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Self-organization of substituted azacrowns based on their discoid and amphiphilic nature

by C. MERTESDORF and H. RINGS DORF

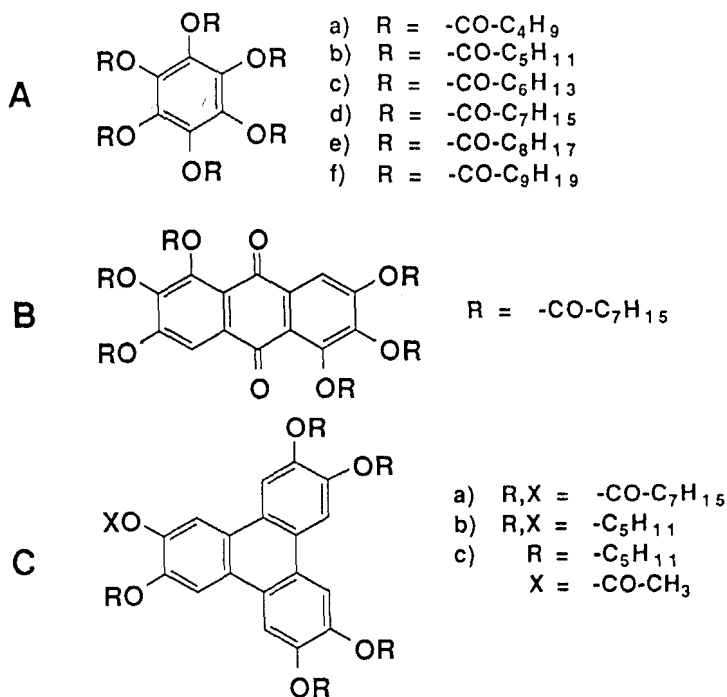
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Cyclame and hexacyclene derivatives, bearing four and six long-chain substituents respectively, were synthesized. They are discussed as monolayer-forming amphiphiles as well as liquid-crystalline-phase-forming thermotropic mesogens. The compounds investigated form ordered monolayers at the gas/water interface. In the monolayer the hydrophilic cyclic head group lies flat on the water surface, whereas the hydrophobic substituents are oriented perpendicularly with respect to the interface. Most derivatives fitted with aromatic substituents exhibit a solid condensed state exclusively. In contrast with this, solid condensed as well as expanded phases can be found when spreading the aliphatic-substituted compounds. In the latter case, the onset of the phase transition takes a bump-like shape, owing to kinetic reasons. A liquid-crystalline columnar order is only achieved with hexacyclenes bearing aromatic substituents, etherified with one alkyl chain. Besides this, the remaining derivatives melt from the crystalline state, transforming directly into the isotropic liquid, or show amorphous behaviour. Preliminary irradiating experiments in the columnar state of cinnamoyl-substituted hexacyclene Hex-7 were carried out in order to obtain polymeric tubes.

1. Introduction: Disc-like molecules as thermotropic and amphiphilic systems

It is well known that water-insoluble amphiphiles spontaneously form two dimensional monomolecular layers when spread at the air/water interface [1]. In addition, some of them are able to form thermotropic liquid-crystalline phases (e.g. phospholipids) [2]. Nevertheless, the spreading behaviour of amphiphilic molecules at interfaces and the determination of the intermolecular arrangement in 'classical' (e.g. rod-like) liquid-crystalline compounds have normally been investigated separately and have seldomly been viewed together. On the other hand, the amphiphilic properties of some polar rod-like thermotropic LCs have also been recognized, and spreading experiments have already been carried out [3-5]. Recently even the monolayer formation of the disc-like mesogens, benzene-hexa-*n*-alkanoates **A** [6-9], rufigallol-hexa-*n*-octanoate **B** [10], triphenylene derivatives **C** [7] and poly(oxysiliconephtalocyanines) [11], at air/water interfaces has attracted particular interest.

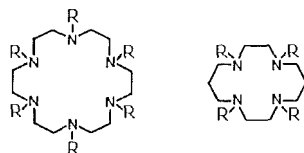
Early studies [6] describe the low-compressibility phase of disc-like benzene-hexa-*n*-alkanoates **A**(*a-f*) classically: all hydrophilic anchoring groups simultaneously face the water surface, resulting in a flat arrangement of the benzene ring with its short axis perpendicular to the air/water interface. According to recent investigations, another possible arrangement of disc-like LCs at the air/water interface, which is quite different from classical amphiphiles, has to be considered: in tightly packed low-compressibility phases the aromatic ring systems of the benzene-hexa-*n*-alkanoate



Disc-like mesogens that have been spread at the gas/water interface [6–11]

A(d) [7] the triphenylenes **C(a–c)** [7] and the anthraquinone derivative **B** [10] are oriented vertically with their short axis parallel to the water surface [7, 10, 11]. According to this arrangement, the aromatic cores adopt a close-packed configuration, leading to a two-dimensional columnar phase, like stems floating on the water.

Considering most of the discotic systems that have been spread so far (**A**, **B**, **C**), it is obvious that these compounds lack distinct amphiphilic properties. For that reason, further investigations studying the relation between the thermotropic nature and the spreading behaviour of discotic molecules require compounds with more pronounced distinction between the hydrophilic and the hydrophobic components as the essential parts of amphiphilic molecules. For these studies cyclic oligoamines fitted with long hydrocarbon chains may be suitable candidates.



hexacyclenes (Hex) cyclames (Cyc)

Lehn *et al.* [12] have already described the mesomorphic behaviour of hexa-(*p*-*n*-dodecyloxybenzoyl)hexacyclene. These macrocyclic mesogens are, like aromatic discotic systems [13], irregularly stacked in columns that are placed in a hexagonal array (D_{hd} phase [13] see figure 8).

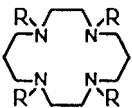
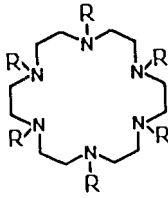
In this paper the synthesis and characterization of a series of acylated and sulphonated azocrowns, cyclame (1,4,8,11-tetraazacyclotetradecane) and hexacyclene

(1,4,7,10,13,16-hexaazacyclooctadecane), differing in the heterocyclic-ring size, are described. The characterization is performed with regard to the spreading behaviour on the one hand and the determination of the thermotropic LC properties on the other.

