calculated toward the end of the refinement, showed a few maxima consistent with the expected positions of hydrogen atoms in all the structures. In **1** and **6**, hydrogen atoms were included at geometrically idealized positions with C–H bond distance at 1.08 Å. Hydrogen atoms were not included in **2**. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[10] and those for hydrogen atoms from Stewart and Davidson.[11] At the conclusion of the refinements, the values of R were 0.082, 0.108, and 0.1354 for **1**, **2**, and **6**, and $wR = [\sum w\Delta^2/\sum wF_0^2]$ were 0.095, 0.146, and 0.1361, respectively. In the refinements, weights were derived from the counting statistics. The programs used in the structure determination were Enraf Nonius SDP for **2** and SHELX76 for **1** and **6**.

Bond lengths and bond angles (Tables I, III, and V) are given in the text. Positional parameters are provided as supplementary material. A summary of crystal data is provided in Table X.

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. and was purified by recrystallization from hexane and sublimation at 50 °C (0.05 mmHg). Tetrahydrofuran (THF) (Fisher) and 1,4-dioxane (Fisher) were dried over sodium benzophenone ketyl. Hexane and methylene chloride were dried over calcium hydride. *sym*-Tetrachloroethane was dried over anhydrous calcium carbonate. All solvents were distilled in an atmosphere of dry nitrogen before use. 4-Phenylphenol (Aldrich) was purified by sublimation. Hexamethyldisilazane (Aldrich) was distilled and stored over molecular sieves. Phosphorus pentachloride (Aldrich) was used as received.

Synthesis of $[NP(O\text{-}C_6H_4\text{–}C_6H_5\text{-}p)_2]_3$ (1). A solution of sodium 4-phenylphenoxide was prepared by the reaction of sodium (1.06 g, 4.6 × 10^{-2} mol) with a solution of 4-phenylphenol (7.9 g, 4.6 × 10^{-2} mol) in tetrahydrofuran (30 mL). The 4-phenylphenoxide solution was decanted from unreacted sodium, and a solution of hexachlorocyclotriphosphazene $(NPCl_2)_3$ in tetrahydrofuran was added to it dropwise with vigorous stirring. After the solution was refluxed for 21 h under a nitrogen atmosphere, the solvent was removed on the rotary evaporator at room temperature and the residue was washed with water to yield a white product. This product was recrystallized from *m*-xylene; mp 202–203 °C. The isolated yield was 84%.

Synthesis of $[NP(O\text{–}C_6H_4\text{–}C_6H_5\text{-}p)_2]_4$ (2). The synthesis of **2** was essentially similar to that of **1**. Octachlorocyclotetraphosphazene, $(NPCl_2)_4$ (2.0 g, 4.3 × 10^{-3} mol) was allowed to react with sodium 4-phenylphenoxide (6.7 × 10^{-2} mol) in tetrahydrofuran (60 mL). The reaction conditions and workup procedure were similar to those in the preparation of **1**; mp 156–158 °C. The isolated yield was 80%.

Synthesis of OP_2NCl_5 (3). Compound **3** was synthesized by a method previously reported.[7] Typically, PCl_5 (187 g, 0.90 mol) was reacted with $(NH_4)_2SO_4$ (26.4 g, 0.20 mol) in *sym*-tetrachloroethane (400 mL). The product **3** was purified by vacuum distillation twice to yield colorless crystals.

Synthesis of OP_3NCl_7 (5). Species **5** was synthesized by the method of Riesel.[8] Species **3** (2.0 g, 7.4 × 10^{-3} mol) was reacted with $NHSi_2Me_6$ (1.2 g, 7.4 × 10^{-3} mol) in CH_2Cl_2 (40 mL). The reaction mixture was refluxed for 12 h. PCl_5 was then added to the reaction flask via a Schlenk addition tube, and the mixture was refluxed for an additional 12 h. The product was used in subsequent reactions without further purification.

Synthesis of $OP_2N(O\text{–}C_6H_4\text{–}C_6H_5\text{-}p)_5$ (4) and $OP_3N_2(O\text{–}C_6H_4\text{–}C_6H_5\text{-}p)_7$ (6). The syntheses of **4** and **6** follow the same general procedure. The compounds were prepared by the reaction of **3** (1.5 g, 5.6 × 10^{-3} mol) and **5** (2.9 g, 7.4 × 10^{-3} mol), respectively, with sodium 4-phenylphenoxide (4.2 × 10^{-2} mol with **3**; 7.8 × 10^{-2} mol with **5**) in dioxane (60 mL). The reaction mixture was cooled with an ice bath and was allowed to warm to room temperature while stirred. The whole process required ~30 min. After the reaction, the solvent was removed and the product was chromatographed on a silica gel column. The products isolated were oils initially. Species **4** was recrystallized from hexane–methylene chloride to give white powders; mp 165–167 °C. Isolated yield was 35%. These failed to form crystals suitable for X-ray analysis. Compound **6** was recrystallized from pentane–methylene chloride to yield white crystals: mp 83–85 °C. The isolated yield was 30%.

Synthesis of $OP_4N_3(O\text{–}C_6H_4\text{–}C_6H_5\text{-}p)_9$ (7). Compound **7** was synthesized by treating the ionic short-chain species $[P_4N_3Cl_{10}]^+PCl_6^-$ (2.0 g, 2.6 × 10^{-3} mol) with sodium 4-phenylphenoxide (5.2 × 10^{-2} mol) in dioxane (75 mL). The reaction and workup procedures were identical with those used in the syntheses of **4** and **6**. Compound **7** was recrystallized from hexane–methylene chloride to give white powders. Isolated yield was 20%. However, all attempts to grow single crystals of **7** acceptable for X-ray analysis were unsuccessful.

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Supplementary Material Available: Tables of selected least-squares planes and distances of atoms from those planes and thermal parameters (18 pages); listing of observed and calculated structure factor amplitudes (96 pages). Ordering information is given on any current masthead page.

Novel Oligo(phenylenevinylenes): Models for the Charging of Extended π Chains

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Abstract: The syntheses as well as the chemical and electrochemical reduction of a series of novel oligo(phenylenevinylenes) are described. The extended π chains are built up by sequences of Wittig reactions, and the corresponding polyanions are generated by electron-transfer reactions and characterized by NMR spectroscopy and quenching experiments. The charge-storage capacity, the charge distribution, and the stereodynamic behavior of the anions are examined as a function of the chain length, the linkage of the stilbene subunits, and the presence of phenyl substituents. The reduction of the title compounds serves as a suitable model experiment for the doping of the corresponding poly(phenylenevinylenes).

1. Introduction

Poly(*p*-phenylenevinylene) (**1**) is the subject of continuing experimental and theoretical efforts, with the emphasis being on the design of battery electrodes and of electrically conducting materials.[1,2] The existence of molecular weight distributions and the insolubility of polymer **1** in organic solvents along with occurring structural inhomogeneities have severely inhibited detailed studies of the charge-storage mechanisms of **1** and of the structures of charged species derived from **1**. In the present work, we have, therefore, considered well-defined oligomeric model systems for

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[†] Max-Planck-Institut für Polymerforschung.

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(1) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327.

(2) (a) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. (b) Friend, R. H.; Bradley, D. D. C.; Townsend, P. D. *J. Phys. D: Appl. Phys.* **1987**, *20*, 1367. (c) Kürti, J.; Kuzmany, H. In *Springer Series in Solid State Sciences*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer Verlag: Berlin, Heidelberg, 1987; Vol. 76, p 43.

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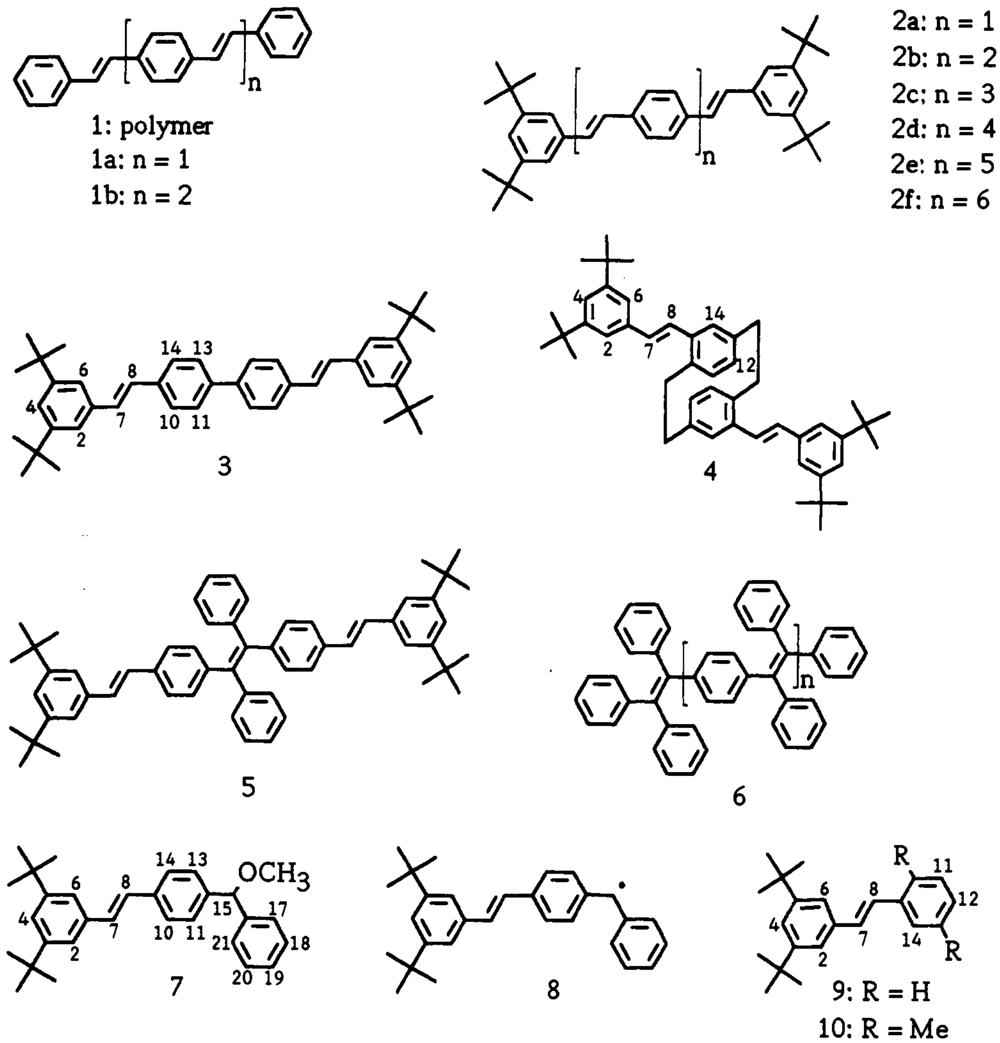
Chart I



1 that possess sufficient solubility in organic solvents due to substitution by alkyl groups. The title compounds in Chart I comprise the following structural variations:

(i) Compounds **2a**–**2f** represent a homologous series of oligo(phenylenevinylenes) with different chain lengths.[3] (ii) Compounds **2b**, **3**, and **4** can be regarded as bis-stilbene systems linked in a different manner.[4] (iii) The role of phenyl substitution can be disclosed by a comparison of **2b** and **5**; this is important since polymer **6** has been proposed as a soluble analogue of parent compound **1**.[5] A useful reference system in the study of ions derived from **5** is ether **7** since its reductive cleavage is supposed to yield monoanion $\mathbf{8}^{-}/\mathrm{M}^{+}$, which can formally be regarded as half the π system of dianion $\mathbf{5}^{2-}/2\mathrm{M}^{+}$.

Herein, we describe the synthesis as well as the chemical and electrochemical reduction of oligo(phenylenevinylenes) **2**–**5**.

The following questions shall be answered: How many electrons can be transferred in an extended reduction sequence, and how does the redox capacity depend upon the chain length, the type of conjugation, and the type of substitution? What is the charge distribution in the carbanions resulting from reduction of the extended π chains? Does the electron transfer induce structural changes, e.g., change of configuration and conformation with respect to the formal double and single bonds?[6] This question is particularly severe for **5** since it comprises a tetraphenylethylene subunit, which is anticipated to suffer from a torsion about the olefinic bond upon dianion formation.[7,8]

2. Results

2.1. Syntheses. The members of the homologous series **2** can be formally regarded as being built up from two 3,5-di-*tert*-butylphenyl end groups and a xylylidene chain with different length. Due to the low solubility of the phenylenevinylene chains, however, it is useful to synthesize soluble terminal units and connect them in a final reaction to the target molecules **2**. From the phosphonium salt **11a**,[9] the chain could be lengthened about a styryl unit via a Wittig reaction with 4-methylbenzaldehyde. The following functionalization was done by bromination of the methyl group with *N*-bromosuccinimide (NBS). The phosphonium salt **11b** was obtained by a subsequent reaction of **13a** with triphenylphosphine in toluene (Scheme I). The larger phosphonium salt **11c** was accessible in a analogous reaction sequence.

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(3) Heinze, J.; Mortensen, J.; Müllen, K.; Schenk, R. *J. Chem. Soc., Chem. Commun.* **1987**, 701.

(4) Schenk, R.; Hucker, J.; Hopf, H.; Räder, H.-J.; Müllen, K. *Angew. Chem.* **1989**, *101*, 942; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 904.

(5) Hörhold, H.-H.; Opfermann, J.; Atrat, P.; Trauer, K. D.; Drehfahl, G. Internat. Symp. Polykondensation 5; Varna, 1975; *Polykondensationsprozesse*; Verlag der Bulg. Akad. Wiss.: Sofia, 1976; p 171.

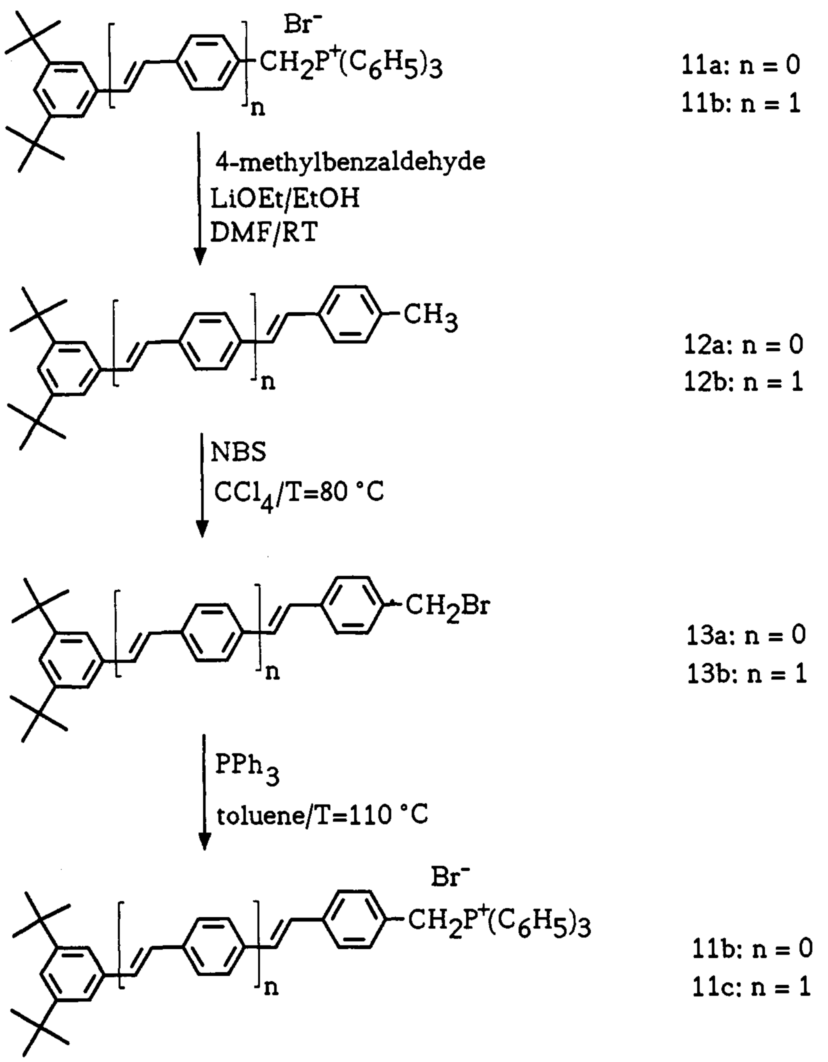
(6) (a) Schenk, R.; Huber, W.; Schade, P.; Müllen, K. *Chem. Ber.* **1988**, *121*, 2201. (b) Huber, W.; Müllen, K. *Acc. Chem. Res.* **1986**, *19*, 300.

(7) Fox, M. A.; Shultz, D. *J. Org. Chem.* **1988**, *53*, 4386.

