

Alkoxy-Substituted Hexastyrylbenzenes

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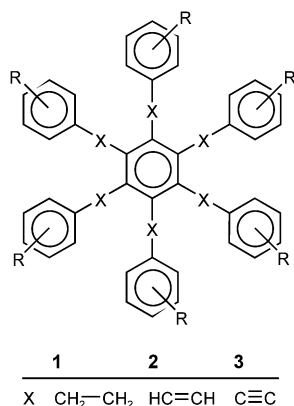
Abstract: Star-shaped compounds **2a–e** with a central benzene ring and six *p*-substituted, (*E*)-configured styryl groups have been prepared by a sequence of three-fold Heck and three-fold Wittig–Horner reactions. Alkoxy chains (OC₃H₇, OC₆H₁₃, OC₁₀H₂₁, OC₁₂H₂₅) on all six arms guarantee a good solubility of **2a–d**, whereas the alternating hexyloxy and cyano substitution in **2e** leads to an almost insoluble push–

pull system. Irradiation into the long-wavelength absorption of **2a–d** (with λ_{max} values of 341–342 nm) results in a statistical photocross-linking, which is characterized by the complete degradation of all stilbene chromophores.

Keywords: CC coupling; conjugation; photocross-linking; star-shaped compounds

Introduction

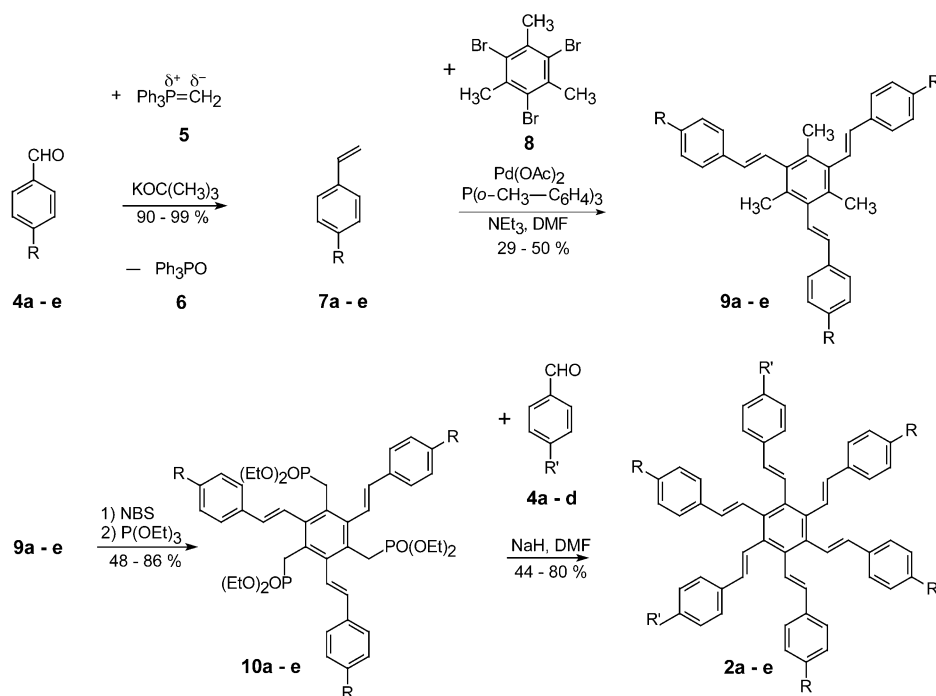
Discotic^[1] and dendritic^[2] molecules in the series of stilbenoid compounds are attracting great attention because of their applications in materials science.^[3] Some time ago, the successful preparation of hexastyrylbenzenes with all-(*E*) configuration was reported.^[3–5] In contrast to hexakis(2-phenylethyl)benzenes **1**^[6–11] and hexakis(2-phenylethynyl)benzenes **3**^[12–21], the poor solubility of hexakis(2-phenylethenyl)benzenes **2** prevented until now detailed studies of these star-like systems in materials science, although these compounds are of interest for applications in the area of liquid crystals (LC), non-linear optics (NLO), photocross-linking and polymer initiators. We report here the preparation of soluble hexastyrylbenzenes [hexakis(2-phenylethenyl)benzenes] **2** which contain alkoxy chains R in *p*-position of all six arms. In spite of the distorted planarity, caused by steric interactions, the compounds should exhibit a six-fold symmetry axis.



Results and Discussion

The Wittig reaction of 4-alkoxybenzaldehydes (**4a–d**) with the phosphorus ylide **5**, obtained from methyltriphenylphosphonium bromide and potassium *tert*-butoxide, gave the 4-alkoxystyrenes **7a–d** in almost quantitative yields. Heck reactions of **7a–d** with 1,3,5-tribromo-2,4,6-trimethylbenzene (**8**) yielded the 1,3,5-tris(2-arylethenyl)-2,4,6-trimethylbenzenes **9a–d**. All attempts to improve the moderate yields by application of the corresponding triiodo compound failed, because a partial reductive dehalogenation occurred. Wohl–Ziegler bromination and Arbusov reaction with triethyl phosphite led to the three-fold phosphonates **10a–e**, which gave in the final step with the aldehydes **4a–d** the target compounds **2a–d**. Due to the high steric demand, a strong basic medium (NaH/DMF) was used and the reaction time at 80 °C was extended to several days. The overall (*E*) configuration of the olefinic double bonds is guaranteed after crystallization. The solubility of **2a–d** in dichloromethane or chloroform is high; however, if the same reaction sequence is applied to 4-cyanobenzaldehyde **4e** the solubility of the system **2e** with a three-fold axis *C*₃ becomes very low. Scheme 1 summarizes the preparative route. An opposite reaction sequence consisting of three Wittig–Horner reactions and three subsequent Heck reactions led to products which are very difficult to purify.

