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Tradition and innovation in science

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Tradition and innovation in science

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A Commentary on the paper "Self-organization of substituted azacrowns based on their discoid and amphiphilic nature", by C. Mertesdorf and H. Ringsdorf. First published in *Liquid Crystals*, **5**, 1757-1772 (1989).

1. Wit is the finder, intelligence the observer [1]: Facts aligning or creative Journals?

Having too many and especially too many new specialised journals [2], it is an enjoyment to be able to help celebrate the 20th Anniversary of *Liquid Crystals*, a journal not yet old but certainly grown up [3, 4]. Congratulations to a journal that from its start was based on tradition and had innovation as its goal. During the past two decades the journal has grown in stature and is now recognized even outside the Liquid Crystal Community as one of the important publishing possibilities for the results of liquid crystal research taken in a broad sense.

The journal did not just develop linearly, it did not stick to new mesogens and old materials only, but the editors were able to attract scientists from several other fields, e.g. the micellar, the mono- and multilayer community, and even from the lipid- and biomembrane side. On the one hand they showed that thermotropic liquid crystals, as self-organizing materials, are interesting and potential candidates in new areas such as non-linear optics, information storage or as self-reinforcing plastics. On the other hand the journal, through the papers it attracted, made it clear that in life science the self-organization of matter in supramolecular assemblies is one of the basic prerequisites for all biological processes: Cellular liquid crystals are necessary tools for all chemical, electrical and mechanical functions of life. The Editors of *Liquid Crystals* were thus able to avoid the normal linear and mostly detrimental growth of journals by the initiation of creative paradigmatic concepts and developments [5]: Steps across borders!

We are glad that we were and are part of the game. Let us thus add some related ideas - ideas about books and dreams, ideas about facts and responsibility - to an old paper we enjoyed when we wrote it, and we came to like once more when we saw it again in this Anniversary Issue.

2. Facts and Dreams in Science: What do Glenn Brown and his old book and Hermann Staudinger and his dreams [6] have in common?

There was a book in the seventies of the last century that influenced our group in Mainz very strongly: *Liquid Crystals and Biological Structures* by G.H. Brown and J.J. Wolken [7]. A book certainly ahead of its time – and never fully accepted and honoured. In those days, we at the University in Mainz had just started to play around with liquid crystals [8], monolayers [9], and polymer pharmaceutics [10]. What an inspiration was Glenn Brown's book for us!

The book did not become very popular and, for many years, it has not been available. In those days liquid crystals, monomeric and polymeric ones, were carefully discussed theoretically, synthesized intensively and were considered to be interesting, useful materials for applications. Their biological side, important since the beginning of life and even essential for its development, belonged to another department: Cell-, Membrane-, and Molecular-Biology. These parts of Science had already reached dizzying heights in those days. But how much did a normal Materials Science oriented liquid crystals expert know about this? Probably less than he could have found in Glenn Brown's book! It is not clear if the book *Liquid Crystals and Biological Systems* was just a remarkably, far-sighted textbook, or if it indirectly described the author's dreams and hopes for the liquid crystal field.

This is the point where it may be allowed – and from a scientific-historical standpoint even be interesting – to compare Glenn Brown and his old book with Hermann Staudinger and his even older dreams. He also had a vision about something that in another department as a

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possible cooperative unit had already reached dizzying heights too: But it remained a dream for Hermann Staudinger. He never really started to bridge the gap between his beloved materials oriented synthetic macromolecules and their wide-open chances and importance in Life Science [6]. When in 1953 Hermann Staudinger was honoured with the Nobel Prize for his discovery in the field of macromolecular chemistry, the classical materials-science oriented polymer community at that time hardly recognized that, at the very same Nobel Prize celebration H.A. Krebs and F.A. Lipmann reported on enzymes and coenzymes as important biological macromolecules [11]. And it was probably even more like news from another star for them that in the same year J.D. Watson and F.H. Crick rang in molecular biology with their *Nature* articles on the DNA-model [12].

In Science, facts and dreams often fall apart [6, 11]. There is no doubt that more is known than we know. The flowers we dream of may just grow in the garden of our neighbours. Many areas of science could and would grow faster and be more creative if we scientists would be more willing to step across borders, to climb out of our speciality boxes [13]: Facts grow out of knowledge – creativity needs dreams.

3. Tradition and Innovation in Science

Two decisive aspects of the field of Science are tradition and innovation. Tradition is the basis, for it is the cummulation of wisdom in the body of knowledge. To know what a subject is all about and to control it creates self-confidence, thus paving the way for innovations. Innovation is the adventure, because with the challenge comes the risk of calling into question or even losing one's own scientific identity, gained through tradition.

Persisting in tradition without innovation, however, soon leads to linear thinking, to tiresome routine and the science of yesterday: The longing for new adventures withers and dies [14]. On the other hand, intuition and pure innovation harbors the danger of superficiality.

The sum of knowledge is immense and growing. Tradition and solid work are honoured and admired. Nevertheless, science can be justified only by challenge and demands the willingness to give up long-held classical or traditional views in an attempt to discover new horizons.

4. Putting the Fizz into Research! Quo vadis University?

Research activities have increased exponentially during the last 50 years and will continue to do so with new players, e.g. China, Korea, and India, vividly and full of ambition entering the game. Today there are already more scientists active than during all centuries before: Research on a high level, an open field, results are abundant. Science is blooming and even adventures across borders - Glenn Brown's and H. Staudinger's dreams! - are part of the game.

Is it then allowed or even necessary at all to ask: Where are we going? Watching the worldwide activities of basic and applied research and some of the newer tendencies in our globalized world a few doubtful remarks may be allowed, not pessimistic at all, but just a little bit worried. Why?

To make us, the teaching and research oriented science community, happy the gurus of our elite societies tell us that we all can be part of this wonderful, brave new world. Just follow the rules: High citation index values for people and papers, first author as often as possible, no publication before the patents, and especially one is expected to like the stock-market induced pressure to produce fantastic results, fast and marketable tomorrow. By the way: Where are the famous industrial research Laboratories, the brain trusts of applied and even basic research, e.g. AT&T Bell Labs, General Electric, the Experimental Station of DuPont? What about the IBM Research laboratories in Almaden and their famous research fellows? Where are the Farbwerke Hoechst and even Aventis? What happened to Schering Berlin, recently? Did they not produce remarkable results and products – or just not the right ones fast enough. The right ones for whom? Or is there more behind the game?

