5	●
1e	C_{16}	—	—		●	48	●	61	●
1e–1f	C_{16}	C_{18}	—	4/1	●	53	●	68	●
1e–1f	C_{16}	C_{18}	—	1/1	●	56·5	●	67	●
1e–1f	C_{16}	C_{18}	—	1/4	●	58·5	●	68	●
1f	—	C_{18}	—		●	58	●	68	●
1d–1e–1f	C_{14}	C_{16}	C_{18}	1/1/1	●	48·5	●	66	●

† Second heating run, 10°C min^{-1}.
‡ Columnar mesophase.

For comparison, in table 2 are reported reproducible transition temperatures for binary and ternary mixtures obtained by mixing the pure derivatives **1b–f**.

3. Results and discussion

3.1. *Influence of the R groups on the core stacking*

The rationale behind this study was the experimental observation of the strong effect of the *R* groups on mesophase formation. In fact, long chain derivatives **1c–f** form columnar hexagonal mesophases, while the corresponding compounds with $R = \mathrm{Et}$, **2b–d**, do not. Such behaviour has been interpreted in terms of differences in bulk of the *R* groups, which influence the optimal core stacking [9]. A further stimulus to undertake this study came from the observation, through X-ray diffraction measurements, of a modulation along the column axis with a period of 11·2 Å in the mesophase. This modulation has been interpreted in terms of pairing of bowl-shaped molecules along the column axis [8].

In order to gain a better understanding of the molecular interactions responsible for the observed phenomena, we performed single crystal X-ray structure analyses of compounds **1a** and **2a**, which differ only in the *R* group (**1a**: $R = \mathrm{Me}$; **2a**: $R = \mathrm{Et}$). The X-ray data were collected only for the non-mesomorphic, short chain derivatives **1a** and **2a** [9], because the corresponding long chain analogues do not form single crystals suitable for X-ray structure analysis, due to the high degree of disorder introduced by the side chains.

Both compounds crystallize in the triclinic crystal system (space group $P\bar{1}$).

As shown in figure 2, both macrocycles assume a slightly deformed, flattened cone conformation [9], with the *R* groups in the axial configuration, oriented almost perpendicularly to the plane intersecting the carbons connecting the benzene rings (molecular reference plane). The orientations of the aromatic rings are described by the torsion angles which involve the bridging carbon atoms (see table 3). The dihedral angles formed by each benzene ring, with respect to the molecular reference plane, are reported in table 4.

In both cases, two opposite benzene rings are almost perpendicular to the reference plane, while the other two deviate from this by *c.* 10° and 20°, respectively. The orientations of the alkanoyloxy chains are also quite similar: both compounds have

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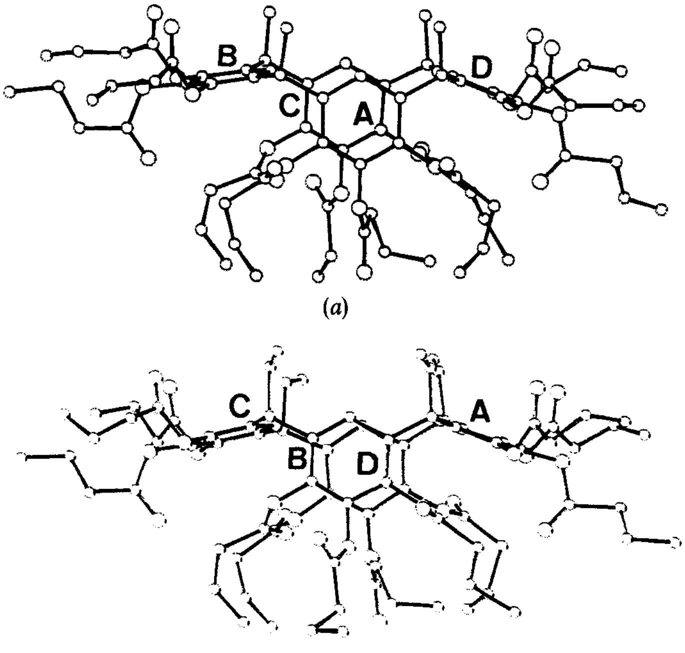

(a)

(b)

Figure 2. (*a*) View of the X-ray crystal structure of compound **1a**. (*b*) View of the X-ray crystal structure of compound **2a**.