2. Synthesis and characterization of the phase behaviour in bulk

Tetra- and hexaacylated and sulphonated cyclic amines were synthesized by the reaction of cyclame and hexacyclene with respectively four and six equivalents of the different aliphatic and aromatic acid chlorides in *N,N*-dimethylformamide (DMF).

Table 1. Phase behaviour of cyclame- and hexacyclene derivatives in bulk

Hydrophilic head group		Hydrophobic tail	Hydrophilic head group
Cyclames (CYC)		Substituents R	Hexacyclenes (HEX)
			
Phase behaviour/°C			
c 115 i	1	$-\text{CO}-(\text{CH}_2)_{10}\text{CH}_3$	—
c 114 i	2	$-\text{CO}-(\text{CH}_2)_{12}\text{CH}_3$	c 107 i
c 114 i	3	$-\text{CO}-(\text{CH}_2)_{14}\text{CH}_3$	c 107 i
c 200 i	4	$-\text{CO}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_{11}\text{CH}_3$	c 108 D _{hd} 140 i
—	5	$-\text{SO}_2-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_{11}\text{CH}_3$	c 186 i
c 196 i	6	$-\text{CO}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_{13}\text{CH}_3$	c 106 D _{hd} 136 i
c 168 i	7	$-\text{CO}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_{13}\text{CH}_3$	c 217 D _{hd} 233 i
—	8	$-\text{CO}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_9\text{CH}_3$	c 237 D 245 i
glassy	9	$-\text{CO}-\text{C}_6\text{H}_3(\text{O}-(\text{CH}_2)_5\text{CH}_3)_2$	glassy
glassy	10	$-\text{CO}-\text{C}_6\text{H}_3(\text{O}-(\text{CH}_2)_8\text{CH}_3)_2$	glassy

The phase behaviour in bulk of the synthesized cyclame and hexacyclene derivatives is shown in table 1.

Only hexacyclene derivatives exhibit LC properties. Substitution of the cyclic hexacyclene moiety by one-fold etherified aromatic carbonic acids leads to thermotropic LC systems (Hex-4, Hex-6, Hex-7, Hex-8). Di- and tri-fold etherified benzoic acid amides (Cyc-9, Cyc-10, Hex-9, Hex-10) show amorphous behaviour and do not crystallize, even upon annealing. The remaining derivatives are high-melting crystalline compounds.

3. Characterization of the monolayer behaviour

Spreading experiments were performed with a computer-controlled film balance, equipped with two Wilhemy pressure pick-up systems [14]. All films were spread on pure water subphase. The water was distilled and purified by a Milli Q water-purification system (Millipore Corp.). Chloroform was used as a spreading solvent. The concentrations of the solutions were about 0.4 mg ml^{-1} . Compression rates of about $15 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ were used. The monolayer properties of all compounds were measured, except those derivatives containing aromatic substituents R (table 1) etherified with two and three alkyl chains (Cyc-9, Cyc-10, Hex-9, Hex-10).

All compounds investigated form ordered monolayers. Expanded as well as condensed states can be found, with pressure/area (Π/A) diagrams comparable to those of simple amphiphiles. A strong dependence of the phase transition on temperature and chain length has been observed, analogous to that of one- and two-chain amphiphiles. The collapse areas of Cyc-1, Cyc-2 and Cyc-3 are, as expected, independent of the chain length and are found to be equal to $82 \text{ \AA}^2 \text{ molecule}^{-1}$ (figures 1 and 2). This result fits well with the area requirement of four alkyl chains ($4 \times 20 \text{ \AA}^2 \text{ molecule}^{-1}$) in the all-*trans* conformation, which are oriented vertically to

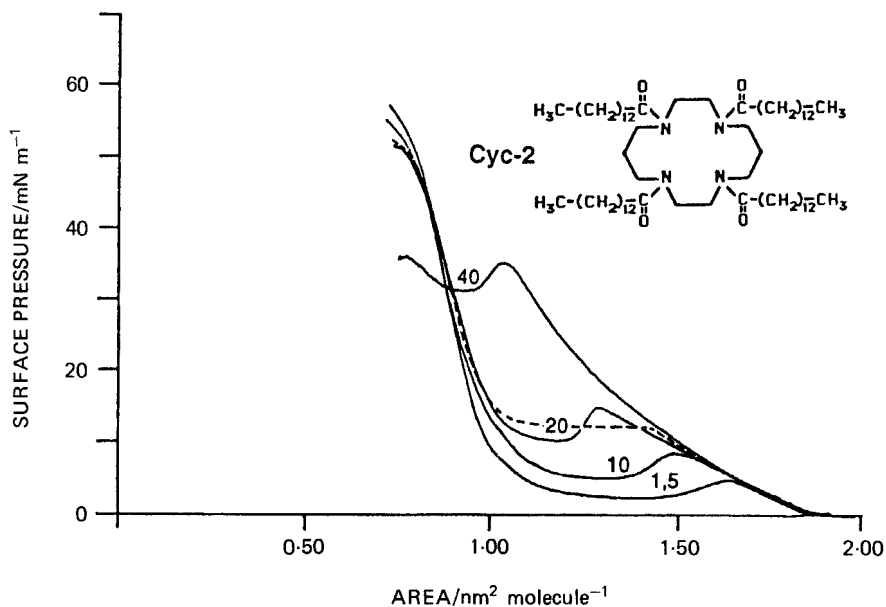


Figure 1. Surface-pressure/area diagram of Cyc-2 (temperatures in °C), dotted line shows slow compression ($1 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$) at 20°C .