Although the autonomy of our Universities and research institutions in most countries worldwide is no longer endangered in a political sense – as, for example, in Germany in the Third-Reich [15, 16] – they exist today in a turbulent atmosphere. In Europe, for example, they are driven by absurd saving plans, sometimes bizarre elitism and influenced by excessive bureaucracy and evaluation games. And there is one more problem, surely at the heart of the matter: It is difficult for our Universities and research institutions to avoid being pulled into the only profit-driven speculations of the absolute open-market economy with the sometimes brutally acting stock-market as its accomplice: They regard research and responsibility only as a shareholder values oriented money making and short-term amusement for our Fun Society. We should not forget that in the nineties of the last century in the USA, Europe and Japan most, perhaps all, big companies reduced their research activities to about 1/10 of what it was before. The international industrial flagships, mentioned previously, are just examples of it.

A period of merger endgames [17] has started: Fast profit increase not by new developments but by stock market driven fusions – not really caring about products and people. Many of the former proud and intrepid galleons of industry no longer have a captain on the bridge, but rather a quartermaster, whose gaze is fixed spellbound on the quarterly balance sheet and the shareholder value: Stock market reports replace research. Certainly worldwide competition and necessary worldwide activities do change our local situations in industry and universities. But many of these negative economic developments cannot simply be justified by the slogan and even by the necessity of globalization [18, 19].

What is the intrinsic value and meaning of knowledge? This question is nowadays often replaced by the question of what type of knowledge do we need to fulfil predetermined functions. This increasing misuse of science - i.e. its transformation mainly to develop and support technology often for purely stock-market effects [17] - threatens to destroy the critical purely truth-oriented function of science. The increasing connection between "Knowledge and Interest" seems to have become the norm to such an extent that the value of science is endangered to vanish in goals and reasons defined outside science: "Truth is what is useful". Does this not demand a response from our Universities?

Where is all this taking us? There is no reason to be pessimistic – we just have to be aware! The main problem of our universities is not pessimism but their naivety! We are in a transition state: Not only in Europe are we under pressure to restructure our shaking Industrial Societies into knowledge based societies. Because we cannot keep the basic industrial productions in our developed [20] countries, knowledge, originality and richness of ideas for further developments are much more in demand than ever before. Thus, we need a science education system that is more vivid than ever. We need universities able to nurture dreams, intuition and creativity, universities and research institutions that can handle an uncomplicated fast and open exchange of scientific and technological aspects with industry – a little bit like in the old times. Basic Science and Applied Science are certainly no contradictions at all. They belong together and depend on each other. We do not need reluctance or even fear of contact, between Universities/Research Institutions and Industry. There is nothing wrong if the application-oriented industrial side helps universities to find interesting perspectives. BUT! But we cannot allow our universities to be instrumentalized: neither politically, for example in the Third Reich [15, 16], nor now political-economically: Universities cannot be the outside laboratories of shareholder-value driven profit-oriented giant companies. We all are responsible for what is to come.

What is to come? What could be the best way to predict the future? *The best way to predict the future is to invent it!* [21, and figure 3] Independent universities and research institutions are a prerequisite for the education of creative, courageous, non-aligned scientists, willing to accept their responsibility as professionals and as citizens of the modern world: Our world is a village!

References

[1] G.C. Lichtenberg (1742–1799, physicist and philosopher in Göttingen/Germany), *Aphorismen*. Insel-Verlag Frankfurt. 202 (1979).

[2] Shall we bet on how many new "Nano-Journals" we will see appearing and disappearing during the next years? Even a journal for *Nano-Liquid Crystals* would not amaze us.

[3] Just wait and see until the journal, *Liquid Crystals*, will be 100 years old! Like the *Journal of Colloid and Polymer Science* this year. To celebrate this they also republished old papers, but only as an appendix [4], including papers from T. Svedberg, W. Ostwald, H. Staudinger, W. Kuhn, I. Langmuir, K.B. Blodgett etc. Not so bad at all. But just wait and see until your journal will reach this age!

[4] *Colloid and Polymer Science – celebrating 100 years*, **284**, A9–A114 (2006).

[5] T.S. Kuhn. *The Structure of Scientific Revolutions* (2^{nd} Edn.), University of Chicago Press Chicago (1970). K.R. Popper. *Objective Knowledge. An Evolutionary Approach*. Oxford Press (1972). Progress in science does not happen through the continuous intelligence driven collection of facts, but by intuition and creativity-induced revolutionary processes, which induce the replacement of existing models (paradigms) by new concepts: A paradigm shift. This is cheerfully demonstrated (see [6], Ref. 14 on page 1071) by the Argentinian caricaturist, G. Mordillo, who seems to know and understand scientists pretty well.

[6] H. Ringsdorf. *Angew. Chem. Int. Ed.*, **43**, 1064 (2004).

[7] G.H. Brown, J.J. Wolken. *Liquid Crystals and Biological Structures*. Academic Press New York (1979).

[8] R. Ackermann, O. Inacker, H. Ringsdorf, u.Z. *Kolloid-Z Polymere*, **249**, 1118 (1971).

[9] E. Perplies, H. Ringsdorf, J.H. Wendorff. *Polymer Letters*, **13**, 243 (1975).

[10] H. Ringsdorf. *J. Polym.Sci. Symp.*, **51**, 135 (1975).

[11] An interesting figure on page 1067 of the paper cited as [6], shows **H. Staudinger**, **H. Krebs**, F. Lipmann and F. Zernike in 1953 a few minutes before the award of the four Nobel Prizes. It is especially interesting and is a delight to look at H. Staudinger and H. Krebs in this figure, and to see a great moment in the history of science: Facts and dreams, tradition and innovation portrayed so openly via these two famous scientists. The creative and innovative strength of **Hermann Staudinger**, University Freiburg, had in 1953 already given room to the Tradition of Science. In his Nobel Lecture he talked only about his most beloved synthetic macromolecules: Middle Age of Polymer Science! And what about his

dreams? His dreams about the unity of chemistry and biology? It was **Hans Krebs**, University Oxford, U.K., who had long before 1953 already fulfilled these dreams. In these days he represented the innovative side of Polymer Science by describing natural macromolecules, enzymes and coenzymes, their functions and their importance in Life Science.

