Synthesis and investigations of new liquid-crystalline compounds by combination of the pyramidic tribenzocyclononene unit and calamitic structural units

Hansjörg Budig,[a] **Siegmar Diele,**[b] **Petra Göring,**[b] **Reinhard Paschke,**[a] **Christiane Sauer**[b] **and Carsten Tschierske** *,[a]
[a] *Institute of Organic Chemistry, Martin-Luther-University Halle, D-06015 Halle/Saale, Weinbergweg 16, Germany*
[b] *Institute of Physical Chemistry, Martin-Luther-University Halle, D-06099 Halle/Saale, Mühlpforte 1, Germany*

Novel liquid crystalline compounds, which consist of five or six calamitic 4-cyanobiphenyl, all-*trans*-bicyclohexyl or 2-alkyl-5-phenyl-1,3,4-thiadiazole units covalently linked by spacers of different length with a bowl-shaped central core (2,3,7,8,12,13-hexa-substituted 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene derivatives) have been synthesized and their phase behaviour was investigated by polarizing microscopy, differential scanning calorimetry and X-ray diffraction. Depending on the spacer length, these compounds exhibit either columnar or lamellar (smectic) mesophases. Some of the new compounds form stable monolayers at the air–water-interface. The force–area isotherms of the thiadiazole derivatives have been recorded and it was found that the films consist of densely packed phenylthiadiazole cores with the carboxylate groups at the tribenzocyclononene unit acting as hydrophilic groups.

It is well known that thermotropic liquid crystalline phases may be formed by rod-like as well as by disc-shaped molecules.[1,2] Thereby the molecular shape determines the kind of mesophase observed. Rod-like molecules give rise to nematic and/or smectic liquid crystalline phases whereas discotic and pyramidic[3–5] molecules self-organize to give discotic nematic phases and/or columnar mesophases. Polycatenar and board-like (sanidic) molecules have recently been designed to bridge the gap between these two different types of mesophases.[6,7] The covalent linkage of differently shaped molecules is an alternative way to create new supramolecular structures. We have found that compounds which consist of six bicyclohexyl or 2-phenyl-1,3,4-thiadiazole calamitic units covalently linked by spacers of different length with a bowl-shaped tribenzocyclononene central core (compounds **1** and **2**) can form either columnar or lamellar mesophases.[8]

In this paper we describe (*i*) the syntheses and detailed investigations of these compounds, (*ii*) new liquid crystalline tribenzocyclononene derivatives which combine the tribenzocyclononene core with the calamitic 4-cyanobiphenyl unit and (*iii*) asymmetric tribenzocyclononene derivatives.

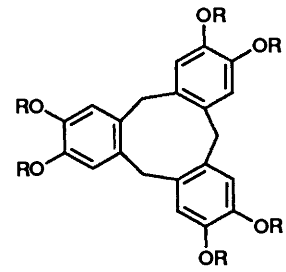
Results and discussion

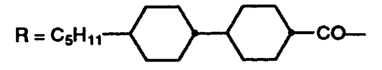
Synthesis

The synthesis of the symmetric compounds **1**, **2**, **9** and **10** was achieved by esterification of cyclotricatechylene (**8**) with appropriate carboxylic acids incorporating bicyclohexyl-, 4-cyanobiphenyl- or 2-phenylthiadiazole rigid cores as displayed in Scheme 1.

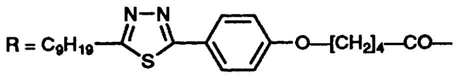
Compound **13** was obtained according to Scheme 2. Thereby 2,3,7,8,12,13-hexakis(10-ethoxycarbonylundecyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene[9] was reduced with lithium aluminium hydride to give the hexakis(11-hydroxyundecyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene **12** which afterwards was esterified with *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexanecarboxylic acid.

For the synthesis of the asymmetric compounds **16** and **17** (Scheme 3) a stepwise condensation procedure[10] was used to prepare 2-methyl-3,7,8,12,13-pentamethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene. The ether groups of this compound were cleaved with boron tribromide and the resulting 2-methyl-3,7,8,12,13-pentahydroxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene **15** was esterified as described above.





1

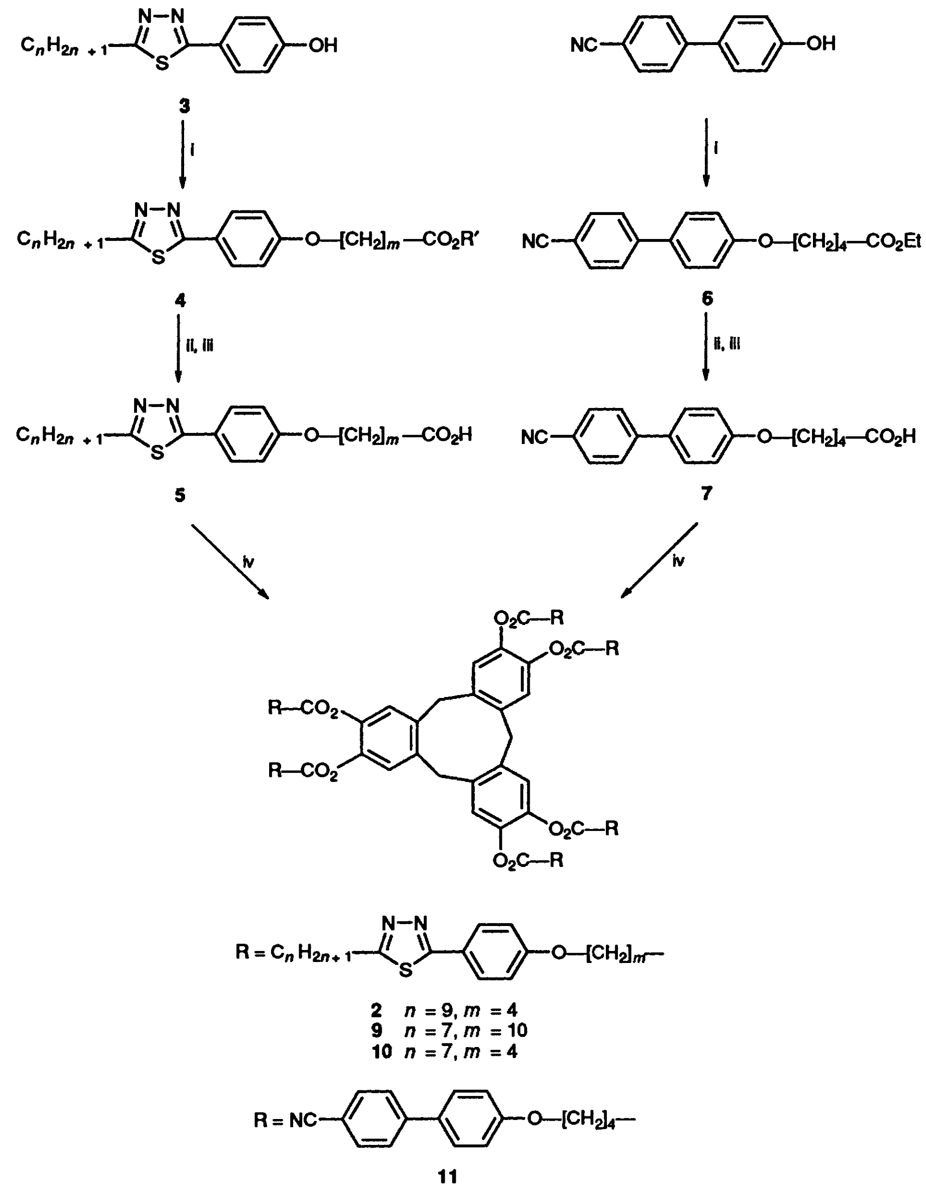


2

Mesomorphic properties

Symmetric tribenzocyclononene derivatives. In Table 1 the properties of the symmetric tribenzocyclononene derivatives **1**, **2**, **9–11** and **13** are summarized and compared with those of a simple hexakis(tridecanoate) **18**[3] and the *trans*-4-octylcyclohexylcarboxylate **19**.[11] The tridecanoate **18** as well as compounds **19** and **1** without a spacer have broad columnar mesomorphic ranges. This was confirmed by polarizing microscopy as well as by X-ray investigations.[8] If one compares compounds **18**, **19** and **1** it is obvious that the mesophase stability increases with increasing number of cyclohexane rings incorporated in the lateral chains. Obviously the stiffness of the side chains supports the stacking of the molecules in columns.