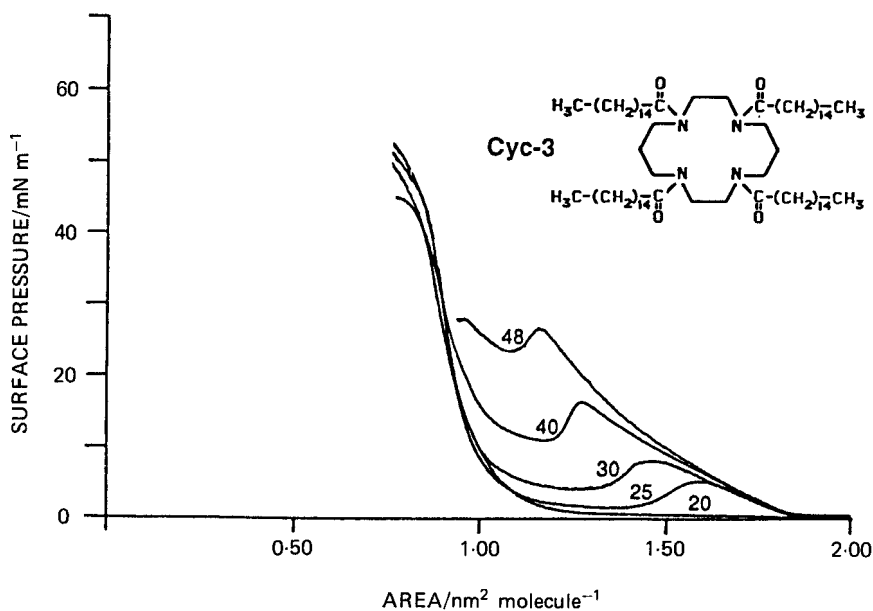


Figure 2. Surface-pressure/area diagram of Cyc-3 (temperatures in °C).

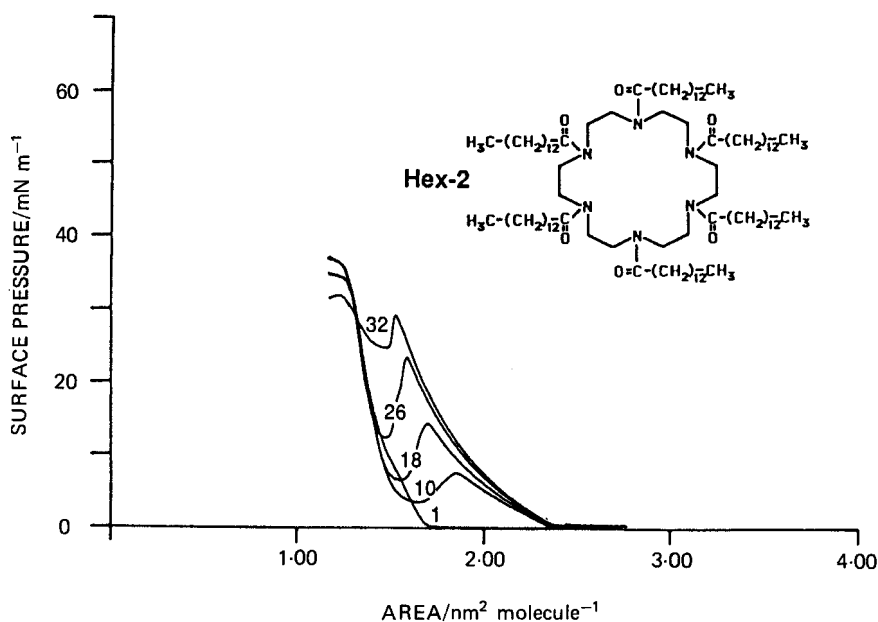


Figure 3. Surface-pressure/area diagram of Hex-2 (temperatures in °C).

the water surface. Consequently, this strongly suggests a molecular orientation with the heterocyclic moiety parallel to the water surface and the amide-bonds serving as polar anchor groups.

The most striking feature appearing in some Π/A diagrams (figures 1–3) is the existence of a bump at the beginning of the phase transition. This effect has also been

observed for diacetylenic compounds [15], and has been explained by the presence of diacetylenic oligomers in the monolayer.

Several possibilities have been investigated to elucidate the mechanism underlying the observations of such a bump in the surface-pressure isotherms of figures 1–3.

- (i) The presence of impurities has been ruled out. Cyc-2 and Hex-2, for example, were recrystallized several times, but no influence on their spreading behaviour could be established.
- (ii) To exclude the influence of incompletely acylated cyclic oligoamines in the product as well, Cyc-2 and Hex-2 were spread on an acidic subphase (0.01 N HCl, pH 2). A protonated amino group in the heterocycle should strongly affect the monolayer behaviour of these compounds. However, no difference in the shape of the isotherms could be detected.
- (iii) Variation of the compression speed indicates that the bump is due to kinetic effects: it was found to become smaller with decreasing compression speed, and vanishes, in the case of Cyc-2, when a speed of $1 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ is reached (figure 1, dotted line). Considering Cyc-2 (figure 1), the reduction of the sweep speed finally provides a clear first-order phase transition, with a curvature in the transition region nearly parallel to the area axis and a pronounced discontinuity marking the phase-transition point.

Presumably, a lattice rearrangement in the solid domains is responsible for the sudden drop in pressure, as indicated by preliminary results of fluorescence microscopy and electron diffraction.

Whether or not a conformational change in the flexible heterocyclic head group causes the lattice rearrangement responsible for the presence of this bump is difficult to show. With regards to this hypothesis, only speculations are possible so far. By means of electron diffraction, only rearrangements in the solid hydrocarbon periphery are detectable.

The time necessary to get rid of the bump in slow-compression-mode experiments is, as one may expect, much larger for Hex-2 and, in fact, exceeds the proper conditions for experimental measurements. Using, for example, a sweep speed of $0.5 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ (compression time 2090 min), the bump is still present but much less pronounced.

The value of $130 \text{ \AA}^2 \text{ molecule}^{-1}$ for the molecular cross-section of Hex-2 (figure 3) and Hex-3 (Π/A diagram not presented) at the collapse pressure strongly suggests that the orientation of the hexacyclene is similar to that postulated for the cyclame derivatives (see above): the heterocyclic head group is oriented in parallel to the interface, with its six amide bonds serving as polar anchor groups on the water surface. With respect to this, the six hydrocarbon chains are oriented perpendicular to the interface in a close-packed all-*trans* conformation (figure 4, cylindrical shape).

According to the interpretation given above, the molecules may change their structure at the phase-transition point from a discoidal to a cylindrical shape. This can be deduced from the areas per molecule occupied in each monolayer state (figures 1–3). In the expanded state, corresponding to the discoidal shape, the chains are more or less laterally extended from the heterocyclic core. This means that the molecule is taking a more or less flat pancake-like structure on the water surface.