The spectroscopic characterization of the hexasubstituted benzenes **9a–e**, **10a–e** and **2a–e** is mainly based on ¹H and ¹³C NMR measurements. Whereas the correlation of the obtained signals with the methyl, methylene and 1,4-phenylene groups is straightforward, the assignment of the olefinic signals proved to be difficult. Both olefinic protons of the styryl groups in **9b**



2, 4, 7, 9, 10	a	b	c	d	e
R	OC ₃ H ₇	OC ₆ H ₁₃	OC ₁₀ H ₂₁	OC ₁₂ H ₂₅	CN
R'	OC ₃ H ₇	OC ₆ H ₁₃	OC ₁₀ H ₂₁	OC ₁₂ H ₂₅	OC ₆ H ₁₃

Scheme 1. Preparation of hexastylbenzenes **2a–e**.

exhibit the same nuclear Overhauser effect on irradiation into the singlet of the methyl groups at 2.35 ppm. This result can be taken as an indication that the styryl substituents are twisted out of the plane of the central benzene ring. (The parent *trans*-stilbene is an essentially planar molecule.^[3]) Figure 1 shows an HMBC spectrum of **9b**. The vicinal couplings ³J(C,H) reveal that the inner olefinic carbon atoms absorb at higher field ($\delta = 127.1$) than the outer carbon atoms ($\delta = 133.9$) – caused as expected, by the electron-releasing hexyloxy groups – but the inner olefinic protons show their resonance at lower field ($\delta = 6.95$) than the outer protons ($\delta = 6.44$). The ¹H and ¹³C NMR data of **9a–e** and **10a–e** are listed in the experimental section; the ¹H NMR data of **2a–e** are summarized in Table 1 and the ¹³C NMR data of **2a–d** in Table 2. The solubility of the cyano-substituted compound **2e** is too low for the ¹³C NMR measurement; the ¹H NMR spectrum of **2e** was obtained at 80 °C in C₂D₂Cl₄.

Figure 2 demonstrates the big difference of the UV spectra of **9b** and **2b**. The intense A → B transition of 1,3,5-tristylbenzenes covers the forbidden A → A transition in the long-wavelength foot of the band.^[22,23] Related to 1,3,5-tris[2-(4-methoxyphenyl)ethenyl]benzene (**11**)^[22], the absorption maximum of **9b** ($\lambda_{\text{max}} = 289$ nm) is shifted by 44 nm to shorter wavelengths. This effect is a consequence of the stronger distortion of

the planarity of the chromophore caused by the additional methyl groups.

In contrast to the cross-conjugation in **9**, the hexastylbenzenes **2** contain conjugated styryl groups; however, the steric hindrance in **2** leads also to a significant deviation from planarity. In comparison to a planar system like 1,4-bis[(*E*)-2-(4-dodecyloxyphenyl)ethenyl]benzene (**12**)^[23] with a λ_{max} value of 369 nm, the absorption maximum of **2d** is hypsochromically shifted to 342 nm (measurement in CH₂Cl₂).

The length of the alkoxy chains in **2a–d** has no influence on the λ_{max} values (see experimental part). The donor-acceptor substituted system **2e** shows in CH₂Cl₂ a bathochromically shifted absorption band ($\lambda_{\text{max}} = 353$ nm) related to the purely donor substituted compound **2d** ($\lambda_{\text{max}} = 342$ nm); but again an undistorted model system like **13**^[24] absorbs at longer wavelengths ($\lambda_{\text{max}} = 376$ nm).

Stilbenoid compounds exhibit a manifold photochemistry which comprises *cis/trans* isomerization reactions, cyclization reactions, [2 π + 2 π] cycloadditions and statistical C–C bond formations yielding oligomers.^[3] The two latter processes are of special interest in the class of hexastylbenzenes, because there exist *monomolecular*, *bimolecular* and *polymolecular* variants of C–C bond formations. Scheme 2 illustrates these possibilities with the unsubstituted hexastylbenzene (R = C₆H₅).

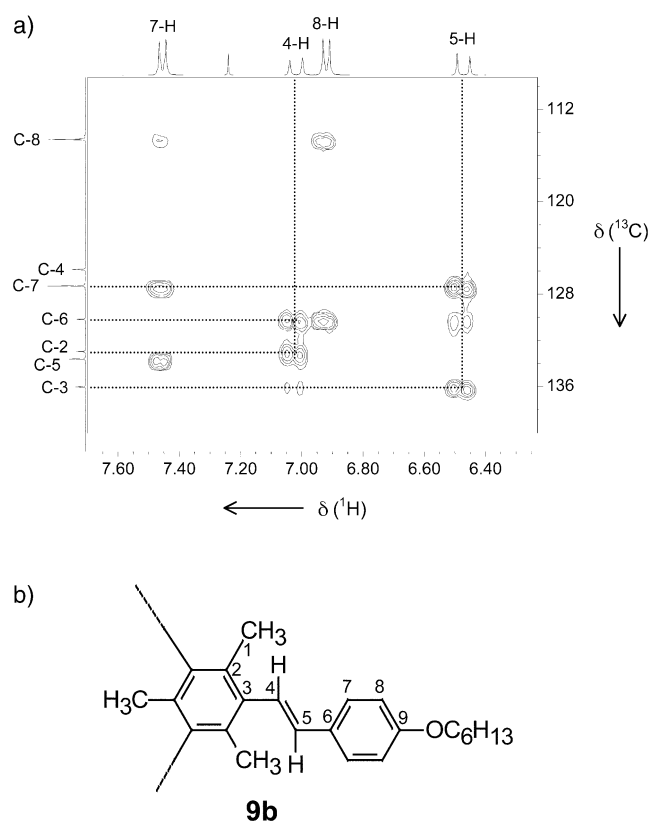


Figure 1. Selected part of the HMBC-spectrum of **9b**. The dotted lines show the $^3J(\text{C,H})$ couplings of the olefinic protons: 4-H/C-2, 4-H/C-6 and 5-H/C-3, 5-H/C-7.

