Pyramidic Mesophases

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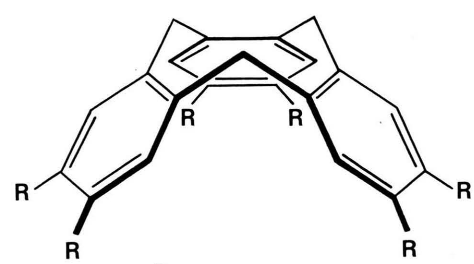
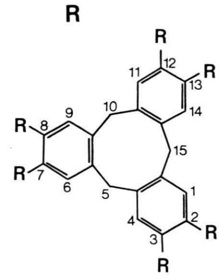
Two series of mesogenic compounds consisting of a rigid pyramidal central core and six equal flexible side chains were synthesized and their mesomorphic properties studied by calorimetry and optical microscopy. The two series of compounds are: I-hexaalkyloxytribenzocyclononene and II-hexaalkanoyloxytribenzocyclononene. In series I, enantiotropic mesophases appear for homologues in which the number, *n*, of carbon atoms in each side chain is equal or larger than six, while for series II mesomorphism is exhibited for all the compounds studied (8–15). Some of these exhibit dimorphism (i.e. I-11 and II-12 to II-14) and even trimorphism (II-11). In total five different mesophases are identified in both series. Several of these are stable at room temperature. Optical measurements indicate that they are not layered, they appear to be columnar. Due to the pyramidal shape of the central core of the constituent molecules special molecular arrangements for these mesophases are possible. It is suggested to call them pyramidic mesophases.

Introduction

The structure and properties of thermotropic mesophases depend on the geometry and chemical nature of their constituent molecules. Thus calamitic liquid crystals (nematic and smectic phases) consist of elongated, usually flexible, molecules; plastic crystals consist of globular molecules, and discotic liquid crystals are formed by flat, disc-like molecules [1–4]. In the present paper we report on the mesophases formed by yet another type of molecular architecture, namely of molecules consisting of a rigid central core with pyramidal symmetry to which long side chains are symmetrically bound at the pyramid base. The compound chosen consists of hexasubstituted tribenzocyclononene (2,3,7,8,12,13-hexasubstituted-5,10,15-dihydrotribenzo[a,d,g]cyclononene).





$\mathbf{I}$ = R = C_nH_{2n+1}–O–

$\mathbf{II}$ = R = $C_{n-1}H_{2n-1}$–C(O)O–

A = R = –OH

B = R = –OCH_3

As may be seen from the structural formula, the central core of these series consist of a rigid crown structure with a trigonal pyramidal symmetry in which the three benzene rings form the three sides of the pyramid while the three methylene groups point towards its apex [5–8]. The molecular structure is thus reminiscent of conventional discogenic compounds [1–4, 9–11] except that their central core is no flat. As a result of this structure, symmetrically substituted homologues will in general possess a net electric dipole moment along the C_3

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symmetry axis of the molecule. This may have important consequences regarding the nature of the molecular packing and other physical properties of the mesophases formed by such compounds.

In analogy with the conventional discogenic compounds we therefore expected that tribenzocyclononenes hexasubstituted with sufficiently long side chains will exhibit such special mesophases. This was indeed the case for the two series, hexaalkyloxytribenzocyclononene (I-n) with $R = C_nH_{2n+1}O-$, and hexaalkanoyloxytribenzocyclononene (II-n) with $R = C_{n-1}H_{2n-1}C(O)-O-$ (in this notation n represents the total number of carbon atoms in the unbranched side chains). In both series of compounds it was found that when the length of the side chains becomes sufficiently long, melting of the solid results in one or several mesophases. In the present paper we report on the preparation of these compounds and on some preliminary observations performed on their mesophases.

Other homologues of tribenzocyclononene derivatives have been known to form special types of complexes and inclusion compounds [12], and have been suggested as solubilizing agents.

Experimental

A) Synthesis

The starting compounds for the synthesis of both the hexaalkyloxy- and hexaalkanoyloxytribenzocyclononenes (I-n and II-n respectively) is the hexahydroxytribenzocyclononene (A). This compound is obtained by hydrolysis of hexamethoxytribenzocyclononene (B), also known as cycloveratrylene [13–17]. The hydrolysis is effected using BBr_3 in benzene followed by recrystallization from water/EtOH to yield colorless crystals of A. Cycloveratrylene (B) is obtained by reacting formaldehyde and veratrol (1,2-dimethoxybenzene) in the presence of a strong acid.

The hexaalkyloxytribenzocyclononene homologues I-n were obtained by alkylation of A with the corresponding n-alkylbromide in EtOH with K_2CO_3 as the base.

Example I-6:

0,5 gr A dissolved in 95% EtOH (50 ml) was refluxed for 30′ with K_2CO_3 (6 gr). n-Hexylbromide (6 gr) in DMF (20 ml) was added and the mixture was stirred and refluxed for 24 hrs. After hot filtration the solution was evaporated under diminished pressure. The resulting product was purified on Silica-gel with $CHCl_3/n$-hexane as eluents.

Yield: 0.9 gr (74%) 2,3,7,8,12,13-hexahexyloxy-5,10,15-trihydro-tribenzo-[a,d,g]-cyclononene (I-6). The ^{1}H-NMR spectrum (270 MH$_z$, $CDCl_3$/TMS) shows the rigid crown-conformation with three exactly equivalent pairs of axial and equatorial hydrogens and a single aromatic resonance, due to equivalency of the aromatic hydrogens.

0.89 ppm (t; $J = 6.8$ Hz; 18H$-\underline{CH_3}$), 1.1–1.6 ppm m; 36H$-CH_2-\underline{CH_2}-\underline{CH_2}-CH_3$), 1.60–1.80 ppm (m; 12H$-O-CH_2-\underline{CH_2}$), 3.49 ppm (d; $J = 14.7$ Hz, Ar$-\underline{CH_2}-$Ar equ.) 3.85–4.0 ppm (m; 12H, $-O-\underline{CH_2}$), 4.70 ppm (d; $J = 14.7$ Hz Ar$-\underline{CH_2}-$ax$-$Ar), 6.82 (S; 12H H$_{arom}$).