All aromatic amides investigated, except Cyc-4 and Cyc-6, exhibit exclusively low-compressibility, condensed phases. The same molecular orientation as that postulated above for Cyc-1, Cyc-2, Cyc-3, Hex-2 and Hex-3 can be established for

these aromatic derivatives in the condensed state. Owing to the interactions of the bulky aromatic groups, the collapse areas are increased in comparison with those of the aliphatic *n*-acyl derivatives. For example, the collapse area obtained in the case of liquid-crystalline Hex-6 ($160 \text{ \AA}^2 \text{ molecule}^{-1}$, figure 5) is $30 \text{ \AA}^2 \text{ molecule}^{-1}$ larger than in the case of Hex-2 ($130 \text{ \AA}^2 \text{ molecule}^{-1}$, figure 3). The same tendency can be observed for Cyc-2 and Cyc-6 (figures 1 and 6).

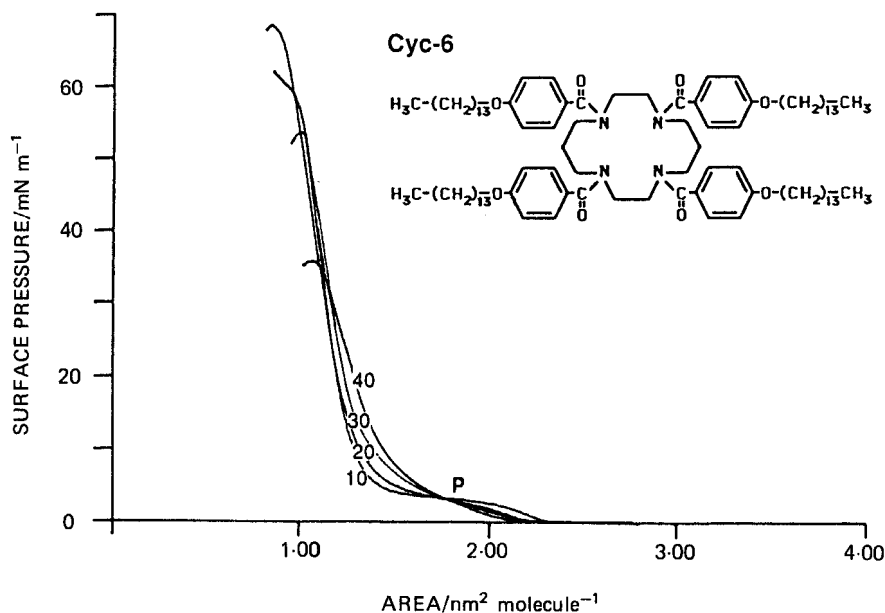


Figure 6. Surface-pressure/area diagram of Cyc-6 (temperatures in °C).

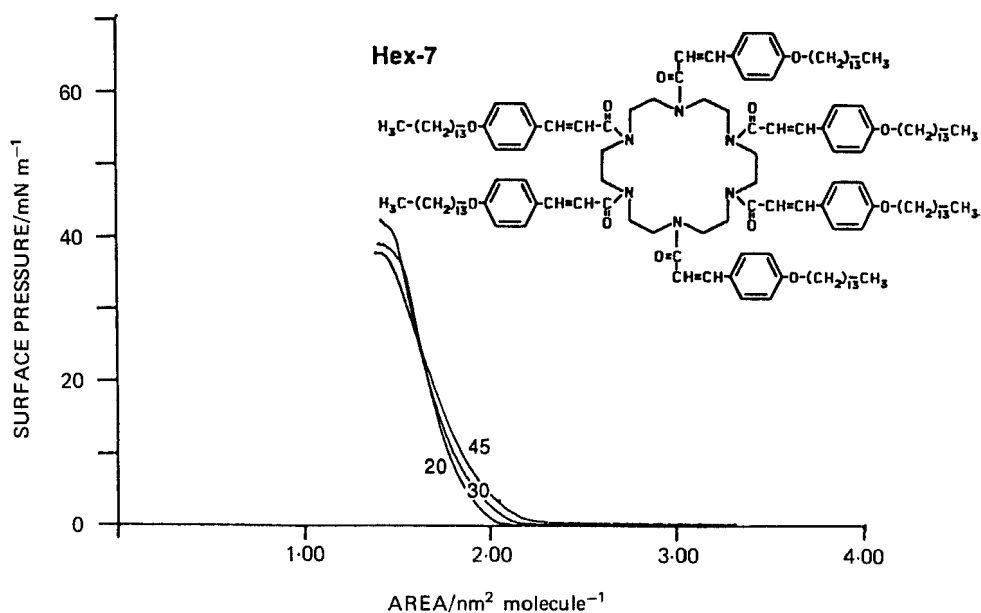


Figure 7. Surface-pressure/area diagram of Hex-7 (temperatures in °C).

The packing situation seems to be improved when spreading the thermotropic cinnamoyl derivative Hex-7 (figure 7), as deduced from the lower compressibilities and a decreased collapse area of $150 \text{ \AA}^2 \text{ molecule}^{-1}$.

At low pressures and high areas, the Π/A diagrams of Cyc-4 (Π/A diagram not presented) and Cyc-6 (figure 6) exhibit an unusual feature: the isotherm measured at 10°C shows a phase transition from an expanded to a solid-condensed state. Usually the surface pressure where the phase transition takes place increases with increasing temperature. However, in this case, the pressure corresponding to the plateau region is temperature-independent, and the onset of the surface pressure of the 'expanded' state is shifted towards smaller molecular areas as a function of increasing temperature. The isotherms recorded at different temperatures intersect at a distinguished point 'P', which is dependent on chain length.

4. Characterization of the liquid-crystalline behaviour

Liquid-crystalline phases were characterized by means of polarizing microscopy equipped with a heating stage (Mettler FP 52, Linkham THM 600), differential scanning calorimetry (Perkin-Elmer DSC-2C) and X-ray analysis performed with a wide angle goniometer (Siemens X-D-500) using CuK_α radiation. The transition temperatures listed in table 1 correspond to the peak maxima of the D.S.C. thermal transitions.

The mesomorphism of Hex-4 and its order within the mesophase were identified by Lehn *et al.* [12] several years ago to be of D_{hd} type (*D*iscotic-*h*exagonal-*d*isordered). The authors suggested the term 'tubular' mesophases, denoted by 'T'. A schematic representation of this phase type is given in figure 8. It corresponds perfectly to the definition of discotic phases [13].

