Synthesis and Characterization of Multinanometer-Sized Expanded Dendralenes with an *iso*-Poly(triacetylene) Backbone

by **Estelle Burri** and **François Diederich***

Laboratorium für Organische Chemie, ETH-Hönggerberg, HCI, CH-8093 Zürich

and

Mogens Brøndsted Nielsen*

Department of Chemistry, University of Southern Denmark, Odense University, Campusvej 55,
DK-5230 Odense M

A series of [*n*]dendralenes (*n* = 3, 4, 8, **3b – d** (*Fig. 1*)) expanded with buta-1,3-diynediyl moieties between the C=C bonds were prepared by repetitive acetylenic scaffolding of 3-(cyclohexylidene)penta-1,4-diyne building blocks (*Scheme*). These remarkably unstable *iso*-poly(triacetylene) (*iso*-PTA) oligomers were characterized by ^{1}H- and ^{13}C−NMR (*Fig. 3* and *Table 1*), IR, and UV/VIS (*Figs. 4* and *6* and *Table 2*) spectroscopy, as well as mass spectrometry (*Fig. 2*). The expanded [8]dendralene contains 40 C(sp)- and C(sp^2)-atoms in the backbone and represents the longest *iso*-PTA oligomer prepared to date. HOMO-LUMO Gap energies were determined as a function of oligomeric length (*Fig. 5* and *Table 3*), providing insight into the degree of π-electron delocalization in these cross-conjugated chromophores. A continous drop in the HOMO-LUMO gap with increasing number of monomeric repeating units provides evidence that cross-conjugation along the oligomeric backbone is effective to some extent. The limiting HOMO-LUMO gap energy for an infinitely long, buta-1,3-diynediyl-expanded dendralene was extrapolated to about 3.3 – 3.5 eV. The conformational preferences of the expanded dendralenes were analyzed in semi-empirical calculations, revealing energetic preferences for planar or slightly twisted s-*cis* and 'U-shaped' geometries.

1. Introduction. – Dendralenes are polyene hydrocarbons in which C=C bonds are aligned in a cross-conjugated arrangement [1a]. This requires the presence of at least three C=C bonds, and the simplest dendralene, therefore, is 3-(methylidene)penta-1,4-diene (a [3]dendralene). Novel synthetic approaches to dendralenes are currently being developed [1d,e], and these chromophores are increasingly investigated for their structural, electronic, and advanced materials properties [1]. Upon insertion of one or more acetylene units between the C=C bonds, series of expanded dendralenes are obtained (*Fig. 1*). *Diederich* and co-workers [2] reported in 1995 the synthesis of the *iso*-poly(triacetylene)s **1a – d** by acetylenic scaffolding starting from appropriate tetraethynylethene (TEE, 3,4-(diethynyl)hex-3-ene-1,5-diyne) precursors. Compounds **1c** and **1d** in this series are the first examples of expanded dendralenes, with buta-1,3-diynediyl bridges inserted between the C=C bonds. More recently, *Tykwinski* and co-workers [3] introduced a new class of expanded dendralenes **2c – i** with the *iso*-poly(diacetylene) backbone, featuring ethynediyl spacers between the C=C bonds (the names *iso*-poly(diacetylene) (*iso*-PDA) and *iso*-poly(triacetylene) (*iso*-PTA) were introduced by *Tykwinski* and co-workers [3b]). In addition to compounds **2a – i**, with peripheral isopropylidene moieties, derivatives with peripheral cyclohexylidene and adamantylidene fragments were also reported [3d].

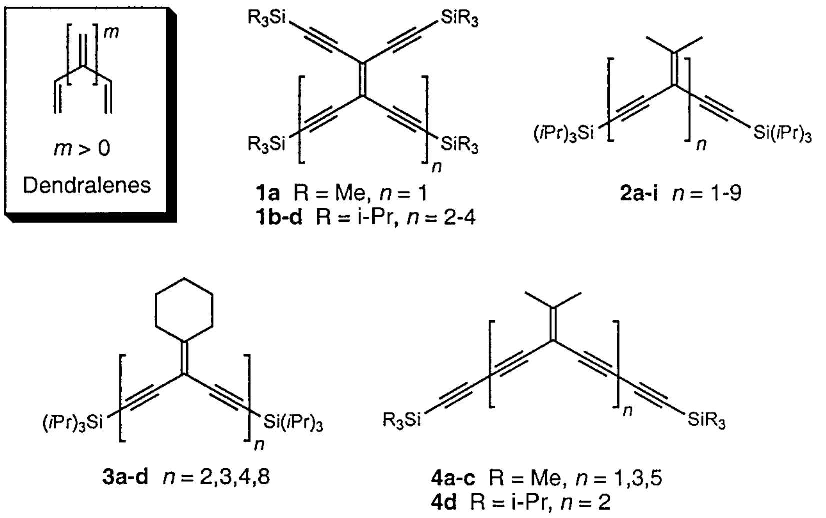
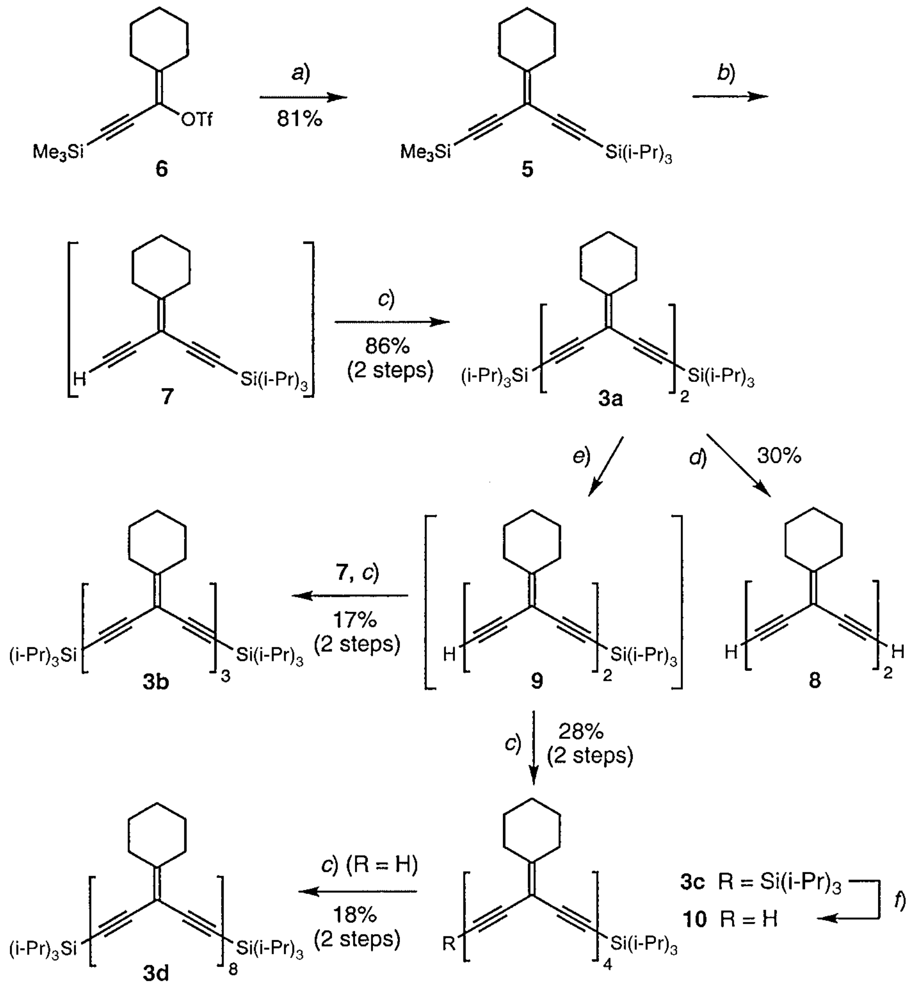


