[16] The structural data used in this calculation are $a = 2.986$ Å, $\alpha = 70.743$, space group $R\bar{3}m$. All calculations are based on the primitive unit cell rather than the conventional one.The symbols of special $\boldsymbol{k}$ points in the BZ and the Cartesian system have been taken from Bradely and Cracknell.[17] EH parameters: H_{ii} [eV] (coefficients ζ_1) for Hg: 6s −13.68 (2.649), 6p −8.47 (2.631); 5d −17.50 (6.436); double ς functions were used: 5d C_1 0.6438, ς_2 3.032, and C_2 0.5215.
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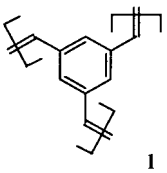
[21] Calculations on the other polymorphs of mercury would serve as test cases for our criteria on the occurrence of superconductivity, however, the lack of knowledge concerning the structures prevents such calculations.

Stilbenoid Dendrimers**

Herbert Meier* and Matthias Lehmann

Stilbenoid compounds show interesting photophysical and photochemical properties and are therefore appropriate for various applications in materials science.[1] Besides use in well-established areas such as optical brighteners, new applications are increasingly becoming apparent, including light-emitting diodes (LED), nonlinear optics (NLO), and optical imaging, storage, and switching techniques.



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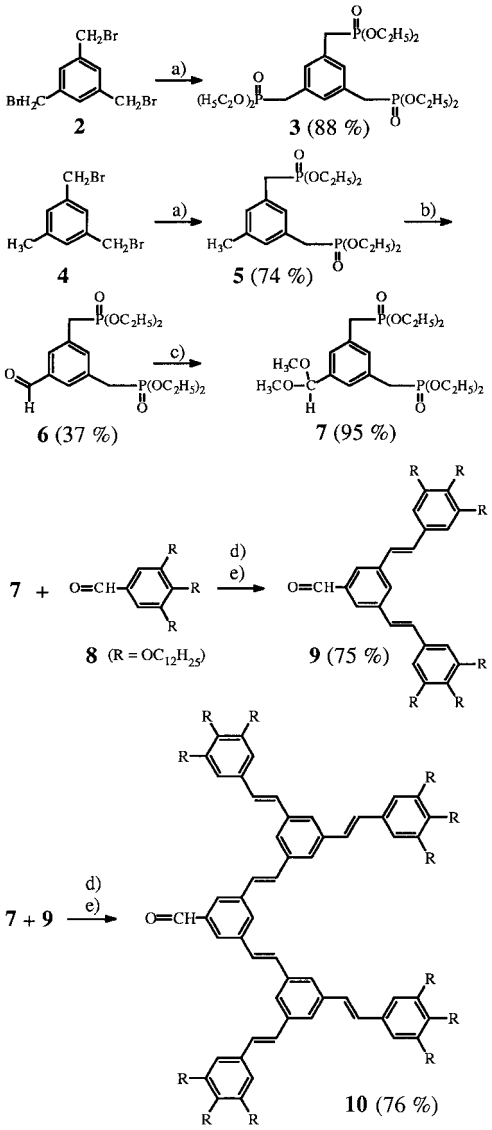
Through the incorporation of stilbenoid chromophores into dendrimers,[2] the design of which is also of considerable interest, we envisioned the new structural concept **1**. The convergent syntheses, coupled for individual generations, are depicted in Schemes 1 and 2. The required *E*-configured double bonds were formed by the Wittig–Horner reaction. The readily available tris(phosphonate) **3**[3] was used as a basic unit to form the core. Aldehyde **8**[4] and the bis(phosphonic acid) derivative **7**[5] with a protected aldehyde functionality served as building blocks for generating the dendrons; aldehydes **9**[6] and **10**[7] were obtained via **7** (Scheme 1). This procedure permitted the preparation of three generations of dendrimers (**1a**–**c**) from **3** and **8**, **9**, and **10** (Scheme 2). Tris(dodecyloxy)phenyl groups were attached to the periphery in order to enhance solubility and, as discussed below, to induce liquid crystalline (LC) behavior. The *trans* selectivity of the Wittig–Horner reaction is sufficiently high in this series of stilbenoid compounds to generate all-*trans* isomers **1a**–**c** within the limits of NMR detection. ^{1}H and ^{13}C NMR spectroscopy confirms the threefold symmetry of dendrimers **1a**–**c**. The observed chemical shifts are all very similar within this series of compounds (Table 1).