$C_{57}H_{90}O_6$: MW = 871.34 Mass-spectrum $M^{\oplus} = 870$
calcul. $C = 78.57\%$ $H = 10.41\%$
found $C = 78.83\%$ $H = 10.61\%$

TLC: Silica-gel F-254 $CDCl_3/n$-hexane: one spot.

The hexaalkanoyloxytribenzocyclononene homologues II-n were obtained either by reacting A with the corresponding acid-chloride under reflux or by reaction in pyridine.

Example II-13:

1 g A and 25 ml n-tridecanoylchloride were heated up to 185 °C while stirring. The excess acid-chloride was removed by vacuum-destillation and the residue was recrystallized twice from EtOH. Subsequent column chromatography on silica-gel using CH_2Cl_2 as eluent yielded 2.5 g (58%) of 2,3,7,8,12,13-hexatridecanoyloxy-5,10,15-trihydro-tribenzo-[a,d,g]-cyclononene (II-13).

$C_{99}H_{162}O_{12} = 1544.37$
calcul. $C = 76.99\%$ $H = 10.57\%$
found $C = 77.20\%$ $H = 10.84\%$.

Example II-15:

0.5 g A was dissolved in 46 ml dry pyridine. While the temperature was kept at 0 °C, pentadecanoylchloride (8.2 g) was added and stirring was continued for 24 hours at 0 °C. After hydrolysis in an excess of diluted HCl, the precipitated solid was filtrated, recrystallized twice from EtOH and purified by column chromatography. Yield = 1.6 g (67%) II-15.

$C_{111}H_{186}O_{12}$ = 1712.70
calcul. $C = 77.84\%$ $H = 10.94\%$
found $C = 77.91\%$ $H = 10.90\%$.

All the compounds I-*n* and II-*n* have been checked by TLC, NMR (270 MH_z) and combustion analysis and found to be of high purity. From the I-*n* homologues correct $M^{\oplus}$ are obtained. The I-*n* and II-*n* compounds are colorless substances. They are stable in air in the temperature range studied, and gave reproducible transition temperatures on repeated measurements.

B) Differential scanning calorimetry (DSC)

Transition temperatures and transition enthalpies were measured using a Mettler T.A. 3000 differential scanning calorimeter. The results are reported for increasing temperatures (0.2 to 5 °C/min).

C) Optical microscopy

The textures as well as the miscibilities of some binary systems were studied using a Leitz polarizing microscope equipped with a Mettler FP 52 hot stage. Binary phase diagrams were constructed by observation of contact preparations [18] and the solubilities calculated using the Le Chatelier-Schröder relation [19].

Table 1. Transition temperatures (in degrees centrigrade) and enthalpies (in kJ/mole) for the hexaalkyloxytribenzocyclononenes ($R = C_nH_{2n+1}O-$) studied in the present work[a].

n	K_1	K_2	P_B	P_A	L
1	•			232	•
4	•			135.6 (22.1)	•
				[• 127]	
5[b]	• 68.4 (21.7)	•		103.8 (16.0)	•
				[• 96.0]	•
6	• 40.9 (15.7)			• 92.2 (14.4)	•
7	• 25.0 (21.1)			• 79.9 (9.3)	•
8	• 24.9 (24.8)			• 71.5 (6.9)	•
9	• 18.7 (28.6)			• 66.1 (6.9)	•
10	• 25.5 (40.4)			• 63.2 (6.7)	•
11	• 34.8 (56.0)		• 44.2 (7.2)	• 62.0 (5.7)	•
12	• 48.3 (76.0)			• 61.6 (6.2)	•

[a] In the table *K* stands for crystal, *P* for mesophases and *L* for the isotropic liquid. The enthalpies are given in parentheses, and in square brackets are indicated virtual transition temperatures.
[b] This compound was deuterated in the methylene sites of the cyclononene ring (positions 5, 10 and 15 in the structural formula).

Results and Interpretation

The list of compounds studied from series I and II and their transition temperatures and enthalpies as determined by DSC are summarized in Tables 1 and 2 and are also shown in a diagramatic form in Figs. 1 and 2. Microscopic observations and misci-

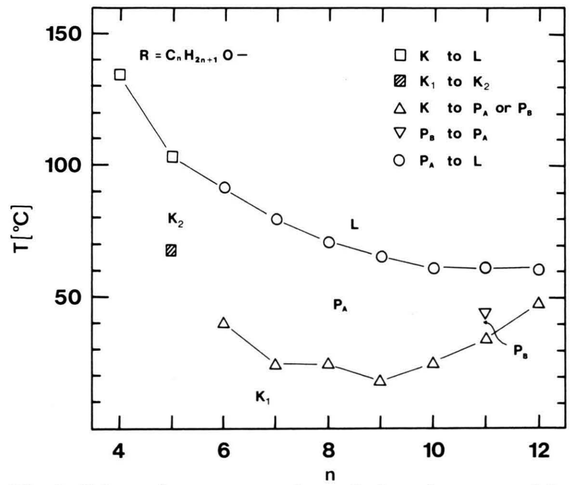


Fig. 1. Schematic representation of the phase transition temperatures of the hexaalkyloxytribenzocyclononene, I-*n*, homologues.

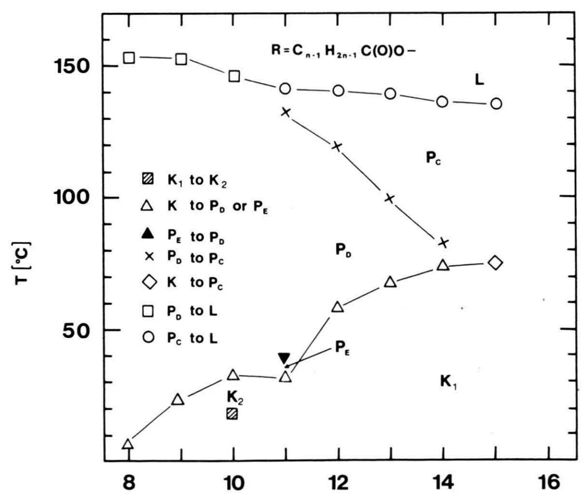


Fig. 2. Same as Fig. 1 for the hexaalkanoyloxytribenzocyclononene, II-*n*, homologues.

