Cyclic alkynes–electronic behaviour as a function of ring strain

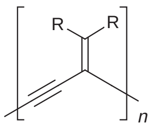
Rik R. Tykwinski

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2.
E-mail: rik.tykwinski@ualberta.ca

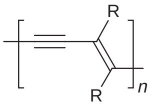
Received (in Corvallis, OR, USA) 2nd February 1999, Accepted 2nd April 1999

UV/Vis spectroscopic analysis of a series of cross-conjugated enediyne macrocycles as a function of increasing ring strain and planarity shows little effect on the electronic absorptions of the macrocycles, despite an obvious rehybridization of the alkylidene carbon atoms as evidenced by ^{13}C NMR spectroscopy.

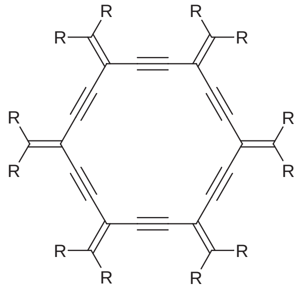
Conjugated organic compounds have considerable potential as materials for electronics and photonics.[1] We are interested in the electronic characteristics of cross-conjugated oligomers such as *iso*-polydiacetylenes (*iso*-PDAs, **1**)[2] and the comparison of their properties to the more prevalently studied compounds, *e.g.* polydiacetylenes **2**, that contain linear conjugation.[3] In the course of investigating the effects of cross conjugation in the cyclic analogues of **1**, namely radialenes **3** and **4**,[4] it became necessary to evaluate the influence of ring strain on the electronic absorption behavior of these molecules.[5–11] Reported herein is the synthesis of a novel series of cross-conjugated, enyne macrocycles[4,12–14] (cyclic expanded dendralenes)[15] and their UV/Vis absorption characteristics as a function of ring strain and planarity.