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Table 3. Torsion angles involving the CHR bridges for compounds **1a** and **2a**†.

	1a
C5A–C6A–C20D–C2D	72·4(8)°
C6A–C20D–C2D–C3D	−128·8(7)°
C5D–C6D–C20C–C2C	128·8(7)°
C6D–C20C–C2C–C3C	−75·2(8)°
C5C–C6C–C20B–C2B	79·1(8)°
C6C–C20B–C2B–C3B	−141·0(6)°
C5B–C6B–C20A–C2A	139·7(6)°
C6B–C20A–C2A–C3A	−71·9(8)°
	2a
C5A–C6A–C30D–C2D	126·7(7)°
C6A–C30D–C2D–C3D	−70·3(7)°
C5D–C6D–C30C–C2C	79·8(7)°
C6D–C30C–C2C–C3C	−141·2(6)°
C5C–C6C–C30B–C2B	137·7(6)°
C6C–C30B–C2B–C3B	−75·3(7)°
C5B–C6B–C30A–C2A	75·4(7)°
C6B–C30A–C2A–C3A	−130·0(6)°

† For the atomic numbering scheme see scheme 2 in the Experimental section.

Table 4. Dihedral angles between least-square planes through the benzene rings (A–D) and the molecular reference plane R.

	A–R	B–R	C–R	D–R
1a	87·0(2)°	9·2(2)°	82·2(2)°	20·1(2)°
2a	20·7(2)°	82·1(2)°	10·9(2)°	82·8(2)°

four of the twelve C=O groups oriented parallel to the C–R bonds. The most significant differences relate to the orientation of some of the terminal Me groups.

In spite of the different steric hindrance of the *R* groups (Me and Et respectively), the molecular packing of the two compounds is quite similar and all the intermolecular contacts are consistent with van der Waals interactions (see figure 3). In both cases, the lattice is built up of molecules oriented with the normal to the reference plane almost parallel to the [010] direction. The angle between the normal to the reference plane and the *Y* axis is 18·4(4)° for **1a** and 18·25(7°) for **2a**. Considering the hollow side of the macrocycle as the upper part of the molecule and that bearing the *R* groups as the lower part, the spacings in any pile represent an alternating sequence of up–up and down–down intermolecular contacts. The up–up intermolecular contacts are comparable in **1a** and **2a** and lie in the range 3·65(1)–3·94(2) Å, as expected, since the alkanoyloxy chains are equal in both compounds.

