Mesomorphic properties and monolayer behaviour of novel liquid crystalline *exo*-calix[4]arene derivatives

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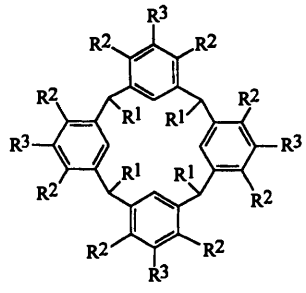
Novel calix[4]arene derivatives are synthesized. These are pyrogallol-derived *exo*-calix[4]arenes with twelve 3-oxaalkanoyloxy chains and *exo*-calix[4]arenes in which eight or twelve rod-like units (phenylthiadiazole and phenylpyrimidine units) are fixed *via* spacers with the calix[4]arene central core. The liquid crystalline properties of these compounds are investigated by thermal optical microscopy between crossed polarizers, by differential scanning calorimetry and some of them also by X-ray diffraction. One of the 3-oxaalkanoates forms a hexagonal columnar mesophase, whereas most of the compounds incorporating calamitic units in the lateral chains give liquid crystalline materials with a smectic A-phase. Furthermore the behaviour of selected compounds as thin films at the air–water interface is studied using the Langmuir technique. They form condensed films whereby the molecular areas at the collapse points are determined by the densely packed lateral chains.

Introduction

In recent years, calixarenes have been identified as new materials with interesting properties. Such compounds were used as catalysts, enzyme mimicrists, stabilizers in polymers and as hosts for small organic molecules.[1,2]

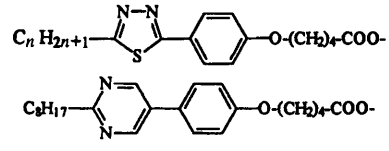
Mesogenic materials with a calix[4]arene central unit were first reported in 1990.[3] These compounds exhibit columnar mesophases if twelve sufficiently long aliphatic chains are connected to an *exo*-calix[4]arene core.[4–8] More recently liquid-crystalline derivatives, based on *endo*-calix[4]arenes, have also been described.[9–12]

Here we wish to report the synthesis, the mesogenic and the monolayer properties of novel *exo*-calix[4]arene derivatives with lateral 3-oxaalkanoyloxy groups (compounds **1**) and *exo*-calix[4]arenes in which calamitic rigid cores are fixed to the macrocyclic calix[4]arene unit (compounds **2–6**).



R^1 = CH_3-, C_3H_7-

R^2 = C_nH_{2n+1}-O-CH_2-COO-



R^3 = H, R^2

Results and discussion

Synthesis

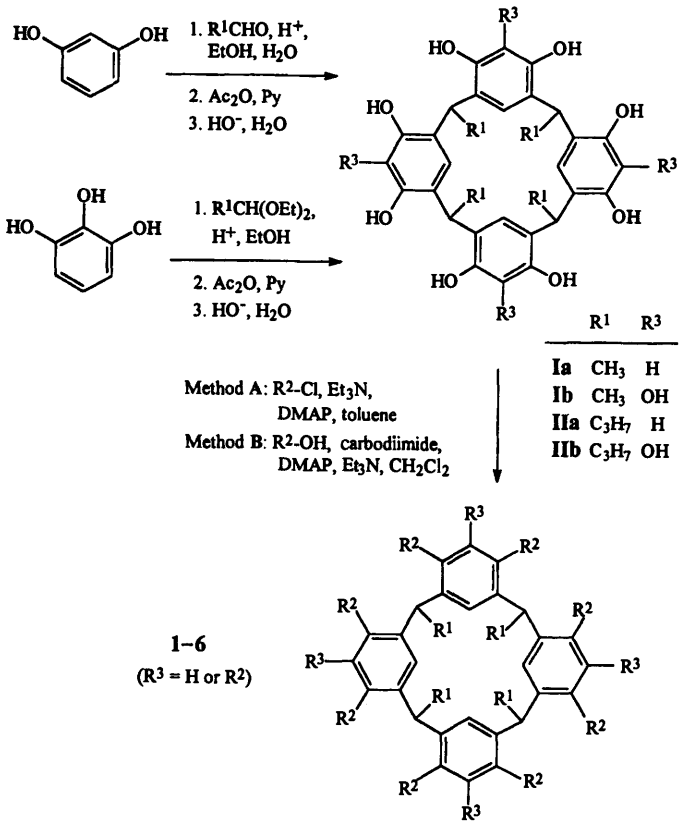
The syntheses of these compounds were carried out according to Scheme 1. The acid-catalysed condensation reactions of resorcinol with aliphatic aldehydes gave the crude calixarenes **Ia** and **IIa**.[13] Purification was achieved by acetylation of the crude phenols followed by repeated crystallization of the octaacetates from ethyl acetate and/or acetonitrile. Saponification of these acetates gave the pure phenolic calixarenes **Ia** and **IIa**.[13] In a similar manner calixarenes with twelve phenolic groups were obtained.[3]

