[6] a) V. W. Day, W. G. Klemperer, O. M. Yaghi, *J. Am. Chem. Soc.* **1989**, *111*, 5959; b) A. Müller, J. Döring, *Z. Anorg. Allg. Chem.* **1991**, *595*, 251.

[7] M. H. Alizadeh, S. P. Harmalker, Y. Jeannin, J. Martin-Frère, M. T. Pope, *J. Am. Chem. Soc.* **1985**, *107*, 2662.

[8] a) A. Müller, E. Krickemeyer, M. Penk, R. Rohlfing, A. Armatage, H. Bögge, *Angew. Chem.* **1991**, *103*, 1720; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1674; b) A. Müller, E. Diemann, E. Krickemeyer, *Naturwissenschaften* **1993**, *80*, 77.

[9] R. Kniep, H. Engelhardt, C. Hauf, *Chem. Mater.* **1998**, *10*, 2930, and references therein.

[10] C. J. Warren, R. C. Haushalter, D. J. Rose, J. Zubieta, *Chem. Mater.* **1997**, *9*, 2694.

[11] R. Bontchev, J. Do, A. J. Jacobson, *Inorg. Chem.* **1999**, *38*, 2231.

[12] C. J. Warren, R. C. Haushalter, D. J. Rose, J. Zubieta, *Inorg. Chem. Commun.* **1998**, *1*, 4.

[13] Crystal structure analyses: a) **1** ($n=6$) at $T=293$ K: monoclinic, space group $P2_1/n$ (no. 14), $a=12.9822(9)$, $b=16.2608(12)$, $c=17.0246(11)$ Å, $\beta=103.412(2)^\circ$, $V=3495(9)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.998$ g cm^{-1}; diffractometer: Siemens SMART 1 K CCD (Mo$_{K\alpha}$ radiation, graphite monochromator); $\mu=1.329$ mm^{-1}; a hemisphere of data (1271 frames at 5-cm detector distance), narrow-frame method with scan widths of 0.30° in ω and exposure time of 30 s per frame, $2\theta_{\max}=53.96^\circ$, 9372 measured reflections, 5582 independent reflections; corrections for Lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate. The program SADABS[14a] was used for the absorption correction; structure solved by direct methods (SHELXTL[14b]) and refined by least-squares methods (all atoms anisotropic, SHELXTL[14c]); 502 free parameters; GOF = 1.126, R values ($I > 2\sigma(I)$): $R1=0.057$, $wR2=0.106$; max./min. residual electron density: $0.586/-0.436$ e^{-1} Å^{-3}.[15] b) **1** ($n=2$): deep blue crystal, space group $P2_1/c$, $a=10.9147(7)$, $b=11.9186(7)$, $c=25.3828(15)$ Å, $\beta=95.011(1)^\circ$, $V=3289(9)$ Å^3. c) **1** ($n=14$): pale blue crystal, space group $P2_1/c$, $a=13.2229(7)$, $b=28.7520(16)$, $c=21.2716(11)$ Å, $\beta=98.916(1)^\circ$, $V=7989(13)$ Å^3. d) **3** ($A=NH_4^+$, $n=12$) at $T=293$ K: rhombohedral, space group $R\bar{3}m$ (no. 166), $a=14.116(2)$ Å, $\alpha=71.96(2)^\circ$, $V=2470.7(5)$ Å^3, $Z=1$, $\rho_{\text{calcd}}=1.651$ g cm^{-1}; data collection, corrections and structure solution as above for **1** ($n=6$); $\mu=1.376$ mm^{-1}, 2689 measured reflections, 1487 independent reflections; 147 free parameters; GOF = 1.037, R values ($I > 2\sigma(I)$): $R1=0.056$, $wR2=0.151$; max./min. residual electron density: $0.415/-0.370$ e^{-1} Å^{-3}.[15] e) **2** at $T=293$ K: monoclinic, space group $P2_1/n$ (no. 14), $a=22.198(1)$, $b=15.3947(8)$, $c=26.118(1)$ Å, $\beta=115.113(1)^\circ$, $V=8081.8(8)$ Å^3. f) Crystallographic data (excluding structure factors) for the structures of **1** and **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115529 and -115530. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

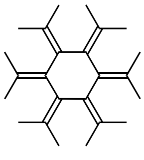
[14] a) G. M. Sheldrick, Program SADABS, Universität Göttingen, **1995**; b) G. M. Sheldrick, SHELXTL, Version 5.03, Siemens Analytical X-ray Instruments, Madison, WI, **1995**; c) G. M. Sheldrick, SHELX-96 Program for Crystal Structure Determination, **1996**.

