Highly Branched Alkanoic Acids from the Preen-Gland Wax of the Domestic Goose as Building Blocks for Chiral Triphenylenes

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

The synthesis of chiral triphenylenes **7a**,**b** bearing side chains derived from enantiomerically pure trimethyloctanoate **1a** and tetramethyldecanoate **1b** from the preen-gland wax of domestic goose was achieved in 3 or 4 steps. Compounds **7a**,**b** were nonmesogenic; however, mixtures of **7a**,**b** with hexakis(octyloxy)triphenylene or hexakis(decyloxy)triphenylene displayed columnar mesophases or soft crystal G phases, as was shown by differential-scanning calorimetry and optical-polarizing microscopy. Circular-dichroism measurements revealed weak associations of **7a**,**b** in solution.

Introduction. – Hexakis(alkyloxy)-substituted triphenylenes are important building blocks for thermotropic columnar liquid crystals [1–3]. As a result of their short-range ordered assembly in the mesophase, several members of this family display high charge-carrier mobilities along the columns, as well as high electrical conductivity and photoconductivity, which make these compounds promising candidates for applications [4][5]. In addition, even in solution, hexakis(alkyloxy)triphenylenes can undergo self-assembly, form charge-transfer complexes with strong electron acceptors [6], or give helical structures with chiral intercalating agents [7]. In contrast, the chemistry and properties of chiral triphenylenes have been used to a much smaller extent [6b][8]. This is probably due to the fact that a convenient access to chiral side-chain precursors is required. It has recently been shown that the preen-gland wax of domestic goose contains large amounts of (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoates and related highly methylated alkanoic acids, which can conveniently be isolated on a gram-scale employing transesterification and Spaltrohr® distillation [9]. Furthermore, it was demonstrated that these alkanoic acids can be used for calamitic liquid crystals giving broader SmC* phases than the corresponding derivatives with a single methyl branching [10]. We were, thus, interested whether such alkanoic acids can be used for

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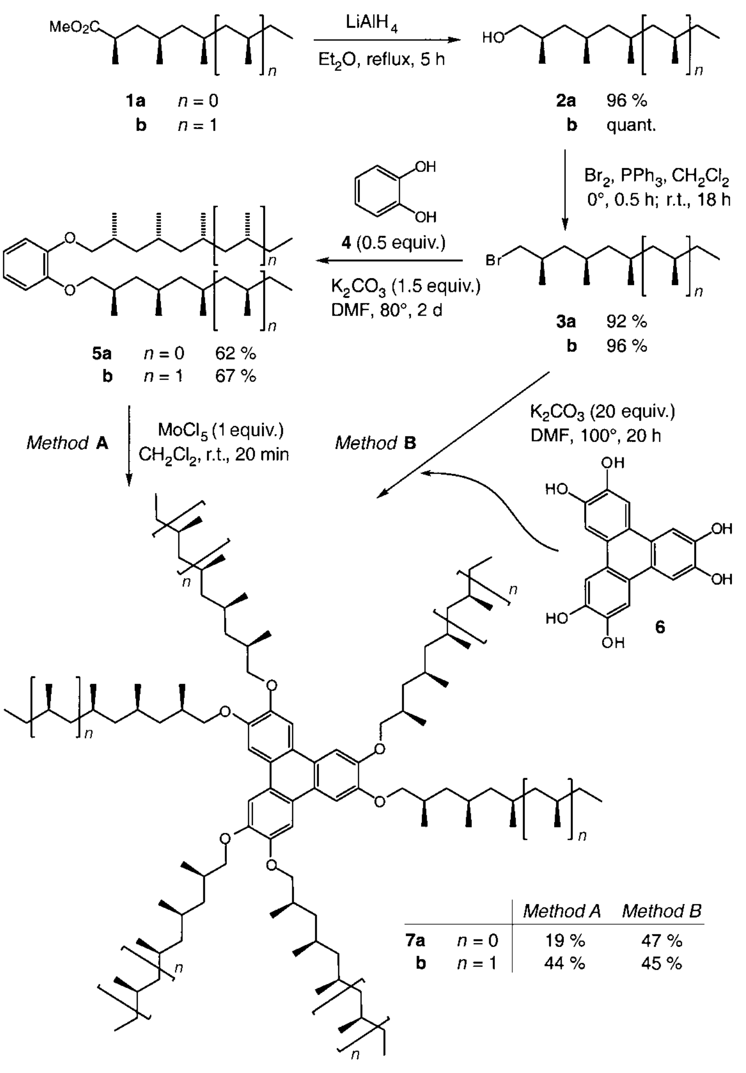
the preparation of chiral triphenylenes as well. The results concerning synthesis and properties are reported below.