Fig. 1. *The parent class of dendralenes [1],* iso-*poly(triacetylene)s* **1a–d** [2], **3a–d** (this work), *and* **4a–d** [5] *featuring buta-1,3-diynediyl-expanded dendralenes, and* iso-*poly(diacetylene)s* **2a–i** [3d] *containing ethynediyl-expanded dendralenes*

We became interested in a direct comparison between the properties of buta-1,3-diynediyl- and ethynediyl-expanded dendralenes [4]. However, the peripheral perethynylation in the earlier *iso*-PTA series **1a–d** prevented direct comparison to the alkyl-substituted *iso*-PDAs such as **2a–i**, and the real consequences of expanding the bridges between the C=C bonds from a C_2- to a C_4-fragment could not be extracted from these two series. Therefore, we decided to prepare the new series of *iso*-PTAs **3a–d**, featuring the expanded dendralenes **3b–d**, with peripheral cyclohexylidene groups rather than alkyne substituents (as in **1a–d**). Here, we report the synthesis and characterization of **3b–d** as well as UV/VIS-spectral investigations on the extent of cross-conjugation in these novel expanded dendralene chromophores. During the preparation of this paper [4], *Tykwinski* and co-workers [5] reported the synthesis of the related *iso*-PTAs **4a–d** but with peripheral Me groups and elongated acetylenic end groups. In addition to the structural differences, the two studies contrast in the synthetic strategy, with the formation of **3a–d** being based on sequential oxidative acetylenic coupling [6] and the preparation of **4a–d** taking advantage of Pd-catalyzed C(sp)–C(sp^2) cross-coupling [7] for the construction of the oligomeric backbone.

2. Results and Discussion. – 2.1. *Synthesis of the Expanded Dendralenes* **3b–d**. The differentially protected penta-1,4-diyne **5** was prepared by Pd-catalyzed cross-coupling between $(i\text{-Pr})_3SiC{\equiv}CH$ and vinyl triflate **6** [3a] (*Scheme*). Next, **5** was selectively deprotected (K_2CO_3 in MeOH/THF) to give **7**, which was oxidatively homo-coupled under *Hay* conditions [8], to afford *iso*-PTA dimer **3a**. Treatment of **3a** with 2 equiv. of Bu_4NF gave the terminally bis-deprotected dimer **8** as a surprisingly stable white solid. The deprotection had to be performed at *ca.* −30°, since the reaction at room temperature led to complete decomposition. Treating **3a** with only 0.1–0.2 equivalents

Scheme. *Synthesis of Expanded Dendralenes* **3b–d**



a) (i-Pr)$_3$SiC≡CH (excess), [Pd(PPh$_3$)$_4$], CuI, Et$_2$NH, THF, r.t. *b*) K$_2$CO$_3$, MeOH, THF, r.t. *c*) CuCl, TMEDA, CH$_2$Cl$_2$, air, r.t. *d*) Bu$_4$NF (2 equiv.), THF, −30°; *e*) Bu$_4$NF (0.1–0.2 equiv.), THF, −30°; *f*) Bu$_4$NF (0.36 equiv.), THF, −30°. Tf = Triflate. TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine.

of Bu$_4$NF at −30° yielded a mixture of unreacted (**3a**), mono-deprotected (**9**), and bis-deprotected (**8**) dimer. Progress of the reaction upon dropwise addition of Bu$_4$NF was conveniently monitored by TLC (SiO$_2$; hexanes/CH$_2$Cl$_2$ 6:1), since the three compounds had significantly different R_f values (**3a**: 0.54, **9**: 0.40, **8**: 0.27). When TLC indicated a product ratio of *ca.* 1:1:1, no more Bu$_4$NF was added. The requirement of less than 0.5 equiv. suggests that the first deprotection step (**3a** → **9**) is significantly faster than the second one (**9** → **8**). After separation by column chromatography, mono-deprotected **9** was hetero-coupled under *Hay* conditions with mono-deprotected **7**, to yield expanded [3]dendralene **3b**, together with **3a** and expanded [4]dendralene **3c** as by-products. To enforce formation of the [3]dendralene as the major product, an excess of monomeric **7** was used. The desired product **3b** was isolated in pure form by repeated column chromatography.

Mono-deprotected *iso*-PTA dimer **9** was also readily homo-coupled, which provided the expanded [4]dendralene **3c**. Gratifyingly, mono-deprotection of **3c** with Bu_4NF could again be monitored by TLC, since unreacted **3c** and the corresponding terminally mono- and bis-deprotected derivatives featured significantly different R_f values. Pure mono-deprotected [4]dendralene **10** was isolated by column chromatography and subsequently homo-coupled under *Hay* conditions, affording expanded [8]dendralene **3d**, the longest *iso*-PTA oligomer prepared so far.

This new series of expanded dendralenes was found to be highly unstable, experiencing both light and temperature sensitivity. In this respect, they are very different from the related series of TEE oligomers **1a** – **d**. Thus, the expanded [3]- and [4]dendralenes **1c** and **1d** are air- and light-stable yellow solids melting above 100° [2]. Interestingly, the two extra geminal acetylene moieties in each monomeric repeat unit in **1a** – **d** add a remarkable stability to the oligomeric *iso*-PTA scaffolds, which is not well-understood at present. The instability possessed by the cyclohexylidene-substituted *iso*-PTAs **3a** – **d** was moreover reflected in the fact that we were not able to obtain the related macrocycles, the expanded radialenes. Thus, all attempts of macrocyclization, starting from **3a** – **c** after desilylation, failed, employing the same dilute *Hay*-coupling conditions that had successfully been used for constructing TEE-based expanded radialenes [9].

2.2. *Characterization of the New Expanded Dendralenes.* The *iso*-PTA dimer **3a** and the [4]- (**3c**) and [8]- (**3d**) dendralenes are solids, whereas [3]dendralene **3b** is an oil. The [8]dendralene is less soluble than the shorter analogs, but it is still possible to dissolve fair amounts in CH_2Cl_2 or $CHCl_3$ for spectral characterization.

The *Fourier*-transform matrix-assisted laser-desorption-ionization (FT-MALDI) mass spectrum of **3d** (*Fig. 2*) confirmed the purity of this long oligomer, which contains a total of 40 C-atoms in the backbone. The base peak in the spectrum corresponds to the $[M+Na]^+$ ion (*m/z* 1473.8990, $C_{106}H_{122}NaSi_2^+$; calc. 1473.8983).