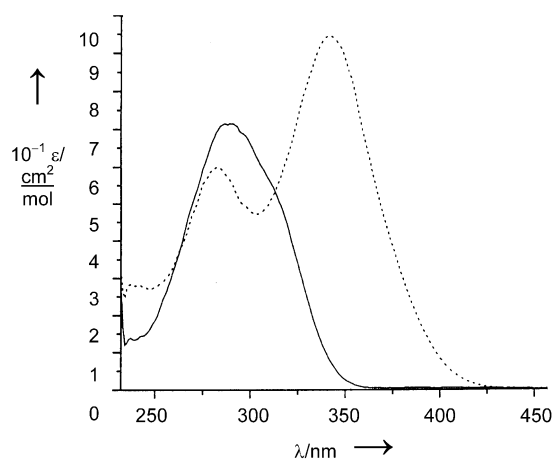
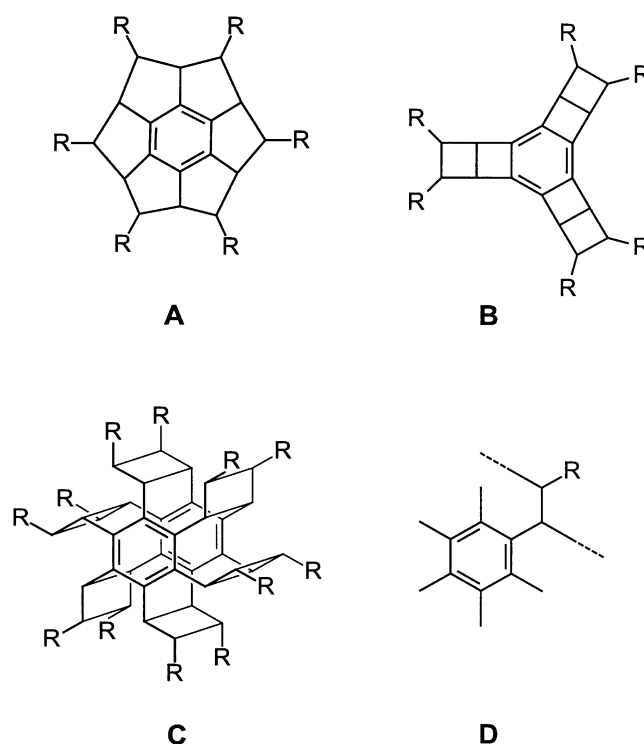
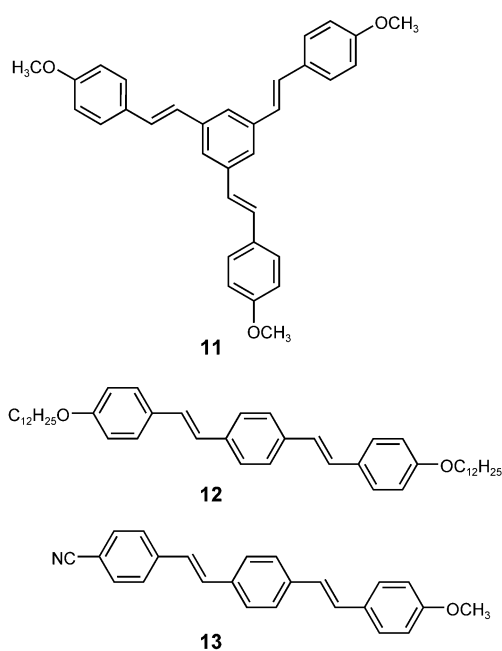


Figure 2. UV spectra of **9b** (—) and **2b** (.....) in chloroform.

The compounds **2** proved to be very light sensitive. Solutions in chloroform change rapidly their UV/Vis absorption in the daylight. Figure 3 shows the corresponding reaction spectra obtained for a monochromatic irradiation of **2b** in benzene. The long-wavelength absorption disappears completely within 120 s.^[25] The other compounds **2a**, **2c** and **2d** behave in the same way.

^1H NMR spectroscopy of the photoproduct proved that a statistical cross-linking **D** occurred; there are no



Scheme 2. Possible products formed by photochemical C–C bond formation in hexastyrilbenzenes: **A** and **B** monomolecular reaction, **C** six-fold bimolecular reaction $[\pi^2s + \pi^2s]$, **D** cross-linking to oligomers.

hints for a monomolecular process to **A** or **B**. The cyclophane structure **C** in Scheme 2 is one of eight possible stereoisomers, which could be generated by six *trans*-selective $[\pi^2s + \pi^2s]$ cycloaddition reactions. The

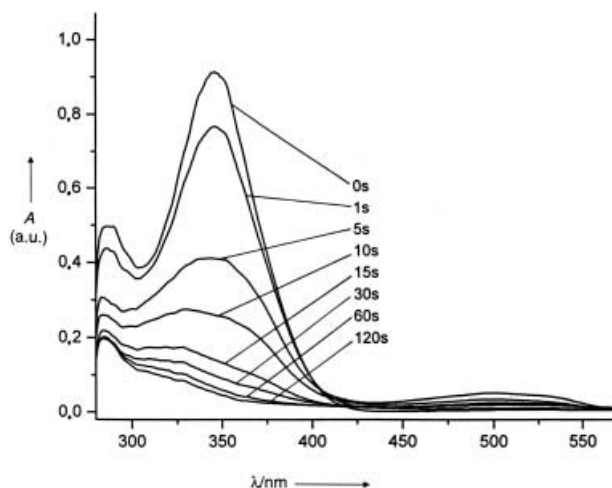


Figure 3. Reaction spectra [absorbance $A(\lambda)$] of a monochromatic irradiation ($\lambda = 366$ nm) of **2b** in benzene.

isomers can be rationalized on the basis of eight different conformers of **2**. The dimer fraction, observed in the FD mass spectrum, could certainly contain such structures. Moreover, the irradiation in the presence of air led to an oxidative cleavage of the styryl groups. Monochromatic irradiation ($\lambda = 366$ nm) of **2b** in chloroform yielded about 5–6% cleavage documented by the signals of 4-hexyloxybenzaldehyde (**4b**) in the ^1H NMR spectrum of the crude photoproduct.