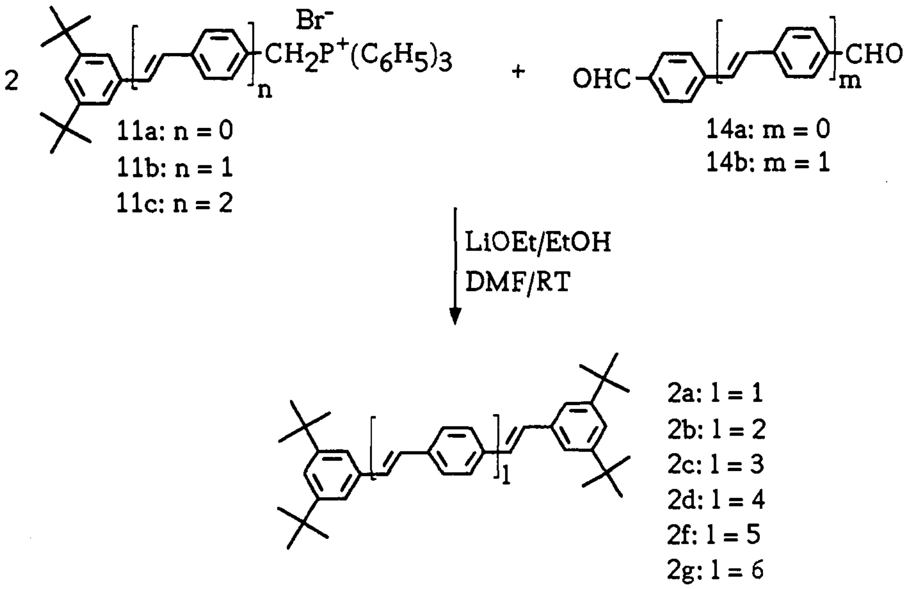
(8) (a) Eargle, D. H., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 3859. (b) Geraldes, C. F. G. C.; Gil, V. M. S.; Eargle, D. H., Jr. *J. Phys. Chem.* **1973**, *59*, 1166. (c) Lundgren, B.; Levin, G.; Claesson, S.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 262. (d) Levin, G.; Claesson, S.; Szwarc, M. *J. Am. Chem. Soc.* **1972**, *94*, 8672. (e) Roberts, R. C.; Szwarc, M. *J. Am. Chem. Soc.* **1965**, *87*, 5542. (f) Cserhegyi, A.; Jagur-Grodzsinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1969**, *91*, 1892. (g) Garst, J. F.; Zabolotny, E. R.; Cole, R. S. *J. Am. Chem. Soc.* **1964**, *86*, 2257. (h) Garst, J. F.; Pacifici, J. G.; Zabolotny, E. R. *J. Am. Chem. Soc.* **1966**, *88*, 3872. (i) Garst, J. F.; Cole, R. S. *J. Am. Chem. Soc.* **1962**, *84*, 4352. (k) Garst, J. F. *J. Am. Chem. Soc.* **1971**, *93*, 6312.

(9) (a) Baas, J. M. A.; von Berkum, H.; Hoefnagel, M. A.; Webster, B. M. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1110. (b) Hearne, G. W.; Evans, T. W.; Buls, V. W.; Schwarzer, C. G.; *Ind. Eng. Chem.* **1955**, *47*, 2311. (c) Paquette, L. A.; Klobucar, W. D.; Snow, R. A. *Synth. Commun.* **1976**, *6*, 575.

Scheme I



Scheme II



The target molecules were obtained in a final bis Wittig reaction of the phosphonium salts **11a**, **11b**, and **11c** (2 equiv) with terephthalaldehyde (**14a**) or 4,4′-stilbenedicarbaldehyde (**14b**)[10] (Scheme II). The pure all-trans isomers of **2a**–**2d** were prepared by heating with a catalytic amount of iodine in toluene.[11] The products were purified by column chromatography on silica gel and subsequent recrystallization. The low solubility of compounds **2e** and **2f** caused problems in the workup procedure. They were

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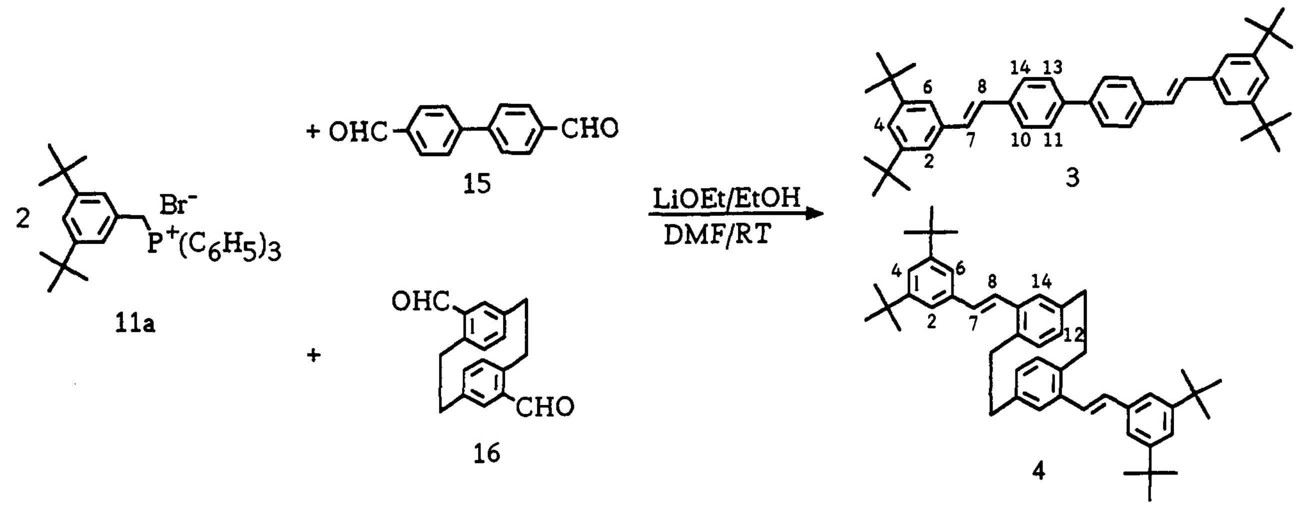
(10) Drehfahl, G.; Plötner, G. *Chem. Ber.* **1958**, *91*, 1274.

(11) Manecke, G.; Lüttke, S. *Chem. Ber.* **1970**, *103*, 700.

Scheme III



isolated by extraction of the crude reaction product with toluene containing small amounts of iodine for the final cis–trans isomerization.

Compounds 3 and 4 could be prepared by a bis Wittig reaction[4] (DMF, lithium ethoxide/ethanol, room temperature) between 4,4′-biphenyldicarbaldehyde (**15**) or 2,5′-[2.2](1,4)cyclophanedicarbaldehyde (**16**),[12] respectively, with 2 equiv of the phosphonium salt **11a** according to Scheme III. The aldehyde **15** could be prepared from 4,4′-dibromobiphenyl according to the literature.[13] As model compounds for the description of 3 and 4, we also prepared the alkyl-substituted stilbenes **9** and **10** from the phosphonium salt **11a** and benzaldehyde or 2,5-dimethylbenzaldehyde, respectively.

Not surprisingly, in view of the close structural relationship, the ^1H NMR chemical shifts of 3 are rather similar to those of **2b**. As expected from the shielding effects generally observed for cyclophanes,[14] the protons H-11 and H-12 of **4** resonate at significantly higher field (δ 6.43, 6.69; ^3J = 8.4 Hz) than the related nuclei in **2b** and **3**. The two doublets for the olefinic protons (δ 6.94, 7.21) can be identified by their coupling constant of ^3J = 16.1 Hz. This is a typical value for trans double bonds. The signals of the terminal phenyl rings (H-2,4,6) do not experience anisotropic shielding effects and closely correspond to those in **3**.

When comparing the UV spectroscopic data of cyclophane **4** and those of stilbene **10**, one notes that the band at highest wavelength of **4** (see Experimental Section) suffers from a bathochromic shift and loses fine structure. This finding is in accord with the behavior of the 1,2-bis(4-methylphenyl)ethane and [2.2]paracyclophane and is ascribed to a transannular π,π interaction within the cyclophane.[15] If the two stilbene units are linked via a single bond, as is the case in **3**, λ_{max} is shifted to longer wavelength (λ = 347 nm, ϵ = 43 500).

Ketone **18** was the key intermediate for the synthesis of the phenylenevinylene **5** and the ether **7**. Compound **18** was readily available in two steps from the phosphonium salt **11a** by a Wittig reaction with 4-cyanobenzaldehyde followed by a Grignard reaction with phenylmagnesium bromide. McMurry coupling of ketone **18** yielded the target molecule **5**. Reduction of **18** with $LiAlH_4$ and subsequent methylation with dimethyl sulfate provided ether **7** (Scheme IV).

2.2. Electrochemical Reduction. Voltammetric experiments were carried out with the compounds **2a–2d**, **3–5**, and **9**. The thermodynamic reduction potentials are summarized in Table I. Voltammetry clearly indicates that the number of redox steps increases with increasing chain length of the oligomer. In THF with $NaBPh_4$ as supporting electrolyte, the highest charged species generated is the pentaanion of **2d**. On the other hand, chemical reduction with alkali metals reveals that even hexaanions can be produced for this species (see section 2.3). This discrepancy results from the fact that, in the THF/$NaBPh_4$ solvent/electrolyte system, the electrochemical background reduction limit lies near −3.0 V, while the reduction power of the alkali metals in the pure solvents clearly exceeds a potential of −3.0 V.

Table I. Redox Potentials of Oligo(phenylenevinylenes)[a]

compd	$E_1°/V$	$E_2°/V$	$E_3°/V$	$E_4°/V$	$E_5°/V$	$E_6°/V$
2a[b]	−2.25	−2.54				
2b[b]	−2.13	−2.32	−2.95			
2b[c]	−1.86	−1.97	−2.79	−3.10		
2c[b]	−2.02	−2.15	−2.70	−2.83		
2d[b]	−1.97	−2.02	−2.46	−2.59	−3.05	
3	−2.30	−2.52	−3.06			
4	−2.44	−2.64				
5	−2.25	−2.25	−2.65			
5[c]	−1.86	−1.86	−2.75	−2.91		
5[d]	−1.86	−1.86	−2.75	−2.89	−3.10	−3.21
9	−2.48	−2.67				
9[c]	−2.26	−2.72				

[a] Cyclic voltammetry was performed at a Pt disk electrode (d = 0.84 mm) with solutions of 10^{-4}–10^{-3} M substrate and 0.1 M $NaBPh_4$/15-crown-5 for THF. All potentials are expressed in volts vs Ag/AgCl (calibration with Cp_2Fe/Cp_2Fe^+ taken to have 0.352 V). Unless noted differently, the scan rate was 0.1 V/s and T = −40 °C. [b] Reference 3. [c] In DMA/(TBA)Br. [d] In TBA/(TBA)Br after addition of $LiClO_4$.

Higher reduction states under electrochemical control were reached, however, when dimethylamine (DMA) was used as solvent. Thus, cyclic voltammetry of **2b** in DMA/tetrabutylammonium bromide ((TBA)Br) indicates the reversible formation of a tetraanion at $E°$ = −3.1 V vs Ag/AgCl (Figure 1a). It should be noted that the redox potentials measured in DMA are, in general, about 0.25 V more positive than those measured in THF.

Some further results can be extracted from Table I. The redox potentials of already existing states are shifted to less negative values for the next higher homologue, thus approaching a common convergence limit. With increasing chain length, both neighboring redox steps tend to approach each other and the energetical gap between the lowest and highest redox states increases. Interesting phenomena are observed when in the 15/15′ position of **2b** additional phenyl substituents are incorporated, resulting in compound **5**. As is shown in Figure 1b, the first two redox steps merge into one and the splitting of redox potentials between the tri- and tetraanion states decreases from 0.31 to 0.16 V.

As was shown by chemical reduction, **5** can be reduced up to a hexaanion (see section 3.3). In pure DMA with (TBA)Br as supporting electrolyte, only a tetraanion of **5** was generated. When small amounts of $LiClO_4$ are added, dramatic changes occur

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(12) Hopf, H.; Raulfs, F.-W. *Isr. J. Chem.* **1985**, *25*, 210.

(13) Thulin, B.; Wennerström, O.; Somfai, I.; Chmielarz, B. *Acta Chem. Scand.* **1977**, *B31*, 135.

(14) Boekelheide, V. *Top. Curr. Chem.* **1979**, *113*, 112.

(15) Misumi, S. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vol. II, p 579.

Table II. ^1H NMR Chemical Shifts of the Alkali-Metal Salts $\mathbf{2a}^{2-}/2M^+$ (M = Li, K), $\mathbf{2b}^{4-}/4Li^+$, $\mathbf{3}^{4-}/4Li^+$, and $\mathbf{9}^{2-}/2Li^+$

	2,6	4	7	8	10,14	11,13	12(15)	*t*-Bu
$\mathbf{2a}^{2-}/2Li^+$, 60 °C	6.20	5.78	4.40	5.46	5.67			1.18
$\mathbf{2a}^{2-}/2K^+$, 60 °C	6.21	5.80	4.41	5.52	5.35, 5.80			1.20
$(\mathbf{2a}')^{2-}/2K^+$, 20 °C	6.19	5.76	4.48	5.51	5.34, 5.79			1.19
$(\mathbf{2a}'')^{2-}/2K^+$, 20 °C	6.17	5.72	4.53	5.51	5.37, 5.83			1.19
$\mathbf{2b}^{4-}/4Li^+$, −20 °C	5.05	4.92	3.17, 3.30		5.03	6.00	(5.38)	1.07
	5.68				5.70	6.11		1.12
$\mathbf{3}^{4-}/4Li^+$, −20 °C	4.78	4.70	2.79, 3.13		5.16	6.14		1.05
	5.54				5.74	6.35		1.10
$\mathbf{9}^{2-}/2Li^+$, −20 °C	4.94	4.82	2.98, 3.04		4.96	5.76	4.55	1.05
	5.58				5.56	6.09		1.10

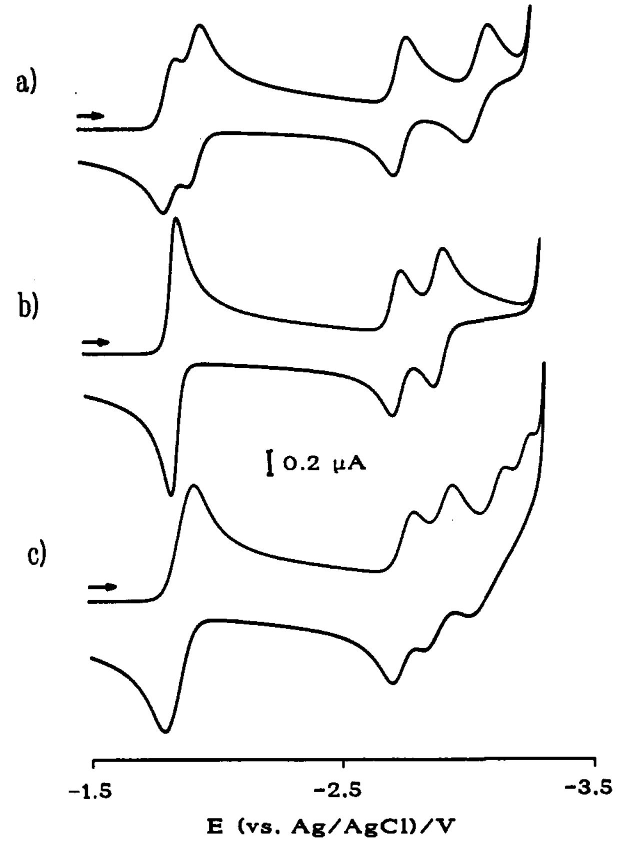


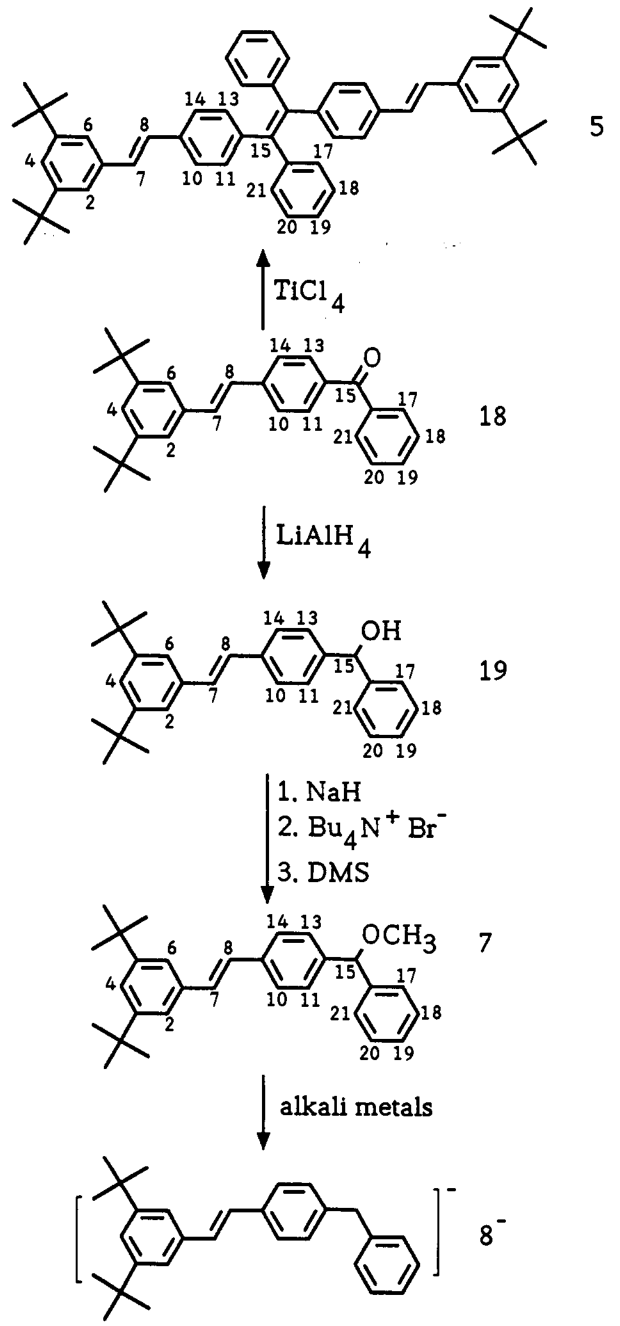
Figure 1. Cyclic voltammograms (corrected for background current) for the reduction of (a) **2b**, (b) **5** in DMA/0.1 M (TBA)Br, and (c) **5** in DMA/0.1 M (TBA)Br (0.01 M $LiClO_4$). Conditions: $c = 5 \times 10^{-4}$ M, scan rate 0.1 V s^{-1}, $T = -60$ °C.