In the ^{1}H-NMR spectra of **3a** – **d**, the cyclohexylidene protons were found to resonate at about the same chemical-shift values, that is as two *multiplets* at δ 1.6 and 2.5 ppm, respectively. The terminal $(i\text{-}Pr)_3Si$ protons appeared as a *singlet* at 1.1 ppm in the whole series. The ratio between the integrated intensities of cyclohexylidene and $(i\text{-}Pr)_3Si$ resonances changed correctly according to the number of monomeric repeating units and, hence, confirmed the structures.

The ^{13}C-NMR spectra are quite informative, especially in the 80 – 170 ppm region. It is possible to observe the different C(sp) and C(sp^2) resonances from the *iso*-PTA backbones as well as the cyclohexylidene C(sp^2) signals. *Fig. 3* and *Table 1* show the spectra of **3a** – **d** and, for comparison, of the bis-(Me_3Si)-protected monomer **11** [10].

The cyclohexylidene C(sp^2) resonances appear at the highest chemical shifts (δ 163 – 170 ppm), while the signals in the region of 75 to 102 ppm correspond to the backbone C-atoms. In the spectra of **3a** – **c** and **11** (as well as of **5**), all the chemically different C(sp^2) resonances can be differentiated, whereas in the spectrum of [8]dendralene **3d**, some C(sp^2) resonances seem to be overlapping. However, the number of C-atoms per signal can be evaluated from the relative signal intensities and

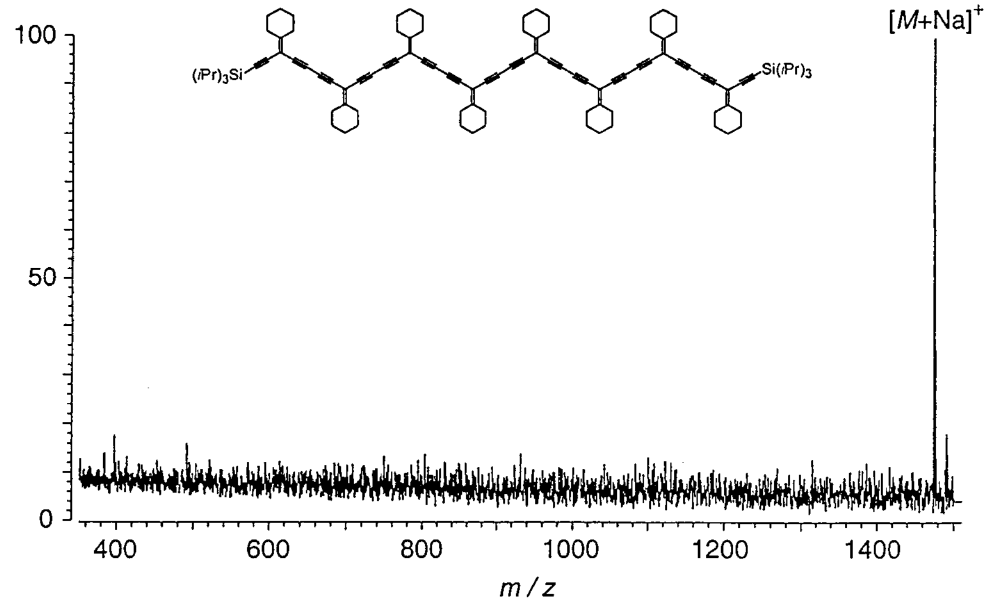


Fig. 2. *FT-MALDI Mass spectrum of* **3d** (matrix: 2,5-dihydroxybenzoic acid)

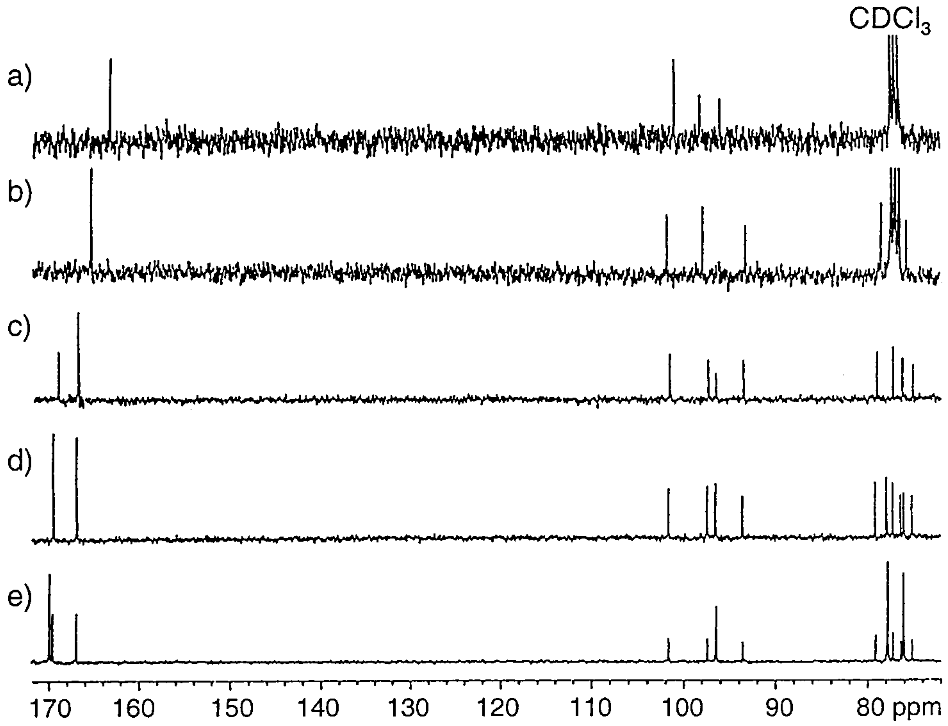
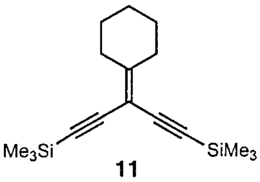


Fig. 3. *Partial* ^{13}*C-NMR spectra of* **11** (a) *and* **3a** (b) *in* $CDCl_3$, *and of* **3b** (c), **3c** (d), *and* **3d** (e) *in* CD_2Cl_2

Table 1. *^{13}C-NMR Chemical Shifts [ppm] for* iso-*PTAs* **3a – d** *and Comparison Compound* **11**. Numbers in brackets refer to the number of C-atoms corresponding to a given resonance.



