Synthesis of Hexastyrylbenzenes

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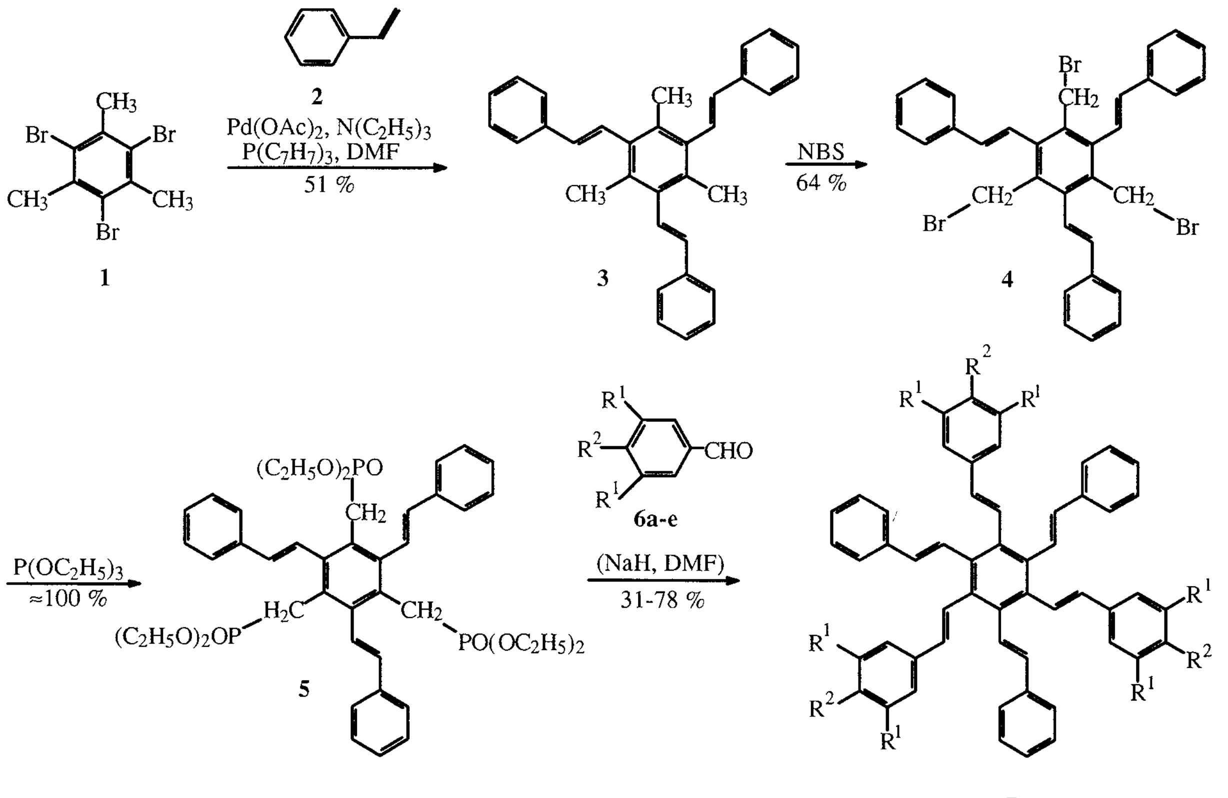
(*E,E,E,E,E,E*)-Hexakis(2-phenylethenyl)benzene (**7a**) and some derivatives **7b–e** with three or nine alkoxy groups were prepared by a synthetic sequence of four steps. Starting from 1,3,5-tribromo-2,4,6-trimethylbenzene (**1**) the first three styryl groups were introduced by a Heck reaction, and the second three styryl groups by a Wittig–Horner reaction.

Disk- or star-shaped molecules with hexakis(2-phenylethyl)benzene[1,2] or hexakis(2-phenylethynyl)benzene[3–10] in the core have received great attention due to their interesting properties such as liquid crystalline systems (LC), hexaarmed polymers and materials for non linear optics (NLO).