(Figure 1c). Whereas the potential separation between the tri- and tetraanion states diminishes, two further redox steps at $E_5° = -3.1$ V and $E_6° = -3.21$ V become visible, indicating a hexaanion formation. Obviously, strong ion-pairing effects caused by the Li^+ counterions shift the redox potentials to less negative values.

2.3. Reduction with Alkali Metals. Compounds **2a–2d**, **3–5**, **7**, **9**, and **10** have been treated with alkali metals (lithium, potassium) in sealed NMR tubes. The experimental details of these experiments were described elsewhere.[16] The progress of the reduction could be followed by NMR spectroscopy.

Thereby, the red (**2a**) or blue (**2b–2d**) radical anions originally formed were characterized by electron spin resonance (ESR) and external nuclear double resonance (ENDOR) spectroscopies,[17] while the final diamagnetic anionic species were characterized by their ^1H and ^{13}C NMR spectra. Careful monitoring of the alkali-metal reduction is crucial since in many cases differently charged ions (e.g., dianions, tetraanions, and hexaanions) are produced. Their detection by highly resolved NMR spectra, however, is only possible if exactly *n* faradays have been transferred. The assignments of signals given for ionic products (shown in Tables II–IV) generally follow from a manifold of criteria such as the splitting patterns, the relative signal intensities, selective

Scheme IV



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(16) (a) Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *J. Am. Chem. Soc.* **1982**, *104*, 5403. (b) Becker, B. C.; Huber, W.; Schnieders, C.; Müllen, K. *Chem. Ber.* **1983**, *116*, 1573. (c) Müllen, K.; Meul, T.; Schade, P.; Schmickler, H.; Vogel, E. *J. Am. Chem. Soc.* **1987**, *109*, 4992.

(17) Schenk, R.; Ehrenfreund, M.; Huber, W.; Müllen, K. *J. Chem. Soc., Chem. Commun.*, in press.

Table III. ^1H NMR Chemical Shifts (Coupling Constants (Hz)) of the Lithium Salts $4^{4-}/4Li^+$ and $10^{2-}/2Li^+$

	2,4,6,14	7,8	11	12	Me (methylene)	*t*-Bu
$4^{4-}/4Li^+$	6.13, 5.99 5.72, 5.36 5.31, 5.15 5.12 (2 H)	3.80 (9.3) 2.70 (9.3) 3.43 (8.8) 3.10 (8.8)	6.17 6.04	5.04 4.42	(2.1–2.8)	1.21 (9 H) 1.18 (9 H) 1.12 (18 H)
$10^{2-}/2Li^+$	5.71, 5.27 5.08, 4.96	3.18 (10.1) 2.80 (10.1)	5.88	4.76	1.80 1.61	1.13 1.08

Table IV. ^1H (δ_H) and ^{13}C (δ_C) NMR Chemical Shifts of the Alkali-metal Salts $5^{2-}/2K^+$, $5^{6-}/6Li^+$, $8^-/M^+$ (M = Li, K), and $8^{3-}/3Li^+$

	2,6	4	7,8	10,11,13,14	15	17,21	18,20	19	t-Bu
$\delta_H(8^-/Li^+)$	7.08	6.92	6.13 6.6–6.8	6.11 6.6–6.8	4.60	6.11 6.6–6.8	6.6–6.8	5.96	1.30
$\delta_H(8^-/K^+)$	7.10	6.96	6.22 6.6–6.8	6.12 6.6–6.8	4.62	6.12 6.6–6.8	6.6–6.8	5.99	1.30
$\delta_H(8^{3-}/3Li^+)$	4.54 5.47	4.43	2.37 3.22	5.34, 6.30 5.80, 6.05	3.35	5.66 6.18	5.94 6.18	4.90	1.03 1.09
$\delta_C(8^{3-}/3Li^+)$	92.4	90.7	51.5 65.1	105.3, 124.1 117.8, 124.8	69.3	118.2 108.4	127.6 129.8	98.7	35.0, 34.5 32.2, 31.8
$\delta_H(5^{2-}/2K^+)$	6.96	6.81	5.95 6.57	6.16 (2 H) 6.51 (4 H) 7.32 (2 H)		7.32	6.74	6.18	1.28
$\delta_H(5^{6-}/6Li^+)$	4.56 5.47	4.50	2.65 3.29	5.29, 6.46 5.80, 6.23		4.98 6.46	5.98 5.80	4.47	1.02 1.09

H,H-decoupling experiments, H,H-correlation spectra, and if necessary a comparison with π charge densities calculated with the Hückel molecular orbital (HMO) method.[18] A typical example is given in the Experimental Section.

For subsequent quenching reactions of the ionic products, the tubes were opened under argon and the solutions treated with electrophiles such as dimethyl sulfate or methanol. The number of electrophilic reagents incorporated into the charged substrate provides independent evidence for the number of extra electrons in the ions.

It is important for the detection of stereoisomerism that the ^1H NMR spectra of some anions exhibit dynamic line-broadening effects. Also it is significant in the structural analysis to count the proton or carbon NMR signals since this provides information on the number of stereoisomers that occur in those cases where rotation about the formal single bonds is slow on the NMR time scale.

Both the electrochemical reduction of compounds **2** under cyclic voltammetric control and the reduction with alkali metals leave no doubt that the maximum number of electrons transferred increases with the chain length; e.g., 2e (**2a**), 4e (**2b**), and 6e (**2c** and **2d**) were transferred by the reduction with potassium. The ^1H NMR spectrum of $\mathbf{2a}^{2-}/2K^+$ exhibits a dynamic line broadening of the signal of H-7 and two broad resonances for the protons of the inner phenylene rings (H-10–14) even at 60 °C (see Figure 2). This does not hold for the spectra of the corresponding lithium salt, so that the barrier for rotation about the C-8–C-9 bond seems to be lower in the latter species. When the sample of $\mathbf{2a}^{2-}/2K^+$ is cooled, the rotations about the formal single bonds C-8–C-9 and C-1–C-7 become slow on the NMR time scale (Table II). Below 30 °C, one obtains two resonances for each aromatic and olefinic proton with a relative intensity of 5:2. This finding shows that the potassium salt of the dianion exists in two conformers as depicted by **2a′** and **2a″** (Chart II). According to the different symmetries of both conformers, the protons H-10/H-14 and H-11/H-13 in **2a′** should be isochronous and should give rise to two doublets, which are, indeed, observed in the spectrum at δ 5.34 and 5.79 (^3J = 8.5 Hz). In contrast for conformer **2a″**, protons H-10/H-11 and H-13/H-14 are equivalent, thus giving rise to the singlets at δ 5.83 and 5.37. The other chemical shifts are given in Table II. At even lower temperature ($T < -60$ °C), the rotation of the terminal phenyl rings about the C-1–C-7 bond is also slow on the NMR time scale. A typical finding, therefore, is the fact that the *tert*-butyl groups give rise to two singlets (relative intensity 1:1).

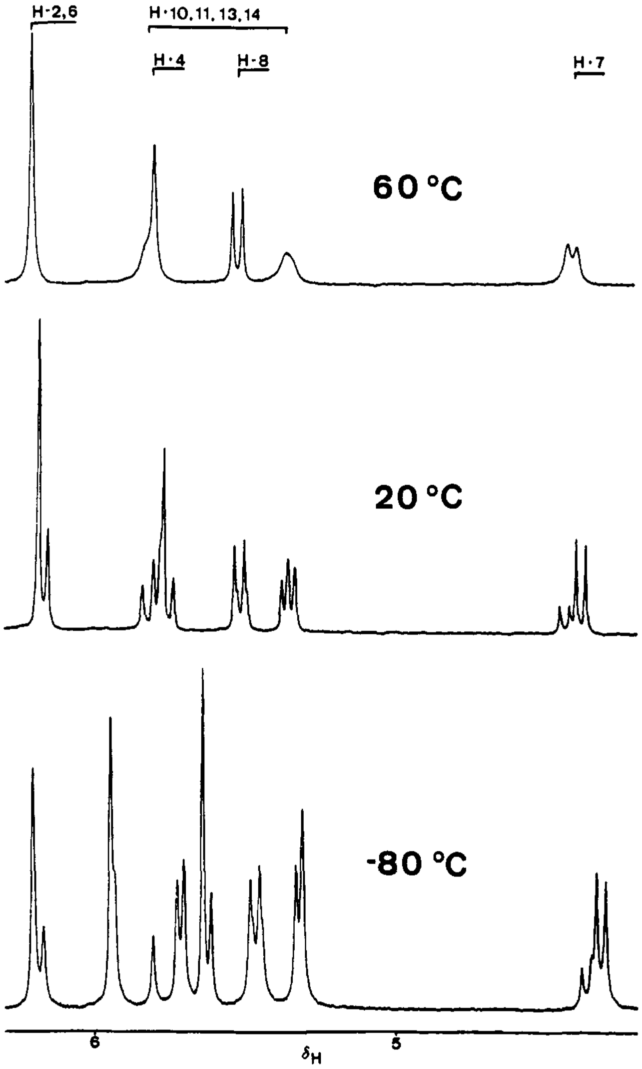

Figure 2. ^1H NMR spectra (400 MHz) of $\mathbf{2a}^{2-}/2K^+$ at different temperatures (THF-d_8).

The quenching products obtained from $\mathbf{2b}^{2-}/2K^+$ with methanol or dimethyl sulfate are identified as the ethane (**20**) and the butane

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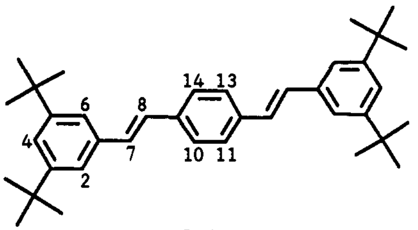
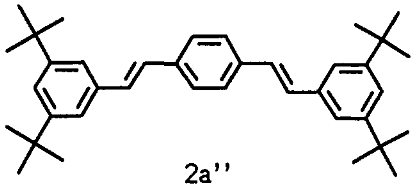
[18] Heilbronner, E.; Bock, H. *Das HMO Modell und seine Anwendung*; Verlag Chemie: Weinheim, West Germany, 1968.

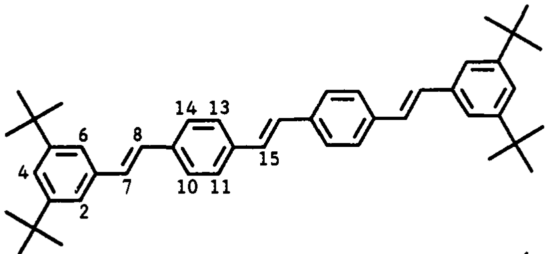
Chart II



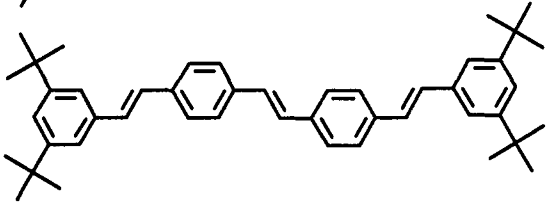
2a'



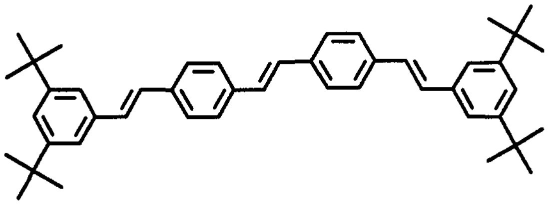
2a''



2b'

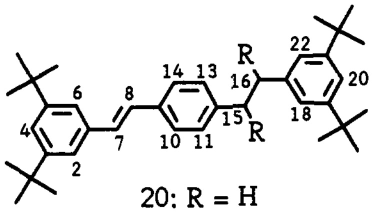


2b''

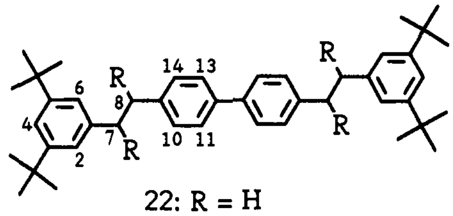


2b'''

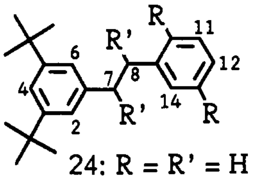
Chart III



20: R = H
21: R = Me



22: R = H
23: R = Me



24: R = R' = H
25: R = H, R' = Me
26: R = Me, R' = H
27: R = R' = Me

(**21**) derivatives, respectively (Chart III).

Prolonged reduction of **2b** with either lithium or potassium at −30 °C gives rise to products that can be identified by highly resolved ^{1}H NMR spectra and by quenching reactions. Quenching with dimethyl sulfate produces tetramethyl adducts, indicating the formation of tetraanions. The absorptions of the aromatic and olefinic protons of the tetraanion $\mathbf{2b}^{4-}/4\mathrm{Li}^+$ (Table II) are detected at significantly higher field (δ 3.1–6.2) than those for the dianion of unsubstituted distyrylstilbene $\mathbf{1b}^{2-}/2\mathrm{M}^+$ (M = Li, K; δ 4.9–6.8).[18] The absorption range for $\mathbf{2b}^{4-}/4\mathrm{Li}^+$ is very similar to that observed for the stilbene dianion $\mathbf{9}^{2-}/2\mathrm{Li}^+$ whereby both species have a similar average charge density per carbon.

Different from $\mathbf{2a}^{2-}/2\mathrm{M}^+$, the NMR spectra of tetraanion $\mathbf{2b}^{4-}/4\mathrm{Li}^+$ fail to exhibit dynamic line broadening upon warming from −80 °C to room temperature. It is clear from the number of proton signals, however, that, in the tetraanion, the rotation about the formal single bonds C-1–C-7, C-8–C-9, and C-12–C-15 is slow within the NMR time scale. It should be noted in this context that the ^{1}H NMR spectra of the corresponding potassium salt are much more complex. It is typical that the resonances of the *tert*-butyl groups appear as a number of singlets between δ 0.9 and 1.2, while the signals of the aromatic and olefinic nuclei were always very numerous.

The reduction of the homologous oligo(phenylenevinylenes) **2c** and **2d** with potassium fails to produce highly resolved NMR spectra even after several months of metal contact. This may be due to the low solubility of the species or to the presence of paramagnetic products. Nevertheless, the number of charges on **2c** and **2d** can be investigated by quenching the final polyanions with dimethyl sulfate. In both cases, the analysis of the products by FD-mass spectrometry indicates the formation of tetra-, hexa-, and octamethyl derivatives. We believe that this finding points toward the formation of hexaanions. An intermolecular electron transfer competes with the quenching reaction so that the hexaanion can give rise to both tetra- and octamethyl derivatives.

