Synthesis, Structure, and Fluorescence Properties of 5,17-Distyryl-25,26,27,28-tetrapropoxycalix[4]arenes in the *Cone* Conformation

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The HWE (Horner−Wadsworth−Emmons) reaction performed on the easily obtainable 5,17-diformylcalix[4]arenes (*cone*) with arylmethyl phosphorus ylides yielded 5,17-distyryl-25,26,27,-28-tetrapropoxycalix[4]arenes (*cone*) in high yield and purely in the *E*/*E* configuration. Compounds **2**−**5** were prepared this way containing bromine. Subsequent bromine−lithium exchange and reaction with trimethoxyborane yielded the dihydroxyboryl-substituted 5,17-distyrylcalix[4]arenes **6**−**7a**. The structures of **3**, **5**, and **7a** were determined by X-ray diffraction. The photophysical properties of **2** were established by absorption and fluorescence spectroscopy and compared to the monomeric fluorophore, 3,5-dimethyl-4-propoxy-(*E*)-stilbene (**10**).

Introduction

Calix[4]arenes[1,2] have become an important class of compounds in supramolecular chemistry because the molecular framework makes them attractive in designing artificial receptors for small neutral molecules.[3] Much effort has been put into the derivatization of calix[4]arenes both at the *upper* rim and the *lower* rim to produce calixarenes with special properties.

We are interested in calix[4]arenes which have fluorescent groups attached at the *upper* rim to monitor a host−guest interaction. It is well-known that the geometry around the C−C double bond in stilbenes has a great effect on the fluorescence quantum yield.[4] Attaching styryl moieties at the *upper* rim of a calix[4]arene, one could expect a response in the fluorescence spectrum when a guest molecule is interacting or incorporated into the receptor. Styrylcalixarenes can be prepared by attaching styryl groups to the *upper* rim by Wittig or HWE (Horner−Wadsworth−Emmons) reactions from the easily obtainable formylcalix[4]arenes and the corresponding arylmethyl phosphorus ylides. These ylides can even contain further functionalities that can bind guest molecules or extend the calix[4]arene. We have prepared six 5,17-distyryltetrapropoxycalix[4]arenes, either unsubstituted or with bromine or boronic acid residues.

Only few reports concerning styrylcalixarenes have been published. They were prepared either by standard Wittig reactions[5] or condensation of 4-methylpyridine and tetraformylcalix[4]arene[6] or a Knoevenagel type reaction of a *p*-cyanomethylcalix[4]arene and benzaldehyde.[7]

Results and Discussion

The 5,17-distyryltetrapropoxycalix[4]arenes **2**-**5** were prepared by a HWE reaction from the corresponding 5,-17-diformyltetrapropoxycalix[4]arene (**1**) and diethyl arylmethylphosphonates in dry THF at 5 °C using *t*-BuOK as base (Scheme 1). The yields are good to excellent (73−92%), and the reaction can be carried out on multigram scale without column chromatography and reduction in yield. The reaction gave the *E*/*E* configuration as the only product, which is expected from the chosen conditions, and this is also confirmed by the X-ray structures. A mixture of *E*/*Z* isomers was obtained when the reaction was carried out under Wittig conditions with benzyltriphenylphosphonium bromide as the ylide precursor. TLC showed only one fluorescent spot in different eluents, but the ^{1}H NMR ($CDCl_3$) spectrum was very complicated and clearly indicated that the isolated product was a mixture of different compounds. To verify that it actually was a mixture of *E*/*Z* isomers, *Z* to *E* isomerization to *E*/*E* was carried out by adding a crystal of iodine to the NMR tube followed by heating the solution for a few minutes with a heat gun. The ^{1}H NMR spectrum then became identical to the spectrum obtained by the HWE route.

The boronic acids (**6** and **7**) were synthesized via a Br−Li exchange reaction with *n*-BuLi in dry THF at −78 °C, followed by quenching with $B(OCH_3)_3$. The boronic acid **7** was insoluble in standard NMR solvents, therefore, it was characterized as its 1,3-propanediol ester (**7a**). The