Conclusion

Hexakis[(*E*)-2-(4-alkoxyphenyl)ethenyl]benzenes **2a–d**, which can be prepared by a sequence of three Heck and three Wittig–Horner reactions, are high-melting compounds that show a good solubility in solvents like chloroform or dichloromethane. On the contrary, the push-pull system **2e**, which has three 4-cyanostyryl groups and three 4-hexyloxystyryl groups, is almost insoluble in organic solvents. The compounds **2a–e** show intense absorption bands with maxima between 341 and 353 nm ($4.94 < \log \varepsilon < 4.98$). Irradiation with 366 nm or daylight leads to the complete disappearance of this band; the preferred photoreaction is a statistical C–C bond formation of the olefinic centers (cross-linking), which yields oligomers.

Experimental Section

Melting points were determined on a Stuart Scientific SMP/3 melting point apparatus and are uncorrected. Elemental microanalysis were performed in the micro-analytical laboratory of the department. FT-IR spectra were recorded in the reflection mode (ATR) with a Nicolet 55XB spectrometer. Mass spectra (FD) were obtained on a Finnigan MAT 95 instrument. ^1H and ^{13}C NMR spectra were measured with the

Bruker machines AC 200, AM 400 and AMX 400. UV/Vis spectra were recorded on a Zeiss MCS 320/340 spectrometer.

General Procedure for the Preparation of the Styrenes **7a–d**

A solution of 91 mmol aldehyde **4a**,^[27] **4b**,^[28] **4c**,^[27] or **4d**^[27] in 200 mL dry THF was added under argon to 43.6 g (122 mmol) methyltriphenylphosphonium bromide and 13.7 g (122 mmol) potassium *tert*-butoxide in 300 mL dry THF. The reaction mixture was stirred at room temperature till the TLC control (SiO_2 , toluene) indicated the complete consumption of **4a–d**. After quenching with methanol, the solvent was removed in the rotavapor and the residue treated with 200 mL diethyl ether. Triphenylphosphine oxide **6** was filtered off and the concentrated solution filtered through silica (10×15 cm SiO_2 , petroleum ether (bp 40–70 °C)/dichloromethane (2:1)).

1-Propoxy-4-vinylbenzene (4-propoxystyrene) (7a): Yield: 99%; colorless oil, which solidifies in the refrigerator. Identification by comparison with an authentic sample.^[29] ^1H NMR (CDCl_3): $\delta = 1.08$ (3H, t, CH_3), 1.85 (2H, m, CH_2), 3.94 (2H, t, OCH_2), 5.17 (1H, dd, $^3J = 10.7$ Hz, $|^2J| = 1.0$ Hz, olefin H), 5.66 (1H, dd, $^3J = 17.6$ Hz, $|^2J| = 1.0$ Hz, olefin H), 6.71 (1H, dd, $^3J = 17.6$ Hz, $^3J = 10.7$ Hz, olefin H), 6.90 (2H, AA' part of AA'BB', 2-H, 6-H), 7.38 (2H, BB', 3-H, 5-H); ^{13}C NMR (CDCl_3): $\delta = 10.5$ (CH_3), 22.5 (CH_2), 69.5 (OCH_2), 111.3 (olefin CH_2), 114.5 (C-2, C-6), 127.3 (C-3, C-5), 130.2 (C-4), 136.3 (olefin CH), 158.9 (C-1).

1-Hexyloxy-4-vinylbenzene (4-hexyloxystyrene) (7b): Yield: 91%; colorless oil, which solidifies in the refrigerator. Identification by comparison with an authentic sample.^[28] ^1H NMR (CDCl_3): $\delta = 0.91$ (3H, t, CH_3), 1.37 (6H, m, CH_2), 1.78 (2H, m, CH_2), 3.95 (2H, t, OCH_2), 5.11 (1H, dd, $^3J = 11.2$ Hz, $|^2J| = 1.0$ Hz, olefin H), 5.60 (1H, dd, $^3J = 17.6$ Hz, $|^2J| = 1.0$ Hz, olefin H), 6.66 (1H, dd, $^3J = 17.6$ Hz, $^3J = 11.2$ Hz, olefin H), 6.85 (2H, AA' part of AA'BB', 2-H, 6-H), 7.33 (2H, BB', 3-H, 5-H); ^{13}C NMR (CDCl_3): $\delta = 14.0$ (CH_3), 22.6, 25.7, 29.2, 31.6 (CH_2), 68.1 (OCH_2), 111.3 (olefin CH_2), 114.6 (C-2, C-6), 127.3 (C-3, C-5), 130.3 (C-4), 136.3 (olefin CH), 159.0 (C-1).

1-Decyloxy-4-vinylbenzene (4-decyloxystyrene) (7c): Yield: 96%, colorless solid, mp 33 °C. Identification by comparison with an authentic sample.^[28] ^1H NMR (CDCl_3): $\delta = 0.92$ (3H, t, CH_3), 1.30 (12H, m, CH_2), 1.46 (2H, m, CH_2), 1.79 (2H, m, CH_2), 3.96 (2H, t, OCH_2), 5.13 (1H, dd, $^3J = 11.0$ Hz, $|^2J| = 0.9$ Hz, olefin H), 5.62 (1H, dd, $^3J = 17.6$ Hz, $|^2J| = 0.9$ Hz, olefin H), 6.67 (1H, dd, $^3J = 17.6$ Hz, $^3J = 11.0$ Hz, olefin H), 6.85 (2H, AA' part of AA'BB', 2-H, 6-H), 7.33 (2H, BB', 3-H, 5-H); ^{13}C NMR (CDCl_3): $\delta = 14.1$ (CH_3), 22.7, 26.1, 29.4, 29.5, 29.6, 32.0 (CH_2 , partly superimposed), 68.1 (OCH_2), 111.3 (olefin CH_2), 114.6 (C-2, C-6), 127.4 (C-3, C-5), 130.4 (C-3), 136.4 (olefin CH), 159.1 (C-1).

