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## Liquid Crystals

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### Substituted tetrabenzocyclophanes as mesogenic units of new polycondensates exhibiting columnar mesophases

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## Substituted tetrabenzocyclophanes as mesogenic units of new polycondensates exhibiting columnar mesophases

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Recently a new family of flexible mesogens has been described namely hexa-alkylated derivatives of cyclotetrameratrylene. We have functionalized these compounds, obtaining monofunctionalized and bifunctionalized derivatives with heptyloxy side groups. A model dimer and polycondensates were synthesized. Calorimetric data as well as optical data prove that they exhibit columnar mesophases. At this point it is not clear whether the conformation of the mesogenic units in the mesophase is tetragonal pyramidal with all of the mesogens being extended in one direction or discotic because of the high internal flexibility of the mesogenic core. The synthesis of the model dimer and the polycondensates as well as the calorimetric and optical data are the subject of this article.

### 1. Introduction

A few years ago a new family of mesogens was derived from cyclotrimeratrylene. These compounds consist of a rigid pyramid-like core with laterally bound side groups (see figure 1) [1, 2, 3, 4]. Several series of compounds exhibiting mesophases were described; for example one with alkoxy side groups and one with alkanoyloxy side groups. Recently it was shown that derivatives of cyclotetrameratrylene with these two types of side groups also exhibit mesophases [5]. Substitution by eight lyotropic side groups leads to both thermotropic and lyotropic mesophases [6]. Unlike the rigid structure of cyclotrimeratrylene the central core of cyclotetrameratrylene is highly flexible and interconverts rapidly between two sofa forms [7]. Although pyramid-like structures seem to be possible, the highly flexible core may result in behaviour more like that of a disc shaped mesogen. The large number of internal degrees of freedom and the considerable variety of possible side groups may facilitate their incorporation into polymers.

We have succeeded in functionalizing these flexible mesogens and have used these derivatives to synthesize a model dimer as well as polycondensates, having heptyloxy side groups; the compounds synthesized are listed in table 1. The synthesis as well as the calorimetric and optical properties of the mesophases are the subject of this paper.

### 2. Experimental part

#### 2.1. Synthesis

Acid catalyzed condensation of 3,4-dimethoxybenzylalcohol leads to the formation of *octamethoxytetrabenzocyclododecatetraene 1* [7]. 3 g of 1 were dissolved in

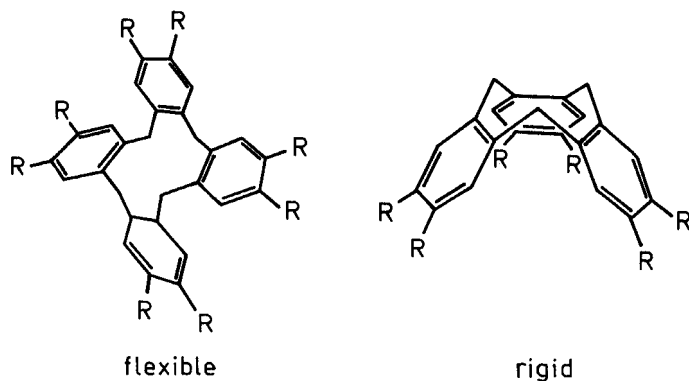
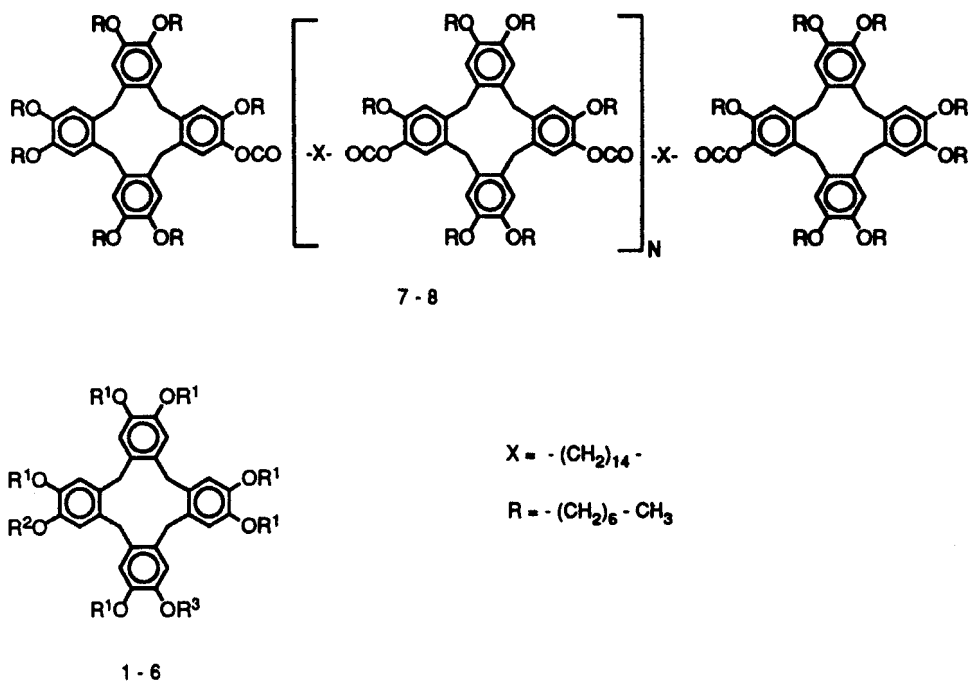