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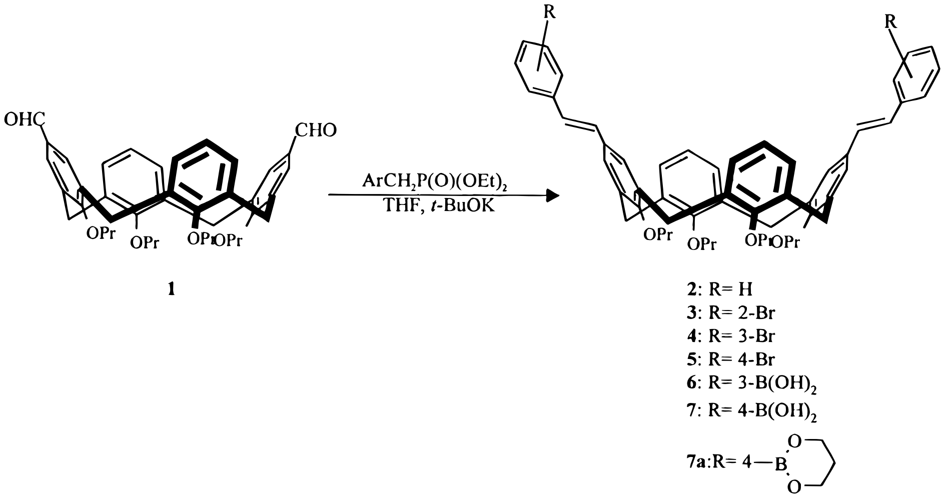
Scheme 1



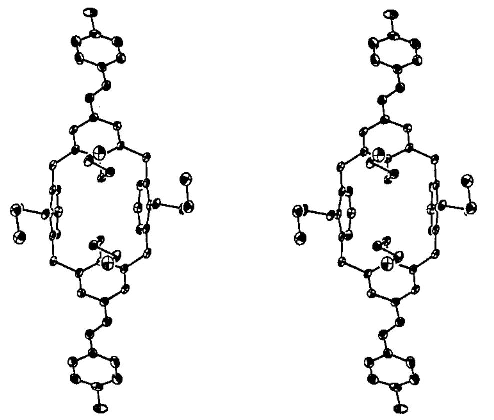


Figure 1. Stereoview of the calixarene moiety of **5** as an ORTEP drawing (methanol molecule and hydrogen atoms omitted). The *E*/*E* conformation is clearly shown.

molecular weight of **6** and **7** is 884.67 g/mol. The MALDI-TOF mass spectra only showed peaks at *m*/*z* 1121, 1143, and 1159.[8]

We prepared **6** and **7** in order to study the complexation of monosaccharides (glucose, fructose, galactose) by means of MALDI-TOF mass spectrometry and fluorescence spectroscopy. The formation of a 1:1 complex is important in order to obtain high selectivity and a high complexation constant. Unfortunately, MALDI-TOF (Sinapinic acid was used as matrix) showed that several monosaccharide/calix[4]arene products with different stoichiometries (2:1, 3:2, 4:3, 5:4 etc) were formed. No 1:1 adduct could be observed under any circumstances. Even when **6** and **7** were in large excess, the 1:1 complex did not form. This is probably due to the rigidity of the styrylcalix[4]arenes in solution. The preferred conformation in solution as well in the solid state is where the stilbene moieties are far apart. This disfavors the formation of a 1:1 complex. The profile of the fluorescence spectra changed dramatically in time when recording the fluorescence spectra. This is attributed to an instability of compounds **6** and **7** in dilute solution (THF/MeOH/water mixture).

X-ray Structure Analysis. The X-ray structures of **3**, **5**, and **7a** shows that the molecular structure in the solid state is the *E*/*E* form for all three compounds (shown for **5** in Figure 1). Two enantiomers exist in the solid state, and they form separate stacks of (*R*) and (*S*) molecules, respectively (head-to-tail). This is a purely solid state phenomenon and arises because the rotation of the styryl unit is not possible in a crystal whereas it occurs readily in solution as observed in the NMR spectra of **3**, **5**, and **7a**. The calix[4]arenes adopt a pinched *cone* conformation where the styryl moieties stick out. The conformation of the calix[4]arene molecules observed in the solid state is similar to the conformation in solution as established by NMR for **3**, **5**, and **7a**. Earlier NMR studies[9] have shown that the aromatic protons of the unsubstituted benzene rings of 5,17-disubstituted calix[4]arenes become more shielded when adopting a pinched cone conformation with these benzene rings being coplanar and the substituents sticking out. The plane of the calix[4]arene benzene rings bearing the styryl units thus forms angles of 53.6° and 56.7° (respectively, for the two different calix[4]arenes in the asymmetric unit) in **3**, 51.1° in **5**, and 51.6° in **7a** with the axis along which the molecules stack (*b*-axis in **5** and **7a**). The planes of the unsubstituted aromatic rings of the calix[4]arene unit are pinched and forms angles of −4.3° and −4.7° in **3**, −5.0° in **5**, and −5.1° in **7a** and are thus all close to parallel with the stacking axis (Figures 2 and 3). These values compares quite well with other values found in the literature[10−13] where values are in the ranges of 45 to 53° and 9.8 to −7.5°, respectively. Interestingly the repeat distance between the calix[4]arene units in the stacks is very similar for all three compounds, 9.1 Å in **3**, 9.3 Å in **5**, and 9.3 Å in **7a**. The bromine atom in **3** inhibits the styryl moieties from being planar due to steric hindrance between the bromine and the vinylic hydrogen. This is reflected in the crystal packing where

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[8] This can be rationalized as the condensation of **6** or **7** and two matrix molecules (2,5-dihydroxybenzoic acid, MW = 154.15 g/mol) and H^+, Na^+, and K^+ peaks, respectively.

