Tubular Mesophases: Liquid Crystals consisting of Macrocyclic Molecules

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The hexa-(*p*-n-dodecyloxybenzoyl) derivatives **(1b)**, **(2b)**, and **(3b)** of the macrocyclic polyamines [18]-N_6, [24]-N_6O_2, and [27]-N_6O_3 display a liquid crystal phase in which the macrocyclic units are stacked, forming a *tubular* mesophase.

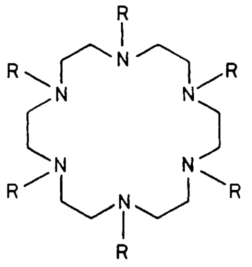
The search for novel types of liquid crystals is of interest because of their physico-chemical properties and their potential applications. A mesomorphic phase may be characterized by the molecular features of the basic units and by the supramolecular arrangement of these units in the mesomorphic state. Of fundamental importance is the determination of how the molecular factors are related to the supramolecular architecture and properties.

In addition to the classical elongated molecules, disc-like flat molecules, containing a rigid core of aromatic[1] or alicyclic type,[2] fitted with six to eight side-chains, have been shown to form thermotropic mesophases. These phases may be either *nematic* N_D, when the only order is a parallel orientation of the molecular discs, or *columnar* D, when the discs are stacked into parallel columns, located at the vertices of a bidimensional lattice of hexagonal, rectangular, or oblique type.[3,4] Columnar type phases have also been observed for substances which do not possess a disc-like core like cyclotriveratrylene[5] or bis-trialkoxybenzene[6] derivatives.†

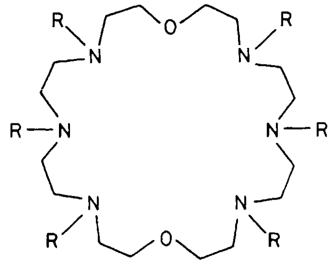
We have investigated the possibility of using macrocyclic molecules fitted with suitable lateral chains as basic units for novel mesomorphic phases. This may in principle be realized with macrocyclic polyamines bearing long chains grafted on nitrogen sites. We now report that *N*-acylated derivatives of saturated macrocyclic hexamines such as [18]-N_6 (hexacyclen, FLUKA AG) (**1a**), as well as similar derivatives of several other macrocyclic polyamines like [24]-N_6O_2 (**2a**)[8] and [27]-N_6O_3 (**3a**),[9] exhibit thermotropic mesomorphism of a novel type.‡

The hexa-acylated compounds (**1b**), (**2b**), and (**3b**) were obtained by treating (95 °C, 48 h) the appropriate macrocyclic polyamine with 6 equiv. of *p*-n-dodecyloxybenzoyl chloride in dimethylacetamide in the presence of 6 equiv. of *p*-dimethylaminopyridine. They were purified by thin-layer chromatography (silica gel; eluant: chloroform + 10% methanol) and crystallized from a methanol–diethyl ether mixture (40—60% yield). The spectral (^1H n.m.r. and i.r. spectra) and microanalytical data are in agreement with the assigned structures. The thermal and optical properties have been studied by differential microcalorimetry and with a polarizing microscope equipped with a variable temperature stage. The transition temperatures and enthalpies are given in Table 1; an example of mesomorphic optical texture is shown in Figure 1.

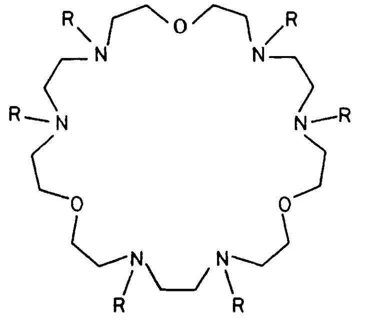
The *X*-ray diffraction patterns of the birefringent viscous mesophases of (**1b**), (**2b**), and (**3b**) are similar: for non-oriented samples only two diffraction rings are seen, the inner is rather sharp and its size varies with the compound, while the outer ring is broad with a maximum of intensity corresponding to the same scattering vector ($2 \sin \theta/\lambda \simeq 1/4.5$ Å) for all the mesophases. Therefore such a pattern could be either that of a smectic A or C or that of a hexagonal columnar phase, since higher order reflections are absent. The ambiguity can be removed by the observation of oriented samples: (1) planar orientation is obtained by stretching the mesophase on a rigid substrate; the extinction directions between crossed polarizers are parallel and perpendicular to the shear direction and the inner ring of the diffraction pattern is split into two crescents lying in a plane perpendicular to the shear direction; (2) homeotropic orientation can be obtained by slow cooling of a thin droplet starting from the isotropic liquid; in such a case the inner ring is in a plane parallel to the homeotropic thin sample; there is no orientation effect upon the outer diffuse ring. These observations do not fit a lamellar structure but are consistent with a hexagonal columnar mesomorphic order. Moreover, the crystallization of oriented samples gives fibres which are also consistent with a columnar organization. The absence of high order reflections in the planar hexagonal



(1)



(2)



(3)

a; R = H
b; R = *p*-n-$C_{12}H_{25}O$–C_6H_4–CO

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† Anhydrous alkaline-earth soaps form columnar-like mesomorphic phases in which the paraffinic chains are organized around a cylindrical core.[7]

‡ Macrocycles bearing long hydrocarbon side-chains have been used in micellar phases,[10] in ion extraction,[11] and in phase transfer[12] processes. Macrocyclic tetra-amines fitted with long chains present lamellar mesophases,[13] and similar compounds with a porphyrin[14] or with a phthalocyanine[15] ring form columnar mesophases.

Figure 1. Optical texture of the mesophase of compound (**1b**) at 133 °C obtained on cooling from the isotropic liquid.