The previous attempts[11–13] to synthesize hexakis(2-phenylethenyl)benzenes suffered from the fact that polymeric byproducts could not easily be separated in the last reaction step; this is especially true for the hardly soluble parent compound **7a** (Scheme). Various optimization processes showed us that one should avoid the Heck reaction[14] as the *final* step. The Scheme depicted below shows a facile reaction sequence for the preparation of the target compounds which starts with 1,3,5-tribromo-2,4,6-trimethylbenzene (**1**).[15] A threefold CC coupling under Heck conditions using tri-*o*-tolylphosphine as ligand yields 1,3,5-trimethyl-2,4,6-tris(2-phenylethenyl)benzene (**3**) which exists, after recrystallization, in a pure *E,E,E*-configuration. Bromination with *N*-bromosuccinimide leads to (*E,E,E*)-1,3,5-tris(bromomethyl)-2,4,6-tris(2-phenylethenyl)benzene (**4**) and the subsequent reaction with triethyl phosphite to the ester **5**. Finally, a threefold Wittig–Horner reaction of **5** and the benzaldehydes **6a–e** yields the hexastyrylbenzenes **7a–e**. The parent compound **7a** precipitates in analytically pure form. It is hardly soluble in organic solvents. The substituted systems **7b–e** can be recrystallized from boiling chloroform by addition of acetone till the solution becomes turbid.

The ^1H and ^{13}C NMR spectra of **7b–e** in solution reveal the all-*E* configuration. A solid state ^{13}C NMR spectrum



6→7	a	b	c	d	e
R^1	H	H	H	OC_6H_{13}	$OC_{12}H_{25}$
R^2	H	OC_6H_{13}	$OC_{12}H_{25}$	OC_6H_{13}	$OC_{12}H_{25}$
Yield [%]	61	67	78	75	31

Scheme

could be obtained for **7a**. It shows well resolved signals for the chemically non-equivalent sp^2 carbon atoms and proves the configurational uniformity and particularly the absence of polymeric byproducts with saturated carbon atoms (Figure). Thus, the CP-MAS ^{13}C NMR spectroscopy is by far the best method for the identification of **7a**.

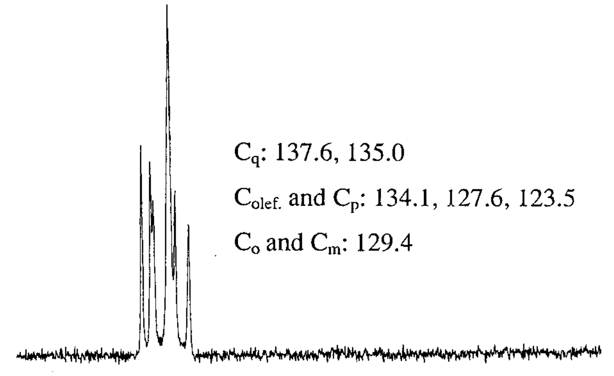


Figure. ^{13}C CP-MAS Spectrum of all-*E* **7a**

^1H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer using TMS or the signal of the solvent ($CDCl_3$) as internal standard and the solid state ^{13}C NMR spectrum was recorded on a Bruker MSL 300 spectrometer. Mass spectra were obtained on a Finnigan MS 95 instrument. IR spectra (KBr pellets) were recorded on a Beckman Acculab 4 spectrometer. Melting points were measured with a Büchi SMP apparatus. Elemental analyses were performed at the microanalytical laboratory of the institute.

(*E*,*E*,*E*)-1,3,5-Trimethyl-2,4,6-tris(2-phenylethenyl)benzene (3):
To a solution of **1**[15] (7.14 g, 20.0 mmol) and styrene (**2**; 8.32 g, 80.0 mmol) in anhyd DMF (50 mL) were added Pd $(OAc)_2$ (450 mg, 2.0 mmol), tri-*o*-tolylphosphine (1.2 g, 4.0 mmol) and anhyd Et_3N (20 mL, 143 mmol). The mixture was thoroughly degassed with argon. After stirring for 3 d at 100 °C in an argon atmosphere, the volatile compounds were removed at 8 Torr, the residue dissolved in $CHCl_3$ (50 mL) and washed with equal amounts of H_2O, dil HCl and again with H_2O. The organic layer was dried ($MgSO_4$) and concentrated. The residue crystallized upon addition of acetone; colorless plates; yield: 4.36 g (51 %); mp 197–198 °C.