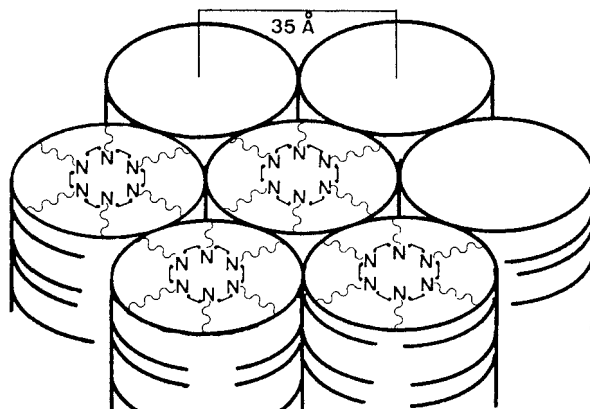


Figure 8. Schematic representation of D_{hd} mesophase.

The findings of the present work are in good agreement with those previously published on D_{hd} phases [12]. As revealed by X-ray scattering measurements of Hex-4, Hex-6 and Hex-7, in the mesophase at elevated temperatures and after subsequent cooling to room temperature, a sharp reflection is found in the small-angle region and a wide halo appears in the wide-angle region. The corresponding molecular spacings are given in table 2. The halo at approximately 4.4 \AA should be related to the scattering of paraffinic chains, typical for liquids and LCs, whereas the sharp signal at approximately 35 \AA corresponds to the intercolumnar distance of the hexagonal lattice.

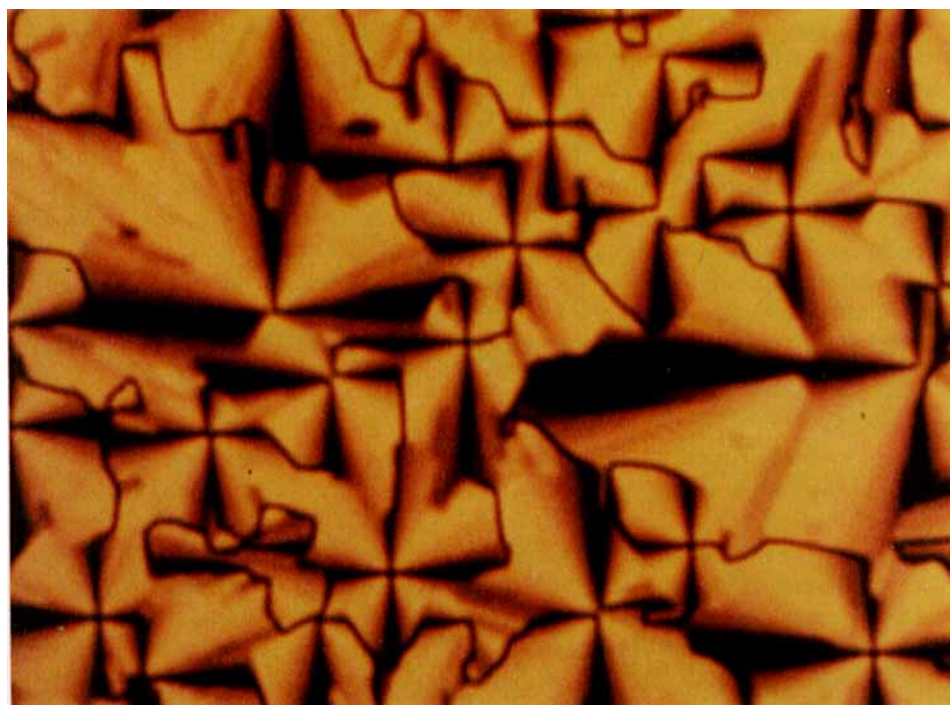


Figure 9. Texture micrograph of Hex-7 at 220°C, obtained by cooling the isotropic liquid.

Table 2. Molecular spacings of the columnar, liquid crystalline hexacyclene derivatives Hex-4, Hex-6 and Hex-7

Hexacyclene derivative	Molecular spacings $d/\text{\AA}$ in the mesophase at elevated temperatures		Molecular spacings $d/\text{\AA}$ after cooling to room temperature	
Hex-7	34.6	4.9	38.4	4.5
Hex-6	35.3	4.7	38.1	4.5
Hex-4	33.3	4.7	35.3	4.5

The optical texture of Hex-7 is shown in figure 9. Focal conics of this type have also been observed with polymorphic hexa-*n*-alkanoyloxytriphenylenes bearing long alkyl chains ($n \geq 10$) [13]. The corresponding columnar phase was assigned to D_{hd} .

In addition, the low heat of the transition from mesophase to isotropic phase of Hex-7 ($0.32 \text{ kcal mol}^{-1}$) indicates the mesophase to be a low-order columnar type. Unfortunately we were not able to perform X-ray measurements on macroscopically oriented Hex-7.

The results of X-ray and D.S.C. investigations of Hex-4, Hex-6 and Hex-7 show that the mesomorphic order can be frozen in the glassy state.

The azobenzene derivative Hex-8 also exhibits a mesophase over a small temperature range, which has not yet been investigated. According to the disc-like shape of the molecule and the texture observed, the mesophase should be of a columnar type too.

In order to investigate whether sulphonamides of hexacyclene are also able to exhibit columnar mesomorphism, Hex-5 was synthesized. Hex-5 melts at 186°C,

transforming directly into the isotropic state (see table 1). $^1\text{H-N.M.R.}$ measurements clearly refer to the unrestricted, free rotation of the sulphonyl substituents R linked to the heterocyclic core. In contrast with this, a restricted rotation was found for the liquid-crystalline derivatives Hex-4, Hex-6, Hex-7 and Hex-8, as indicated by a broadening of the signals in the aromatic region ($\delta = 6\text{--}8$ ppm).

In summary, the following criteria can be established as being important for the formation of columnar mesomorphism of the azacrown derivatives presented in table 1.

- (i) *A six-fold symmetry of the hexacyclene moiety.* This leads to a circular structure of the resulting amide. No cyclame derivative with two-fold symmetry (Cyc-1-10) exhibits the LC-state (table 1: left column).
- (ii) *Lateral extension of the azacrown via planar rigid substituents.* Only aromatic carbonic acids serving as substituents R lead to thermotropic mesomorphism (table 1: right column). sp^2 carbons exhibiting trigonal symmetry—carbonyl-, aromatic-, double-bonded carbons—linked to the cyclic oligoamine seem to be important for the stiffening of the whole system. Presumably the hindrance of the aromatic groups organized side by side, and consequently the restricted rotation of the benzene cores in this sterically fixed orientation, allows a single molecule to take a disc-like shape.
- (iii) *Optimized space filling of aliphatic hydrocarbon tails.* Sufficient space filling in the periphery of the molecule is obtained by a single n -alkyl chain per substituent R. Substituents R bearing two or three hydrocarbon chains (R-9, R-10) prevent the bulky amide (Cyc-9, Cyc-10, Hex-9, Hex-10) from adopting a certain ordered arrangement—crystalline and/or liquid-crystalline.