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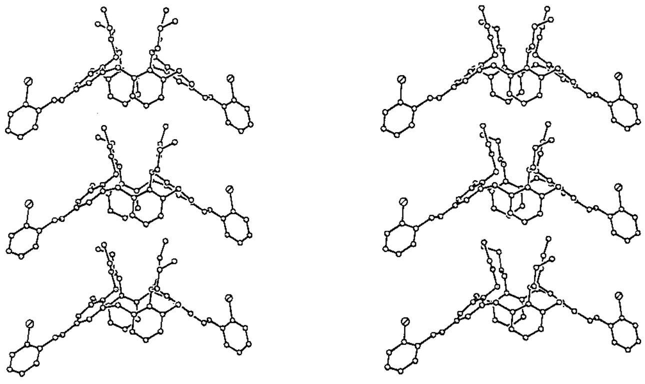


Figure 2. Stereoview of the stacking of the calixarene moiety of **3** with a twisted stilbene unit (hydrogen atoms omitted).

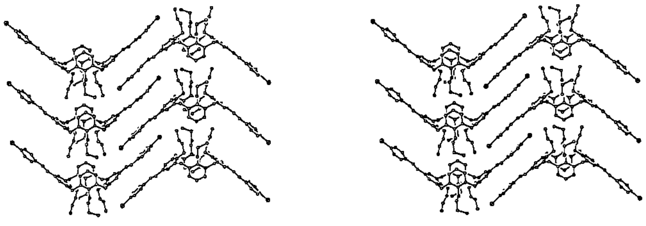


Figure 3. Stereoview of the stacking of **5** (hydrogen atoms omitted). Notice the opposite chirality of the molecules in the two stacks. The stilbene units overlap molecules between.

the calix[4]arenes retain the stacking in essentially the same manner as observed for **5** and **7a** (Figures 2 and 3). However, the interstack arrangement is very different and stacks do not interpenetrate as seen for **5** and **7a** (Figure 3) but instead the styryl units are twisted (Figure 2). This twist can be elaborated further by considering the three torsion angles defining the conformation around the styryl double bond. In compound **3** the torsion angle around the bond linking the calix[4]arene and the ethenylidene bridge have values of 1.1° and 1.2° for one molecule and 25.4° and 26.8° for the other molecule in the asymmetric unit. For **5** and **7a**, values of 0.4° and 2.6° are found, respectively. One part of the asymmetric unit in **3** thus differs significantly from planarity. The torsion angle around the ethenylidene bridge itself is close to 180° as expected for a trans double bond. Finally the torsion angle around the bond linking the ethenylidene bridge with the aromatic substituent has values of 16.8° and 17.2° for one molecule and 33.7° and 34.7° for the other molecule in the asymmetric unit in **3**. For **5** and **7a**, values of 7.1° and 5.2° are found, respectively. Both parts of the asymmetric unit in **3** thus differ significantly from planarity. The comparison of these torsion angles thus distinguishes **3** from **5** and **7a**. The observed conformation of the calix[4]arene units in **5** and **7a** (Figure 3) give rise to a good overlap between the conjugated styryl units in alternate stacks. The molecules in **5** and **7a** have an exact crystallographic 2-fold symmetry. Two methanol molecules are found for each calix[4]arene molecule for **5**, and they fill in the gaps between the stacks of calix[4]arene molecules. In the case of **7a** two methylene chloride molecules are found for each calix[4]arene unit. They also fill in the gaps between the stacks of calix[4]arene molecules.

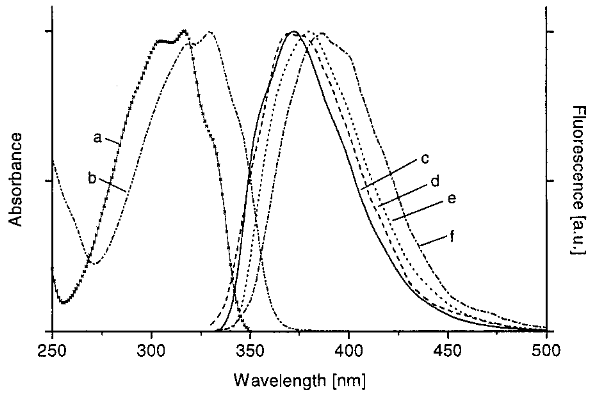
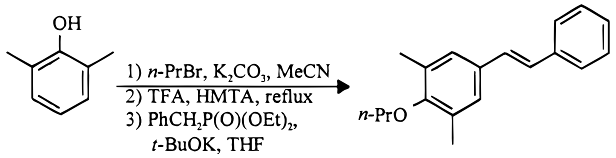