Results and Discussion. – The synthesis of chiral triphenylenes **7a**,**b** is outlined in the *Scheme*. Starting from enantiomerically pure methyl (2*R*,4*R*,6*R*)-2,4,6-trimethyloctanoate (**1a**), reduction with $LiAlH_4$ yielded alcohol **2a** in 96% yield [9]. Reduction of the corresponding methyl (2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecanoate (**1b**) gave alcohol **2b** almost quantitatively. Reaction of **2a** and **2b** with Br_2 in the presence of PPh_3 provided the bromides **3a** and **3b** in 92 and 96% yield, respectively. Subsequent alkylation of catechol (**4**) with bromides **3a** and **3b** in the presence of K_2CO_3 in DMF gave the chiral 1,2-bis(alkyloxy)benzenes **5a** and **5b** in 62 and 67% yield, respectively. Compounds **5a**,**b** turned out to be highly volatile and, therefore, precautions had to be taken during workup and evaporation of solvents. Oxidative trimerization of 1,2-bis(alkyloxy)benzenes **5a**,**b** was achieved in the presence of 1 equiv. of $MoCl_5$ in CH_2Cl_2 at room temperature [11] yielding the desired triphenylenes **7a**,**b** in 19 and 44% (*Method A*). As an alternative route, direct alkylation of triphenylenehexal **6** [12] with bromides **3a**,**b** in the presence of 20 equiv. of K_2CO_3 in DMF at 100° was attempted (*Method B*); to our delight the yield of compound **7a** could be improved (47%), and compound **7b** was obtained in 45%.

Differential-scanning calorimetry (DSC) and optical-polarizing microscopy revealed no mesomorphic properties of **7a**,**b**. Both compounds were colorless isotropic oils at room temperature. During the first cooling cycle, triphenylene **7a** showed a melting transition from the isotropic liquid to the crystalline phase at $-36°$ and a crystal-to-crystal transition at $-132°$. The corresponding transition temperatures for compound **7b** were observed at -37 and $-134°$. Comparison with the known chiral hexakis{[(3*R*)-3,7-dimethyloctyl]oxy}triphenylene derived from (3*R*)-dihydrocitronellol, which displays a disordered hexagonal columnar mesophase between 19 and 36° [8a], indicates that the introduction of additional branching points in the side chain severely damages mesophase stability.

Next, mixtures of chiral triphenylenes **7a** and **7b** with hexakis(octyloxy)triphenylene (**HAT8**) [13] and hexakis(decyloxy)triphenylene (**HAT10**) [13], respectively, were studied by DSC and optical-polarizing microscopy. The results are summarized in the *Table*. Whereas **HAT8** displays a hexagonal columnar mesophase between 67 and 87° (*Entry 1*), admixture of the chiral triphenylene **7a** and **HAT8** resulted in an overall decrease of the phase-transition temperatures and a change of the phase behavior in most cases (*Entries 2–13*). For the 10:1 mixture **HAT8/7a**, only a melting transition was obtained by DSC (*Entries 2–4*). However, on cooling from the isotropic phase, a mosaic texture with star-shaped domains typical of a soft crystal G phase (formerly assigned as SmG) [14][15] was detected under the microscope between 59 and 47° (*Fig. 1*). Upon further cooling to room temperature, the mixture crystallized. The 5:1 mixture **HAT8/7a** displayed a crystal-to-crystal transition at 45° and a melting transition at 62° during first heating (*Entry 5*). Further cooling/heating cycles revealed only one phase transition (*Entries 6* and *7*). DSC Results were supported by optical investigations. In contrast, the 2:1 mixture displayed monotropic mesomorphic behavior. A melting transition was detected at 46° and a clearing transition at 58° (*Entry 8*). During subsequent heating cycles, similar transition temperatures were

Scheme



		Method A	Method B
7a	$n = 0$	19 %	47 %
b	$n = 1$	44 %	45 %

found (*Entries 9* and *10*). Optical investigations revealed a columnar texture with spherulitic domains upon rapid cooling between 48 and 58° (*Fig. 2*). The 1:1 mixture displayed enantiotropic melting behavior (*Entries 11–13*). Under the microscope, fan-shaped textures typical of columnar mesophases were detected at 63° upon cooling. **HAT10** displays a hexagonal columnar mesophase between 58 and 69° (*Entry 15*). Addition of **7b** to **HAT10** again resulted in a dramatic change of the phase behavior. For all three mixtures (10:1, 5:1, and 2:1), a crystal-to-crystal transition and a melting transition can be observed on first heating (*Entries 16, 19,* and *22*). Subsequent cooling cycles lead immediately to crystallization. Under the microscope, crystalline fibres were detected. However, a 1:1 contact preparation of **HAT10** and **7b** yielded a fan-

Table. *Phase-Transition Temperatures and Enthalpies of Chiral Triphenylenes* **7a**,**b** *and Mixtures with Achiral Triphenylenes* **HAT8** *or* **HAT10**[a])