Contrary to this, compound **13** with the tribenzocyclononene

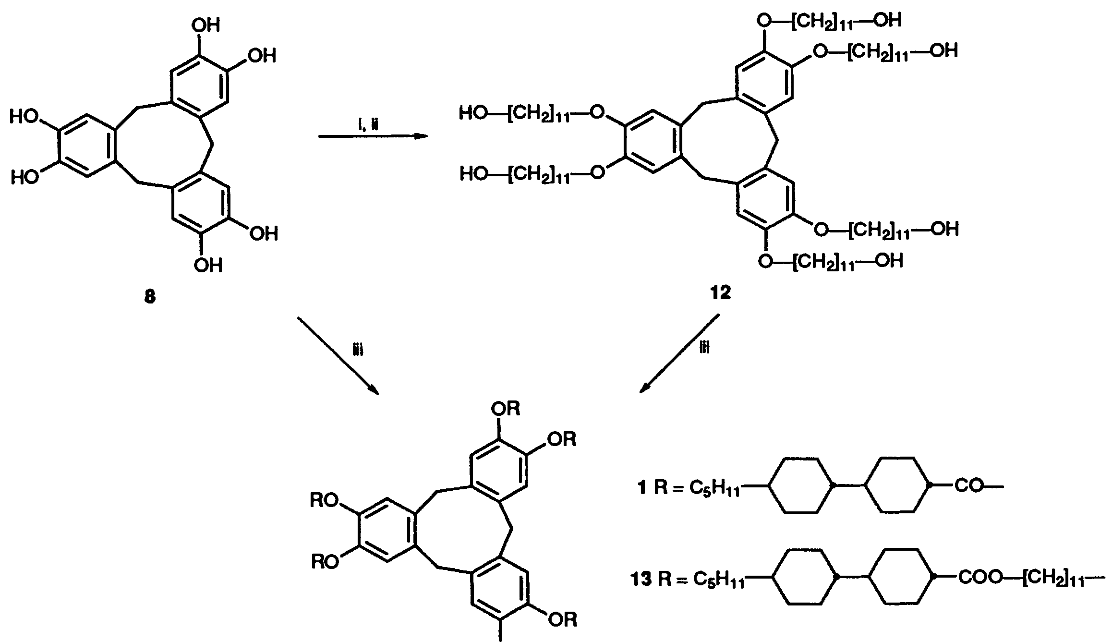


Scheme 1 Synthesis of the symmetric tribenzocyclononene derivatives **2**, **9**–**11**. *Reagents and conditions:* i, Br[CH$_2$]$_m$CO$_2$R′ (R′ = Me, Et), K$_2$CO$_3$, KI, EtCOMe; ii, KOH, MeOH, H$_2$O; iii, H$^+$; iv, compound **8** (see Scheme 2), C$_6$H$_{11}$–N=C=N–[CH$_2$]$_2$–N$^+$(Me)[CH$_2$]$_2$OCH$_2$CH$_2$ TsO$^-$, DMAP, CH$_2$Cl$_2$, DMF.

unit decoupled from the bicyclohexyl rigid core by an undecamethylene spacer is a crystalline solid without any mesophase. This is also true for the thiadiazole derivative **9**. Obviously, the mesomorphic properties are lost, if the rod-like units are decoupled from the central part by a long spacer.

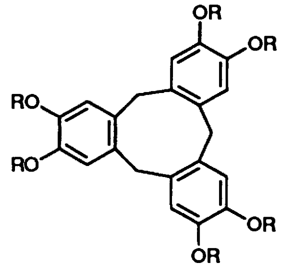
However, as proven by X-ray diffraction and polarizing microscopy compounds **2** and **10** with medium spacer lengths form a lamellar smectic phase. On cooling the isotropic liquid of compound **2** down to 160 °C, a rapid formation of batonnets can be observed. These coalesce to give a focal conic fan texture; a behaviour characteristic of a smectic A-type phase. At 134 °C crystallization occurs. These crystals melt at 152 °C. Unoriented samples of compound **2** were investigated using a Guinier X-ray goniometer. The diffraction was characteristic of an S$_A$ phase showing a sharp reflection corresponding to the interlayer spacing (d = 5.3 nm) and weak higher orders and a diffuse outer scattering corresponding to the 0.46 nm average separation in the plane. The dependence of the d-values on the temperature is given in Fig. 1. Oriented samples of this compound were obtained by applying a magnetic field or by drawing threads from the molten sample. In the pattern of the oriented samples the inner and outer rings shrink to crescent-like maxima oriented at right angles to each other. This proves the presence of an S$_A$ (rather than S$_C$) phase.

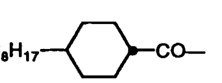
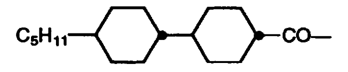
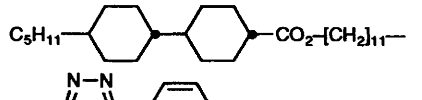
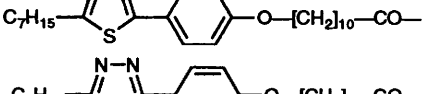
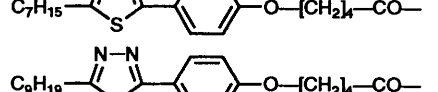
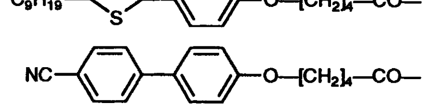
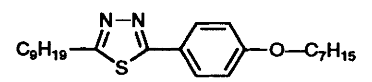
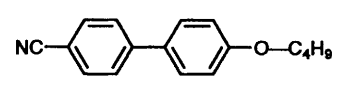
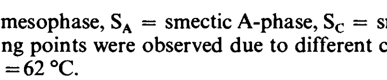
The texture of the mesophase of compound **10** is the same as that of compound **2**. The complete miscibility confirms that both are S$_A$-phases. This indicates that in these derivatives of tribenzocyclononene a columnar stacking of the molecules is not possible. The competition between the disc-like middle part of the molecule and the calamitic units is increased by the decoupling of both different structural elements. Now the calamitic units adapts a parallel packing, which leads to the lamellar self organization. At 140 °C a d-value of 5.3 nm was calculated for compound **2**. The layer period of the S$_A$-phase is significantly larger than the length of the single calamitic moieties. Using molecular modelling (CERIUS) and CPK-models two possible models could be proposed (Fig. 2). In the first one a parallel arrangement of all calamitic units directed in the same direction is assumed. The molecular length of a single molecule in such a conformation would be *ca.* 3.0 nm. If the formation of a double layer according to Fig. 2(*a*) is assumed, a layer thickness of 5.3–5.4 nm could be estimated. This value



Scheme 2 Synthesis of the symmetric tribenzocyclononene derivatives **1** and **13**, incorporating the *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexane core. *Reagents and conditions:* i, $Br[CH_2]_{10}Co_2Et$, NaH, DMF, 70 °C; ii, $LiAlH_4$, Et_2O, 70 °C; iii, C_5H_{11}–C_6H_{10}–C_6H_{10}–COCl, Et_3N, DMAP, toluene, 20 °C.

Table 1 Phase transition temperatures[a] of the symmetric tribenzocyclononene derivatives **1**,[8] **2**,[8] **9–11**, **13**,[8] **18**[3] and **19**[11] and the calamitic compounds **20**[14] and **21**[12]



Compound	R	T/°C
18	$C_{12}H_{25}$—CO—	C 67 D 139 I
19		C 60 D 278 I (13.5)[b] (22.2)[b]
1		C 118 D 355 I (dec.) (63.8)[b]
13		C 114–115 I
9		C 140–142 I
10		C 117 S_A 159 I
2[c]		C 144/152 S_A 160[d] I (43.1)[b] (38.8)[b]
11[e]		C 165 (S_A 133)[d] I (76.7)[b] (6.6)[b]
20		C 77 S_C 89 I
21		C 78 (N 75.5)[d] I

[a] Abbreviations: C = crystalline, D = discotic mesophase, S_A = smectic A-phase, S_C = smectic C-phase, N = nematic phase, I = isotropic phase. [b] Enthalpy, ΔH/kJ mol^{-1}. [c] Two different melting points were observed due to different crystalline modifications. [d] Value of temperature refers to cooling data. [e] Glass transition temperature T_g = 62 °C.

