

The phenylenes

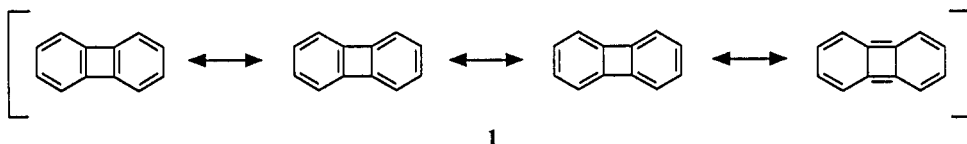
K. Peter C. Vollhardt

Department of Chemistry, University of California at Berkeley, and the Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, U.S.A.

Abstract - Exploration of the synthesis and chemistry of a new class of hydrocarbons is described, the "phenylenes", composed of alternating fused benzene and cyclobutadiene rings. Related structures include extended *sp*-carbon nets and heterocyclic analogs. These molecules are of great theoretical and potentially practical interest in the search for novel molecules that may exhibit (super)conductive behavior. Their unique topology makes them also excellent candidates as precursors to novel (hydro)carbon cages and related assemblies. Facile access to these compounds is made possible by the application of transition metal catalysis.

INTRODUCTION

Aromaticity is one of the fundamental concepts of organic chemistry (ref. 1), its essence epitomized by Hückel's rule (ref. 2). Pivotal in the attempts to understand the behavior of cyclic conjugated π -systems has been the juxtaposition between *the* aromatic molecule par excellence, benzene, and its antiaromatic (ref. 3) counterpart, cyclobutadiene. In the words of Maier (ref. 4), "benzene and cyclobutadiene are worlds apart," and therefore organic molecules containing both fragments are of special importance in efforts aimed at understanding the basic features associated with π -conjugation. Prior to the work described here, the only simple stable molecule on which to probe these matters was biphenylene (**1**) (ref. 1).



In a nutshell, this molecule combines the properties of the component rings, revealing physical and chemical characteristics reflecting both antiaromaticity and aromaticity, in addition to those related to the ring strain inherent in its topology. The interpretations of these data has been controversial, particularly in light of recent developments that pinpoint the σ -frame in benzene as being responsible for its symmetry and, ultimately, its "aromatic" behavior (ref. 4). Not surprising, therefore, is the degree of scrutiny to which **1**, its benzoderivatives, and its higher and lower "homologs" have been subjected (ref. 1,5). Notably absent from the literature have been until recently the simple benzocyclobutadienologs of **1**, for which we have coined the term [*N*]phenylenes where *N* denotes the number of benzene rings. Examples are found in the series of linear and angular phenylenes **2** and **3**.



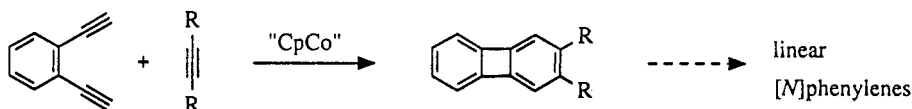
Activated molecules of this nature are important fundamentally, because their study sheds light on the limits of chemical bonding to carbon, and, in a more practical vein, because they are protagonists in current efforts directed toward the elucidation of the mechanism(s) of carcinogenesis by polycyclic benzenoid hydrocarbons (ref. 6), the activation of benzene and related petroleum and coal-derived

compounds as a source of industrial raw materials (ref. 7), and the development of organic electroactive materials, such as potential conductors, ferromagnets, memory storage devices, etc. (ref. 8). Connected with these topics is the anticipated novel organometallic chemistry of the strained and electronically reactive π -framework. Finally, the direct connections of the component benzene rings might be exploited in the assembly of the shortest "spacer" analogs of the corresponding acenes, a facet that has already been put to use in the synthesis of biphenylene-bridged porphyrins (ref. 9).