[15] Selected bond lengths [Å] and angles [°] for **1** ($n=6$): V–O 1.932–2.001, V=O 1.588–1.613, P–O 1.497–1.579, B–O 1.452–1.497; O-P-O 105.5–114.0, O-B-O 104.5–112.4; for **3** ($A=NH_4^+$, $n=12$): V–O 1.932–2.022, V=O 1.590, P–O 1.496–1.569, B–O 1.461–1.480; O-P-O 107.5–112.0, O-B-O 105.1–111.0.

Expanded Radialenes: Modular Synthesis and Characterization of Cross-Conjugated Enyne Macrocycles[**]

Sara Eisler and Rik R. Tykwinski[*]

Structurally intermediate between the radialenes **1**[1] and expanded radialenes **3**[2] are a class of hitherto unknown enyne macrocycles **2** constructed of 3-alkylidene-1-propynyl [–C≡C–C(=CR$_2$)–] building blocks.[3] Our interest in the electronic effects of cross-conjugation[4] in iso-polydiacetylenes (iso-PDAs, **4**), the acyclic analogues of **2**, led us to explore the synthesis of macrocycles such as **2** with a view to extending our understanding of π-electron delocalization in this intriguing class of molecules.



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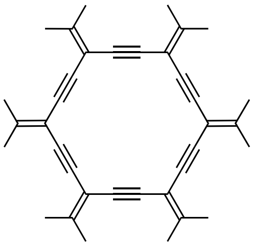

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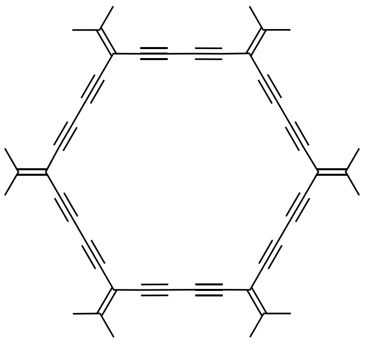

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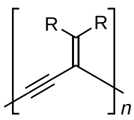

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Our initial studies of the electronic absorption behavior of iso-PDAs showed that π-electron delocalization in these compounds is not limited to the longest linearly conjugated segment; instead, it increases as a function of oligomer length and reaches saturation around the length of the nonamer (**4**; R = Me, $n=9$).[5] This analysis suggested a subtle contribution from cross-conjugation to the overall electronic communication along the enyne framework of iso-PDAs. It was anticipated that the more structurally rigid enyne framework of **2** would allow evaluation of electronic effects from cross- or

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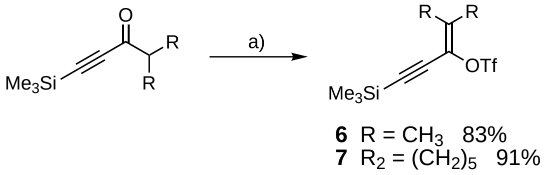
homoconjugation that may not be observable in the rotationally flexible iso-PDAs.

