

Prospecting for a 5-Center 4-Electron (C - - H - - C - - H - - C)⁺ Bonding Array

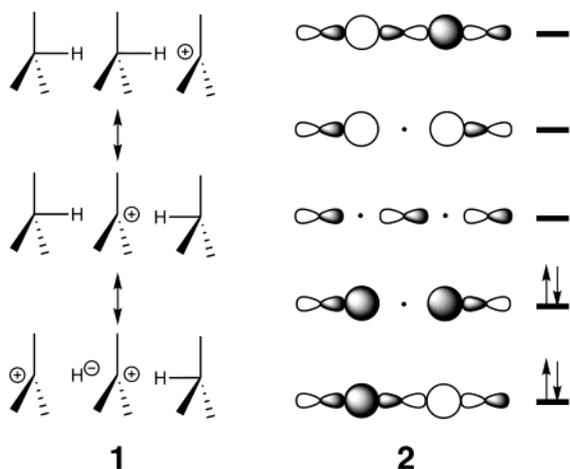
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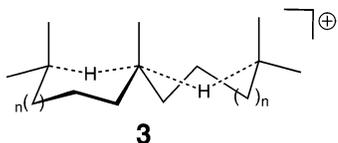
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Can a hydrocarbon with a 5-center 4-electron bonding array exist? Acyclic electron-deficient bonding arrays of the 3-center 2-electron C - - H - - C variety are well-precedented in hydrocarbon chemistry,¹ but whether σ -delocalization can be extended over larger arrays is not yet known.

Linear 5-center 4-electron C - - H - - C - - H - - C bonding arrays can be described as hybrids of classical resonance structures, such as those shown in **1**, which delocalize positive charge throughout the array. The molecular orbital description of these structures (using a simple basis set that consists of a p-orbital on each carbon and an s-orbital on each hydrogen) is shown in **2**. All four electrons reside in bonding orbitals, but whether delocalization prevails will depend on how favorable localized alternatives are.

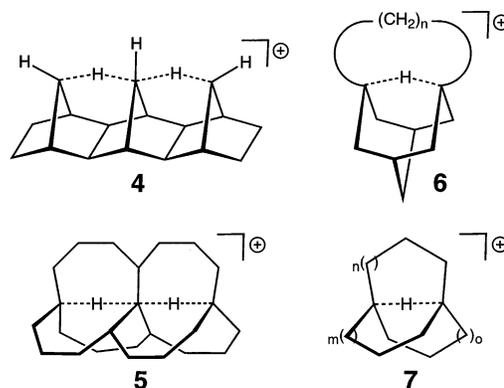


Initially we surveyed (via calculations at the B3LYP/6-31G(d) level²) a number of potential support structures based on helical backbones, as shown in **3**. These were inspired by our previous investigations on helical sigmatropic shiftamers—systems with exceptionally expressed delocalization in their transition structures.³ In short, we were unable, unfortunately, to locate minima for any of these systems which contained the desired delocalized 5-center array.



Additional frameworks (for example, **4** and **5**)—inspired by structures that had previously been shown to support acyclic 3-center 2-electron arrays (**6** and **7**)¹—were also explored. Again, no minima with truly delocalized 5-center C - - H - - C - - H - - C arrays were found. Structure **4** relaxed to a localized structure with a central secondary cation and two 1.1 Å C—H bonds pointing toward it, but with their hydrogens 2.1 Å away from the cationic center. Structure **5** relaxed to an interesting asymmetric structure

with four different C—H distances in the C - - H - - C - - H - - C array (1.2, 1.5, 2.3, and 1.1 Å, in that order), resembling a 3-center 2-electron array aligned with a localized C—H bond.



Hoping that stricter geometric constraints might encourage formation of a symmetrical, delocalized array, we explored relatives of **5** with rigid, unsaturated bridges. Gratifyingly, cation **8** (Figure 1), derived from three anthracenes “joined up” around a C - - H - - C - - H - - C core,⁴ turned out to possess a 5-center 4-electron array with four short C - - H distances (the geometrical features of this core are highlighted in **8'**, Figure 1). This remarkable structure contains two approximately trigonal pyramidal carbons and one five-coordinate trigonal bipyramidal carbon!⁵ Although isomers with one or two localized C—H bonds pointing “out” from the termini instead of “in” toward the central carbon are thermodynamically more stable (by ~20 and ~30 kcal/mol, respectively), we believe that cation **8** may still display some measure of kinetic stability; note that the ends of the 5-center array are sterically shielded, by C—H bonds of the anthracenes, from external attack.