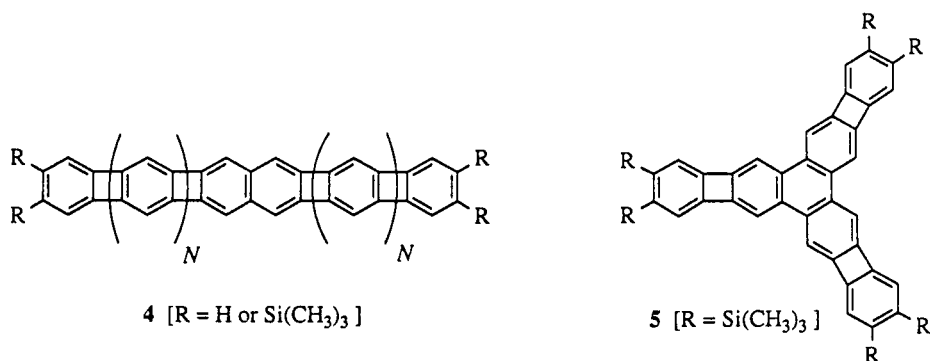
RESULTS AND DISCUSSION

The reason for the original dearth of information on this class of compounds was the absence of viable and general synthetic methods for their construction. This state of affairs has been drastically altered by our discovery that $\eta^5\text{-C}_5\text{H}_5\text{CoL}_2$ ($\text{L} = \text{CO}, \text{CH}_2\text{CH}_2$) catalyzes the cocyclization of σ -diethynylarenes with alkynes to furnish biphenylenes (Scheme I) (ref. 10).

Scheme I

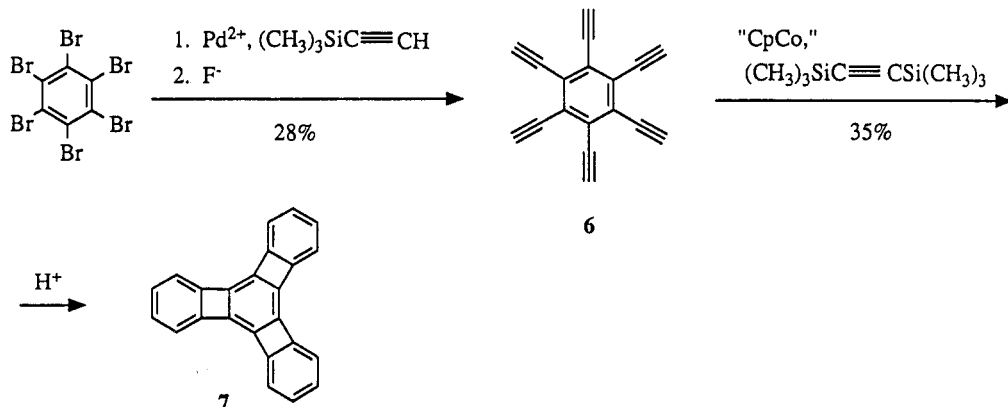


As the requisite alkynylarenes are readily prepared from the corresponding haloarenes by Pd-catalyzed alkylation and because R (Scheme I), when equal to $\text{Si}(\text{CH}_3)_3$, can function as a masked halogen, the method lends itself to an iterative protocol providing access to the higher linear phenylenes, up to $N = 5$ (ref. 10,11). Dramatic improvements in convergence are achieved by utilizing "bidirectional" multicyclizations (involving 1,2,4,5-tetraethynylbenzene or 2,3,6,7-tetraethynylbiphenylene) in conjunction with the regioselective cooligomerization of 1,6-bis(triisopropylsilyl)-1,3,5-hexatriyne (ref. 11a,b). Extension of this strategy has allowed the assembly of the two "phenylenonaphthalenes" **4** ($N = 0$ and 1) (ref. 12) and the triangular derivative **5**

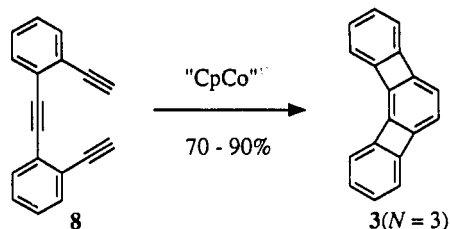


(ref. 13), the latter endowed with a topology that, on further elaboration, holds promise in ferromagnetic applications (ref. 14). Along these lines, most striking has been the synthesis of **7** (ref. 15) via hexaethynylbenzene **6** (ref. 16). The 30π system **6** is of separate intrinsic interest (Scheme II).