Entry	Compound(s)	Ratio	Temp. Cycle	Phase I[b])	T_{trans1} [°] ($\Delta H_{\mathrm{trans1}}$ [kJ mol^{-1}])	Phase II[b])	T_{trans2} [°] ($\Delta H_{\mathrm{trans2}}$ [kJ mol^{-1}])	Phase III[b])
1	**HAT8**	–	1st heating[c])	K	67	$\mathrm{Col_h}$	87	I
2	**HAT8/7a**	10 : 1	1st heating	K	56 (62.5)	I		
3	**HAT8/7a**	10 : 1	1st cooling[a])[d])	I	44 (59.1)	$\mathrm{G_{cr}}$		
4	**HAT8/7a**	10 : 1	2nd heating	K	64 (79.4)	I		
5	**HAT8/7a**	5 : 1	1st heating	$\mathrm{K_1}$	45 (6.7)	$\mathrm{K_2}$	62 (64.8)	I
6	**HAT8/7a**	5 : 1	1st cooling	I	42 (56.9)	$\mathrm{K_1}$		
7	**HAT8/7a**	5 : 1	2nd heating	$\mathrm{K_1}$	54 (60.9)	I		
8	**HAT8/7a**	2 : 1	1st heating	K	46 (0.8)	Col	58 (65.1)	I
9	**HAT8/7a**	2 : 1	1st cooling	I	37 (58.4)	K		
10	**HAT8/7a**	2 : 1	2nd heating	K	48 (54.1)	Col	58 (2.1)	I
11	**HAT8/7a**	1 : 1	1st heating[d])	K	47	Col	67	I
12	**HAT8/7a**	1 : 1	1st cooling[d])	I	66	Col	51	K
13	**HAT8/7a**	1 : 1	2nd heating[d])	K	47	Col	60	I
14	**7a**	–	1st heating	$\mathrm{K_1}$	– 132 (38.0)	$\mathrm{K_2}$	– 36 (5.2)	I
15	**HAT10**	–	1st heating[c])	K	58	$\mathrm{Col_h}$	69	I
16	**HAT10/7b**	10 : 1	1st heating	$\mathrm{K_1}$	54 (11.9)	$\mathrm{K_2}$	58 (81.1)	I
17	**HAT10/7b**	10 : 1	1st cooling	I	46 (73.5)	$\mathrm{K_1}$		
18	**HAT10/7b**	10 : 1	2nd heating	$\mathrm{K_1}$	57 (76.1)	I		
19	**HAT10/7b**	5 : 1	1st heating	$\mathrm{K_1}$	53 (32.7)	$\mathrm{K_2}$	57 (84.4)	I
20	**HAT10/7b**	5 : 1	1st cooling	I	45 (72.0)	$\mathrm{K_1}$		
21	**HAT10/7b**	5 : 1	2nd heating	$\mathrm{K_1}$	56 (75.5)	I		
22	**HAT10/7b**	2 : 1	1st heating	$\mathrm{K_1}$	44 (88.2)	$\mathrm{K_2}$	52 (93.3)	I
23	**HAT10/7b**	2 : 1	1st cooling	I	41 (72.7)	$\mathrm{K_1}$		
24	**HAT10/7b**	2 : 1	2nd heating	$\mathrm{K_1}$	53 (73.3)	I		
25	**HAT10/7b**	1 : 1	1st heating[d])	K	48	Col	72	I
26	**HAT10/7b**	1 : 1	1st cooling[d])	I	66	Col	42	K
27	**HAT10/7b**	1 : 1	2nd heating[d])	K	47	Col	71	I
28	**7b**	–	1st heating	$\mathrm{K_1}$	– 134 (23.4)	$\mathrm{K_2}$	– 37 (6.6)	I

[a]) Transition temperatures were determined by DSC (heating rate 10 K min^{-1}). [b]) The following phases were observed: K (crystalline), $\mathrm{Col_h}$ (hexagonal columnar), $\mathrm{G_{cr}}$ (soft crystalline G phase), and I (isotropic). [c]) See [14]. [d]) Transition temperatures were determined by optical-polarizing microscopy.

shaped texture between 48 and 72° on heating (between 66 and 42° on cooling) (*Entries 25–27*). The texture was assigned to a hexagonal columnar mesophase.

Thus, it seems that with increasing concentration of the chiral triphenylene **7a**,**b**, stable mesophases can be obtained. Unfortunately, further confirmation of these assignments by X-ray diffraction were not possible.

Next, CD spectra of solutions of chiral triphenylenes **7a**,**b** in $CHCl_3$ and hexane were examined (*Figs. 3* and *4*). The spectra in $CHCl_3$ differ from those in hexane. In particular, the ellipticity of **7a** increases in hexane as compared to $CHCl_3$. The same result was found for **7b**. Noteworthy are the sharp and relatively intense peaks at *ca.* 277 nm for both **7a** and **7b** in hexane, showing opposite signs. The reason for this remains to be investigated. The solvent-dependence of the circular dichroism is probably caused by an increased association of the triphenylene moieties in the nonpolar solvent resulting from π-π stacking interactions [7]. The fact that the observed ellipticities were relatively small may be either due to weak aggregation or