Figure 4. Electronic absorption and fluorescence ($\lambda_{ex} = 300$ nm) spectra of **2** and **10**: (a) absorption of **10** in CH_2Cl_2; (b) absorption of **2** in CH_2Cl_2; (c) fluorescence of **2** in cyclohexane; (d) fluorescence of **10** in CH_2Cl_2; (e) fluorescence of **2** in benzene; (f) fluorescence of **2** in CH_2Cl_2. All spectra are normalized at maximum.

Scheme 2



10

Electronic Absorption and Emission Spectra. Compound **2** displays fluorescence and so does 3,5-dimethyl-4-propoxy-stilbene **10**, which can be considered as the isolated fluorophore of **2**. Compound **10** was prepared by standard reactions (Scheme 2). The absorption and fluorescence spectra of **2** and **10** are shown in Figure 4. The absorption spectrum of **2** in CH_2Cl_2 (trace b, $\lambda_{max} = 330$ nm, $e = 6.2 \times 10^4$ M^{-1} cm^{-1}) is red shifted relative to the absorption of **10** (trace a, $\lambda_{max} = 316$ nm, $\epsilon = 2.9 \times 10^4$ M^{-1} cm^{-1}) in the same solvent. This means that the conjugation in **2** is at least as efficient as that in **10**. The total planarity of the extended π-system in **2** is not distorted by the molecular environment. Instead, the absorption spectra extend the conclusion from the solid state X-ray structure and indicate conformationally relaxed alkoxy stilbene chromophores in the dissolved molecules of both **2** and **10**. The modest bathochromic shift observed in the absorption spectra when going from **10** to **2** is taken as an indication of an excited state being even further polarized than the ground state. Electron density is donated from the nonbonding orbital on the propoxy oxygens into the empty π-orbital of the ring, giving the excited state some CT character. The positive charge on the oxygen of the chromophore is stabilized by the oxygen atoms of the neighboring propoxy groups of the calixarene through a seven-membered transition state.

In analogy, the fluorescence of **2** undergoes a bathochromic shift when the solvent polarity is increased from cyclohexane (trace c, $\lambda_{max}^{FLU} = 372.5$ nm), through benzene (trace e, $\lambda_{max}^{FLU} = 380$ nm) to CH_2Cl_2 (trace f, $\lambda_{max}^{FLU} = 387$ nm), indicating an excited state with a dipole moment larger than and having the same direction as that of the ground state. The monomer **10** fluoresces in CH_2Cl_2 with a maximum (trace d, $\lambda_{max}^{FLU} = 370$ nm) which almost coincides with the calixarene spectrum in cyclohexane (trace c). This means that the fluorophore enjoys the same level of stabilization from the supramolecular environment of the calixarene as the monomer does in CH_2Cl_2. The relative fluorescence quantum yield of **2** was found to be 32% larger than that of **10**. This is considered a marginal effect. If the 4-propoxystilbene units of **2** were suffering from conformational constraint, the *E*/*Z*-isomerization deactivation pathway of the excited singlet state would be hindered in **2** relative to **10**, and a more dramatic increase in fluorescence efficiency would be anticipated.

Experimental Section

Melting points are uncorrected. The mass spectra of compounds **2**-**7** were recorded on a MALDI-TOF MS with 2,5-dihydroxybenzoic acid as matrix. ^{1}H and ^{13}C NMR spectra were recorded on a 250 MHz instrument with TMS as internal reference and at 300 K. All the NMR spectra were taken in $CDCl_3$ unless otherwise stated. All commercially available chemicals were used without further purification. All solvents were reagent grade and used without further purification, except for THF which was freshly distilled from sodium/benzophenone ketyl. Compound **1** was synthesized by the method described previously.[14] The phosphonates were synthesized from the corresponding benzyl bromides and triethyl phosphite (Arbuzov reaction) and distilled under reduced pressure to give satisfactory ^{1}H and ^{13}C NMR spectra. All reactions were carried out in a flame-dried glass apparatus and in an argon atmosphere. The temperatures given are internal temperatures. Chromatographic separations were performed on silica gel 60 (SiO_2, particle size 0.040−0.063 mm, 230−240 mesh). Thin-layer chromatography was carried out on hard TLC plates (SiO_2 60, F-254). Microanalytical samples were dried for at least 4 h at 60 °C/0.1 mmHg.

