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Liquid crystalline paracyclophane derivatives

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Various paracyclophane derivatives incorporating 4,4′-biphenyl, 2,5-diphenyl-1,3,4-thiadiazole, phenyl benzoate and 2,6-disubstituted naphthyl rigid cores were synthesized and their mesomorphic behaviour was studied using polarizing microscopy, DSC and X-ray diffraction. Most of these macrocyclic compounds possess liquid crystalline properties with unexpectedly high clearing temperatures compared to those of conventional calamitic mesogens. In this way, the coupling of two appropriate rigid units using flexible chains to form a macrocycle constitutes a new and powerful approach towards mesophase induction and stabilization. The types of mesophase formed by these macrocycles do not depend only on the nature of the bridging chains, but also strongly on the structure of the rigid aromatic system. The smectic A phase and the E phase are formed by polyetherbiphenylophanes. Polyethercyclophanes incorporating the 2,5-diphenylthiadiazole rigid core form nematic and smectic C phases. The nematic phase is the only mesophase when the rigid core is the phenyl benzoate unit. No mesomorphic properties could be detected for macrocycles which featured either the benzyl phenyl ether moiety or the 2,6-disubstituted naphthalene unit in their constitution.

1. Introduction

Most liquid crystalline materials consist of form-anisotropic (calamitic or discotic) single molecules, associates or polymeric compounds. Much less attention has been focused on mesogenic dimers, which feature two rigid units in their constitution. In these chain-like dimers, the anisotropic units may be connected via their terminal chains [1] or via laterally attached groups (Siamese twins) [2, 3]. Percec has recently reported macrocyclic compounds [4] which contain flexible mesogenic units. These compounds display slightly increased mesophase stabilities when compared with the analogous non-cyclic main chain oligomers.

We have recently reported the synthesis of liquid crystalline polyetherbiphenylophanes [5]. These compounds may be regarded as cyclic dimers, obtained by joining two 4,4′-disubstituted biphenyl rigid cores together by two chains.

2. Biphenylophane derivatives

The transition temperatures of the polyether biphenylophane **1a**, as well as those of its acyclic counterparts **2** [6] and **3** are compared in figure 1.

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Unlike its acyclic counterpart, 4,4′-bis-(1,4,7-trioxaoctyl)biphenyl **3** which does not form a mesophase at all, the macrocyclic compound **1a**, possesses liquid crystalline properties. Moreover, the clearing temperature of 209°C is unexpectedly high when compared to those of conventional biphenyl mesogens [7]. The coupling of two appropriate rigid units via flexible linking chains to yield cyclic compounds seems to constitute a new and powerful approach towards mesophase induction and stabilization. In order to investigate the generality of this observation we have synthesized a number of compounds with structures related to **1a**, but having linking polyether chains of different lengths (**1b–1d** in figure 2) [5].

The shortening of one bridging chain (**1b**) increases the melting temperature as well as the clearing temperature. Lengthening of the linking polyether chains (**1c**) lowers the clearing and melting temperatures. Compound **1d** is a constitutional isomer of **1a**, containing one longer and one shorter polyether chain. This 'desymmetrization' leads, as expected, to a lower melting and clearing temperature and a smaller mesomorphic range. The type of mesophase exhibited is not affected by varying the length of the linking polyether chains.

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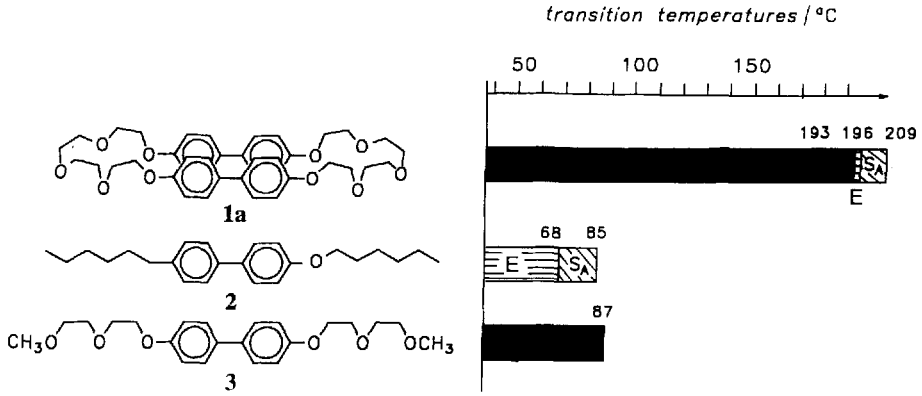


Figure 1. Comparison of the thermotropic properties of the polyethercyclophane **1 a** with those of the structurally related biphenyl derivatives **2** [6] and **3** (black areas indicate the crystalline state).

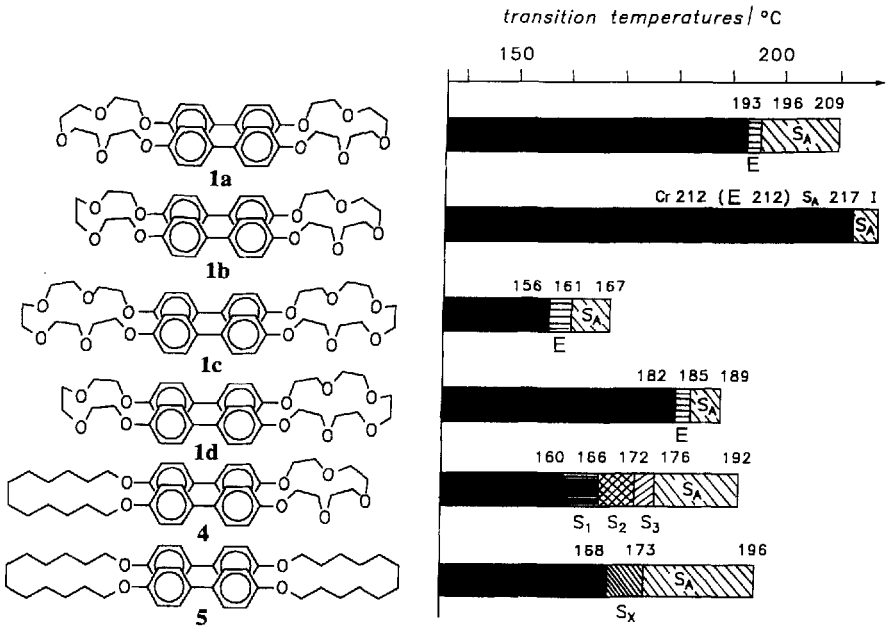


Figure 2. Comparison of the thermotropic properties of the biphenylophane derivatives **1 a–d**, **4** and **5** (black areas indicate the crystalline state).

For example, on cooling the isotropic liquid of compound **1 d** down to 189°C, a rapid formation of bâtonnets can be observed. These then coalesce to a focal-conic fan-like texture with pseudo-isotropic areas indicating a smectic A mesophase. At 185°C the focal-conic texture changes to an arced focal-conic texture, while the homeotropic areas which appeared dark originally, start to show birefringent platelet areas with transparent platelets overlapping each other. This feature is unique for the crystal E phase. Further cooling leads to crystallization at 180°C.

This designation of the mesophases was additionally confirmed by X-ray investigations. The Guinier pattern of compound **1 d** at 188°C shows the expected interferences for the S_A phase. The low temperature phase, assumed to be an E phase by way of texture observations, exhibits the inner layer reflection and several outer interferences (see figure 3). These interferences can be indexed assuming an orthorhombic cell. Table 1 displays the observed reflections and the calculated lattice parameters.

Further investigations have shown [5] that one or both of the polyether linking chains can be replaced by aliphatic polymethylene chains without a significant decrease of the clearing temperature (**4** and **5** in figure 2).