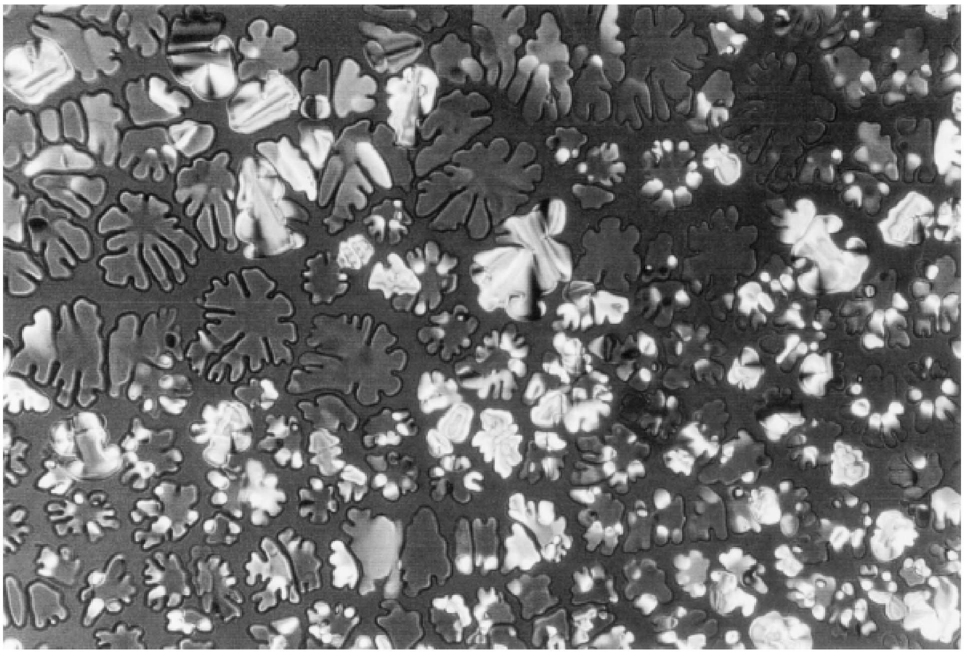


Fig. 1. *Mosaic texture with star-shaped domains of* **HAT8/7a** *10 : 1.* The photomicroscopic image of the mesophase was obtained at 50° on cooling (2° min^{-1}) from the isotropic liquid (crossed polarizers, magnification × 100)

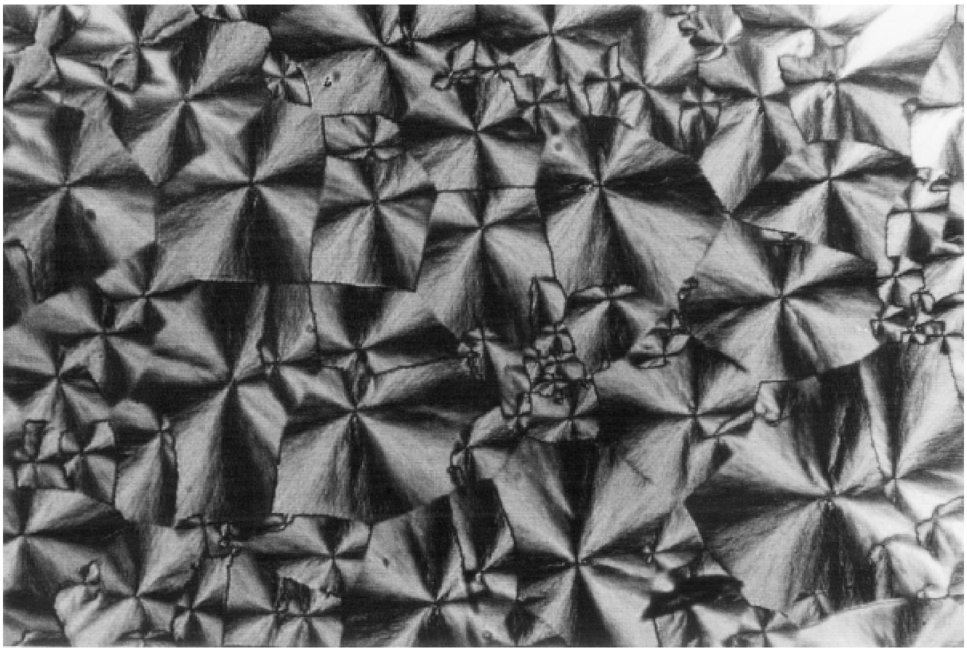


Fig. 2. *Columnar texture with spherulitic domains of* **HAT8/7a** *2 : 1.* The photomicroscopic image of the mesophase was obtained at 51° on cooling (10° min^{-1}) from the isotropic liquid (crossed polarizers, magnification × 100).

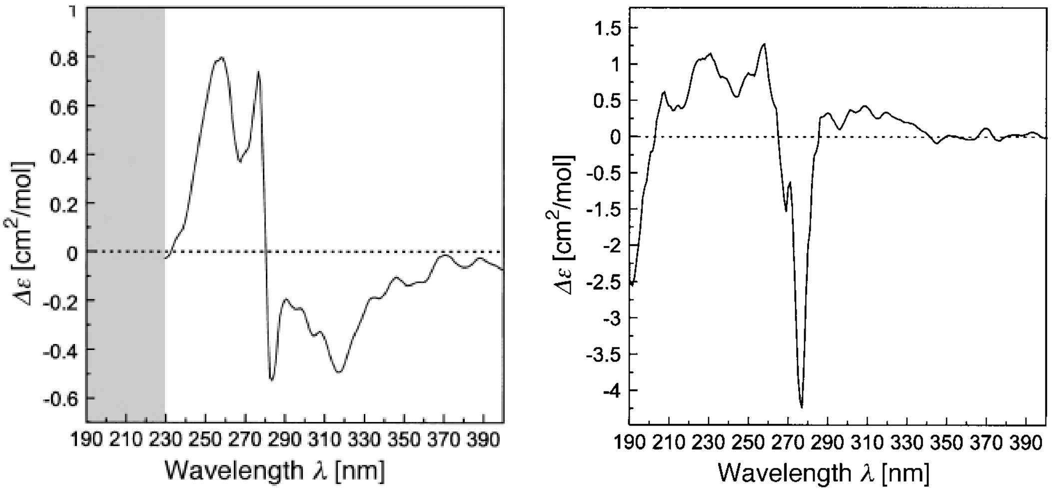


Fig. 3. *CD Spectrum of triphenylene* **7a** *in* $CHCl_3$ ($c = 10^{-3}$ mol l^{-1}) (left) *and in hexane* ($c = 10^{-3}$ mol l^{-1}) (right). The grey area indicates the range of wavelength where no significant measurement is possible due to the absorption of the solvent.