The two bis-stilbene systems **3** and **4** can be transformed into tetraanion salts (lithium, potassium), which are stable even at room temperature.[4] While the tetraanions give rise to highly resolved NMR spectra, the intermediate dianions could not be detected by NMR spectroscopy in spite of careful monitoring of the reduction. The chemical evidence for the formation of tetraanions comes from the detection of tetramethyl derivatives upon quenching with dimethyl sulfate. Likewise, protonation of $\mathbf{3}^{4-}/4\mathrm{M}^+$ produces the tetrahydro derivative **22**. The reduction and protonation of the tetraanion $\mathbf{3}^{4-}/4\mathrm{M}^+$ is, thus, completely analogous to that of the stilbene model systems $\mathbf{9}^{2-}/2\mathrm{Li}^+$ and $\mathbf{10}^{2-}/2\mathrm{Li}^+$, which affords the diphenylethane systems **24** and **26**.

It is not surprising in light of these findings that the ^{1}H NMR chemical shifts of the tetraanions $\mathbf{3}^{4-}/4\mathrm{Li}^+$ and $\mathbf{4}^{4-}/4\mathrm{Li}^+$ closely correspond to those of the dianions $\mathbf{9}^{2-}/2\mathrm{Li}^+$ and $\mathbf{10}^{2-}/2\mathrm{Li}^+$ (see Tables II and III and Figure 3). It is also characteristic that the chemical shifts of the cyclophane tetraanion $\mathbf{4}^{4-}/4\mathrm{Li}^+$ and of the linear analogue $\mathbf{3}^{4-}/4\mathrm{Li}^+$ exhibit only slight differences.

Reaction of the diphenyl-substituted phenylenevinylene **5** with potassium (THF-d_8) for about 5 min at −78 °C affords a species that can be identified as the dianion $\mathbf{5}^{2-}/2\mathrm{K}^+$ (see Figure 4). This finding follows safely from the formation of a dimethyl derivative upon quenching with dimethyl sulfate. Prolonged reduction fails to produce a resolved NMR spectrum of a further diamagnetic product. In contrast, similar reduction of **5** with lithium produces a diamagnetic anion $\mathbf{5}^{n-}/n\mathrm{Li}^+$ possessing a higher charge than the dianion. This is obvious from the NMR signals of $\mathbf{5}^{n-}/n\mathrm{Li}^+$ (see Table IV and Figure 3), which appear at significantly higher field than those of $\mathbf{5}^{2-}/2\mathrm{K}^+$. Quenching of the highly charged product with dimethyl sulfate produces a hexamethyl derivative that is identified by FD-MS. The mass spectrum exhibits the signals

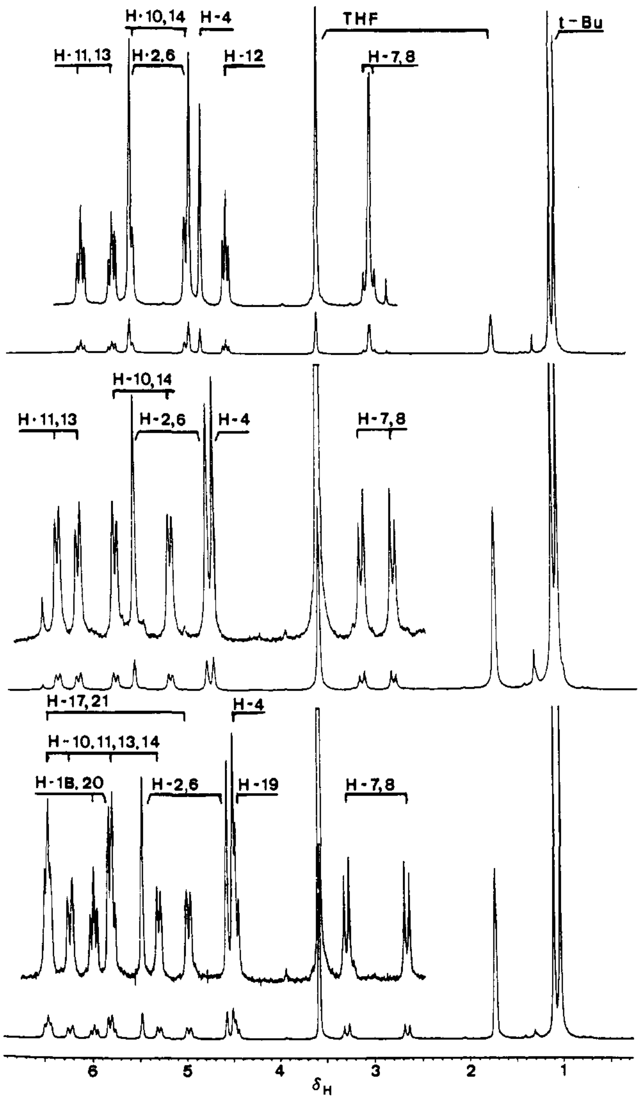


Figure 3. ^{1}H NMR spectra (200 MHz) of $9^{2-}/2Li^+$ (top), $3^{4-}/4Li^+$ (center), and $5^{6-}/6Li^+$ (bottom) at −20 °C (THF-d_8).

of tetramethyl and hexamethyl derivatives and not those of a dimethyl derivative. We, therefore, conclude that a hexaanion $5^{6-}/6Li^+$ has been formed upon reduction of **5**. The formation of a tetramethyl adduct in the quenching reaction must be ascribed to a partial reoxidation of the hexaanion by traces of oxygen. The signal at m/z = 847 is due to a pentamethyl monohydro derivative, which may result from a hexaanion via partial protonation and subsequent methylation.[20] Analogously, protonation of $5^{6-}/6Li^+$ with methanol leads to the hexahydro adduct **28** (Chart IV).

The ^{1}H NMR spectrum of $5^{2-}/2K^+$ exhibits one singlet for the *tert*-butyl groups, which indicates that the rotation of the phenyl group about the C-1–C-7 bond is rapid on the NMR time scale. In contrast in the higher charged species $5^{6-}/6Li^+$, rotation about all formal single bonds (C-1–C-7, C-8–C-9, C-12–C-15, and C-15–C-16) is slow on the NMR time scale.

If a THF-d_8 solution of the ether **7** is treated with lithium or potassium, one obtains the monoanion $8^-/M^+$ (see Table IV and Figure 4) in a clean reaction. This process can be monitored by NMR spectroscopy from the disappearance of the signals of the starting material and by the appearance of product signals since no line broadening is observed throughout the reaction. Prolonged metal contact of the solution of $8^-/Li^+$ gives rise to the trianion $8^{3-}/3Li^+$ (see Table IV). The corresponding tripotassium salt is insoluble in THF-d_8.

The structures of the monoanion and trianion can be proved by their highly resolved ^{1}H NMR spectra (see below) and by quenching reactions. Thus, quenching with dimethyl sulfate affords mono- and trimethyl adducts, respectively, which are identified by mass spectrometry. Protonation of $8^-/M^+$ and $8^{3-}/Li^+$ provides 3,5-di-*tert*-butyl-4′-benzylstilbene (**29**) and 1-(3,5-di-*tert*-butylphenyl)-2-(4-benzylphenyl)ethane (**30**), respectively (see Experimental Section). When the temperature is increased from −20 to +60 °C, the spectrum of $8^-/M^+$ exhibits dynamic line broadening. The doublet signal at δ 6.15 (relative intensity 1) disappears, and a new doublet can be observed at δ 6.48 (relative intensity 2). This finding indicates that, at low temperatures, the rotation about the C-8–C-9 or C-12–C-15 bond is slow within the NMR time scale. The Gibbs free energy of activation of this process can be estimated from the coalescence

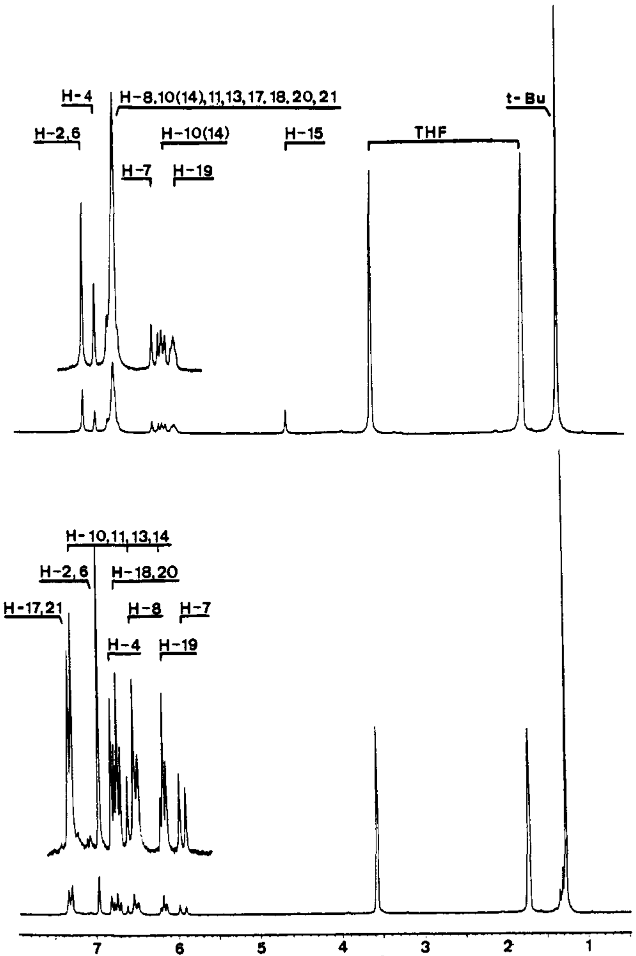
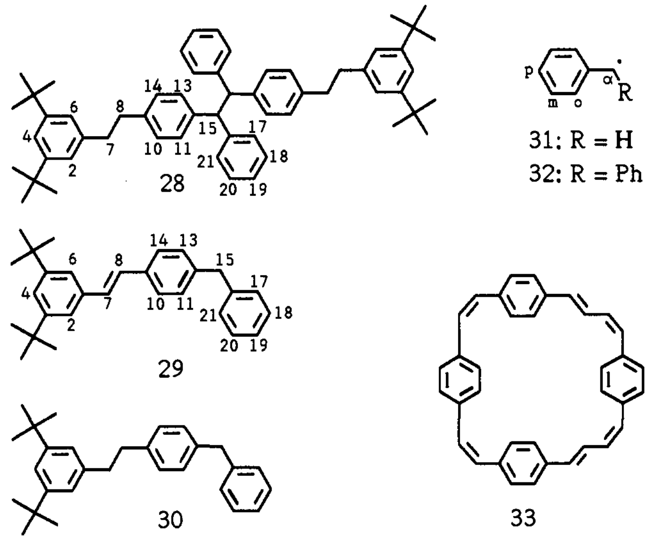


Figure 4. ^{1}H NMR spectra (200 MHz) of $8^-/K^+$ (top) and $5^{2-}/2K^+$ (bottom) at −20 °C (THF-d_8).

Chart IV



temperature as $\Delta G^\ddagger = 60 \pm 3$ kJ/mol.

The number of NMR signals in the spectrum of $8^{3-}/3Li^+$ shows that the rotations about the formal single bonds are slow within the NMR time scale. Particularly significant is the existence of two singlet signals for the *tert*-butyl groups (δ 1.03 and 1.09 and relative intensity 9:9).

Torsion about the formal single bonds C-15–C-16 of **5** would decouple the phenyl groups from the linear π system, and ions derived from **5** should resemble those from the non-phenyl-substituted analogue **2b**.

3. Discussion

Number of Electrons That Can Be Transferred. The maximum number of electrons that are transferred in an extended redox sequence is generally deduced from cyclic voltammetric evidence (see above), the NMR spectroscopic description of the ionic products, and the results of quenching reactions (i.e., the number of electrophilic groups being incorporated). Cyclic voltammograms for the reduction of the homologous series **2a–2d** clearly indicate that the number of accessible redox states increases with the chain length. There is no doubt, however, that alkali-metal reduction of the hydrocarbon precursors can produce highly charged products, which in some solvent/electrolyte systems are not detected by cyclic voltammetry. Thus, while **2b** produces in THF a tetraanion salt upon reduction with lithium, cyclic voltammetry carried out in the same solvent with $NaBPh_4$ as supporting electrolyte only exhibits three redox steps but shows the reversible formation of a tetraanion in DMA/TBABr. It can be concluded that, in any case, the title hydrocarbons serve as very efficient electron acceptors.

An interesting case can be made by describing **2b** and **3–5** as being made up of differently linked stilbene units. Thus, **2b**, **3**, and **4** represent bis-stilbene systems, which interact via a vinylene group, a single bond, or space, respectively. In all cases, stable tetraanionic products are formed, which point toward an effective decrease of the Coulombic repulsion between the stilbene dianion subunits. One must also conclude that phenyl substitution within a phenylenevinylene chain increases the redox activity because compound **5** gives rise to a hexaanion, while the analogous reaction of **2b** only leads to a tetraanion. Ether cleavage in **7** is much more rapid than electron transfer into the electrophoric stilbene unit so that pure monoanion $8^-/M^+$ can readily be prepared. Only after prolonged reduction does the latter accept two additional electrons with the formation of the corresponding trianion.

The correlation of local π charge densities and corresponding chemical shifts provides additional evidence for the number of charges acquired by the π system.[21] It is well-known that ^{13}C NMR chemical shifts are more reliable than the corresponding proton data in a description of the local π charge densities.[21] The low solubility of the large ionic hydrocarbons, however, excludes ^{13}C NMR as a general tool in the analysis of the title systems. There is ample evidence that, in the linear π systems[6,22] considered here (absence of significant ring current and ion-pairing effects), ^1H NMR chemical shifts mainly reflect local π charge densities. The carbanions $3^{4-}/4Li^+$, $4^{4-}/4Li^+$, $9^{2-}/Li^+$, $10^{2-}/2Li^+$, $8^{3-}/3Li^+$, and $5^{6-}/6Li^+$ have in common that one electron is delocalized over seven sp^2-hybridized carbon atoms. The olefinic protons typically absorb in a range of δ 2.5–3.5. As a result, the signals of protons in corresponding π centers suffer from only minor shifts in going from a stilbene dianion to the bis-stilbene tetraanion. However, if the π system is lengthened without increasing the charge, the signals are shifted downfield. This can be seen from a comparison between $2a^{2-}/2K^+$, $1b^{2-}/2K^+$, and $5^{2-}/2K^+$. The resonances of $5^{6-}/6Li^+$ are at higher field than those of $2b^{4-}/4Li^+$, which again suggests that **5** has transformed into a hexa- instead of a tetraanion.

The electrochemical reduction of **2a–2d** under cyclic voltammetric control shows three effects:

The redox potentials of already existing states are shifted to less negative potentials, thereby approaching borderline values.

With increasing chain lengths, neighboring redox steps (e.g., mono- and dianion formation) tend to approach each other, although no typical two-electron transfers with $E_{i+1}{}^0 > E_i{}^0$ are observed. There is, thus, no extrastabilization of diionic states.

The number of accessible redox states increases with the chain length. Thus, while **2a** transforms into a dianion, homologue **2d** reversibly forms a pentaanion.

On extrapolating these findings toward a corresponding polymer, one concludes that the interaction energy between the two extra electrons in a diionic state decreases to a minimum only if the chain is made up of at least eight repeating units. In other words in a polymer with the degree of polymerisation n, $n/4$ charges can be stored, which interact only by spin pairing. However, recent solid-state voltammetry carried out with defined oligomers of oligo(phenylenes) shows that, even in tetramers, thermodynamically favorable two-electron transfer reactions occur. This leads to the conclusion that results obtained in solution may not fit the properties of the solid state.[23]

π Charge Distribution. Having firmly established the number of charges in the carbanions, one can proceed to an interpretation of the π charge distribution.

In the dianion of 4,4'-distyrylstilbene (**1b**), the calculated π charge densities (q_π) decrease in the series C-15 > C-7 > C-8, and this is in accord with the sequence of proton resonances of $1b^{2-}/2M^+$.[19] Upon going from the dianion to the tetraanion, the additional charge is mainly localized in the terminal olefinic units so that the resulting sequence of local π charge densities is q_π(C-7) > q_π(C-8) > q_π(C-15). As expected, the protons H-7,8 in $2b^{4-}/4Li^+$ absorb at highest field.