Table 2. Transition temperatures (in degrees centigrade) and enthalpies (in kJ/mole) for the hexaalkanoyloxytribenzocyclononene homologues studied in the present work[a].

n	K_1	K_2	P_E	P_D	P_C	L
8	• 5.2 (16.1)			• 153.1 (31.0)		•
9	• 23.9 (28.2)			• 152.6 (30.2)		•
10	• 18.2 (22.1)	• 32.7 (14.8)		• 146.2 (29.2)		•
11	• 31.5 (22.0)		• 38.6 (17.3)	• 131.6 (3.7)	• 140.8 (18.8)	•
12	• 58.1 (48.4)			• 118.8 (3.1)	• 140.6 (20.2)	•
13	• 67.4 (67.0)			• 99.5 (2.3)	• 139.2 (20.9)	•
14	• 73.4 (81.0)			• 81.4 (1.4)	• 136.2 (18.5)	•
15	• 80.5 (118.4)				• 134.6 (19.1)	•

[a] The notation is the same as in Table 1.

bility experiments were made on the various mesogens of these two series and the results are described in the following sections in some detail.

A) The hexaalkyloxytribenzocyclononene series (I-n)

Upon increasing the length of the side chains in this series of compounds the normal melting temperature of the solid gradually decreases until at $n = 6$ it has reduced sufficiently to allow the formation of a mesophase. Compound I-5 does not possess an enantiotropic mesophase but it exhibits two different crystalline phases (see Plate 1) labeled K_1 and K_2 in Table 1 and in Figure 1. Each of the I-6 to I-12 homologues exhibits a thermodynamically stable mesophase. Optical microscopy observation of the melting solids show disordered birefringent patterns which disappear upon further heating to the isotropic liquid. On very slow cooling of these liquids they undergo strong supercooling and eventually exhibit birefringent patterns with nonuniform extinction as shown in Plate 2. Further cooling results in packed areas with irregularly curved boundaries (Plate 3), exhibiting defects with rectilinear axes similar to those occuring in columnar discotic mesophases [1, 20]. If these samples are observed with polarized light but with the analyzer removed, the rectilinear axes are not visible when the electric field vector of the light is parallel to the defect axis. Areas with defect axes oriented in different directions, observed between crossed polarizers and with an auxiliary wave plate, appear blue in the quadrants parallel to the slow neutral line of the wave plate and red in the two other quadrants. Thus the sign of the optical anisotropy of these mesophases is negative [21]. By pressing the cover slip numerous defects appear with locally parallel orientation, which persist for a very long period of time due to the high viscosity of the mesophase.

One often observes dark areas between crossed polarizers which are not changed by rotation of the microscope stage. These domains must therefore correspond to normally oriented areas indicating that the mesophases of I-n are uniaxial. On the other hand the boundaries of these domains usually exhibit finger-like contours suggesting that the symmetry axis of the phase is of finite order.

Near rectilinear axes the neutral lines are either parallel or perpendicular to the defect axes. Thus the optical axes are everywhere perpendicular to the defect axes, and the normal surfaces (surfaces which at each point are perpendicular to the optical axes [22]) constitute cylinders parallel to these lines. Without analyzer and by shifting the focus plane above a defect axis, the latter turns sombre indicating [22] that the optical axes are not radial but rather concentric around the defect axis as indicated in Figure 3. Isolated domains with only one defect axis exhibit uniform extinction, two plane surfaces perpendicular to this defect and lateral boundaries with finger-like profiles.

Droplets of mesophases with free surfaces obtained from the isotropic phase by slow cooling (say 1 °C/min) show near the boundaries birefringencies which increase continuously with the thickness and no Grandjean's terraces are observed. Similar observations were made on monotropic phases obtained at room temperature by evaporation of the solvent from benzene solutions.

When a crystalline sample is remelted the resulting mesophase exhibits pseudomorphosis of the crystal structure (see Plate 4). Crystalline prepara-