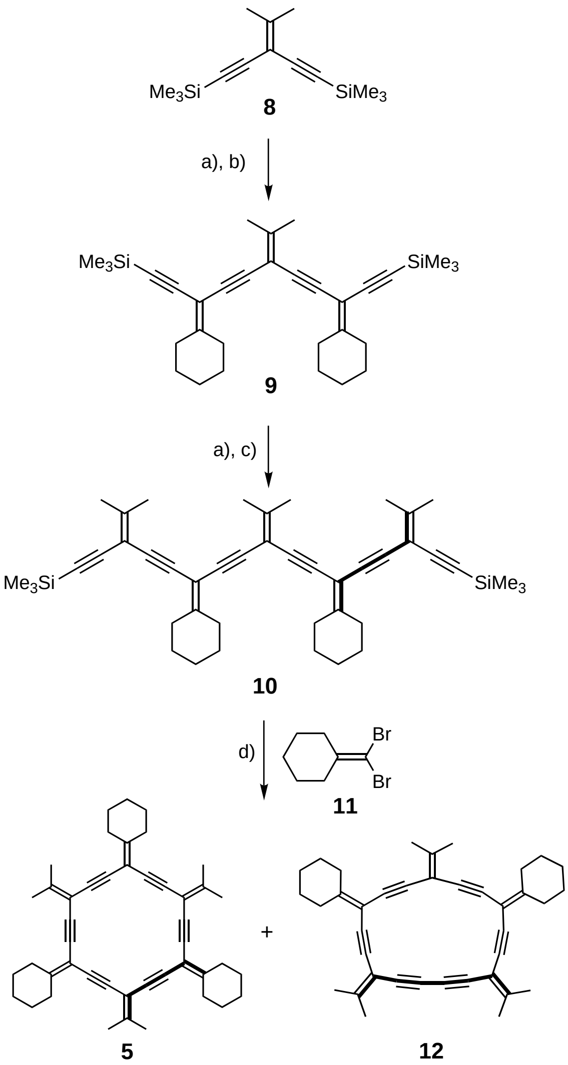
An iterative method of chain elongation was used to assemble the cross-conjugated precursors to the radialenes **2**[6] by utilizing palladium-catalyzed cross-coupling of terminal alkynes with vinyl triflates.[7] Our coupling sequence is sufficiently mild to tolerate the unsaturated iso-PDA framework, and its versatility allows modular incorporation of the different substituents required to maintain solubility or vary electronic effects. The target compound **5** (see Scheme 2) demonstrates our ability to selectively append different substituents to the same radialene framework.

The vinyl triflate building block **6** was synthesized from the corresponding ketone as described by Stang and Fisk,[8] and an analogous method gave vinyl triflate **7** (Scheme 1). The stepwise synthesis of radialene **5** is outlined in Scheme 2. Cross-conjugated enediyne **8**[5] was desilylated with K_2CO_3 in wet THF/MeOH (1/1) to afford the deprotected diyne, which, after work-up, was cross-coupled with vinyl triflate **7** to give the mixed trimer **9**. Cross-coupling to form **9** proceeds rapidly at room temperature in DMF with $[Pd(PPh_3)_4]$ as catalyst, CuI as co-catalyst, and a slight excess of the vinyl triflate **7**. Trimer **9** was subjected to a second iteration of the protodesilylation and cross-coupling procedure, in this case with vinyl triflate **6**, to give pentamer **10** in a modest yield of 28 %.[9]



Scheme 1. Synthesis of vinyl triflates **6** and **7**. a) 2,6-tBu$_2$-4-CH_3-C_5NH_2, $(CF_3SO_2)_2O$, CH_2Cl_2, room temperature.

The assembly of radialene **5** required protodesilylation of **10** followed by cross-coupling with dibromoolefin **11** (Scheme 2). To minimize the intramolecular Cu^{II}-catalyzed oxidative coupling[10] of deprotected **10** to give the hybrid radialene **12**, precursor **10** was desilylated in situ.[11] Tetrabutylammonium fluoride (TBAF, 1 M in THF) was added to a dilute degassed solution (ca. 0.006 M) of **10** and **11**[12] in THF in the presence of $[Pd(PPh_3)_4]$, CuI, and piperidine. The reaction mixture was stirred at room temperature and the reaction monitored by TLC, which showed sequentially the slow desilylation of **10**, cross-coupling with **11**, and finally cyclization to **5** (oxidative coupling to give **12** was observed as well). Although the dilute reaction conditions ultimately favored cyclization to **5** rather than the formation of linear oligomers, the reaction reached completion only after seven days. Work-up and column chromatography gave the pure macrocycles **5** and **12** in modest yields as a result of decomposition during purification. As pure solids, radialenes **5** and **12** are stable at room temperature under argon for only short periods of time (hours). They can, however, be stored in dilute, degassed solutions for days at room temperature or months under refrigeration with minimal loss. In spite of their modest environmental stability, both radialenes were completely characterized (Table 1).