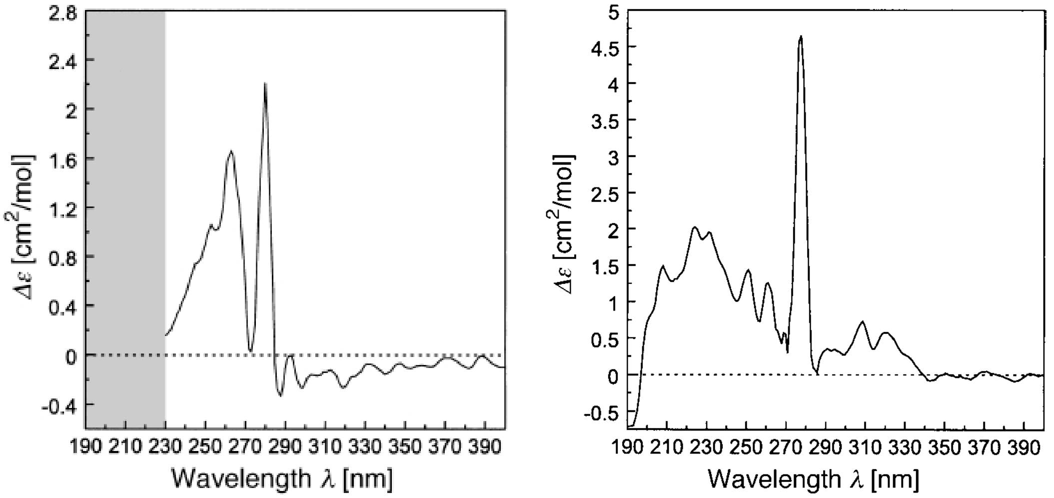


Fig. 4. *CD Spectrum of triphenylene* **7b** *in* $CHCl_3$ ($c = 10^{-3}$ mol l^{-1}) (left) *and in hexane* ($c = 10^{-3}$ mol l^{-1}) (right). The grey area indicates the range of wavelength where no significant measurement is possible due to the absorption of the solvent.

small helical twisting of the columnar aggregates resulting from the in part quite remote chiral centers in the side chain with respect to the central triphenylene chromophore.

Conclusions. – We have shown that chiral triphenylenes **7a**,**b** with highly branched alkanoic acid derived side chains can be used to form mesophases in mixtures with achiral triphenylenes although compounds **7a**,**b** are nonmesomorphic. In addition, compounds **7a**,**b** form helical aggregates in solution.

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Experimental Part

General. FC = flash chromatography. NMR Spectra: *Bruker AM-400* and *Bruker AC-200-P*; δ in ppm and J in Hz. Differential-scanning calorimetry: *Rheometric Scientific DSC-SP* and *Perkin-Elmer DSC-7*; heating and cooling rate, 10 K $\min^{-1}$. Polarizing microscopy: *Olympus-BX50* polarizing microscope combined with a *Linkam LTS350* hot stage and *Linkam TP-93* central processor. Circular dichroism spectra: *Jasco J-715*; cell length 0.5 mm, band width 1.0 nm, scanning speed 200 nm $\min^{-1}$, response time 0.25 s. EI-MS: in *m/z* (rel. %).

Triphenylene-2,3,6,7,10,11-hexol (**6**) was prepared according to [12], *2,3,6,7,10,11-hexakis(octyloxy)triphenylene* (**HAT8**) and *2,3,6,7,10,11-hexakis(decyloxy)triphenylene* (**HAT10**) were prepared according to [13].

*(*2R,4R,6R*)-2,4,6-Trimethyloctan-1-ol* (**2a**). *Methyl (*2R,4R,6R*)-2,4,6-trimethyloctanoate* (**1a**; 12.0 g, 0.06 mol) was added dropwise to a suspension of $LiAlH_4$ (7.30 g, 0.19 mol) in Et_2O (70 ml) while maintaining gentle refluxing. Then the mixture was refluxed for 5 h. After cooling to r.t., the mixture was carefully hydrolyzed under ice-cooling by subsequent dropwise addition of H_2O (7 ml), 10% NaOH soln. (7 ml), and H_2O (21 ml), and the resulting suspension was stirred for 1 h. The precipitate was removed by filtration and washed with Et_2O, and the combined org. layer was dried ($MgSO_4$) and evaporated: 9.94 g (96%) of **2a**. Colorless liquid. $[\alpha]_D^{20} = +6.1$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.53 (*dd*, $J = 5.0$, 10.4, H_a–C(1)); 3.36 (*dd*, $J = 6.8$, 10.4, H_b–C(1)); 1.76–1.68 (*m*, H–C(2)); 1.61–1.51 (*m*, H–C(4)); 1.54–1.18 (*m*, H–C(6), H_a–C(7), H_a–C(5), H_a–C(3)); 1.08–0.99 (*m*, H_b–C(7)); 0.92 (*d*, $J = 6.6$, Me–C(2)); 0.86 (*d*, $J = 6.3$, Me–C(4)); 0.83 (*d*, $J = 6.6$, Me–C(6)); 0.93–0.82 (*m*, H_b–C(5), H_b–C(3), Me(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 68.3 (C(1)); 44.7 (C(5)); 41.3 (C(3)); 33.1 (C(2)); 31.5 (C(6)); 28.8 (C(7)); 27.5 (C(4)); 20.9 (*Me*–C(4)); 19.9 (*Me*–C(6)); 17.5 (*Me*–C(2)), 11.1 (C(8)).