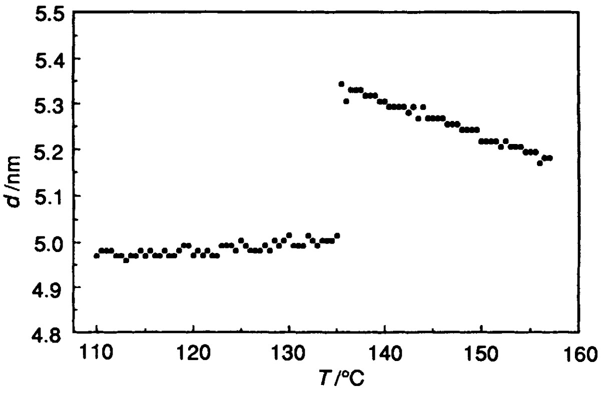
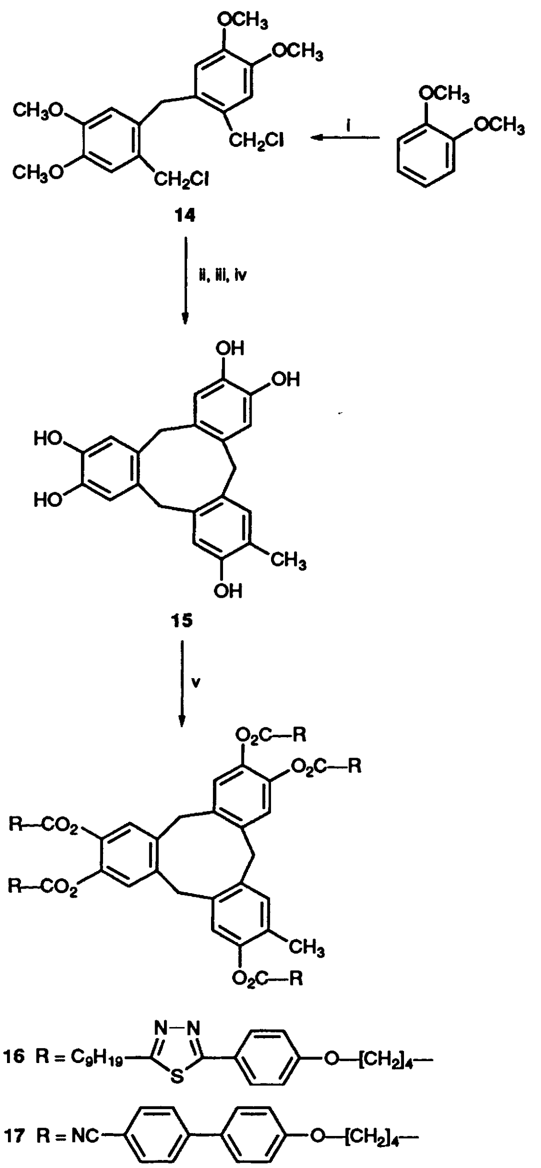


Fig. 1 Temperature dependence of the layer thickness of compound **2**



Scheme 3 Synthesis of the asymmetric tribenzocyclononene derivatives **16** and **17**. *Reagents and conditions*: i, HCl, HCHO, 0 °C; ii, 2-methylanisole, AcOH, reflux; iii, BBr_3, C_6H_6, reflux; iv, H_2O; v, RCO_2H, C_6H_{11}-N=C=N-$[CH_2]_2$-$N^+(Me)[CH_2]_2O$-CH_2CH_2 TsO^-, DMAP, CH_2Cl_2, DMF, 20 °C.

agrees fairly well with the experimentally determined *d*-value of 5.3 nm. This lamellar arrangement would give rise to a layer of tribenzocyclononene cores laying more or less perpendicular to the layer normal of the smectic layers of the calamitic units [see Fig. 2(*a*)]. In the second model [Fig. 2(*b*)] a statistical distribution of the calamitic units of one molecule in two smectic layers is assumed. In this way an arrangement of the tribenzocyclononene units parallel to the smectic layers is obtained. The layer thickness of this arrangement amounts to 5.8–5.9 nm and thus it is significantly (*ca.* 0.5 nm) larger than the determined layer thickness. However it must be taken into account that all molecular models are constructed assuming an all-*trans* conformation of the alkyl chains. Increasing the temperature would cause an enhanced population of gauche conformers in the conformational equilibrium and thus the effective molecular length should be significantly shorter.

Though the exact arrangement of the molecules is not clear yet it is obvious that the tribenzocyclononene moieties support the lamellar structure. This conclusion is drawn from the fact that the tribenzocyclononene derivatives **2** and **10** exhibit a significantly higher mesophase stability than the corresponding monomeric calamitic thiadiazole derivative **20**.† With respect to this, these compounds could be regarded as a special kind of oligomeric liquid crystals.

Symmetric tribenzocyclononene derivatives incorporating the rigid 4-cyanobiphenyl core. Can tribenzocyclononene derivatives with nematic properties be obtained by attaching six 4-cyanobiphenyl rigid cores by spacers of a medium length to the tribenzocyclononene central unit? Compound **11** was synthesized according to the procedure given in Scheme 1. This compound has a sharp melting point at 165 °C. However, on cooling the appearance of a non-specific birefringent texture was observed at 133 °C, indicating the formation of a monotropic mesophase. Its clearing temperature is significantly higher than that of the structurally related 4-butoxy-4′-cyanobiphenyl **21**[12] (see Table 1). This again demonstrates the mesophase stabilizing influence of the tribenzocyclononene connecting unit.

In order to investigate this mesophase, a sample of compound **11** was rapidly supercooled from the isotropic liquid to 0 °C. At room temperature this sample was investigated using a Guinier goniometer. The typical diffraction of a layered structure without order within the layers was observed. The layer thickness was calculated to be 3.03 nm. Since the length of the molecule is about 0.8–0.9 nm smaller than the molecular length of compound **2** the structure can be correlated directly to that of compound **2**. Obviously, the nematic phase of the cyanobiphenyl derivative **21** is replaced by a smectic phase in compound **11**, which also means that the tribenzocyclononene linking unit stabilizes a layered arrangement of the individual calamitic units. Due to the rapid crystallization no oriented samples could be obtained. Also, the other six-fold substituted tribenzocyclononene derivatives exhibit rather high melting points due to their highly symmetric molecular structure.

Asymmetric tribenzocyclononene derivatives. In order to get compounds with lower melting temperatures, *i.e.* liquid crystals with larger mesomorphic ranges, the compounds **16** and **17**, both combining the tribenzocyclononene unit with only five calamitic units have been synthesized according to Scheme 3. Table 2 summarizes the mesomorphic properties of comparable penta- and hexa-substituted tribenzocyclononene derivatives. The pentasubstituted compounds **16** and **17** have only slightly lower clearing temperatures than the hexasubstituted ones (compounds **2** and **11**), which means that the loss of one calamitic unit is almost negligible in terms of mesophase stability. This is in sharp contrast to the behaviour of simple cyclotricatechylene alkanoates **22** and **23** (Table 2) in which the loss of only one side chain causes the disappearance of any liquid crystalline properties, probably due to the disturbed space filling around the central core.[13]

---

† This compound was prepared using the procedure given in ref. 14.

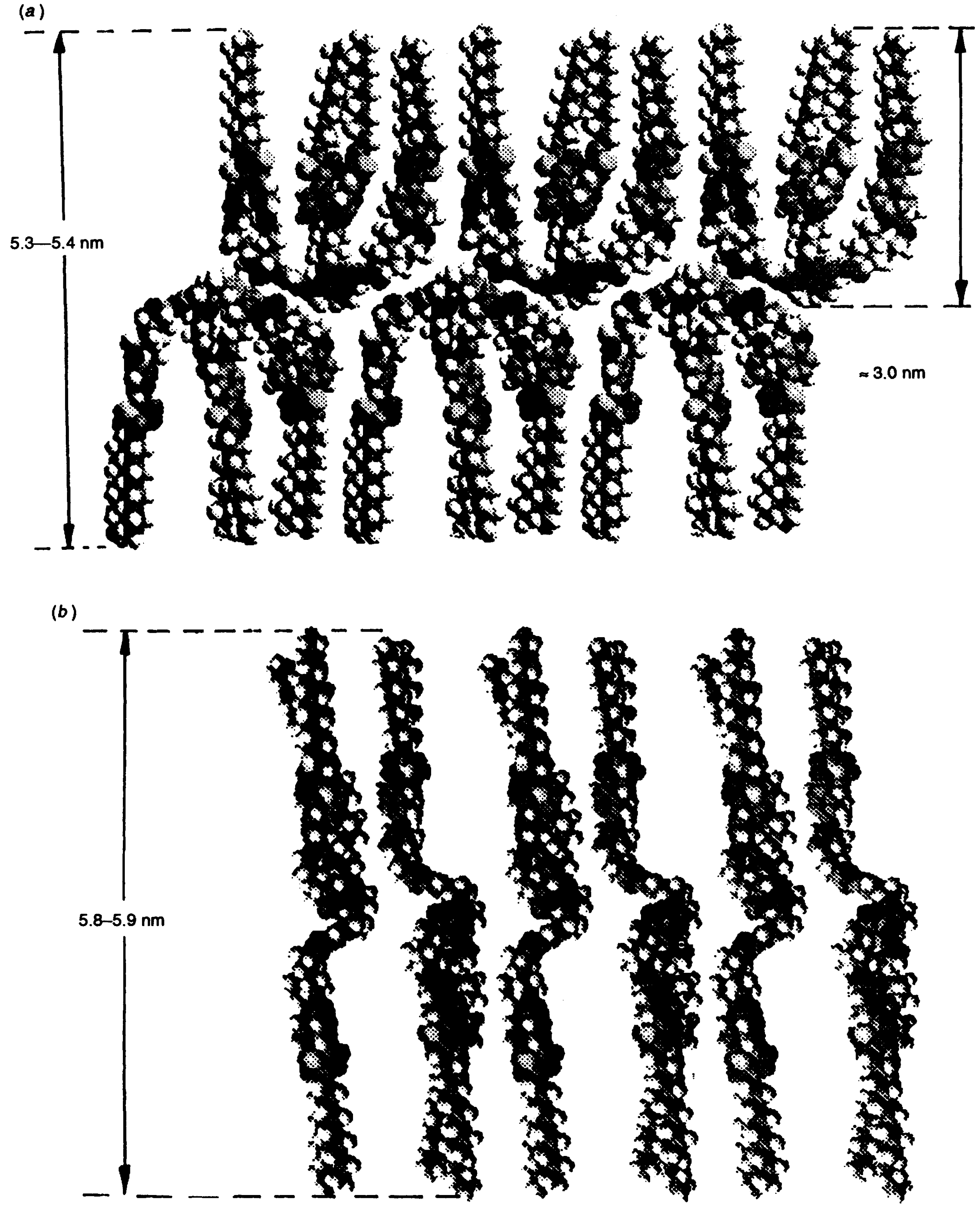
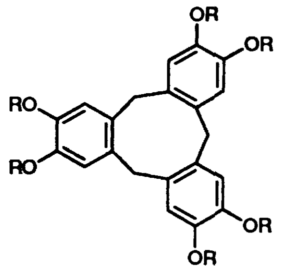