If one looks 20 years back from this Nobel Prize event in 1953 there is an additional very interesting and – in our opinion – very important socio-political point to be made: One has to realize that in the 1930s these two Nobel Prize Winners indeed worked at the very same University, the University of Freiburg, Germany. Did they know each other? Did Hermann Staudinger know that at his University there was Hans Krebs, a young, highly talented biomedical scientist working on Biopolymers working on his dreams? Did he know that Hans Krebs was Jewish? Despite all the offers for chairs, he had received in Germany, he was kicked out from the University in Freiburg already in 1933 and had to leave his native country [16].

[12] J.D. Watson, F.H. Crick. *Nature* 171, 737 and 964 (1953).

[13] Ronald Searle, the famous British cartoonist, called his following caricature "Human Beings". In analogy we scientists usually sit in the boxes of our speciality areas: naturally we are interested in what is going on next door! But beyond that? Admitted, admitted: This point has already been made very often! But here we can sit back and relax and just cite André Gide, the famous French writer: *All this has been said before – but because nobody has listened, it all has to be said again.*

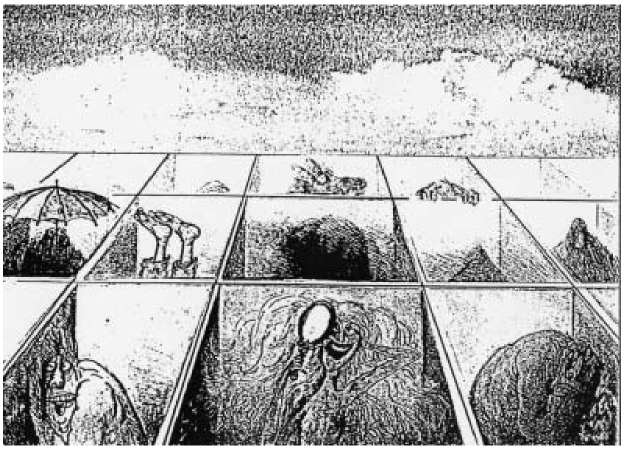

Figure 1.

[14] Already in 1788 (!) Georg Christoph Lichtenberg, the great critical philosopher and physicist from Göttingen, knew about that and he was very clear and outspoken in this respect when he characterized one of his colleagues: *….he was still hanging at his university like a wonderful chandelier without a tiny candle lit for years* (G.C. Lichtenberg, "Sudelbücher"). This certainly was a Full-Professor who made it! He could have overlooked the whole scientific world from his high position – but he only viewed the problems through the key-hole of his office door. And what do you think he saw? An exception?

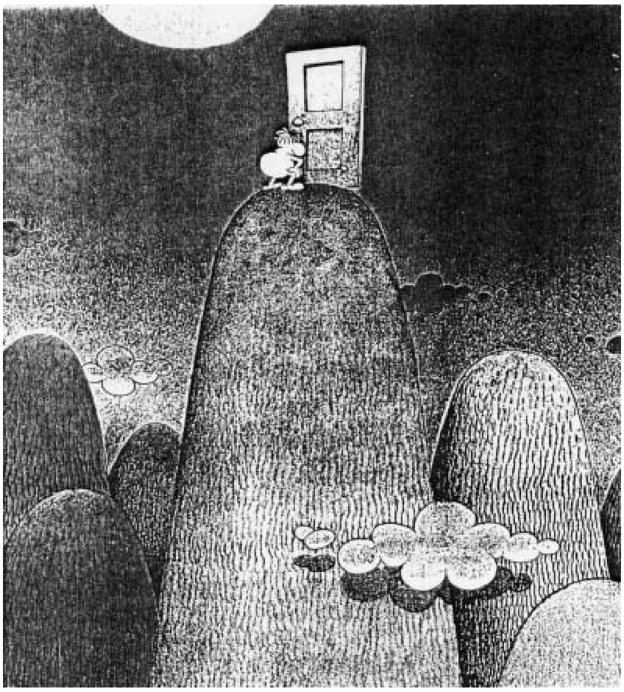

Figure 2.

[15] U. Deichmann. *Flüchten, Mitmachen, Vergessen. Chemiker und Biochemiker in der NS-Zeit* (To flee, to participate, to forget. Chemists and Biochemists in the Third Reich), Wiley-VCH, Weinheim (2001). And a publication as a shorter version in English: U. Deichmann. *Angew.Chem., Int. Ed.,* **41**, 1310 (2002).

[16] Even nowadays elderly German scientists sometimes claim that in the Third Reich (1938–1945) nobody at the German universities could have known what the Nazis had in mind. Wide of the mark! This opinion – in my opinion – is just a hint of not enough moral courage or too much patriotism! In 1937 – E.Y. Hartshorne, Tutor in Sociology at Harvard University published a book: "The German Universities and National Socialism", G.Allen Ltd., London. He had spent the year 1935–1936 in Germany with a fellowship to study the new German university system. Did he have to work under cover, underground? Not at all! The German officials were only too happy to let him have a detailed insight into their attempts to politicize and restructure the German universities – many of which were at this time world leading. We all could have known already in 1933–1936 how many university professors were planned to be kicked out - and then were really kicked out – most of them Jewish and one of them Hans Krebs. The names are all in Hartshorne's book in 1937 – and the numbers of the professors thrown out were reconfirmed after the war [15]. Just as an example the percentage of them at different German universities in the 1930s: Berlin 32.4%, Heidelberg 24.3%, Freiburg (see H. Krebs, [10]) 18.8%, Göttingen 18.6%, Hamburg 18.5%, München 8.3%, and so on, and so on!

[17] G.K. Deans, F. Krüger, St. Zeisel. *Winning the Merger Endgames*. MacGraw-Hill (2002). A shocking, realistically

written book based on the believe of the absolute necessity of unmerciful fusions.

[18] N. Chomsky. *Profit over People* Europa Verlag Hamburg 6 (2001) J. Stiglitz. *Globalization and its Discontents*, W. Norton Corp., New York (2001). J. Stiglitz. *Making Globalization work*, W.Norton Corp., New York (2006).

[19] Those who do not want to read the book of N. Chomsky [18], may be are willing to listen to the opinion of two quite different, but both pretty famous personalities. **Pope John Paul II**: *Market capitalism has become the most successful religion of all time*.

George Soros, Investment Manager: *The unrestricted increase of laissez-faire capitalism and extension of the market to all areas of our lifes endangers the future of our democratic society*. These statements are in agreement with an increasing fear that in the final analysis Neo-Liberalism is not concerned with the empirical justification of its policies, but rather with the blind belief in the infallibility of the unregulated market place.