Scheme 2. Modular synthesis of radialenes **5** and **12**. a) K_2CO_3, wet MeOH/THF (1/1), room temperature, 2 h; b) **7**, $[Pd(PPh_3)_4]$, CuI, Et_2NH, DMF, room temperature, 2 h, 41 % (from **8**); c) **6**, $[Pd(PPh_3)_4]$, CuI, Et_2NH, DMF, room temperature, 2.5 h, 28 % (from **9**); d) **11**, TBAF, $[Pd(PPh_3)_4]$, CuI, piperidine, THF, 9 % **5**, 5 % **12** (from **10**).

Table 1. Selected spectroscopic data for **5**, **12**, and **15**.

5: White solid; m.p. 150 °C (decomp); IR (solid): $\tilde{\nu} = 2927, 2854, 2198, 1577\ cm^{-1}$; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 2.80$ (m, 12 H), 2.12 (s, 18 H), 1.70 (m, 18 H); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 160.7, 153.3, 102.1, 98.6, 88.3, 88.2, 33.4, 28.1, 26.5, 23.0$; UV/Vis ($CHCl_3$): λ_{max} $(\varepsilon) = 286$ nm (53 600); HR-MS calcd for $C_{45}H_{48}$: m/z: 588.3756; found (EI, 70 eV): 588.3750.

12: White solid; m.p. 140 °C (decomp); IR (solid): $\tilde{\nu} = 2928, 2854, 2201, 2134, 1577\ cm^{-1}$; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 2.60$ (m, 8 H), 2.14 (s, 6 H), 2.08 (s, 6 H), 2.07 (s, 6 H), 1.66 (m, 12 H); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 160.7, 154.7, 153.1, 102.3, 102.1, 98.8, 89.4, 89.0, 88.6, 88.4, 83.0, 77.2, 33.6, 33.4, 28.1, 28.1, 26.6, 23.3, 23.2, 22.9$; UV/Vis ($CHCl_3$): λ_{max} $(\varepsilon) =$ 336 (13 200), 293 nm (47 000); HR-MS calcd for $C_{38}H_{38}$: m/z: 494.2974; found (EI, 70 eV): 494.2967.

15: White solid; m.p. 136–138 °C; IR (solid): $\tilde{\nu} = 2931, 2227, 2133, 1604\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.35$ (m, 4 H), 1.96 (s, 6 H), 1.95 (s, 6 H), 1.55 (m, 8 H), 1.29 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 151.3, 101.8, 93.8, 81.7, 79.1, 75.9, 30.3, 29.6, 28.9, 22.6, 22.5, 19.6; UV/Vis ($CHCl_3$): λ_{max} $(\varepsilon) = 328$ (24 500), 309 (26 500), 290 (15 700), 276 (8400), 260 nm (25 000); HR-MS calcd for $C_{23}H_{26}$: m/z: 302.2035; found (EI, 70 eV): 302.2035.

A comparison of the UV/Vis spectrum of radialene **5** with that of iso-PDA oligomer **10** (Figure 1) distinguishes the electronic absorptions resulting from the *cis* and *trans* orientations of the ene–yne–ene segments that represent the longest linearly conjugated paths in these molecules (Scheme 2, shown in bold for **5** and **10**). Rotationally unencumbered acyclic **10** shows two low-energy absorptions at 283 nm and about 305 nm for *cisoid* and *transoid* ene–yne–ene orientations, respectively.[13] Structurally rigid radialene **5** shows only one major low-energy absorption, at 286 nm, which is ascribed to the *cisoid* ene–yne–ene configuration of this molecule.