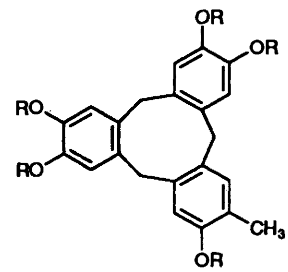
Fig. 2 Two possible packing models of the molecules of compound **2** in the smectic A-phase

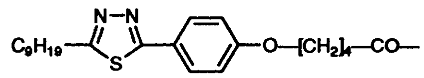
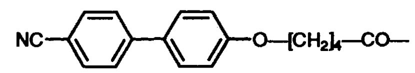
As was expected, the tendency to crystallization could be dramatically diminished by lowering the molecular symmetry. In contrast to the highly symmetrical hexasubstituted tribenzocyclononene derivatives no crystallization was observed in the case of the pentasubstituted compounds **16** and **17**. On cooling from the isotropic liquid, the thiadiazole derivative **16** forms a fan-like texture [Fig. 3(*a*)], typical of the smectic A-phase. At 126 °C this develops into a paramorphotic broken fan texture [Fig. 3(*b*)] indicating a phase transition to a more ordered smectic phase.

The optical texture of the cyanobiphenyl derivative **17** looks rather strange. On cooling to 118 °C no significant change can be observed. By further decreasing the temperature small birefringent islands with no specific texture were formed [see the right upper corner in Fig. 4(*a*)]. Their number slowly increases with decreasing temperature and the rest of the sample becomes homeotropic. However slight pressure on the cover slip causes the appearance of a large Schlieren-texture [see the middle of Fig. 4(*a*)]. It seems that the material has become homeotropically oriented and the mechanical distortion causes

Table 2 Comparison of the transition temperatures[a] (T/°C) of the symmetric tribenzocyclononene derivatives **2**, **11** and **22** with those of the asymmetric tribenzocyclononene derivatives **16**, **17** and **23**





R	Compd.	T/°C	Compd.	T/°C
	**2**	C 144/152 S_A 160 I	**16**	C < 20 S_X 126 S_A 142 I $(0.8)^b$ $(38.0)^b$
	**11**[c]	C 165 (S_A 133)[d] I	**17**[e]	C < 20 S_A 118 I $(7.1)^b$
$C_{12}H_{25}$–O–CH_2–CO–	**22**	C 93 D_{hd} 164 I $(11.1)^b$ $(12.9)^b$	**23**	C 65 I $(18.8)^b$

[a] Abbreviations: S_X = unknown smectic phase, D_{hd} = hexagonal disordered discotic phase, for an explanation of the other abbreviations see Table 1. [b] Enthalpy ΔH/kJ mol^{-1}. [c] Glass transition temperature, T_g = 62 °C. [d] Value of temperature refers to cooling data. [e] Glass transition temperature, T_g = 76 °C.

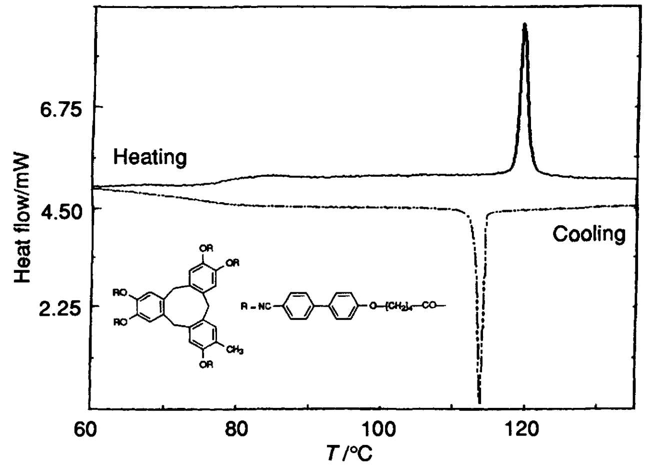


Fig. 5 DSC heating and cooling traces of compound **17** (5 K min^{-1})

a reorientation of the molecules. The DSC-trace of the cyanobiphenyl derivative **17** displays an endotherm at 118 °C and a glass transition at 76 °C (see Fig. 5).

On annealing the sample close to the clearing temperature the formation of a fan texture in the birefringent regions is observed [see Fig. 4(*b*)]. From these observations and from the X-ray pattern we conclude the existence of a smectic A-phase. Comparing the layer periods d of substance **16** (d = 5.2 nm at 100 °C) and substance **17** (d = 3.25 nm at 100 °C) with those of the symmetrically substituted compounds **2** (d = 5.3 nm at 140 °C) and **11** (d = 3.03 nm at 0 °C) no essential influence of the number of calamitic units connected with the central tribenzocyclononene unit on the layer structure can be seen.

Thin films at the air–water interface

Furthermore, we were interested in the investigation of the behaviour of our tribenzocyclononene derivatives as thin films at the air–water interface by means of the Langmuir technique. The F-A-isotherms of the pentasubstituted and the hexasubstituted tribenzocyclononene derivatives **2** and **16**, both incorporating phenylthiadiazole rigid cores as well as that one of the parent calamitic thiadiazole derivative **4.2** (see Table 3) are given in Fig. 6.

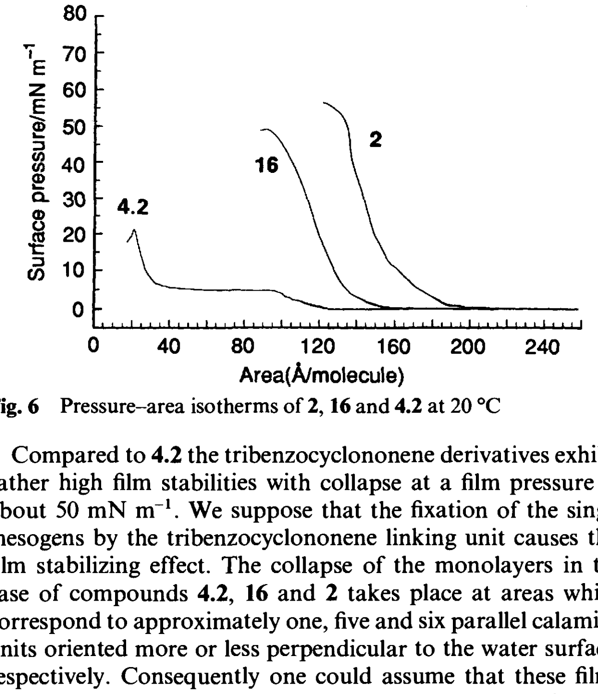


Fig. 6 Pressure–area isotherms of **2**, **16** and **4.2** at 20 °C

Compared to **4.2** the tribenzocyclononene derivatives exhibit rather high film stabilities with collapse at a film pressure of about 50 mN m^{-1}. We suppose that the fixation of the single mesogens by the tribenzocyclononene linking unit causes this film stabilizing effect. The collapse of the monolayers in the case of compounds **4.2**, **16** and **2** takes place at areas which correspond to approximately one, five and six parallel calamitic units oriented more or less perpendicular to the water surface, respectively. Consequently one could assume that these films consist of densely packed phenylthiadiazole cores with the carboxylate groups at the tribenzocyclononene unit acting as hydrophilic groups.