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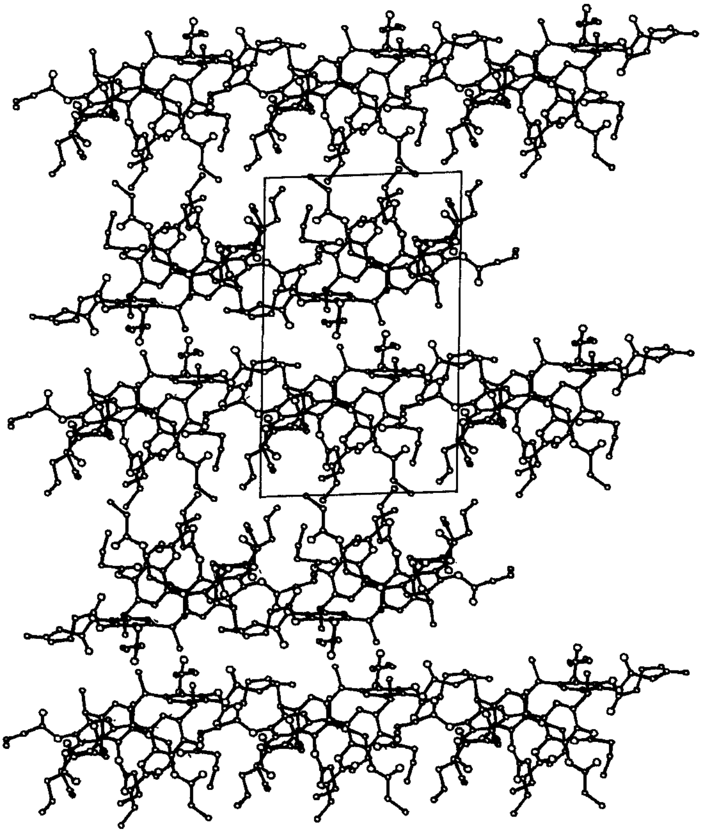
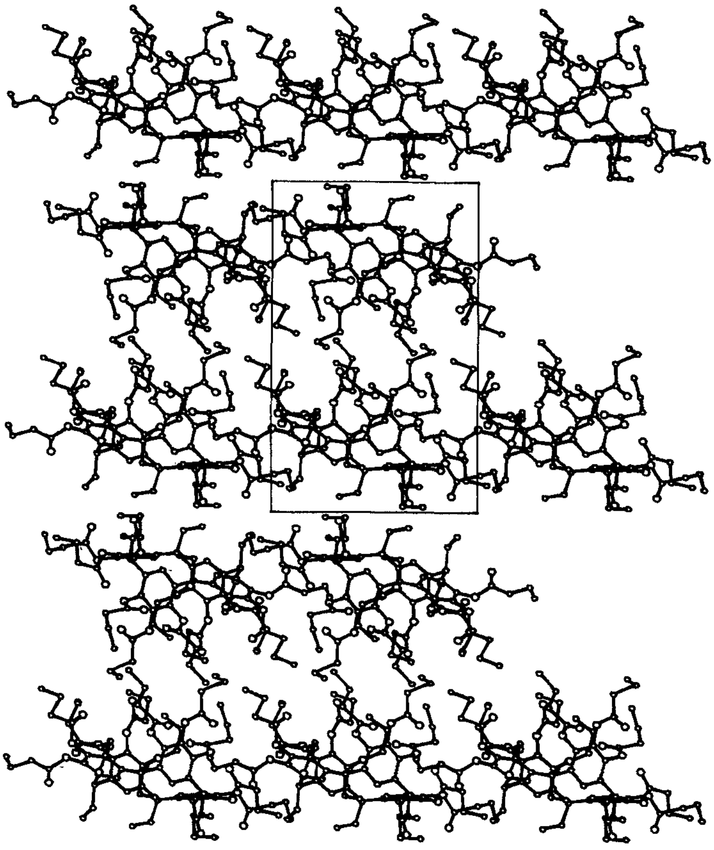


(*a*)



(b)

Figure 3. (a) View of the molecular packing of **1a** along the [001] direction. (b) View of the molecular packing of **2a** along the [001] direction.

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In the down–down intermolecular contacts, substitution of four methyl by four ethyl groups increases the separation between the reference planes. Calculation of the distance between the centres of gravity of atoms defining the reference planes of two adjacent molecules gives 9·44(9) Å for **2a**, whereas 8·04(2) Å is obtained for **1a** (see figure 4). The overall molecular packing is more efficient for the methyl derivative **1a**. As expected, the calculated density decreases from 1·171 g cm^{-3} to 1·147 g cm^{-3} for **1a** and **2a**, respectively. The more efficient packing mode of **1a** with respect to **2a** is in agreement with the higher melting point of the methyl derivative (mp 475 K) compared to that of the ethyl derivative (mp 463 K). In spite of this, the shortest intermolecular down–down contact is 3·63(2) Å in **1a** and 3·49(1) Å in **2a**.

Variation of the *R* substituents from methyl (**1a**) to ethyl (**2a**) does not change molecular conformation, columnar organization and pairing of the molecules within the columns. The only significant difference lies in the 1·40 Å additional distance observed for **2a** in the down–down contacts with respect to **1a** (see figure 4). The crystal structures of **1a** and **2a** are comparable with the solid state picture obtained for mesogens **1d–f**. In fact in the solid form obtained by rapid cooling of the mesophases of **1d–f**, both columnar organization, pairing of the molecules within the columns (observed by X-ray diffraction [8]), and flattened cone conformation of the cores

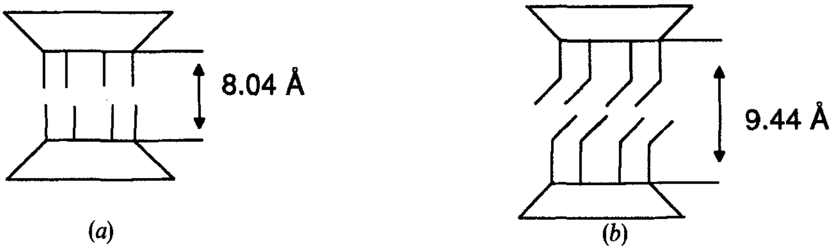

Figure 4. Columnar stacking of **1a** (*a*) and **2a** (*b*) in the solid state. The spacing between two reference planes in the down–down packing mode represents the shortest core stacking distance.