General Procedure for the Synthesis of 5,17-Bis-(*E*)-styryltetrapropoxycalix[4]arenes (2−5). Compound **1** (3.24 g, 5.0 mmol) and diethyl arylmethylphosphonate (15.0 mmol) were dissolved in dry THF (100 mL) and cooled to 5 °C. A solution of *t*-BuOK (1.68 g, 15.0 mmol) in dry THF (15 mL) was added over 1 min at 5 °C. The yellow mixture was stirred for 45 min at 25 °C, poured into ice cold 1 M hydrochloric acid (200 mL), and extracted with CH_2Cl_2 (3×80 mL). The yellow organic phase was washed with brine (100 mL) and dried (Na_2SO_4), and the solvent was removed on a rotary evaporator to give a light yellow solid. The crude product was purified by being dissolved in a minimum of CH_2Cl_2 and precipitated by slow addition of two volumes of MeOH. The products were obtained as colorless crystals. A mixture of *n*-hexane/$CHCl_3$ (2:1, v/v) was used as TLC eluent.

5,17-Bis((*E*)-2-phenyl-1-ethenyl)-25,26,27,28-tetrapropoxycalix[4]arene (2): yield 73%: mp 260−262 °C; $R_f \approx 0.50$; ^{1}H NMR δ 7.43 (d, 4H, $J = 7.0$ Hz), 7.35−7.15 (m, 6H), 7.01 (d, 2H, $J = 16.3$ Hz), 6.92 (d, 2H, $J = 16.3$ Hz), 6.36 (s, broad, 6H), 4.46 (d, 4H, $J = 13.3$ Hz), 3.98 (t, 4H, $J = 7.9$ Hz), 3.75 (t, 4H, $J = 7.0$ Hz), 3.18 (d, 4H, $J = 13.3$ Hz), 2.05−1.70 (m, 8H), 1.08 (t, 6H, $J = 7.4$ Hz), 0.93 (t, 6H, $J = 7.4$ Hz; ^{13}C NMR δ 157.7, 155.6, 137.8, 136.6, 133.6, 131.1, 129.0, 128.6, 127.7, 127.0, 126.9, 126.8, 126.2, 122.2, 76.9, 76.6, 31.1, 23.4, 23.1, 10.7, 10.0; MS *m*/*z* 797 ($M + H^+$), 818 ($M + Na^+$), 834 ($M + K^+$). Anal. Calcd for $C_{56}H_{60}O_4$: C, 84.38; H, 7.59. Found: C, 84.10; H, 7.67.

5,17-Bis((*E*)-2-(2-bromophenyl)-1-ethenyl)-25,26,27,28-tetrapropoxycalix[4]arene (3): yield 88%: mp 245−246 °C; $R_f \approx 0.59$; ^{1}H NMR δ 7.66−7.40 (m, 4H), 7.18 (d, 2H, $J = 16.1$ Hz), 7.13−6.92 (m, 8H), 6.84 (d, 2H, $J = 16.1$ Hz), 6.48 (s, 6H), 4.47 (d, 4H, $J = 13.3$ Hz), 3.95 (t, 4H, $J = 7.7$ Hz), 3.80 (t, 4H, $J = 7.2$ Hz), 3.20 (d, 4H, $J = 13.3$ Hz), 2.00−1.85 (m, 8H), 1.05 (t, 6H, $J = 7.4$ Hz), 0.96 (t, 6H, $J = 7.4$ Hz); ^{13}C NMR δ 157.7, 155.9, 137.5, 136.2, 134.0, 132.9, 131.6, 130.9, 128.1, 128.0, 127.4, 127.1, 126.4, 125.3, 123.8, 122.2, 76.9, 76.7, 31.1, 23.4, 23.2, 10.6, 10.2; MS *m*/*z* 955 ($M + H^+$), 977 ($M + Na^+$), 993 ($M + K^+$). Anal. Calcd for $C_{56}H_{58}Br_2O_4$: C, 70.44; H, 6.12. Found: C, 70.27; H, 6.00.

5,17-Bis((*E*)-2-(3-bromophenyl)-1-ethenyl)-25,26,27,28-tetrapropoxycalix[4]arene (4): yield 81%: mp 218−220 °C; $R_f \approx 0.58$; ^{1}H NMR δ 7.50−7.45 (s, broad, 2H), 7.27−7.20 (m, 4H), 7.06 (t, 2H, $J = 7.8$ Hz), 6.94 (s, 4H), 6.86 (d, 2H, $J = 16.3$ Hz), 6.70 (d, 2H, $J = 16.3$ Hz), 6.50 (s, 6H), 4.46 (d, 4H, $J = 13.3$ Hz), 3.93 (t, 4H, $J = 7.6$ Hz), 3.81 (t, 4H, $J = 7.2$ Hz), 3.17 (d, 4H, $J = 13.3$ Hz), 2.00−1.85 (m, 8H), 1.04 (t, 6H, $J = 7.4$ Hz), 0.97 (t, 6H, $J = 7.4$ Hz); ^{13}C NMR δ 157.6, 156.0, 139.9, 136.1, 134.1, 130.6, 130.3, 130.0, 129.7, 128.9, 128.0, 126.8, 124.9, 124.6, 122.8, 122.2, 76.8, 76.7, 31.1, 23.3, 23.2, 10.5, 10.2; MS *m*/*z* 955 ($M + H^+$), 977 ($M + Na^+$), 993 ($M + K^+$). Anal. Calcd for $C_{56}H_{58}Br_2O_4$: C, 70.44; H, 6.12. Found: C, 70.14; H, 6.29.