Finally, we conclude that the fixing of calamitic rod-like molecules by a tribenzocyclononene unit *via* appropriate spacers is a useful approach to new oligomeric materials, which exhibit lamellar mesophases and form stable monomolecular layers at the air–water interface.

Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H and ^{13}C NMR spectroscopy (Bruker WP 200 spectrometer and a Varian Unity 500; coupling constants J are given in Hz), IR spectroscopy (Specord 71 IR) and mass spectrometry (Intectra GmbH, AMD 402, electron impact, 70 eV; electrospray-MS, VG Bio-Q Fisons Instruments). Microanalyses were performed using a Carlo-Erba 1102 elemental

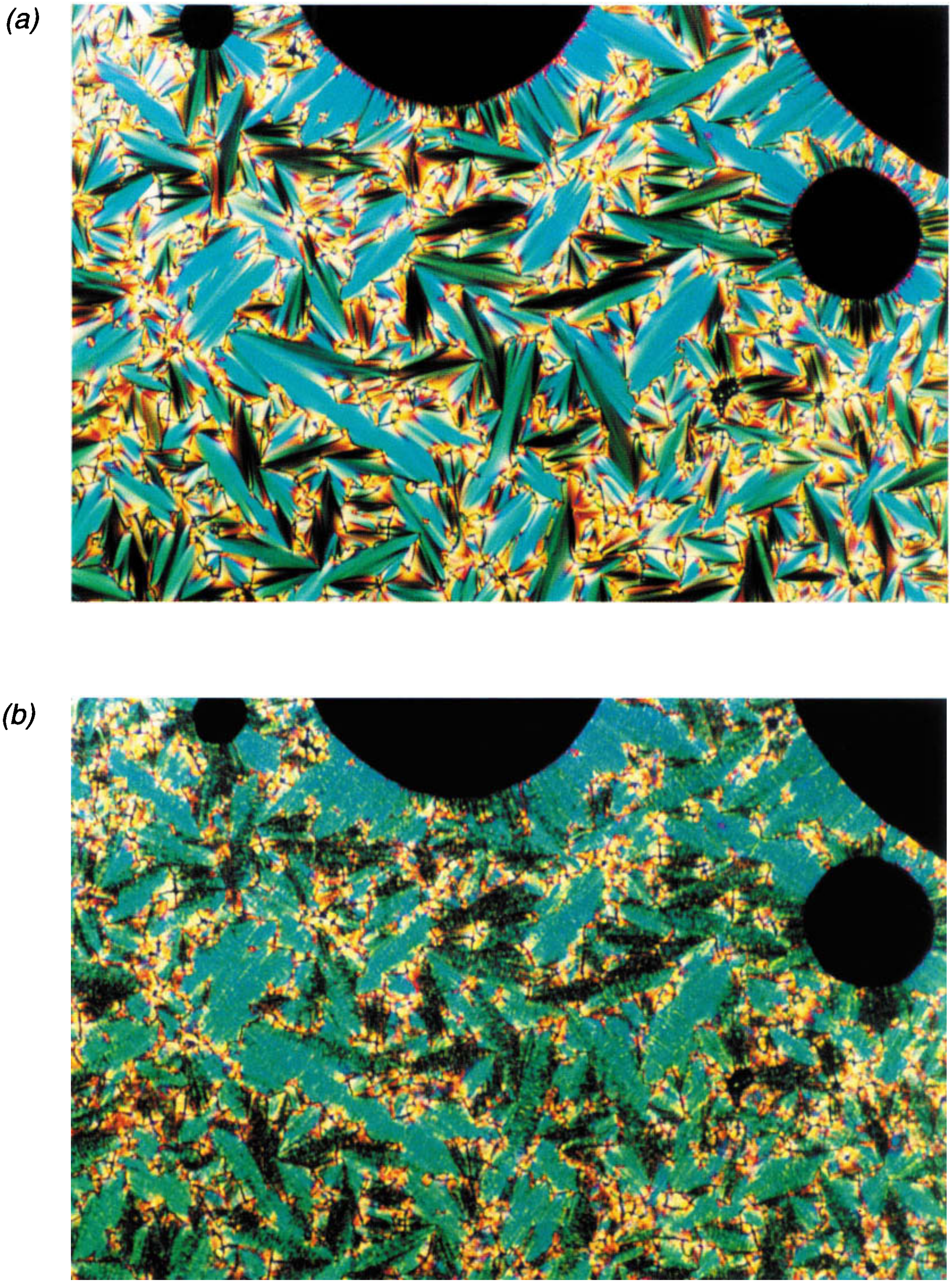


Fig. 3 Optical photomicrographs of the textures of the asymmetric thiadiazole derivative **16** as obtained by cooling from the isotropic melt (crossed polarizers): (*a*) characteristic of S_A, at 140 °C; (*b*) paramorphotic broken fans characteristic for the more ordered smectic phase at 126 °C

Table 3 Compounds **4.1–4.3**[a]

Comp.	*n*	R′	*m*	Mp/°C	Yield (%)
4.1	7	Me	4	71	64
4.2	9	Et	4	65	89
4.3	7	Me	10	83	84

[a] See Scheme 1.

Table 4 Compounds **5.1–5.3**

Comp.	*n*	*m*	Mp/°C	Yield (%)
5.1	7	4	106	92
5.2	9	4	104	90
5.3	7	10	106	81

analyser. Transition temperatures (given in °C) were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7). Pressure–area-isotherms were recorded using a R & K film balance equipped with a teflon-coated Langmuir trough (60 × 10 cm) and a continuous Wilhelmy type measuring system. The temperature of the experimental system was 20 °C and was controlled within ±0.1 K. The substances were dissolved in chloroform. Typically, the solutions were between 1 and 2 mmol dm^{-3}. The measurements were started 10 min after spreading. The films were compressed with a velocity of 0.08 nm^2 $molecule^{-1}$ min^{-1}. The spreading solvent was chromatography grade chloroform stabilized by a small amount of purified methanol. Water used for measuring the surface properties was of Millipore quality. The purity of all compounds was checked by thin layer chromatography (Merck, silica gel 60 F_{254}). The 5-alkyl-2-(4-hydroxyphenyl)-1,3,4-thiadiazoles (**3**) were synthesized according to literature procedures.[15] 4′-Cyano-4-hydroxybiphenyl, *trans*-4′-pentylbicyclohexane-4-carboxylic acid and 11-bromoundecanoic acid were obtained from Merck. Methyl 5-bromopentanoate and ethyl 5-bromopentanoate (Lancaster) were used as obtained.

Alkyl ω-[4-(5-alkyl-1,3,4-thiadiazol-2-yl)phenoxy]alkanoates (4.1–4.3) and ethyl 5-(4′-cyanobiphenyl-4-yloxy)pentanoate (6)

The appropriate 5-alkyl-2-(4-hydroxyphenyl)-1,3,4-thiadiazole (**3**) or 4-cyano-4′-hydroxybiphenyl (38 mmol) was dissolved in dry butan-2-one (400 cm^3), alkyl ω-bromoalkanoate (76 mmol), K_2CO_3 (15.8 g, 114 mmol) and KI (50 mg) were added and the resulting mixture was stirred at reflux temperature for 10 h. After cooling, the solvent was evaporated and the residue was dissolved in water and dichloromethane. The organic phase was washed with sodium hydrogen carbonate 10% hydrochloric acid and water successively. Afterwards the solution was dried and the solvent was removed under reduced pressure. The thiadiazole derivatives **4** were crystallized twice from hexane (see Table 3) and the 4-cyanobiphenyl derivative **6** was crystallized twice from light petroleum (bp 60–85 °C)–ethyl acetate.

4.2. δ_H(200 MHz; $CDCl_3$) 7.81 (2 H, d, *J* 8.9, Ar–H), 6.90 (2 H, d, *J* 8.9, Ar–H), 4.09 (2 H, q, *J* 7.1, $\mathrm{OC}H_2$–CH_3), 3.98 (2 H, t, *J* 5.8, $\mathrm{OC}H_2$–CH_2), 3.06 (2 H, t, *J* 7.6, Ar–CH_2), 2.35 (2 H, t, *J* 6.9, CH_2–CO_2), 1.70–1.83 (6 H, m, CH_2), 1.18–1.32 (15 H, m, CH_2, OCH_2–$\mathrm{C}H_3$) and 0.84 (3 H, t, *J* 6.4, CH_3).