(observed by CP/MAS ^{13}C spectroscopy [14]) are maintained. On these bases, we attribute the suppression of the mesomorphic properties in all derivatives of **2** to the specific steric interaction between the ethyl groups in the down–down intermolecular contact, which prevents the optimal core stacking necessary for the formation of columnar mesophases.

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3.2. *Random mixtures of dodecasubstituted* [1_4]*-metacyclophanes*

By reacting a dodecahydroxy [1_4]-metacyclophane like **3** with two different acyl chlorides A and B, 13 derivatives having different molecular weight can be obtained statistically (all range from A_{12} to B_{12}; see figure 1). For most of them several structural isomers are possible, resulting from the random introduction of A and B side chains on the same macrocyclic core.

The statistical side chain distribution on the core and the structural heterogeneity of each component of the mixture have the effect of widening the temperature range of the mesophases formed with respect to those of the pure derivatives **1c–f** (see table 1).

This effect is especially evident when the A component is a short chain derivative, as in mixtures **4b** and **4e**. Both melting points (C–Col. transitions) and clearing points (Col.–I transitions) are depressed in the random mixtures compared to those of the pure mesogens, with the C–Col. transition temperature the more affected. Branching of side chains widens the mesophase temperature range in one case, **4d**, $\Delta T = 22°C$ versus **1e**, $\Delta T = 13°C$, while in the other, **4c**, an isotropic liquid stable is produced at $-15°C$.

The positive effect of the random side chain introduction on the mesophase formation is even more evident when compared with the opposite trend showed by mixtures of pure mesogens (see table 2). By mixing pure compounds with different side chains, the mesophase temperature range shrinks with respect to that of the pure components. This unusual behaviour can be explained by assuming that perfect space filling is an important factor for the generation of discotic mesophases [15]. In our case, the irregularly shaped mesogens forming the random mixtures should give a better space filling at the periphery of the core with respect to mixtures of bowls having different sizes. Random side chain mixtures of **2** showed no mesomorphic behaviour, indicating the fundamental importance of optimal core stacking in the formation of columnar mesophases.

4. Conclusions

The crystal structures of **1a** and **2a** show that the columnar organization and the pairing of the molecules within the columns are features already present in the solid state. These results are consistent with the X-ray diffraction measurements performed on the mesophases of **1d–f** [8]. The main difference between the two crystal structures lies in the distance between the molecules in the down–down packing mode along the column axis (see figure 4), due to the different bulkiness of the respective *R* groups. The 1·40 Å additional distance observed for **2a** accounts for the suppression of the mesomorphic properties of derivatives **2b–d** by preventing optimal core stacking.

Incorporation of dissimilar side chains on the same core produces, when the difference in length between the alkyl chains is appropriate, random mixtures having wide mesomorphic temperature ranges. This procedure, however, is not sufficient to generate bowlic mesogens when the requirement of optimal core stacking is not fulfilled. This simple method for the direct production of liquid crystal mixtures can be technologically useful in the case of mesogens possessing several side chains [11].

Our findings are consistent with the model proposed by Lillya [12], which predicts that, for discotic liquid crystals, the C–Col. transition is caused by the side chain melting without affecting core stacking. Also, in our case, the effect of the random side chain distribution on the clearing temperature is not preducted by the model.