Interestingly, however, as the nature of the bridging links in these biphenylophane derivatives becomes more aliphatic, the types of smectic mesophase observed

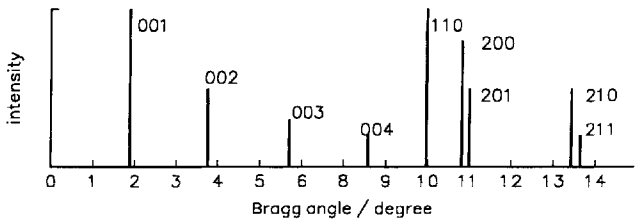


Figure 3. Schematic plot of observed interferences in the E phase of compound **1 d** at 183°C.

Table 1. Structural parameters of the E phase of **1 d**.

θ_{exp}/°	θ_{calc}/°	$\Delta\theta$	hkl
2·025	–	–	001
4·068	–	–	002
6·131	–	–	003
8·162	–	–	004
9·656	–	–	110
10·593	–	–	200
10·793	10·799	0·006	201
13·371	13·373	0·002	210
13·618	13·53	0·088	211

Calculated lattice parameters: a = 0·838 nm; b = 0·550 nm; c = 2·174 nm.

change. The smectic A phase is evident in all compounds, but the E phase of compounds **1a–1d** is no longer seen and additional low temperature smectic phases appear.

The DSC heating trace of compound **4** with one polyether chain and one aliphatic polymethylene linking chain is shown in figure 4.

It is obvious that several phase transitions take place. These are accompanied by substantial changes in the textures. The different textures observed by cooling compound **4** from the isotropic liquid are displayed in figure 5, suggesting for the S_A–S_3–S_2–S_1 phase sequence an S_A–S_I–S_F–G–polymorphism. Unfortunately, owing to the limited amount of material available, neither miscibility studies nor detailed X-ray investigations could be carried out to confirm this proposed phase sequence.

The replacement of both polyether chains by polymethylene chains gives compound **5** with a clearing temperature between those of compound **1 a** and **4**. The polymorphism is simplified, with only one low temperature mesophase below the S_A phase. The texture of this low temperature mesophase obtained by cooling the pseudo-isotropically oriented smectic A phase is given in figure 6.

3. Polyethercyclophanes with various mesogenic units

The types of mesophase formed by these macrocycles might be expected to depend not only on the nature of the bridging groups, but also on the structural type of the incorporated aromatic rigid core. Accordingly, we have synthesized cyclophane derivatives with various mesogenic units.

3.1. *Synthesis*

We have synthesized the macrocyclic esters **10 a** and **10 b** as outlined in scheme 1.

Starting with the etherification of the respective ethyleneglycol bis-*p*-tosylates with methyl 4-hydroxybenzoate and 4-benzyloxyphenol, respectively, two halves (**8** and **9**) of the final macrocycle were prepared via several steps (compound **9** is shown after removal of the benzyl protective groups). The final step of the reaction sequence involved the esterification of the benzoyl chlorides **8** with the diphenol **9** under conditions of high dilution. Owing to the lack of a template supporting the cyclization, the macrocycles **10 a** and **10 b** were obtained in very low yields (< 1 per cent).

The cyclophane **14** incorporating benzylether units was synthesized according to scheme 2.

To investigate whether the introduction of heteroaromatic rings into the rigid cores has the same strong influence on the types of mesophase for the macrocycles as that observed in the case of non-cyclic compounds, we synthesized a macrocycle similar to **1 b**, but containing two additional 2,5-disubstituted 1,3,4-thiadiazole units in the aromatic core.

The cyclophane containing 2,5-disubstituted 1,3,4-thiadiazole units (**19**) was made as outlined in scheme 3 using a one pot thiadiazole ring closure [8] as the key step. The macrocyclization was performed under conditions of high dilution, in the presence of an excess of potassium tosylate as a template. The yield in the final step (27 per cent) was considerably higher than that for our previous [5] cyclizations.

Extending our investigations into 'desymmetrized' macrocycles (i.e. macrocycles incorporating two different calamitic units) we prepared compound **22** in which one biphenyl unit of the prototype biphenylophane **1 a** is replaced by a 2,6-naphthyl unit.

The synthesis of **22** was easily achieved, following the reaction pathway given in scheme 4, in relatively high yield (27·1 per cent).

3.2. *Results and discussion*

As we expected, the structural variation of the calamitic units in the polyether cyclophanes has a strong impact on the mesomorphic properties (see table 2).

The macrocyclic phenyl benzoates **10 a** and **10 b** do not form smectic phases, but exhibit instead a nematic phase with significantly lower clearing temperatures than the biphenylophane derivatives **1 a–d**. However, the mesophase stabilizing effect of cyclization is still clear when one compares **10 b** with the conventional non-cyclic phenyl benzoate **7** [9]. Interestingly, replacement

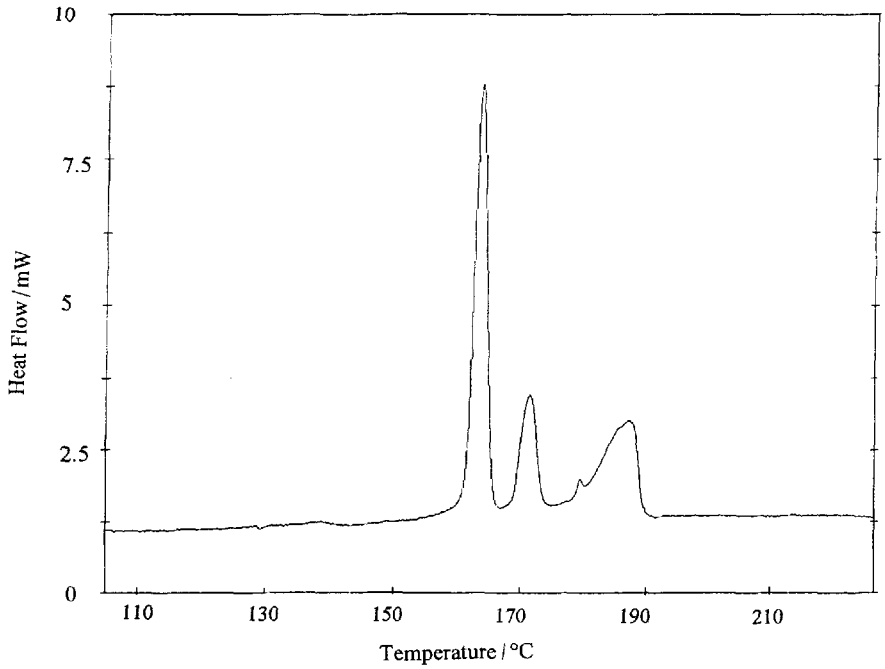
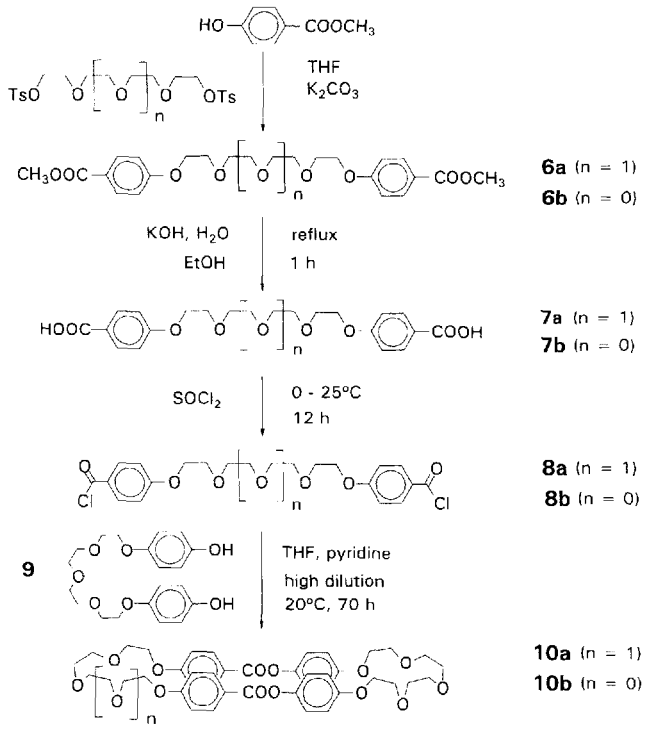
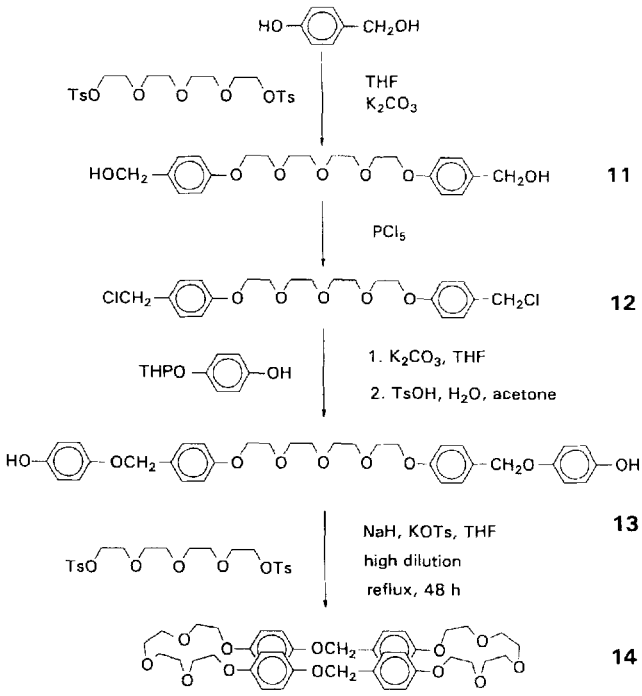