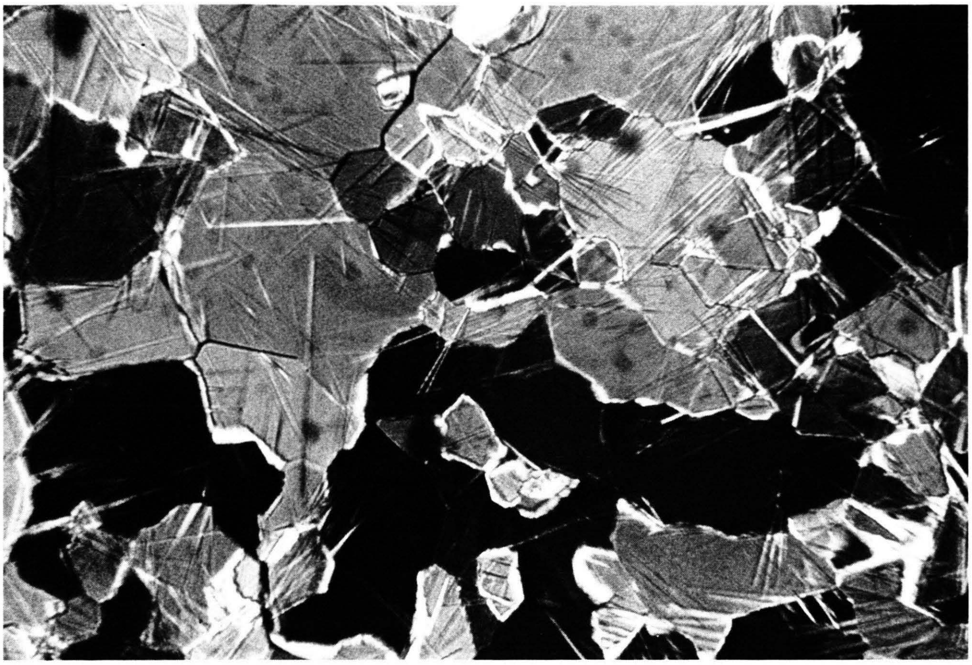
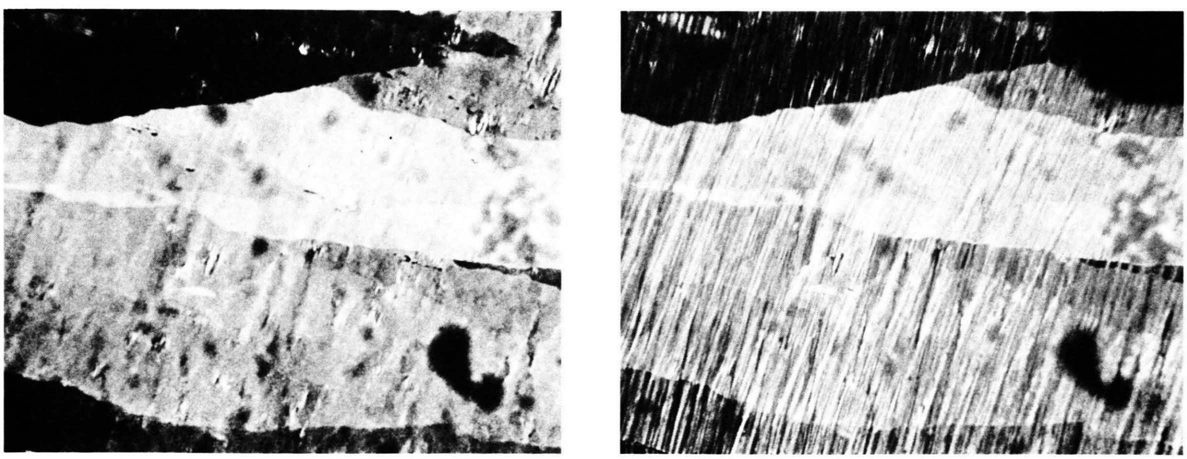


Plate 1. Crystalline polymorphism in I-5. The crystal phase K_1 (large domains) is transformed to the crystalline phase K_2 (needles) upon heating to above 68 °C (× 125).



a) **b)**

Plate 4. Pseudomorphism between the crystalline and P_A phases of I-6. Picture **a** is of the crystalline form at 30 °C. Picture **b** is of the mesophase at 81 °C (× 125).

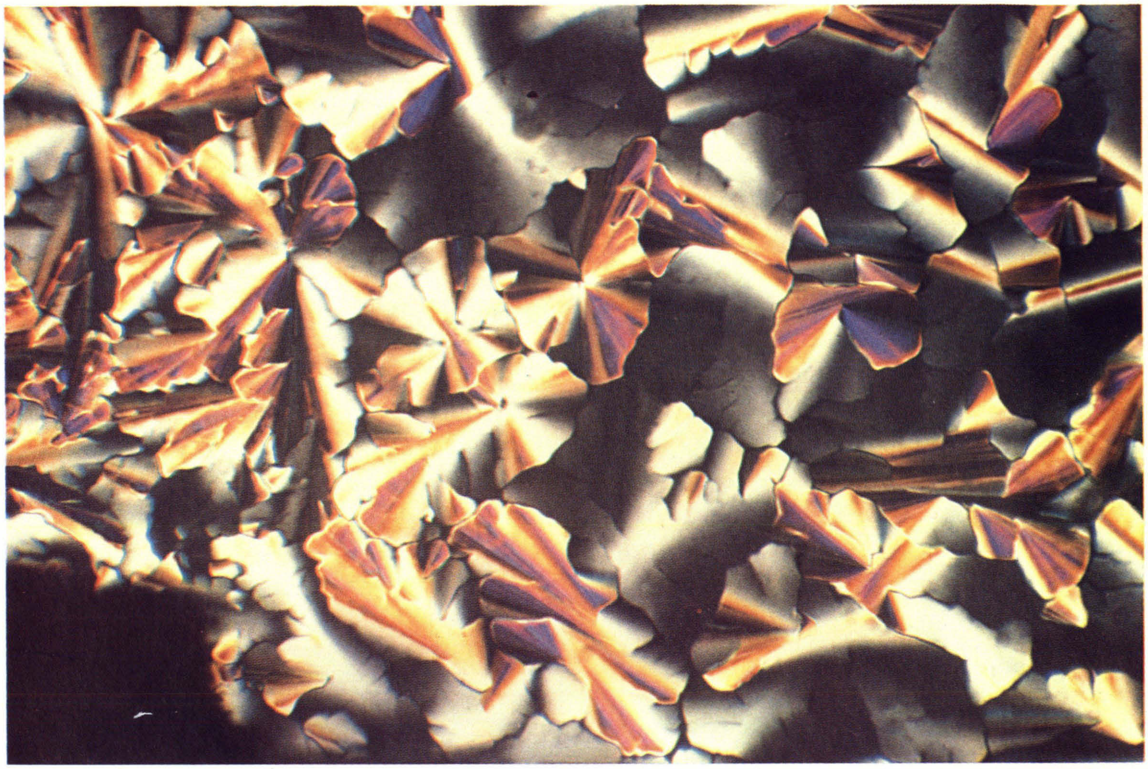


Plate 3. Same as in Plate 2 upon further cooling to 71 °C.