1-Dodecyl-4-vinylbenzene (4-dodecylstyrene) (7d): Yield: 92%, colorless solid mp 45 °C. ^1H NMR (CDCl_3): $\delta = 0.91$ (3H, t, CH_3), 1.37 (18H, m, CH_2), 1.78 (2H, m, CH_2), 3.95 (2H, t, OCH_2), 5.11 (1H, dd, $^3J = 10.9$ Hz, $|^2J| = 0.9$ Hz, olefin H), 5.60 (1H, dd, $^3J = 17.6$ Hz, $|^2J| = 0.9$ Hz, olefin H), 6.66 (1H, dd, $^3J = 17.6$ Hz, $^3J = 10.9$ Hz, olefin H), 6.85 (2H, AA' part of AA'BB', 2-H, 6-H), 7.33 (2H, BB', 3-H, 5-H); ^{13}C NMR (CDCl_3): $\delta = 14.0$ (CH_3), 22.7, 26.1, 29.3, 29.4, 29.6, 31.9 (CH_2 , partly superimposed), 68.1 (OCH_2), 111.3 (olefin CH_2), 114.6

(C-2, C-6), 127.3 (C-3, C-5), 130.3 (C-4), 136.3 (olefin CH), 159.0 (C-1); FD MS: m/z = 288 (100%, M^+); anal. calcd. for $C_{20}H_{32}O$ (288.5): C 83.27, H 11.18; found: C 83.18, H 11.35.

4-Vinylbenzonitrile (7e): commercially available.

General Procedure for the Preparation of the 1,3,5-Trimethyl-2,4,6-tristyrilbenzenes (9a–e)

1,3,5-Tribromo-2,4,6-trimethylbenzene (**8**)^[30] (9.0 g, 25.0 mmol), styrene **7a–e** (100.0 mmol), $Pd(OAc)_2$ (1.0 g, 4.5 mmol) and tri-*o*-tolylphosphine (3.6 g, 11.8 mmol) were dissolved under argon in 60 mL DMF/30 mL triethylamine and heated to 100 °C. As soon as the TLC control (SiO_2 , toluene) indicated the end of the reaction, chloroform (50 mL) was added and the solution filtered and evaporated. The residue was dissolved in 100 mL chloroform and extracted with 50 mL 2 M HCl and 100 mL water. The organic layer was dried with Na_2SO_4 , concentrated and filtered through silica (10 × 15 cm SiO_2 , CH_2Cl_2).

1,3,5-Trimethyl-2,4,6-tris[(E)-2-(4-propoxyphenyl)ethenyl]benzene (9a): Yield 43%; colorless solid, mp 80 °C [recrystallized from petroleum ether (bp 40–70 °C)]. 1H NMR ($CDCl_3$): δ = 1.06 (9H, t, CH_3), 1.83 (6H, m, CH_2), 2.38 (9H, s, CH_3), 3.96 (6H, t, OCH_2), 6.47 (3H, d, 3J = 16.7 Hz, outer olefin H), 6.92 (6H, AA' part of AA'BB', aromat H), 7.02 (3H, d, 3J = 16.7 Hz, inner olefin H), 7.46 (6H, BB', aromat H); ^{13}C NMR ($CDCl_3$): δ = 10.5 (CH_3), 19.1 (CH_3), 22.6 (CH_2), 69.6 (OCH_2), 114.7, 127.3 (aromat CH), 125.9, 133.7 (olefin CH), 130.2, 133.0, 136.1, 158.8 (aromat C_q); FD MS: m/z = 600 (100%, M^+); anal. calcd. for $C_{42}H_{48}O_3$ (600.8): C 83.96, H 8.05; found: C 83.77, H 8.26.

1,3,5-Tris[(E)-2-(4-hexyloxyphenyl)ethenyl]-2,4,6-trimethylbenzene (9b): Yield 29%; colorless solid, mp 76 °C [recrystallized from petroleum ether (bp 40–70 °C)]. 1H NMR ($CDCl_3$): δ = 0.91 (9H, t, CH_3), 1.35 (12H, m, CH_2), 1.46 (6H, m, CH_2), 1.79 (6H, m, CH_2), 2.35 (9H, s, CH_3), 3.97 (6H, t, OCH_2), 6.45 (3H, d, 3J = 16.4 Hz, outer olefin H), 6.90 (6H, AA' of AA'BB', aromat H), 7.00 (3H, d, 3J = 16.4 Hz, inner olefin H), 7.43 (6H, BB', aromat H); ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 19.1 (CH_3), 22.6, 25.7, 29.2, 31.6 (CH_2), 68.1 (OCH_2), 114.7, 127.3 (aromat CH), 125.9, 133.7 (olefin CH), 130.2, 133.0, 136.1, 158.8 (aromat C_q); FD MS: m/z = 727 (100%, M^+); anal. calcd. for $C_{51}H_{66}O_3$ (727.1): C 84.25, H 9.15; found: C 84.24, H 9.29.

1,3,5-Tris[(E)-2-(4-decyloxyphenyl)ethenyl]-2,4,6-trimethylbenzene (9c): Yield 50%; colorless crystals, mp 67 °C (recrystallized from acetone). 1H NMR ($CDCl_3$): δ = 0.87 (9H, t, CH_3), 1.26 (36H, m, CH_2), 1.45 (6H, m, CH_2), 1.78 (6H, m, CH_2), 2.34 (9H, s, CH_3), 3.96 (6H, t, OCH_2), 6.44 (3H, d, 3J = 16.7 Hz, outer olefin H), 6.89 (6H, AA' of AA'BB', aromat H), 6.98 (3H, d, 3J = 16.7 Hz, inner olefin H), 7.42 (6H, BB', aromat H); ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 19.1 (CH_3), 22.7, 26.1, 29.3, 29.4, 29.6, 31.9 (CH_2 , partly superimposed), 68.2 (OCH_2), 114.8, 127.4 (aromat CH), 126.1, 133.8 (olefin CH), 130.4, 133.1, 136.1, 158.9 (aromat C_q); FD MS: m/z = 895 (100%, M^+); anal. calcd. for $C_{63}H_{90}O_3$ (895.4): C 84.51, H 10.13; found: C 84.74, H 10.19.