The calixarene derivatives **1** were prepared by esterification of the phenols with the appropriate 3-oxaalkanoyl chlorides[14] (Method **A**). The synthesis of the compounds **2–6** incorporating 2-phenyl-1,3,4-thiadiazole or 5-phenylpyrimidine rigid cores was achieved by esterification of phenolic calix[4]arenes with appropriate carboxylic acids using a modified carbodiimide method[15] (Method **B**).

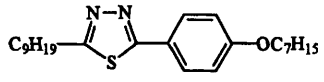
Liquid crystalline properties

In Table 1 the mesomorphic properties of these new compounds are summarized. Compounds **1** represent calix[4]arene derivatives, with twelve 3-oxaalkanoyloxy chains. Only the long chain derivative **1b** exhibits a columnar mesophase. Polarizing optical microscopy and X-ray scattering proved the existence of a D_{hd}-phase in the temperature range 45–52 °C.

If one compares the compounds **1** with compound **3** it is obvious that the mesophase stability increases if calamitic 2-phenylthiadiazole units are connected to the calix[4]arene core by flexible spacer units. Also the calixarene derivatives **2** and **5** are monotropic or enantiotropic liquid crystals. More detailed investigations, however, have shown that the mesophase type has changed. Contrary to the 3-oxapentadecanoate **1b**, which has a hexagonal disordered columnar mesophase, the compounds **2**, **3** and **5** incorporating the phenylthiadiazole units form a layered smectic A-type mesophase. In all these compounds the transition from the isotropic liquid to the mesophase can be seen between crossed polarizers by the formation of small batonnets that coalesce to a focal conic fan



Scheme 1 Synthesis of the calix[4]arene derivatives (R^1, R^2 and R^3 of the compounds **1**–**6** are explained in Table 1)



7 cr 77 S_C 89 is

texture indicating the smectic A-phase. This means that in these derivatives of *exo*-calix[4]arene the calamitic rigid units determine the mesophase type. A columnar stacking of the molecules is not possible, but the calamitic units can adopt a parallel packing, which leads to the smectic self-organization. Obviously, the calix[4]arene moieties support this lamellar structure and act as something like a 'cyclooligomer backbone'.[17] This conclusion can be drawn from the fact that the calamitic compound **7**[18] exhibits a significantly lower mesophase stability than the corresponding calix[4]arene derivatives **2**, **3** and **5**.

Furthermore, the mesophase stability rises with the increasing number of phenylthiadiazole units coupled with the calix[4]arene central unit. This is especially evident from the comparison of the propyl derivatives **4** and **5**. The resorcinol based compound **4** with eight phenylthiadiazole units is only a crystalline solid, whereas the pyrogallol-based calix[4]arene derivative **5**, in which twelve thiadiazole units are fixed to each other, has a smectic A-phase.

The mesophase stability is additionally influenced by the size of the groups arranged at the bridging positions of the calixarene central core. In the case of calixarenes with simple aliphatic lateral chains, relative large groups at the bridging positions (R^1), such as the propyl group, prevent the molecular stacking of these molecules into columns while the analogous methyl-substituted compounds display a columnar mesophase.[4] Also in the case of the resorcinol-based calixarene **2** the replacement of the methyl groups in the bridging position by the larger propyl groups causes the loss of mesogenic properties (compound **4**). However, liquid crystallinity is maintained in the case of the pyrogallol-derived calixarene **5**.