Scheme II



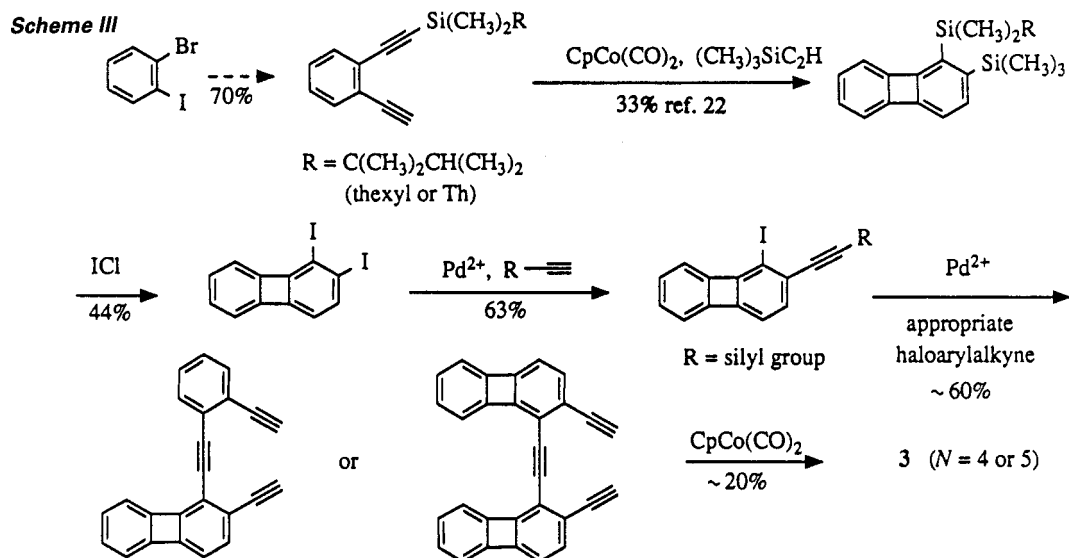
Indications that the angular series may be tackled synthetically were provided by the successful isomerization of **8** to **3** ($N = 3$), remarkable because of the extraordinary degree of strain (~ 110 kcal mol⁻¹), that is introduced in this step (ref. 17). Finally, Ni(O) catalyzes the efficient conversion of a number of the systems (made by the Pd-Co-"tandem catalysis" route outlined above) to the corresponding tetrabenzocyclooctatetraenes, opening yet other avenues towards hitherto inaccessible frameworks (ref. 18).



The phenylenes have shown the anticipated unprecedented physical and chemical behavior. Preliminary (and some more extensive, especially in the case of **2**, $N = 3$) investigations have ranged from calculations to X-ray analyses, electrochemistry, stoichiometric redox behavior (to give the corresponding dianions and dications), organometallic transformations, catalytic hydrogenations, and some thermal and photochemical reactions (ref. 4,10-13,15-19).

Of the linear systems, the parent **2** ($N = 3$) and silylated derivatives of **2** ($N = 4,5$) have been made (ref. 10,11). Most notable along the series **2** ($N = 2-5$) is the increasing air-sensitivity, the increasing tenacity with which the π -system binds to CpCo (via the innermost cyclobutadiene units), the relatively large (yet decreasing) incremental bathochromic shift of the highest-wavelength electronic absorptions ($363 \rightarrow 432 \rightarrow 492 \rightarrow 530$ nm), and the regularly decreasing chemical shift for the innermost benzene hydrogens [$\Delta\delta \sim 0.35$ ppm; $\delta(\text{C}_6\text{D}_6)$ for these nuclei in 2,3,9,10-tetrakis(trimethylsilyl)[5]phenylene **9**: 5.56 ppm; c.f. the corresponding absorption in benzocyclobutadiene: $\delta(\text{CD}_3\text{CN}) = 5.75$ ppm (ref. 20)]. These properties are consistent with increasing paratropic character, a rapidly diminishing HOMO-LUMO gap, and consequently with the presence of an increasingly activated π -system, as confirmed recently by theory (ref. 21). They also show that Hückel's rule (note that the series is alternating in the "Hückel-sense") is inapplicable.