¹H and ¹³C NMR chemical shifts were also computed as a measure of the electron density around the atoms in the delocalized array of **8** (Figure 1).⁶ Experimentally determined chemical shifts were used previously in characterizing the structures of delocalized cations such as **6** and **7**;¹ in general, experimental shifts for bridging H's range from -7 to -3 ppm (shifts computed with B3LYP range from -7 to -4), and shifts for the carbons that flank them range from +135 to +180 ppm (computed shifts range from +150 to +200).¹ The computed chemical shifts for the hydrogens (+2.9 ppm) and the carbons (+112 and +182 ppm) of the 5-center array in cation **8** differ considerably, however, from those found in typical 3-center 2-electron systems. Nonetheless, we believe that these chemical shifts are still indicative of delocalization.

To probe this issue further, cation **8** was dissected into three pieces: two identical triphenylmethanes, each with the same geometry as the ends of **8** (**9**, Figure 2) and a trityl cation with the geometry of the central portion of **8** (**10**, Figure 2). Chemical shifts were computed for **9** and **10**, without allowing any geometric relaxation to occur.⁶ Clearly, the shifts in **9** and **10** are quite different

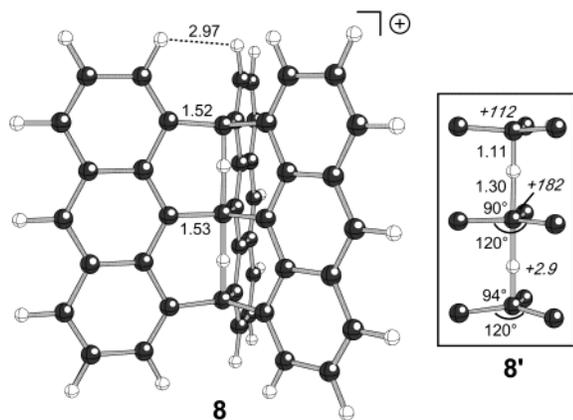


Figure 1. Optimized structure of 5-center 4-electron cation **8**, (with its core highlighted in **8'**). Selected distances (Å), angles (deg), and computed chemical shifts (ppm relative to TMS, italics) are shown.

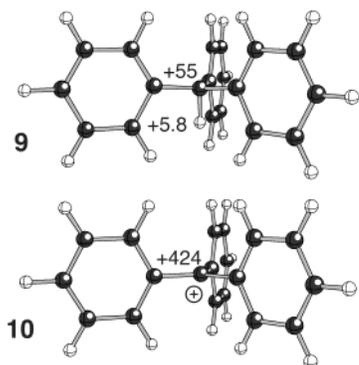


Figure 2. Computed chemical shifts (ppm relative to TMS) for structures derived from portions of **8**.

from those in **8**, indicating that there is substantial interaction between all five atoms of the electron-deficient array of **8**. Comparison of the shifts in **8**, **9**, and **10** indicates that the terminal carbons in **8** are in fact deshielded upon interaction with the central carbon, while this carbon is greatly shielded⁷—exactly what one would expect for a strong interaction of the type shown in **1** and **2**.

One additional feature of **8** warrants discussion: the fact that the terminal C—H distances in the 5-center array are 0.2 Å shorter than the central C—H distances. This variation in C—H distance is actually nicely accounted for by the simple orbital picture shown in **2**. The electron distribution in the two occupied MOs makes for stronger terminal bonds, much as one would have in a pentadienyl cation. In accord with this, an extended Hückel calculation on a hypothetical geometry with four equal C—H distances gave substantially larger overlap populations for the terminal C—H units.⁸

In conclusion, we have described a structure, cation **8**, that we predict will possess a delocalized 5-center 4-electron bonding array. We think this structure could be made.

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Supporting Information Available: Coordinates and low-frequency vibrational modes for structure **8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For leading references on the pioneering work of Sorensen and McMurry on *cyclic* 3-center 2-electron carbocations, see: McMurry, J. E.; Lectka,

T. *Acc. Chem. Res.* **1992**, *25*, 47–53. For general reviews that also describe *cyclic* 3-center 2-electron cations, see: Saunders, M.; Jimenez-Vazquez, H. A. *Chem. Rev.* **1991**, *91*, 375–397; Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426–431; Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432–440.