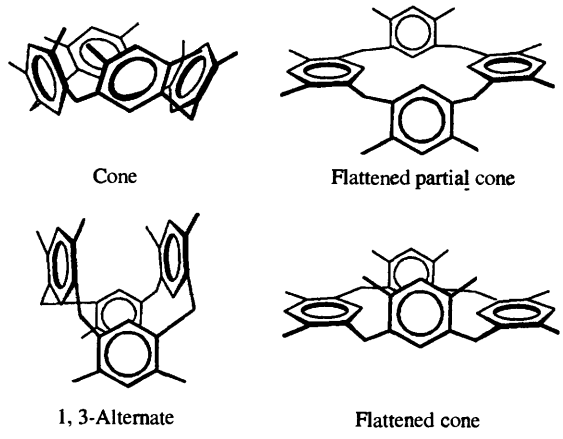


Fig. 1 Possible conformations of *exo*-calix[4]arenes

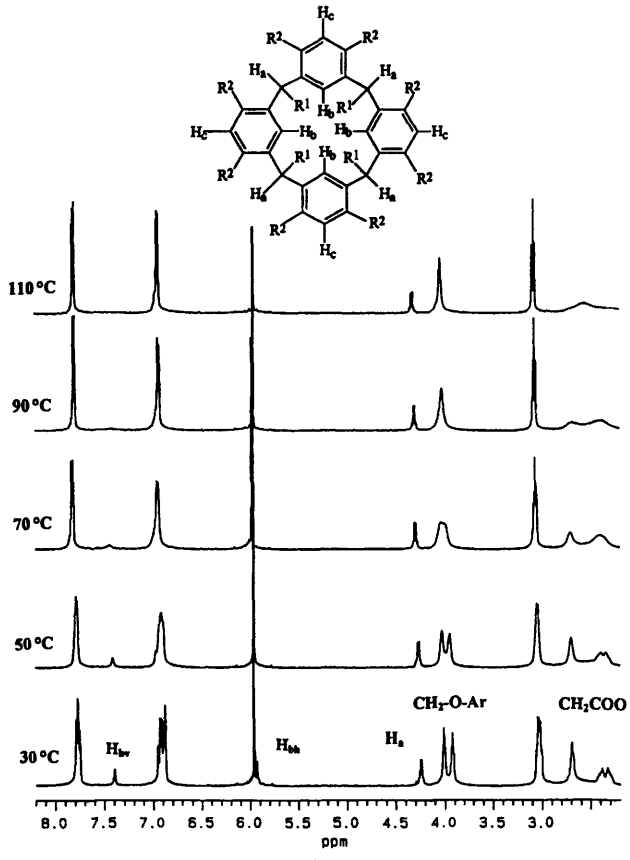


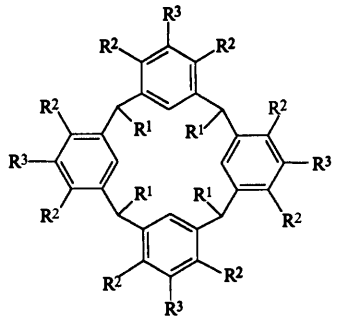
Fig. 2 Sections of the 500 MHz ^{1}H NMR spectra of compound **2** in 1,1,2,2-tetrachloro[$^2H_2$]ethane solution at 30, 50, 70, 90 and 110 °C ($SiMe_4$ as internal standard)

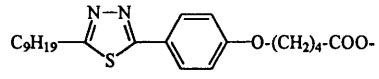
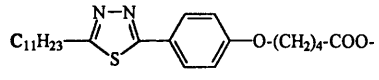
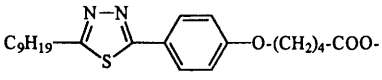
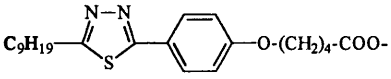
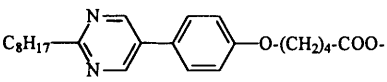
The pyrimidine derivative **6** is a crystalline solid. It seems that the bent 2-phenylthiadiazole[19] units represent better mesogenic units in the case of these calixarene derivatives. The reason for this behaviour is not clear yet.

The ^{1}H NMR spectra of all synthesized calix[4]arene derivatives in $CDCl_3$ solution at room temperature are consistent with the presence of a C_{2v} flattened cone conformation. Rapid interconversion of the two identical flattened cone conformations may take place and is dependent on the temperature and substituents (Figs. 1 and 2).

At elevated temperatures the ^{1}H NMR spectra therefore are consistent with the presence of a C_{4v} symmetric crown conformation, which is the average structure resulting from the rapid interconversion between the two equivalent flattened cone conformers. For compound **2** the coalescence points of the aromatic H_b protons was determined by means of temperature-dependent ^{1}H NMR spectroscopy in deuteriated 1,1,2,2-

Table 1 Phase transition temperatures[a] T/°C of the calix[4]arene derivatives **1a**,[16] **1b** and **2–6**. The values in parentheses (lower lines) refer to the transition enthalpies ΔH/kJ mol^{-1}.