*(*2R,4R,6R,8R*)-2,4,6,8-Tetramethyldecan-1-ol* (**2b**). As described for **2a**, with **1b**: 11.5 g (quant.) of **2b**. Colorless liquid. $[\alpha]_D^{20} = +2.95$ ($c = 1.08$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.54 (*dd*, $J = 5.0$, 10.4, H_a–C(1)); 3.36 (*dd*, $J = 6.8$, 10.4, H_b–C(1)); 1.76–1.68 (*m*, H–C(2)); 1.62–1.52 (*m*, H–C(4), H–C(6)); 1.46–1.15 (*m*, H–C(8), H_a–C(9), H_a–C(3), H_a–C(7), H_a–C(5)); 1.09–0.99 (*m*, H_b–C(9)); 0.93 (*d*, $J = 6.8$, Me–C(2)); 0.86 (*d*, $J = 6.3$, Me–C(4)); 0.84 (*d*, $J = 6.6$, Me–C(8)); 0.83 (*d*, $J = 6.6$, Me–C(6)); 0.92–0.80 (*m*, H_b–C(3), H_b–C(5), Me(10), H_b–C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 68.2 (C(1)); 45.5 (C(5)); 44.6 (C(7)); 41.1 (C(3)); 33.1 (C(2)); 31.5 (C(8)); 28.7 (C(9)); 27.5 (C(4), C(6)); 21.0 (*Me*–C(4), *Me*–C(6)); 20.0 (*Me*–C(8)); 17.6 (*Me*–C(2)); 11.1 (C(10)).

Bromides **3a**,**b**: *General Procedure.* A soln. of Br_2 (5.1 ml, 0.10 mol) in CH_2Cl_2 (15 ml) was added dropwise at 0° to a soln. of PPh_3 (26.2 g, 0.10 mol) in CH_2Cl_2 (300 ml), and the resulting suspension was stirred for 30 min at 0°. Then **2a**,**b** (0.10 mol) was added at 0°, and the mixture was stirred for 18 h at r.t. The org. layer was washed with sat. Na_2SO_3 soln. (200 ml) and H_2O (200 ml) and dried ($MgSO_4$). Upon evaporation of the solvent, Ph_3PO precipitated from the soln., which was removed by filtration. The precipitate was washed with pentane, the combined filtrate evaporated, and the residue purified by FC (SiO_2; pentane): **3a**,**b** as colorless liquids.

*(*2R,4R,6R*)-1-Bromo-2,4,6-trimethyloctane* (**3a**): 10.8 g (92%). $[\alpha]_D^{20} = -15.0$ ($c = 2.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.42 (*dd*, $J = 4.0$, 9.8, H_a–C(1)); 3.32 (*dd*, $J = 6.0$, 9.8, H_b–C(1)); 1.93–1.86 (*m*, H–C(2)); 1.59–1.52 (*m*, H–C(4)); 1.47–1.30 (*m*, H–C(6), H_a–C(3), H_a–C(7)); 1.24–1.17 (*m*, H_a–C(5)); 1.11–1.02 (*m*, H_b–C(7)); 1.01 (*d*, $J = 6.6$, Me–C(2)); 0.86 (*d*, $J = 6.0$, Me–C(4)); 0.85 (*d*, $J = 6.6$, Me–C(6)); 0.99–0.84 (*m*, H_b–C(3), H_b–C(5), Me(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 44.8 (C(5)); 42.6 (C(3)); 41.6 (C(1)); 32.3 (C(2)); 31.5 (C(6)); 29.0 (C(7)); 27.4 (C(4)); 20.6 (*Me*–C(4)); 19.8 (*Me*–C(6)); 19.7 (*Me*–C(2)); 11.1 (Me(8)).

*(*2R,4R,6R,8R*)-1-Bromo-2,4,6,8-tetramethyldecane* (**3b**): 13.2 g (95%). $[\alpha]_D^{20} = -13.6$ ($c = 2.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.43 (*dd*, $J = 4.0$, 9.8, H_a–C(1)); 3.32 (*dd*, $J = 6.0$, 9.8, H_b–C(1)); 1.93–1.85 (*m*, H–C(2)); 1.63–1.52 (*m*, H–C(6), H–C(4)); 1.47–1.32 (*m*, H–C(8), H_a–C(3), H_a–C(9)); 1.24–1.15 (*m*, H_a–C(7), H_a–C(5)); 1.01 (*d*, $J = 6.6$, *Me*–C(2)); 1.09–0.84 (*m*, H_b–C(9), H_b–C(3), H_b–C(5), Me(10), H_b–C(7), Me–C(4), Me–C(6), Me–C(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 45.6 (C(5)); 44.7 (C(7)); 42.3 (C(3)); 41.5 (C(1)); 32.3 (C(2)); 31.5 (C(8)); 28.9 (C(9)); 27.4 (C(4), C(6)); 20.9 (*Me*–C(8)); 20.7 (*Me*–C(4)); 20.0 (*Me*–C(6)); 19.8 (*Me*–C(2)); 11.2 (Me(10)). EI-MS: 278 (2), 276 (2, M^+), 249 (2), 247 (2), 207 (4), 205

(4), 179 (6), 177 (6), 165 (36), 163 (37), 151 (1), 149 (1), 141 (8), 125 (11), 111 (7), 99 (18), 85 (21), 83 (43), 71 (42), 57 (100), 55 (39).