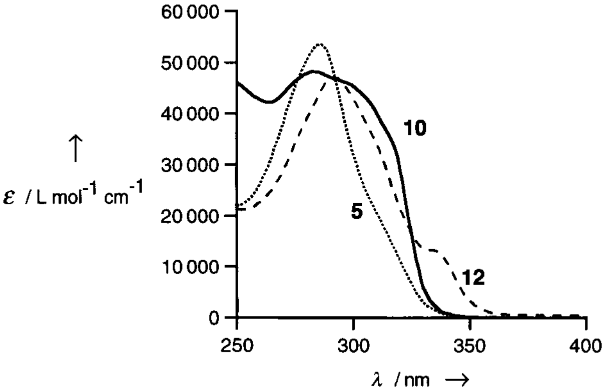
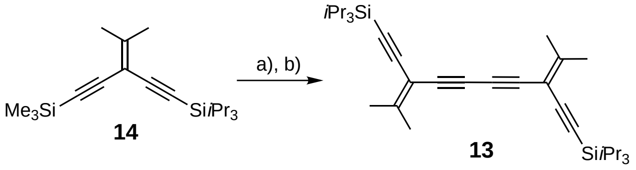


Figure 1. Electronic absorption spectra of **5**, **10**, and **12** in $CHCl_3$ at room temperature.

Molecular modeling studies predict a somewhat flattened chair conformation for the hexameric radialene **5**.[14] Despite this nonplanar structure, the rigid macrocycle is constrained to an orientation that is nearly optimal for overlap of the in-plane sp orbitals of the acetylenic units. The UV/Vis spectra suggest, however, that homoconjugation contributes little to the overall π-electron delocalization in **5**, since the radialene **5** has similar absorption characteristics to acyclic **10** (Figure 1).[15] The similar absorption energies of **5** and **10** predict virtually the same extent of overall π-delocalization in these two molecules as a sum of linear and cross-conjugation.[5]

Comparing the UV/Vis spectrum of **5** with that of the hybrid radialene **12** (Figure 1) shows that major electronic absorption of **12** is slightly red-shifted by 10 nm to 293 nm, possibly the result of increased planarity in **12**, as was observed for other radialenes.[16] The absorption spectrum of **12** has an additional low-energy band around 336 nm. This new band was initially attributed to the longer linearly conjugated segment present in **12** (Scheme 2, ene–yne–yne–ene, shown in bold). To confirm the assignment of this electronic transition, the synthesis of two model compounds, each containing the linearly conjugated C_8 segment of **12**, was undertaken.

The first model compound, dimer **13**, was readily derived from the enediyne **14** (Scheme 3).[5, 17] The UV/Vis spectrum of **13** (Figure 2) showed absorption maxima at 262 and 269 nm and lower energy absorptions at 288, 307, and 328 nm. The lowest energy absorption of **13** (328 nm) corresponds approximately to that of radialene **12**, although it is slightly blue-shifted by about 8 nm. The rotational freedom of **13**, however, is expected to result in individual absorptions for the *cis* and *trans* rotamers (vide supra), which were not clearly assignable in the spectrum of **13**. Hence, the origin of the low-energy absorption in **12** is still uncertain.



Scheme 3. Synthesis of **13**. a) K_2CO_3, wet MeOH/THF (1/1), room temperature, 2 h; b) CuI, TMEDA, O_2, CH_2Cl_2, room temperature, 2 h, 95 % (from **14**). TMEDA = *N,N,N′,N′*-tetramethylethylenediamine.

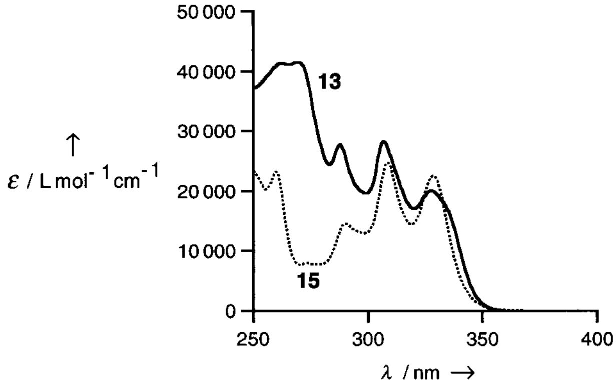
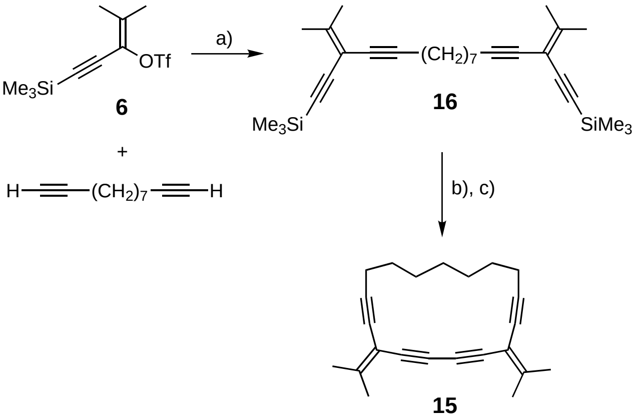