Compound	R^1	R^2	R^3	Transition temperatures T/°C (Transition enthalpies ΔH/kJ mol^{-1})
1a-	CH_3-	$C_{10}H_{21}$-O-CH_2-COO-	R^2	cr 46 is
1b	CH_3-	$C_{12}H_{25}$-O-CH_2-COO-	R^2	cr 45 D_{hd} 52 is (6.6) (8.6)
2	CH_3-		H	cr 159 (S_A 149) is (113) (54)
3	CH_3-		R^2	cr 196 S_A 211 is (49) (29)
4	C_3H_7-		H	cr 126 is (126)
5	C_3H_7-		R^2	cr 150 S_A 165 is
6	CH_3-		R^2	cr 168 is (107)

[a] Abbreviations: cr = crystalline, D_{hd} = disordered hexagonal columnar mesophase; S_A = smectic A-phase; is = isotropic phase.

tetrachloroethane as solvent (T_c = 100 °C, 500 MHz). Using eqn. (1), the activation energy ($\Delta G^{\ddagger}$) for the pseudo-rotation was determined to be 69.2 kJ mol^{-1}.

$$\Delta G^{\ddagger} = RT_c\left(22.96 + \ln\frac{T_c}{\Delta\nu}\right) \quad (1)$$

Therefore one can conclude that in the temperature range of the liquid crystalline phases the calix[4]arene derivatives **2**, **3** and **5** are in a dynamic equilibrium of different conformations. This means, that the calixarene central unit represents a rather flexible structural unit and therefore these compounds can be regarded as novel oligomeric liquid crystals with an exactly defined molecular mass.[20–23]

Monolayer behaviour

Besides the mesomorphic properties we were also interested in the monolayer behaviour of these calix[4]arene derivatives as thin films at the air–water interface.[24,25]

In Fig. 3, the pressure–area isotherm of the 3-oxapentadecanoate **1b** is displayed. It shows a condensed phase with a collapse at *ca.* 210 Å^2 molecule^{-1} and a film pressure of 40 mN m^{-1}. This corresponds to an area occupied by the twelve aliphatic chains (18 Å^2 per chain[26]) arranged more or less perpendicular to the water surface. Thus, the molecular area at the collapse is determined by the densely packed alkyl chains. A kind of 'side-on' arrangement of the calix[4]arene central unit can be assumed with the carboxylate groups acting as hydrophilic parts. The conformation of the calix[4]arene unit

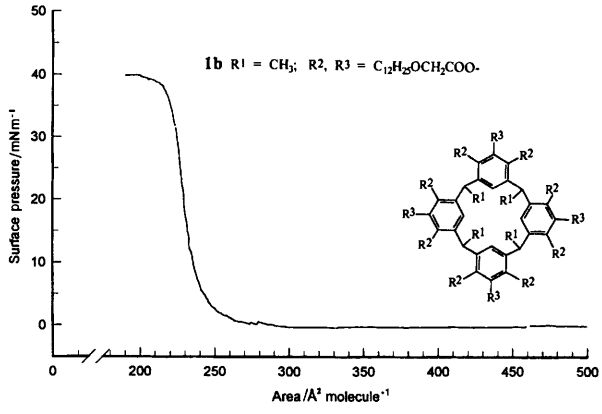


Fig. 3 Pressure–area isotherm (T = 20 °C) of the calix[4]arene **1b**

in the organized films[25] was not investigated, but it seems likely that the flattened cone conformation should allow an efficient interaction of the carboxylate groups with the aqueous subphase and also the most dense packing of the alkyl chains.

Fig. 4 displays the spreading behaviour of selected calix[4]arenes, which incorporate the 2-phenylthiadiazole rigid units. The pyrogallol-derived calixarenes **3** and **5** with twelve calamitic structural units collapse at *ca.* 250 Å^2 molecule^{-1} and film pressures of 28 and 37 mN m^{-1}, respectively. The resorcinol-derived calix[4]arene **2** with only eight lateral chains exhibits a collapse at 160 Å^2 molecule^{-1} and 45 mN m^{-1}. These