5,17-Bis((*E*)-2-(4-bromophenyl)-1-ethenyl)-25,26,27,28-tetrapropoxycalix[4]arene (5): yield 92%; mp 243−245 °C; $R_f \approx 0.50$; ^{1}H NMR δ 7.34 (d, 4H, $J = 8.4$ Hz), 7.19 (d, 4H, $J = 8.4$ Hz), 6.92 (s, 4H), 6.84 (d, 2H, $J = 16.3$ Hz), 6.72 (d, 2H, $J = 16.3$ Hz), 6.53 (s, 6H), 4.47 (d, 4H, $J = 13.4$ Hz), 3.93 (t, 4H, $J = 7.6$ Hz), 3.83 (t, 4H, $J = 7.3$ Hz), 3.18 (d, 4H, $J = 13.4$ Hz), 2.05−1.80 (m, 8H), 1.05 (t, 6H, $J = 7.4$ Hz), 0.98 (t, 6H, $J = 7.5$ Hz); ^{13}C NMR δ 157.4, 156.1, 136.6, 136.0, 134.2, 131.6, 130.8, 129.6, 128.0, 127.6, 126.7, 125.3, 122.1, 120.6, 76.8, 76.7, 31.0, 23.3, 23.2, 10.5, 10.2; MS *m*/*z* 955 ($M + H^+$), 977 ($M + Na^+$), 993 ($M + K^+$). Anal. Calcd for $C_{56}H_{58}Br_2O_4$: C, 70.44; H, 6.12. Found: C, 70.69; H, 6.24.

General Procedure for the Synthesis of Dihydroxyboryl-Substituted 5,17-Bis-(*E*)-styryltetrapropoxycalix[4]arenes (6−7). To a stirred solution of **4** or **5** (0.50 g, 0.524 mmol) in dry THF (40 mL) at −78 °C was added 1.45 M *n*-BuLi (0.72 mL, 1.05 mmol). The yellow solution was stirred at −78 °C for 10 min. Trimethoxyborane (0.35 mL, 3 mmol) was added, and the mixture was stirred for 30 min at −78 °C, poured into water (300 mL), and acidified with 1 M hydrochloric acid until pH $\gg$ 4. The THF was evaporated on a rotary evaporator. The crude boronic acid was filtered off, washed water (200 mL) and MeOH (30 mL), and dried at 40 °C for 24 h. No resonance from the C atom which is attached to boron was observed in the ^{13}C NMR spectra due to line broadening.

5,17-Bis((*E*)-2-(3-dihydroxyborylphenyl)-1-ethenyl)-25,26,27,28-tetrapropoxycalix[4]arene (6). Compound **6** was isolated as a colorless powder in 49% yield: mp > 280 °C (dec); $R_f \approx 0.20$ (*n*-hexane/EtOAc (1:2, v/v)); ^{1}H NMR (acetone-d_6) δ 8.10 (s, 2H), 7.76 (d, 2H, $J = 7.2$ Hz), 7.60 (d, 2H, $J = 7.8$ Hz), 7.37−7.25 (m, 6H), 7.20 (d, 2H, $J = 16.3$ Hz), 7.19 (s, 4H), 7.12 (d, 2H, $J = 16.3$ Hz), 6.42−6.29 (m, 6H), 4.53 (d, 4H, $J = 13.2$ Hz), 4.09 (t, 4H, $J = 7.8$ Hz), 3.79 (t, 4H, $J = 6.8$ Hz), 3.26 (d, 4H, $J = 13.2$ Hz), 2.12−1.85 (m, 8H), 1.15 (t, 6H, $J = 7.4$ Hz), 1.00 (t, 6H, $J = 7.4$ Hz); ^{13}C NMR (acetone-d_6) δ 158.0, 155.1, 137.4, 137.0, 133.7, 133.3, 132.5, 131.9, 129.0, 128.5, 128.2, 128.1, 127.4, 127.3, 122.4, 77.2, 76.9, 31.1, 23.7, 23.4, 10.6, 9.9; MS *m*/*z* 1121 ($M + H^+$), 1143 ($M + Na^+$), 1159 ($M + K^+$). Anal. Calcd for $C_{56}H_{62}B_2O_8$: C, 76.02; H, 7.06. Found: C, 76.23; H, 7.16.