- (2) (a) All calculations were performed with GAUSSIAN 98, revision A.9: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Geometries were optimized without symmetry constraints at the B3LYP/6-31G(d) level (Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652; Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377; Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789; P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627). Several recent reports have discussed the use of B3LYP for computing geometries and energetics of 3-center 2-electron cations (Vrcek, I. V.; Vrcek, V.; Siehl, H.-U. *J. Phys. Chem. A* **2002**, *106*, 1604–1611 and Farcasiu, D.; Lukinskas, P.; Pamidighantam, S. V. *J. Phys. Chem. A* **2002**, *106*, 11672–11675). These papers suggest that B3LYP tends to underestimate the stability of delocalized structures relative to MP2, but that B3LYP gives comparable results to CCSD. (c) Structure **8** was characterized as a minimum by frequency calculations at the B3LYP/3-21G level (we are aware of the issues associated with using B3LYP/3-21G calculations to characterize the nature of this stationary point, but all attempts to perform frequency calculations on **8** with the larger 6-31G(d) basis set proved computationally unfeasible; we believe, on the basis of our experience with related systems, that B3LYP/6-31G(d) frequency calculations would also show **8** to be a true minimum).
- (3) Tantillo, D. J.; Hoffmann, R. *J. Am. Chem. Soc.* **2002**, *124*, 6836–6837.
- (4) (a) Related architectures have been proposed as supports for *o*-allyl cations, but the C—C distances in such systems appear to be too large to allow for direct carbon—carbon interaction. See, for example: Olson, L. P. *Org. Lett.* **2000**, *2*, 3059–3062 and Lipkowitz, K. B.; Larter, R. M.; Boyd, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 85–92. (b) For a discussion of hypothetical polyradicals built from similar triple acene architectures, see: Hoffmann, R.; Eisenstein, O.; Balaban, A. T. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5588–5592. (c) Another similar architecture, comprised of boron atoms and infinitely extended in one dimension, is found in the solid-state structure of U₅Mo₁₀B₂₄ and its relatives. See Merschrod, E. F.; Hoffmann, R. *Chem. Mater.* **1999**, *11*, 341–351 and references therein. We might ponder further extension of **8** towards an infinite one-dimensional polycation.
- (5) (a) A related 3-center 4-electron O—C—O cation, supported by a monoanthracene framework, also boasts a central trigonal bipyramidal carbon, in this case substituted by four oxygen atoms. See: Akiba, K.; Yamashita, M.; Yamamoto, Y.; Nagase, S. *J. Am. Chem. Soc.* **1999**, *121*, 10644–10645. (b) Trigonal bipyramidal carbons have also been found in some cases where a carbon atom is surrounded by five metals (such as Li or Au). See, for example: Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4275–4276 and Scherbaum, F.; Grohmann, A.; Müller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 463–465. (c) A variant of **8** with a simple saturated support system (three CH₂CH₂CH₂ units) has subsequently been shown to also boast a 5-center 4-electron array. P. v. R. Schleyer, personal communication, a “holiday gift” to us, 12/13/02.
- (6) (a) ¹H and ¹³C chemical shifts (relative to TMS) were computed at the GIAO-B3LYP/6-31G(d) level.² For a classic example of the use of computed chemical shifts in characterizing carbocation structures, see: Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300–301. (b) For leading references on the use of ¹³C chemical shifts as probes of electron density in carbocations, see: Forsyth, D. A.; Spear, R. J.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2512–2518. (c) In some cases, using absolute chemical shifts as a measure of local electron density can be a somewhat risky endeavor (See, for example: Bethell, D. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1978; Chapter 4, Vol. 1), but we believe that the risk is minimal in our case due to the fact that we are primarily interested in relative shifts for closely related structures.
- (7) For comparison, we compute a chemical shift of +191 ppm for the central carbon of fully relaxed trityl cation (the experimental value is +211 ppm; see: Ray, G. J.; Kurland, R. J.; Colter, A. K. *Tetrahedron* **1971**, *27*, 735–752; Abarca, B.; Asensio, G.; Ballesteros, R.; Varea, T. *J. Org. Chem.* **1991**, *56*, 3224–3229 and references therein) and a shift of +370 ppm for the carbon in naked methyl cation (all relative to TMS).
- (8) Extended Hückel calculations were performed with Greg Landrum’s Yet Another Extended Hückel Molecular Orbital Package (YAEHMOP), available through <http://sourceforge.net/projects/yaehmop/>.

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