Figure 1. Molecular structures of substituted cyclotetraeratrlylene (left) and cyclotrimeratrlylene (right).

Table 1. Molecular structures and weight-average molecular weights of the compounds 1–8. studied. The structure of compound 6 is not unambiguous because the synthesis results in a mixture of three isomers.



System	<sup>1</sup> R	<sup>2</sup> R	<sup>3</sup> R	N	$\overline{M}_w/\text{g mol}^{-1}$
1	-CH <sub>3</sub>	-CH <sub>3</sub>	-CH <sub>3</sub>		
2	-H	-H	-H		
3	-CO-CH <sub>3</sub>	-CO-CH <sub>3</sub>	-CO-CH <sub>3</sub>		
4	$-(\text{CH}_2)_6-\text{CH}_3$	$-(\text{CH}_2)_6-\text{CH}_3$	$-(\text{CH}_2)_6-\text{CH}_3$		
5	$-(\text{CH}_2)_6-\text{CH}_3$	$-(\text{CH}_2)_6-\text{CH}_3$	-CO-CH <sub>3</sub>		
6	$-(\text{CH}_2)_6-\text{CH}_3$	CO-CH <sub>3</sub>	-CO-CH <sub>3</sub>		
7				0	
8a				10	15000
8b				32	44000

dichloromethane. An equimolar amount per methoxy unit of boron tribromide in dichloromethane was added dropwise at room temperature. After evaporating the dichloromethane, the residue containing the octahydroxyderivative 2 was treated with acetic anhydride and one drop of concentrated sulphuric acid. The reaction mixture was poured over ice (500 g) and filtered. The residue was washed with water and then recrystallized from nitromethane/ethanol, giving the *octaacetoxytetrabenzocyclo-dodecatetraene* 3 in an 80 per cent yield. Alkylation of 3 in an isobutylmethylketone/potassium carbonate mixture was done at 390 K with 10 per cent more than eight equivalents of the alkylbromide. The reaction was monitored via thin layer chromatography and stopped after 24–26 h to give the functionalized ether mixture 4–6. The separation of this mixture was done by middle pressure liquid chromatography, using a 2:1 mixture of dichloromethane/cyclohexane as a solvent.