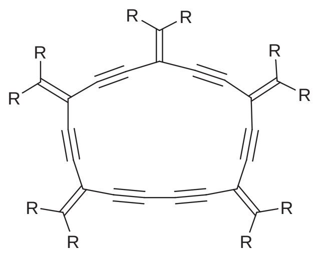
1



2



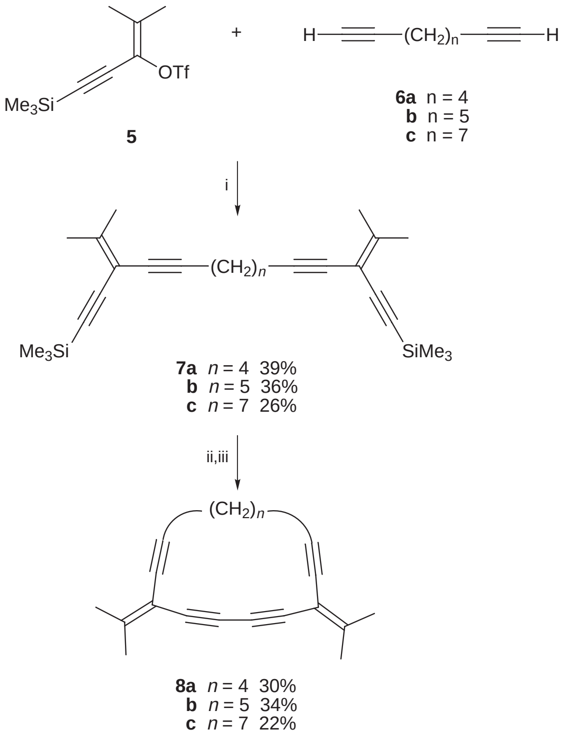
3



4

The macrocyclic enynes **8a–c** were constructed as outlined in Scheme 1. Vinyl triflate **5** (2.2 equiv.)[16] was coupled with the commercially available diynes **6a**,**b** and **6c**[17] in DMF in the presence of Et_2NH, CuI and $Pd(PPh_3)_4$.[2] The coupling process proceeded rapidly at room temperature as monitored by TLC, and column chromatography (silica gel, hexanes–CH_2Cl_2 20:1) afforded fair yields of tethered enediynes **7a–c**.† Compounds **7a-c** were protodesilylated with K_2CO_3 in MeOH–THF (1 : 1) for 2–3 h to afford the terminal alkynes. The desilylation was essentially quantitative, and (following aqueous work-up) the products were immediately carried on to the next step. Oxidative acetylenic coupling of the respective terminal alkynes of **7a–c** was conducted in CH_2Cl_2 (*ca.* 0.001 M) in the presence of CuI and TMEDA.[18] Under these relatively dilute conditions, the coupling reactions were complete in *ca.* 4–5 h. Macrocycles **8a–c** were isolated in modest yields as white solids by column chromatography (SiO_2, hexanes–CH_2Cl_2 4:1).‡ Oligomers resulting from intermolecular oxidative coupling of the acetylenic precursors were observed as the major side-products. Unfortunately, this intermolecular coupling process effectively competed with intramolecular cyclization despite the use of increasingly dilute reaction conditions. The isolated macrocycles are thermally stable, and even the highly strained **8a** was stable as a crystalline solid to well above 100 °C. Under ambient conditions in the presence of oxygen, all cycles slowly decompose over a period of days. They can, however, be stored under refrigeration for months with minimal decomposition.

The structure of the most strained cyclic dendralene **8a** was confirmed by X-ray crystallographic analysis of a single crystal grown by diffusion of MeOH into a $CHCl_3$ solution at 4 °C.§ An ORTEP drawing of **8a** is shown in Fig. 1, and, interestingly, it shows that in the solid state this molecule is not C_2 symmetrical as might be expected. Whereas all of the alkyne moieties are strained, with angles much smaller than an ideal 180°, the angles of enediyne segment C(4)–C(5)–C(6)–C(7)–C(8) bear the majority of this strain with C(4)–C(5)–C(6) bent to just over 160°. The conjugated enyne portion of macrocycle **8a** is only slightly twisted from planarity, with a torsion angle between C(14)–C(13) • • • C(7)–C(8) of 3°. The enediyne bond angles C(14)–C(1)–C(2) and C(5)–C(6)–C(7) at *ca.* 111 and 108° are both smaller than the analogous angles of an acyclic *iso*-PDA at *ca.* 115°.[2] Despite the strained nature of macrocycle **8a**, there are no anomalous bond lengths when compared to the *iso*-PDA. The crystal structure of **8a** provides a quite remarkable example of the significant ability of packing forces to distort molecular structure in the solid state as compared to solution.¶



Scheme 1 *Reagents and conditions*: i, $Pd(PPh_3)_4$, CuI, Et_2NH, DMF, rt; ii, K_2CO_3, MeOH–THF; iii, CuI, TMEDA, O_2, CH_2Cl_2.

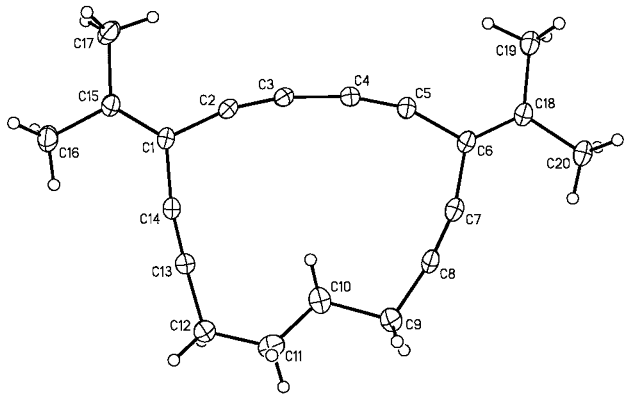


Fig. 1 X-Ray crystal structure of **8a**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.439(5), C(2)–C(3) 1.196(5), C(3)–C(4) 1.378(5), C(4)–C(5) 1.207(5), C(5)–C(6) 1.433(5), C(6)–C(7) 1.444(6), C(7)–C(8) 1.188(5), C(13)–C(14) 1.180(5), C(1)–C(15) 1.337(5), C(6)–C(18) 1.341(5); C(1)–C(2)–C(3) 166.5(4), C(2)–C(3)–C(4) 169.0(4), C(3)–C(4)–C(5) 168.3(4), C(4)–C(5)–C(6) 161.6(4), C(5)–C(6)–C(7) 108.4(3), C(6)–C(7)–C(8) 165.4(4), C(7)–C(8)–C(9) 170.5(4), C(12)–C(13)–C(14) 176.6(5), C(1)–C(13)–C(14) 171.0(4), C(2)–C(1)–C(14) 110.9(3).