^1H NMR ($CDCl_3$): $\delta = 2.40$ (s, 9 H, CH_3), 6.56, 7.19 (AB, $^3J = 16.6$ Hz, 6 H, CH=CH), 7.30 (t, 3 H_{arom}, *p*-H), 7.40 (t, 6 H_{arom}, *m*-H), 7.54 (d, 6 H_{arom}, *o*-H).

^{13}C NMR ($CDCl_3$): $\delta = 19.0$ (CH_3), 126.3 (C_o, Phenyl), 128.7 (C_m, Phenyl), 127.5, 128.2, 134.4 (C_p, Phenyl and C=C), 133.2, 135.9, 137.6 (C_q).

EI-MS (70 eV): *m/z* (%) = 426 (100, M^+), 335 (31), 86 (39), 84 (63).

$C_{33}H_{30}$	calc.	C 92.91	H 7.09
(426.6)	found	92.85	7.10

(*E*,*E*,*E*)-1,3,5-Tris(bromomethyl)-2,4,6-tris(2-phenylethenyl)benzene (4):
To a solution of **3** (4.27 g, 10.0 mmol) in anhyd CCl_4 (300 mL) were added NBS (5.7 g, 32.0 mmol) and a small portion of AIBN and the mixture was vigorously stirred and refluxed. After about 2 h, the mixture was cooled to r.t. and filtered, the solvent was removed and the residue treated with acetone. Colorless crystals; yield: 4.24 g (64 %); mp 175–176 °C.

^1H NMR ($CDCl_3$): $\delta = 4.69$ (s, 6 H, CH_2), 7.10, 7.38 (AB, $^3J = 16.7$ Hz, 6 H, CH=CH), 7.36 (t, 3 H_{arom}, *p*-H), 7.44 (t, 6 H_{arom}, *m*-H), 7.63 (d, 6 H_{arom}, *o*-H).

^{13}C NMR ($CDCl_3$): $\delta = 31.8$ (CH_2), 126.9 (C_o, Phenyl), 128.9 (C_m, Phenyl), 123.3, 128.4, 136.1 (C_p, Phenyl and C=C), 134.1, 136.5, 140.6 (C_q).

EI-MS (70 eV): *m/z* (%) = 660, 662, 664, 666 (M^+, Br_3-pattern, 4,13,13,4), 581, 583, 585 (Br_2-pattern, 25, 52, 28), 501, 503 (Br_2-pattern, 48, 58), 423 (67), 422 (86), 421 (100), 331 (46), 158 (87).

$C_{33}H_{27}Br_3$	calc.	C 59.76	H 4.10
(663.3)	found	59.63	4.07

(*E*,*E*,*E*)-1,3,5-Tris(diethoxyphosphorylmethyl)-2,4,6-tris(2-phenylethenyl)benzene (5):
Compound **4** (3.32 g, 5.0 mmol) was stirred in $(EtO)_3P$ (20 mL, 117 mmol) for 2 h at 160 °C. The EtBr formed in the reaction was distilled off through a cooling tube which was kept at 50 °C. The excess $(EtO)_3P$ was then removed thoroughly at 10 Torr. The highly viscous raw product could be used for the subsequent step without further purification; yield: 4.17 g (~ 100 %).

^1H NMR ($CDCl_3$): $\delta = 1.18$ t, 18 H, CH_3), 3.49 (d, $^2J_{PH} = 23.1$ Hz, 6 H, CH_2), 3.95 (m, 12 H, OCH_2), 6.63, 7.52 (AB, $^3J = 16.9$ Hz, 6 H, CH=CH), 7.25 (t, 3 H_{arom}, *p*-H), 7.34 (t, 6 H_{arom}, *m*-H), 7.55 (d, 6 H_{arom}, *o*-H).