5,17-Bis((*E*)-2-(4-(1,3,2-dioxaborinane-2-yl)phenyl)-1-ethenyl)-25,26,27,28-tetrapropoxycalix[4]arene (7a). The yield of the boronic acid **7** was almost quantitative. The crude product was suspended in toluene (50 mL), 1,3-propanediol (2.2 equiv) was added and water was distilled off. The toluene phase was washed with water (2×20 mL), dried (Na_2SO_4), and evaporated to dryness. Recrystallization from *n*-heptane/CH_2Cl_2 (4:1, v/v) gave **7a** as colorless crystals (flakes) in 78% yield: mp 242−245 °C (dec); ^{1}H NMR δ 7.73 (d, 4H, $J = 8.0$ Hz), 7.46 (d, 4H, $J = 8.0$ Hz), 7.21 (s, 4H), 7.13 (d, 2H, $J = 16.3$ Hz), 7.00 (d, 2H, $J = 16.3$ Hz), 6.35−6.18 (m, 6H), 4.46 (d, 4H, $J = 13.3$ Hz), 4.16 (t, 8H, $J = 5.3$ Hz), 4.02 (t, 4H, $J = 7.9$ Hz), 3.71 (t, 4H, $J = 6.8$ Hz), 3.18 (d, 4H, $J = 13.3$ Hz), 2.13−1.80 (m, 12H), 1.09 (t, 6H, $J = 7.4$ Hz), 0.91 (t, 6H, $J = 7.4$ Hz); ^{13}C NMR δ 158.0, 155.3, 139.9, 137.0, 134.0, 133.1, 131.0, 129.5, 127.6, 127.2, 127.0, 125.5, 122.2, 76.9, 76.5, 61.9, 31.1, 27.5, 23.5, 23.1, 10.8, 9.9; MS *m*/*z* 1121 ($M + H^+$), 1143 ($M + Na^+$), 1159 ($M + K^+$). Anal. Calcd for $C_{62}H_{70}B_2O_8$: C, 77.18; H, 7.31. Found: C, 77.40; H, 7.54.

2,6-Dimethyl-1-propoxybenzene (8). 2,6-Xylenol (61 g, 0.5 mol), K_2CO_3 (dry, 69 g, 0.50 mol), and *n*-propyl bromide (55 mL, 0.55 mol) were stirred in dry MeCN (400 mL) for 18 h at 50 °C. The mixture was filtered, and the filtercake was

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(14) Larsen, M.; Jørgensen, M. *J. Org. Chem.* **1996**, *61*, 6651.

Table 1. Crystallographic Data for the 5,17-Distyryltetrapropoxycalix[4]arenes

compound	**3**	**5**	**7a**
formula	$C_{56}H_{58}O_4Br_2$	$C_{56}H_{60}O_4Br_2 \cdot 2CH_3OH$	$C_{62}H_{70}O_8B_2 \cdot 2CH_2Cl_2$
formula wt	954.84	1018.93	1134.65
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2/c$	$C2/c$
Z	4	2	4
a, Å	9.1290(18)	14.516(3)	36.794(7)
b, Å	18.759(4)	9.307(2)	9.303(2)
c, Å	28.179(6)	18.285(4)	17.937(4)
α, deg	104.02(3)	90	90
β, deg	90.01(3)	92.89(3)	110.42(3)
γ, deg	90.02(3)	90	90
V, Å^3	4681.9(16)	2467.2(9)	5753.9(20)
ρ, g cm^3	1.355	1.372	1.310
crystal dimensns, mm	0.50 × 0.37 × 0.035	0.33 × 0.28 × 0.28	0.40 × 0.23 × 0.05
type of radiation	Mo-Kα	Mo-Kα	Mo-Kα
μ, cm^{-1}	1.778	1.695	0.262
T, K	120(2)	120(2)	120(2)
no. of reflctns	49300	25594	29743
unique reflctns (with $I > 2\sigma$)	9747	4380	3687
R_{int}	0.1017	0.0271	0.0732
$R(F)$, $R_w(F^2)$ all data	0.0573, 0.1438	0.0513, 0.1577	0.0773, 0.2404

washed with MeCN (100 mL). The solvent was removed in vacuo, and the resulting orange oil was vacuum distilled, bp 60−62 °C/0.3 mmHg, yielding **8** as a clear oil in 82% (67 g) yield: ^{1}H NMR δ 7.00−6.80 (AB$_2$ system, 3H), 3.71 (t, 2H, J = 7.5 Hz), 2.27 (s, 6H), 1.90−1.70 (m, 2H), 1.07 (t, 3H, J = 7.5 Hz); ^{13}C NMR δ 156.0, 130.9, 128.7, 123.5, 73.7, 23.6, 16.2, 10.6; MS m/z 107 (70), 122 (100), 164 (33).