[20] What means “developed”? Are not most of the “developed” countries for quite some time already over-developed? And to defend this is problematic!

[21] *The best way to predict the future is to invent it*. A quotation of Richard Feynman, Physics Nobel Prize 1965. This is perfectly demonstrated in figure 3: A figure not too realistic for the necessarily more direct goal-oriented industrial side – but absolutely essential and imperative for our universities!

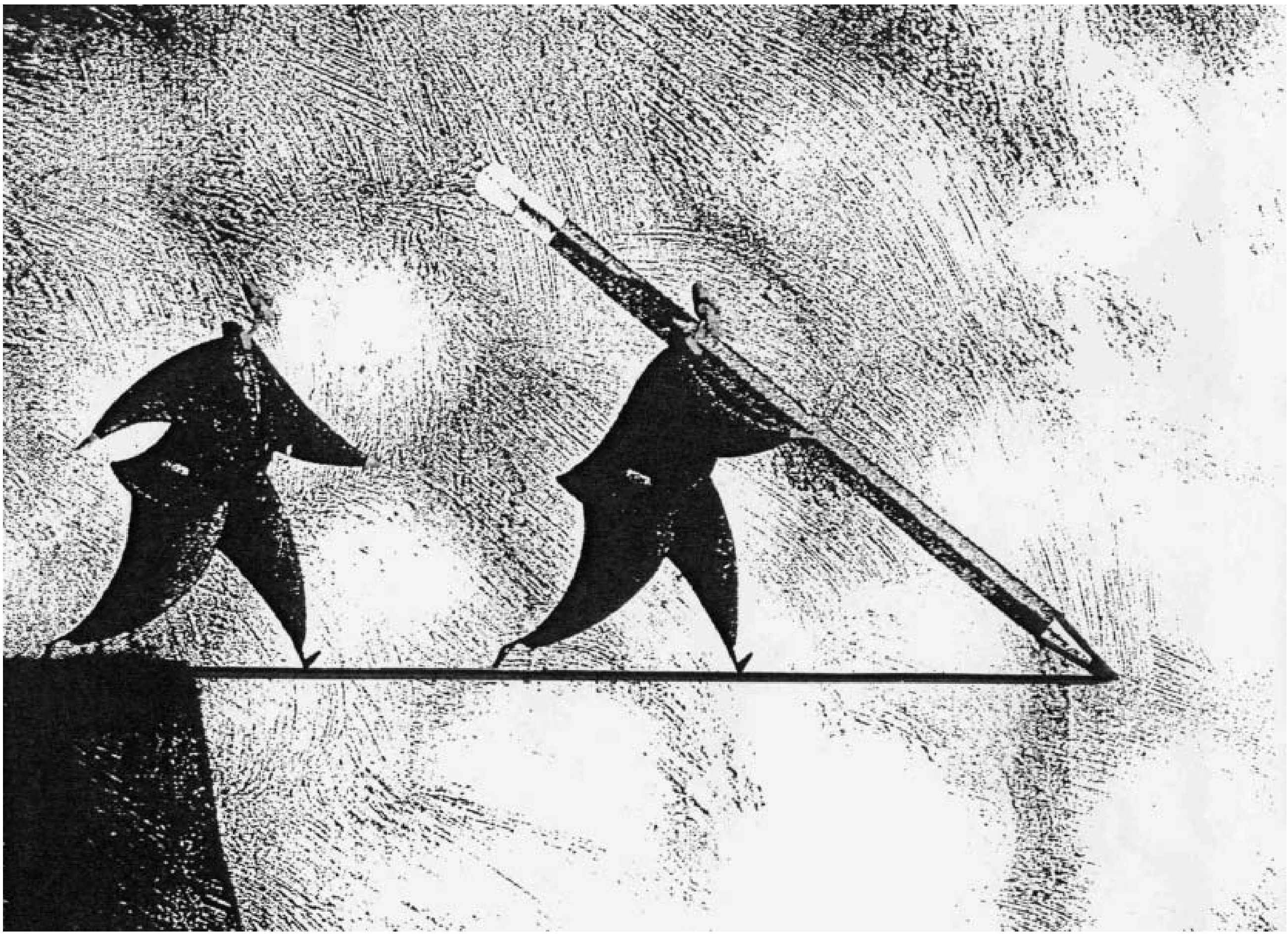

Figure 3.

LIQUID CRYSTALS, 1989, VOL. 5, NO. 6, 1757-1772

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

by C. MERTESDORF and H. RINGSDORF
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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

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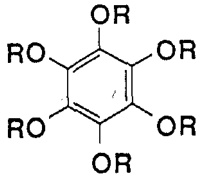
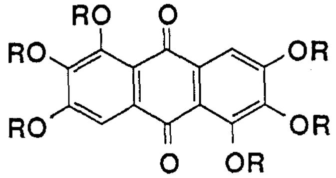
A



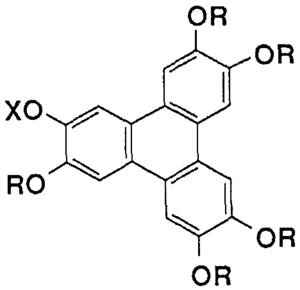
a) R = $-CO-C_4H_9$
b) R = $-CO-C_5H_{11}$
c) R = $-CO-C_6H_{13}$
d) R = $-CO-C_7H_{15}$
e) R = $-CO-C_8H_{17}$
f) R = $-CO-C_9H_{19}$

B



R = $-CO-C_7H_{15}$

C

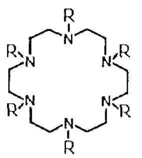


a) R,X = $-CO-C_7H_{15}$
b) R,X = $-C_5H_{11}$
c) R = $-C_5H_{11}$
X = $-CO-CH_3$

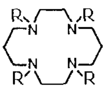
Disc-like mesogens that have been spread at the gas/water interface [6–11]

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).