An electrostatic repulsion effect within the cyclophane moiety of $4^{4-}/4Li^+$, which might result in a shift of the excess charge toward the terminal styrene units, cannot be detected. The coupling of the stilbene systems in $3^{4-}/4Li^+$ by a torsion about the biphenyl single bonds cannot be observed since the calculated charge densities at C-7 and C-8 are not affected by the torsion about the central single bond. The NMR spectroscopic characterization of all tetraanions and a comparison with the model dianions $9^{2-}/2Li^+$ and $10^{2-}/2Li^+$ are in agreement with the existence of two separate stilbene dianion subunits possessing only a weak electronic interaction. The degree of interaction between the stilbene subunits of $2b^{4-}$, 3^{4-}, and 4^{4-} can also be deduced from the experimental reduction potentials (see Table I).

It follows from the cyclic voltammetric data that **2b** is reduced to the monoanion at a somewhat more positive potential than **3** and **4**, which can readily be ascribed to the existence of the additional ethylene unit. The conjugative interaction between the stilbene moieties of **3** readily explains that **3** is reduced to the monoanion with greater ease than **4**. Nevertheless, the radical anion of **4** appears to be more stable than the model compounds **9** and **10**.

The potential difference $E_1{}^0 - E_2{}^0$ serves as an experimental measure of the interaction energy between excess electrons in the dianions of **2b**, **3**, and **4** (see Table I). The data (0.22 (**3**), 0.20 (**4**), 0.19 (**2b**)) can be rationalized by assuming that the interaction energy between the charged stilbene units in the dianions of **2b**, **3**, and **4** is small and essentially independent of the mode of coupling.

It is obvious from an inspection of the ^1H NMR spectra that anions $8^-/M^+$ and $5^{2-}/2K^+$ are similar, while $8^{3-}/3Li^+$ and $5^{6-}/6Li^+$ closely correspond to each other. A significant difference is only observed for the resonances of H-12 and H-13. This must be due to additional nonbonding interactions, which prevail in **5**

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(19) Unterberg, H. Ph.D. Thesis, University of Cologne, 1985.

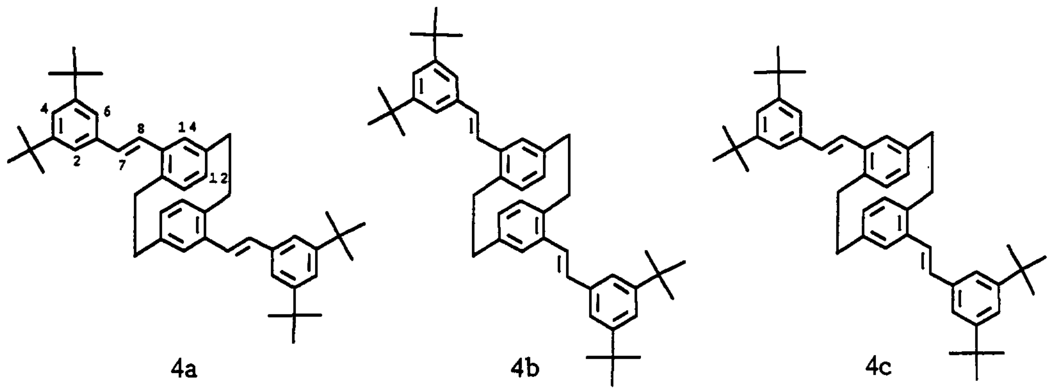
(20) It is, in principle, possible that a hexamethyl derivative may result from quenching of a tetraanion. Thereby, a tetraanion can serve as an electron donor during the quenching reaction. This would give rise to di- and hexamethyl derivatives. Since a dimethyl derivative is not observed, the detection of a hexamethyl derivative of **5** can be taken as evidence for the presence of a hexaanion $5^{6-}/6Li^+$.

(21) (a) O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (b) Müllen, K. *Chem. Rev.* **1984**, *84*, 603. (c) Eliasson, B.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 937.

(22) Bohnen, A.; Heitz, W.; Müllen, K.; Räder, H.-J.; Schenk, R. Submitted for publication.

(23) Meerholz, K.; Heinze, J. *Angew. Chem.* **1990**, in press.

Chart V



but not in **8** (see below). The terminal styryl units of $\mathbf{8}^-/M^+$ and $\mathbf{5}^{2-}/2K^+$ carry only a small charge, which is obvious from the resonances of the ortho protons H-2,6 and of the para proton H-4. Furthermore, the olefinic protons H-7 and H-8 in $\mathbf{8}^-/M^+$ and $\mathbf{5}^{2-}/2K^+$ are not shielded with respect to the aromatic protons, which is clearly different from the situation in stilbene dianions $\mathbf{9}^{2-}/2Li^+$ and $\mathbf{10}^{2-}/2Li^+$. Otherwise, the ^1H NMR spectra of the more highly charged species $\mathbf{8}^{3-}/3Li^+$ and $\mathbf{5}^{6-}/6Li^+$ are more similar to those of stilbene dianion and bis-stilbene tetraanion systems. The olefinic resonances are now significantly shifted with respect to the aromatic proton signals and appear with a vicinal coupling constant of 10.0 Hz ($\mathbf{8}^{3-}/3Li^+$) and 10.2 Hz ($\mathbf{5}^{6-}/6Li^+$). The protons H-2,6, and H-4 of the terminal phenyl rings resonate in the same region as those of the other aromatic signals (H-10,11,13,14,17–21). Accordingly, the terminal styryl moieties in $\mathbf{8}^{3-}/3Li^+$ and $\mathbf{5}^{6-}/6Li^+$ carry a charge similar to those in the above mentioned stilbene systems with one electron per seven carbon atoms. It must be emphasized that the weakly charged carbanions $\mathbf{8}^-/M^+$ and $\mathbf{5}^{2-}/2K^+$ tend toward the localization of the excess charge in the diphenylmethyl and tetraphenylethylene subsystems, respectively. This is particularly surprising for dianion $\mathbf{5}^{2-}/2K^+$ in view of the prevailing Coulomb repulsion. In general, an increasing number of electrons enhances the tendency toward a uniform charge distribution over the whole π system. It is characteristic that the ^1H NMR spectrum of $\mathbf{5}^{6-}/6Li^+$ fails to exhibit resonances with a chemical shift larger than δ 6.5 and that the resonances of para protons H-4 (δ 4.50) and H-19 (δ 4.47) point toward the uniform charge distribution. This finding implies that the distribution of the excess charge also affects the phenyl substituents at C-15 and C-15′ and, thus, excludes a strongly twisted arrangement of the phenyl substituents at C-15 and C-15′ with respect to the π chain. This finding will be referred to in the discussion of the prevailing conformations.

With the structure of $\mathbf{5}^{2-}/2K^+$, reference to benzyllithium (potassium) ($\mathbf{31}^-/M^+$) and the corresponding diphenylmethyl species ($\mathbf{32}^-/M^+$) is appropriate. From benzyllithium to (diphenylmethyl)lithium, the more pronounced π charge delocalization causes a downfield shift both of the signals of H_α and of the ring protons ($\mathbf{31}^-/Li^+$, δ_α 1.62, δ_{phenyl} 5.50–6.30; $\mathbf{32}^-/Li^+$, δ_α 4.22, δ_{phenyl} 5.65–6.54).[24] The similar resonance of H-15 in monoanion $\mathbf{8}^-/Li^+$ and of H_α in the diphenylmethyl anion and the weak shielding of H-2,6 upon going from $\mathbf{32}^-/Li^+$ to $\mathbf{8}^-/Li^+$ point toward a small π charge in the styryl group of the latter; thus, $\mathbf{8}^-/Li^+$ can adequately be described as a (diphenylmethyl)lithium salt weakly perturbed by a styryl substituent.

Conformational and Configurational Changes upon Electron Transfer. The vicinal coupling constants of the olefinic protons are a function of the corresponding π bond order and decrease with increasing charge: $\mathbf{8}^-/M^+$ (J = 15.1 Hz), $\mathbf{5}^{2-}/2K^+$ (J = 15.0 Hz), $\mathbf{2a}^{2-}/2K^+$ (J = 12.9 Hz), $\mathbf{2b}^{4-}/4Li^+$ (J = 10.8 Hz), $\mathbf{3}^{4-}/4Li^+$ (J = 10.3 Hz), $\mathbf{8}^{3-}/3Li^+$ (J = 10.0 Hz), and $\mathbf{5}^{6-}/6Li^+$ (J = 10.1 Hz). These values do not show whether the trans configuration prevailing in the neutral starting compound is maintained upon ion formation. This is particularly obvious from a comparison with the data of the cyclic dianion $\mathbf{33}^{2-}/2Li^+$, which contains both cis (J = 11.0 Hz) and trans (J = 13.3 Hz) olefinic bonds.[25] The fact that mono- and dianions derived from *cis*- and *trans*-stilbene possess a trans configuration of the olefinic bond[26] supports the conservation of the trans double bonds upon doping in the oligo(pheneylenevinylenes). The conformation about the formal single bonds of the charged π systems is less evident. There is evidence, however, from related examples[6] that an electron transfer will increase the π bond order of the formal single bond and, thus, increase the tendency toward planar structures. What one would expect, however, from the increasing π bond order of formal single bonds is that conformational isomerism might become detectable.

The temperature-dependent ^1H NMR spectra of $\mathbf{2a}^{2-}/2K^+$ reveal that rotation about the C-1–C-7 single bond requires a lower activation barrier than that about the C-8–C-9 single bond. Steric effects cannot be responsible for the observed difference. However, a straightforward explanation comes from a simple HMO model according to which the π bond order of the C-1–C-7 bond is lower than that of the C-8–C-9 bond.

In principle, **2b** can exist in the nonisodynamic conformations **2b′**, **2b″**, and **2b‴**. Two of them possess a C_2 axis (**2b′** and **2b″**) perpendicular to the neutral double bond. Accordingly, each aromatic and olefinic proton can give four and the *tert*-butyl protons eight NMR resonances. From the number of ^1H NMR signals of $\mathbf{2b}^{4-}/4Me^+$, one concludes, however, that the lithium salt exists as only one centrosymmetric conformer (**2b′** or **2b″**), while the potassium salt forms all three possible stereoisomers.

Analogous anions $\mathbf{9}^{2-}/2Li^+$, $\mathbf{10}^{2-}/2Li^+$, $\mathbf{3}^{4-}/4Li^+$, and $\mathbf{4}^{4-}/4Li^+$ have in common that, at room temperature, rotation of the terminal phenyl rings about the neighboring C-1–C-7 single bonds is slow within the NMR time scale. This can be safely deduced from the detection of two singlets for the *tert*-butyl groups and of separate resonances for the hydrogens H-2 and H-6. The analysis of the ^1H NMR spectrum of $\mathbf{4}^{4-}/4Li^+$ is severely inhibited by the occurrence of conformational isomerism resulting from hindered rotation about the C-8–C-9 bonds. Particularly characteristic is the occurrence of four doublets (δ 2.70, 3.80, 3.10, 3.43) with pairwise coupling and different coupling constants (^3J = 9.3 and 8.8 Hz) for the olefinic protons (H-7,8). In principle, $\mathbf{4}^{4-}/4M^+$ can exist in three nonisodynamic conformers, only two of which (**4a** and **4b**) are centrosymmetric (Chart V). The observation that all NMR signals have equal intensity seems to indicate the existence of the nonsymmetric conformer $\mathbf{4c}^{4-}/4Li^+$ with different torsional angles (about 0° and 180°) with respect to the C-8–C-9 and C-8′–C-9′ bonds.

It has been deduced from the NMR spectra of $\mathbf{8}^-/M^+$ that, at low temperatures (<–20 °C), the rotation about the C-8–C-9 or

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[24] O'Brien, D. H. In *Comprehensive Carbanion Chemistry, Part A*; Buncel, E., Durst, T., Eds.; Elsevier Scientific Publishing Co.: Amsterdam, Oxford, New York, 1980; p 271.

[25] Müllen, K.; Unterberg, H.; Huber, W.; Wennerström, O.; Norinder, U.; Tanner, D.; Thulin, B. *J. Am. Chem. Soc.* **1984**, *106*, 7514.

[26] (a) Gerson, F.; Ohya-Nishiguchi, H.; Swarc, M.; Levin, G. *Chem. Phys. Lett.* **1977**, *52*, 587. (b) Stucky, G. D. *Adv. Chem. Ser.* **1974**, *130*, 50. (c) Walczak, M.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *98*, 5531. (d) Schade, P.; Müllen, K. Unpublished results.

C-12–C-15 bond is slow within the NMR time scale. According to an HMO model, the C-12–C-15 bond possesses a higher π order than the C-8–C-9 bond. Therefore, we conclude that rotation about the C-12–C-15 bond is slow on the NMR time scale. The Gibbs free energy of activation of this process is $\Delta G^{\ddagger} = 60 \pm 3$ kJ/mol, which is quite close to the values observed for related π systems.[27] In contrast, it can be deduced from the number of NMR signals in the spectrum of $\mathbf{8}^{3-}/3\mathrm{Li}^+$ that the rotation of the terminal phenyl ring (C-1–C-7 bond) is slow. Thus, a comparison of data for $\mathbf{8}^-/\mathrm{M}^+$ and $\mathbf{8}^{3-}/3\mathrm{Li}^+$ points toward the increasing rigidity of the highly charged species. The same trend appears from a comparison of dianion $\mathbf{5}^{2-}/2\mathrm{K}^+$ and hexaanion $\mathbf{5}^{6-}/6\mathrm{Li}^+$ since only in the latter the rotation of the terminal phenyl groups (C-1–C-7 bond) is slow on the NMR time scale.

A crucial question is the structure of the carbanions $\mathbf{5}^{2-}/2\mathrm{K}^+$ and $\mathbf{5}^{6-}/6\mathrm{Li}^+$ because they contain a tetraphenylethylene subunit whose geometry upon dianion formation has not been unambiguously determined.[7,8] Model considerations reveal that a planar arrangement of this tetraphenylethylene moiety in **5** is not possible since the hydrogens H-13,17′ and H-13′,17 closely approach each other. A relief of the resulting steric strain is possible by a torsion about the bonds C-12–C-15, C-15–C-16, or C-15–C-15′. In the case of a strong twist about the formal double bond C-15═C-15′, the dianion and the hexaanion can be regarded as being made up of two styryl-substituted diphenylmethyl anion subunits. It is for this reason that monoanion $\mathbf{8}^-/\mathrm{M}^+$ and trianion $\mathbf{3}^{3-}/3\mathrm{Li}^+$ have been included as reference compounds. On the other hand, torsions about the formal single bonds C-15–C-16 of **5** would decouple the phenyl groups from the linear π system, and ions derived from **5** should resemble those obtained for the non substituted analogue **2b**.

The ^{1}H NMR spectrum of $\mathbf{5}^{2-}/2\mathrm{K}^+$ shows that the ortho hydrogens H-17,21 resonate at lower field than the neighboring meta protons H-18,20. A related finding was made for the highly charged lithium salt $\mathbf{5}^{6-}/6\mathrm{Li}^+$, with the only difference being that, due to the slow phenyl rotation, only one of the two ortho protons is deshielded with respect to the corresponding meta proton. This unusual chemical shift sequence must be due to the nonplanar geometry of the carbanions. In that respect, $\mathbf{5}^{2-}/2\mathrm{K}^+$ and $\mathbf{5}^{6-}/6\mathrm{Li}^+$ resemble the dianion of tetraphenylethylene but differ from the stilbene systems $\mathbf{9}^{2-}/2\mathrm{Li}^+$, $\mathbf{10}^{2-}/2\mathrm{Li}^+$, $\mathbf{3}^{4-}/4\mathrm{Li}^+$, $\mathbf{4}^{4-}/4\mathrm{Li}^+$, $\mathbf{8}^-/\mathrm{M}^+$, and $\mathbf{8}^{3-}/3\mathrm{Li}^+$. In the tetraphenylethylene dianion,[7] the shielding is ascribed to a van der Waals interaction of protons from neighboring rings and is supported by the short relaxation times (T_1) expected for sterically hindered protons. For the central C_α–$C_{\alpha'}$ bond in the tetraphenylethylene dianion, torsional angles between 0° (planar) and 90° (orthogonal) have been reported in the literature.[8] From a recent investigation of ^{13}C/^{13}C coupling constants, the angle has been estimated to lie between 8° and 28°.[7]

A crystal structure determination of the disodium salt of tetraphenylethylene dianion shows that there are two different types of phenyl rings and two different sodium cations.[28] The torsional angle about the C_α–$C_{\alpha'}$ bond is 56°, and those about the formal single bonds are 10° and 14°, respectively. It is not possible for that compound to adopt a similar structure in solution because all four rings are equivalent in the tetraphenylethylene dianion according to NMR spectroscopy.