5. Experimental

ACS Grade reagents were used without further purification. Flash chromatography was performed by using silica gel 60 (Merck, 400–230 mesh ASTM). Analytical TLC was conducted on precoated silica gel 60 plates. Mass spectra were recorded on a Finnigan MAT 8400 spectrometer, using the DCI technique (source temperature set to 90°C, isobutene as reagent gas, values corrected for mass defect and ^{13}C isotropic abundance). ^{1}H NMR spectra were recorded on a Brucker AMX-400 spectrometer. Chemical shifts are given in parts per million ($\delta_{TMS} = 0$) using the solvent peak referred to TMS (7·25 ppm for chloroform) as internal reference. Optical microscopy was performed using a Leitz–Panphot polarizing microscope, equipped with a Mettler FP 82 hot stage. DSC measurements were made with a Perkin–Elmer DSC 7 thermal analyser.

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5.1. *X-ray data collection and structure refinement*

Single crystal X-ray diffraction measurements were performed on a Siemens A.E.D. 3-circle diffractometer. The most relevant parameters used in the experiment are summarized in table 5. The intensities were calculated from profile analysis according to the Lehman and Larsen procedure [16]. The intensities were corrected for Lorentz and polarization effects. No corrections were performed for absorption effects. Both structures were solved by direct methods and refined with the SHELX86 [17] and SHELX76 [18] crystallographic computer programs. The atomic numbering schemes are depicted in scheme 2.

During the isotropic refinement the structure of **1a** showed disorder in the alkanoyloxy side chains attached to the rings C and D, whereas a disordered terminal CH_3 of the *R* groups was found in **2a**. In both cases, the disorder was resolved by the refinement of the site occupancy factors. For both compounds, anisotropic temperature factors were assigned to all non-hydrogen atoms, with the exception of the disordered atoms of the benzene rings and of the terminal CH_2–CH_3 of the alkanoyloxy chains, for which isotropic temperature factors were taken. The refinements converged at $R = 0{\cdot}085$ for **1a** and $R = 0{\cdot}102$ for **2a**. Unit weights were assumed. Atomic scattering factors were taken from the literature [19]. The highest peak in the final F map was 0·35 e · Å^{-3} in **1a** and 0·40 e · Å^{-3} in **2a**. Geometrical calculations were performed by PARST [20]. All the calculations were carried out on the GOULD 6040

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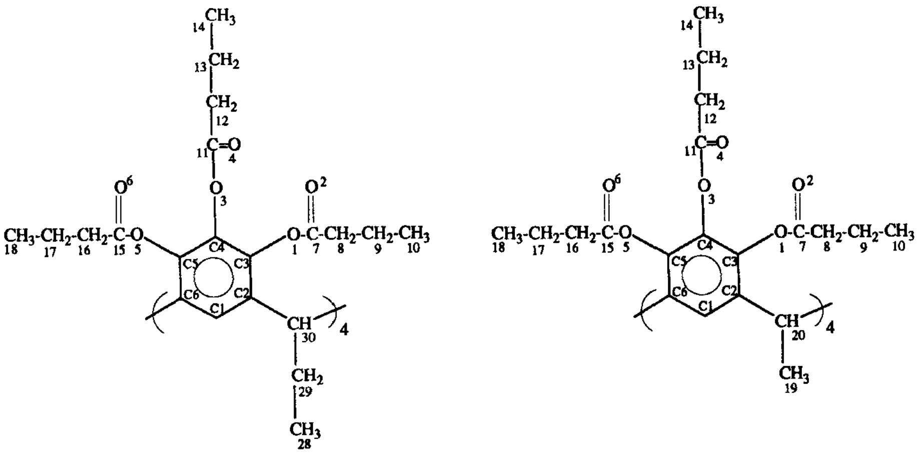

Scheme 2.

Table 5. Experimental data for the X-ray diffraction studies on compounds **1a** and **2a**.