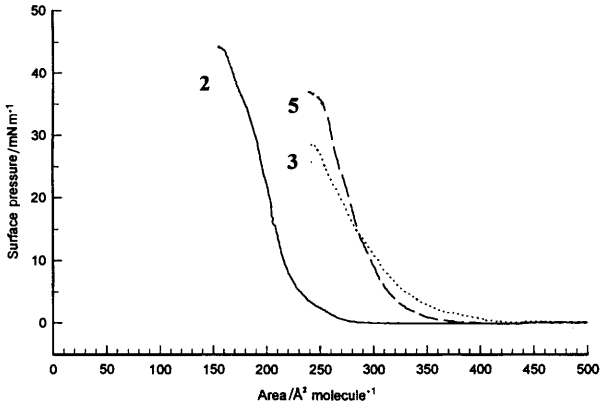


Fig. 4 Pressure–area isotherms (T = 20 °C) of the calix[4]arenes **2**, **3** and **5**

areas at the collapse points are in agreement with a densely packed arrangement of twelve (compounds **3** and **5**) or eight (compound **2**) calamitic 2-phenylthiadiazole cores, orientated more or less perpendicular to the air–water interface (20–22 Å^2 for each phenylthiadiazole unit[27]). This arrangement is very similar to that of the alkyl derivative **1b**.

A related arrangement of the molecules has recently been observed for the monomolecular films of analogous cyclotribenzylene derivatives incorporating calamitic 2-phenylthiadiazole units.[21] In all these cases the areas at the collapse points are determined by the number of calamitic units.

Conclusions

In summary we have synthesized the first examples of calix[4]arene derivatives which exhibit smectic liquid crystalline phases. These compounds may be regarded as novel macrocyclic oligomeric liquid crystals with an exactly defined molecular mass. Furthermore the arrangement of the calixarene units in smectic layers and the preparation of defined monomolecular films of these compounds could be tools to influence their molecular recognition ability and their inclusion behaviour.

Experimental

General

The calix[4]arenes **Ia**, **Ib**, **IIa** and **IIb** were synthesized according to literature procedures.[13] *N*-Cyclohexyl-*N'*-[2-(4-methylmorpholinio)ethyl]carbodiimide toluene-*p*-sulfonate (Fluka) was used as received. Confirmation of the structures of the intermediates and products was obtained by ^{1}H NMR spectroscopy (VARIAN Unity 500 or Aspekt 200 spectrometer) and IR spectroscopy (SPECORD 71 IR). The purity of all compounds was checked by thin layer chromatography (Merck, silica gel 60 F_{254}). Chloroform–methanol mixtures (10:0.5) were used as eluents and the spots were detected by UV irradiation and/or by means of bromothymol blue solution. Microanalyses were performed using a LECO CHNS-932 elemental analyser.

Transition temperatures 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). X-Ray studies were performed by means of a Guiniergoniometer (Fa. Huber). Pressure–area isotherms were recorded using a film balance (Riegler & Kirstein GmbH) equipped with a Teflon-coated Langmuir trough and a continuous Wilhelmy-type measuring system. The temperature of the experimental system was 20 °C. The substances were dissolved in chloroform (0.25 and 0.5 mmol). The measurements were started 10 min after spreading. The films were compressed with a velocity of 0.05 nm^2 molecule^{-1} min^{-1}. Water was of millipore quality.

1,3,5,7(1,3)-Tetrabenzena-2,4,6,8-tetramethyl-1$^{4.5.6}$,3$^{4.5.6}$5$^{4.5.6}$,7$^{4.5.6}$-dodecakis(3-oxatridecanoyloxy)-cyclooctaphane (1a)