6. (70%) mp 94 °C (Found: C, 74.4; H, 6.6; N, 4.3. $C_{20}H_{21}NO_3$ requires C, 74.28; H, 6.55; N, 4.35%); δ_H(80 MHz; $CDCl_3$) 7.63 (4 H, s, Ar–H), 7.51 (2 H, d, *J* 8.9, Ar–H), 6.94 (2 H, d, *J* 8.9, Ar–H), 4.12 (2 H, q, *J* 7.1, CO_2CH_2), 4.01 (2 H, t, br, CH_2O), 2.38 (2 H, t, br, CH_2CO_2), 1.75–1.91 (4 H, m, br, CH_2) and 1.24 (3 H, t, *J* 7.1, CH_3).

ω-[4-(5-Alkyl-1,3,4-thiadiazol-2-yl)phenoxy]alkanoic acids (5.1–5.3) and 5-(4′-cyanobiphenyl-4-yloxy)pentanoic acid (7)

The appropriate alkanoate **4.1–4.3** or **6** (29.6 mmol) was dissolved in methanol (250 cm^3). A solution of potassium hydroxide (6.3 g, 112 mmol) in water (20 cm^3) was added under stirring at room temperature. Afterwards the solution was refluxed for 2 h in the cases of compounds **4.1–4.3** and only for 5 min in the case of compound **6**. After cooling, the mixture was poured onto crushed ice. The precipitate which was formed by acidification with dilute hydrochloric acid was filtered off, washed with water and crystallized twice from light petroleum (bp 60–85 °C)–ethyl acetate (see Table 4).

5.2. (Found: C, 65.3; H, 7.9; N, 6.8; S, 7.9. $C_{22}H_{32}N_2O_3S$ requires C, 65.31; H, 7.98; N, 6.93; S, 7.91%); δ_H(200 MHz; $CDCl_3$) 7.82 (2 H, d, *J* 8.8, Ar–H), 6.91 (2 H, d, *J* 8.8, Ar– H), 3.99 (2 H, t, *J* 5.5, CH_2O), 3.07 (2 H, t, *J* 7.6, Ar–CH_2), 2.43 (2 H, t, *J* 6.6, CH_2–CO_2), 1.74–1.84 (6 H, m, CH_2), 1.23–1.37 (12 H, m, CH_2) and 0.84 (3 H, t, *J* 6.4, CH_3).

7. (67%) C 137 (N 126) I (Found: C, 73.2; H, 5.8; N, 4.4. $C_{18}H_{17}NO_3$ requires C, 73.19; H, 5.81; N, 4.74%); δ_H(200 MHz; $CDCl_3$) 7.67 (2 H, d, *J* 8.6, Ar–H), 7.61 (2 H, d, *J* 8.3, Ar–H), 7.51 (2 H, d, *J* 8.6, Ar–H), 6.96 (2 H, d, *J* 8.7, Ar–H), 4.01 (2 H, br s, CH_2O), 2.45 (2 H, br s, CH_2–CO_2) and 1.85–1.87 (4 H, m, CH_2).

2,3,7,8,12,13-Hexakis{ω-[4-(5-alkyl-1,3,4-thiadiazol-2-yl)phenoxy]alkanoyloxy}-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononenes (2, 9 and 10) and 2,3,7,8,12,13-hexakis[5-(4′-cyanobiphenyl-4-yloxy]pentanoyloxy)-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene (11)

N-Cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide metho-toluene-*p*-sulfonate [4-(cyclohexyliminomethylideneiminoethyl)-4-methylmorpholin-4-ium 4-methylbenzenesulfonate] (2.44 g, 5.8 mmol) was added to a stirred solution of **5.1–5.3** or **7** (4.8 mmol), cyclotricatechylene[10] (**8**) (10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene-2,3,7,8,12,13-hexaol) (0.18 g, 0.5 mmol) and a catalytic quantity of 4-(dimethylamino)pyridine (DMAP) in a mixture of dry dichloromethane (60 cm^3) and dry *N*,*N*-dimethylformamide (DMF) (10 cm^3). The mixture was stirred at room temperature for 24 h. After complete reaction water was added to the mixture, the organic phase was separated, washed with aqueous sodium hydrogen carbonate, brine and water, successively. Afterwards the solution was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The product was purified by column chromatography using a chloroform–methanol (50:1) mixture followed by crystallization from nitromethane.

2,3,7,8,12,13-Hexakis{5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-10,15-dihydro-5*H*-tribenzo[*a,d,g*]-cyclononene (2). (0.37 g, 29%) C 152 S_A 160 I (Found: C, 68.1; H, 7.5; N, 6.3; S, 7.4. $C_{153}H_{198}N_{12}O_{18}S_6$ requires C, 68.42; H, 7.44; N, 6.26; S, 7.15%); ν_{max}(KBr)/cm^{-1} 2920 (s), 2840 (s), 1760 (s, CO), 1600 (s), 1570 (w), 1520 (m), 1460 (m), 1440 (m), 1420 (m), 1310 (m), 1260 (s), 1170 (s), 1130 (s) and 830 (s); δ_H(200 MHz, $CDCl_3$) 7.79 (12 H, d, *J* 8.8, Ar–H), 7.13 (6 H, s, Ar–H of 10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene), 6.88 (12 H, d, *J* 8.9, Ar–H), 4.74 (3 H, d, *J* 13.3, Ar–CH_2–Ar, H_a), 3.96 (12 H, br t, CH_2O), 3.66 (3 H, d, *J* 13.8, Ar–CH_2–Ar, H_e), 3.05 (12 H, t, *J* 7.6, Ar–CH_2), 2.57 (12 H, br t, CH_2–CO_2), 1.71–1.86 (36 H, m, CH_2), 1.11–1.33 (72 H, m, CH_2) and 0.85 (18 H, t, *J* 6.4, CH_3); Electrospray-MS: 2683.54 ± 1.27; calc. 2683.33.

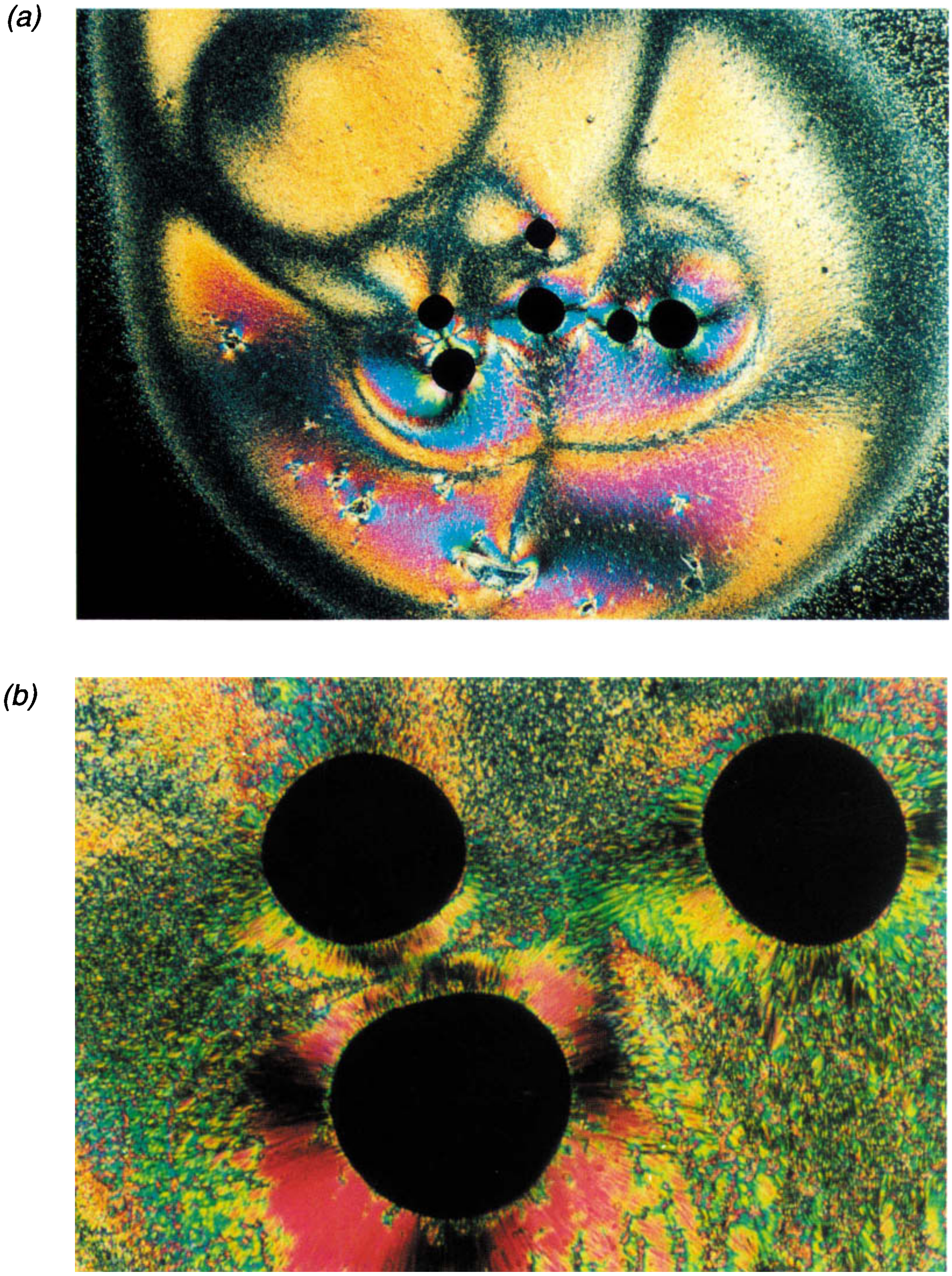


Fig. 4 Optical photomicrographs of the textures of the asymmetric cyanobiphenyl derivative **17** as obtained by cooling from the isotropic melt (crossed polarizers): (*a*) after mechanical distortion at 118 °C (S_A); (*b*) enlarged part of (*a*) after storage at 118 °C for 1 h