Figure 2. Electronic absorption spectra of **13** and **15** in $CHCl_3$ at room temperature.

To provide more definitive information, the conformationally restricted analogue of **13**, cyclic **15** (Table 1), was assembled as outlined in Scheme 4.[18] The electronic absorption spectrum of **15** (Figure 2) shows major low-energy absorptions similar to those of **13** at 290, 309, and 328 nm. A direct comparison of the absorption spectra of **13** and **15** suggests that the bands of the *cis* and *trans* forms of **13** are similar in energy; the latter is barely visible as a shoulder at about 336 nm for **13** and absent from the spectrum of **15**. As observed for **13**, the lowest energy absorption of **15** at 328 nm



Scheme 4. Synthesis of **15**. a) $[Pd(PPh_3)_4]$, CuI, Et_2NH, DMF, room temperature, 5 h, 26 %; b) K_2CO_3, wet MeOH/THF, room temperature, 3 h; c) CuI, TMEDA, O_2, CH_2Cl_2, 4 h, 22 % (from **16**).

is also blue-shifted by about 8 nm versus that of radialene **12**. There is little doubt, however, that in all three molecules this absorption band is due to the linearly conjugated ene–yne–yne–ene segment.

The slight bathochromic shift of the lowest energy absorption of radialene **12** relative to **13** or **15** is interesting as it could signify an increased contribution from cross- or homoconjugation to the overall electronic communication that results from the constricted interior yne–ene–yne bond angles of **12** relative to those of **15**.[15] At this point, however, it can not be ruled out that this red shift results from inductive effects or the increased planarity and/or ring strain of **12** versus **15**. However, these explanations seem less likely, given the similar absorption spectra of **13** and **15** (Figure 2). Additional model compounds are now being synthesized in an effort to resolve this question.

The synthesis and characterization of radialenes **5** and **12** provides preliminary details of the electronic properties of these cross-conjugated enyne macrocycles. The hexameric radialene **5**, with nearly optimal sp^2 interior bond angles, shows no enhanced π-electron delocalization attributable to homoconjugation, as shown by comparison with acyclic iso-PDA analogues. The absorption spectrum of hybrid radialene **12**, however, suggests that a reduction of the interior bond angles could lead to additional electronic effects in these molecules that ultimately result in a red shift of the lowest energy absorption. The syntheses of the tri-, tetra-, and pentameric members of this new class of expanded radialenes represented by hexamer **5** are currently being conducted. The more rigorously planar structure of these smaller rings and the smaller interior bond angles promise to provide a more detailed view of the π-electron delocalization in expanded radialenes.

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[1] a) G. Maas, H. Hopf in *The Chemistry of Dienes and Polyenes, Vol. 1* (Ed.: Z. Rappoport), Wiley, Chichester, **1997**, pp. 927–977; b) H. Hopf, G. Maas, *Angew. Chem.* **1992**, *104*, 953–977; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 931–954.

[2] a) A. M. Boldi, F. Diederich, *Angew. Chem.* **1994**, *106*, 482–485; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 468–471; b) J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, P. Seiler, C. B. Knobler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 797–817; c) M. Schreiber, R. R. Tykwinski, F. Diederich, R. Spreiter, U. Gubler, C. Bosshard, I. Poberaj, P. Günter, C. Boudon, J.-P. Gisselbrecht, M. Gross, U. Jonas, H. Ringsdorf, *Adv. Mater.* **1997**, *9*, 339–343.