^{13}C NMR ($CDCl_3$): $\delta = 16.3$ (CH_3), 30.2 (d, $^1J_{PH} = 136.9$ Hz, CH_2), 61.6 (d, $^2J_{PC} = 3.6$ Hz, OCH_2), 126.5 (C_o, Phenyl), 128.5 (C_m, Phenyl), 127.6, 128.8, 134.4 (C_p, Phenyl and CH=CH), 128.3, 139.1, (C_q), 137.2 (C_q, Phenyl).

$C_{45}H_{57}O_9P_3$	calc.	C 64.74	H 6.88
(834.9)	found	64.58	6.70

(*E*,*E*,*E*,*E*,*E*,*E*)-Hexakis(2-phenylethenyl)benzenes 7a–e; General Procedure:
A solution of **5** (835 mg, 1.0 mmol) and the corresponding aldehyde **6a–e** (4.0 mmol) in anhyd DMF (50 mL) was added dropwise under argon to a stirred suspension of NaH (120 mg, 5.0 mmol) in anhyd DMF (50 mL). After 1 h at r.t. the mixture was kept 4 d at 90 °C. Crushed ice was added till the product precipitated. The solid material was separated, washed twice with H_2O and then with acetone. The yellow products could be recrystallized from $CHCl_3$/acetone; an exception is the hardly soluble parent compound **7a**.

(E,E,E,E,E,E)-Hexakis(2-phenylethenyl)benzene (**7a**): Yield: 422 mg (61 %); mp 306–308 °C.

IR (KBr): $\nu = 3050$, 3020, 1590, 1490, 1445, 980, 970, 770, 750, 700 cm^{-1}.

^{13}C NMR (solid state): $\delta = 123.5$, 127.6, 129.4, 129.4, 134.1, 135.0, 137.6.

EI-MS (70 eV): *m/z* (%) = 690 (M^+, 100), 602 (12), 599 (12).

$C_{54}H_{42}$	calc.	C 93.87	H 6.13
(690.9)	found	93.79	6.21

(E,E,E,E,E,E)-1,3,5-Tris[2-(4-hexyloxyphenyl)ethenyl]-2,4,6-tris(2-phenylethenyl)benzene (**7b**): Yield: 664 mg (67 %); mp 268–270 °C.

^1H NMR ($CDCl_3$): $\delta = 0.95$ (t, 9 H, CH_3), 1.38 (m, 12 H, CH_2), 1.46 (m, 6 H, CH_2), 1.73 (m, 6 H, CH_2), 3.77 (t, 6 H, OCH_2), 6.04 (AA′, 6 H, H-Phenyl), 6.26 (m, 18 H, BB′, 12 H_{arom}, *o*-H, 6 × CH=), 6.51 (t, 6 H_{arom}, *m*-H), 6.78 (AB, $^3J = 16.5$ Hz, 3 H, 3 × CH=), 6.93 (m, 6 H, 3 H_{arom}, *p*-H + 3 × CH=).

^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3), 22.7, 25.8, 29.3, 31.7 (CH_2), 67.9 (OCH_2), 114.4, 126.2, 126.4, 126.8, 127.4, 128.3, 128.9, 133.9, 134.1 (CH), 130.3, 133.2, 134.0, 137.4, 158.1 (C_q).

FD-MS: *m/z* = 991 (M^+, 100), 992 (68), 993 (24).

$C_{72}H_{78}O_3$	calc	C 87.23	H 7.93
(991.4)	found	87.12	7.90

(E,E,E,E,E,E)-1,3,5-Tris[2-(4-dodecyloxyphenyl)ethenyl]-2,4,6-tris(2-phenylethenyl)benzene (**7c**): Yield: 970 mg (78 %); mp 246–249 °C.

^1H NMR ($CDCl_3$): $\delta = 0.90$ (t, 9 H, CH_3), 1.32 (m, 48 H, CH_2), 1.47 (m, 6 H, CH_2), 1.77 (m, 6 H, CH_2), 3.81 (t, 6 H, OCH_2), 6.14 (AA′, 6 H, H-Phenyl), 6.43 (m, 18 H, BB′, 12 H_{arom} + CH=), 6.62

(t, 6 H_{arom}, *m*-H), 6.87 (AB, ^3J = 16.4 Hz, 3 H, 3 H, CH=), 7.02 (m, 6 H, 3 H_{arom}, *p*-H and CH=).