The *model-dimer* 7 was prepared by an acid catalyzed esterification of the heptaheptyloxyderivative 5 with 1,16-hexadecadecarboxylic-acid under melt condensation conditions. The *polycondensates* 8a,b were obtained by acid-catalyzed melt polycondensation of the bifunctionalized hexaheptyloxyderivative 6 with 1,16 hexadecadecarboxylic acid. Toluenesulphonic acid was added to all of the condensation-reactions as a catalyst.

## 2.2. Characterization

All of the compounds were characterized by  $^1\text{H}$  N.M.R. and  $^{13}\text{C}$  N.M.R. The molecular weights of the polycondensates were estimated using gel permeation chromatography, with polystyrene as a reference, and  $^1\text{H}$  N.M.R. end group determination. Both techniques gave similar results.

## 2.3. Differential scanning calorimetry

The transition temperatures and transition enthalpies were measured on a Mettler D.S.C. 30. A heating rate of 5 K/min was used.

## 2.4. Optical microscopy

The textures were studied using a Leitz microscope equipped with a Mettler FP52 hot stage. Thin samples were examined between two untreated cover slips. The samples were first heated to the isotropic phase. Slow cooling with cooling rates from 1–10 K/h resulted in the textures shown in figure 3.

# 3. Results and discussion

## 3.1. Differential scanning calorimetry

The results obtained by D.S.C. measurements are presented in table 2. The phase transitions from the mesophase to the isotropic liquid ( $T_i$ ) do not undergo significant supercooling as is typical for this kind of transition. The transition enthalpies  $\Delta H_i$  range from 12.9 J/g up to 18.0 J/g. This is typical of highly ordered discotic mesophases of the  $D_h$  type. In order to facilitate comparison between the different systems we also give the transition entropies per mole disc unit,  $\Delta S_m$  disc. It is highest for the symmetric monomer 4 and decreases significantly on functionalizing with acetoxy-groups, compounds 5 and 6. In the dimer 7,  $\Delta S_m$  disc is almost as high as in the symmetric monomer and decreases only slightly on polymerization.

Looking at the monomeric precursors, the octaheptyloxyderivative 4 which is completely alkylated, shows a mesophase over a temperature interval of 28 K,

Table 2. Phase transition temperatures and enthalpies of transitions for compounds 4–8.

Compound	$T_m$ or $T_g$ /K	$T_i$ /K	$\Delta H_i/\text{J g}^{-1}$	$\Delta S_m \text{ disc}/\text{J mol}^{-1}$
4	403	431	18.0	53.1
5	406	435	13.5	37.5
6	395	434	12.9	33.9
7	400g	452	16.1	46.2
8a	343g	460	14.2	40.9
8b	343g	459	13.9	40.2

functionalization increases the width of the mesophase slightly. The derivative 5 having one acetoxygroup and seven heptyloxygroups, exhibits a mesophase over 29 K and the derivative 6 having two acetoxygroups and six heptyloxygroups has a 39 K mesophase range.

For the compounds with higher molecular weights, there is an increase in the transition temperature  $T_i$ . The monomeric precursors 4–6 show a liquid crystalline to liquid transition at about 430 K, while for the model-dimer 7 it increases to 452 K and for the main chain polycondensates the transition occurs at about 460 K. The glass-transition-temperature  $T_g$  of the polycondensates 8a,b, which corresponds to the temperature of mesophase formation, is lower than the melting temperatures of the low molecular weight compounds 4–6. Consequently the mesophase range increases with molecular weight, from 39 K for the monomeric bifunctionalized compound 6 to 52 K for the model-dimer 7, and about 115 K for the polymers 8a,b, as shown in figure 2.

