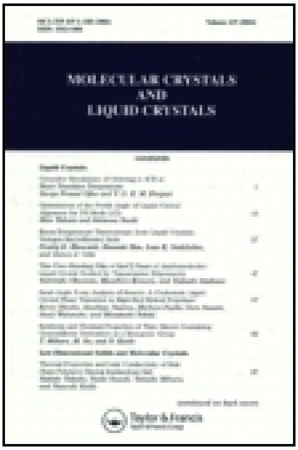

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Photoreactive Liquid Crystals in the Series of Dendritic and Cyclic Stilbenoid Compounds

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Photoreactive Liquid Crystals in the Series of Dendritic and Cyclic Stilbenoid Compounds

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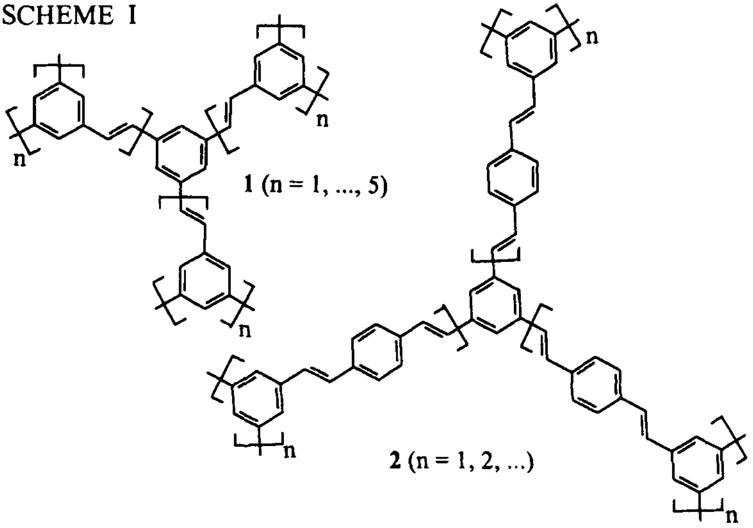
The dendrimers **1** and **2** and the areno-condensed annulenes **3** and **4** represent new mesogens for the generation of discotic mesophases. The stilbenoid building blocks of these compounds provide the molecular basis for interesting photochemical and photophysical effects like dimerisation, oligomerisation or the formation of charge carriers.

Keywords: Dendrimers; Annulenes; Conformational dynamics; Columnar dynamics; Photoreactivity; Photoconductivity

MOLECULAR DESIGN

Stilbenoid chromophores represent the molecular basis for various applications in photochemistry and photophysics [1]. Recently we succeeded in the preparation of dendrimers which consist of (*E*)-stilbene building blocks [2]. We conceived a convergent and between the different generations coupled synthesis in order to generate constitutionally and configurationally pure dendrimers [2]. The two most important symmetrical structures [3] are shown in Scheme 1. Alkoxy chains fixed on the periphery enhance the solubility and are a precondition for the generation of liquid crystalline phases. The number

SCHEME I



1 (n = 1, ..., 5)

2 (n = 1, 2, ...)

of stilbene units and naturally also the molecular masses grow fast from generation to generation. Table 1 gives a survey over the first five obtained generations of the series **1**.

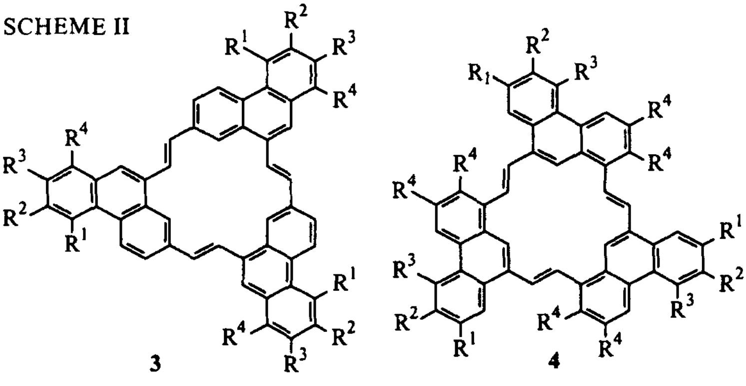
TABLE 1 Generations of the dendrimers **1** (n = 1 – 5) with tris(hexyloxy) substituted peripheral benzene rings

Compound **1** (generation n)	Number of olefinic double bonds $3\,(2^n - 1)$	Hydrocarbon skeleton $C_{24\cdot 2^n-18}H_{18\cdot 2^n-12}$	Entire formula	Molecular mass
a (1)	3	$C_{30}H_{24}$	$C_{84}H_{132}O_9$	1286
b (2)	9	$C_{78}H_{60}$	$C_{186}H_{276}O_{18}$	2800
c (3)	21	$C_{174}H_{132}$	$C_{390}H_{564}O_{36}$	5829
d (4)	45	$C_{366}H_{276}$	$C_{798}H_{1140}O_{72}$	11886
e (5)	93	$C_{750}H_{564}$	$C_{1614}H_{2292}O_{144}$	24000

trans-Stilbene is essentially planar; it is located in a flat minimum of the energy hypersurface with low barriers for the torsion around the single bonds. Thus one could assume that stilbenoid dendrimers represent flat discs; however, this is only valid for the first two generations. The steric repulsions in the higher generations force an extension into the third dimension. Molecular modelling [4] reveals that cylinders are formed with a strongly growing height and a diameter, which grows less than linearly with increasing number n. So it is not so surprising, that liquid crystalline phases are restricted to the first two generations of **1** and presumably also of **2**.