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Compound	Cyclohexylidene C(sp^2)	Backbone C(sp) and C(sp^2)
11	163.4 [1]	96.1 [2], 98.3 [2], 101.1 [1]
3a	165.5 [2]	75.8 [2], 78.5 [2], 93.3 [2], 97.9 [2], 101.9 [2]
3b	167.0 [2], 169.2 [1]	75.2 [2], 76.3 [2], 77.3 [2], 79.1 [2], 93.6 [2], 96.6 [1], 97.4 [2], 101.7 [2]
3c	167.0 [2], 169.6 [2]	75.1 [2], 76.0 [2], 76.4 [2], 77.1 [2], 77.9 [2], 79.1 [2], 93.6 [2], 96.5 [2], 97.4 [2], 101.7 [2]
3d	167.0 [2], 169.6 [2], 169.9 [4]	75.2 [2], 76.0 [2], 76.1 [8], 76.4 [2], 77.2 [2], 77.8 [8], 77.9 [2], 79.1 [2], 93.6 [2], 96.4 [4], 96.5 [2], 97.4 [2], 101.7 [2]

is in accordance to the structure. The different cyclohexylidene C(sp^2) resonances are readily differentiated as well (*Table 1*). In the IR-spectrum of bis-deprotected dimer **8**, a strong band appears at 3312 cm^{-1}, corresponding to the C–H vibration of the terminal acetylenes. Since a similar band does not appear in any of the spectra of the silyl-protected *iso*-PTA oligomers **3a – d**, it establishes the absence of unprotected products in these compounds.

2.3. *UV/VIS Spectroscopy.* The UV/VIS spectra in CHCl$_3$ of the *iso*-PTA oligomers **5** and **3a – d** (with expanded dendralenes **3b – d)** are shown in *Fig. 4*. All compounds in the series, except from monomer **5**, show the same vibrational fine-structure pattern. Moreover, it is evident that the molar extinction coefficient increases almost proportionally as the number of monomeric repeat units (n) increases. It ranges from $\varepsilon = 18600$ M^{-1} cm^{-1} at $\lambda_{max} = 308$ nm for **3a** to $\varepsilon = 99000$ M^{-1} cm^{-1} at $\lambda_{max} = 316$ nm for **3d** (*Table 2*).

Table 2. *Molar Extinction Coefficients of the Band at ca. λ_{max} 310 mm Compared to the Increasing Number of Monomeric Repeat Units (n) in the* iso-*PTA Oligomers*

Compound	λ_{max} [nm]	ε [M^{-1} cm^{-1}]	ε/n [M^{-1} cm^{-1}]
3a	308	18600	9300
3b	312	32200	10700
3c	313	42200	10600
3d	316	99000	12400

Another interesting observation is the red-shift of the end-absorption as the number of repeat units in the dendralenes increases. Three different approaches were used to estimate the HOMO-LUMO gap, either from *i*) the longest-wavelength absorption maximum λ_{max} (with ε_{max}), *ii*) the wavelength at $\varepsilon_{max}/2$, or *iii*) the intercept value (λ_{tg}) of the tangent to the curve close to the end-absorption [3d]. The obtained

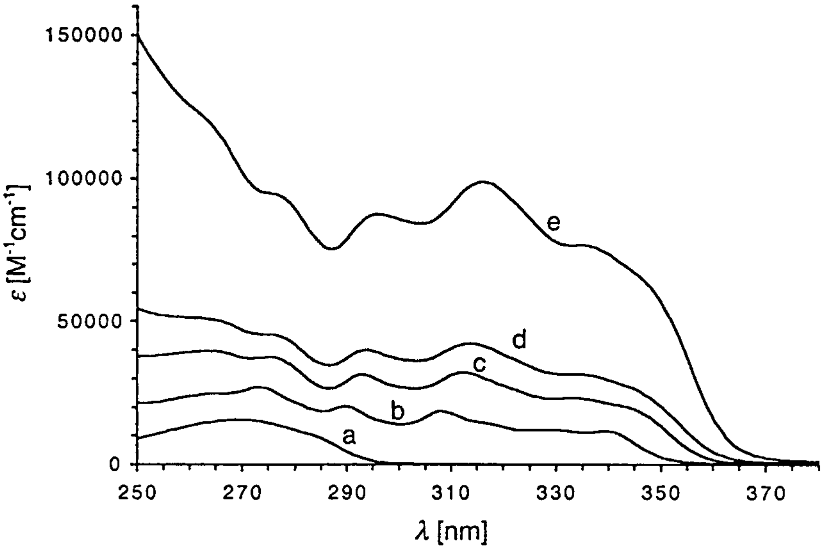


Fig. 4. *UV/VIS Spectra in $CHCl_3$ of* **5** (a), **3a** (b), **3b** (c), **3c** (d), *and* **3d** (e)

Table 3. *HOMO-LUMO Gap Energies* (E_g) *Calculated by Three Different Methods*

Compound	E_g (λ_{max}) [eV]	E_g ($\lambda(\varepsilon_{max}/2)$) [eV]	E_g (λ_{tg}) [eV]
5	4.35	4.28	4.16
3a	3.65	3.58	3.49
8	3.68	3.61	3.50
3b	3.61	3.52	3.42
3c	3.59	3.50	3.39
3d	3.56	3.48	3.35

energies are tabulated in *Table 3*. All three methods show the same trend: the HOMO-LUMO gap energy decreases as *n* increases.

The HOMO-LUMO gaps of **5** and **3a–d** (series *a*, *Fig. 5*) were compared to those of *iso*-PTAs **1a–d** [2] composed of monomeric TEE units (series *b*) and of *iso*-PDAs **2b–i** [3d] (series *c*). This comparison allows analysis of the influence of peripheral substituents and the number of acetylenes between the C=C bonds on the electronic properties of the expanded dendralenes.

The two extra acetylenes in each TEE repeating unit expectedly lower the HOMO-LUMO gap in the *iso*-PTA series *b* by *ca.* 0.8 eV compared to *iso*-PTA series *a* with peripheral cyclohexylidene residues. This lowering is readily explained by more-extended linear π-electron conjugation.

The influence of the number of acetylene moieties between the C=C bonds is evident when comparing series *a* and *c:* Upon moving from *iso*-PDA to *iso*-PTA oligomers, the HOMO-LUMO gap energy is lowered by 0.4 eV. The difference between the peripheral groups (cyclohexylidene *vs.* isopropylidene) is negligible as

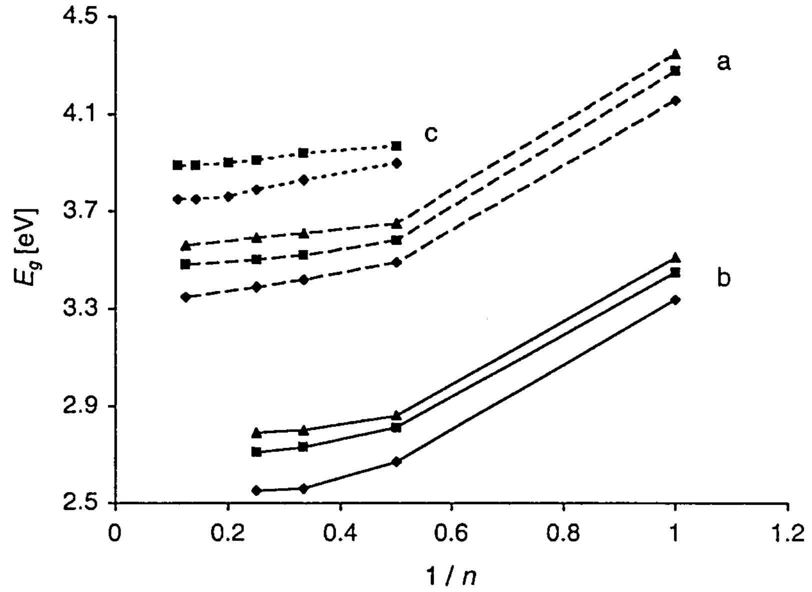


Fig. 5. *Correlations of the HOMO-LUMO gaps in* iso-*PTAs* **5** and **3a-d** (series *a*), iso-*PTAs* **1a – d** (series *b*) [2], *and* iso-*PDAs* **2b – i** (series *c*) [3d]. ▲ Corresponds to λ_{max}, ■ to λ at $\varepsilon_{max}/2$, and ◆ to λ_{tg}.

shown by comparison of the UV/VIS spectra of *iso*-PTA dimers containing the two types of peripheral groups [11].