Compound	**1a**	**2a**
Formula	$C_{80}H_{104}O_{24}$	$C_{84}H_{112}O_{24}$
FW	1449·69	1505·79
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
TK	295	295
Cell parameters†		
a Å	13·528(3)	13·973(3)
b Å	21·648(4)	22·055(4)
c Å	14·614(3)	14·816(3)
α°	90·08(2)	86·74(2)
β°	74·22(2)	72·99(2)
γ°	86·97(2)	89·20(2)
VÅ^3	4112(2)	4359(2)
Z	2	2
D_{calc}g cm^{-3}	1·171	1·147
Radiation	Cu–K$_\alpha$	Cu–K$_\alpha$
μ(Cu–K$_\alpha$) cm^{-1}	6·72	6·50
Reflection measured	$\pm h, \pm k, l$	$\pm h, \pm k, l$
θ range°	$3° \leqslant \theta \leqslant 70°$	$3° \leqslant \theta \leqslant 70°$
Total collected data	16315	17235
Observed data	9290($I \geqslant 2\sigma(I)$)	8549($I \geqslant 2\sigma(I)$)
R (unit weight)	0·085	0·102
$(\blacktriangle/\sigma)_{\max}$	0·01	0·02

† Unit cell parameters were obtained by least-squares fitting of the setting angles of 30 $(\theta, \chi, \Phi)_{hkl}$ reflections in the range $30° \leqslant \theta \leqslant 38°$ for **1**, and 30 $(\theta, \chi, \Phi)_{hkl}$ reflections in the range $36° \leqslant \theta \leqslant 45°$ for **2**.

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Final atomic coordinates, thermal parameters, and observed and calculated structure factors have been deposited as supplementary material. Copies of this material which comprises 89 pages may be obtained from the British Library, Lending Division, by quoting the number SUP 16522 according to the procedure described at the end of this issue.

5.2. *Preparation of random mixtures*

Compounds **1a–f**, **2a–d** and **3** were obtained following a published procedure [9].

Mixture **4a**. 0·609 g (1 mmol) of **1** were added to a stirred, homogeneous mixture of 8·15 ml (30 mmol) of tetradecanoyl chloride and 4·19 ml (30 mmol) of hexanoyl chloride. The mixture was heated at 140°C for 16 h. The excess of acyl chlorides was removed by vacuum distillation (1×10^{-2} mm Hg). The residue was dissolved in dichloromethane and the resulting solution was washed with 0·2 M sodium hydroxide, then with water to neutrality, and dried over sodium sulphate. After filtration and evaporation of the solvent, the residue was purified by flash chromatography with dichloromethane/hexane (4 : 1) as eluant.

4a (0·83 g) was obtained as a waxy white solid. DCI-MS. Theoretical range: 1784 ($12C_6$ residues)-3128 ($12C_{14}$ residues). Observed molecular weight distribution: 2232 ($8C_6$-$4C_{14}$, 5 per cent), 2344 ($7C_6$-$5C_{14}$, 40 per cent), 2456 ($6C_6$-$6C_{14}$, 95 per cent), 2568 ($5C_6$-$7C_{14}$, 100 per cent), 2680 ($4C_6$-$8C_{14}$, 90 per cent), 2792 ($3C_6$-$9C_{14}$, 50 per cent), 2904 ($2C_6$-$10C_{14}$, 15 per cent), 3016 ($1C_6$-$11C_{14}$, 5 per cent). Mixtures **4b–h** were obtained following the above procedure, using in each case the mixture of acyl chlorides reported in table 1.

4b. DCI-MS. Theoretical range: 2120 ($12C_8$ residues)-3128 ($12C_{14}$ residues). Observed molecular weight distribution: 2288 ($10C_8$-$2C_{14}$, 5 per cent), 2372 ($9C_8$-$3C_{14}$, 10 per cent), 2456 ($8C_8$-$4C_{14}$, 35 per cent), 2540 ($7C_8$-$5C_{14}$, 50 per cent), 2624 ($6C_8$-$6C_{14}$, 80 per cent), 2708 ($5C_8$-$7C_{14}$, 100 per cent), 2792 ($4C_8$-$8C_{14}$, 85 per cent), 2876 ($3C_8$-$9C_{14}$, 40 per cent), 2960 ($2C_8$-$10C_{14}$, 15 per cent), 3044 ($1C_8$-$11C_{14}$, 5 per cent).