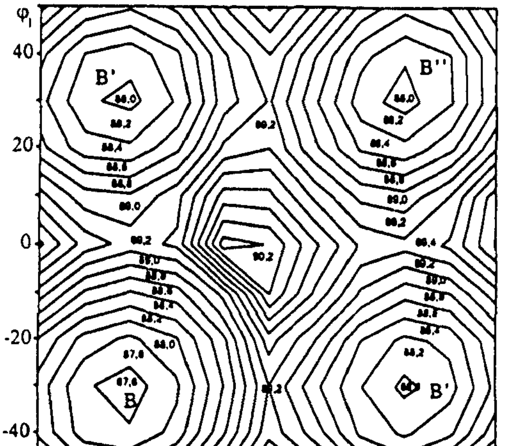
Another type of stilbenoid compounds is realized in areno-condensed annulenes [5-7]. This article shall be focused on [18]annulenes, which are condensed with three naphthalene or phenanthrene units. Especially in the series **3** and **4**, there are good chances for the generation of mesophases, provided that a suitable

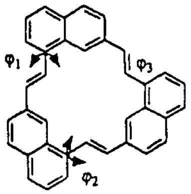
SCHEME II



3 **4**

number of long flexible side chains is fixed on the periphery. Whereas for example **3a** ($R^1 = R^2 = R^3 = OC_6H_{13}$, $R^4 = H$) forms a hexagonal columnar phase Col$_{hd}$ in a more than 300 K broad temperature interval [7], **4a** ($R^1 = R^3 = H$, $R^2 = R^4 = OC_6H_{13}$) does not form a mesophase. Both tri(phenanthro)[18]annulenes bear 9 hexyloxy chains. If three of the 9 hexyloxy chains are omitted, compound **4b** ($R^1 = R^2 = R^3 = H$, $R^4 = OC_6H_{13}$) generates between 115 and 192 °C a nematic discotic phase N_D. Another important factor is the planarisation of the central macrocyclic ring. Figure 1 demonstrates that areno-condensed [18]annulenes like **5** exist in a C_3 symmetrical, pyramidal conformation B (torsional angles: $\varphi_1 = \varphi_2 = \varphi_3 = -32$ °). The diastereomeric pair of enantiomers B' ($\varphi_1 = \varphi_3 = -32$ °, $\varphi_2 = 32$ °) and B'' ($\varphi_1 = \varphi_2 = 32$ °, $\varphi_3 = -32$ °) can be formed with low activation barriers. Thus the chiral C_3 conformation B can be transformed to its mirror image via C_1 conformations.





5

FIGURE 1 Contour plot of the MMX energies [8] (in kcal · mol^{-1}) of the conformations of **5**. (The torsional angles φ_1 and φ_2 were systematically varied; φ_3 and all other molecular parameters were optimized).

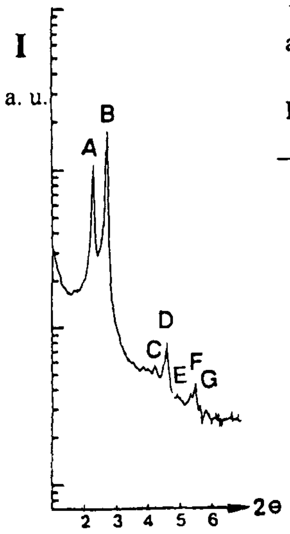
Such conformational dynamics are typical of the [18]annulenes. The situation of the areno-condensed [24]annulenes is much more complicated. We found in this latter series systems, which behave similar to the [18]annulenes (enantiotopic OCH_2 protons) and systems with an S_4 conformation, which cannot invert (diastereotopic OCH_2 protons). Interestingly LC phases were only detected for those areno-condensed annulenes, which show a fast inversion of the central macrocyclic ring, thus they appear to be planar on average.

CHARACTERISATION OF THE LC PHASES

The mesophases mentioned above were characterized by DSC, polarization microscopy and X-ray scattering measurements. Compound **1b'** ($R = OC_{12}H_{25}$), which serves here as an example, shows in the heating curve a transition of the crystalline state to the Col_{hd} phase at an offset temperature of 0 °C ($\Delta H = 52\ kJ \cdot mol^{-1}$), a transition to the Col_{ob} phase at 32 °C ($\Delta H = 4\ kJ \cdot mol^{-1}$) and a clearing point at 99 °C ($\Delta H = 17\ kJ \cdot mol^{-1}$). Figure 2 demonstrates the identification of the Col_{ob} phase by X-ray small angle scattering. The measured d values fit excellently to the values which can be calculated for the Bragg reflections.