Scheme 1. Synthesis of the dendrimer precursors. a) $P(OC_2H_5)_3$, 160 °C; b) NBS (CCl_4), Fe (H_2O), 100 °C; c) CH_3OH, $HC(OCH_3)_3$, Dowex 50W-X8; d) $KOC(CH_3)_3$ (THF); e) HCl ($CHCl_3$).

The MALDI-TOF technique proved to be excellent for determining the molecular masses of **1a**–**c**. The discrepancy between the measured and calculated *m/z* values amounts to no more than one mass unit. For example, for **1c** with the molecular formula $C_{606}H_{996}O_{36}$ we obtained the value 8859.6, whereas the calculated mean for the peak of this molecular ion M^+ is 8858.6. The yields presented in Scheme 2 refer to dendritically pure compounds whose formation is assured by the convergent synthesis. A small amount of the "two-branched" compound, formed when only two molecules of **10** reacted with **3**, could only be detected in the crude product of **1c** with the MALDI-TOF method.

The aggregation of the stilbenoid dendrimers is especially interesting. Neat **1a** and **1b** generate two liquid crystalline phases each (D_{hd}: discotic hexagonal disordered phase; D_{rd}: discotic rectangular disordered phase; D_{ob}: discotic oblique

[*] Prof. Dr. H. Meier, Dipl.-Chem. M. Lehmann
Institut für Organische Chemie der Universität
J.-J. Becherweg 18-22, D-55099 Mainz (Germany)
Fax: (+49) 6131 395-396
E-mail: hmeier@mzdmza.zdv.uni-mainz.de

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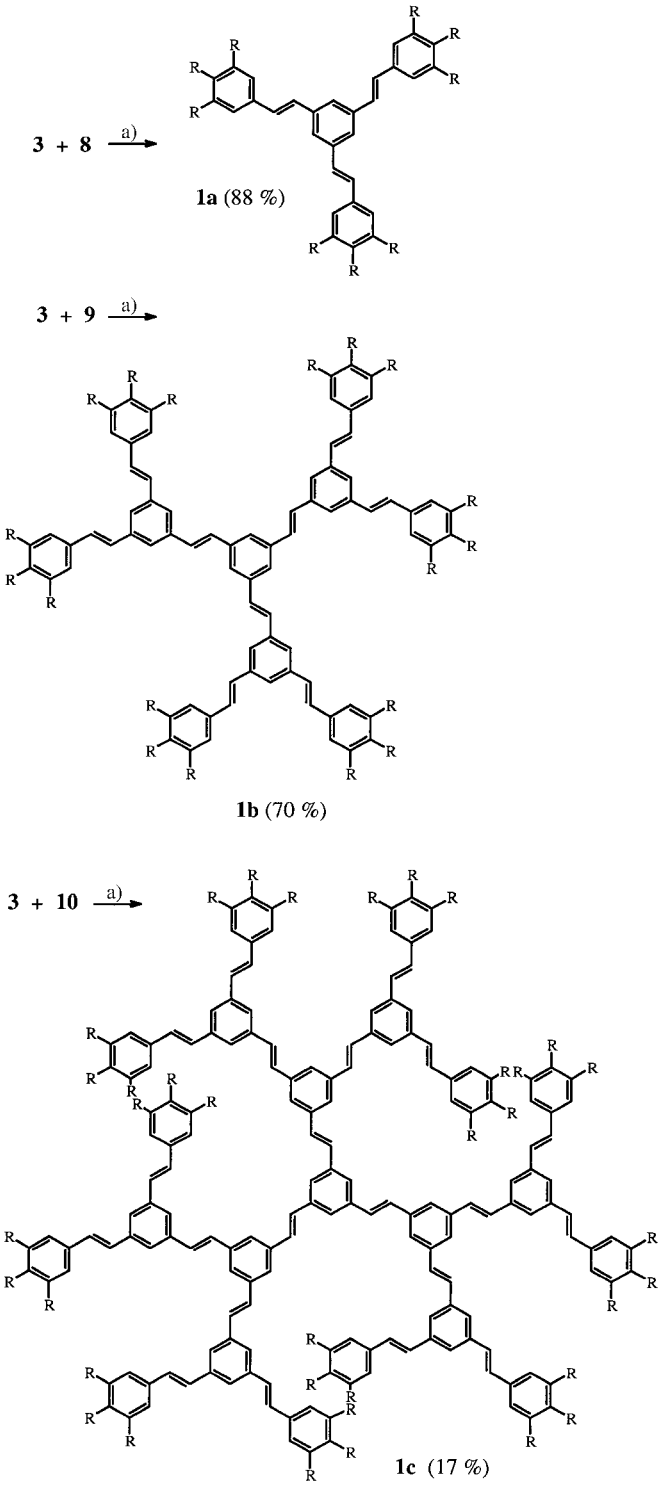