Ib (0.91 g, 1.5 mmol), 4-dimethylaminopyridine (DMAP) (50 mg) and dry triethylamine (1.92 g, 19.0 mmol) were placed in dry toluene (50 ml). 3-Oxatridecanoyl chloride (4.46 g, 19.0 mmol) was added drop by drop at 0 °C. After stirring for 3 h at 80 °C, the mixture was cooled and poured into water. The organic layer was separated and the solvent was removed by distillation. To remove the excess of acyl chloride the residue was dissolved in $CHCl_3$ and stirred with an aqueous NaOH solution (150 ml of a 0.2 M solution) for 2 h at room temperature. The organic layer was separated and washed several times with water. After drying over Na_2SO_4 and evaporation of the solvent the product was obtained by column chromatography on silica gel (eluent: $CHCl_3$–ethyl acetate, 20:1) followed by recrystallization (four times) from EtOH–PrOH (1.50, 33%), mp 46 °C (Found: C, 70.7; H, 9.9. $C_{176}H_{296}O_{36}$ requires C, 70.7; H, 10.0%); δ_H(200 MHz, $CDCl_3$, 25 °C, flattened cone conformation) 0.85 (36 H, t, CH_3, J = 6.3 Hz), 1.10–1.24 (168 H, m, CH_2), 1.47 (12 H, d, CH_3–CH, J = 6.9 Hz), 1.57 (24 H, br m, CH_2–CH_2–O), 3.44–3.60 (24 H, m, CH_2–CH_2–O), 3.92–4.42 (28 H, m, CH_2–COO and CH_3–CH), 6.01 (2 H, s, Ar–H_{bh}) and 7.32 (2 H, s, Ar–H_{bv}); δ_H(200 MHz, $C_2D_2Cl_4$, 90 °C, cone conformation) 0.96 (36 H, t, CH_3, J = 6.5 Hz), 1.36 (168 H, m br, CH_2), 1.58 (12 H, d, CH_3–CH, J = 7.2 Hz), 1.68 (24 H, m br, CH_2–CH_2–O), 3.60–3.66 (24 H, m, CH_2–CH_2–O), 4.01–4.36 (28 H, m, CH_2–COO and CH_3–CH) and 6.77 (4 H, s, Ar–H_b).

1,3,5,7(1,3)-Tetrabenzena-2,4,6,8-tetramethyl-1$^{4.5.6}$,3$^{4.5.6}$,5$^{4.5.6}$,7$^{4.5.6}$-dodecakis(3-oxapentadecanoyloxy)-cyclooctaphane (1b)

Prepared as described for compound **1a**. Quantities: **Ib** (0.83 g, 1.4 mmol), DMAP (50 mg), dry triethylamine (1.77 g, 17.5 mmol), 3-oxapentadecanoyl chloride (4.60 g, 17.5 mmol). Purification by column chromatography on silica gel [eluents: $CHCl_3$–acetyl acetate (35:1), then light petroleum–ethyl acetate (5:1)] and recrystallization (three times) from MeOH–PrOH (0.90 g, 20%), phase transitions (°C): cr 45 D_{hd} 52 is (Found: C, 72.2; H, 10.2. $C_{200}H_{344}O_{36}$ requires C, 72.2; H, 10.4); δ_H(200 MHz, $CDCl_3$, 25 °C, flattened cone conformation) 0.86 (36 H, t, CH_3, J = 6.8 Hz), 1.24–1.28 (216 H, m, CH_2), 1.47 (12 H, d, CH_3–CH, J = 7.1 Hz), 1.50–1.61 (24 H, m, CH_2–CH_2–O), 3.41–3.57 (24 H, m, CH_2–CH_2–O), 3.95–4.37 (28 H, m, CH_2–COO and CH_3–CH), 6.01 (2 H, s, Ar–H_{bh}) and 7.32 (2 H, s, Ar–H_{bv}).

1,3,5,7(1,3)-Tetrabenzena-2,4,6,8-tetramethyl-1$^{4.6}$,3$^{4.6}$,5$^{4.6}$,7$^{4.6}$-octakis{5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}cyclooctaphane (2)

Ia (90 mg, 0.16 mmol), 5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoic acid (0.90 g, 2.22 mmol), *N*-cyclohexyl-*N'*-[2-(4-methylmorpholinio)ethyl]carbodiimide toluene-*p*-sulfonate (1.13 g, 2.66 mmol) and DMAP (50 mg) were placed in dry CH_2Cl_2 (50 ml). The reaction mixture was stirred at room temperature for 24 h. Afterwards the mixture was poured into water (100 ml). The organic layer was separated, washed once with water and dried over Na_2SO_4. After evaporation of the solvent the crude product was worked up by column chromatography on silica gel [eluent: $CHCl_3$–MeOH (10:1)] and recrystallized (twice) from acetone–toluene (0.10 g, 17%), phase transitions (°C): cr 159 S_A 149 is (Found: C, 68.0; H, 7.4; N, 6.2; S, 6.9. $C_{208}H_{272}N_{16}O_{24}S_8$ requires C, 68.7; H, 7.5; N, 6.2; S, 7.1%); δ_H(500 MHz, $CDCl_3$, 25 °C, flattened cone conformation) 0.85 (24 H, t, CH_3–CH_2, J = 7.0 Hz), 1.24–1.93 (144 H, m, CH_2), 1.45 (12 H, d, CH_3–CH, J = 6.8 Hz), 2.30–