4c. DCI-MS. Theoretical range: 2456 [$12C_9$(4-Me) residues]-3128 ($12C_{14}$ residues). Observed molecular weight distribution: 2512 [$11C_9$(4-Me)-$1C_{14}$, 5 per cent], 2568 [$10C_9$(4-Me)-$2C_{14}$, 10 per cent], 2624 [$9C_9$(4-Me)-$3C_{14}$, 20 per cent], 2680 [$8C_9$(4-Me)-$4C_{14}$, 40 per cent], 2736 [$7C_9$(4-Me)-$5C_{14}$, 70 per cent], 2792 [$6C_9$(4-Me)-$6C_{14}$, 100 per cent], 2848 [$5C_9$(4-Me)-$7C_{14}$, 70 per cent], 2904 [$4C_9$(4-Me)-$8C_{14}$, 50 per cent], 2960 [$3C_9$(4-Me)-$9C_{14}$, 15 per cent], 3016 [$2C_9$(4-Me)-$10C_{14}$, 10 per cent].

4d. DCI-MS. Theoretical range: 2120 [$12C_6$(2-Et) residues]-3464 ($12C_{16}$ residues). Observed molecular weight distribution: 3128 [$3C_6$(2-Et)-$9C_{16}$, 15 per cent], 3240 [$2C_6$(2-Et)-$10C_{16}$, 40 per cent], 3352 [$1C_6$(2-Et)-$11C_{16}$, 100 per cent], 3464 ($12C_{16}$, 40 per cent).

4e. DCI-MS. Theoretical range: 2120 ($12C_8$ residues)-3800 ($12C_{18}$ residues). Observed molecular weight distribution: 2540 ($9C_8$-$3C_{18}$, 15 per cent), 2680 ($8C_8$-$4C_{18}$, 20 per cent), 2820 ($7C_8$-$5C_{18}$, 40 per cent), 2960 ($6C_8$-$6C_{18}$, 75 per cent), 3100 ($5C_8$-$7C_{18}$, 100 per cent), 3240 ($4C_8$-$8C_{18}$, 65 per cent), 3380 ($3C_8$-$9C_{18}$, 15 per cent).

4f. DCI-MS. Theoretical range: 2792 ($12C_{12}$ residues)-3800 ($12C_{18}$ residues). Observed molecular weight distribution: 3212 ($7C_{12}$-$5C_{18}$, 5 per cent), 3296 ($6C_{12}$-$6C_{18}$, 35 per cent), 3380 ($5C_{12}$-$7C_{18}$, 75 per cent), 3464 ($4C_{12}$-$8C_{18}$, 100 per cent), 3548 ($3C_{12}$-$9C_{18}$, 85 per cent), 3632 ($2C_{12}$-$10C_{18}$, 60 per cent), 3716 ($1C_{12}$-$11C_{18}$, 20 per cent).

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4g. DCI-MS. Theoretical range: 3128 ($12C_{14}$ residues)-3800 ($12C_{18}$ residues). Observed molecular weight distribution: 3184 ($11C_{14}$-$1C_{18}$, 10 per cent), 3240 ($10C_{14}$-$2C_{18}$, 20 per cent), 3296 ($9C_{14}$-$3C_{18}$, 50 per cent), 3352 ($8C_{14}$-$4C_{18}$, 70 per cent), 3408 ($7C_{14}$-$5C_{18}$, 95 per cent), 3464 ($6C_{14}$-$6C_{18}$, 100 per cent), 3520 ($5C_{14}$-$7C_{18}$, 55 per cent), 3576 ($4C_{14}$-$8C_{18}$, 40 per cent), 3632 ($3C_{14}$-$9C_{18}$, 20 per cent), 3688 ($2C_{14}$-$10C_{18}$, 5 per cent).

4h. DCI-MS. Theoretical range: 3128 ($12C_{14}$ residues)-3800 ($12C_{18}$ residues). Observed molecular weight distribution: 3296(35 per cent), 3324(40 per cent), 3352(50 per cent), 3380(75 per cent), 3408(80 per cent), 3436(100 per cent), 3464(80 per cent), 3492(75 per cent), 3520(50 per cent), 3548(30 per cent), 3576(15 per cent), 3604(10 per cent), 3632(5 per cent).

All the mixtures synthesized present three diagnostic peaks in the NMR spectrum: ^{1}H NMR ($CDCl_3$, boat conformation): δ4·20 (q, CH), 6·02 (bs, Ar–H), 7·30 ppm (bs, Ar–H). Mixtures of derivatives **1b–f** (see table 2) were prepared by vacuum drying of solutions of the two/three components in dichloromethane.

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