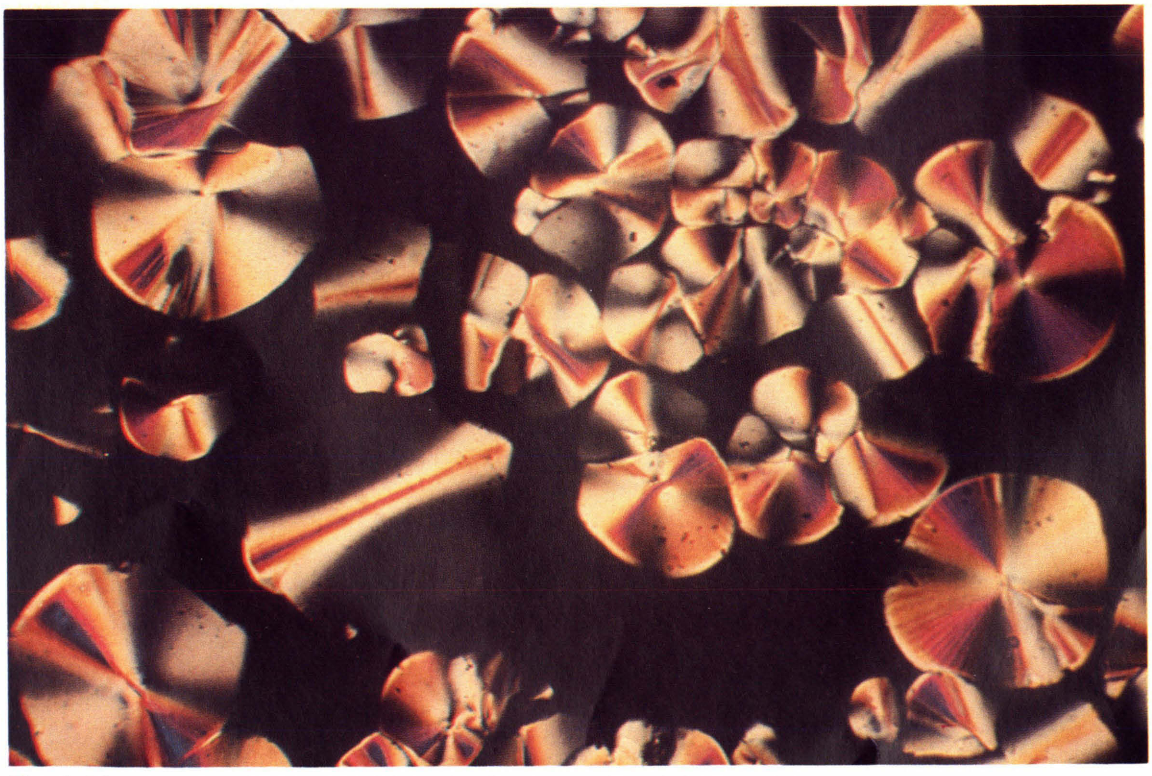


Plate 5. Mesophase P_C of II-13 at 138 °C obtained by slow cooling (0.2 °C/min) from the isotropic liquid (× 125).

Plate 2. The mesophase P_A of I-6 obtained on slow cooling (0.2 °C/min) from the isotropic liquid. Temp. = 82 °C (× 125).

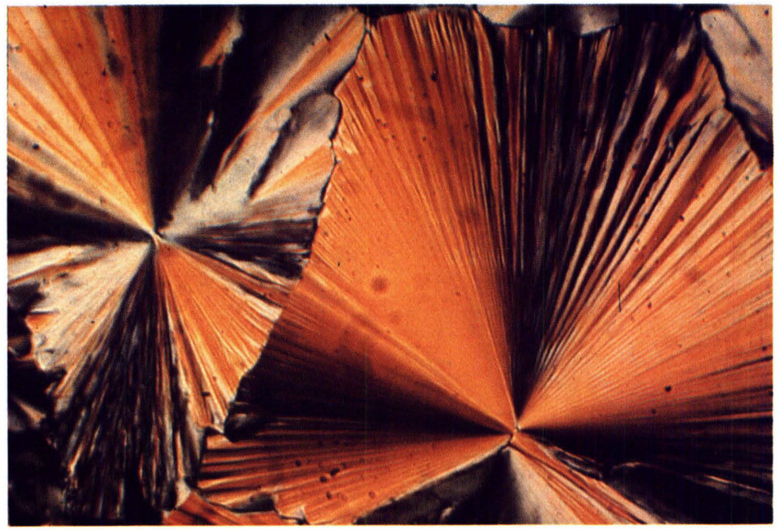


Plate 7. Mesophase P_D of II-13 at 75 °C obtained by cooling (3 °C/min) from the P_C phase shown in Plate 6 (× 125).

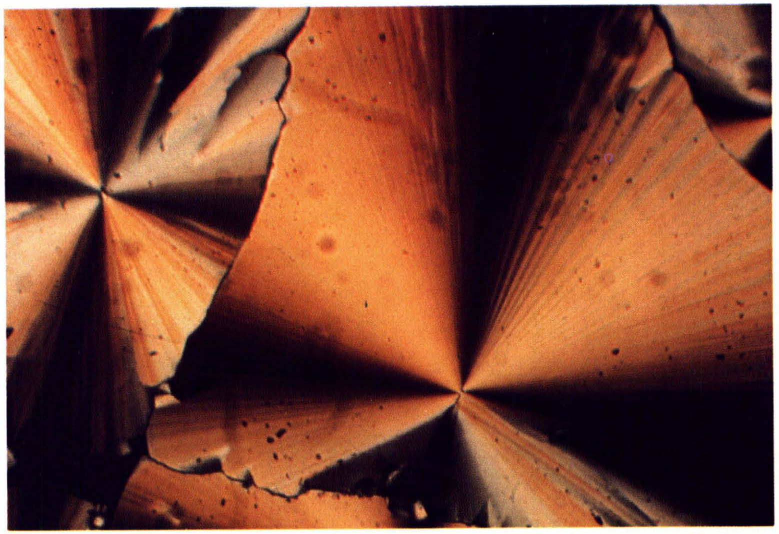


Plate 6. Mesophase P_C, as Plate 5 at 133 °C.