Scheme 2. Synthesis of the three dendrimer generations **1a–c**. a) $KOC(CH_3)_3$ (THF).

phase). We obtained the following phase transitions for the two dendrimers from differential scanning calorimetric (DSC) measurements:

1a: k – 11 °C/59 kJ mol^{-1} – D_{hd} – 31 °C/4 kJ mol^{-1} – D_{rd} – 61 °C/8 kJ mol^{-1} – i

1b: k – 0 °C/52 kJ mol^{-1} – D_{hd} – 32 °C/4 kJ mol^{-1} – D_{ob} – 99 °C/17 kJ mol^{-1} – i

The data represent onset temperatures for phase transitions and the corresponding changes in enthalpy ΔH_o in the second heating curve. The DSC diagram for **1c** shows only melting of the alkoxy chains at −36 °C. Steric hinderance in the periphery of **1c** is probably too great for formation of an LC phase.

The mesophases of **1a** and **b** were characterized by polarization microscopy and X-ray scattering. Figure 1 shows

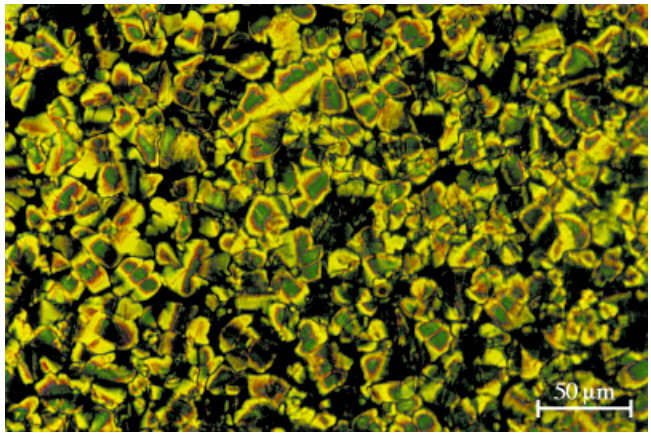

Figure 1. Texture of the D_{ob} phase of the second-generation dendrimer **1b**. The photograph was made with a polarization microscope after cooling to 45.9 °C.

the texture of the D_{ob} phase of **1b**; the corresponding parameters from X-ray analysis are provided in Table 2.

Table 2. Parameters for X-ray scattering of the D_{ob} phase of **1b** (determined at 86 °C with CuK_α irradiation: $a = 42.0$ Å, $b = 38.0$ Å, $\gamma = 115°$).

Bragg reflections			d [Å]	
h	k	l	measured	calculated
1	0	0	38.0	38.0
0	1	0	32.4	32.6
0	−1	0	32.4	32.4
1	1	0	21.0	20.8
2	−1	0	21.0	20.7
2	0	0	19.2	19.0
−1	2	0	18.1	18.0
0	2	0	16.6	16.3
2	2	0	16.1	16.2

Table 1. Chemical shifts in the ^{1}H NMR spectra of **1a–c** (δ values in $CDCl_3$, TMS as internal standard).

1	CH_3	CH_2	*p*-OCH_2	*m*-OCH_2	Peripheral arom. H	Other arom. H	Peripheral olef. H[a]	Other olef. H[b]
a	0.85	1.1–1.9	3.96	4.02	6.72 (6H)	7.49 (3H)	7.00, 7.10	–
b	0.85	1.2–1.9	3.96	4.02	6.74 (12H)	7.55 (9H), 7.62 (3H)	7.02, 7.11	7.23 (6H)
c	0.83	1.1–1.8	3.7–4.0		6.69 (24H)	7.53 (6H), 7.55 (12H) 7.62 (3H), 7.69 (6H) 7.71 (3H)	6.97, 7.07	7.27 (12H), 7.34 (6H)

[a] AB, $^3J = 16.1 \pm 0.1$ Hz. [b] Singlets.

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Electron-scattering investigations and model calculations that are currently in progress should provide more detailed characterization of the molecular self-assembly. Liquid crystalline properties are presumably destroyed by the segment mobility of an increasing number of stilbene units; in principle, the number of conformers is doubled per double bond, but for symmetry reasons the maximum number of 2^n (e.g., 2^{21} for the third generation) cannot be reached.