The resonance for the para proton H-19 in $\mathbf{5}^{6-}/6\mathrm{Li}^+$ appears at significantly higher field than in $\mathbf{8}^{3-}/3\mathrm{Li}^+$. In the former compound, the two different para protons H-4 and H-19 give rise to signals with rather similar chemical shifts. Both findings suggest that, in $\mathbf{5}^{6-}/6\mathrm{Li}^+$, the phenyl rings (C-16–21) behave as part of a stilbene dianion moiety rather than of a benzyllithium system. This result would point to a significant conjugative interaction of the trianionic phenylstilbenylmethyl subunit and, thus, only a small twist about the C-15–C-15′ bond. The actual size of the prevailing torsional angle, however, cannot be deduced from the present NMR data. The electrochemical data support this view. Although the change of redox potentials from **2b** to **5** indicates a stabilization of the charged states due to a larger conjugation system, there is no evidence for the formation of thermodynamically favorable diphenylmethyl anion subunits. In the latter case, the potential difference $E_2^0 - E_3^0$ should become essentially smaller in going from **2b** to **5**.[29] This effect was never observed.

4. Conclusion

The three introductory questions concerning the (i) redox capacity of the title phenylenevinylenes, (ii) charge distribution in the resulting carbanions, and (iii) electron-transfer-induced structural changes can now be answered as follows:

All oligo(phenylenevinylene) systems studied herein are most effective electron acceptors. The number of transferrable electrons increases with the chain length but remains essentially unaffected when the mode of connection of stilbene subunits is varied as in the bis-stilbene systems **2b**, **3**, and **4**.

The substitution of the olefinic protons H-15 in **2b** with phenyl rings to give compound **5** increases the redox activity.

As expected from π MO models, injection of two electrons into phenylenevinylene **2b** creates the highest π charge at the central olefinic bond; injection of further electrons significantly increases the charge at the terminal styrene moieties.

While the neutral oligo(phenylenevinylenes) fail to exhibit conformational isomerism due to rapid rotation about all formal single bonds, ion formation significantly increases the corresponding rotational barriers and gives rise to detectable stereoisomers.

5. Experimental Section

Electrochemical Measurements. Our standard electrochemical instrumentation consisted of an AMEL potentiostat, Model 553, and a PAR universal programmer, Model 175. Cyclic voltammograms were recorded with a Model PM 8131 Philips X–Y recorder. A three-electrode configuration was employed throughout. The working electrode was a Pt disk (diameter 0.8 mm) sealed in soft glass. The counter electrode was a Pt wire coiled around the glass mantel of the working electrode. The reference electrode was an Ag wire, on which AgCl had been deposited electrolytically, immersed in the electrolyte solution. Potentials were calibrated against the formal potential of the $[\mathrm{Cp_2Co^+}]/[\mathrm{Cp_2Co}]$ couple (−0.940 V vs Ag/AgCl) or of the $[\mathrm{Cp_2Fe}]/[\mathrm{Cp_2Fe^+}]$ couple (+0.352 V vs Ag/AgCl). All manipulations were carried out under an argon atmosphere.

The experiments were performed in specially designed cells, details of which are described elsewhere.[30] The solvents used were purified by published methods: THF[31] and dimethylamine.[32]

Alkali-Metal Reductions. The neutral compounds **2a–2d**, **3–5**, **7**, **9**, and **10** have been treated with alkali metals (lithium, potassium) in sealed NMR tubes. The experimental details of these experiments were described elsewhere.[16] The progress of the reduction could be followed by NMR spectroscopy. The ^{1}H NMR signal assignments rest on various pieces of experimental evidence (see text). A typical example is that of $\mathbf{2a}^{2-}/2\mathrm{K}^+$ (T = 60 °C): The two resonances of the olefinic protons (H-7,8) at δ 4.41 and 5.52 are recognized by their large coupling constant of 12.1 Hz. The ortho (H-2,6) and para (H-4) aromatic protons of the terminal phenyl rings give rise to two singlets at δ 6.21 and 5.80 with a relative intensity of 2:1. The remaining two broad resonances of aromatic protons at δ 5.35 and 5.80 must then be assigned to the protons H-10,11,13,14 of the central phenylene unit. From the calculated π charge densities at positions 7 and 8 of $\mathbf{2a}^{2-}$, the high-field signal is assigned to H-7. For additional information of the shift assignments, see ref 33.

General procedures: Melting points, Büchi Dr. Tottoli apparatus (uncorrected), commercial solvents purified according to standard procedures; IR spectra, Beckman IR 4220 spectrometer; UV spectra, Perkin-Elmer Lambda 15 spectrometer; ^{1}H NMR spectra, Bruker WH 90 (90 MHz), Bruker AC 200 (200 MHz), Bruker AM 400 (400 MHz) spectrometers; ^{13}C NMR spectra, Bruker AC 200 (50-MHz), Bruker AM 400 (100-MHz) spectrometers; MS (EI), Varian MAT CH 7 A; MS (FD), Varian 711; Elemental analyses, inhouse.

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[27] Huber, W.; May, A.; Müllen, K. *Chem. Ber.* **1981**, *114*, 1318.

[28] Bock, H.; Ruppert, K.; Fenske, D. *Angew. Chem.* **1989**, *101*, 1717; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1685.

[29] Evans, D. H.; O'Conell, K. M. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1979; Vol. 14, p 268.

[30] Hinkelmann, K.; Heinze, J.; Schacht, H. T.; Field, J. S.; Vahrenkamp, H. *J. Am. Chem. Soc.* **1989**, *111*, 5078.

[31] Lund, H.; Iverson, P. In *Organic Electrochemistry*; Baizer, M. M., Ed.; Dekker: New York, 1979; p 165.

[32] Meerholz, K.; Heinze, J. *J. Am. Chem. Soc.* **1989**, *111*, 2325.

[33] Schenk, R. Ph.D. Thesis, University of Mainz, 1990.

General procedure for the Wittig reaction: The Wittig reactions were carried out in a three-necked flask equipped with a stirrer, a gas inlet tube, and a dropping funnel with a pressure equalizing side arm. The phosphonium salts and aldehydes were dissolved or suspended in dimethylformamide (DMF). During the reaction, which was run at room temperature, a slow stream of argon was bubbled through the reaction mixture. A freshly prepared solution of lithium ethoxide in ethanol (0.2–0.3 M) was added dropwise so the colored ylide was consumed between successive additions. When no color change was observed (usually after 0.5–4 h) upon addition of the base, the reaction mixture was diluted with an equal volume of water. The mixture was extracted with diethyl ether three times, the ether extract washed with water several times and dried over sodium sulfate, and the solvent distilled. Usually the olefin was separated by chromatography on silica gel (70–230 mesh ASTM) with tetrachloromethane as eluent. The first fractions gave pure olefins ($R_f \cong 0.9$) on evaporation and recrystallization from tetrachloromethane/methanol. The pure all-trans isomers were obtained by heating the olefins in toluene with a catalytic amount of iodine.

3,5-Di-*tert*-butyl-4′-methylstilbene (12a) was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (50 mmol) and 4-methylbenzaldehyde (6 g, 50 mmol). Yield: 9 g (28.5 mmol, 57%). Mp 81 °C. ^{1}H NMR (200 MHZ, CDCl$_3$): δ 7.43 (d, ^3J = 8.1 Hz, 2 H, H-10, 14), 7.32–7.38 (m, 3 H, H-2,4,6), 7.16 (d, ^3J = 8.1 Hz, 2 H, H-11,13), 7.12, 7.04 (2 d, ^3J = 16.4 Hz, 2 H, H-7,8), 2.36 (s, 3 H, Me), 1.36 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, CDCl$_3$): δ 151.1 (C-3,5), 137.3, 137.0, 135.1 (C-1,9,12), 129.5, 126.6 (C-10,11,13,14), 129.1, 128.2 (C-7,8), 122.0 (C-4), 120.9 (C-2,6), 35.0, 31.7 (*t*-Bu), 21.4 (Me). MS (70 eV), *m/z* (%): 306 (100, M$^+$), 291 (29.9, M$^+$ – CH$_3$), 57 (95.5, *t*-Bu).

4-(3,5-Di-*tert*-butylstyryl)-4′-methylstilbene (12b) was synthesized in a Wittig reaction (see experimental conditions above) from **11b** (50 mmol) and 4-methylbenzaldehyde (6 g, 50 mmol). Yield: 12.7 g (31 mmol, 62%). Mp: 174–175 °C. ^{1}H NMR (90 MHz, CDCl$_3$): δ 7.51–7.09 (m, 15 H), 2.36 (s, 3 H, Me), 1.36 (s, 18 H, *t*-Bu). MS (70 eV), *m/z* (%): 408 (100, M$^+$), 393 (5.1, M$^+$ – CH$_3$), 57 (56.9, *t*-Bu).

4-(Bromomethyl)-3′,5′-di-*tert*-butylstilbene (13a). A suspension of **12a** (9.2 g, 30 mmol), *N*-bromosuccinimide (NBS) (5.1 g, 29 mmol), and a catalytic amount of azobisisobutyronitrile (AIBN) (100 mg) were heated in dry tetrachloromethane (30 mL) to 80 °C for 3 h. After the reaction mixture had cooled to room temperature, the succinimide separated. The solvent was removed and the product examined by ^{1}H NMR spectroscopy. Further purification was unnecessary, because remaining methyl compound does not react in the next step. ^{1}H NMR (90 MHz, CDCl$_3$): δ 7.55–7.05 (m, 9 H), 4.51 (s, 2 H, CH$_2$Br), 1.35 (s, 18 H, *t*-Bu).

[4-(3,5-Di-*tert*-butylstyryl)benzyl]triphenylphosphonium Bromide (11b). The bromomethyl compound **13a** (25 mmol) and triphenylphosphine (6.5 g, 24.8 mmol) were dissolved in toluene. The reaction mixture was heated to 110 °C for 3 h. The product **11b** forms a colorless precipitate, which was separated, washed with toluene, and dried in vacuo. Yield: 12 g (17.1 mmol, 57% based on **12a**). ^{1}H NMR (90 MHz, CDCl$_3$): δ 7.87–7.55 (m, 15 H), 7.42–6.99 (m, 9 H), 5.42 (d, J = 14.3 Hz, 2 H, CH$_2$), 1.35 (s, 18 H, *t*-Bu).

4-(Bromomethyl)-4′-(3,5-di-*tert*-butylstyryl)stilbene (13b) was synthesized as described for **13a** from **12b** (12.2 g, 30 mmol), NBS (5.1 g, 29 mmol), and AIBN (100 mg) in CCl$_4$ (180 mL). ^{1}H NMR (90 MHz, CDCl$_3$): δ 7.51–7.10 (m, 15 H), 4.51 (s, 2 H, CH$_2$Br), 1.35 (s, 18 H, *t*-Bu).

[4-[4-(3,5-Di-*tert*-butylstyryl)styryl]benzyl]triphenylphosphonium bromide (11c) was synthesized as described for **11b** from **13b** (25 mmol) and triphenylphosphine (6.5 g, 24.8 mmol) in toluene (300 mL). Yield: 12.4 g (19 mmol, 63% based on **12b**). ^{1}H NMR (90 MHz, CDCl$_3$): δ 7.78–7.43 (m, 15 H), 7.34–6.99 (m, 15 H), 5.40 (d, J = 14.4 Hz, 2 H, CH$_2$), 1.35 (s, 18 H, *t*-Bu).

1,4-Bis(3,5-di-*tert*-butylstyryl)benzene (2a) was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (3.5 g, 6.4 mmol) and terephthaldicarbaldehyde (0.43 g, 3.2 mmol). Yield: 0.64 g (1.3 mmol, 39%). Mp: 224–225 °C. IR (KBr): ν 3020 (=C—H), 2960–2840 (–C–H), 1583 (C=C), 1388, 1358 (CH$_3$), 1242, 1195, 955, 895, 877, 857, 802, 785, 705 cm^{-1}. UV (CHCl$_3$): λ_{max} (log ϵ) 359.8 nm (4.75). ^{1}H NMR (400 MHz, THF-d_8): δ 7.56 (s, 4 H, H-10,11,13,14), 7.44 (d, ^4J = 1.8 Hz, 2 H, H-2,6), 7.37 (t, ^4J = 1.8 Hz, 1 H, H-4), 7.26, 7.14 (2 d, ^3J = 16.3 Hz, 2 H, H-7,8), 1.37 (s, 36 H, *t*-Bu). ^{13}C NMR (100 MHz, CDCl$_3$): δ 151.1 (C-3,5), 136.9, 136.7 (C-1,9), 129.7 (C-7), 127.7 (C-8), 126.8 (C-10,11,13,14), 122.1 (C-4), 120.9 (C-2,6), 34.9, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 506 (80.0, M$^+$), 491 (4.6, M$^+$ – CH$_3$), 57 (100, *t*-Bu). Anal. Calcd for C$_{38}$H$_{50}$: C, 90.06; H, 9.94. Found: C, 89.32; H, 9.83.

4,4′-Bis(3,5-di-*tert*-butylstyryl)stilbene (2b) was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (3.59 g, 6.5 mmol) and 4,4′-stilbenedicarbaldehyde (0.78 g, 3.3 mmol). Yield: 1.15 g (1.9 mmol, 58%). Mp: 260 °C. IR (KBr): ν 3015 (=C—H), 2940–2860 (–C–H), 1585 (C=C), 1388, 1358 (CH$_3$), 1245, 1195, 952, 895, 872, 848, 810, 790, 700 cm^{-1}. UV (CHCl$_3$): λ_{max} (log ϵ) 386.9 nm (4.94). ^{1}H NMR (400 MHz, THF-d_8): δ 7.56 (s, 4 H, H-10,11,13,14), 7.44 (d, ^4J = 1.8 Hz, 4 H, H-2,6), 7.37 (t, ^4J = 1.8 Hz, 2 H, H-4), 7.26, 7.14 (2 d, ^3J = 16.3 Hz, 2 H, H-7,8), 1.37 (s, 36 H, *t*-Bu). ^{13}C NMR (100 MHz, CDCl$_3$): δ 151.1 (C-3,5), 137.2, 136.7 (C-1,9,12), 129.9, 128.2, 127.7 (C-7,8,15), 126.9 (C-10,11,13,14), 122.1 (C-4), 120.9 (C-2,6), 34.9, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 608 (100, M$^+$), 57 (11.7, *t*-Bu). Anal. Calcd for C$_{46}$H$_{56}$: C, 90.73; H, 9.27. Found: C, 90.85; H, 9.38.

1,4-Bis[4-(3,5-di-*tert*-butylstyryl)styryl]benzene (2c) was synthesized in a Wittig reaction (see experimental conditions above) from **11b** (3.41 g, 5.3 mmol) and terephthaldicarbaldehyde (0.35 g, 2.6 mmol). Yield: 0.65 g (0.9 mmol, 33%). Mp: 294 °C. IR (KBr): ν 3018 (=C—H), 2940–2840 (–C–H), 1586 (C=C), 1390, 1360 (CH$_3$), 1245, 1195, 953, 898, 872, 848, 818, 791, 702 cm^{-1}. UV (CHCl$_3$): λ_{max} (log ϵ) 402.7 nm (5.05). ^{1}H NMR (400 MHz, THF-d_8): δ 7.57 (s, 12 H, aromatic H), 7.44 (d, ^4J = 1.6 Hz, 4 H, H-2,6), 7.37 (t, ^4J = 1.6 Hz, 2 H, H-4), 7.26, 7.17 (2 d, ^3J = 16.2 Hz, 2 H, H-7,8), 7.23 (s, 4 H, H-15,16), 1.37 (s, 36 H, *t*-Bu). MS (70 eV), *m/z* (%): 710 (100, M$^+$), 57 (30.7, *t*-Bu). Anal. Calcd for C$_{54}$H$_{62}$: C, 91.19; H, 8.81. Found: C, 91.01; H, 8.73.

4,4′-Bis[4-(3,5-di-*tert*-butylstyryl)styryl]stilbene (2d) was synthesized in a Wittig reaction (see experimental conditions above) from **11b** (3.4 g, 5.3 mmol) and 4,4′-stilbenedicarbaldehyde (0.62 g, 2.6 mmol). The chromatography was done with chloroform/tetrachloromethane (1:1) as eluent. Yield: 0.6 g (0.74 mmol, 30%). Mp: 307 °C. IR (KBr): ν 3015 (=C—H), 2935–2860 (–C–H), 1585 (C=C), 1390, 1360 (CH$_3$), 1243, 1198, 955, 898, 875, 848, 822, 788, 702 cm^{-1}. UV (CHCl$_3$): λ_{max} (log ϵ) 412.0 nm (5.05). ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$, T = 70 °C): δ 7.48 (br s, 16 H, aromatic H), 7.30 (br s, 6 H, H-2,4,6), 7.13, 7.04 (2 d, ^3J = 16.3 Hz, 4 H, H-7,8), 7.08 (s, 6 H, olefinic H), 1.34 (s, 36 H, *t*-Bu). MS (70 eV), *m/z* (%): 812 (100, M$^+$), 57 (90.5, *t*-Bu). Anal. Calcd for C$_{62}$H$_{68}$: C, 91.57; H, 8.43. Found: C, 91.36; H, 8.26.