1,3,5-Tris[(E)-2-(4-dodecyloxyphenyl)ethenyl]-2,4,6-trimethylbenzene (9d): Yield 37%, colorless powder, mp 58 °C [recrystallized from petroleum ether (bp 40–70 °C)]. 1H NMR ($CDCl_3$): δ = 0.86 (9H, t, CH_3), 1.25 (48H, m, CH_2), 1.44 (6H, m, CH_2), 1.77 (6H, m, CH_2), 2.33 (9H, s, CH_3), 3.96 (6H, t,

OCH_2), 6.43 (3H, d, 3J = 16.7 Hz, outer olefin H), 6.88 (6H, AA' of AA'BB', aromat H), 6.98 (3H, d, 3J = 16.7 Hz, inner olefin H), 7.42 (6H, BB', aromat H); ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 19.1 (CH_3), 22.7, 26.1, 29.3, 29.4, 29.6, 31.9 (CH_2 , partly superimposed), 68.2 (OCH_2), 114.8, 127.4 (aromat CH), 126.1, 133.7 (olefin CH), 130.4, 133.0, 136.1, 158.9 (aromat C_q); FD MS: m/z = 979 (100%, M^+); anal. calcd. for $C_{69}H_{102}O_3$ (979.6): C 84.60, H 10.50; found: C 84.31, H 10.36.

2,4,6-Tris[(E)-2-(4-cyanophenyl)ethenyl]-2,4,6-trimethylbenzene (9e): Yield 46%, colorless powder, mp 199 °C (recrystallized from acetone). 1H NMR ($CDCl_3$): δ = 2.32 (9H, s, CH_3), 6.52 (3H, d, 3J = 16.7 Hz, outer olefin H), 7.26 (3H, d, 3J = 16.7 Hz, inner olefin H), 7.57/7.65 (12H, AA'BB', aromat H); ^{13}C NMR ($CDCl_3$): δ = 19.0 (CH_3), 111.0, 133.5, 135.4, 141.7 (aromat C_q), 118.8 (CN), 126.7, 132.5 (aromat CH), 131.6, 133.2 (olefin CH). FD MS: m/z = 501 (100%, M^+); anal. calcd. for $C_{36}H_{27}N_3$ (501.4): C 86.20, H 5.43, N 8.38; found: C 85.98, H 5.67, N 8.31.

General Procedure for the Preparation of the Triphosphonates 10a–e

A mixture of 2.00 mmol **9a–e**, 1.175 g (6.60 mmol) NBS and 13 mg (0.08 mmol) AIBN was refluxed in 20 mL dry CCl_4 , until the whole succinimide was gathered on the surface. The mixture was cooled to room temperature, filtered and the volatile parts removed in the rotavapor. The residue was heated with 3.88 g (23.35 mmol) triethyl phosphite to 150 °C and the formed bromoethane continuously removed. The excess triethylphosphite was distilled off under reduced pressure (3 kPa) and the raw product purified by column filtration (6 × 12 cm SiO_2 , ethyl acetate/acetone 1:1).

1,3,5-Tris[(diethoxyphosphoryl)methyl]-2,4,6-tris[(E)-2-(4-propoxyphenyl)ethenyl]benzene (10a): Yield 86%, viscous oil. 1H NMR ($CDCl_3$): δ = 1.02 (9H, t, CH_3), 1.17 (18H, t, CH_3), 1.80 (6H, m, CH_2), 3.48 (6H, d, $|^2J(H,P)|$ = 23.0 Hz, CH_2P), 3.92 (18H, m, OCH_2), 6.53 (3H, d, 3J = 17.1 Hz, outer olefin H), 6.87 (6H, AA' of AA'BB', aromat H), 7.32 (3H, d, 3J = 17.1 Hz, inner olefin H), 7.45 (6H, BB', aromat H); ^{13}C NMR ($CDCl_3$): δ = 10.4 (CH_3), 16.3 (CH_3), 25.5 (CH_2), 30.2 (d, $^1J(C,P)$ = 136.6 Hz, CH_2P), 62.1 ($POCH_2$), 69.5 (OCH_2), 114.6, 127.6 (aromat CH), 126.5, 133.7 (olefin CH), 128.3, 130.3, 139.3, 158.9 (aromat C_q); FD MS: m/z = 1009 (100%, M^+); anal. calcd. for $C_{54}H_{75}O_{12}P_3$ (1009.1): C 64.27, H 7.49; found: C 63.98, H 7.77.

1,3,5-Tris[(diethoxyphosphoryl)methyl]-2,4,6-tris[(E)-2-(4-hexyloxyphenyl)ethenyl]benzene (10b): Yield 62%, viscous oil. 1H NMR ($CDCl_3$): δ = 0.89 (9H, t, CH_3), 1.17 (18H, t, CH_3), 1.33 (12H, m, CH_2), 1.44 (6H, m, CH_2), 1.76 (6H, m, CH_2), 3.48 (6H, d, $|^2J(H,P)|$ = 22.9 Hz, CH_2P), 3.94 (18H, m, OCH_2), 6.53 (3H, d, 3J = 16.7 Hz, outer olefin H), 6.86 (6H, AA' of AA'BB', aromat H), 7.33 (3H, d, 3J = 16.7 Hz, inner olefin H), 7.45 (6H, BB', aromat H); ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 16.4 (CH_3), 22.6, 25.7, 29.2, 31.6 (CH_2), 30.2 (d, $^1J(C,P)$ = 136.6 Hz, CH_2P), 61.8 ($POCH_2$), 68.1 (OCH_2), 114.6, 127.7 (aromat CH), 126.4, 133.8 (olefin CH), 128.3, 129.9, 139.3, 158.9 (aromat C_q); FD MS: m/z = 1135 (100%, M^+); anal. calcd. for $C_{63}H_{93}O_{12}P_3$ (1135.3): C 66.65, H 8.26; found: C 66.31, H 8.50.