1,2-Bis(alkyloxy)benzenes **5a**,**b**: *General Procedure.* Compound **3a**,**b** (27.0 mmol) was added dropwise to a suspension of K_2CO_3 (5.60 g, 40.5 mmol) and catechol (=benzene-1,2-diol; **4**; 1.49 g, 13.5 mmol) in DMF (40 ml), and the resulting mixture was stirred at 80° for 2 d. After cooling to r.t., H_2O (100 ml) was added, the aq. layer extracted with Et_2O (2 × 100 ml) and the combined org. layer washed with H_2O (4 × 100 ml), dried ($MgSO_4$), and evaporated. Purification by FC (SiO_2, hexanes/ethyl AcOEt 40 : 1) yielded **5a**,**b** as colorless liquids.

*1,2-Bis{[(2*R*,4*R*,6*R*)-2,4,6-trimethyloctyl]oxy}benzene* (**5a**): 3.48 g (62%). $[\alpha]_D^{20} = -14.4$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.89 (*m*, 4 arom. H); 3.88 (*dd*, $J = 5.0$, 8.8, 2 H, H_a–C(1′)); 3.71 (*dd*, $J = 7.0$, 8.8, 2 H, H_b–C(1′)); 2.14–2.06 (*m*, 2 H, H–C(2′)); 1.70–1.61 (*m*, 2 H, H–C(4′)); 1.53–1.34 (*m*, 6 H, H_a–C(3′), H–C(6′), H_a–C(7′)); 1.31–1.24 (*m*, 2 H, H_a–C(5′)); 1.12–1.01 (*m*, 4 H, H_b–C(7′), H_b–C(3′)); 1.08 (*d*, $J = 6.6$, 6 H, Me–C(2′)); 0.96–0.88 (*m*, 2 H, H_b–C(5′)); 0.91 (*d*, $J = 6.6$, 6 H, Me–C(4′)); 0.87 (*t*, $J = 7.3$, 6 H, Me–C(8′)); 0.85 (*d*, $J = 6.6$, 6 H, Me–C(6′)). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.5 (C(1), C(2)); 120.9 (C(4), C(5)); 113.9 (C(3), C(6)); 74.2 (C(1′)); 44.7 (C(5′)); 41.7 (C(3′)); 31.5 (C(6′)); 30.8 (C(2′)); 28.9 (C(7′)); 27.5 (C(4′)); 21.0 (*Me*–C(4′)); 19.9 (*Me*–C(6′)); 18.1 (*Me*–C(2′)); 11.1 (Me(8′)). EI-MS: 418 (10, M^+), 264 (11), 125 (2), 121 (3), 110 (100), 97 (6), 85 (14), 71 (15), 57 (38). Anal. calc. for $C_{28}H_{50}O_2$: C 80.31, H 12.04; found: C 79.93, H 12.10.

*1,2-Bis{[(2*R*,4*R*,6*R*,8*R*)-2,4,6,8-tetramethyldecyl]oxy}benzene* (**5b**): 3.39 g (67%). $[\alpha]_D^{20} = -7.90$ ($c = 1.01$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.88 (*m*, 4 arom. H); 3.88 (*dd*, $J = 5.0$, 8.8, 2 H, H_a–C(1′)); 3.70 (*dd*, $J =$ 7.1, 8.8, 2 H, H_b–C(1′)); 2.12–2.04 (*m*, 2 H, H–C(2′)); 1.69–1.55 (*m*, 4 H, H–C(4′), H–C(6′)); 1.52–1.33 (*m*, 6 H, H_a–C(3′), H–C(8′), H_a–C(9′)); 1.27–1.19 (*m*, 4 H, H_a–C(5′), H_a–C(7′)); 1.07 (*d*, $J = 6.6$, 6 H, Me–C(2′)); 1.10–0.97 (*m*, 4 H, H_b–C(9′), H_b–C(3′)); 0.90 (*d*, $J = 6.6$, 6 H, Me–C(4′)); 0.85 (*d*, $J = 6.6$, 6 H, Me–C(8′)); 0.83 (*d*, $J = 6.6$, 6 H, Me–C(6′)); 0.93–0.82 (*m*, 10 H, H_b–C(5′), H_b–C(7′), Me(10′)). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.5 (C(1), C(2)); 120.9 (C(4), C(5)); 114.0 (C(3), C(6)); 74.2 (C(1′)); 45.5 (C(5′)); 44.6 (C(7′)); 41.5 (C(3′)); 31.5 (C(8′)); 30.8 (C(2′)); 28.8 (C(9′)); 27.5 (C(4′), C(6′)); 21.1, 21.0 (*Me*–C(4′), *Me*–C(6′)); 20.0 (*Me*–C(8′)); 18.2 (*Me*–C(2′)); 11.1 (Me(10′)). EI-MS: 502 (44, M^+), 306 (18), 196 (2), 149 (1), 139 (5), 125 (11), 110 (100), 71 (54), 69 (76), 57 (96). Anal. calc. for $C_{34}H_{62}O_2$: C 81.20, H 12.44; found: C 80.99, H 12.60.

Hexakis(alkyloxy)triphenylenes **7a**,**b**: *General Procedures. Method A.* $MoCl_5$ (410 mg, 1.50 mmol) was added to a soln. of **5a**,**b** (1.50 mmol) in CH_2Cl_2 (3 ml), and the mixture was stirred for 20 min at r.t. Then the mixture was treated subsequently with MeOH (5 ml) and H_2O (6 ml), and the aq. layer was extracted with hexanes (4 × 50 ml). The combined org. layer was washed with brine (2 × 75 ml), dried ($MgSO_4$), and evaporated. Purification by FC (2 × ; SiO_2; hexanes/CH_2Cl_2 3 : 1) yielded **7a**,**b** as colorless oils.