4-Propoxy-3,5-dimethylbenzaldehyde (9). Hexamethylenetetraamine (28.0 g, 0.20 mol) and **8** (16.4 g, 0.10 mol) were refluxed in TFA (150 mL) for 18 h. The dark mixture was poured into crushed ice (500 g) and neutralized with solid Na_2CO_3. The product was isolated by steam distillation and purified by vacuum distillation, bp 114−118 °C/0.5 mmHg, yielding **9** as a slightly yellow oil in 47% yield: ^{1}H NMR δ 9.86 (s, 1H), 7.53 (s, 2H), 3.78 (t, 2H, J = 6.6 Hz), 2.33 (s, 6H), 1.90−1.80 (m, 2H), 1.09 (t, 3H, J = 7.4 Hz); ^{13}C NMR δ 191.2, 161.6, 132.0, 131.9, 130.6, 73.9, 23.6, 16.3, 10.5; MS m/z 149 (100), 192 (20).

3,5-Dimethyl-4-propoxy-(*E*)-stilbene (10). To a solution of **9** (3.00 g, 15.6 mmol) and diethyl benzylphosphonate (4.57 g, 20.0 mmol) in dry THF (100 mL) at 5 °C was added a solution of *t*-BuOK (3.36 g, 30 mmol) in dry THF (20 mL) while keeping the temperature below 5 °C. The yellow mixture was stirred for another 1 h, at 5 °C and the THF was evaporated. The residue was dissolved in CH_2Cl_2 (100 mL), washed with 1 M hydrochloric acid (150 mL), and dried (Na_2SO_4), and the solvent was removed in vacuo. Recrystallization from MeOH gave **10** as colorless flakes in 68% (2.84 g) yield; mp 58−59 °C; ^{1}H NMR δ 7.50−7.43 (m, 2H), 7.36−7.30 (m, 2H), 7.25−7.17 (m, 1H), 7.16 (s, 2H), 6.99 (s, 2H, alkene-H, accidental isochrony), 3.73 (t, 2H, J = 6.6 Hz), 2.29 (s, 6H), 1.90−1.75 (m, 2H), 1.08 (t, 3H, J = 7.4 Hz); ^{13}C NMR δ 155.9, 137.6, 132.6, 131.1, 128.6, 128.4, 127.4, 127.2, 127.0, 126.3, 73.9, 23.6, 16.4, 10.6; MS m/z 165 (34), 224 (100), 266 (45).

Crystallography Methods. Crystals of compound **5** and **7a** lost solvent upon exposure to air. Crystals of **3**, **5**, and **7a** were drawn directly from the mother liquor, coated with a thin layer of oil, mounted on a glass capillary using grease (Apiezon), and transferred quickly to the cold nitrogen stream on the diffractometer. Data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. Absorption corrections were made using SADABS.[15] Direct methods for the structure solution and full-matrix least-squares refinements were used. Hydrogen atoms were included in calculated positions but not refined. Programs used were SMART, SAINT and SHELXTL from Siemens.[16,17] The weighting schemes, $w = 1/[\sigma^2(F_o^2) + 0.0545P^2]$ for **3**, $w = 1/[\sigma^2(F_o^2) + 0.1002P^2 + 8.0115P]$ for **5**, $w = 1/[\sigma^2(F_o^2) + 0.1028P^2 + 34.5050P]$ for **7a**, where $[P = (F_o^2 + 2F_c^2)/3]$ and with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analysis. For compound **7a** carbon-5 in the 1,3,2-dioxaborinane-2-yl moiety was found to be disordered. Further, the methylene chloride solvent molecule was found to be disordered. This was in both instances modeled as two mutually exclusive groups and refined with respect to the sof, which was found to be 0.496 and 0.569, respectively. The structure was checked for overlooked symmetry using MISSYM and for voids in PLATON.[18] Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

Spectroscopic Methods. Absorption spectra were recorded on a UV−vis spectrophotometer using ca. 10^{-5} M solutions in 1 cm cells. Fluorescence spectra were recorded on an LS 50B luminescence spectrometer using solutions (ca. 10^{-6} M) with $A < 0.05$ at the maximum absorbance. In all spectra shown, excitation and emission bandpass were 5 nm. All fluorescence spectra were corrected for any solvent background including Raman scatter. No correction was performed for the wavelength-dependent response function of the detection system. Relative fluorescence quantum yields were estimated from the integrated fluorescence spectra and corrected for the small differences between absorbancies at λ_{ex} = 300 nm of the solutions.

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Supporting Information Available: Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, bond lengths, and bond angles (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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