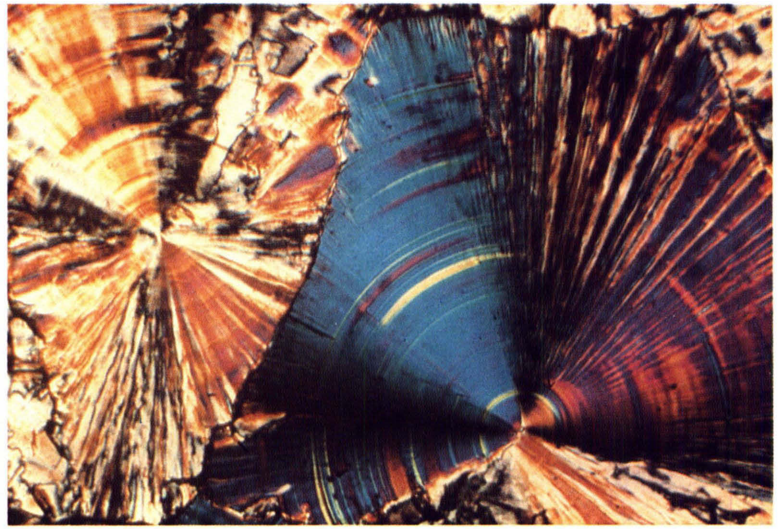


Plate 8. Concentric arcs in the crystalline phase of II-13 at 40 °C (× 125); same preparation for Plates 6, 7 and 8.

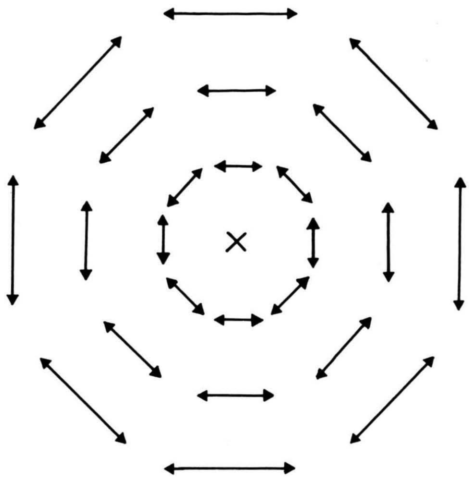


Fig. 3 Disposition of the optical axes (arrows) near a defect line in the mesophases P_A and P_D. The defect axis is perpendicular to the figure's plane and crosses it at the center.

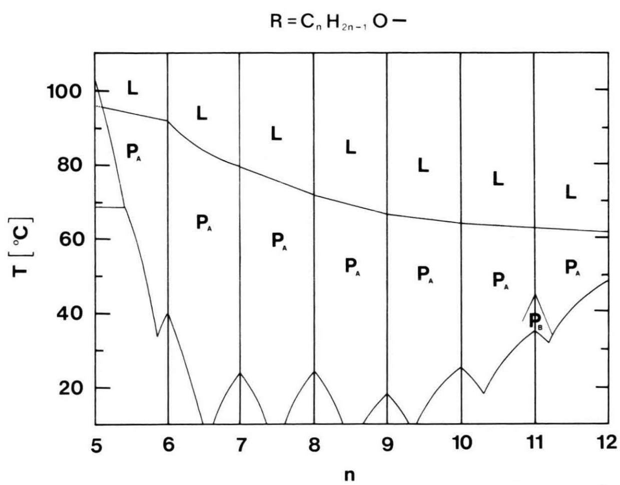


Fig. 4. Phase diagram of the binary mixtures of I-*n* and I-(*n* + 1) for *n* equal 5 to 11 of the hexaalkyloxytribenzocyclononene.

tions obtained by cooling often exhibit fissures, which on remelting get filled up, indicating that the molar volume change associated with melting is positive.

Miscibility measurements were made on binary mixtures of the I-*n* homologues and the results for neighboring members in the series are presented in Figure 4. These results show that the mesophases obtained on cooling from the isotropic liquid of all mesogenic compounds in this series are completely miscible and must therefore be the same. We call this mesophase P_A. Note that compound I-11 exhibits an additional mesophase (P_B) which does not occur in its neighboring homologues. Solid solutions are detected everywhere. The pure I-9 and some binary mixtures (Fig. 4) exhibit P_A stable at room temperature. Miscibility measurements of mixtures between enantiotropic mesogens and non-mesogenic homologues with not too different side chains (e.g. I-6 with I-5 and I-4) may provide information on the virtual clearing temperature of the latter compounds. The measurements on mixtures of I-6 and I-5 are included in Fig. 4, yielding a virtual $L - P_A$ transition temperature of 96 °C. A similar procedure applied to mixtures of I-6 and I-4 yield a virtual $L - P_A$ transition temperature of 127 °C for the latter. This result is, however, uncertain because the coexistance curve for the P_A and L phases in the I-6 and I-4 mixtures exhibits a pronounced minimum, making the extrapolation procedure unreliable. Mixtures of non-neighboring members of the I-*n* series also exhibit minima in their miscibility curves, e.g. I-10 with I-12 at 58 °C, and I-8 with I-12 at 40.1 °C. These results show that even for the mesogenic members of the series, when the side chains are not very similar their binary mixtures are not ideal [23, 24]. For that reason we were unable to obtain the virtual L-P_A transition temperatures for the lower members of the I-*n* series.

B) The hexaalkanoyloxytribenzocyclononene series (II-n)

We have performed similar optical microscopy and miscibility experiments on the homologues of the II-*n* series. Their transition temperatures and enthalpies are summarized in Table II and in Figure 2. Compounds II-8 and II-9 are highly viscous birefringent pastes at room temperature. Both these compounds as well as II-10 give on slow cooling from the isotropic liquid birefringend domains having mainly two rectilinear, parallel sides, and axicular extremities with uniform extinction between crossed polarizers. Sometimes the sides are curved and a neutral line appears which is everywhere parallel to these sides. No normally oriented areas have been observed, indicating that these mesophases (labeled as P_D in Fig. 2 and Table 2) are most probably biaxial. Rarely domains with rectilinear defect axes distributed radially, are observed. By pressing strongly the microscope cover slip the larger domains with uniform extinction split up into elongated smaller domains, with sharp extremities, slightly curved contours and small defects with rectilinear axes.