5. Photoisomerization and photopolymerization in ordered structures

The crystal-lattice geometry plays an important role in the photodimerization of cinnamic acids in the solid state [16]. In order to investigate the influence of a fluid-like ordered environment on the photocycloaddition, cinnamoyl moieties have either been embedded into liquid-crystalline host matrices [17] or incorporated as a part of the mesogenic units themselves [18].

According to the columnar order of disc-like Hex-7, the photocycloaddition between cinnamoyl substituents R-7 linked to different heterocycles within one column should lead to polymeric tubes. Owing to their hydrophobic exterior and hydrophilic interior, those tubes may serve for example as ion channels when incorporated into lipid membranes. To facilitate conductivity, metal ions have to be inserted into the central cavity of the molecule via coordinative bonds to the nitrogen atoms. Through this pathway, one dimensional materials with interesting technological applications may be achieved.

Preliminary irradiating experiments were performed using a high-pressure mercury lamp as a light source and an interference filter (296 nm) in order to prevent side- and back-reactions.

Hex-7 was irradiated in the mesomorphic state at 220°C under nitrogen. For that purpose, a thin film was prepared by heating in each case, in the isotropic liquid, 0.5 mg of the crystalline sample between two glass slides, the upper one being made of quartz. After the subsequent slow cooling to 220°C (columnar mesophase), irradiation was started. To investigate the progress of the photolysis, the samples were dissolved in CHCl_3 . G.P.C. diagrams using polystyrene as internal standard, as well

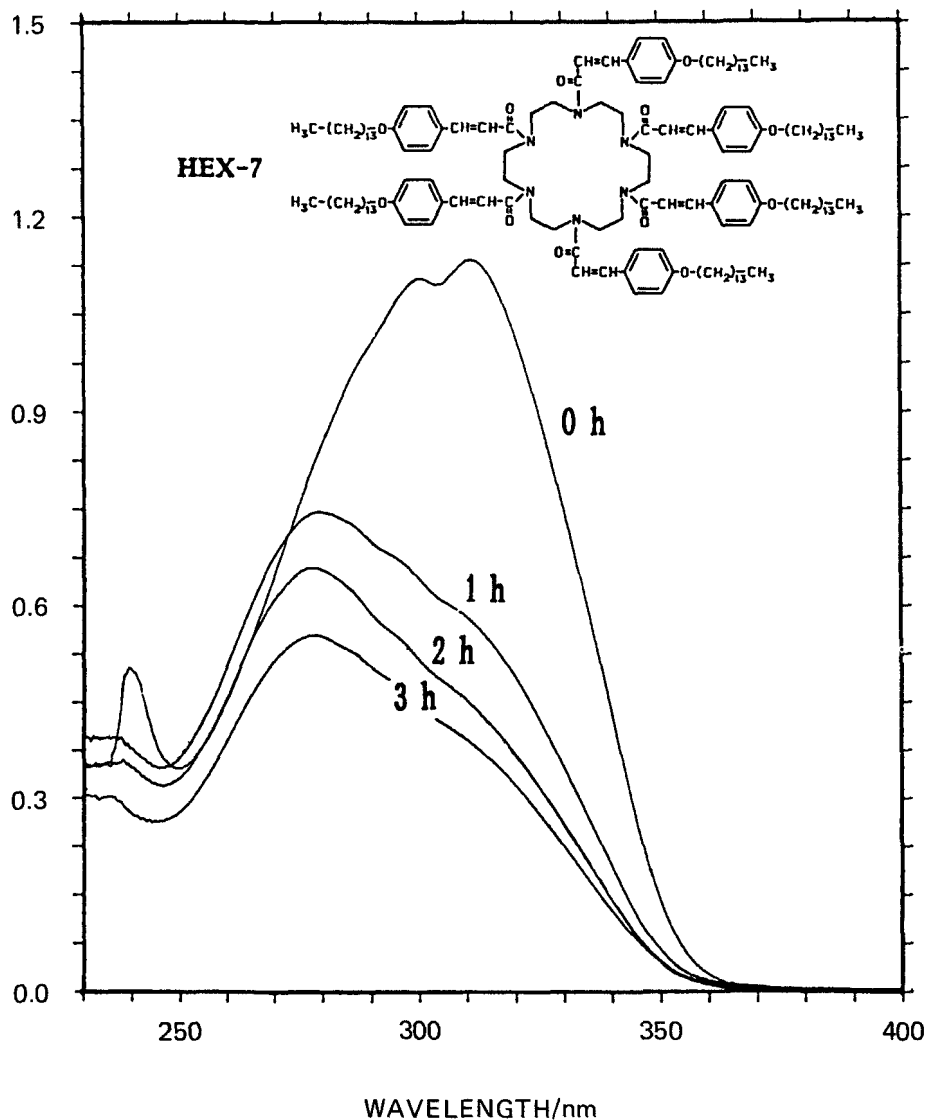


Figure 10. U.V. absorption spectra of Hex-7 in CHCl_3 after irradiation in the columnar state. as U.V. spectra of the solutions in adequate concentration (figure 10), were then recorded.

A reduction in the intensity of the absorption between 298 nm and 310 nm on continued irradiation is observed, connected with a shift in the absorption maximum to shorter wavelength (278 nm). Presumably the shift and the large drop in the intensity after one hour of irradiation is due to the *trans/cis* isomerization of the substituents R, as indicated by short-time photolysis experiments in dilute solution. This is a disadvantage of the desired polymerization in order to obtain polymeric columns, because the *cis* isomer is hardly ever known to exhibit the 2 + 2 cycloaddition. Furthermore, it is not clear whether the *cis* isomer destroys the mesomorphic order. However, G.P.C. measurements reveal the formation of dimers (MW = 4340) and oligomers in small yields.