Table 1. Transition temperatures and enthalpies for (**1b**), (**2b**), and (**3b**); lattice constant and specific area per molecule of the T phase.[a]

Compound	K ⟷ T	T ⟷ I	Lattice constant (Å)	Specific area cm^2/g × 10^7
(**1b**)	121.5	141.5	37.3	3.48
	35.7	*0.7*		
(**2b**)	101[b]	(97.5)	34.5	2.86
		2.3		
(**3b**)	85[b]	(80)	37.5	3.31
		1.9		

[a] Temperatures are in °C and enthalpies (italics) in kcal mol^{-1} (1 kcal = 4.184 kJ); K: crystal, T: *tubular* mesophase, I: isotropic liquid; [b] Crystalline polymorphism. ( ): Monotropic transition temperature.

lattice of the mesophase is due to a large amplitude of fluctuations and may be related to the flexibility of each column.§

It is likely that the three compounds display the same type of mesophase. The values of the lattice constants and of the specific area per molecule for each compound (Table 1) are rather larger than the usual values for columnar mesophases (the specific area is less than 2.9 × 10^{-7} cm^2/g for triphenylene derivatives and less than 3.1 × 10^{-7} cm^2/g for truxene derivatives[4]).

All the results are consistent with a supramolecular arrangement of the macrocyclic mesogens into parallel columns placed at the vertices of a hexagonal lattice. So the stacked basic macrocyclic units should form hollow columns, *tubes*, since they are expected to contain a central void, and the phases may be termed: *tubular mesophases*, noted T. A schematic representation of such a phase and of the stacking arrangement is given in Figure 2. Molecular models indicate that the total diameter of macrocyclic hexa-amides is larger than the corresponding lattice constant; for example the diameter of (**1b**) is about 50 Å and the lattice constant is 37.3 Å. This may indicate partial interpenetration of the six lateral chains between neighbouring tubes. The central macrocyclic cavity may also be more or less compressed depending on the nature of the macrocycle.

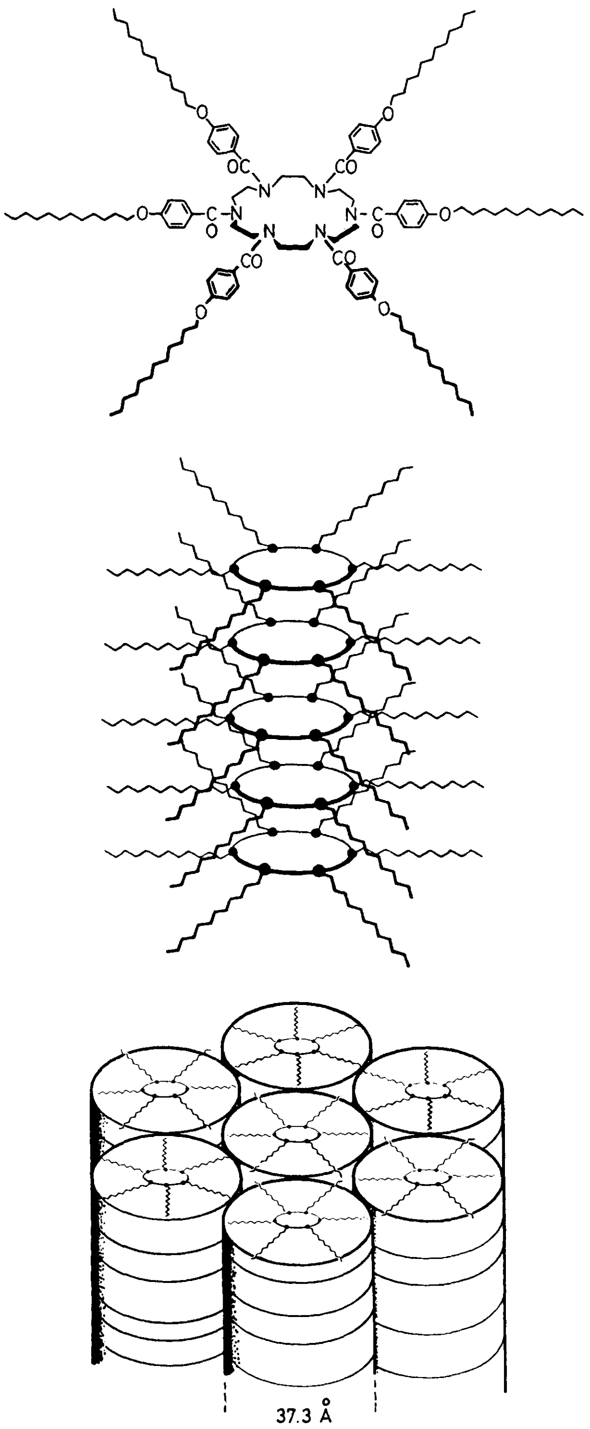

Figure 2. Structure of the mesogenic macrocyclic molecule (**1b**) (top); schematic representation of the stacking of macrocycles in the mesomorphic phase (middle, for clarity, the molecules are arbitrarily drawn with the same orientation); and of the tubular mesophase thus formed (bottom).

In view of the numerous macrocyclic molecules which may be obtained (including those which contain more rigid groups like α,α′-bipyridine or phenanthroline), a great variety of tubular mesophases may become available. Polymerisation of

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§ Optical observations of homeotropic droplets are indicative of an easy distortion of the structure in the plane parallel to the free surface (P. Oswald, personal communication).

such stacks might lead to extended molecular channels. Finally, the combination of the complexation properties of macrocyclic compounds with the supramolecular arrangements provided by the mesophases may open ways to the design of functional polymolecular devices.

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