Compound II-10 shows fragile crystals at room temperature (20 °C). Therefore the first order transition observed by calorimetry at 18.2 °C is a solid-solid transition. Crystalline preparations of this compound are obtained from the mesophase after several days at room temperature. They exhibit fissures, which upon melting near 33 °C fill up indicating that the volume change associated with this transition is positive.

For compounds II-11 to II-15, slow cooling of the isotropic liquid gives, upon strong supercooling, birefringent patterns as shown in Plates 5 and 6. They exhibit defects with rectilinear axes similar to those observed in the phase P_A of series I-*n*. Normally oriented domains are also observed. Consequently this mesophase indicated by P_C in Fig. 2 and Table II is uniaxial with negative optical anisotropy. The optical axes seem to form concentric contours around the defect line (Figure 3). We have observed that isolated domains with only one defect axis exhibit uniform extinctions and often two parallel planes perpendicular to the defect axis. Occasionally one of these planes and one point and lateral surfaces with finger-like profiles are observed. Droplets of this mesophase with free surfaces obtained by slow cooling (1 °C/min) of the liquid exhibit near their boundaries birefringencies which increase continuously with the thickness but no Grandjean's terraces are observed.

For compounds II-11 to II-14 further cooling of the phase P_C results in considerable supercooling (relative to the transition temperatures given in Table II for heating), and in a transformation to a second mesophase (cf. Plates 6, 7 and 8) which was found to be identical to the mesophase P_D of compounds II-8 to II-10 . During the transformation normally oriented domains break up into separate domains with neutral lines inclined at 45° to each other and the limits between areas are more indented. Areas with defect axes in phase P_C exhibit in the P_D phase striations perpendicular to these axes which disappear upon reheating the sample, and normally oriented domains are reformed. These mesomorphic transitions are more clearly observed on free surface preparations.

Compound II-11 exhibits an additional phase, labeled P_E, which is stable between 31.5 and 38.6 °C. Experiments performed on this phase indicate that it is not crystalline but rather a mesophase. For example, pressing with a fine steel needle on preparation with a free surface, does not cause fracture of fissures but rather small craters, indicating that this phase can support considerable deformations when stresses are applied.

To compare the mesophases of the II-*n* series miscibility measurements, on binary mixtures were carried out. The results for neighboring members of the series are shown in Figure 5. It may be seen that compounds II-11 to II-15 all exhibit the same P_C phase, compounds II-11 to II-14 also have a lower P_D phase while II-11 is trimorphic and in addition exhibits the phase P_E. The P_D phase is also identified as the mesophase of compounds II-8 to II-10. Contact preparation of II-*n* with II-(*n* + 1) homologues show no minima for $n \gg 10$ indicating that these mixtures form ideal solutions in the *L* and P_C phases. However, minima are observed in mixtures of II-8 with II-9 and II-9 with II-10 indicating that these mixtures are not ideal. Pure II-8 and II-9 exhibit stable P_D mesophase at room temperature.

Miscibility studies were also made on binary mixtures of homologues from the I-*n* and II-*n* series. These studies show that the mesophases P_A and P_B identified in series I are apparently different from

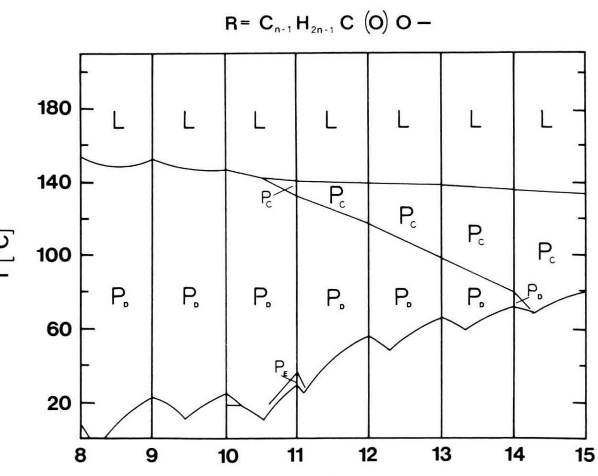


Fig. 5. Phase diagram of the binary mixtures of neighboring homologues of the hexaalkanoyloxytribenzocyclononene (II-*n*) series.

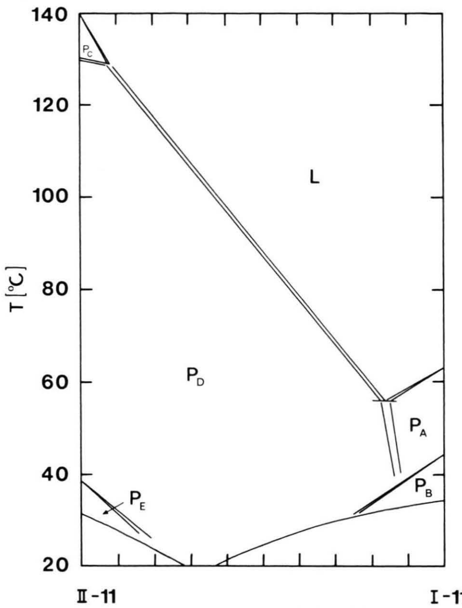


Fig. 6. The phase diagram of the binary mixture consisting of I-11 and II-11.

P_E, P_D and P_C of series II. As an example we reproduce in Fig. 6, the phase diagram of the mixture consisting of I-11 and II-11. Clearly neither P_A nor P_B mix with P_D. This diagram also shows that the sequence of phases, with increasing temperatures (from left to right) is

$$\begin{matrix} P_E & P_D & P_C \\ P_B & & P_A \end{matrix}$$

The relative order of P_E and P_B or P_C and P_A could, however, not be obtained due to the limited miscibilities in P_A and P_C states of compounds exhibiting the respective phases.

Finally we have also studied the miscibilities of compounds from series I and II with several discotic forming mesogens, in particular with members of the hexaalkyloxytriphenylene series [1–4, 9, 10]. These compounds have a molecular symmetry similar to that of the I and II series and the size of their central core matches the projection of the tribenzocyclononene moiety perpendicular to its threefold axis. However, in all these experiments no total miscibility in a mesomorphic state of the respective mesogens was found.