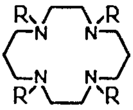
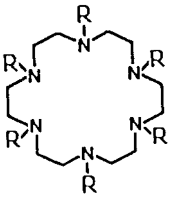
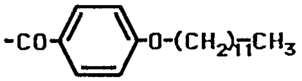
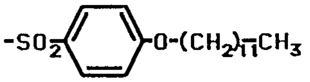
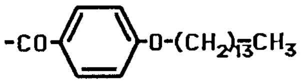
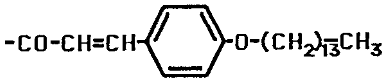
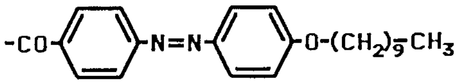
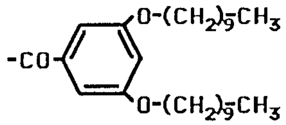
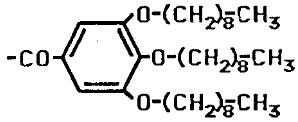
In this paper the synthesis and characterization of a series of acylated and sulphonated azocrowns, cyclame (1,4,8,11-tetraazacyclotetradecane) and hexacyclene

(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	$-CO-(CH_2)_{10}CH_3$	—
c 114 i	2	$-CO-(CH_2)_{12}CH_3$	c 107 i
c 114 i	3	$-CO-(CH_2)_{14}CH_3$	c 107 i
c 200 i	4	 	c 108 D_{hd} 140 i
—	5	 	c 186 i
c 196 i	6	 	c 106 D_{hd} 136 i
c 168 i	7	 	c 217 D_{hd} 233 i
—	8	 	c 237 D 245 i
glassy	9	 	glassy
glassy	10	 	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 Å^2 molecule^{-1} 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 Å^2 molecule^{-1} (figures 1 and 2). This result fits well with the area requirement of four alkyl chains (4 × 20 Å^2 molecule^{-1}) in the all-*trans* conformation, which are oriented vertically to

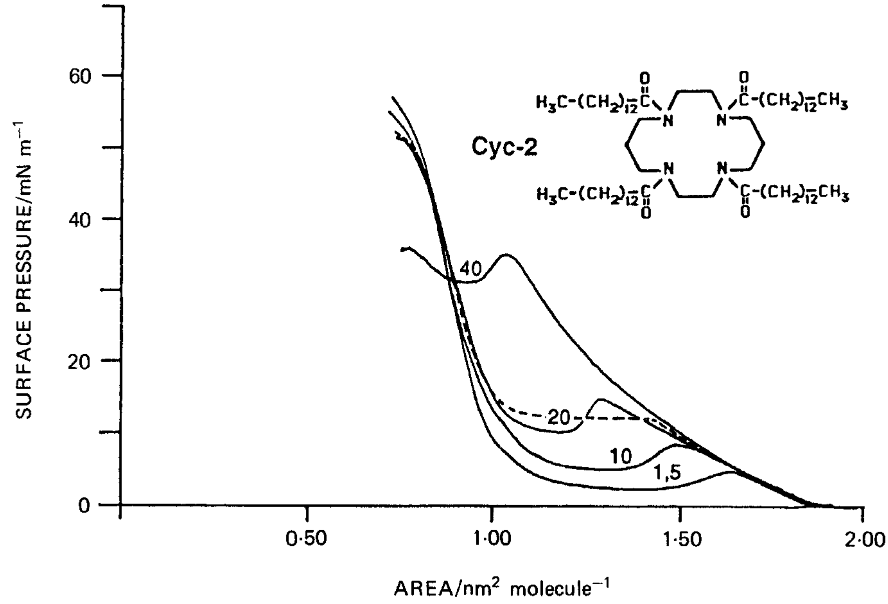


Figure 1. Surface-pressure/area diagram of Cyc-2 (temperatures in °C), dotted line shows slow compression (1 Å^2 molecule^{-1} min^{-1}) at 20°C.

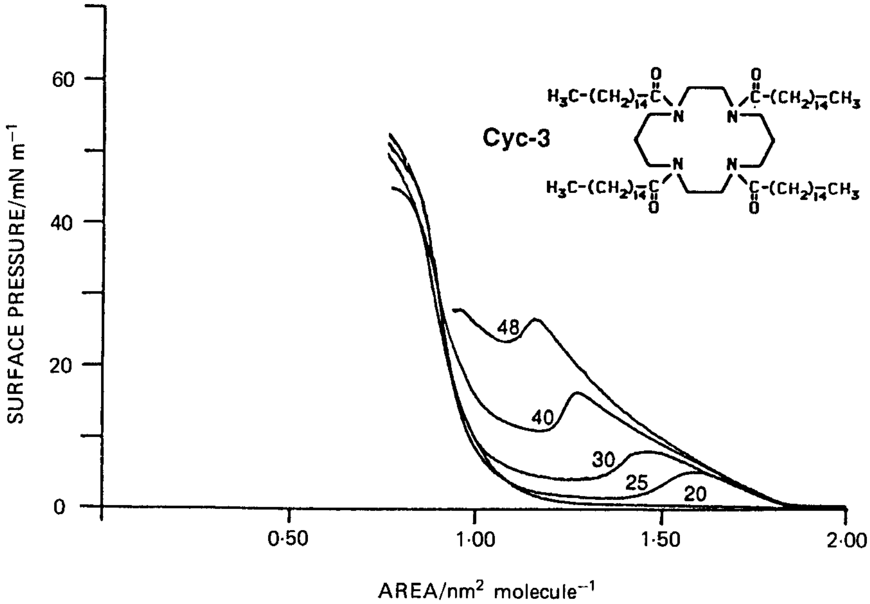


Figure 2. Surface-pressure/area diagram of Cyc-3 (temperatures in °C).

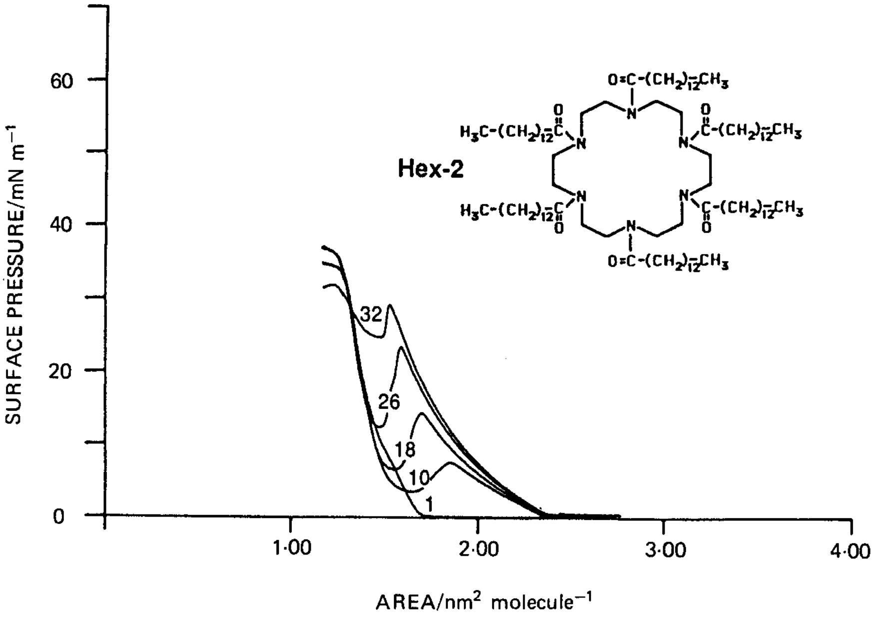


Figure 3. Surface-pressure/area diagram of Hex-2 (temperatures in °C).