Figure 4. DSC heating trace (10 K min^{-1}) of compound **4**.

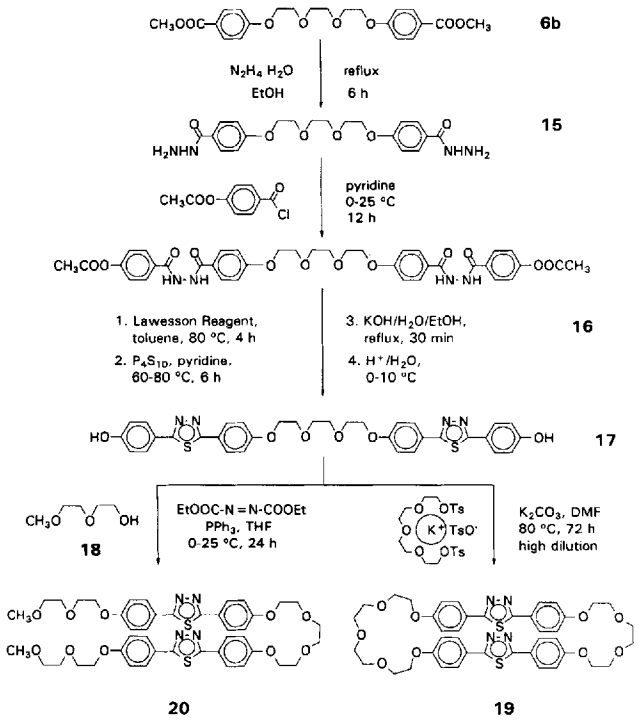


Scheme 1. Synthesis of the polyethercyclophanes **10a** and **b**.



Scheme 2. Synthesis of the cyclophane **14**.

of the carboxylic groups by the more flexible oxymethylene groups (**14**) leads to a macrocycle without mesomorphic properties. From the results obtained so far, we conclude that the type of mesophases exhibited by the macrocycles is strongly influenced by the structure of the rigid aromatic core units. The introduction of a thiadiazole unit into the rigid part of the mesogenic molecules is a powerful tool in the synthesis of liquid crystals with smectic C phases [10, 11]. As we had



Scheme 3. Synthesis of the thiadiazole derivatives **19** and **20**†.

hoped, our macrocycle **19**, incorporating the two 2,5-diphenyl-1,3,4-thiadiazole units indeed exhibits a smectic C phase, with a transition to a nematic phase at 221°C. The clearing temperature could not be determined because of the onset of decomposition at $T > 330$°C. Nevertheless, the mesophase stabilizing effect of the cyclization becomes clear when comparing **19** with the now acyclic liquid crystalline thiadiazole derivative **20** which was synthesized from the same precursor **18** and which consists of two identical mesogenic moieties connected via only one chain. The ring closure leads to a mesophase stabilization of more than 120°C for the nematic phase and 66°C for the smectic C phase.

Guinier diffraction experiments on compounds **19** and **20** confirm the observed S_C phase, showing the required inner layer reflection and the diffuse outer scattering. In the nematic phase, diffuse inner and outer reflection have been detected. The diffraction pattern observed for an oriented sample of compound **20** in the S_C phase shows crescent-like reflections (and their second order) in the small angle region and diffuse scattering in the wide angle region. The maxima of both scatterings are not perpendicularly aligned with each other, indicating that the molecules must be tilted. The calculated *d*-values and tilt angles are given in table 1. In the nematic phase of an oriented sample of compound **20**, cybotactic groups have been observed. If one compares the *d*-values of compounds **19** and **20** in the S_C phases, it is clear that the layers of compound **20** have a thickness about twice that of compound **19**. This means, that the molecules of compound **20** arrange themselves in a stretched, extended molecular conformation in this phase.

To widen our investigations, it was considered interesting to synthesize and examine mesogenic cyclophanes with two different aromatic units to see how the physical properties of the different mesogenic cores affect the properties of the new macrocyclic liquid crystal. As a first example of such a 'desymmetrized' macrocycle, we prepared **22** in which one biphenyl unit of the prototype biphenylophane **1** is replaced by a 2,6-naphthyl unit. This change to the molecular structure lowered the melting point by 43°C, but unfortunately, also caused the loss of the liquid crystalline properties.

In conclusion, from the results obtained so far, we have shown that the combination of suitable mesogenic groups into macrocycles will generally have an enormous mesophase stabilizing effect. The CPK model of compound **1c** is shown in figure 7.

By inspection of this molecular model we conclude that increased molecular form-anisotropy is not responsible for the significant mesophase stabilization observed. It seems more likely that the reason for this results from the restricted mobility of the now linked calamitic units. The types of mesophase formed by these macrocycles depend strongly on the nature of the linking chains, as well as on the type of the incorporated rigid core.

4. Experimental

4.1. *General considerations*

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP-200, AC 300 and an AMX 400 spectrometer, respectively, with tetramethylsilane as internal standard. Transition temperatures were determined using a Mettler FP HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope, and were confirmed by calorimetric measurements with a Perkin–Elmer DSC-7. Mass spectra were recorded on an AMD 402 mass spectrometer (EIMS, 70 eV) and on a Kratos MS80RF mass spectrometer (FABMS), accelerating voltage 3 kV.

A 3-nitrobenzyl alcohol matrix was used for the latter. Thin-layer chromatography was performed on TLC aluminium sheets (silica gel 60 F_{254}) from Merck and developed by using a solution of 3′,3″-dibromothymolsulfonphthalein, KOH in EtOH/H_2O, and NH_3 or UV light. Silica gel 60 (0·063–0·200) from Merck was used

† Recently we found, that the yield of **20** can be increased by etherification of **17** with the tosylate of **18** and K_2CO_3 in DMF, for details see Experimental section.