Method B. Compound **6** (1.54 mmol) and **3a**,**b** (0.01 mol) were added to a suspension of K_2CO_3 (2.76 g, 0.02 mol) in DMF (25 ml), and the resulting mixture was stirred at 100° for 20 h. After cooling to r.t., the mixture was diluted with H_2O (60 ml) and extracted with pentane (3 × 60 ml). The combined org. layer was washed with H_2O (4 × 60 ml), dried ($MgSO_4$), and evaporated, and the crude **7a**,**b** purified as described in *Method A*.

*2,3,6,7,10,11-Hexakis{[(2*R*,4*R*,6*R*)-2,4,6-trimethyloctyl]oxy}triphenylene* (**7a**): 120 mg (19%) by *Method A*; 910 mg (47%) by *Method B.* $[\alpha]_D^{20} = -29.1$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.82 (*s*, 6 arom. H); 4.14 (*dd*, $J = 5.0$, 8.8, 6 H, H_a–C(1′)); 3.96 (*dd*, $J = 6.8$, 8.8, 6 H, H_b–C(1′)); 2.27–2.19 (*m*, 6 H, H–C(2′)); 1.75–1.69 (*m*, 6 H, H–C(4′)); 1.65–1.58 (*m*, 6 H, H_a–C(3′)); 1.55–1.27 (*m*, 18 H, H–C(6′), H_a–C(7′), H_a–C(5′)); 1.17 (*d*, $J = 6.8$, 18 H, Me–C(2′)); 1.18–1.04 (*m*, 12 H, H_b–C(3′), H_b–C(7′)); 1.00–0.93 (*m*, 6 H, H_b–C(5′)); 0.97 (*d*, $J = 6.6$, 18 H, Me–C(4′)); 0.89–0.86 (*m*, 36 H, Me(8′), Me–C(6′)). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.2 (C(2), C(3), C(6), C(7), C(10), C(11)); 123.5 (C(1a), C(4a), C(5a), C(8a), C(9a), C(12a)); 106.9 (C(1), C(4), C(5), C(8), C(9), C(12)); 74.4 (C(1′)); 44.7 (C(5′)); 41.7 (C(3′)); 31.5 (C(6′)); 30.9 (C(2′)); 29.0 (C(7′)); 27.5 (C(4′)); 21.1 (*Me*–C(4′)); 19.9 (*Me*–C(6′)); 18.2 (*Me*–C(2′)); 11.2 (Me(8′)). EI-MS: 1249 (43, M^+), 1094 (4), 939 (5), 785 (3), 631 (14), 477 (7), 324 (30), 295 (10), 218 (16), 125 (3), 83 (24), 69 (33), 57 (100). Anal. calc. for $C_{84}H_{144}O_6$: C 80.70, H 11.62; found: C 80.71, H 11.91.

*2,3,6,7,10,11-Hexakis{[(2*R*,4*R*,6*R*,8*R*)-2′,4′,6′,8′-tetramethyldecyl]oxy}triphenylene* (**7b**): 1.10 g (44%) by *Method A*; 1.03 g (45%) by *Method B.* $[\alpha]_D^{20} = -16.8$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.82 (*s*, 6 arom. H); 4.14 (*dd*, $J = 5.0$, 8.8, 6 H, H_a–C(1′)); 3.96 (*dd*, $J = 6.8$, 8.8, 6 H, H_b–C(1′)); 2.26–2.18 (*m*, 6 H, H–C(2′)); 1.78–1.57 (*m*, 18 H, H–C(4′), H–C(6′), H_a–C(3′)); 1.49–1.22 (*m*, 24 H, H–C(8′), H_a–C(9′), H_a–C(5′), H_a–C(7′)); 1.18 (*d*, $J = 6.6$, 18 H, Me–C(2′)); 1.14–1.00 (*m*, 12 H, H_b–C(3′), H_b–C(9′)); 0.97 (*d*, $J = 6.6$, 18 H, Me–C(4′)); 0.98–0.84 (*m*, 66 H, H_b–C(5′), H_b–C(7′), Me–C(6′), Me–C(8′), Me(10′)).

^{13}C-NMR (100 MHz, CDCl$_3$): 149.2 (C(2), C(3), C(6), C(7), C(10), C(11)); 123.5 (C(1a), C(4a), C(5a), C(8a), C(9a), C(12a)); 106.9 (C(1), C(4), C(5), C(8), C(9), C(12)); 74.3 (C(1′)); 45.4 (C(5′)); 44.7 (C(7′)); 41.4 (C(3′)); 31.6 (C(8′)); 30.9 (C(2′)); 28.8 (C(9′)); 27.5 (C(4′), C(6′)); 21.3, 21.0 (*Me*−C(4′), *Me*−C(6′)); 20.0 (*Me*−C(8′)); 18.3 (*Me*−C(2′)); 11.2 (Me(10′)). EI-MS: 1501 (56, M^+), 1304 (10), 1108 (4), 913 (2), 715 (18), 519 (10), 323 (42), 295 (17), 149 (21), 97 (36), 85 (60), 71 (81), 57 (100). Anal. calc. for $C_{102}H_{180}O_6$: C 81.53, H 12.08; found: C 81.35, H 12.28.

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