As shown in the previous section, the mesomorphic order is maintained in the glassy state at room temperature. In order to reduce competitive side-reactions—*trans/cis* isomerisation, photocleavage—it is planned to carry out the irradiation experiments of Hex-7 in a supercooled thin film.

Several synthetic approaches are in progress to increase the efficiency of the photocycloaddition.

6. Experimental

6.1. Synthesis of the substituents R (benzoic, cinnamic, sulphonic acid derivatives)

6.1.1. 4-n-Alkyloxybenzoic acids (see R-4, R-6) [19]

65 mmol of 4-hydroxybenzoic acid were dissolved in 50 ml ethanol by gentle heating. Then 160 mmol of potassium hydroxide and some crystals of potassium iodide dissolved in 10 ml of water and 72 mmol of the *n*-alkyl bromide were subsequently added. The mixture was heated to reflux. After some hours, plate-like crystals started to form. To complete the reaction, refluxing was continued for two days. The crystalline precipitate was suction-filtered at room temperature. The collected crystals were washed with dilute acetic acid and recrystallized from glacial acetic acid. The acetic acid was removed by drying the product *in vacuo* at 80°C for one day and then at room temperature for four more days.

Yield approximately 80 per cent.

4-n-Dodecyloxybenzoic acid: phase behaviour (transitions in °C): k 87 s 126 i (LC). Elemental analysis (C₁₉H₃₀O₃): found: 75.36 per cent C; 9.62 per cent H; calc. 74.47 per cent C; 9.86 per cent H. ¹H-N.M.R. (CDCl₃, 200 MHz), δ/ppm: 0.9 t (—CH₃); 1.3 m (—(CH₂)₉—); 1.8 m (—CH₂—CH₂—O); 4.0 t (—CH₂—O); 6.9 d (ArH 3.5); 8.0 d (ArH 2.6).

4-n-Tetradecyloxybenzoic acid: phase behaviour (transitions in °C): k 97 s 126 i (LC). Elemental analysis (C₂₁H₃₄O₃): found: 76.34 per cent; 10.11 per cent; calc.: 75.40 per cent C; 10.24 per cent H. ¹H-N.M.R. (CDCl₃, 200 MHz), δ/ppm: 0.9 t (—CH₃); 1.3 m (—(CH₂)₁₁—); 1.8 m (—CH₂—CH₂—O); 4.0 t (—CH₂—O); 6.9 d (ArH 3.5); 8.0 d (ArH 2.6).

6.1.2. 4-n-Tetradecyloxycinnamic acid (see R-7)

The etherification of 4-hydroxycinnamic acid with tetradecyl bromide was performed according to the procedure given in §6.1.1.

Yield 81 per cent. Phase behaviour (transitions in °C): k 128 s 158 i (LC). Elemental analysis (C₂₃H₃₆O₃): found: 77.52 per cent C; 9.92 per cent H; calc.: 76.62 per cent C; 10.06 per cent H. ¹H-N.M.R. (CDCl₃, 200 MHz), δ/ppm: 0.9 t (—CH₃); 1.3 m (—(CH₂)₁₁—); 1.8 m (—CH₂—CH₂—O); 4.0 t (—CH₂—O); 6.9 d (ArH 3.5); 7.5 d (ArH 2.6); 6.3/7.7 d (ViH, *trans*).

6.1.3. 4-n-Decyloxyphenylazobenzoic acid (see R-8)

4-Hydroxy-4'-carboxyazobenzene was etherified with decyl bromide according to the procedure described in §6.1.1. Because of its lower solubility compared with 4-hydroxybenzoic and 4-hydroxycinnamic acids (see §6.1.1 and 6.1.2 respectively), the etherification of 19 mmol 4-hydroxy-4'-carboxyazobenzene with 20 mmol decyl bromide was carried out in 130 ml of a basic ethanol/water mixture (4/1).

Yield 62 per cent. Phase behaviour (transitions in °C): k 220 s 255 i (LC). Elemental analysis ($C_{23}H_{30}N_2O_3$): found: 71.84 per cent C; 7.87 per cent H; 7.33 per cent N; calc.: 72.22 per cent C; 7.91 per cent H; 7.32 per cent N. 1H -N.M.R. ($CDCl_3$, 400 MHz), δ /ppm: 0.85 t ($-CH_3$); 1.26 m ($-(CH_2)_6-$); 1.43 m ($-CH_2-CH_2-CH_2-O$); 1.75 m ($-CH_2-CH_2-O$); 4.08 t ($-CH_2-O$); 7.12 d (ArH 3.5); 7.90 d (ArH 2.6); 7.92 d (ArH 2',6'); 8.00 d (ArH 3',5').

6.1.4. 3,5-Di-*n*-decyloxybenzoic acid (see R-9)

(a) *3,5-Di-*n*-decyloxybenzoic acid methyl ester.* 2.4 g of sodium were dissolved in 130 ml of absolute ethanol. Then 42 mmol of 3,5-dihydroxybenzoic acid methyl ester, some crystals of potassium iodide and 92 mmol of decyl bromide were subsequently added. In order to prevent oxidation, the reaction was carried out under a nitrogen atmosphere. After 12 h reflux, ethanol was evaporated extensively. The residue was poured into 50 ml of an aqueous solution of sodium hydroxide (5 per cent). The organic layer was removed and the basic aqueous layer was extracted twice with diethyl ether. The combined organic layers were dried over sodium sulphate. The solvent was then evaporated and the product was purified by flash chromatography (silica gel: 40 μ m; petroleum ether/ethyl acetate = 60/1 as eluent).

Yield 56 per cent.

(b) *3,5-Di-*n*-decyloxybenzoic acid.* Saponification of the diether was carried out by refluxing 10 mmol with a two-fold excess of sodium hydroxide in 70 ml of an ethanol/water mixture (4/1) for 4 h. The reaction mixture was then acidified with concentrated hydrochloric acid at room temperature. The precipitate was suction-filtered, washed with dilute hydrochloric acid and recrystallized from ethanol.

Yield 70 per cent; m.p. 53/59°C. 1H -N.M.R. ($CDCl_3$, 200 MHz), δ /ppm: 0.9 t ($2(-CH_3)$); 1.3 m ($2(-(CH_2)_7-)$); 1.8 m ($2(-CH_2-CH_2-O)$); 4.0 t ($2(-CH_2-O)$); 6.7 t (ArH 4); 7.2 d (ArH 2.6).