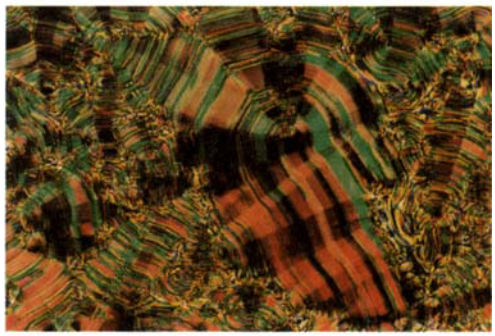
(*a*)

(*b*)

(*c*)

Figure 5. Optical photomicrographs of the textures of compound **4** as obtained by cooling from the isotropic melt (crossed polarizers) (*a*) at 178°C (S_A), (*b*) at 173°C (S_3), (*c*) at 171°C (S_2), (*d*) at 165°C (S_1) and (*e*) at 163°C (crystalline).

(*d*)



(*e*)

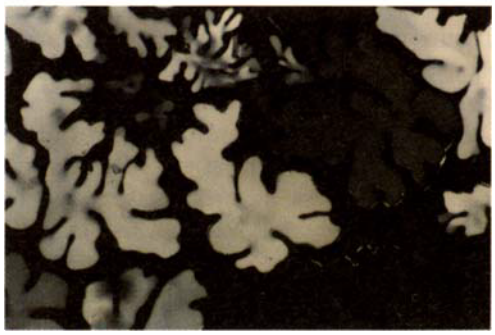
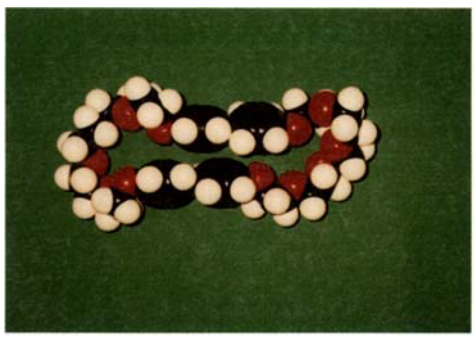
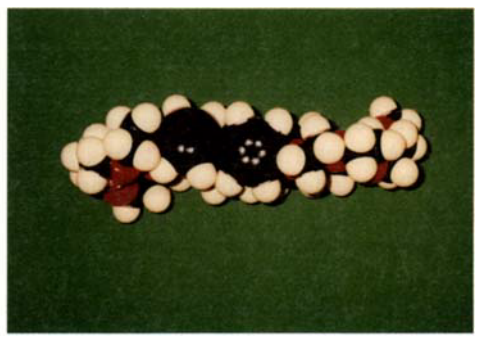


Figure 6. Optical photomicrograph of the texture observed at the transition from the smectic A phase (homeotropically oriented sample between crossed polarizers) to the low temperature mesophase of compound **5** at 173°C.

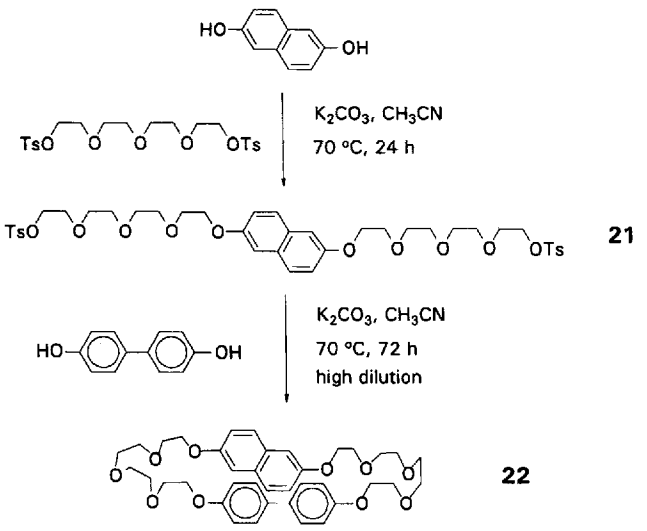


(*a*)



(*b*)

Figure 7. CPK model of compound **1c**.



Scheme 4. Synthesis of the paracyclonaphthalenophane **22**.

for column chromatography. Solvents were purified and dried according to standard procedures [12].

4.2. *Synthesis of paracyclophanes* **10a** *and* **10b**

4.2.1. *Dimethyl 4,4'-(1,13-diphenyl-1,4,7,10,13-pentaoxatridecane)dicarboxylate* **6a**

K_2CO_3 (11·1 g, 80·0 mmol) was added to a solution of methyl 4-hydroxybenzoate (6·7 g, 44·0 mmol) in dry THF (100 ml) with stirring. The mixture was heated to reflux and a solution of tetraethylene glycol di-*p*-tosylate (10·0 g, 20·0 mmol) in dry THF (250 ml) was added dropwise over 1 h. The mixture was stirred at 50–60°C for 9 h, allowed to cool to room temperature and filtered. The solid residue was extracted with CH_2Cl_2 (3 × 150 ml). The THF solution was evaporated to dryness and the residue was dissolved in the CH_2Cl_2 solution obtained previously. The solution was washed with H_2O, dilute HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The resulting solution was dried over Na_2SO_4. Removal of the solvent *in vacuo* gave an oily residue which was treated with diethyl ether leading to precipitation of the crude product. This was purified by two recrystallizations from *n*-hexane/ethyl acetate to give pure **6a** as a white solid. Yield 21·5 g (77·6 per cent); m.p. 68–70°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7{\cdot}79$ (m, 4H, H-aromatic), 6·92 (m, 4H, H-aromatic), 4·16 (t, 4H, α-CH_2–O–, $^3J = 4{\cdot}8$ Hz), 3·90–3·84 (m, 4H, β-CH_2–O–), 3·88 (s, 6H, O–CH_3), 3·76–3·66 (m, 8H, γ,δ-CH_2–O–). ^{13}C NMR (75·5 MHz, $CDCl_3$): δ = 166·8, 162·6, 131·5, 122·8, 114·2, 70·9, 70·7, 69·6, 67·6, 51·8. FABMS *m/z* (relative intensity, per cent): 463 $[M + H]^+$ (15), 431 (100), 223 (8), 179 (42).

4.2.2. *4,4'-(1,13-Diphenyl-1,4,7,10,13-pentaoxatridecane)dicarboxylic acid* **7a**

A solution of NaOH (0·39 g, 10·0 mmol) in H_2O (2 ml) was added to a suspension of **6a** (0·92 g, 2·0 mmol) in MeOH (20 ml). The mixture was heated under reflux for 1 h and after cooling to room temperature, the solvent was evaporated. The residue was dissolved in H_2O (30 ml) and acidified by careful addition of concentrated HCl. The white precipitate was filtered off and washed three times with H_2O (3 × 50 ml). The crude product was recrystallized from CH_3COOH/CH_3CN to afford pure **7a** as a fine white powder. Yield 0·76 g (87·5 per cent); m.p. 191°C. Elemental analysis. Found (calculated for $C_{22}H_{26}O_9$): C 60·93 per cent (60·82 per cent), H 6·11 per cent (6·03 per cent). ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 12{\cdot}60$ (s, COOH, weak), 7·87 (m, 4H, H-aromatic), 7·00 (m, 4H, H-aromatic), 4·14 (t, 4H, α-CH_2–O–, $^3J = 4{\cdot}7$ Hz), 3·74 (t, 4H, β-CH_2–O–, $^3J = 4{\cdot}7$ Hz), 3·62–3·40 (m, 8H, β,γ-CH_2–O–). ^{13}C NMR (75·5 MHz, DMSO-d_6): δ = 167·1, 162·1, 131·4, 123·1, 114·3, 70·0, 69·9, 68·8, 67·5. FABMS *m/z* (relative intensity, per cent): 457 $[M + Na]^+$ (43), 435 $[M + H]^+$ (24), 417 (100), 391 (19), 369 (56), 337 (9).