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 $Å^2$ molecule^{-1} 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 $Å^2$ molecule^{-1} min^{-1} (compression time 2090 min), the bump is still present but much less pronounced.

The value of 130 $Å^2$ 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, corresonding 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

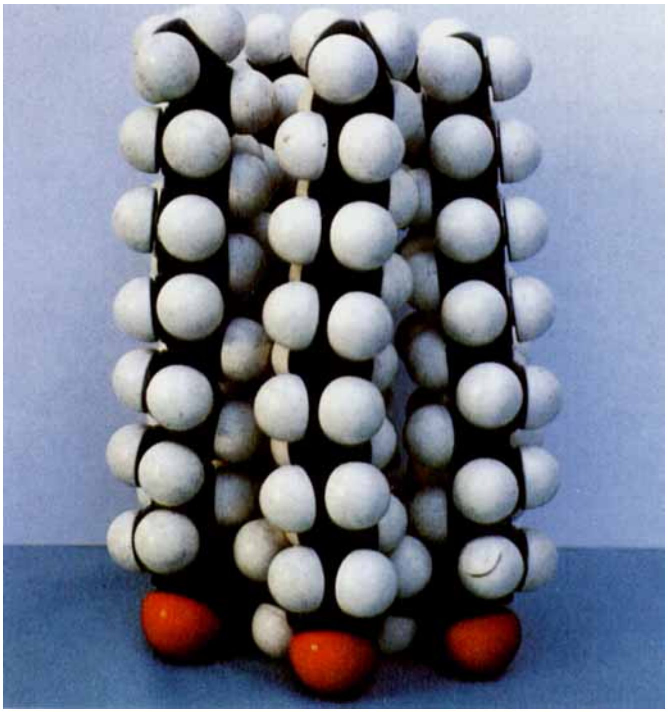


Figure 4. Molecular model of Hex-2: arrangement in the solid-condensed monolayer (cylindrical shape).

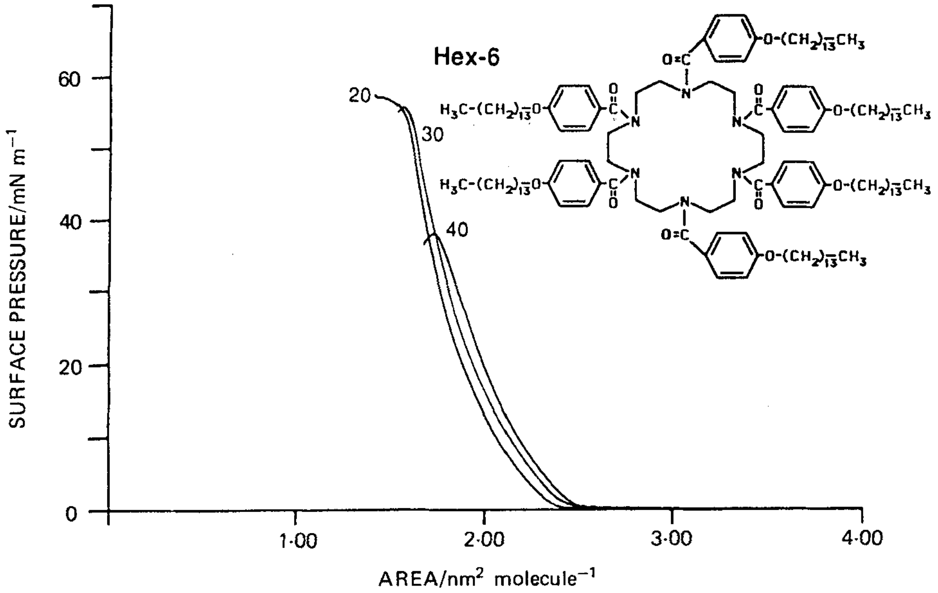


Figure 5. Surface-pressure/area diagram of Hex-6 (temperatures in °C).

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 Å^2 molecule^{-1}, figure 5) is 30 Å^2 molecule^{-1} larger than in the case of Hex-2 (130 Å^2 molecule^{-1}, figure 3). The same tendency can be observed for Cyc-2 and Cyc-6 (figures 1 and 6).

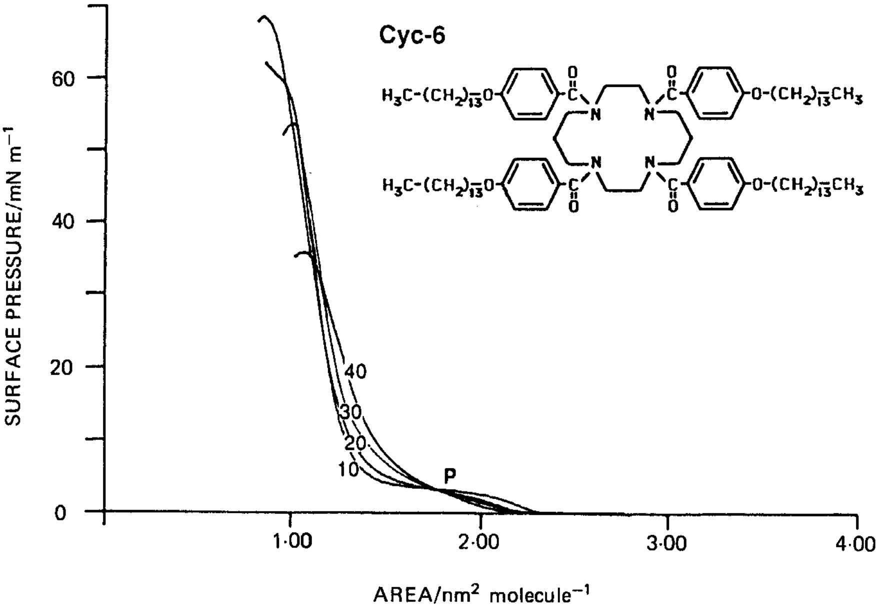


Figure 6. Surface-pressure/area diagram of Cyc-6 (temperatures in °C).