The ^{1}H and ^{13}C NMR spectra of macrocycles **8a-c** are completely consistent with their macrocyclic structures. Particularly interesting are the shifts of the alkylidene carbons. As the size of the macrocycle is decreased from 17 to 15 to 14 carbons in **8c**, **8b** and **8a**, respectively, a consistent shift is observed for the ^{13}C resonances of the olefinic carbons. The ^{13}C resonance of the endocyclic vinylidene carbon of **8c**, representing that of an unstrained system, is found at δ 82, whereas the analogous ^{13}C resonances of **8b** and **8a** are deshielded to δ 88 and 90, respectively. These shifts likely result from rehybridization effects as bond angle deformation imparts greater p character to the σ-bonds of the ring and, consequently, more s character to the olefin. The chemical shifts of the exocyclic vinylidene carbons, affected to a lesser extent, are consistently shifted upfield from δ 151 in **8c** to δ 149 and 147 for **8b** and **8a**, respectively. These ^{13}C resonances clearly reflect the expected rehybridization of the ring carbons as a function of decreased bond angles and increased ring strain.[12,19]

The UV/Vis spectra of the new macrocycles **8a-c** were examined to determine if the varied hybridization of the ring carbons affected the electronic absorption characteristics. In addition, the increased rigidity and enforced planarity as the ring size is decreased could also influence the respective electronic absorptions as observed previously for radialenes.[20] Unexpectedly, the electronic absorption spectra for **8a-c** (Fig. 2) show no variation in energy of the lowest energy electronic absorptions. These absorptions, presumably arising from the linearly conjugated dienediyne segment of each macrocycle, are observed at virtually identical values of 290, 309 and 329 nm. The absorption peaks do, however, gradually broaden as the ring size, and hence flexibility, is increased from 14 to 15 to 17 carbons. The absence of electronic absorption changes between *e.g.* **8a** and **8c** also suggests little or no contribution to π-electron delocalization *via* homoconjugation, as might be anticipated from the constricted ring size that forces the in-plane acetylenic sp orbitals to closer spatial proximity.[21]

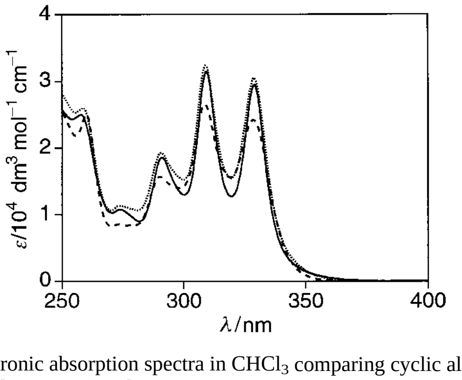


Fig. 2 Electronic absorption spectra in $CHCl_3$ comparing cyclic alkynes **8a** (———), **8b** (• • • • •) and **8c** (– – – – –).

The syntheses of more strained derivatives of **8** (n = 2, 3) are currently being pursued, as is the analogous series of macrocycles containing the ene-yne-ene segment of **3**. Together, these additional analogues will further detail the influence of ring strain on π-electron delocalization.

This work was supported by a Gen-Science Endowment from the University of Alberta and by NSERC of Canada. I thank Dr R. McDonald for the X-ray structural determination of **8a**.

Notes and references

† The purity and structures of all new compounds were confirmed by ^{1}H and ^{13}C NMR, IR, UV, MS and either EA or HRMS.

‡ *Selected data* for **8a**: white solid, mp 129–130 °C; ν(solid)/cm^{-1} 2905, 2214, 2192, 2118, 1618, 1334; δ_H(300 MHz, $CDCl_3$) 2.35 (4 H, m), 1.91 (6 H, s), 1.89 (6 H, s), 1.74 (4 H, AA'BB'); δ_C(75.5 MHz, $CDCl_3$) 146.9, 102.8, 94.6, 90.4, 80.7, 80.0, 29.2, 22.9, 22.2, 19.9; λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 329 (29 500), 309 (31 500), 290 (18 600), 275 (10 700), 258 (25 000) [Calc. for ($C_{20}H_{20}$): 260.1565. Found 260.1564]. For **8b**: white solid, mp 168 °C; ν(solid)/cm^{-1} 2905, 2215, 2130, 1617, 1349; δ_H(300 MHz, $CDCl_3$) 2.42 (4 H, t, J 5.6), 1.92 (6 H, s), 1.89 (6 H, s), 1.70 (2 H, m), 1.54 (4 H, m); δ_C(125 MHz, $CDCl_3$) 148.5, 102.2, 93.7, 88.4, 79.5, 78.2, 29.8, 28.9, 22.9, 22.2, 19.9; λ_{max}($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 329 (30 500), 309 (32 400), 291 (19 300), 275 (11 300), 259 (26 000) [Calc. for ($C_{21}H_{22}$): 274.1722. Found: 274.1726]. For **8c**: see ref. 4.