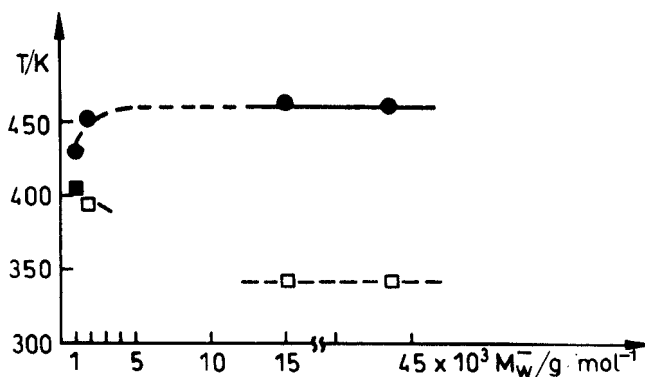


Figure 2. Transition temperatures of compounds 4–8 as a function of their weight-average molecular weights (see table 2). ● =  $T_i$ ; ■ =  $T_m$ ; □ =  $T_g$ .

As observed previously for similar compounds having substituted triphenylenes as discotic mesogens [9, 10] the dimer can serve as a model for the corresponding main chain polymers. It has the advantage of being a well defined compound and the considerably lower viscosity makes textural studies much easier. Upon cooling it does not crystallize but forms a glass. Thus the molecular order generated in the liquid-crystalline mesophase can be frozen in permanently [8]. As opposed to the monomeric compounds,  $T_i$  for the model dimer is comparable to that for the polycondensates, as evident from the molecular weight dependence for the transition temperature plotted in figure 2.

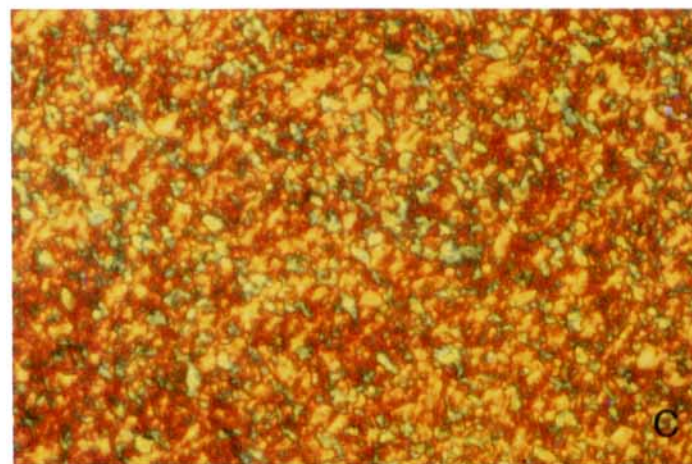
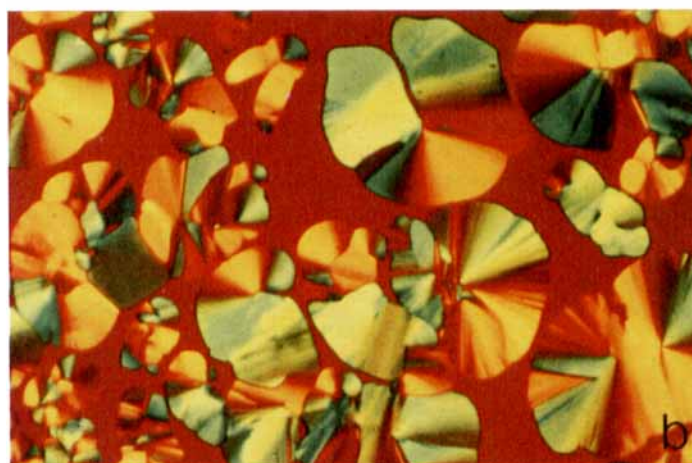
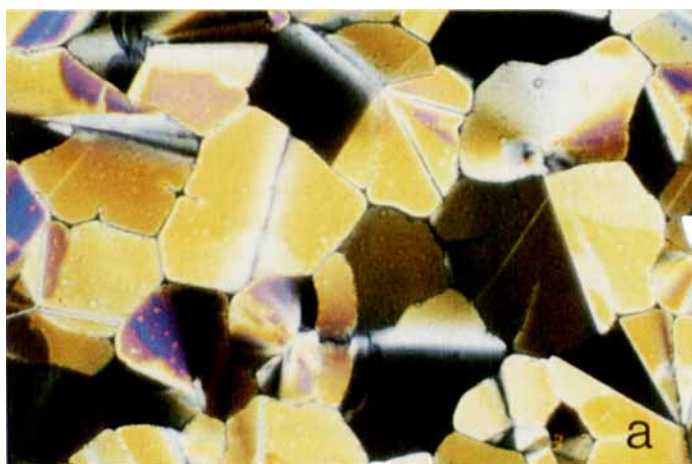