1,3,5-Tris[(E)-2-(4-decyloxyphenyl)ethenyl]-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene (10c): Yield 57%, viscous oil. 1H NMR ($CDCl_3$): δ = 0.85 (9H, t, CH_3), 1.17 (18H, t, CH_3),

Table 1. ^1H NMR data of the hexastyrylbenzenes **2a–d** in CDCl_3 and **2e** in $\text{C}_2\text{D}_2\text{Cl}_4$ (δ values, TMS as internal standard).

Compound	Aromatic protons		Olefinic protons		$^3J[\text{Hz}]$	Alkoxy chains		
	AA'	BB'	A	B		OCH_2 t (12H)	CH_2 m (H)	CH_3 t (18H)
2								
a	6.33	6.64	6.43	6.95	16.7	3.83	1.80 (2H)	1.06
b	6.35	6.65	6.44	6.95	16.6	3.86	1.40 (36H)	0.94
							1.78 (12H)	
c	6.47	6.85	6.55	7.04	16.7	3.89	1.28 (72H)	0.88
							1.48 (12H)	
							1.79 (12H)	
d	6.53	6.93	6.58	7.07	16.7	3.90	1.26 (96H)	0.87
							1.47 (12H)	
							1.78 (12H)	
e ^[a]	6.81	7.22	6.63	7.04	16.7	3.92	1.34 (18H)	0.88
	7.52	7.40	6.78	7.37	17.0		1.74 (6H)	

^[a]Measurement in $\text{CDCl}_2\text{--CDCl}_2$ at 80°C ; upper row: alkoxy arms; lower row: cyano arms.

Table 2. ^{13}C NMR data of the hexastyrylbenzenes **2a–d** (δ values in CDCl_3 , TMS as internal standard)

Compound	Aromatic C			Olefinic C		Alkoxy chains		
	C_q	C_qO	CH	CH		OCH_2	CH_2	CH_3
a	133.9	130.6	158.3	114.6	127.4	133.9	127.1	69.4
b	133.7	130.6	158.2	114.5	127.4	133.9	127.1	67.9
c	134.2	130.7	158.6	114.8	127.5	134.4	127.1	68.1
d	134.0	130.6	158.4	114.6	127.4	134.2	127.0	68.0

^[a] Partly superimposed.

1.25 (36H, m, CH_2), 1.43 (6H, m, CH_2), 1.76 (6H, m, CH_2), 3.48 (6H, d, $|^2J(\text{H,P})| = 22.9$ Hz, CH_2P), 3.94 (18H, m, OCH_2), 6.53 (3H, d, $^3J = 17.0$ Hz, outer olefin H), 6.86 (6H, AA' of AA'BB', aromat H), 7.34 (3H, d, $^3J = 17.0$ Hz, inner olefin H), 7.45 (6H, BB', aromat H); ^{13}C NMR (CDCl_3): $\delta = 14.0$ (CH_3), 16.3 (CH_3), 22.6, 26.0, 29.2, 29.3, 29.5, 31.8 (CH_2 , partly superimposed), 29.8 (d, $^1J(\text{C,P}) = 138.1$ Hz, CH_2P), 61.6 (POCH_2), 68.1 (OCH_2), 114.6, 127.7 (aromat CH), 126.5, 133.8 (olefin CH), 128.3, 130.0, 139.3, 158.8 (aromat C_q). FD MS: $m/z = 1305$ (100%, M^+); anal. calcd. for $\text{C}_{75}\text{H}_{117}\text{O}_{12}\text{P}_3$ (1303.7): C 69.10, H 9.05; found: C 68.73, H 9.38.

1,3,5-Tris[(diethoxyphosphoryl)methyl]-2,4,6-tris[(E)-2-(4-dodecyloxyphenyl)ethenyl]benzene (10d): Yield 57%, viscous oil. ^1H NMR (CDCl_3): $\delta = 0.85$ (9H, t, CH_3), 1.17 (18H, t, CH_3), 1.24 (48H, m, CH_2), 1.43 (6H, m, CH_2), 1.76 (6H, m, CH_2), 3.48 (6H, d, $|^2J(\text{H,P})| = 21.9$ Hz, CH_2P), 3.95 (18H, m, OCH_2), 6.53 (3H, d, $^3J = 17.0$ Hz, outer olefin H), 6.86 (6H, AA' of AA'BB', aromat H), 7.33 (dd, $^3J = 17.0$ Hz, $|^5J(\text{H,P})| = 1.8$ Hz, inner olefin H), 7.45 (BB', aromat H); ^{13}C NMR (CDCl_3): $\delta = 14.1$ (CH_3), 16.4 (CH_3), 22.6, 26.0, 29.3, 29.4, 29.6, 31.8 (CH_2 , partly superimposed), 29.8 (d, $^1J(\text{C,P}) = 136.6$ Hz, CH_2P), 61.7 (POCH_2), 68.1 (OCH_2), 114.7, 127.7 (aromat CH), 126.6, 133.9 (olefin CH), 128.3, 130.1, 139.3, 159.0 (aromat C_q). FD MS: $m/z = 1388$ (100%, M^+); anal. calcd. for $\text{C}_{81}\text{H}_{129}\text{O}_{12}\text{P}_3$ (1387.8): C 70.10, H 9.37; found: C 69.86, H 9.61.