2.68 (16 H, m, CH_2–COO), 3.02–3.06 (16 H, m, Ar–CH_2), 3.90–4.00 (16 H, m, CH_2–O), 4.24 (4 H, q, CH_3–C*H*, J = 7.0 Hz), 5.96 (2 H, s, Ar–H_{bh}), 6.81–6.93 (20 H, m, Ar–H and Ar–H_c), 7.37 (2 H, s, Ar–H_{bv}) and 7.76–7.80 (16 H, m, Ar–H); δ_H(500 MHz, $C_2D_2Cl_4$, 120 °C, cone conformation) 0.92 (24 H, t, CH_3–CH_2, J = 6.5 Hz), 1.33–1.90 (144 H, m, CH_2), 1.52 (12 H, d, C*H*$_3$–CH, J = 6.6 Hz), 2.58 (16 H, br m, CH_2–COO), 3.08 (16 H, t, Ar–CH_2, J = 7.3 Hz), 4.05 (16 H, br m, CH_2O), 4.34 (4 H, q, CH_3–C*H*, J = 6.6 Hz), H_b collapsed, 6.94–6.96 (20 H, m, Ar–H and Ar–H_c) and 7.81–7.82 (16 H, m, Ar–H).

1,3,5,7(1,3)-Tetrabenzena-2,4,6,8-tetramethyl-$1^{4.5.6}$,$3^{4.5.6}$,$5^{4.5.6}$,$7^{4.5.6}$-dodecakis{5-[4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}cyclooctaphane (3)

Prepared as described for compound **2**. Quantities: **Ib** (91 mg, 0.15 mmol), 5-[4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenoxy]-pentanoic acid (1.35 g, 3.12 mmol), *N*-cyclohexyl-*N*′-[2-(4-methylmorpholinio)ethyl]carbodiimide toluene-*p*-sulfonate (1.44 g, 3.75 mmol), DMAP (50 mg); purification by column chromatography on silica gel [eluent: $CHCl_3$–MeOH (10:1)] and recrystallization (twice) from ethyl acetate–toluene (0.31 g, 37%), phase transitions (°C): cr 196 S_A 211 is (Found: C, 68.8; H, 7.9; N, 5.9; S, 7.0. $C_{320}H_{440}N_{24}O_{36}S_{12}$ requires C, 68.8; H, 7.9; N, 6.0; S, 6.9%); δ_H(500 MHz, $CDCl_3$, 25 °C, flattened cone conformation) 0.85 (36 H, t, C*H*$_3$–CH_2, J = 6.6 Hz), 1.23–1.91 (264 H, m, CH_2), 1.47 (12 H, d, C*H*$_3$–CH, J = 6.1 Hz), 2.34–2.65 (24 H, m, CH_2–COO), 3.02 (24 H, br m, Ar–CH_2), 3.75–3.96 (24 H, m, CH_2–O), 4.29 (4 H, br q, CH_3–C*H*), 6.10 (2 H, s, Ar–H_{bh}), 6.79–6.86 (24 H, m, Ar–H), 7.36 (2 H, s, Ar–H_{bv}) and 7.69–7.76 (24 H, m, Ar–H).

1,3,5,7(1,3)-Tetrabenzena-$1^{4.6}$,$3^{4.6}$,$5^{4.6}$,$7^{4.6}$-octakis{5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-2,4,6,8-tetrapropylcyclooctaphane (4)

Prepared as described for compound **2**. Quantities: **IIa** (0.14 g, 0.21 mmol), 5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoic acid (1.20 g, 2.97 mmol), *N*-cyclohexyl-*N*′-[2-(4-methylmorpholinio)ethyl]carbodiimide toluene-*p*-sulfonate (1.50 g, 3.55 mmol), DMAP (50 mg); purification by column chromatography on silica gel [eluent: $CHCl_3$–MeOH (10:1)] and recrystallization from acetone–MeOH (80 mg, 10%), mp 126 °C (Found: C, 69.0; H, 7.7; N, 5.9; S, 6.9. $C_{216}H_{288}N_{16}O_{24}S_8$ requires C, 69.2; H, 7.7; N, 6.0; S, 6.8%); δ_H(500 MHz, $CDCl_3$, 25 °C, flattened cone conformation) 0.84–0.90 (36 H, 2 t, CH_3), 1.25–1.91 (160 H, m, CH_2), 2.35–2.66 (16 H, m, CH_2–COO), 3.05 (16 H, br m, Ar–CH_2), 3.92–3.99 (16 H, m, CH_2O), 4.16 (4 H, t, CH_2–C*H*, J = 7.1 Hz), 6.06 (2 H, s, Ar–H_{bh}), 6.88 (20 H, br m, Ar–H and Ar–H_c), 7.32 (2 H, s, Ar–H_{bv}) and 7.79 (16 H, br m, Ar–H).