4.2.3. *4,4'-(1,13-Diphenyl-1,4,7,10,13-pentaoxatridecane)dicarbonyl chloride* **8a**

A suspension of **7a** (1·09 g, 2·5 mmol) in $SOCl_2$ (30 ml) was stirred at 60°C until the gas evolution ceased and a clear solution was obtained. The excess of $SOCl_2$ was evaporated to give an oily residue which was dissolved in dry toluene (30 ml). The solvent and any remaining $SOCl_2$ were removed *in vacuo* to afford crude **8a** in quantitative yield; this was used in the next reaction step (synthesis of **10a**) without further purification.

4.2.4. *1,4,7,10,13,21,28,31,34,37,40,47-Dodecaoxa-20,48-dioxo[13.2.13.2]paracyclophane* **10a**

A solution of **8a** ($n = 1$, scheme 1) (1·18 g, 2·5 mmol) and 1,11-bis(4-hydroxyphenoxy)-3,6,9-trioxaundecane (0·95 g, 2·5 mmol) in dry THF (360 ml) was added dropwise to a stirred solution of dry pyridine (20 ml) and 4-dimethylaminopyridine (0·20 g, 1·6 mmol) in dry THF (150 ml) at 20°C over 18 h. The solution was then stirred at this temperature for a further 52 h. The THF was removed *in vacuo*, and the oily residue was partitioned between $CHCl_3$ and dilute HCl. The organic layer was separated and washed with a small amount of H_2O and saturated aqueous NaCl. After drying over Na_2SO_4 the solvent was evaporated and the resulting oil was subjected to column chromatography (SiO_2; CH_2Cl_2/Et_2O, 4:1). The crude product obtained was further purified by several recrystallizations from EtOH and hexane/ethyl acetate (1:1) to afford pure **10a** in the

Table 2. Phase transitions, associated temperatures and transition enthalpies [kJ mol $^{-1}$] (lower lines in brackets of the paracyclophane derivatives **10**, **14**, **19**, **20** and **22**, and the structurally related phenyl benzoate **23** [9].

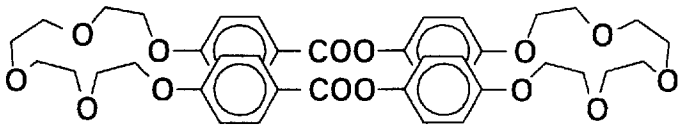
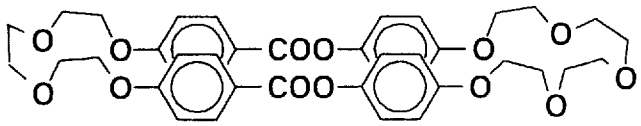
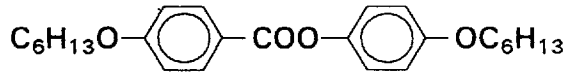
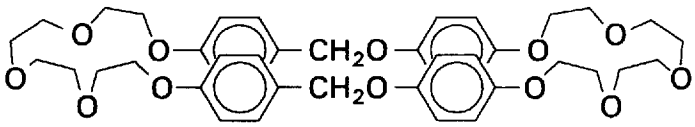
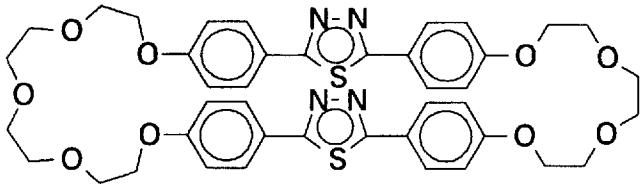
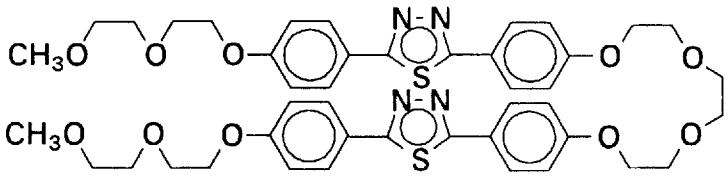
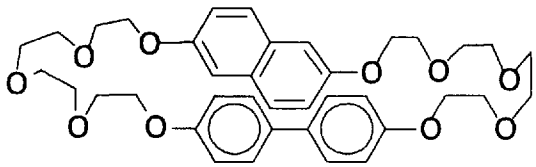
Compound	Structure	Phase transition/°C
10a		Cr 135 N 162 I
10b		Cr 145 N 172 I (55·3) (1·8)
23		Cr 64 N 90 I
14		Cr 148 I
19		Cr 168 S_C 221 N 330 dec. (39·9) (1·7)
20		Cr 139 S_C 155 N 207 I (30·5) (3·6) (2·1)
22		Cr 148 I (69·9)

Table 3. Structural parameters of the S_C phases of compounds **19** and **20** (*L* was estimated using CPK models).

Compound	θ/°C	*d*/nm	*L*/nm	Tilt angle/°C
19	180	1·92	2·6	≈42
20	150	3·92	5·1	≈44

form of small white crystals. Yield: 5·0 mg (0·3 per cent); transitions (°C): Cr 135 N 162 I. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8{\cdot}00$ (m, 4H, H-aromatic), 6·98 (m, 4H, H-aromatic), 6·89–6·77 (m, 8H, H-aromatic), 4·09 (t, 4H, $^3J = 8{\cdot}0$ Hz, α-CH_2–O–), 4·03 (t, 4H, $^3J = 8{\cdot}0$ Hz, α′-CH_2–O–), 3·95–3·85, (m, 8H, β,β′-CH_2–O–), 3·79–3·68 (m, 16H, γ,γ′,δ,δ′-CH_2–O–). FABMS *m/z* (relative intensity, per cent): 799 $[M + Na]^+$ (17), 777 $[M + H]^+$ (100), 641 (9), 597 (9), 553 (7), 509 (19), 417 (12), 401 (35), 373 (6).

4.2.5. *1,4,7,10,13,20,28,31,34,37,45-Decaoxa-21,44-dioxo[13.2.10.2]paracyclophane* **10b**

Compound **10b** was prepared from compound **8b** using an analogous procedure to that for **10a**. Yield 3·0 mg (0·6 per cent); transitions (°C): Cr 145 N 172 I. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7{\cdot}99$ (m, 4H, H-aromatic), 6·99 (m, 4H, H-aromatic), 6·88–6·75 (m, 8H, H-aromatic), 4·13–4·05 (m, 4H, α-CH_2–O–), 4·05–3·97 (m, 4H, α′-CH_2–O–), 3·94–3·86 (m, 8H, β,β′-CH_2–O–), 3·80–3·77 (m, 12H, γ,γ′,δ-CH_2–O–). ^{13}C

NMR (75·5 MHz, $CDCl_3$): δ = 164·9, 162·2, 156·4, 144·0, 132·1, 123·9, 122·6, 115·1, 114·3, 71·1, 71·0, 70·0, 69·7, 69·6, 68·0, 67·6. FABMS *m/z* (relative intensity, per cent): 755 $[M+Na]^+$ (4), 733 $[M+H]^+$ (100), 641 (5), 597 (9), 553 (10), 509 (9), 465 (22), 373 (18), 357 (39), 329 (10).