1,4-Bis[4-[4-(3,5-di-*tert*-butylstyryl)styryl]styryl]benzene (2e) was synthesized in a Wittig reaction (see experimental conditions above) from **11c** (3.28 g, 4.4 mmol) and terephthaldicarbaldehyde (0.29 g, 2.2 mmol). Purification procedure: After the reaction had ended, the solvent was removed and the crude product extracted with toluene, containing a catalytic amount of iodine. During the extraction, the product formed a yellow precipitate and was separated after 2 weeks. Yield: 0.3 g (0.33 mmol, 15%). Mp: >310 °C. IR (KBr): ν 3005 (=C—H), 2935–2860 (–C–H), 1583 (C=C), 1388, 1357 (CH$_3$), 1242, 1192, 951, 893, 870, 842, 822, 782, 700 cm^{-1}. UV (CHCl$_3$): λ_{max} (log ϵ) 417.9 nm (5.13). FD-MS (20–25 mA), *m/z* (%): 914 (53.7, M$^+$), 457 (100, M^{2+}). Anal. Calcd for C$_{70}$H$_{74}$: C, 91.85; H, 8.15. Found: C, 91.63; H, 8.11.

4,4′-Bis[4-[4-(3,5-di-*tert*-butylstyryl)styryl]styryl]stilbene (2f) was synthesized in a Wittig reaction (see experimental conditions above) from **11c** (3.4 g, 5.3 mmol) and 4,4′-stilbenedicarbaldehyde (0.62 g, 2.6 mmol). The purification was done analogous to that for **2e**. Yield: 0.13 g (0.13 mmol, 7%). Mp: >310 °C. IR (KBr): ν 3015 (=C—H), 2940–2860 (–C–H), 1587 (C=C), 1390, 1360 (CH$_3$), 1243, 1200, 953, 898, 872, 845, 830, 785, 702 cm^{-1}. UV (CHCl$_3$): λ_{max} 415.0 nm.

4,4′-Bis(3,5-di-*tert*-butylstyryl)biphenyl (3) was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (1.6 g, 2.9 mmol) and 4,4′-biphenyldicarbaldehyde (300 mg, 1.4 mmol). Yield: 0.5 g (0.9 mmol, 30%). Mp: 203 °C. UV (CHCl$_3$): λ_{max} (log ϵ) 347 nm (4.62). ^{1}H NMR (200 MHz, THF-d_8), δ 7.70, 7.64 (2 d, ^3J = 8.8 Hz, 8 H, H-10,11,13,14), 7.45 (d, ^4J = 1.6 Hz, 4 H, H-2,6), 7.38 (t, ^4J = 1.6 Hz, 2 H, H-4), 7.31, 7.19 (2 d, J = 16.2 Hz, 4 H, H-7,8), 1.38 (s, 36 H, *t*-Bu). ^{13}C NMR (50 MHz, CDCl$_3$): δ 151.1 (C-3,5), 139.6 (C-12), 136.8, 136.6 (C-1,9), 130.0 (C-7), 127.5 (C-8), 127.0, 126.9 (C-10,11,13,14), 122.2 (C-4), 120.9 (C-2,6), 34.9, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): = 582 (51.6, M$^+$), 57 (100, *t*-Bu). Anal. Calcd for C$_{44}$H$_{54}$: C, 90.65; H, 9.34. Found: C, 90.42; H, 9.22.

2,5′-Bis(3,5-di-*tert*-butylstyryl)[2.2]paracyclophane (4) was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (1.24 g, 2.3 mmol) and 2,5′-[2.2](1,4)paracyclophandicarbaldehyde (**16**) (300 mg, 1.1 mmol). Yield: 300 mg (0.47 mmol, 42%). Mp: 273 °C. UV (CHCl$_3$): λ_{max} (log ϵ) 309, 323 (sh) nm (4.66, 4.61). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.38–7.45 (m, 6 H, H-2,4,6), 7.21, 6.94 (2 d, J = 16.1 Hz, 4 H, H-7,8), 6.71 (s, 2 H, H-14), 6.69, 6.43 (2 d, J = 8.4 Hz, 4 H, H-11,12), 2.8–3.7 (m, 8 H, CH$_2$), 1.40 (s, 36 H, *t*-Bu). ^{13}C NMR (50 MHz, CDCl$_3$), δ 151.2 (C-3,5), 139.5, 138.1, 137.7, 137.2, (C-1,9,10,13), 133.6, 130.5, 130.1, 129.4, 126.6 (C-7,8,11,12,14), 122.1 (C-4), 120.9 (C-2,6), 35.0, 31.6 (*t*-Bu), 34.6, 33.5 (CH$_2$). MS (70 eV), *m/z* (%): 636 (100, M$^+$), 318 (46.4, (M/2)$^+$), 57 (56.1, *t*-Bu). Anal. Calcd for C$_{48}$H$_{60}$: C, 90.51; H, 9.49. Found: C, 90.42; H, 9.45.

3,5-Di-*tert*-butylstilbene (9) was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (8.18 g, 15 mmol) and benzaldehyde (1.48 g, 14 mmol). Yield: 1.58 g (5.4 mmol, 39%). Mp: 57 °C. UV ($CHCl_3$): λ (log ε) 297, 309, 323 (sh) nm (4.44, 4.42, 4.22). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.20–7.55 (m, 8 H), 7.17, 7.07 (2 d, ^{3}J = 16.3 Hz, 2 H, H-7,8), 1.36 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.2 (C-3,5), 137.9, 136.8 (C-1,9), 130.1 (C-7), 128.2, 127.5 (C-8,12), 128.8, 126.6 (C-10,11,13,14), 122.2 (C-4), 121.0 (C-2,6), 35.0, 31.7 (*t*-Bu). MS (70 eV), *m/z* (%): 292 (100, M^+), 277 (59.2, $M^+ - CH_3$), 57 (85.6, *t*-Bu).

3,5-Di-*tert*-butyl-2′,5′-dimethylstilbene (10) was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (6.8 g, 12.4 mmol) and 2,5-dimethylbenzaldehyde (1.7 g, 12.7 mmol). Yield: 2.2 g (6.9 mmol, 54%). Mp: 78 °C. UV ($CHCl_3$): λ_{max} (log ε) 297, 317 (sh), 333 (sh) nm (4.35, 4.25, 3.88). ^{1}H NMR (200 MHz, THF-d_8): δ 7.44 (br s, 1 H, H-14), 7.40 (d, ^{4}J = 1.8 Hz, 2 H, H-2,6), 7.36 (t, ^{4}J = 1.8 Hz, 1 H, H-4), 7.34, 7.06 (2 d, ^{3}J = 16.0 Hz, 2 H, H-7,8), 7.03, 6.93 (2 d, ^{3}J = 7.8 Hz, 2 H, H-11,12), 2.37, 2.31 (2 s, 6 H, Me), 1.36 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.1 (C-3,5), 137.2, 136.6, 135.5, 132.7 (C-1,9,10,13), 131.1, 130.3, 128.2, 126.3, 126.2 (C-7,8,11,12,14), 122.1 (C-4), 121.0 (C-2,6), 34.9, 31.6 (*t*-Bu), 21.1, 19.5 (Me). MS (70 eV), *m/z* (%): 320.2 (100, M^+), 305.1 (24.7, $M^+ - CH_3$), 57 (64.5, *t*-Bu).

3′,5′-Di-*tert*-butyl-4-cyanostilbene was synthesized in a Wittig reaction (see experimental conditions above) from **11a** (10.3 g, 19 mmol) and 4-cyanobenzaldehyde (2.5 g, 19 mmol). Yield: 2.8 g (8.8 mmol, 47%). Mp: 146.5 °C. IR (KBr): ν 2950–2860 (–C–H), 2220 (CN), 1595 (C=C), 1392, 1362 (CH_3), 1247, 1196, 1175, 965, 950, 880, 863, 848, 814, 707 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.61 (m, 4 H, H-10,11,13,14), 7.53–7.45 (m, 3 H, H-2,4,6), 7.26, 7.06 (2 d, ^{3}J = 16.3 Hz, 2 H, H-7,8), 1.37 (s, 18 H, *t*-Bu).

3′,5′-Di-*tert*-butylstilbenyl Phenyl Ketone (18). A suspension of magnesium powder (0.32 g) in dry diethyl ether (10 mL) was heated to the boiling point. Solutions of bromobenzene (2.06 g, 13.1 mmol) and 3′,5′-di-*tert*-butyl-4-cyanostilbene (3.8 g, 12 mmol) in ether (20 mL) were successively added. The resulting greenish mixture was heated for 2 h. After being cooled to room temperature, the suspension was poured on ice; ethanol (200 mL) and concentrated HCl (200 mL) were added. The mixture was stirred for 5 h at room temperature. The product was isolated by extracting with ether (three times). The organic layers were successively washed with a Na_2CO_3 solution and with water and dried with sodium sulfate. After chromatography (silica gel, $CHCl_3$, $R_f \cong 0.5$) and recrystallization (methanol), the yellow product was isolated. Yield: 2 g (5 mmol, 42%). Mp: 124.5 °C. IR (KBr): ν = 2950–2860 (–C–H), 1642 (C=O), 1592 (C=C), 1393, 1362 (CH_3), 1313, 1278, 1249, 960, 937, 920, 868, 792, 744, 705, 697, 662 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81, 7.61 (2 d, ^{3}J = 8.5 Hz, 4 H, H-10,11,13,14), 7.79 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 2 H, H-17,21), 7.58 (tt, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 1 H, H-19), 7.48 (tt, ^{3}J = 7.5 Hz, 1 H, H-18,20), 7.38 (s, 3 H, H-2,4,6), 7.27, 7.13 (2 d, ^{3}J = 16.5 Hz, 2 H, H-7,8), 1.38 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.1 (C-15), 151.3 (C-3,5), 141.9, 138.0, 136.2, 136.1 (C-1,9,12,16), 132.7, 132.2, 126.9 (C-7,8,19), 130.7, 129.9, 128.3, 126.2, (C-10,11,13,14,17,18,20,21), 122.8 (C-4), 121.2 (C-2,6), 34.9, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 396.2 (100, M^+), 381.3 (33.2, $M^+ - CH_3$), 105.1 (61.4, C_7H_5O), 77.2 (17.4, C_6H_5), 57.2 (60.6, *t*-Bu).

3′,5′-(Di-*tert*-butylstilbenyl)phenylmethanol (19). A solution of **18** (12.8 g, 32 mmol) in diethyl ether (100 mL) was added dropwise to a suspension of lithium aluminum hydride (340 mg, 9 mmol) in ether (50 mL). The reaction mixture was heated for 2 h. The excess of $LiAlH_4$ was destroyed by adding water until the evolution of hydrogen had stopped. Upon addition of 4 N sulfuric acid, a white precipitate was formed. The organic layer was separated, washed with a saturated solution of sodium chloride (three times), and dried with sodium sulfate. Evaporation of the solvent and recrystallization from hexane yielded the white product **19**. Yield: 11.8 g (29.4 mmol, 91%). Mp: 141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8 Hz, 2 H, H-10,14), 7.3–7.4 (m, 9 H, H-2,4,6,12,13,17,18,20,21), 7.25 (tt, ^{3}J = 7 Hz, ^{4}J = 1.5 Hz, 1 H, H-19), 7.11, 7.04 (2 d, ^{3}J = 16.2 Hz, 2 H, H-7,8), 5.85 (s, 1 H, H-15), 2.22 (s, 1 H, OH), 1.38 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.1 (C-3,5), 143.9, 143.1 (C-12,16), 137.2, 136.6, (C-1,9), 130.2 (C-7), 127.7, 127.6 (C-8,19), 128.5, 127.0, 126.7, 126.6 (C-10,11,13,14,17,18,20,21), 122.2 (C-4), 120.9 (C-2,6), 76.1 (C-15), 34.9, 31.6 (*t*-Bu). MS (70 eV), *m/z* (%): 398.2 (90.9, M^+), 383.1 (16.0, $M^+ - CH_3$), 105.1 (30.7, C_7H_5O), 57.1 (100, *t*-Bu).

1-(3′,5′-Di-*tert*-butylstilbenyl)-1-methoxy-1-phenylmethane (7). A suspension of the alcohol **19** (2.6 g, 6.5 mmol) and of an excess of sodium hydride (750 mg, 30 mmol) in tetrahydrofuran (THF) (130 mL) was stirred for 1 h. Tetrabutylammonium bromide (170 mg, 0.55 mmol) and, after 3 h, an excess of dimethyl sulfate (2.5 mL) were added. After the mixture had been stirred for 2 days at room temperature, the remaining dimethyl sulfate was destroyed with an ammonia solution. The organic layer was separated and dried with sodium sulfate. Purification by column chromatography on silica gel with chloroform/tetrachloromethane (1:1) as eluent yielded the white ether **7**. Mp: 84 °C. UV ($CHCl_3$): λ (log ε) 302, 315, 328 (sh) nm (4.52, 4.52, 4.31). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.8 Hz, 2 H, H-10,14), 7.2–7.4 (m, 10 H, aromatic H), 7.18, 7.08 (2 d, ^{3}J = 16.1 Hz, 2 H, H-7,8), 5.30 (s, 1 H, H-15), 3.47 (s, 3 H, OCH_3), 1.40 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.1 (C-3,5), 142.1, 141.4 (C-12,16), 137.0, 136.6 (C-1,9), 129.9 (C-7), 127.7, 127.5 (C-8,19), 128.4, 127.3, 127.0, 126.5 (C-10,11,13,14,17,18,20,21), 122.1 (C-4), 120.9 (C-2,6), 85.3 (C-15), 57.0 (OCH_3), 34.9, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 412.2 (100, M^+), 397.2 (6.7, $M^+ - CH_3$), 381.2 (59.0, $M^+ - OCH_3$), 335.1 (10.9, $M^+ - C_6H_5$), 121.1 (14.5, C_8H_9O), 105.1 (18.5, C_7H_5O), 91.1 (12.9, C_7H_7), 77.1 (8.5, C_6H_5), 57.1 (65.6, *t*-Bu).

4,4′-Bis(3,5-di-*tert*-butylstyryl)-α,α′-diphenylstilbene (5). A three-necked flask equipped with a magnetic stirrer, dropping funnel, condenser, and a gas inlet tube was cooled in an ice bath. Under argon, titanium(IV) chloride (0.65 g, 0.37 mL, 3.4 mmol), zinc powder in small portions (0.46 g), pyridine (0.5 mL), and a solution of 3′,5′-di-*tert*-butylstilbenyl phenyl ketone (**18**) (1.27 g, 3.2 mmol) in THF (50 mL) were successively added. The reaction mixture was heated for 16 h at 65 °C. After the mixture had been cooled to room temperature, a K_2CO_3 solution (150 mL) was added. The aqueous layer was separated and extracted three times with ether. The organic fractions were washed twice with water and dried over sodium sulfate. Purification by column chromatography on silica gel with tetrachloromethane as eluent and subsequent recrystallization with methanol yielded the greenish olefin **5**. Yield: 100 mg (0.13 mmol, 8%). Mp: 264 °C. UV ($CHCl_3$): λ (log ε) 322, 359 (sh) nm (4.68, 4.56). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.9–7.4 (m, 28 H), 1.36 (s, 36 H, *t*-Bu). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.1 (C-3,5), 143.9, 143.1 (C-12,16), 140.9 (C-15), 136.7, 135.8 (C-1,9), 131.8, 131.6, 127.9, 125.8 (C-10,11,13,14,17,18,20,21), 129.6 (C-7), 127.9, 126.6 (C-8,19), 122.1 (C-4), 120.9 (C-2,6), 34.9, 31.6 (*t*-Bu). MS (70 eV), *m/z* (%): 760.5 (61.0, M^+), 57.1 (100, *t*-Bu).

Quenching Studies. The sealed NMR tubes were opened under argon, and a few drops of the electrophilic reagent (methanol or dimethyl sulfate) was added to the polyanion solution. The color of the solution disappeared immediately. The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel (Merck Kieselgel 60, 70–230 mesh ASTM) with chloroform as eluent.