6.1.5. 3,4,5-Tri-*n*-nonyloxybenzoic acid (see R-10) [20, 21]

By refluxing 10 mmol of 3,4,5-trihydroxybenzoic acid ethyl ester (ethyl gallate) with an excess of powdered potassium carbonate (70 mmol), a catalytic amount of potassium iodide and 33 mmol of nonyl bromide in acetone for 48 h, the corresponding triether was formed in approximately 70 per cent yield. Saponification of the triether was performed according to the procedure in §6.1.4 (b). Elemental analysis ($C_{34}H_{60}O_5$) [21]: found: 74.20 per cent C; 10.88 per cent H; calc.: 74.70 per cent C; 11.02 per cent H. ^{13}C -N.M.R. [21] ($CDCl_3$, 400 MHz), δ /ppm: 153, 143, 124, 109 (ArC); 74, 69 (Ar-O-C). EI-M.S. [21]: M^+ (100 per cent) = 548.

6.1.6. 4-*n*-dodecyloxybenzene sulphonyl chloride (see R-5)

The starting *n*-dodecyl phenyl ether was synthesized according to the Williamson method, by reacting dodecyl bromide and phenol in a freshly prepared solution of sodium ethanolate in absolute ethanol. Chlorosulphonation of the *n*-dodecyl phenyl ether led to the final aromatic sulphonyl chloride. The procedure is as follows. 38 mmol of *n*-dodecyl phenyl ether was dissolved in 35 ml dry chloroform. Then, while stirring vigorously, 76 mmol of chlorosulphonic acid (5 ml) were added cautiously at $-10^\circ C$. The reaction mixture initially became pasty at the beginning and liquified

again later. Stirring was continued for several hours in order to complete the reaction. After evaporation of the solvent, the residue was poured onto 100 g of crushed ice. The aqueous layer was immediately extracted twice with petroleum ether. Shaking had to be performed with great care because the heterogeneous mixture could easily be emulsified. Separation of the organic layer from the aqueous one could be accelerated by adding sodium chloride. The combined organic layers were first washed with a solution of sodium hydrogen carbonate and subsequently with water. Drying of the solution with calcium chloride and evaporation of the solvent yielded the sulphonyl chloride as a nearly white crystalline material.

Yield 46 per cent; m.p. 35°C. $^1\text{H-N.M.R.}$ (CDCl_3 , 400 MHz), δ/ppm : 0.87 t ($-\text{CH}_3$); 1.27 m ($-(\text{CH}_2)_8-$); 1.45 m ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}$); 1.8 m ($-\text{CH}_2-\text{CH}_2-\text{O}$); 4.04 t ($-\text{CH}_2-\text{O}$); 7.00 d (ArH 3.5); 7.94 d (ArH 2.6).

The transition temperatures of the liquid-crystalline aromatic acids were determined by means of polarizing microscopy.

Benzoic and cinnamic acids, as well as the azobenzene derivative (§6.1.1.–6.1.5.) were converted into the acid chlorides by the following general method. 5 mmol of the acid was suspended in 10 ml of dry benzene. A five-fold excess of oxalyl chloride was subsequently added dropwise at 0°C. Stirring at room temperature was continued for 24 h in order to complete the reaction. If necessary, the mixture was gently heated at 50°C for 1–2 h. The excess of oxalyl chloride as well as the solvent was evaporated at 40–50°C. The residue was used as acylating agent without further purification. The *n*-aliphatic acid chlorides (see R-1, R-2, R-3) were purchased and distilled prior to use.

6.2. Acylation and sulphonation of the cyclic oligoamines (cyclame, hexacyclene)

Four- and six-fold acylation and sulphonation of cyclame and hexacyclene respectively was achieved according to the following general procedure [12]. 2 mmol of cyclame (hexacyclene) and 8 mmol (12 mmol) of 4-dimethylaminopyridine were stirred with 8 mmol (12 mmol) of the corresponding acid chloride in 25 ml of *N,N*-dimethylformamide (DMF) under a nitrogen atmosphere at 80°C for 12 h. The amidation of the azobenzene acid chloride (§6.1.3) required more rigorous conditions (5 days/90°C) in order to obtain complete conversion. The 4-dimethylaminopyridinium chloride formed could easily be removed by evaporating DMF *in vacuo*, adding chloroform to the solid residue and extracting the obtained solution twice with water. The solvent was then evaporated and the residue purified by flash chromatography (silica gel: 40 μm ; chloroform/methanol as eluent) and recrystallization from either ethanol, THF/ethanol or acetone. The polarity of the eluent mixture was adjusted for each compound. For example, a ratio of chloroform/methanol = 80/1 was used in the case of Hex-7.

All compounds showed correct elemental analysis data. Moreover, the I.R. and $^1\text{H-N.M.R.}$ spectra are in agreement with the proposed structures. For example, the following data have been obtained for Cyc-7 and Hex-7.

Cyc-7. Elemental analysis ($\text{C}_{102}\text{H}_{160}\text{N}_4\text{O}_8$): found: 77.66 per cent C; 10.04 per cent H; 3.68 per cent N; calc.: 78.01 per cent C; 10.27 per cent H; 3.57 per cent N. $^1\text{H-N.M.R.}$ (CDCl_3 , 200 MHz), δ/ppm : 0.9 t 4($-\text{CH}_3$); 1.3 m 4($-(\text{CH}_2)_{11}-$); 1.8 m 4($-\text{CH}_2-\text{CH}_2-\text{O}$); 2.0 m 2($-\text{CH}_2-\text{N}$); 3.7 m 8 ($-\text{CH}_2-\text{N}$); 4.0 m 4($-\text{CH}_2-\text{O}$); 6.5–7.8 m 4(ArH, ViH).

Hex-7. Elemental analysis ($C_{150}H_{234}N_6O_{12}$): found: 77.80 per cent C; 10.28 per cent H; 3.71 per cent N; calc.: 77.87 per cent C; 10.19 per cent H; 3.63 per cent N. 1H -N.M.R. ($CDCl_3$, 200 MHz), δ /ppm: 0.9 t 6($-CH_3$); 1.3 m 6($-(CH_2)_{11}-$); 1.8 m 6($-CH_2-CH_2-O$); 3.8 m 12($-CH_2-N$); 4.0 m 6($-CH_2-O$); 6.4–7.8 m 6(ArH, ViH).

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