4.3. *Synthesis of the paracyclophane* **14**

4.3.1. *4,4'-Bis(4-hydroxymethylphenyl)-1,4,7,10,13-pentaoxatridecane* **11**

K_2CO_3 (13·8 g, 0·1 mol) was added to a solution of 4-hydroxymethylphenol (5·6 g, 44·0 mmol) and tetraethylene glycol di-*p*-tosylate (10·0 g, 20·0 mmol) in dry acetonitrile (130 ml) with stirring. The mixture was heated to reflux for 5 h, allowed to cool to room temperature and filtered. The solid residue was extracted with acetone (3 × 150 ml). The combined solutions were evaporated and the oily residue was dissolved in ethyl acetate (150 ml). The solution was washed twice with dilute KOH and brine. The resulting solution was dried over Na_2SO_4. Removal of the solvent *in vacuo* gave an oily residue which was treated with diethyl ether (20 ml) leading to precipitation of the crude product. After filtration the product was washed with diethyl ether (10 ml) to give **11** as a white solid. Yield 4·2 g, (52 per cent); m.p. 80°C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7·26 (m, 4 H, H-aromatic), 6·87 (m, 4 H, H-aromatic), 4·56 (d, 4 H, $-CH_2-OH$, ^3J = 5·2 Hz), 4·08 (t, 4 H, α-CH_2-O, ^3J = 4·7 Hz), 3·84 (t, 4 H, β-CH_2-O-, ^3J = 4·7 Hz), 3·75–3·64 (m, 8 H, γ,δ-CH_2-O-), 2·11 (t, 2 H, $-OH$, ^3J = 5·2 Hz). ^{13}C NMR (75·5 MHz, $CDCl_3$): δ = 158·4, 133·4, 128·6, 114·7, 70·8, 70·7, 69·7, 67·5, 64·9. FABMS *m/z* (relative intensity, per cent): 406 $[M]^+$ (26), 389 (100), 371 (30), 359 (59), 239 (25), 193 (70).

4.3.2. *4,4'-Bis(4-chloromethylphenyl)-1,4,7,10,13-pentaoxatridecane* **12**

A solution of **11** (2·03 g, 5·0 mmol) in dry chloroform (20 ml) was added at 0–5°C to a stirred suspension of PCl_5 (2·29 g, 11 mmol). The mixture was stirred at this temperature for 20 h. The solvent and $POCl_3$ were evaporated and the oily residue was dissolved in methylene chloride (150 ml). The solution was washed twice with water and once with saturated aqueous $NaHCO_3$ and once with brine. After having dried the solution over Na_2SO_4, the solvent was evaporated and the resulting oil was subjected to column chromatography (SiO_2; light petroleum/ethyl acetate, 1:2). Evaporation of the solvent gave a colourless oil, which slowly solidified. Yield: 1·7 g (77 per cent); m.p. 42°C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7·29 (m, 4 H, H-aromatic), 6·88 (m, 4 H, H-aromatic), 4·55 (s, 4 H, $-CH_2-Cl$), 4·11 (t, 4 H, α-CH_2-O, ^3J = 4·8 Hz), 3·84 (t, 4 H, β-CH_2-O-, ^3J = 4·8 Hz), 3·76–3·65 (m, 8 H, γ,δ-CH_2-O-). ^{13}C NMR (75·5 MHz, $CDCl_3$): δ = 158·9, 130·0, 129·9, 114·9, 70·9, 70·7, 69·7, 67·6, 46·3. FABMS *m/z* (relative intensity, per cent): 443 $[M]^+$ (1), 243 (95), 199 (100), 155 (37), 91 (45).

4.3.3. *4,4'-Bis[4-(4-hydroxyphenyl)oxymethylphenyl]-1,4,7,10,13-pentaoxatridecane* **13**

A mixture of **12** (1·5 g, 3·4 mmol), 4-tetrahydropyranyloxyphenol (1·36 g, 7·0 mmol), K_2CO_3 (1·65 g, 12 mmol) and KI (0·5 g) in THF (50 ml) was heated at reflux for 20 h, allowed to cool to room temperature and filtered. The solid residue was extracted with ethyl acetate (2 × 50 ml) and acetone (2 × 50 ml). After evaporation of the solvents, the residue was partitioned between ethyl acetate (100 ml) and water (50 ml). The organic layer was washed with 10 per cent HCl and saturated aqueous $NaHCO_3$. After drying over Na_2SO_4 and evaporation of the solvent, an oil was obtained, which was pure enough to be used for the deprotection by boiling for 2 h in an acetone/water mixture (10:1, 100 ml) in the presence of *p*-toluene sulphonic acid (20 mg). The solvent was evaporated and the residue was partitioned between chloroform (100 ml) and water (50 ml). The organic layer was washed with water and brine, dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (SiO_2; methylene chloride/diethyl ether, 4:1). Yield 0·12 g (6 per cent); m.p. 103°C. ^1H NMR (300 MHz, acetone-d_6): δ = 7·88 (s, 2 H, OH), 7·36 (m, 4 H, H-aromatic), 6·94 (m, 4 H, H-aromatic), 6·84 (m, 4 H, H-aromatic), 6·75 (m, 4 H, H-aromatic), 4·92 (s, 4 H, ar-CH_2-O), 4·15–4·09 (m, 4 H, α-CH_2-O), 3·84–3·78 (m, 4 H, β-CH_2-O-), 3·69–3·59 (m, 8 H, γ,δ-CH_2-O). ^{13}C NMR (75·5 MHz, $CDCl_3$): δ = 159·5, 152·2, 130·7, 129·9, 116·7, 116·5, 115·2, 71·3, 71·2, 70·8, 70·2, 68·3.

4.3.4. *1,4,7,10,13,21,28,31,34,37,40,47-Dodecaoxa[13.2.13.2]-paracyclophane* **14**

A solution of **13** (120 mg, 0·2 mmol) and tetraethylene glycol di-*p*-tosylate (100 mg, 0·2 mmol) in dry THF (80 ml) was added over 4 h at 70°C to a stirred mixture of NaH (300 mg, 7·2 mmol) and KOTos (920 mg, 4·0 mmol) in dry THF (20 ml) kept under an argon atmosphere. After the resulting mixture had been stirred for a further 48 h at this temperature, it was allowed to cool to room temperature. Methanol (10 ml) was added and the mixture was stirred for 10 min to destroy excess of NaH. The solvent was evaporated and the residue was partitioned between $CHCl_3$ (100 ml) and brine. After phase separation, the chloroform solution was washed with brine (50 ml) and dried over Na_2SO_4. Evaporation of the solvent gave a mixture which was separated by column chromatography (SiO_2; CH_2Cl_2/Et_2O, 10:4). Yield 1 mg (1 per cent); m.p. 148°C. ^1H NMR (200 MHz,

$CDCl_3$): $\delta = 7{\cdot}35$–$7{\cdot}15$ (m, 6H, H-aromatic), 6·88–6·72 (m, 10H, H-aromatic), 4·77 (s, 4H, ar-$\mathbf{CH_2}$–O), 4·08–3·96 (m, 8H, α,α′-$\mathbf{CH_2}$–O), 3·90–3·80 (m, 8H, β,β′-$\mathbf{CH_2}$–O–), 3·78–3·66 (m, 16H, γ,γ′δ,δ′-$\mathbf{CH_2}$–O). FABMS *m/z* (relative intensity, per cent): 787 $[M + K]^+$ (6), 748 (100), 613 (5), 460 (47), 371 (51).