2,3,7,8,12,13-Hexakis{11-[4-(5-heptyl-1,3,4-thiadiazol-2-yl)-phenoxy]undecanoyloxy}-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene (9). (0.62 g, 43%) mp 140–142 °C (Found: C, 70.2; H, 8.3; N, 5.4; S, 6.5. $C_{177}H_{246}N_{12}O_{18}S_6$ requires C, 70.34; H, 8.21; N, 5.56; S, 6.35%); δ_H(200 MHz; $CDCl_3$) 7.83 (12 H, d, Ar-H), 7.12 (6 H, s, Ar-H of 10,15-dihydro-5*H*-tribenzo-[*a*,*d*,*g*]cyclononene), 6.92 (12 H, d, Ar-H), 4.73 (3 H, d, Ar–CH_2–Ar, H_a), 3.99 (12 H, t, CH_2O), 3.69 (3 H, d, Ar–CH_2–Ar, H_e), 3.08 (12 H, t, Ar–CH_2), 2.50 (12 H, t, CH_2–CO_2), 1.24–1.89 (156 H, m, CH_2) and 0.90 (18 H, t, CH_3); δ_C(50.3 MHz; $CDCl_3$) 170.84, 169.53, 168.10, 161.24, 141.80, 137.00, 129.23, 124.58, 122.73, 114.88, 68.12 (CH_2O), 36.00 (Ar–*C*H_2–Ar), 34.03, 31.58, 30.11, 30.02, 29.47, 29.34, 29.23, 29.10, 28.90, 28.81, 25.96, 25.86, 24.81, 22.52 (CH_2) and 14.00 (CH_3).

2,3,7,8,12,13-Hexakis{5-[4-(5-heptyl-1,3-4-thiadiazol-2-yl)-phenoxy]pentanoyloxy}-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene (10). (0.70 g, 58%) C 117 S_A 159 I; δ_H(200 MHz; $CDCl_3$) 7.82 (12 H, d, Ar-H), 7.28 (6 H, s, Ar-H of 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene), 6.90 (12 H, d, Ar-H), 4.76 (3 H, d, Ar–CH_2–Ar, H_a), 3.99 (12 H, br t, CH_2O), 3.69 (3 H, d, Ar–CH_2–Ar, H_e), 3.09 (12 H, t, Ar–CH_2), 2.59 (12 H, br t, CH_2–CO_2), 1.20–2.00 (84 H, m; CH_2) and 0.90 (18 H, t, CH_3); δ_C(50.3 MHz; $CDCl_3$) 170.45, 169.60, 167.97, 160.91, 140.63, 137.10, 129.29, 123.09, 114.83, 67.47 (CH_2O), 36.20 (Ar–*C*H_2–Ar), 33.63, 31.61, 30.15, 30.04, 28.96, 28.84, 28.48, 22.55, 21.58 (CH_2) and 14.03 (CH_3).

2,3,7,8,12,13-Hexakis[5-(4′-cyanobiphenyl-4-yloxy)pentanoyloxy]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (11). (0.15 g, 15%), C 165 (S_A 133) I (Found: C, 75.7; H, 5.3; N, 4.0. $C_{129}H_{108}N_6O_{18}$ requires C, 76.30; H, 5.37; N, 4.14%); ν_{max}(KBr)/cm^{-1} 2920m, 2860w, 2220m (CN), 1750s (CO), 1600s, 1490s, 1250s, 1170s, 1140s, 710s and 520m; δ_H(200 MHz; $CDCl_3$) 7.64 (12 H, d, *J* 8.5, Ar-H), 7.53 (12 H, d, *J* 8.6, Ar-H), 7.46 (12 H, d, *J* 8.7, Ar-H), 7.13 (6 H, s, Ar-H of 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene), 6.92 (12 H, d, *J* 8.8, Ar-H), 4.74 (3 H, d, *J* 13.3, Ar–CH_2–Ar, H_a), 3.98 (12 H, br t, CH_2O), 3.66 (3 H, d, *J* 13.8, Ar–CH_2–Ar, H_e), 2.58 (12 H, br t, CH_2–CO_2) and 1.87 (24 H, br m, CH_2).

2,3,7,8,12,13-Hexakis(4′-pentylbicyclohexan-4-ylcarbonyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (1)

A solution of *trans*-4′-pentylbicyclohexane-4-carbonyl chloride (2.40 g, 8.0 mmol), freshly prepared by treatment of *trans*-4′-pentylbicyclohexane-4-carboxylic acid with thionyl chloride and careful evaporation of excess thionyl chloride) in toluene (10 cm^3) was added to a cooled solution (0 °C) of cyclotricatechylene[10] (0.37 g, 1.0 mmol), DMAP (10 mg) and triethylamine (0.81 g, 8.0 mmol), in dry toluene (40 cm^3). The mixture was stirred at room temperature for 24 h and for an additional 2 h at 80 °C. The mixture was poured into water and the organic layer was separated, washed with aqueous sodium hydrogen carbonate and water. Afterwards the solution was dried (Na_2SO_4) and the solvent was removed *in vacuo*. The crude product was crystallized from ethyl acetate–toluene and further purified by column chromatography (silica gel) using a chloroform–ethyl acetate (10:2) mixture. Finally it was again crystallized twice from ethyl acetate–toluene to give pure **1** (0.74 g, 38%). C 118 D 355 (dec.) I (Found: C, 79.3; H, 10.1. $C_{129}H_{198}O_{12}$ requires C, 79.81; H, 10.29%); δ_H(500 MHz; $CDCl_3$) 7.08 (6 H, s, Ar-H), 4.69 (3 H, d, *J* 13.8, Ar–CH_2–Ar, H_a), 3.62 (3 H, d, *J* 14.1, Ar–CH_2–Ar, H_e), 2.34–2.40 (6 H, m, CH–CO_2), 2.07–2.10 (12 H, m, CH-cyclohexane), 1.69–1.83 (36 H, m, CH-cyclohexane) and 0.80–1.53 (132 H, m, CH-cyclohexane, CH_2 and CH_3); δ_C(125.7 MHz; $CDCl_3$) 173.14 (CO), 140.88, 136.88, 124.51, 43.54, 43.24, 42.56, 37.94, 37.45, 36.22 (Ar–*C*H_2–Ar), 33.58, 32.23, 30.07, 29.33, 29.29, 29.17, 29.14, 26.66, 22.69 and 14.07 (CH_3).

2,3,7,8,12,13-Hexakis(11-hydroxyundecyl-1-oxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (12)

A solution of hexakis(10-ethoxycarbonyldecyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene[9] (11.30 g, 6.9 mmol) in dry diethyl ether (50 cm^3) was added dropwise to a stirred solution of lithium aluminium hydride (1.25 g, 33.0 mmol) in dry diethyl ether (50 cm^3). The mixture was stirred for 4 h at room temperature and afterwards was hydrolysed by careful dropwise addition of water until no hydrogen evolution was observed. Afterwards 10% sulfuric acid (100 cm^3) was added dropwise. The remaining precipitate was sucked off and crystallized from nitromethane to yield **12** (3.0 g, 31%). Mp 94–96 °C (Found: C, 74.9; H, 10.7. $C_{87}H_{150}O_{12}$ requires C, 75.26; H, 10.90%); δ_H(200 MHz; $CDCl_3$) 7.13 (6 H, s, CH_2O*H*), 6.83 (6 H, s, Ar–H), 4.71 (3 H, d, Ar–CH_2–Ar, H_a), 3.92 (12 H, m, CH_2O), 3.63 (12 H, t, C*H*$_2$OH), 3.50 (3 H, d, Ar–CH_2–Ar, H_e) and 1.20–1.90 (108 H, m, CH_2).