1,3,5,7(1,3)-Tetrabenzena-$1^{4.5.6}$,$3^{4.5.6}$,$5^{4.5.6}$,$7^{4.5.6}$-dodecakis{5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoyloxy}-2,4,6,8-tetrapropylcyclooctaphane (5)

Prepared as described for compound **2**. Quantities: **IIb** (86 mg, 0.12 mmol), 5-[4-(5-nonyl-1,3,4-thiadiazol-2-yl)phenoxy]pentanoic acid (1.01 g, 2.50 mmol), *N*-cyclohexyl-*N*′-[2-(4-methylmorpholinio)ethyl]carbodiimide toluene-*p*-sulfonate (1.27 g, 3.00 mmol); purification by column chromatography on silica gel [eluent: $CHCl_3$–MeOH (10:1)] and recrystallization (twice) from acetone–toluene (50 mg, 8%), phase transitions (°C): cr 150 S_A 165 is (Found: C, 67.7; H, 7.5; N, 6.2; S, 7.0. $C_{304}H_{408}N_{24}O_{36}S_{12}$ requires C, 67.5; H, 7.6; N, 6.2; S, 7.1%); δ_H(500 MHz, $CDCl_3$, 25 °C, flattened cone conformation) 0.84–0.89 (48 H, 2 t, CH_3), 1.24–1.77 (232 H, m, CH_2), 2.44–2.64 (24 H, m, CH_2–COO), 3.03 (24 H, br m, Ar–CH_2), 3.76–3.95 (24 H, m, CH_2–O), 4.17 (4 H, t, CH_2–CH, J = 7.2 Hz), 6.15 (2 H, s, Ar–H_{bh}), 6.80–6.86 (24 H, m, Ar–H), 7.30 (2 H, s, Ar–H_{bv}) and 7.71–7.76 (24 H, m, Ar–H).

1,3,5,7(1,3)-Tetrabenzena-2,4,6,8-tetramethyl-$1^{4.5.6}$,$3^{4.5.6}$,-$5^{4.5.6}$,$7^{4.5.6}$-dodecakis{5-[4-(2-octylpyrimidin-5-yl)phenoxy]-pentanoyloxy}cyclooctaphane (6)

Prepared as described for compound **2**. Quantities: **Ib** (73 mg, 0.12 mmol), 5-[4-(2-octylpyrimidin-5-yl)phenoxy]pentanoic acid (0.96 g, 2.50 mmol), *N*-cyclohexyl-*N*′-[2-(4-methylmorpholinio)ethyl]carbodiimide toluene-*p*-sulfonate (1.27 g, 3.00 mmol), DMAP (50 mg); purification by column chromatography on silica gel [eluent: $CHCl_3$–MeOH (10:1)] and recrystallization (twice) from acetone (0.20 g, 33%), mp 168 °C (Found: C, 73.6; H, 7.8; N, 6.6. $C_{308}H_{392}N_{24}O_{36}$ requires C, 73.9; H, 7.9; N, 6.7%); δ_H(500 MHz, $CDCl_3$, 25 °C, flattened cone conformation) 0.86 (36 H, t, C*H*$_3$–CH_2, J = 6.6 Hz), 1.24–1.90 (192 H, m, CH_2), 1.47 (12 H, d, C*H*$_3$–CH, J = 7.1 Hz), 2.35–2.62 (48 H, m, CH_2–COO and Ar–CH_2), 3.75–3.95 (24 H, m, CH_2O), 4.28 (4 H, q, CH_3–C*H*, J = 6.8 Hz), 6.11 (2 H, s, Ar–H_{bh}), 6.78–6.91 (24 H, m, Ar–H), 7.36 (2 H, s, Ar–H_{bv}) and 8.22–8.48 (48 H, m, Ar–H).

Acknowledgements

This work was supported by the BASF-AG, the BMFT and the Fonds der Chemischen Industrie.

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Paper 6/01725H
Received 11*th March* 1996
Accepted 11*th April* 1996