UV/VIS and structural data [1] strongly indicate the absence of cross-conjugation in the parent, nonexpanded dendralenes. In contrast, all three series of expanded dendralenes show some extent of cross-conjugation as indicated by the shift of the end-absorption with increasing number of monomeric subunits (and increased possible longest-conjugation path). However, it is not straightforward to extrapolate when saturation occurs, *i.e.,* at which oligomeric length the E_g value of an infinite polymer is reached [12], in particular since the differently-sized oligomers in one series may have different conformational preferences (*vide infra*). A tentative extrapolation for series *a* (**3a – d**) indicates a minimal E_g value of 3.3 to 3.5 eV for infinite buta-1,3-diynediyl-expanded dendralenes.

It is also interesting to compare the new *iso*-PTA series **3a – d** with the linearly-conjugated PTAs composed of (*E*)-1,2-diethynylethene (DEE, (*E*)-hex-3-ene-1,5-diyne) repeating units [13]. The effective conjugation length in these oligomers is reached at *ca.* 10 monomeric DEE units, corresponding to a limiting HOMO-LUMO gap of 2.5 – 2.8 eV, that is a reduction of *ca.* 0.8 eV relative to cross-conjugated *iso*-PTAs.

The spectrum of bis-deprotected *iso*-PTA dimer **8** was recorded to obtain more information on the influence of the (i-Pr)$_3$Si end groups on the UV/VIS absorptions (*Fig. 6*). Compared with bis-protected dimer **3a**, the spectrum of unprotected **8** reveals a small blue-shift of the longest-wavelength absorptions (*ca.* 3 nm) and some changes in the spectral shape are also apparent. But overall, the (i-Pr)$_3$Si end groups seem to have

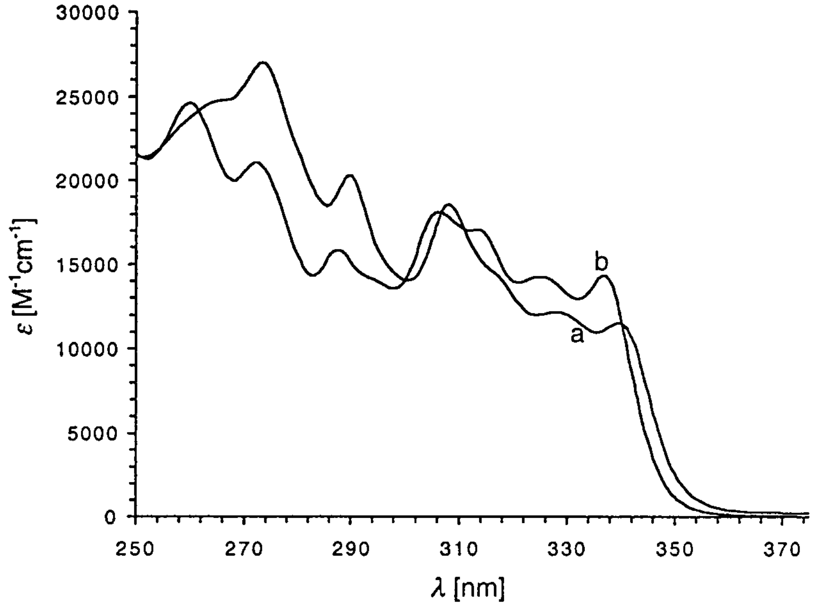
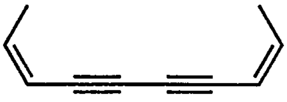


Fig. 6. *UV/VIS Spectra of bis[(i-Pr)$_3$Si]-protected dimer* **3a** (a) *and bis-deprotected dimer* **8** (b)

only a small influence on the electronic absorptions as is also evident from the comparision of the HOMO-LUMO gap energies in *Table 3*.

A comparison of lowest-energy absorptions was also made between **8** and a related compound devoid of cross-conjugation. Thus, (*Z*,*Z*)-deca-2,8-diene-4,6-diyne (**12**) [14] possesses a linear conjugation pathway of exactly the same length as the longest possible one in **8**. The two lowest-energy absorptions of **8** occur at $\lambda_{\max}$ 325 and 337 nm, whereas the lowest-energy absorption for **12** is at $\lambda_{\max}$ 312 nm, with a very small shoulder at 326 nm (in hexane). The bathochromic shifts observed for **8** relative to **12** indicate a significant degree of cross-conjugation in **8**.



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The analysis of the UV/VIS spectral data, including the control experiments, indicates that the slight but non-negligible red-shifts of the longest wavelength maxima and the optical end-adsorption with increasing length of the expanded dendralene do reflect some further extension of π-electron delocalization *via* cross-conjugative pathways as the number of monomeric repeat units increases.

2.4 *PM3 Calculations.* To gain insight into possible conformational preferences of the cyclohexylidene-substituted *iso*-PTAs **3a**, **c** and **d**, semi-empirical geometry optimizations were performed at the PM3 (perturbation method 3) level with

Hyperchem [15], with the terminal $(i\text{-}Pr)_3Si$ groups substituted, for computational ease, by H-atoms. Various starting geometries were used, and some of the obtained local conformational minima are depicted in *Fig. 7.*