^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.2, 29.4, 29.5, 29.6, 29.7, 32.0 (CH_2, superimposed), 67.9 (OCH_2), 114.4, 126.2, 126.3, 126.8, 127.4, 128.4, 128.9, 133.9, 134.1 (CH), 130.3, 133.2, 134.0, 137.4, 158.1 (C_q).

FD-MS: *m*/*z* = 1243 (M^+, 100), 1244 (91), 1245 (48).

$C_{90}H_{114}O_3$ calc. C 86.90 H 9.24
(1243.9) found 86.80 9.19

(E,E,E,E,E,E)-1,3,5-Tris{2-[3,4,5-tris(hexyloxy)phenyl]ethenyl}-2,4,6-tris(2-phenylethenyl)benzene (**7d**): Yield: 1.19 g (75 %); mp 230–235 °C.

^{1}H NMR ($CDCl_3$): δ = 0.90 (2 t, 27 H, CH_3), 1.34 (m, 48 H, CH_2), 1.49 (m, 6 H, CH_2), 1.69 (m, 12 H, CH_2), 1.76 (m, 6 H, CH_2), 3.74 (t, 12 H, OCH_2), 3.97 (m, 6 H, OCH_2), 6.56 (s, 6 H_{arom}, *o*-H), 6.78, 6.87, 7.20, 7.37 (2AB, ^3J = 16.6 Hz, 12 H, CH=CH), 7.27 (t, 3 H_{arom}, *p*-H), 7.29 (t, 6 H_{arom}, m-H), 7.49 (d, 6 H_{arom}, *o*-H).

^{13}C NMR ($CDCl_3$): δ = 13.9, 14.0 (CH_3), 22.6, 22.7, 25.7, 25.8, 29.3, 30.5, 31.8 (CH_2), 68.9, 73.5 (OCH_2), 104.6, 126.3, 128.7 (C_o, C_m, Phenyl), 127.6, 128.0, 128.9, 135.8, 136.1 (C_p, Phenyl and CH=CH), 133.2, 134.6, 134.8, 137.7, 138.1, 153.3 (C_q).

FD-MS: *m*/*z* = 1591 (M^+, 44), 1592 (100).

$C_{108}H_{150}O_9$ calc. C 81.46 H 9.49
(1592.4) found 81.30 9.40.

(E,E,E,E,E,E)-1,3,5-Tris{2-[3,4,5-tris(dodecyloxy)phenyl]ethenyl}- 2,4,6-tris(2-phenylethenyl)benzene (**7e**): Yield: 729 mg (31 %); mp > 200 °C.[16]

^{1}H NMR ($CDCl_3$): δ = 0.89 (2t, 27 H, CH_3), 1.28 (m, 156 H, CH_2), 1.50 (m, 6 H, CH_2), 1.69 (m, 12 H, CH_2), 1.77 (m, 6 H, CH_2) 3.72 (t, 12 H, OCH_2), 3.97 (t, OCH_2), 6.56 (s, 6 H_{arom}, *o*-H), 6.78, 6.88, 7.21, 7.37 (2AB, ^3J = 16.6 Hz, 12 H, CH=CH), 7.28 (m, 9 H_{arom}, *m*- and *p*-H), 7.48 (d, 6 H_{arom}, *o*-H).

^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 26.2, 29.4, 29.7, 29.8, 30.4, 31.9 (CH_2, superimposed), 68.9, 73.5 (OCH_2), 104.6, 126.3, 128.7 (C_o, C_m, Phenyl), 127.7, 128.0, 129.0, 135.7, 136.1 (C_p, Phenyl and C=C), 133.2, 134.5, 134.9, 137.7, 138.2, 153.5 (C_q).

FD-MS: *m*/*z* = 2348 (M^+, 42), 2349 (100), 2350 (32), 2351 (33), 2352 (15).

$C_{162}H_{258}O_9$ calc. C 82.81 H 11.07
(2349.8) found 82.78 10.98

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(16) The LC properties will be discussed elsewhere in context with photochemical switching processes.