Figure 3. Optical textures of the monomeric compound 6 (a), the model dimer 7 (b) and the polycondensate 8b (c). The magnification is the same in all three cases.

### 3.2. Optical microscopy

In figure 3 the textures of the bifunctionalized monomeric compound 6 (figure 3(a)), the model dimer 7 (figure 3(b)) and the polycondensate 8b (figure 3(c)) are shown. The monomeric precursor 6 exhibits mesophase textures typical of highly ordered columnar mesophases. Upon slow cooling from the isotropic liquid, defect axes appear and then grow spherulitic-like contours. The size of the contours is dependent on the cooling rate, a lower cooling rate results in larger optical structures. The model dimer 7 shown in figure 3(b) exhibits a similar texture with smaller contours. The polycondensates 8a,b show textures in which the domain areas are much smaller, giving blurred contours. Even extremely slow cooling does not result in larger domain areas (see figure 3(c)).

### 4. Summary and conclusion

Using functionalized derivatives of octaheptyloxytetrabenzocyclododecatetraene, we have created a new family of polycondensates exhibiting columnar liquid-crystalline mesophases. A model dimer as well as polycondensates were synthesized. D.S.C. measurements and the textures observed under a polarizing microscope prove that these compounds possess columnar mesophases. At this point it is not clear, whether the conformation of the mesogenic units is tetragonal pyramidal with all mesogens being extended in one direction or discotic because of the high internal flexibility of the mesogens (see figure 4). Although rigid trigonal pyramids based on tribenzocyclophanes can be incorporated into dimers and polymers, we have not succeeded in obtaining liquid-crystalline phases from these polymers [9].

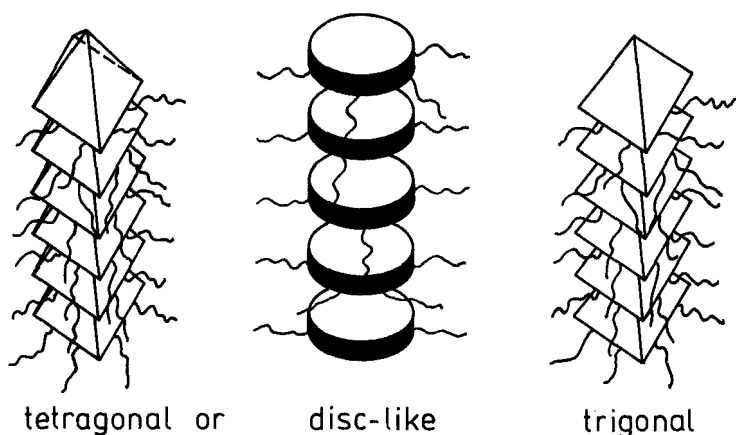


Figure 4. Different possibilities of columnar stacking of the cyclotetraveratrylene core (left) compared to the stacking of trigonal pyramids based on cyclotrimeratrylene (right).

Since thermal behaviour of dimer and polymer are similar and the space is adjusted in length to twice that of the side groups it is likely that even in the dimer the columns are interlinked. Thus the packing of the columns in the mesophases of both, the dimer and the polycondensates can be expected to be rather similar. More information about molecular order and dynamics of these new polymeric liquid crystals can be obtained from  $^2\text{H}$  N.M.R. and X-ray scattering. This work is in progress and will be published at a later date.

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