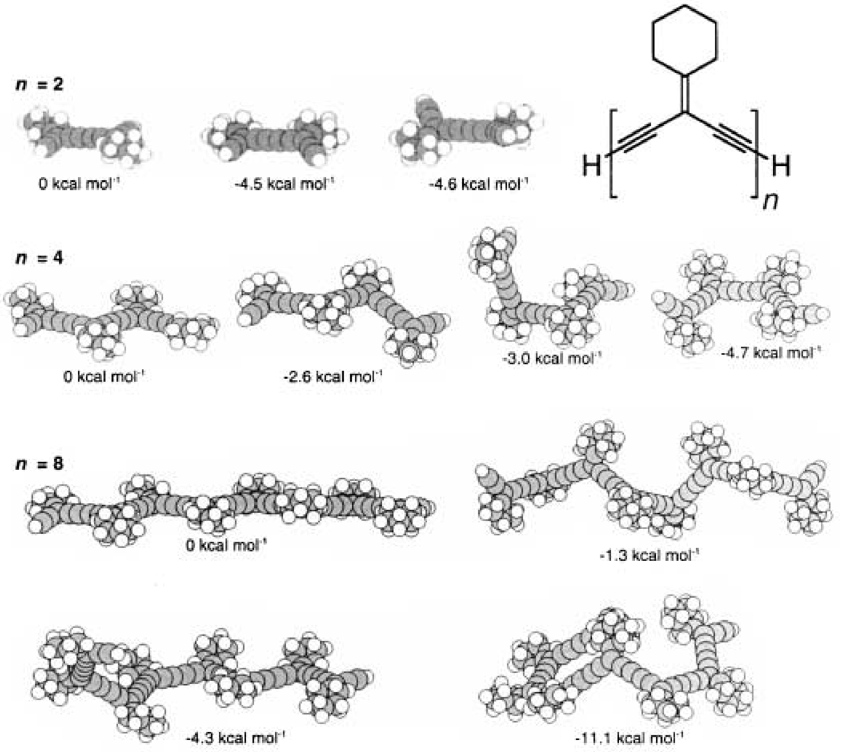

Fig. 7. *PM3-Optimized structures of* iso-*PTA oligomers* **3a, c, d**. The $(i\text{-}Pr)_3Si$ terminal groups are replaced in the calculations by H-atoms. Energies are given relative to the near-planar all-s-*trans* conformation of the oligomer.

For the dimer, the planar s-*trans* conformation, which was observed in several X-ray crystal structures of PTA oligomers [2][16], was not found to be the most favorable geometry. Thus, the s-*cis* and a slightly twisted s-*trans* conformer were -4.5 and -4.6 kcal mol^{-1}, respectively, lower in energy than the planar s-*trans* conformer. This relative sequence of conformational energies was confirmed by single-point calculations on the PM3-optimized structures, employing the Gaussian 98 program package [17]. At the HF/6-31 + G(d) level of theory; the calculated relative energies were 0 (planar s-*trans*), -8.9 (s-*cis*), and -9.2 (twisted s-*trans*) kcal mol^{-1}.

The planar all-s-*trans* conformation of the expanded [4]dendralene was also calculated as the highest-energy geometry. A slightly twisted s-*trans* conformation was found to be by -2.6 kcal mol^{-1} lower in energy whereas a geometry with a dihedral angle, defined by the four C(sp^2)-atoms in the *iso*-PTA backbone, of *ca.* 90° was lower in energy by -3.0 kcal mol^{-1}. In the most-stable calculated conformation (-4.7 kcal mol^{-1}), this dihedral angle approachs 0°, leading to a partly planar U-shaped conformation.

A significant difference between the parent and buta-1,3-diynediyl-expanded dendralenes becomes apparent: the [4]dendralene prefers a dihedral angle of *ca.* 72° [1c,e], whereas the expanded [4]dendralene seems to be more stable in the near-planar U-shape with a dihedral angle approaching 0°, which should be favorable for π-electron conjugation. Apparently, the spacing induced by the four acetylenic C-atoms between the C=C bonds is enough to reduce the steric interactions between the peripheral cyclohexylidene moieties, thereby allowing a more-planar π-chromophore. Furthermore, it has been previously shown [18] that effective π-electron conjugation between directly connected C≡C and C=C bonds does not require full planarity of the C_4 fragment in view of the cylindrical π-electron conjugation in the acetylenic bond. Both factors should enhance cross-conjugation in the expanded dendralenes as compared to the parent compounds.

The calculations performed on the expanded [8]dendralene showed once more that the planar all-s-*trans* conformation was not the most-stable one. The lowest energy (-11.1 kcal mol^{-1}) was calculated for a U-shaped geometry with five monomeric repeating units in one plane and the remaining three in another one.

It should be pointed out that the lowest-energy conformations obtained in this study are not necessarily the global minima. However, the present data do indeed reveal one general trend for *iso*-PTA oligomers: planar or slightly twisted s-*cis* and U-shaped conformations are energetically more favorable than the all-s-*trans* conformations, which is in contrast to the findings in PTAs with linearly conjugated backbones.

3. Conclusions. – A series of expanded [*n*]dendralenes **3b**–**d** ($n = 3, 4, 8$) with an *iso*-poly(triacetylene) (*iso*-PTA) backbone and peripheral cyclohexylidene substituents were synthesized from mono- and dimeric precursors and fully characterized. These compounds are remarkably less stable than the TEE-based expanded dendralenes and are sensitive to both light and temperature. The UV/VIS spectra of **3b**–**d** reveal interesting electronic properties: their HOMO-LUMO gap energies (E_g) are located between those of the corresponding TEE-based expanded dendralenes (**1c** and **d**) and expanded dendralenes with the *iso*-poly(diacetylene) (*iso*-PDA) backbone (**2c**–**i**). Their spectra show a slight red-shift as the number of monomeric repeat units increases, which indicates a small but non-negligible degree of π-electron cross-conjugation along the oligomeric backbone. The HOMO-LUMO gap energy for an infinitely long buta-1,3-diynediyl-expanded dendralene is estimated to 3.3–3.5 eV. Calculations performed at the PM3 level suggest that planar or slightly twisted s-*cis* and U-shaped conformations of *iso*-PTA oligomers are of lower energy than all-*s-trans* conformations, which is in contrast to the experimentally demonstrated conformational preferences of linearly π-conjugated PTA oligomers. The study once again underlines the great value of the oligomeric approach in exploring the electronic properties of polymers with novel conjugated backbones [12][19].

Experimental Part

General. Chemicals were purchased from *Aldrich* and *Fluka*, and used as received. All reactions, except *Hay* couplings, were carried out under a positive pressure of Ar. For the *Hay* couplings, the following mixture was used as *Hay* catalyst: CuCl (0.13 g) and *N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA, 0.16 g) in CH_2Cl_2 (4.5 ml). Column chromatographic (CC) purification refers to flash chromatography with the solvent mixture in the given ratio on SiO_2-*60* (230–400 mesh). M.p.: *Büchi 510* melting-point apparatus; uncorrected. UV/VIS (λ_{max} [nm] (ε [M^{-1} cm^{-1}])): *CARY 500 UV/VIS-NIR* spectrophotometer. IR [cm^{-1}]: *Nicolet 600 FT-IR* spectrometer. ^{1}H- and ^{13}C-NMR: *Varian Gemini 300 MHz* spectrometer; chemical-shift values are reported in ppm relative to residual solvent peaks. EI-MS *VG-Tribid* instrument; high-resolution- (HR) MALDI spectra: *IonSpec Fourier Transform* instrument by a two-layer technique (tl), with 2,5-dihydroxybenzoic acid (DHB) as matrix and the compound typically dissolved in CH_2Cl_2. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich.