§ *Crystal data* for **8a**: $C_{20}H_{20}$, M = 260.4, monoclinic ,space group $P2_1/c$ (No. 14), D_c = 1.079 g cm^{-3}, Z = 4, a = 9.2119(8), b = 12.5305(12), c = 14.5747(10) Å, b = 107.744(7)°, V = 1602(2) Å^3, μ = 0.061 mm^{-1}. Final $R(F)$ = 0.076, $wR_2(F^2)$ = 0.20 for 185 variables and 2814 data with $F_o^2 \geq -3\sigma(F_o^2)$ (1399 observations [$F_o^2 \geq 2\sigma(F_o^2)$]. CCDC 182/1213. See http://www.rsc.org/suppdata/cc/1999/905/ for crystallographic files in .cif format.

¶ No evidence of symmetry distortion was observed in solution on the time scale of NMR analysis.

1 *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*, ed. W. R. Salaneck, I. Lundström and B. Rånby, OUP, Oxford, 1993.
2 Y. Zhao and R. R. Tykwinski, *J. Am. Chem. Soc.*, 1999, **121**, 458.
3 *Polydiacetylenes*, ed. D. Bloor and R. R. Chance, Martinus Nijhoff, Dordrecht, 1985.
4 S. Eisler and R. R. Tykwinski, *Angew. Chem.*, in the press.
5 W. Sander, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1455.
6 H. Meier, N. Hanold, T. Molz, H. J. Bissinger, H. Kolshorn, and J. Zountsas, *Tetrahedron*, 1986, **42**, 1711.
7 G. Maas and H. Hopf, in *The Chemistry of Dienes and Polyenes*, ed. Z. Rappoport, Wiley, Chichester, 1997, pp. 927–977.
8 A. Krebs and J. Wilke, *Top. Curr. Chem.*, 1983, **109**, 189.
9 R. Gleiter and W. Schäfer, in *The Chemistry of Triple-Bonded Functional Groups: Supplement C2*, ed. S. Patai, Wiley, Chichester, 1994, pp. 153–189.
10 R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 27.
11 R. Gleiter and R. Merger, in *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995, pp. 285–319.
12 J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, P. Seiler, C. B. Knobler and F. Diederich, *Helv. Chim. Acta*, 1995, **78**, 797.
13 R. Faust, F. Diederich, V. Gramlich and P. Seiler, *Chem. Eur. J.*, 1995, **1**, 111.
14 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 and H. Ringsdorf, *Adv. Mater.*, 1997, **9**, 339.
15 H. Hopf, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 948.
16 P. J. Stang and T. E. Fisk, *Synthesis*, 1979, 438-440.
17 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1988.
18 A. S. Hay, *J. Org. Chem.*, 1962, **27**, 3320.
19 H. N. C. Wong and F. Sondheimer, *Tetrahedron*, 1981, **37**, W99.
20 H. Hopf and G. Maas, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 931.

[21] A change in absorption energy as a result of angle deformation would also be expected for the in-plane π-system of the central butadiyne moiety of **8a-c**, as has been previously shown for cycloalkynes (ref. 8). Whereas absorptions are observed in the expected region of the butadiyne segment (*ca.* 250–275 nm) of **8a-c**, interpretation of shifts is, at this point, inconclusive. The expected absorption range of 250–275 nm is based on the lowest energy absorptions of known butadiyne derivatives, see: J. B. Armitage and M. C. Whiting, *J. Chem. Soc.*, 1952, 2005. I thank one of the reviewers for helpful suggestions.

Communication 9/00910H