2,3,7,8,12,13-Hexakis[11-(*trans*-4′-pentylbicyclohexan-4-ylcarbonyloxy)undecyloxy]-10,15-dihydro-5*H*-tribenzo-[*a*,*d*,*g*]cyclononene (13)

The same experimental procedure as described for the preparation of compound **1** was used. Quantities: **12** (1.00 g, 0.7 mmol), *trans*-4′-pentylbicyclohexane-4-carbonyl chloride (1.93 g, 6.5 mmol), triethylamine (0.65 g, 6.5 mmol) and DMAP (20 mg) dry toluene (45 cm^3). The residue was recrystallized twice from ethyl acetate to yield **13** (0.60 g, 28%), mp 114–115 °C (C, 78.8; H, 11.2. $C_{195}H_{330}O_{18}$ requires C, 79.04; H, 11.23%); δ_H(200 MHz; $CDCl_3$) 6.81 (6 H, s, Ar–H), 4.70 (3 H, d, Ar–CH_2–Ar, H_a), 4.05 (12 H, t, CH_2–OCO), 3.91 (12 H, m, CH_2O), 3.49 (3 H, d, Ar–CH_2–Ar, H_e), 2.20 (6 H, m, CH–CO_2) and 0.88–2.28 (288 H, m, CH-cyclohexane, CH_2, CH_3).

2-Methyl-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene-3,7,8,12,13-pentaol (15)

BBr_3 (1.50 g, 6.0 mmol) was added to a solution of 3,7,8,12,13-pentamethoxy-2-methyl-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene[10] (0.50 g, 1.2 mmol) in dry benzene (100 cm^3). The solution was stirred for 2 h at reflux temperature. After cooling to room temperature 50 cm^3 water was carefully added drop by drop and the precipitate formed was sucked off and washed with cold water. The crude product was purified by column chromatography (silica gel) using chloroform–methanol (5:1) as eluent. Finally it was crystallized from ethanol–water to yield **15** as a slightly brown solid (0.21 g, 50%), mp > 350 °C (dec.); δ_H(200 MHz; [$^2H_6$]acetone 7.45 (1 H, s, Ar–OH), 7.49 (1 H, s, Ar–OH), 7.58 (1 H, s, Ar–OH), 7.66 (1 H, s, Ar–OH), 7.82 (1 H, s, Ar–OH), 6.77, 6.78, 6.85, 7.04 (4 s, 6 H, Ar–H), 4.66 (2 H, d, *J* 13.2, Ar–CH_2–Ar, H_a), 4.62 (1 H, d, *J* 13.5, Ar–CH_2–Ar, H_a), 3.40 (1 H, d, *J* 13.4, Ar–CH_2–Ar, H_e), 3.36 (1 H, d, *J* = 13.4, Ar–CH_2–Ar, H_e), 3.34 (1 H, d, *J* = 13.5, Ar–CH_2–Ar, H_e) and 2.08 (3 H, s, Ar–CH_3); *m*/*z*(%) (70 eV) 364 (71, M^+), 349 (29, $M^+ - CH_3$), 331 (8), 254 (38), 241 (100), 226 (39), 211 (19), 197 (20), 167 (12), 149 (28), 123 (23), 102 (10) and 57 (34).

2-Methyl-3,7,8,12,13-pentakis{5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (16)

The same experimental procedure as described for the preparation of compound **2** was used. Quantities: **15** (0.17 g, 0.5 mmol), **5.2** (1.88 g, 4.7 mmol), *N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide metho-toluene-*p*-sulfonate (2.37 g, 5.6 mmol), DMAP (50 mg), dry methylene chloride (50 cm^3) and dry DMF (7 cm^3). The crude product was purified by column chromatography (silica gel) using chloroform–methanol (50 : 1) as eluent. The residue was recrystallized twice from nitromethane to give **16** (0.28 g, 36%). C < 20 S_X 126 S_A 142 I (C, 68.9; H, 7.5; N, 6.1; S, 7.0. $C_{132}H_{170}N_{10}O_{15}S_5$ requires C, 69.02; H, 7.46; N, 6.10; S, 6.97%); δ_H(200 MHz; $CDCl_3$) 7.77–7.85 (10 H, m, Ar–H), 7.11, 7.14, 7.18 (6 H, 3 s, Ar–H, 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene), 6.86–6.95 (10 H, m, Ar–H), 4.68–4.79 (3 H, m, Ar–CH_2–Ar, H_a), 3.96–4.03 (10 H, m, CH_2O), 3.65 (3 H, br d, *J* 13.9, Ar–CH_2–Ar, H_e), 3.06 (10 H, t, *J* 7.6, Ar–CH_2), 2.57–2.62 (10 H, m, CH_2–CO_2), 2.06 (3 H, s, Ar–CH_3), 1.71–1.92 (30 H, m, CH_2), 1.24–1.55 (60 H, m, CH_2) and 0.85 (15 H, t, *J* 6.4, CH_3); Electrospray-MS 2295.88 ± 0.43, calc. 2295.14.

3,7,8,12,13-Pentakis[5-(4′-cyanobiphenyl-4-yloxy)pentanoyloxy]-2-methyl-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene (17)

The same experimental procedure as described for the preparation of compound **2** was used. Quantities: **15** (0.17 g, 0.5 mmol), **7** (1.38 g, 4.7 mmol), *N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide metho-toluene-*p*-sulfonate (2.37 g, 5.6 mmol), DMAP (50 mg), dry methylene chloride (50 cm^3) and dry DMF (7 cm^3). The crude product was purified by column chromatography (silica gel) using chloroform–methanol (100 : 1) as eluent. The residue was recrystallized twice from ethyl acetate–butanol to yield the pure compound **17** (0.18 g, 21%). C < 20 S_A 118 I (Found: C, 76.5; H, 5.4; N, 3.8. $C_{112}H_{95}N_5O_{15}$ requires C, 76.81; H, 5.47; N, 4.00%); ν_{max}(Nujol)/cm^{-1} 2220m (CN), 1760s (CO), 1600s, 1500s, 1300m, 1260s, 1180s, 1140s and 1100m; δ_H(200 MHz, $CDCl_3$) 6.91–7.66 (46 H, m, Ar–H, 10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene), 4.68–4.78 (3 H, m, Ar–CH_2–Ar, H_a), 3.91–4.00 (10 H, m, CH_2O), 3.65 (3 H, br d, *J* 13.5, Ar–CH_2–Ar, H_e), 2.59–2.61 (10 H, m, CH_2–CO_2), 2.07 (3 H, s, Ar–CH_3) and 1.89 (20 H, br m, CH_2).

Acknowledgements

This work was supported by the BASF-AG, the BMFT, and the *Fonds der Chemischen Industrie*. We thank Merck (Darmstadt) for the donation of chemicals.

References

1 C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121.
2 S. Chandrasekhar, *Liq. Cryst.*, 1993, **14**, 3.
3 H. Zimmermann, R. Poupko, Z. Luz and J. Billard, *Z. Naturforsch., A Phys. Sci.*, 1985, **40**, 149.
4 H. Zimmermann, R. Poupko, Z. Luz and J. Billard, *Z. Naturforsch., A Phys. Sci.*, 1986, **41**, 1137.
5 J. Malthete and A. Collet, *J. Am. Chem. Soc.*, 1987, **109**, 7544.
6 J. Malthete, N. H. Tinh and C. Destrade, *Liq. Cryst.*, 1993, **13**, 171.
7 M. Ebert, O. Herrmann-Schönherr, J. H. Wendorff, H. Ringsdorf and P. Tschirner, *Makromol. Chem.*, 1988, **9**, 45.
8 H. Budig, S. Diele, P. Göring, R. Paschke, C. Sauer and C. Tschierske, *J. Chem. Soc., Chem. Commun.*, 1994, 2359.
9 F. M. Menger, M. Takeshita and J. F. Chow, *J. Am. Chem. Soc.*, 1981, **103**, 5938.
10 A. S. Lindsey, *J. Chem. Soc.*, 1965, 1685.
11 H. Budig, R. Paschke, S. Diele, I. Letko and G. Pelzl, *Ber. Bunsenges. Phys. Chem.*, 1993, **97**, 1355.
12 G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton and E. P. Raynes, *Liquid Crystals and Ordered Fluids*, 1974, **2**, 617.
13 B. Kohne and K. Praefcke, *Chem.-Ztg.*, 1985, **109**, 121.
14 C. Tschierske, H. Zaschke, H. Kresse, A. Mädicke, D. Demus, D. Girdziunaite and G. Y. Bak, *Mol. Cryst. Liq. Cryst.*, 1990, **191**, 223.
15 C. Tschierske and D. Girdziunaite, *J. Prakt. Chem.*, 1991, **333**, 135.

Paper 4/06036I
Received 3rd *October* 1994
Accepted 24*th November* 1994