4.4. *Syntheses of 1,4,7,10,13,31,34,37,40-nonaoxa[13]-paracyclo[0](2,5)thiadiazolo[0](1,4)pheno[10](1,4)-pheno[0](2,5)thiadiazolo[0](1,4)phenophane* **19** *and 1,10-bis{4-[5-(4-(1,4,7-trioxaoctyl)phenyl)-1,3,4-thiadiazol-2-yl]phenyl}-1,4,7,10-tetraoxadecane* **20**

4.4.1. *Dimethyl 4,4′-(1,10-diphenyl-1,4,7,10-tetraoxadecane)dicarboxylate* **6b**

Compound **6b** was synthesized by a procedure similar to that for **6a**, using methyl 4-hydroxybenzoate (33·4 g, 220 mmol) in dry THF (100 ml), K_2CO_3 (41·5 g, 300 mmol) and triethylene glycol di-*p*-tosylate (45·9 g, 0·10 mol). The crude product gave, after a recrystallization from EtOH, pure **6b** as a white solid. Yield 24·0 g (57·4 per cent); m.p. 105–107°C. Elemental analysis: found (calculated for $C_{22}H_{26}O_8$): C 63·19 per cent (63·15 per cent), H 6·39 per cent (6·26 per cent). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7{\cdot}97$ (m, 4H, H-aromatic), 6·92 (m, 4H, H-aromatic), 4·17 (t, 4H, $^3J = 4{\cdot}8$ Hz, α-$\mathbf{CH_2}$–O–), 3·92–3·85 (m, 10H, β-$\mathbf{CH_2}$–O–, –O–$\mathbf{CH_3}$), 3·75 (s, 4H, γ-$\mathbf{CH_2}$–O–). ^{13}C NMR (75·5 MHz, $CDCl_3$): $\delta = 166{\cdot}8$, 162·5, 131·6, 122·8, 114·2, 71·0, 69·6, 67·9, 67·6, 51·8. FABMS *m/z* (relative intensity, per cent): 439 $[M + Na]^+$ (4), 419 $[M + H]^+$ (20), 416 (17), 387 (100), 223 (7), 199 (6), 179 (38), 165 (9).

4.4.2. *4,4′-(1,10-Diphenyl-1,4,7,10-tetraoxadecane)dicarboxylic acid dihydrazide* **15**

Small portions of **6b** (10·5 g, 25·0 mmol) were added to a stirred solution of hydrazine hydrate (6·40 g, 200 mmol) in boiling EtOH (30 ml) over 5 h. After boiling the mixture for a further 16 h, more EtOH was added to dissolve any precipitated material. When a clear solution was obtained, it was allowed to cool to room temperature. The precipitate was separated by filtration and recrystallized from EtOH to give pure **15** in the form of fine white needles. Yield: 8·60 g (87·0 per cent); m.p. 198°C. Elemental analysis: found (calculated for $C_{20}H_{26}O_6N_4$): C 57·32 per cent (57·40 per cent), H 6·41 per cent (6·26 per cent), N 13·26 per cent (13·39 per cent). ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 9{\cdot}62$ (s, 2H, –C(O)–N**H**–), 7·78 (m, 4H, H-aromatic), 6·97 (m, 4H, H-aromatic), 4·42 (br, 4H, –$\mathbf{NH_2}$), 4·17–4·06 (m, 4H, α-$\mathbf{CH_2}$–O–), 3·77–3·71 (m, 4H, β-$\mathbf{CH_2}$–O–), 3·59 (s, 4H, γ-$\mathbf{CH_2}$–O–), ^{13}C NMR (75·5 MHz, $CDCl_3$): $\delta =$ 165·7, 160·7, 128·8, 125·6, 114·1, 70·0, 68·9, 67·4. FABMS *m/z* (relative intensity, per cent): 552 $[M + Cs]^+$ (34), 520 (27), 460 $[M + K]^+$ (47), 440 (12), 419 $[M + H]^+$ (48), 387 (100), 373 (21), 354 (23), 329 (17).

4.4.3. *4,4′-Bis[N′-(4-acetoxybenzoyl)hydrazocarbonyl]-(1,10-diphenyl-1,4,7,10-tetraoxadecane)* **16**

A solution of 4-acetoxybenzoyl chloride (4·95 g, 25·0 mmol) in dry THF (15 ml) was added dropwise to a stirred solution of **15** (4·18 g, 10·0 mmol) in a mixture of dry *N*-methyl-2-pyrrolidinone (60 ml) and dry pyridine (25 ml) over 10 min at 0–5°C. The solution obtained was allowed to equilibrate to ambient temperature and stirring was continued for 12 h at this temperature. The solution was then poured into ice/H_2O (400 ml) and kept in a refrigerator for 20 h. The precipitate was filtered off and washed several times with H_2O. The crude product was recrystallized from MeOH to give pure **16** as a white solid. Yield 6·10 g (82·2 per cent); m.p. 226–228°C. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta =$ 10·50, (s, 2H, –C(O)–N**H**–), 10·40 (s, 2H, –C(O)–N**H**–), 8·02–7·87 (m, 8H, H-aromatic), 7·29 (m, 4H, H-aromatic), 7·07 (m, 4H, H-aromatic), 4·20 (t, 4H, $^3J =$ 4·3 Hz, α-$\mathbf{CH_2}$–O–), 3·84–3·75 (m, 4H, β-$\mathbf{CH_2}$–O–), 3·64 (s, 4H, γ-$\mathbf{CH_2}$–O–), 2·32 (s, 6H, –$\mathbf{CH_3}$). ^{13}C NMR (75·5 MHz, DMSO-d_6): $\delta = 169{\cdot}0$, 165·4, 165·3, 161·4, 153·2, 130·3, 129·4, 129·0, 124·8, 122·0, 114·3, 70·0, 68·9, 67·5, 20·9, FABMS *m/z* (relative intensity, per cent): 743 $[M + H]^+$ (100), 701 (4), 549 (51), 531 (66), 460 (17), 387 (14), 357 (12).

4.4.4. *1,10-Bis{4-[5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl}-1,4,7,10-tetraoxadecane* **17**

A suspension of **16** (3·71 g, 5·0 mmol) and Lawesson reagent (5·26 g, 13·0 mmol) was heated at reflux under N_2 for 4 h. The solvent was removed *in vacuo* and the oily residue was dissolved in dry pyridine (25 ml). After addition of P_4S_{10} (2·20 g, 5·0 mmol), the mixture was stirred for 2 h at 60°C and for 4 h at 80°C. After cooling to room temperature, EtOH (2·5 ml) was added with stirring. After 10 min the mixture was poured into ice/H_2O (300 ml). The yellow precipitate was filtered off and washed twice with water. It was then suspended in a solution of KOH (1·12 g, 20·0 mmol) in MeOH and heated at reflux for 30 min. The solvent was evaporated off and the yellowish solid residue was dissolved in H_2O (200 ml). The solution was cooled in an ice/H_2O bath and then carefully acidified to pH 1 by the dropwise addition of concentrated HCl. The off-white precipitate was collected by filtration, washed with water and dried. After two recrystallizations from DMF/EtOH (1:3) pure **17** was obtained. Yield 2·55 g (76·8 per cent); m.p. 223–224°C. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta =$ 10·23 (br, 2H, –O**H**), 7·84 (m, 4H, H-aromatic), 7·78 (m, 4H, H-aromatic), 7·06 (m, 4H, H-aromatic), 6·91 (m, 4H, H-aromatic), 4·14 (t, 4H, $^3J = 4{\cdot}3$ Hz, α-$\mathbf{CH_2}$–O–),

3·76 (t, 4H, $^3J = 4·3$ Hz, β-CH_2–O–), 3·62 (s, 4H, γ-CH_2–O–). FABMS *m/z* (relative intensity, per cent): 655 $[M + H]^+$ (100), 504 (13), 440 (6), 385 (10), 341 (7).