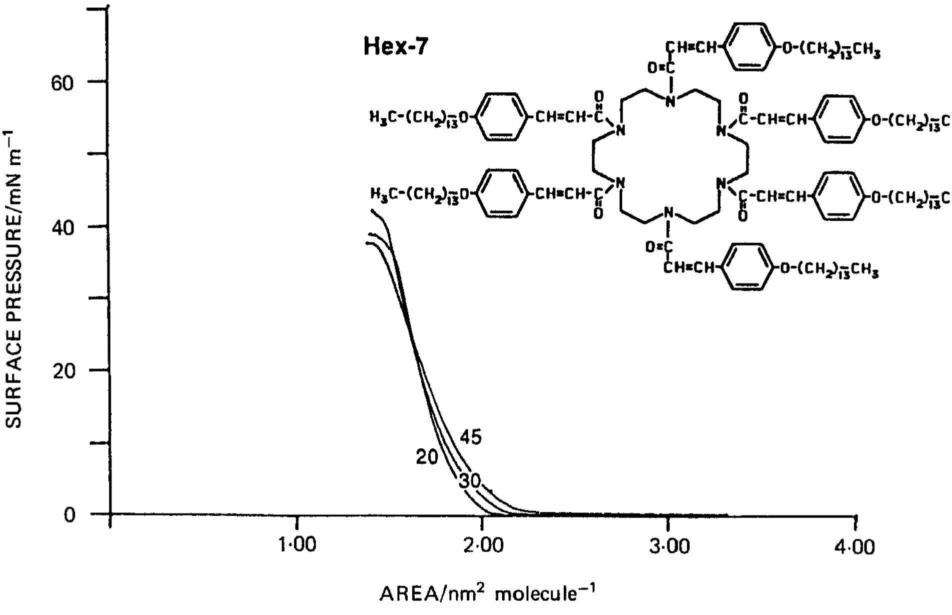


Figure 7. Surface-pressure/area diagram of Hex-7 (temperatures in °C).

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 Å^2 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 an 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].

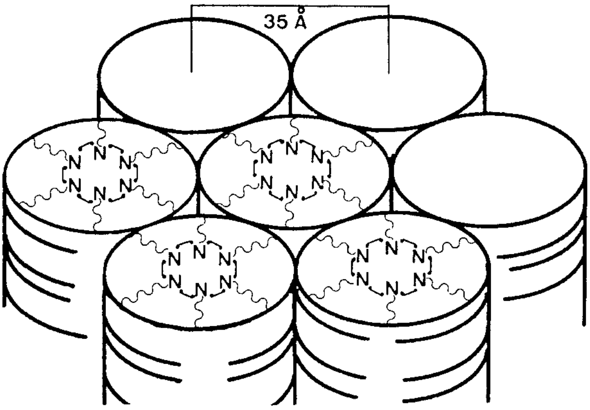


Figure 8. Schematic representation of D_{hd} mesophase.

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 Å should be related to the scattering of paraffinic chains, typical for liquids and LCs, whereas the sharp signal at approximately 35 Å corresponds to the intercolumnar distance of the hexagonal lattice.

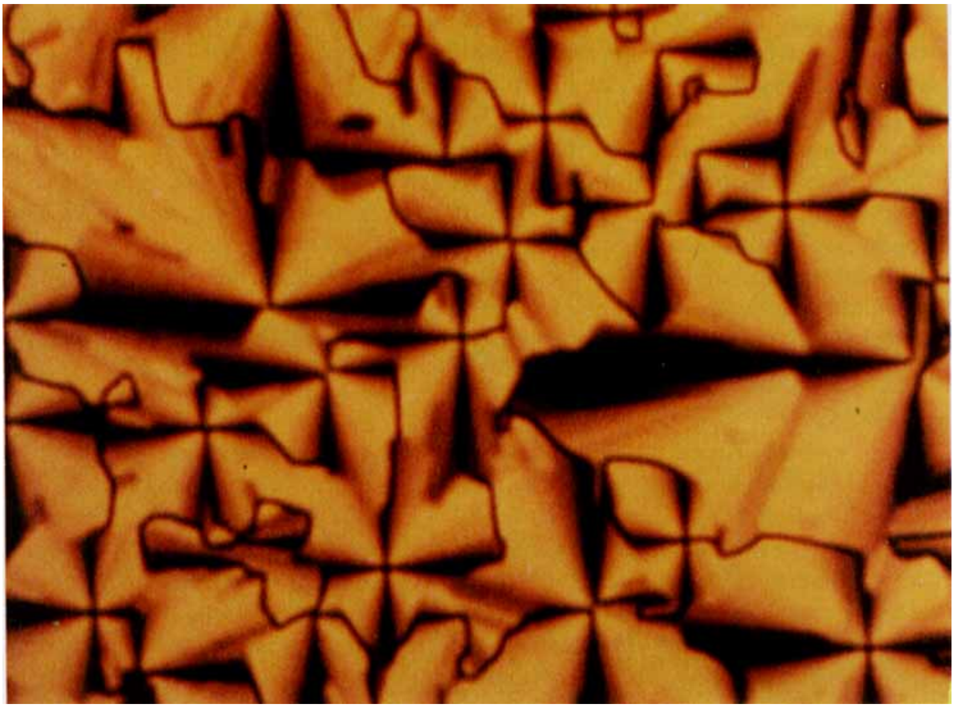


Figure 9. Texture micrograph of Hex-7 at 220°C, obtained by cooling the isotropic liquid.