The tendency to aggregate increases from **1a** through **1b** to **1c**. Figure 2 shows the temperature dependence of ^{1}H NMR

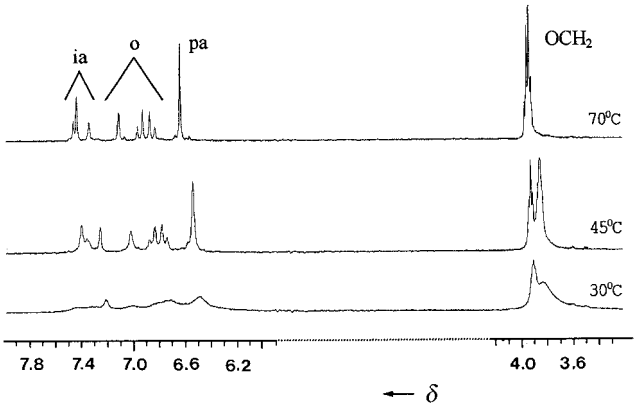

Figure 2. Temperature-dependent ^{1}H NMR spectra (400 MHz) of **1b** in C_6D_{12} (4.6×10^{-3} M). ia: inner aromatic protons; o: olefinic protons; pa: aromatic protons on the peripheral benzene rings.

spectra of **1b** in [D_{12}]cyclohexane. Whereas the spectrum in $CDCl_3$ at 20 °C exhibits quite normally resolved signals, aggregation in cyclohexane causes considerable line broadening, which has its origin in reduced segment mobility. The effect is so pronounced for **1c** that no highly resolved ^{1}H NMR spectrum can be obtained even by heating the sample.

Temperature- and concentration-dependent aggregation in nonpolar solvents can also be followed with fluorescence spectroscopy. For example, a 10^{-8} M solution of **1b** in cyclohexane shows two fluorescence maxima at $\lambda = 399$ and $\lambda = 419$ nm; however, only a broad band with a single bathochromically shifted maximum at 424 nm is obtained for a 10^{-4} M solution. In chloroform or dichloromethane the fluorescence band is independent of concentration. The interaction especially between the electron-rich peripheral benzene rings and the solvent molecules (which exhibit acceptor properties) is apparently so strong that dendrimer molecules no longer form aggregates. In dichloromethane, all three dendrimers **1a**–**c** show a UV absorption with $\lambda_{max} =$ 329 nm, which decreases upon irradiation. Decomposition progresses are especially fast in the aggregated state in cyclohexane.[8]

With respect to structure, **1a**–**c** are most closely related to the stiff dendrimers consisting of tolan building blocks.[9, 10] However, the aggregation, phase behavior, and photochemistry of the stilbenoid dendrimers have not been found with the tolan system so far,[11] nor was this expected in the case of photochemistry. Further investigations of conformational mobility and charge and energy transfers are currently in progress.

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[6] **9**: M.p. 66 °C, ^{1}H NMR ($CDCl_3$): $\delta = 0.86$ (m, 18H, CH_3), 1.40–1.85 (m, 120H, CH_2), 3.98 (t, 4H, OCH_2), 4.01, (t, 8H, OCH_2), 6.72 (s, 4H, arom. H), 7.00/7.13 (AB, $^3J = 16.2$ Hz, 4H, olef. H), 7.80 (t, 1H, 4-H), 7.85 (d, 2 H, 2-H, 6-H), 10.04 (s, 1H, CHO).
[7] **10**: M.p. 106 °C, ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (m, 36H, CH_3), 1.24–1.86 (m, 240H, CH_2), 3.97 (t, 8H, OCH_2), 4.03 (t, 16H, OCH_2), 6.74 (s, 8H, arom. H), 7.24/7.29 (AB, $^3J = 16.1$ Hz, 4H, olef. H), 7.55 (m, 6 H, arom. H), 7.88 (t, 1H, 4-H), 7.94 (d, 2H, 2-H, 6-H), 10.09 (s, 1H, CHO).
[8] Decomposition of the stilbenoid chromophores is almost complete; that is, the C–C double bonds disappear through formation of intermolecular C–C single bonds. For the 21 double bonds of **1c** and the 9 double bonds of **1b** these are processes that lead to very complex structures. In the case of **1a** we were able to isolate two diastereomeric dimers with three four-membered rings each; see J. Juriew, T. Skorochodova, J. Merkushew, W. Winter, H. Meier, *Angew. Chem.* **1981**, *93*, 285; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 269.
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