Turning to the angular isomers of **3**, the series has been completed up to $N = 5$, through the expedient exploitation of Co, Pd, and Si, in what amounts to a "stitching-iterative" strategy. Scheme III depicts the syntheses of angular [4]- and [5]phenylene.



Remarkably in light of the published theoretical data (ref. 21) and in comparison to the linear series, the angular systems appear considerably less sensitive (air, CpCo, H₂-cat (ref. 17)), show much attenuated bathochromic UV shifts [longest wavelength band for biphenylene and **3** ($N = 3,4,5$): 363, 428, 448, 470], and, perhaps most significantly, reveal increasing *deshielding* of the "inside" aromatic hydrogens [**3** ($N = 3,4,5$): $\delta(\text{CD}_2\text{Cl}_2)$ 6.176, 6.312 (isochronous), 6.511]. Our (currently tentative)

interpretation of the data proposes that these molecules maximize local aromatic (benzenic) circuits at the expense of generating (a minimum) of cyclohexatrienic moieties [e.g. **3** ($N = 5$) would thus be best described as composed of three "aromatic" benzenes at the termini and at the center, the remaining two suffering bond fixation]. Nevertheless, theory suggests the series to be destabilized relative to **2**! Clearly, much work needs to be done to understand the behavior of these hydrocarbons.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract DE-AC03-76SF00098 and (in part) by the National Science Foundation (CHE-9202152).