[3] Other examples of cross-conjugated macrocycles: a) A. Sekiguchi, T. Matsuo, H. Sakurai, *Angew. Chem.* **1998**, *110*, 1751–1754; *Angew. Chem. Int. Ed.* **1998**, *37*, 1662–1664; b) S. Kammermeier, R. R. Tykwinski, P. Siemsen, P. Seiler, F. Diederich, *Chem. Commun.* **1998**, 1285–1286; c) J. Nitschke, T. D. Tilley, *J. Org. Chem.* **1998**, *63*, 3673–3676; d) A. Stanger, N. Ashkenazi, R. Boese, D. Bläser, P. Stellberg, *Chem. Eur. J.* **1997**, *3*, 208–211; e) T. Enomoto, T. Kawase, H. Kurata, M. Oda, *Tetrahedron Lett.* **1997**, *38*, 2693–2696; f) R. Gleiter, H. Röckel, B. Nuber, *Tetrahedron Lett.* **1995**, *36*, 1835–1838; g) R. Faust, F. Diederich, V. Gramlich, P. Setler, *Chem. Eur. J.* **1995**, *1*, 117; h) R. Gleiter, H. Röckel, H. Irngartinger, T. Oeser, *Angew. Chem.* **1994**, *106*, 1340–1342; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1270–1272; i) G. M. Pilling, F. Sondheimer, *J. Am. Chem. Soc.* **1971**, *93*, 1977–1984.

[4] a) M. Traetteberg, H. Hopf, *Acta Chem. Scand.* **1994**, *48*, 989–993; b) N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, *45*, 633–637.

[5] Y. Zhao, R. R. Tykwinski, *J. Am. Chem. Soc.* **1998**, *120*, 458–459.

[6] N. Feuerbacher, F. Vögtle, *Top. Curr. Chem.* **1998**, *197*, 1–18.

[7] K. Ritter, *Synthesis* **1993**, 735–762.

[8] P. J. Stang, T. E. Fisk, *Synthesis* **1979**, 438–440.

[9] The purity and structure of all new compounds were confirmed by ^{1}H and ^{13}C NMR, IR, UV, MS, and either elemental analysis or HR-MS.

[10] A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320–3321.

[11] D. A. Shultz, K. P. Gwaltney, H. Lee, *J. Org. Chem.* **1998**, *63*, 4034–4038.

[12] R. Hässig, D. Seebach, H. Siegel, *Chem. Ber.* **1984**, *117*, 1877–1884.

[13] The absorption band for the *transoid* form at 305 nm, visible as a shoulder in the spectrum of **10**, is more clearly discernible in **9** and other shorter iso-PDAs.[5]

[14] Calculations were performed on an SGI Indigo^2 with Macromodel 5.5.

[15] For a similar discussion of homoconjugation in percyclines, see L. T. Scott, M. J. Cooney in *Modern Acetylene Chemistry* (Eds.: P. J. Stang, F. Diederich), VCH, Weinheim, **1995**, pp. 321–351.

[16] M. Iyoda, S. Tanaka, H. Otani, M. Nose, M. Oda, *J. Am. Chem. Soc.* **1988**, *110*, 8494–8500.

[17] The trimethylsilyl group of **14** was selectively removed with methanolic K_2CO_3 to give the terminal alkyne, which was then oxidatively coupled[10] to give **13** as a colorless solid.

[18] Vinyl triflate **6** was coupled with 1,10-undecadiyne to give the tethered bis-enediyne **16**. Protodesilylation of **16** gave the terminal alkynes, which were then oxidatively coupled[10] to give **15** as a white solid.

A New Radical Vinylation Reaction of Iodides and Dithiocarbonates[**]

Frédérique Bertrand, Béatrice Quiclet-Sire, and
Samir Z. Zard[*]

Aryl and vinyl halides can be coupled to vinylic or acetylenic groups by a number of reactions mediated by transition metals, particularly palladium.[1] In contrast, the analogous direct reaction with aliphatic halides is much more limited and remains a challenge in organic synthesis.[1e] Recently, an attempt to fill this gap was reported by Bräse, Waegell, and de Meijere,[2] but the scope of their study remains limited to bromoadamantane so far. Radical arylations and vinylations are more useful,[3] especially when such groups are delivered internally. Intermolecular addition–elimination is more sensitive to competing side reactions but can

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