PHOTOREACTIVITY

Photoreactions in the crystalline state are topochemically controlled; in LC phases the mobility of the molecules is higher and therefore an unfavorable arrangement of neighboring molecules may be overcome. Compound **3a** represents a typical example. The Col_{hd} phase is photochemically inert till temperatures of 150 °C are reached. Then a



Parameters

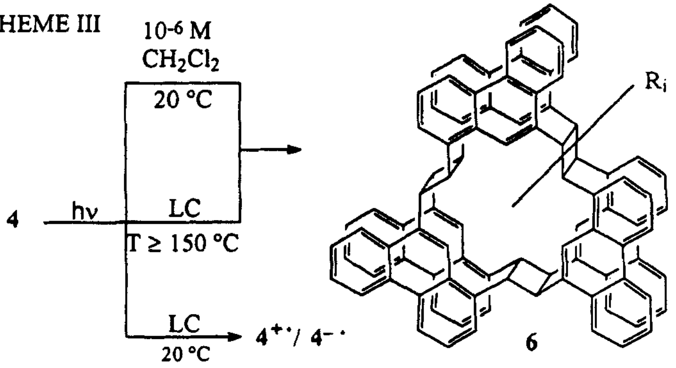
a = 42 Å b = 36 Å γ = 115 °

Bragg reflections				measured		calcd.
h	k	l		2Θ[°]	d [Å]	d [Å]
1	0	0	A	2.3	38.0	38.1
0	1	0	B_1	2.7	32.4	32.6
1	-1	0	B_2	2.7	32.4	32.5
1	1	0	C_1	4.2	21.0	20.8
2	-1	0	C_2	4.2	21.0	20.7
2	0	0	D	4.6	19.2	19.0
-1	2	0	E	4.9	18.1	18.0
0	2	0	F	5.3	16.6	16.3
2	-2	0	G	5.5	16.1	16.2

FIGURE 2 X-ray small angle scattering of **1b'** (R = $OC_{12}H_{25}$) at 86 °C (The calculation with $d^{-2} = \sin^{-2}\gamma\,(h^2a^{-2} + k^2b^{-2} - 2\,hk\,a^{-1}b^{-1}\cos\gamma)$ corresponds to the Col_{ob} phase).

slow photodimerisation starts which becomes a quantitative process above 200 °C. The energy-lowest arrangement of neighboring molecules in the columns is determined by the interaction of alkoxy substituted, electron-rich benzene rings with olefinic π centers. However, this interaction is not suitable for the photodimerisation to belt cyclophanes **6**. As soon as the uniaxial rotation in the column becomes so fast that the olefinic π centers of an electronically excited molecule can interact within its average lifetime with the olefinic π centers of a molecule in the ground state, a concerted [2π + 2π] reaction can start. The average lifetimes were measured (in solution) to be in the range of 3 – 10 ns [6]; consequently the photoreaction has this unusually high temperature effect. This theory is based on *ab initio* calculations and solid state NMR measurements of the LC phases of **3** and **4** which were deuteriated in different positions [9].

SCHEME III



In the series of the dendrimers **1** such highly regio- and stereoselective photodimerisation reactions were only observed for **1a** in solution; due

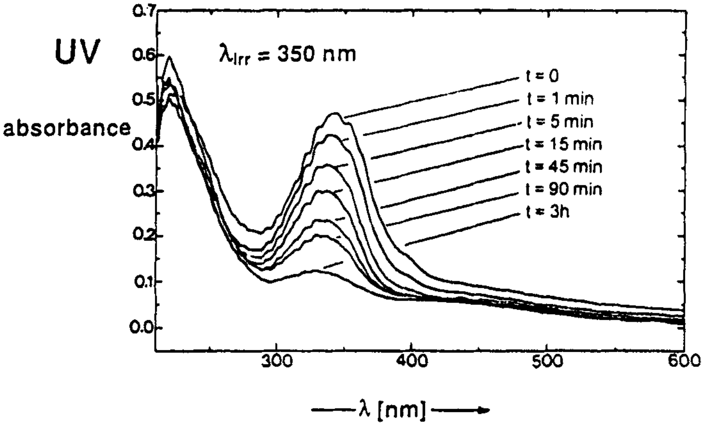


FIGURE 3 Time-dependent photocrosslinking of **1b'** (R = $OC_{12}H_{25}$) in a spincoat-film at room temperature

to a statistical formation of CC bonds, the LC phases of **1a,b** generate oligomers. Interestingly the stilbenoid chromophores disappear almost completely by irradiation (Figure 3). The mesophases tolerate only a few percent of turnover.

APPLICATIONS IN MATERIALS SCIENCE

The columnar phases of **3** and **4** represent photoconductive LC materials provided that the irreversible photochemistry at temperatures above 150 °C is avoided (Scheme III). Charge carriers are formed which have average lifetimes of 200 ns [10]. The charge carrier mobilities are high, they amount to $3 \cdot 10^{-1} \cdot cm^2 \cdot V^{-1} \cdot s^{-1}$. For reversible phase transitions induced by irradiation of stilbenoid compounds (optical switching) calamitic systems are more suitable than columnar phases [10].

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