Summary and Discussion

Both homologous series of the tribenzocyclononene derivatives studied exhibit mesophases once the attached side chains are sufficiently long. Evidence has been presented for the existence of five new mesophases in these compounds. Their clearing enthalpies are generally large, so are the enthalpies for some of the interphase transitions, e.g. P_B to P_A and P_E to P_D, but the enthalpy changes associated with the P_D to P_C transitions are small. In some cases (e.g. II-8 to 10) the clearing enthalpies are larger than the melting enthalpies, as was also found in some discogens [25].

The mesophases P_A and P_C are optically uniaxial, while P_B and P_D are apparently biaxial. In the uniaxial phases strong anisotropy of interfacial tensions with the liquid occur as evidenced by the parallel plane faces in isolated domains of P_A and P_C. These mesophases exhibit rectilinear defects which are surrounded concentrically by the optical axes of the domains (see Figure 3). Since the circulation of $\boldsymbol{n}$ (the director) along a closed path surrounding the defect axis is non zero and we have

$$\nabla \times \boldsymbol{n} \neq 0 .$$

There can be two possible structures for such domains: non-layered, or layered with the director non-orthogonal to the layers [26]. However, the absence of Grandjean's terraces in droplets with free surfaces rules out the possibility of a layered structure for P_A and P_C. Although we do not yet have structural information from X-ray studies, it is natural to assume that these phases have columnar structures similar to those occuring in the conventional columnar discotics. The textural studies showed that the normal surfaces have single curvatures, so that if the molecules are indeed stacked into columns the distance between them remains unchanged upon bending.

Since the tribenzocyclononene core has a net electric dipole along its C_3 axis it is most likely that the stacking of the molecules in the columns is with their dipoles parallel to each other resulting in a net macroscopic electric dipole as indicated in Figure 7. We thus obtain a two-dimensional array of columns with dipoles pointing either up or down. This may result in paraelectric, ferroelectric or anti-ferroelectric mesophases, depending on the interaction nature between the columns. Energetically it would

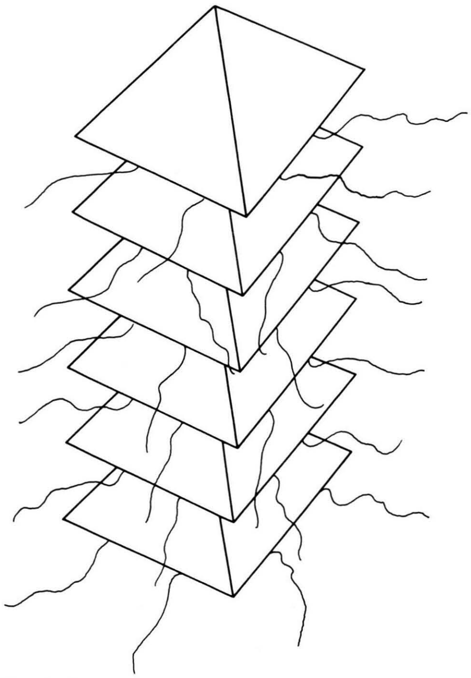


Fig. 7. Schematic model for the stacking of the substituted tribenzocyclononene molecules into columnar structures.

be more favourable for neighboring columns to have opposite direction (anti-ferroelectric), however this imposes restriction on the symmetry of the columnar array: As may be seen in Fig. 8, while both parallel and alternant directions are possible for tetragonal (and rectangular) arrays, only parallel arrangement (ferroelectric) is possible for the hexagonal array of columns. In this connection it is interesting to note that domains of P_D obtained from single domains of P_C exhibit neutral lines inclined at 45°, suggesting a tetragonal symmetry for the latter phase. It should also be emphasized that if the interactions between the molecules within the columns are sufficiently strong, the columns will retain the trigonal symmetry of the isolated molecules, and it would be impossible to construct mesophases with simple two or four fold symmetry axes.

Clearly more research into the structure and physical properties of these mesophases is needed, in particular X-ray measurements on the structure of the mesophases and studies of the effect of electric fields on the transformation between phases, relaxation dispersion in alternating fields etc.

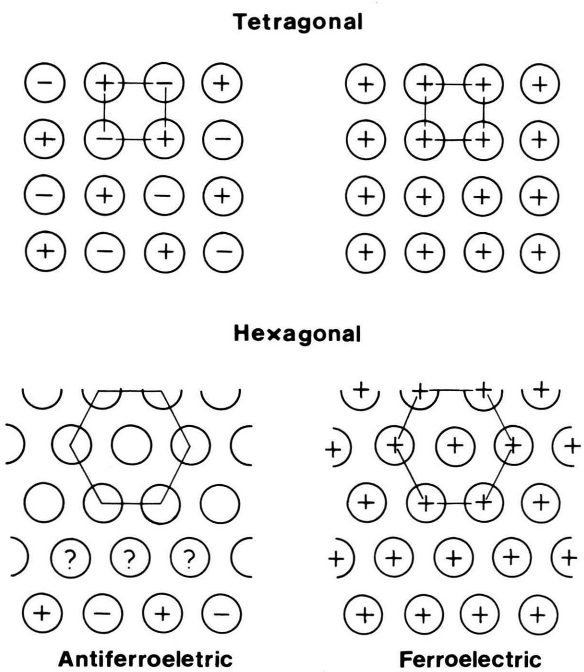


Fig. 8. Schematic representation of two dimensional arrays of polar columns in tetragonal and hexagonal lattices. + and − indicate the directions of the columnar dipoles.

Conclusions

The studies of the pyramidic derivatives of tribenzocyclononene resulted in the discovery of five new non-layered mesophases. It is anticipated that further work on similar compounds will reveal a new area of mesomorphic polymorphism.

Globular molecules can be assembled into plastic crystals, elongated molecules into calamitic (καλαμος-reed) mesophases; and disc-like molecules into discotic (δισκος-quoit) mesophases. In accordance with this tradition we propose to name these phases pyramidic (πυραμις-pyramid). We have surmised their existence before their observation.

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