1,3,5-Tris[(E)-2-(4-cyanophenyl)ethenyl]-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene (10e): Yield 48%, viscous oil, isolated by filtration over SiO_2 (4×40 cm) with ethyl acetate/methanol (2:1). ^1H NMR (CDCl_3): $\delta = 1.15$ (18H, t, CH_3), 3.36

(6H, d, $|^2J(\text{H,P})| = 22.9$ Hz, CH_2P), 3.92 (12H, m, OCH_2), 6.66 (3H, d, $^3J = 16.7$ Hz, outer olefin H), 7.60 (12H, AA'BB', aromat H), 7.62 (3H, m, inner olefin H); ^{13}C NMR (CDCl_3): $\delta = 16.3$ (CH_3), 30.4 (d, $^1J(\text{C,P}) = 138.1$ Hz, CH_2P), 61.8 (POCH_2), 111.1, 128.4, 138.4, 141.4 (aromat C_q), 118.7 (CN), 126.9, 132.4 (aromat CH), 132.3, 133.2 (olefin CH). FD MS: $m/z = 910$ (100%, M^+); anal. calcd. for $\text{C}_{48}\text{H}_{54}\text{N}_3\text{O}_9\text{P}_3$ (909.9): C 63.36, H 5.98, N 4.62; found: C 63.12, H 6.17, N 4.59.

General Procedure for the Preparation of the Hexastyrylbenzenes **2a–e**

A solution of 1.0 mmol triphosphonate **10a–e** and 5.0 mmol of the corresponding aldehyde **4a–d** in 100 mL dry DMF was dropped under argon to 500 mg (12.5 mmol) of a 60% dispersion of NaH in mineral oil and 100 mL DMF warmed to 80°C . After 5d the reaction mixture was cooled to room temperature and treated with 200 mL water. The precipitated solid was filtered off, dispersed in 100 mL acetone and stirred for several hours in order to dissolve all byproducts. The target compounds **2a–e** were isolated as faint yellow powders. The ^1H and ^{13}C NMR data of **2a–e** are summarized in the Tables 1 and 2.

1,2,3,4,5,6-Hexakis[(E)-2-(4-propoxyphenyl)ethenyl]benzene (2a): Yield 4%, yellowish powder, which melts at 300°C under decomposition. UV (CH_2Cl_2): $\lambda_{\text{max}} = 342$ nm, $\epsilon = 88,500$ $\text{cm}^2 \cdot \text{mmol}^{-1}$; IR (ATR): $\nu = 3033, 2964, 2932, 2874, 1603, 1573, 1508, 1470, 1420, 1389, 1301, 1236, 1172, 1112, 1069,$

1049, 1022, 978, 967, 866, 846, 820 cm^{-1} . FD MS: $m/z = 1039$ (100%, M^+); anal. calcd. for $\text{C}_{72}\text{H}_{78}\text{O}_6$ (1039.4): C 83.20, H 7.56; found: C 83.34, H 7.52.

1,2,3,4,5,6-Hexakis[(E)-2-(4-hexyloxyphenyl)ethenyl]benzene (2b): Yield 73%, yellowish powder, which melts at 271 °C (decomp.). UV (CH_2Cl_2): $\lambda_{\text{max}} = 341 \text{ nm}$, $\epsilon = 94,400 \text{ cm}^2 \cdot \text{mmol}^{-1}$; IR (ATR): $\nu = 3033, 2954, 2929, 2856, 1602, 1574, 1508, 1468, 1420, 1389, 1300, 1243, 1172, 1110, 1033, 983, 966, 935, 866, 850, 821, 804, 725 \text{ cm}^{-1}$. FD MS: $m/z = 1292$ (100%, M^+); anal. calcd. for $\text{C}_{90}\text{H}_{114}\text{O}_6$ (1291.9): C 83.67, H 8.89; found: C 83.52, H 8.68.

1,2,3,4,5,6-Hexakis[(E)-2-(4-decyloxyphenyl)ethenyl]benzene (2c): Yield 65%, yellowish powder, which melts at 263 °C (decomp.). UV (CH_2Cl_2): $\lambda_{\text{max}} = 341 \text{ nm}$, $\epsilon = 93,700 \text{ cm}^2 \cdot \text{mmol}^{-1}$; IR (ATR): $\nu = 3034, 2917, 2850, 1603, 1574, 1508, 1469, 1427, 1390, 1301, 1246, 1172, 1110, 1029, 984, 966, 822, 719 \text{ cm}^{-1}$. FD MS: $m/z = 1628$ (100%, M^+); anal. calcd. for $\text{C}_{114}\text{H}_{162}\text{O}_6$ (1628.5): C 84.08, H 10.03; found: C 84.17, H 9.82.

1,2,3,4,5,6-Hexakis[(E)-2-(4-dodecyloxyphenyl)ethenyl]benzene (2d): Yield 80%, yellowish powder, which melts at 268 °C (decomp.). UV (CH_2Cl_2): $\lambda_{\text{max}} = 342 \text{ nm}$, $\epsilon = 87,900 \text{ cm}^2 \cdot \text{mmol}^{-1}$; IR (ATR): $\nu = 2917, 2850, 1629, 1603, 1573, 1503, 1469, 1426, 1379, 1295, 1245, 1171, 1111, 1033, 979, 876, 833, 806, 791, 719 \text{ cm}^{-1}$. FD MS: $m/z = 1797$ (100%, M^+); anal. calcd. for $\text{C}_{126}\text{H}_{186}\text{O}_6$ (1796.9): C 84.22, H 10.43; found: C 84.13, H 10.50.

1,3,5-Tris[(E)-2-(4-cyanophenyl)ethenyl]-2,4,6-tris[(E)-2-(4-hexyloxyphenyl)ethenyl]benzene (2e): Yield 62%, yellow powder, mp 306 °C (decomp.). UV (CH_2Cl_2): $\lambda_{\text{max}} = 353 \text{ nm}$, $\epsilon = 94,800 \text{ cm}^2 \cdot \text{mmol}^{-1}$; IR (ATR): $\nu = 3035, 2926, 2858, 2222, 1600, 1572, 1508, 1468, 1412, 1390, 1302, 1247, 1172, 1111, 1014, 986, 968, 935, 872, 822 \text{ cm}^{-1}$. FD MS: $m/z = 1066$ (100%, M^+); anal. calcd. for $\text{C}_{75}\text{H}_{75}\text{N}_3\text{O}_6$ (1066.4): C 84.47, H 7.09, N 3.94; found: C 84.30, H 7.23, N 3.87.

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