REFERENCES

1. P. Garratt and K.P.C. Vollhardt, *Aromatizität*, Thieme Verlag, Stuttgart (1973). D. Lloyd, *The Chemistry of Conjugated Cyclic Compounds*, Wiley, New York (1989).
2. E. Hückel, *Grundzüge der Theorie Ungesättigter und Aromatischer Verbindungen*, Verlag Chemie, Berlin (1938).
3. R. Breslow, *Acc. Chem. Res.* **6**, 393 (1973).
4. See: A. Stanger and K.P.C. Vollhardt, *J. Org. Chem.* **53**, 4889 (1988). K. Jug and A.M. Köster, *J. Am. Chem. Soc.* **112**, 6772 (1990).
5. K.P.C. Vollhardt, *Top. Curr. Chem.* **59**, 113 (1975).
6. See: R.G. Harvey, Ed., *Polycyclic Hydrocarbons and Carcinogenesis*, ACS Monograph 283, American Chemical Society, Washington, D.C. (1985). T. Vo-Dinh, Ed., *Chemical Analysis of Polycyclic Aromatic Compounds*, Wiley, New York (1989).
7. P.H. Spitz, *Petrochemicals*, Wiley, New York (1988). J. Falbe, *Chemierohstoffe aus Kohle*, Thieme, Stuttgart (1977).
8. See: *Isr. J. Chem.* **27**, issue 4 (1986). T.J. Skotheim, Ed., *Handbook of Conducting Polymers*, Marcel Dekker, New York (1956); Vols. 1 and 2. M. Emmelius, G. Pawlowski and H.W. Vollmann, *Angew. Chem., Int. Ed. Engl.* **28**, 1445 (1989). For a recent study of immediate relevance: R. Schenk, H. Gregorius, R. Meerholz, J. Heinze and K. Müllen, *J. Am. Chem. Soc.* **113**, 2634 (1991). See also: Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.* **27**, 1633 (1988). D.J. Sagl and J.C. Martin, *J. Am. Chem. Soc.* **110**, 5827 (1988). L.Y. Chiang, D.C. Johnston, D.P. Goshorn and A.N. Bloch, *J. Am. Chem. Soc.* **111**, 1925 (1989). D.A. Dixon, J.C. Calabrese and J.S. Miller, *Angew. Chem., Int. Ed. Engl.* **28**, 90 (1989). D.A. Dixon, J.C. Calabrese, R.L. Harlow and J.S. Miller, *Angew. Chem., Int. Ed. Engl.* **28**, 92 (1989).
9. A. Osuka and K. Maruyama, *J. Am. Chem. Soc.* **110**, 4454 (1988). J.P. Collman, J.E. Hutchison, M.A. Lopez, R. Guilard and R.A. Reed, *J. Am. Chem. Soc.* **113**, 2794 (1991). J.P. Fillers, K.G. Ravichandran, I. Abdalmuhdi, A. Tulinsky and C.K. Chang, *J. Am. Chem. Soc.* **108**, 417 (1986). See also: P.W. Kenny and L.L. Miller, *J. Chem. Soc., Chem. Commun.* **84** (1984).
10. B.C. Berris, G.H. Hovakeemian, Y.-H. Lai, H. Mestdagh and K.P.C. Vollhardt, *J. Am. Chem. Soc.* **107**, 5670 (1985).
11. (a) M. Hirthammer and K.P.C. Vollhardt, *J. Am. Chem. Soc.* **108**, 2481 (1986). (b) L. Blanco, H.E. Helson, M. Hirthammer, H. Mestdagh, S. Spyroudis and K.P.C. Vollhardt, *Angew. Chem., Int. Ed. Engl.* **26**, 1246 (1987). (c) A low-yielding, limited approach to both linear and angular [3]phenylene (only) based on flash-pyrolytical techniques was developed independent of our strategy: J.W. Barton and R.B. Walker, *Tetrahedron Lett.* **1005** (1978). J.W. Barton and D.J. Rowe, *Tetrahedron Lett.* **24**, 299 (1983).
12. H.E. Helson, K.P.C. Vollhardt and Z.-Y. Yang, *Angew. Chem., Int. Ed. Engl.* **24**, 114 (1985).
13. K.P.C. Vollhardt, *Angew. Chem., Int. Ed. Engl.* **23**, 539 (1984).
14. R. Breslow, *Pure Appl. Chem.* **54**, 927 (1982). T.J. LePage and R. Breslow, *J. Am. Chem. Soc.* **109**, 6412 (1987). J.S. Miller, D.A. Dixon, J.C. Calabrese, C. Vazquez, P.J. Krusic, M.D. Ward, E. Wasserman and R.L. Harlow, *J. Am. Chem. Soc.* **112**, 381 (1990).
15. R. Diercks and K.P.C. Vollhardt, *J. Am. Chem. Soc.* **108**, 3150 (1986).
16. R. Diercks, J.C. Armstrong, R. Boese and K.P.C. Vollhardt, *Angew. Chem., Int. Ed. Engl.* **25**, 268 (1986).
17. R. Diercks and K.P.C. Vollhardt, *Angew. Chem., Int. Ed. Engl.* **25**, 266 (1986).
18. H. Schwager, S. Spyroudis and K.P.C. Vollhardt, *J. Organomet. Chem.* **382**, 191 (1990).
19. For most recent results, see: D.L. Mohler, K.P.C. Vollhardt and S. Wolff, *Angew. Chem., Int. Ed. Engl.* **29**, 1151 (1990).
20. W.S. Trahanovsky and D.R. Fischer, *J. Am. Chem. Soc.* **112**, 4971 (1990).
21. N. Trinajstić, T.G. Schmalz, T.P. Zivković, S. Nikolic, G.E. Hite, D.J. Klein and W.A. Seitz, *New J. Chem.* **15**, 27 (1991).
22. We have observed precedence for this regioselectivity: R.L. Hillard III and K.P.C. Vollhardt, *J. Am. Chem. Soc.* **99**, 4058 (1977).