3-Cyclohexylidene-1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyne (**5**). Compound **6** (1.38 g, 4.06 mmol) [3a] was dissolved in Ar-degassed THF (35 ml) and Et_2NH (5 ml). (Triisopropylsilyl)acetylene (2.70 ml, 12.2 mmol), $[Pd(PPh_3)_4]$ (116 mg, 0.100 mmol), and CuI (62 mg, 0.326 mmol) were added, and the mixture was stirred at r.t. under Ar for 19 h. Et_2O (200 ml) was added, and the org. phase was washed with H_2O (200 ml) and sat. aq. NH_4Cl soln. (2 × 100 ml), dried ($MgSO_4$), and concentrated *in vacuo*. CC (SiO_2; hexanes, then hexanes/CH_2Cl_2 10:1) afforded **5** (1.22 g, 81%). Colorless oil. UV/VIS ($CHCl_3$): 268 (15600), 285 (sh, 9100). IR (CCl_4): 2958*s*, 2942*s*, 2892*m*, 2865*s*, 2150*m*, 2120*w*, 1593*w*, 1462*m*, 1448*w*, 1408*w*, 1383*w*, 1366*w*, 1348*w*, 1337*w*, 1283*w*, 1250*m*, 1231*w*, 1187*w*, 1132*w*, 1113*w*, 1072*w*, 1011*m*, 996*w*, 940*w*, 919*w*, 897*w*, 883*m*, 858*s*, 853*s*, 845*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.19 (*s*, 9 H); 1.09 (*s*, 21 H); 1.55–1.66 (*m*, 6 H); 2.47–2.54 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 0.12; 11.5; 18.8; 26.2; 27.6 (2 ×); 32.8; 32.9; 92.7; 96.0; 98.7; 101.5; 103.1; 162.3. EI-MS: 372 (M^+), 329 ($[M - Pr]^+$), 287, 259, 129, 73, 59. Anal. calc. for $C_{23}H_{40}Si_2$ (372.74): C 74.11, H 10.82; found: C 74.22, H 10.82.

3,8-Bis(cyclohexylidene)-1,10-bis(triisopropylsilyl)deca-1,4,6,9-tetrayne (**3a**). A mixture of **5** (300 mg, 0.805 mmol) and K_2CO_3 (111 mg, 0.805 mmol) in wet MeOH (10 ml) and THF (10 ml) was stirred at r.t. under Ar for 1.5 h. Et_2O (200 ml) and H_2O (200 ml) were added, and the org. phase was dried ($MgSO_4$) and concentrated *in vacuo* to a few ml. The residue was dissolved in CH_2Cl_2 (15 ml), whereupon *Hay* catalyst (1.5 ml) was added, and the mixture was stirred under air for 19.5 h. CC (SiO_2; hexanes/CH_2Cl_2 6:1) afforded **3a** (207 mg, 86%) as an oily product that solidified upon standing. White solid. M.p. 73°. UV/VIS ($CHCl_3$): 265 (24800), 273 (27000), 290 (20300), 308 (18600), 317 (sh, 14400), 328 (12200), 340 (11500). IR (CCl_4): 2941*s*, 2891*m*, 2865*s*, 2146*m*, 1578*w*, 1462*m*, 1448*m*, 1383*w*, 1366*w*, 1348*w*, 1336*w*, 1317*w*, 1281*w*, 1255*w*, 1229*w*, 1177*w*, 1130*w*, 1117*w*, 1071*w*, 1052*w*, 1018*w*, 1006*w*, 996*w*, 921*w*, 883*m*, 854*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.09 (*s*, 42 H); 1.55–1.67 (*m*, 12 H); 2.50–2.58 (*m*, 8 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.4; 18.8; 26.2; 27.7; 27.9; 33.2 (2 ×); 75.8; 78.5; 93.3; 97.9; 101.9; 165.5. EI-MS: 599 (M^+), 556 ($[M - Pr]^+$), 513, 471, 256, 193, 157, 115, 87, 59. Anal. calc. for $C_{40}H_{62}Si_2$ (599.10): C 80.19, H 10.43; found: C 80.36, H 10.24.

3,8,13-Tris(cyclohexylidene)-1,15-bis(triisopropylsilyl)pentadeca-1,4,6,9,11,14-hexayne (**3b**). A soln. of **3a** (118 mg, 0.197 mmol) in THF (25 ml) was degassed under Ar and cooled to – 30°. Bu_4NF (1M in THF, 0.04 ml, 0.04 mmol) was added dropwise over 30 min, and the reaction was carefully followed by TLC (SiO_2; hexanes/CH_2Cl_2 6:1). To the mixture containing **3a**, **8**, and **9**, Et_2O (200 ml) was added, and the org. phase was washed with H_2O (2 × 200 ml), dried ($MgSO_4$), and concentrated to a few ml. CC (SiO_2; hexanes/CH_2Cl_2 6:1) gave pure **9** (R_f 0.40) as the second fraction.

A mixture of **5** (100 mg, 0.268 mmol) and K_2CO_3 (37 mg, 0.27 mmol) in wet MeOH (5 ml) and THF (5 ml) was stirred at r.t. under Ar for 1 h. Et_2O (200 ml) and H_2O (200 ml) were added, and the org. phase, containing **7**, was dried ($MgSO_4$) and concentrated to a few ml.

Mono-deprotected **7** and **9** were dissolved in CH_2Cl_2 (15 ml), and *Hay* catalyst (3 ml) was added. After stirring under air for 18 h, CH_2Cl_2 (200 ml) was added, and the org. phase was washed with H_2O (2 × 200 ml), dried ($MgSO_4$), and concentrated to a few ml. CC (SiO_2; hexanes/CH_2Cl_2 8:1) afforded **3b** (25 mg, 17%). White oily solid. UV/VIS ($CHCl_3$): 263 (39600), 275 (37600), 292 (31200), 312 (32200), 332 (23200), 343 (sh, 20400). IR (CCl_4): 2941*s*, 2891*m*, 2865*s*, 2147*m*, 1578*w*, 1462*m*, 1448*m*, 1439*w*, 1383*w*, 1367*w*, 1348*w*, 1336*w*, 1316*w*, 1281*w*, 1271*w*, 1255*w*, 1229*w*, 1173*w*, 1124*w*, 1110*w*, 1072*w*, 1017*m*, 1004*w*, 996*m*, 920*w*, 883*m*, 854w. ^{1}H-NMR (300 MHz, CD_2Cl_2): 1.07 (*s*, 42 H); 1.54–1.68 (*m*, 18 H); 2.48–2.60 (*m*, 12 H). ^{13}C-NMR (75 MHz, CD_2Cl_2): 11.3; 18.6; 26.0; 26.1; 27.8; 28.0; 33.3; 33.5; two coincident peaks not observed; 75.2; 76.3; 77.3; 79.1; 93.6; 96.6; 97.4; 101.7; 167.0; 169.2. HR-MALDI-MS (DHB-tl): 740.5137 (M^+, $C_{51}H_{72}Si_2^+$; calc. 740.5173), 763.5070 ($[M+Na]^+$, $C_{51}H_{72}NaSi_2^+$; calc. 763.5065).