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

Hexacyclene derivative	Molecular spacings d/Å in the mesophase at elevated temperatures		Molecular spacings d/Å 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 ($n \geqslant 10$) [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 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}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 (δ = 6–8 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

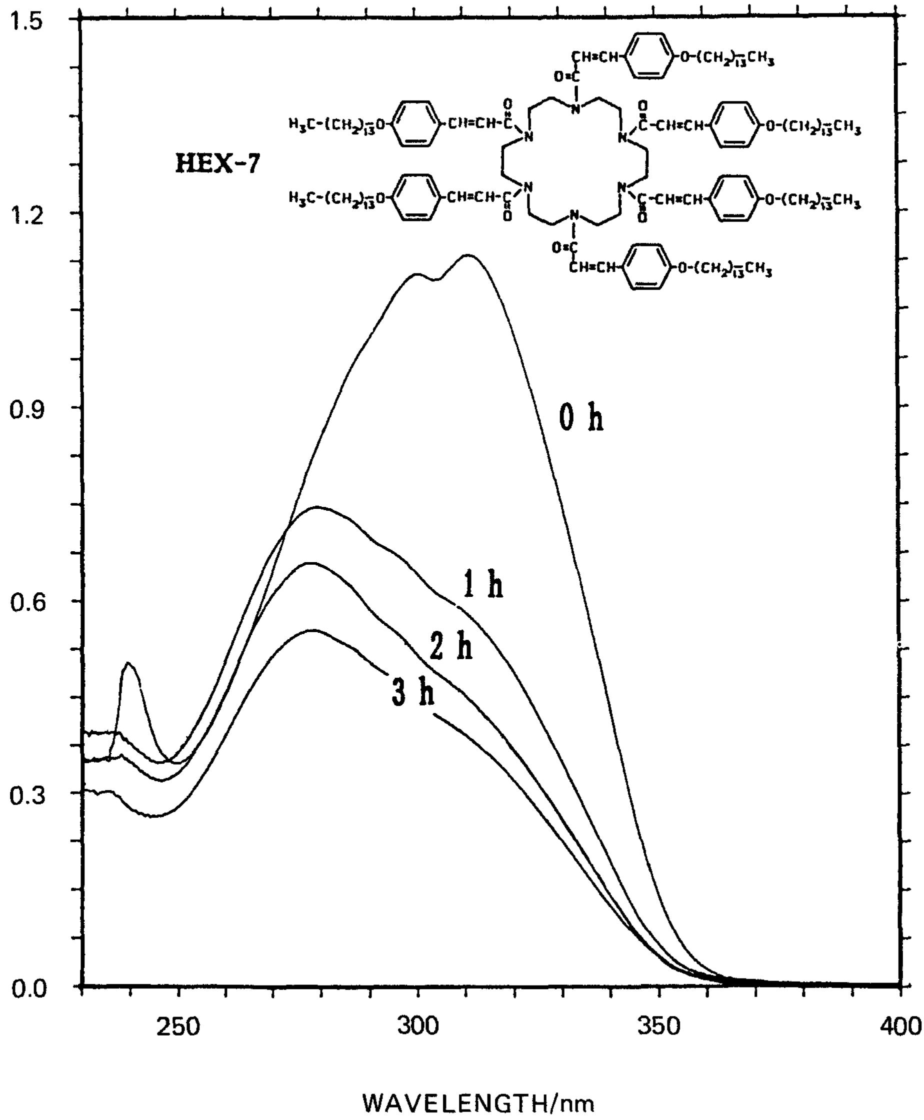


Figure 10. U.V. absorption spectra of Hex-7 in $CHCl_3$ after irradiation in the columnar state.

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 than 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 ($C_{19}H_{30}O_3$): found: 75·36 per cent C; 9·62 per cent H; calc. 74·47 per cent C; 9·86 per cent H. ^{1}H-N.M.R. ($CDCl_3$, 200 MHz), δ/ppm: 0·9 t (-**CH$_3$**); 1·3 m (-(**CH$_2$**)$_9$-); 1·8 m (-**CH$_2$**—CH$_2$—O); 4·0 t (-**CH$_2$**—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 ($C_{21}H_{34}O_3$): found: 76·34 per cent; 10·11 per cent; calc.: 75·40 per cent C; 10·24 per cent H. ^{1}H-N.M.R. ($CDCl_3$, 200 MHz), δ/ppm: 0·9 t (-**CH$_3$**); 1·3 m (-(**CH$_2$**)$_{11}$-); 1·8 m (-**CH$_2$**—CH$_2$-O); 4·0 t (-**CH$_2$**—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 ($C_{23}H_{36}O_3$): found: 77·52 per cent C; 9·92 per cent H; calc.: 76·62 per cent C; 10·06 per cent H. ^{1}-N.M.R. ($CDCl_3$, 200 MHz), δ/ppm: 0·9 t (-**CH$_3$**); 1·3 m (-(**CH$_2$**)$_{11}$-); 1·8 m (-**CH$_2$**—CH$_2$—O); 4·0 t (-**CH$_2$**-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. ^{1}H-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 μm; 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. ^{1}H-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. ^{13}C-N.M.R. [21] ($CDCl_3$, 400 MHz), δ/ppm: 153, 143, 124, 109 (ArC); 74, 69 (Ar-O-C). El-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°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}H-N.M.R. ($CDCl_3$, 400 MHz), δ/ppm: 0·87 t ($-\mathbf{CH_3}$); 1·27 m ($-(\mathbf{CH_2})_8-$); 1·45 m ($-\mathbf{CH_2}-CH_2-CH_2-O$); 1·8 m ($-\mathbf{CH_2}-CH_2-O$); 4·04 t ($-\mathbf{CH_2}-O$); 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 been 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}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 ($C_{102}H_{160}N_4O_8$): 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}H-N.M.R. ($CDCl_3$, 200 MHz), δ/ppm: 0·9 t 4($-\mathbf{CH_3}$); 1·3 m 4($-(\mathbf{CH_2})_{11}-$); 1·8 m 4($-\mathbf{CH_2}-CH_2-O$); 2·0 m 2($-\mathbf{CH_2}-N$); 3·7 m 8 ($-\mathbf{CH_2}-N$); 4·0 m 4($-\mathbf{CH_2}-O$); 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. ^{1}H-N.M.R. ($CDCl_3$, 200 MHz), δ/ppm: 0·9 t 6(–$\mathbf{CH_3}$); 1·3 m 6(–$(\mathbf{CH_2})_{11}$–); 1·8 m 6(–$\mathbf{CH_2}$—CH_2—O); 3·8 m 12(–$\mathbf{CH_2}$—N); 4·0 m 6(–$\mathbf{CH_2}$—O); 6·4–7·8 m 6(ArH, ViH).

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