4.4.5. *1,4,7,10,13,31,34,37,40-Nonaoxa[13]paracyclo[0](2,5)thiadiazolo[0](1,4)pheno[10](1,4)pheno[0](2,5)-thiadiazolo[0](1,4)phenophane* **19**

A solution of **17** (0·65 g, 1·0 mmol) and tetraethylene glycol di-*p*-tosylate (0·55 g, 1·1 mmol) in dry DMF (250 ml) was added dropwise with stirring to a suspension of K_2CO_3 (1·35 g, 10·0 mmol) and KOTs (2·11 g, 10·0 mmol) in dry DMF (50 ml) over 24 h at 80°C. The reaction mixture was stirred at this temperature for 48 h. The solvent was removed *in vacuo* and the residue was partitioned between $CHCl_3$ and dilute HCl. The organic layer was separated, washed with H_2O and saturated aqueous NaCl. After drying over Na_2SO_4 the solvent was evaporated and the residue was subjected to column chromatography (SiO_2; $CHCl_3$/MeOH, 49 : 1). The fractions containing **19** were combined, and after evaporation of the solvent recrystallized from DMF/EtOH (1 : 1) to give pure **19** in the form of fine white needles. Yield: 0·22 g (27·1 per cent); transitions (°C): Cr 168 S_C 221 N 330 I (dec.). Elemental analysis: found (calculated) for $C_{42}H_{44}O_9N_4S_2$): C 62·00 per cent (62·05 per cent), H 5·37 per cent (5·46 per cent), N 6·68 per cent (6·89 per cent). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7·73–7·63$ (m, 8H, H-aromatic), 6·87–6·77 (m, 8H, H-aromatic), 4·08–3·98 (m, 8H, α,α′-CH_2–O–), 3·96–3·83 (m, 8H, β,β′-CH_2–O–), 3·81–3·70 (m, 12H, γ,γ′,δ-CH_2–O–). ^{13}C NMR (75·5 MHz, $CDCl_3$): $\delta = 166·9$, 160·9, 129·2, 129·1, 122·9, 115·0, 114·9, 71·1, 70·8, 69·6, 67·8, 67·5. FABMS *m/z* (relative intensity, per cent): 813 $[M + H]^+$ (100), 460 (7), 391 (6).

4.4.6. *1,10-Bis{4-[5-(4-(1,4,7-trioxaoctyl)phenyl)-1,3,4-thiadiazol-2-yl]phenyl}-1,4,7,10-tetraoxadecane* **20**

K_2CO_3 (1·38 g, 10·0 mmol) was added to a solution of **17** (0·33 g, 0·5 mmol) and 3,6-dioxaheptyl *p*-toluenesulphonate (1·4 g, 5·0 mmol) in dry DMF (25 ml) kept under a nitrogen atmosphere. The mixture was stirred for 10 h at 70°C. After cooling to room temperature, the solvent was distilled off *in vacuo* and the residue obtained was partitioned between $CHCl_3$ (100 ml) and dilute HCl (50 ml). The organic layer was separated, washed with H_2O and saturated aqueous NaCl. After drying over Na_2SO_4, the solvent was evaporated off and the residue was recrystallized from EtOH/ethyl acetate to give pure **20** as white needles. Yield 0·21 g (48·9 per cent); transitions (°C): Cr 139 S_C 155 N 207 I. Elemental analysis: found (calculated for $C_{44}H_{50}O_{10}N_4S_2$): C 61·82 per cent (61·52 per cent), H 5·88 per cent (5·87 per cent), N 6·42 per cent (6·12 per cent). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7·91–7·81$ (m, 8H, H-aromatic), 7·01–6·91 (m, 8H, H-aromatic), 4·23–4·08 (m, 8H, α,α′-CH_2–O–), 3·92–3·82 (m, 8H, β,β′-CH_2–O–), 3·75 (s, 4H, γ′-CH_2–O–), 3·74–3·68 (m, 4H, γ-CH_2–O–), 3·61–3·54 (m, 4H, δ-CH_2–O–), 3·37 (s, 6H, –CH_3). ^{13}C NMR (75·5 MHz, $CDCl_3$): $\delta = 167·0$, 161·0, 129·3, 123·2, 123·1, 115·1, 71·9, 71·0, 70·8, 69·7, 69·6, 67·6, 59·1. FABMS m/z (relative intensity, per cent): 859 $[M + H]^+$ (100), 606 (12), 487 (13), 443 (10), 399 (16), 372 (37).

4.5. *Synthesis of 1,4,7,10,13,26,29,32,35,38-decaoxa[13·0]paracyclo[13](2,6)naphthalenophane* **22**

4.5.1. *2,7-Bis-[10-(4-toluenesulphonyloxy)-1,3,7,10-tetraoxadodecyl]naphthalene* **21**

K_2CO_3 (11·1 g, 80 mmol) was added to a stirred solution of tetraethylene glycol di-*p*-tosylate (100 g, 200 mmol) and 2,6-dihydroxynaphthalene (3·2 g, 20 mmol) in dry acetonitrile (30 ml) kept under an argon atmosphere. The temperature of the resulting mixture was raised to 80°C. After having stirred the reaction mixture for 18 h at this temperature, the solvent was removed *in vacuo*. The residue was extracted with toluene and the solution obtained was washed with water (3 × 50 ml) and saturated aqueous NaCl (50 ml). After having dried the solution over $CaCl_2$, the solvent was evaporated off and the resulting oil was subjected to column chromatography (SiO_2; light petroleum/EtOAc, 1 : 1). The crude product was recrystallized from pentane/ethyl acetate to afford pure **21** as a fine white powder. Yield 8·40 g (51·7 per cent); m.p. 63°C. Elemental analysis: found (calculated for $C_{40}H_{52}O_{14}S_2$): C 58·25 per cent (58·52 per cent), H 6·21 per cent (6·39 per cent), S 7·76 per cent (7·80 per cent). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7·79–7·73$ (m, 4H, H-aromatic), 7·61–7·56 (m, 2H, H-aromatic), 7·31–7·27 (m, 4H, H-aromatic), 7·14–7·06 (m, 4H, H-aromatic), 4·21–4·19 (m, 4H, –CH_2–O–Tos), 4·17–4·09 (m, 4H, –CH_2–O–naphth.), 3·90–3·85 (m, 4H, –CH_2–O–), 3·74–3·85 (m, 12H, –CH_2–O–), 3·56 (s, 8H, –CH_2–O–), 2·39 (s, 6H, –CH_3). EIMS *m/z* (relative intensity, per cent): 820 $[M]^+$ (5), 732 (10), 644 (8), 560 (19), 534 (11), 472 (7), 446 (7), 402 (6), 243 (11), 230 (11), 199 (100), 172 (37), 160 (24), 155 (69).

4.5.2. *1,4,7,10,13,26,29,32,35,38-Decaoxa[13·0]paracyclo[13](2,6)naphthalenophane* **22**

A solution of **21** (1·62 g, 2 mmol) and a solution of 4,4′-dihydroxybiphenyl (each in 100 ml of dry DMF) were added simultaneously over a 4 h period at 70°C to a stirred mixture of K_2CO_3 (2·80 g, 20 mmol) and KOTos (4·22 g, 20 mmol) in dry DMF (100 ml) kept under an argon atmosphere. After the resulting mixture had been

stirred for a further 60 h at this temperature, the solvent was distilled off *in vacuo* and the residue was partitioned between $CHCl_3$ and dilute HCl. The organic phase was separated and washed with dilute HCl and saturated aqueous NaCl (2 × 50 ml). After drying over Na_2SO_4, the solvent was evaporated off and the resulting oil was subjected to column chromatography (SiO_2; CH_2Cl_2/Et_2O, 3:1). The chromatographically purified product was recrystallized several times from CH_3CN/EtOH to afford pure **22** as fine white crystals. Yield 0·36 g (27·1 per cent); m.p. 148°C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7{\cdot}41$–$7{\cdot}36$ (m, 2 H, H-aromatic), 7·18–7·14 (m, 4 H, H-aromatic), 7·05–6·99 (m, 2 H, H-aromatic), 6·92–6·91 (m, 2 H, H-aromatic), 6·79–6·75 (m, 4 H, H-aromatic), 4·08–4·03 (m, 8 H, α,α′-CH_2–O–), 3·91–3·86 (m, 8 H, β,β′-CH_2–O–), 3·85–3·69 (m, 16 H, γ,γ′,δ,δ′-CH_2–O–). EIMS *m/z* (relative intensity, per cent): 662 $[M]^+$ (100), 618 (3), 574 (7), 530 (3), 486 (3), 443 (3), 344 (3), 331 (3), 318 (3), 257 (5), 239 (6), 213 (15), 187 (21).

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