1-(3,5-Di-*tert*-butylphenyl)-2-(3′,5′-di-*tert*-butylstilbenyl)ethane (20) was obtained by the reaction of **2a**$^{2-}$/2M^+ (M = Li, K) with methanol. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.48, 7.22 (2 d, ^{3}J = 8.2 Hz, 4 H, H-10,11,13,14), 7.36 (m, 3 H, H-2,4,6), 7.30 (t, ^{4}J = 1.7 Hz, 1 H, H-20), 7.12 (s, 2 H, H-7,8), 7.05 (d, ^{4}J = 1.7 Hz, 2 H, H-18,22), 2.97 (s, 4 H, H-15,16), 1.38, 1.34 (2 s, 36 H, *t*-Bu). ^{13}C NMR (200 MHz, $CDCl_3$): δ 151.0, 150.7 (C-3,5,19,21), 141.5, 140.8 (C-17,12), 136.7, 135.5 (C-1,9), 129.1, 128.0 (C-7,8), 128.8, 126.4 (C-10,11,13,14), 122.7 (C-18,22), 121.9 (C-4), 120.8 (C-2,6), 119.9 (C-20), 38.4, 38.0 (C-15,16), 34.9, 34.8, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 508 (45.1, M^+), 305 (100, $C_{23}H_{29}$), 203 (46.3, $C_{15}H_{23}$), 57.1 (88.3, *t*-Bu).

2-(3,5-Di-*tert*-butylphenyl)-3-(3′,5′-di-*tert*-butylstilbenyl)butane (21) was obtained by the reaction of **2a**$^{2-}$/2M^+ (M = Li, K) with dimethyl sulfate. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.48 (d, ^{3}J = 8 Hz, 2 H, H-10,14), 7.4–7.0 (m, 8 H), 6.91 (d, ^{3}J = 14.8 Hz, 1 H, olefinic H), 6.78 (d, ^{4}J = 1.8 Hz, 2 H, H-18,22), 2.81–2.95 (m, 2 H, H-15,16), 1.38, 1.34 (2 s, 36 H, *t*-Bu), 1.3–1.4 (m, 3 H, Me), 1.09 (d, ^{3}J = 6.3 Hz), 1.05 (d, ^{3}J = 6.2 Hz) (3 H, Me). ^{13}C NMR (200 MHz, $CDCl_3$): δ 151.1, 151.0, 150.3, 149.7 (C-3,5,19,21), 146.1, 145.4, 144.9, 144.2 (C-12,17), 136.8, 135.5, 135.1 (C-1,9), 129.0, 128.7, 128.1, 128.0 (C-7,8), 128.2, 128.0, 126.3, 125.8 (C-10,11,13,14), 122.3, 121.9 (C-18,22), 121.9, 121.8 (C-4), 120.8, 120.7 (C-2,6), 119.8, 119.4 (C-20), 47.5, 47.2, 47.0, 46.8 (C-15,16), 34.83, 34.77, 34.65, 31.6, 31.5 (*t*-Bu), 20.5, 20.4, 18.2, 18.1 (Me). MS (70 eV), *m/z* (%): 536 (6.9, M^+), 319 (100, $C_{24}H_{31}$), 217 (10.3, $C_{16}H_{25}$), 57 (53.0, *t*-Bu).

2b(CH_3)$_4$ was obtained by the reaction of **2b**$^{4-}$/4M^+ (M = Li, K) with dimethyl sulfate. MS (70 eV), *m/z* (%): 668 (1.4, **2b**(CH_3)$_4$), 481 (4.3, $C_{36}H_{49}$), 451 (14.9, $C_{34}H_{43}$), 421 (3.2, $C_{32}H_{37}$), 349 (35.6, $C_{26}H_{37}$), 319 (76.5, $C_{24}H_{31}$), 234 (7.6, $C_{18}H_{18}$), 217 (100, $C_{16}H_{25}$), 132 (21.9, $C_{10}H_{12}$), 57 (69.6, *t*-Bu).

2c(CH_3)$_6$ was obtained by the reaction of **2c**$^{6-}$/6K^+ with dimethyl sulfate. FD-MS (20–25 mA), *m/z* (%): 832 (54.6, **2c**(CH_3)$_8$), 802 (100, **2c**(CH_3)$_6$), 772 (96.3, **20**(CH_3)$_4$).

2d(CH_3)$_6$ was obtained by the reaction of **2d**$^{6-}$/6K^+ with dimethyl sulfate. FD-MS (20–25 mA), *m/z* (%): 933 (83.4, **2d**(CH_3)$_8$), 903 (75.1, **2d**(CH_3)$_6$, 873 (100, **2d**(CH_3)$_4$).

4,4′-Bis[2-(3,5-di-*tert*-butylphenyl)ethyl]biphenyl (22) was obtained by the reaction of **3**$^{4-}$/4M^+ (M = Li, K) with methanol. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.50 (d, ^{3}J = 8.1 Hz, 4 H, H-11,13), 7.23–7.28 (m, 6 H, H-4,10,14), 7.03 (d, ^{4}J = 1.7 Hz, 2 H, H-2,6), 2.95 (s, 8 H, H-7,8), 1.31 (s, 36 H, *t*-Bu). ^{13}C NMR (50 MHz, CDCl$_3$): δ 150.6 (C-3,5), 140.9, 140.7, 138.8 (C-1,9,12), 128.9, 126.9 (C-10,11,13,14), 122.7 (C-2,6), 119.8 (C-4), 38.4, 37.8 (C-7,8), 34.8, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 586 (50.1, M$^+$), 383 (100, $C_{29}H_{35}$), 203 (23.3, $C_{15}H_{23}$), 180 (18.1, $C_{14}H_{12}$), 57 (33.4, *t*-Bu).

4,4′-Bis[2-(3,5-di-*tert*-butylphenyl)-1,2-dimethylethyl]biphenyl (23) was obtained by the reaction of $\mathbf{3}^{4-}/4M^+$ (M = Li, K) with dimethyl sulfate. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.84–7.62 (m, 12 H, aromatic H), 6.78, 6.76 (2 d, ^4J = 1.8 Hz, 2 H, H-2,6), 2.8–3.0 (m, 4 H, H-7,8), 1.32, 1.31, 1.22, 1.21 (4 s, 36 H, *t*-Bu), 0.8–1.4 (m, 12 H, Me). ^{13}C NMR (50 MHz, CDCl$_3$): δ 150.3, 149.7 (C-3,5), 145.4, 145.2, 144.91, 144.86, 144.7, 144.5, 144.2 (2 C) (C-1,9), 139.0, 138.9, 138.7, 138.6 (C-12), 128.3, 128.2, 128.1, 128.0, 126.71, 126.68, 126.2 (2 C) (C-10,11,13,14), 122.4, 122.0 (C-2,6), 119.8, 119.4, 119.3 (C-4), 47.5, 47.2, 46.9, 46.83, 46.79 (C-7,8), 34.8, 34.7, 31.6, 31.5 (*t*-Bu), 20.4, 20.3, 18.3, 18.2 (Me). MS (70 eV), *m/z* (%): 642 (12.8, M$^+$), 425 (100, $C_{32}H_{41}$), 217 (59.1, $C_{16}H_{25}$), 208 (51.7, $C_{16}H_{16}$), 57.1 (62.4, *t*-Bu).

$\mathbf{4}(CH_3)_4$ was obtained by the reaction of $\mathbf{4}^{4-}/4M^+$ (M = Li, K) with dimethyl sulfate. MS (70 eV), *m/z* (%): 696 (4.6, $\mathbf{10}(CH_3)_4$), 217.1 (78.6, $C_{16}H_{25}$), 57.1 (100, *t*-Bu).

1-(3,5-Di-*tert*-butylphenyl)-2-phenylethane (24) was obtained by the reaction of $\mathbf{9}^{2-}/2M^+$ (M = Li, K) with methanol. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.18–7.28 (m, 6 H, H-4,10,11,12,13,14), 7.02 (d, ^4J = 1.7 Hz, 2 H, H-2,6), 2.91 (s, 4 H, H-7,8), 1.31 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, CDCl$_3$): δ 150.6 (C-3,5), 142.1, 140.8 (C-1,9), 128.5, 128.3 (C-10,11,13,14), 125.8 (C-12), 122.7 (C-2,6), 119.9 (C-4), 38.6, 38.3 (C-7,8), 34.8, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 294 (100, M$^+$), 280 (34.8, M$^+$ − CH$_3$), 203 (96.9, $C_{15}H_{23}$), 57.1 (*t*-Bu).

2-(3,5-Di-*tert*-butylphenyl)-3-phenylbutane (25) was obtained by the reaction of $\mathbf{9}^{2-}/2M^+$ (M = Li, K) with dimethyl sulfate. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.89–7.36 (m, 7 H, aromatic H), 6.75 (d, ^4J = 1.8 Hz, 2 H, H-2,6 (one diastereomer)), 2.78–2.93 (m, 2 H, H-7,8), 1.31, 1.22 (2 s, 18 H, *t*-Bu), 1.30, 1.04 (2 m, 6 H, Me). ^{13}C NMR (50 MHz, CDCl$_3$): δ 150.2, 149.6 (C-3,5), 146.7, 145.8, 145.0, 144.2 (C-1,9), 128.1, 128.0, 127.8, 127.6 (C-10,11,13,14), 125.9, 125.5 (C-12), 122.3, 121.9 (C-2,6), 119.8, 119.4 (C-4), 47.6, 47.2, 47.1, 47.0 (C-7,8), 34.8, 34.6, 31.6, 31.4 (*t*-Bu), 20.53, 20.50, 18.2, 18.0 (Me). MS (70 eV), *m/z* (%): 322 (2.5, M$^+$), 217 (100, $C_{16}H_{25}$), 105 (7.0, C_8H_9), 57 (51.1, *t*-Bu).

1-(3,5-Di-*tert*-butylphenyl)-2-(2,5-dimethylphenyl)ethane (26) was obtained by the reaction of $\mathbf{10}^{2-}/2M^+$ (M = Li, K) with methanol. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.28 (t, ^4J = 1.7 Hz, 1 H, H-4), 7.03 (d, ^4J = 1.7 Hz, 2 H, H-2,6), 6.9–7.1 (m, 3 H, H-11,12,13), 2.85 (s, 4 H, H-7,8), 2.30, 2.24 (2 s, 6 H, Me), 1.32 (s, 18 H, *t*-Bu). ^{13}C NMR (50 MHz, CDCl$_3$): δ 150.6 (C-3,5), 141.1, 140.0 (C-1,9), 135.2, 132.8 (C-10,13), 130.0, 129.7, 126.6 (C-11,12,14), 122.6 (C-2,6), 119.9 (C-4), 37.5, 35.6 (C-7,8), 34.8, 31.5 (*t*-Bu), 21.0, 18.7 (Me). MS (70 eV), *m/z* (%): 322 (33.0, M$^+$), 307 (13.6, M$^+$ − CH$_3$), 203 (100, $C_{15}H_{23}$), 119.1 (25.6, C_9H_{11}), 57 (37.1, *t*-Bu).

2-(3,5-Di-*tert*-butylphenyl)-3-(2,5-dimethylphenyl)butane (27) was obtained by the reaction of $\mathbf{10}^{2-}/2M^+$ (M = Li, K) with dimethyl sulfate. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.7–7.2 (m, 6 H, aromatic H), 2.8–3.2 (m, 2 H, H-7,8), 2.30, 2.27, 1.92 (3 s, 6 H, Me), 1.32, 1.20 (2 s, 18 H, *t*-Bu), 1.25–1.47 (m, 3 H), 1.08, 0.95 (2 d, ^3J = 6.8 Hz, Me). ^{13}C NMR (50 MHz, CDCl$_3$): δ 150.2, 149.6 (C-3,5), 145.0, 144.7 (C-1,9), 135.2, 134.6, 132.6, 132.2 (C-10,13), 130.0, 129.7, 127.3, 126.8, 126.1, 125.9 (C-11,12,14), 122.0, 121.9 (C-2,6), 119.8, 119.3 (C-4), 47.3, 46.1, 41.8, 41.2 (C-7,8), 34.8, 34.6, 31.6, 31.4 (*t*-Bu), 21.2, 21.1, 20.14, 20.10, 19.4, 18.9, 18.5, 17.8 (Me). MS (70 eV), *m/z* (%): 350 (4.3, M$^+$), 217 (100, $C_{16}H_{25}$), 133 (56.4, $C_{10}H_{13}$), 57 (76.2, *t*-Bu).

4′-Benzyl-3,5-di-*tert*-butylstilbene (29) was obtained by the reaction of $\mathbf{8}^{-}/M^+$ (M = Li, K) with methanol. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.45 (d, ^3J = 8.2 Hz, 2 H, H-10,14), 7.34 (s, 3 H, H-2,4,6), 7.10–7.30 (m, 7 H, H-7,8,11,13,18,19,20), 7.08 (d, ^4J = 1.5 Hz, 2 H, H-17,21), 3.98 (s, 2 H, H-15), 1.35 (s, 18 H, *t*-Bu). ^{13}C NMR (100 MHz, CDCl$_3$): δ 151.0 (C-3,5), 141.0, 140.4 (C-12,16), 136.7, 135.7 (C-1,9), 129.4, 127.8 (C-7,8), 129.3, 129.0, 128.5, 126.6 (C-10,11,13,14,17,18,20,21), 126.1 (C-19), 122.0 (C-4), 120.8 (C-2,6), 41.7 (C-15), 34.9, 31.5 (*t*-Bu). MS (70 eV), *m/z* (%): 382 (100, M$^+$), 367 (34.4, M$^+$ − CH$_3$), 203 (55.9, $C_{15}H_{23}$), 91 (58.6, C_7H_7), 57 (95.4, *t*-Bu).

$\mathbf{8}(CH_3)$ was obtained by the reaction of $\mathbf{8}^{-}/M^+$ (M = Li, K) with dimethyl sulfate. MS (70 eV), *m/z* (%): 396 (16.7, $\mathbf{8}(CH_3)$), 381 (5.8, **8**), 57 (100, *t*-Bu).

1-(3,5-Di-*tert*-butylphenyl)-2-(4-benzylphenyl)ethane (30) was obtained by the reaction of $\mathbf{8}^{3-}/3Li^+$ with methanol. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.35–7.15 (m, 6 H, H-4,17–21), 7.12 (s, 4 H, H-10,11,13,14), 7.01 (d, ^4J = 1.8 Hz, 2 H, H-2,6), 3.96 (s, 2 H, H-15), 2.89 (s, 4 H, H-7,8), 1.31 (s, 18 H, *t*-Bu). ^{13}C NMR (100 MHz, CDCl$_3$): δ 150.6 (C-3,5), 141.4, 140.9, 139.8, 138.6, (C-1,9,12,16), 129.0, 128.9, 128.7, 128.5 (C-10,11,13,14,17,18,20,21), 126.0 (C-19), 122.7 (C-2,6), 119.9 (C-4), 41.7 (C-15), 38.6, 37.8 (C-7,8), 34.8, 31.6 (*t*-Bu). MS (70 eV), *m/z* (%): 384 (31.7, M$^+$), 369 (21.8, M$^+$ − CH$_3$), 203 (100, $C_{15}H_{23}$), 91 (23.3, C_7H_7), 57 (58.9, *t*-Bu).

$\mathbf{8}(CH_3)_3$ was obtained by the reaction of $\mathbf{8}^{3-}/3Li^+$ with dimethyl sulfate. MS (70 eV): *m/z* (%): 426 (1.0, M$^+$), 217 (9.6, $C_{16}H_{25}$), 105 (49.7, C_8H_9), 91 (100, C_7H_7), 57 (9.6, *t*-Bu).

$\mathbf{5}(CH_3)_2$ was obtained by the reaction of $\mathbf{5}^{2-}/K^+$ with dimethyl sulfate. FD-MS (20–25 mA), *m/z* (%): 791 (100, $\mathbf{5}(CH_3)_2$), 761 (17.6, **5**).

1,2-Bis[4-[2-(3,5-di-*tert*-butylphenyl)ethyl]phenyl]-1,2-diphenylethane (28) was obtained by the reaction of $\mathbf{5}^{6-}/6Li^+$ with methanol. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.9–7.4 (m, 24 H, aromatic H), 4.74 (s, 2 H, H-15), 2.77 (m, 4 H, H-7,8), 1.27 (s, 36 H, *t*-Bu). ^{13}C NMR (100 MHz, CDCl$_3$). δ 150.6 (C-3,5), 144.0, 141.00, 140.95, 139.4 (C-1,9,12,16), 128.6, 128.4, 128.3, 128.2, 128.1, 128.0 (C-10,11,13,14,17,18,20,21), 125.7 (C-19), 122.6 (C-2,6), 119.8 (C-4), 56.0 (C-15), 38.1, 37.7, 37.6 (C-7,8), 34.7, 31.5 (*t*-Bu).

$\mathbf{5}(CH_3)_6$ was obtained by the reaction of $\mathbf{5}^{6-}/6Li^+$ with dimethyl sulfate. FD-MS (20–25 mA), *m/z* (%): 851 (53.2, $\mathbf{5}(CH_3)_6$), 837 (32.0, $\mathbf{5}(CH_3)_5H$), 821 (100, $\mathbf{5}(CH_3)_4$).

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