3,8,13,18-Tetrakis(cyclohexylidene)-1,20-bis(triisopropylsilyl)icosa-1,4,6,9,11,14,16,19-octayne (**3c**). A soln. of **3a** (821 mg, 1.37 mmol) in THF (150 ml) was degassed under Ar and cooled to – 30°. Bu_4NF (1M in THF, 0.15 ml, 0.15 mmol) was added dropwise over 70 min, and the reaction was followed carefully by TLC (SiO_2; hexanes/CH_2Cl_2 6:1). To the mixture containing **3a**, **8**, and **9**, Et_2O (200 ml) was added, and the org. phase washed with H_2O (3 × 200 ml), dried ($MgSO_4$), and concentrated to a few ml. CC (SiO_2; hexanes/CH_2Cl_2 6:1) gave pure **9** (R_f 0.40) as the second fraction. The residue was dissolved in CH_2Cl_2 (60 ml), then *Hay* catalyst

(5.5 ml) was added, and the mixture was stirred under air for 17 h. Et_2O (200 ml) was added, and the org. phase was washed with H_2O (3 × 200 ml), dried ($MgSO_4$), and concentrated *in vacuo*. CC (SiO_2; hexanes/CH_2Cl_2 4 : 1) afforded **3c** (171 mg, 28%). White solid. M.p. 70°. UV/VIS ($CHCl_3$): 263 (51100), 275 (45500), 293 (39900), 313 (42200), 334 (31600), 345 (sh, 26400). IR (CCl_4): 2940*s*, 2892*m*, 2864*s*, 2145*w*, 1576*w*, 1462*m*, 1448*m*, 1440*w*, 1383*w*, 1367*w*, 1348*w*, 1337*w*, 1281*w*, 1261*w*, 1255*w*, 1229*w*, 1172*w*, 1144*w*, 1127*w*, 1109*w*, 1071*w*, 1041*w*, 1018*m*, 1010*m*, 1003*m*, 997*m*, 919*w*, 883*m*, 854*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.09 (*s*, 42 H); 1.55 – 1.69 (*m*, 24 H); 2.48 – 2.58 (*m*, 16 H). ^{13}C-NMR (75 MHz, CD_2Cl_2): 11.5; 18.6; 26.0; 26.1; 27.8; 28.0; 33.3 (2 ×), 33.3; 33.5; two coincident peaks not observed; 75.1; 76.0; 76.4; 77.1; 77.9; 79.1; 93.6; 96.5; 97.4; 101.7; 167.0; 169.6. HR-MALDI-MS (DHB-tl): 905.5867 ($[M+\mathrm{Na}]^+$, $C_{62}H_{82}NaSi_2^+$; calc. 905.5858). Anal. calc. for $C_{62}H_{82}Si_2$ (883.50): C 84.29, H 9.35; found: C 84.27, H 9.39.

3,8,13,18,23,28,33,38-Octakis(cyclohexylidene)-1,40-bis(triisopropylsilyl)tetraconta-1,4,6,9,11,14,16,19,21,24,26,29,31,34,36,39-hexadecayne (**3d**). A soln. of **3c** (171 mg, 0.194 mmol) in THF (50 ml) was degassed under Ar and cooled to – 30°. Bu_4NF (1M in THF, 0.07 ml, 0.07 mmol) was added dropwise over 60 min, and the reaction was carefully followed by TLC (SiO_2; hexanes/CH_2Cl_2 5 : 1). To the mixture containing unreacted, mono-, and bis-deprotected **3c**, Et_2O (200 ml) was added, and the org. phase was washed with H_2O (2 × 200 ml), dried ($MgSO_4$), and concentrated to a few ml. CC (SiO_2; hexanes/CH_2Cl_2 5 : 1) afforded pure **10** as the second fraction. This compound was dissolved in CH_2Cl_2 (20 ml), then *Hay* catalyst (1.5 ml) was added, and the mixture was stirred under air for 17 h. CC (SiO_2; hexanes/CH_2Cl_2 5 : 1) afforded **3d** (26 mg, 18%) containing a slight amount of impurities. Pure **3d** was obtained by precipitation from CH_2Cl_2/hexanes in the refrigerator. White solid. M.p. dec. > 120°. UV/Vis ($CHCl_3$): 263 (sh, 120800), 277 (94200), 296 (87600), 316 (99000), 335 (76900), 348 (sh, 62000). IR (CCl_4): 2960*m*, 2933*s*, 2890*w*, 2862*m*, 2145*w*, 1700*w*, 1653*w*, 1559*m*, 1460*w*, 1448*m*, 1439*w*, 1347*w*, 1336*w*, 1281*w*, 1261*s*, 1228*w*, 1171*w*, 1098*s*, 1015*s*, 885*w*, 856*w*. ^{1}H-NMR (300 MHz, CD_2Cl_2): 1.07 (*s*, 42 H); 1.51 – 1.68 (*m*, 48 H); 2.46 – 2.58 (*m*, 32 H). ^{13}C-NMR (75 MHz, CD_2Cl_2): 11.5; 18.6; 26.0; 26.1; 27.8; 28.0; 33.3; 33.5; fourteen coincident peaks not observed; 75.2; 76.0; 76.1 (4 ×); 76.4; 77.2; 77.8 (4 ×); 77.9; 79.1; 93.6; 96.4 (2 ×); 96.5; 97.4; 101.7; 167.0; 169.6; 169.9 (2 ×). HR-MALDI-MS (DHB-tl): 1473.8990 ($[M+\mathrm{Na}]^+$, $C_{106}H_{122}NaSi_2^+$; calc. 1473.8983).

3,8-Bis(cyclohexylidene)deca-1,4,6,9-tetrayne (**8**). A soln. of **3a** (103 mg, 0.172 mmol) in THF (20 ml) was degassed under Ar and cooled to – 30°, then Bu_4NF (1M in THF, 0.34 ml, 0.34 mmol) was added dropwise. Et_2O (200 ml) was added, and the org. phase was washed with H_2O (2 × 200 ml), dried ($MgSO_4$), and concentrated to a few ml. CC (SiO_2; hexanes/CH_2Cl_2 6 : 1) provided **8** (15 mg, 30%). White solid. M.p. 113°. UV/VIS ($CHCl_3$): 259 (24500), 271 (20900), 287 (15800), 293 (sh, 14300), 306 (18100), 313 (17100), 325 (14300), 337 (14400). IR (CCl_4): 3312*s*, 2962*m*, 2936*s*, 2894*w*, 2859*m*, 2837*w*, 1584*w*, 1448*m*, 1440*w*, 1348*w*, 1281*w*, 1261*s*, 1230*w*, 1161*w*, 1099*s*, 1015*s*, 855*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.55 – 1.68 (*m*, 12 H); 2.51-2.57 (*m*, 8 H); 3.09 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 26.0; 27.7; 27.8; 33.1; 33.2; 75.9; 78.4; 79.1; 79.7; 96.4; 166.6. MALDI-MS (DHB-tl): 286 (M^+). Anal. calc. for $C_{22}H_{22}$ (286.42): C 92.26, H 7.74; found: C 92.18, H 7.66.

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