JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Thermal Isomerizations of Diethynyl Cyclobutadienes and Implications for Fullerene Formation

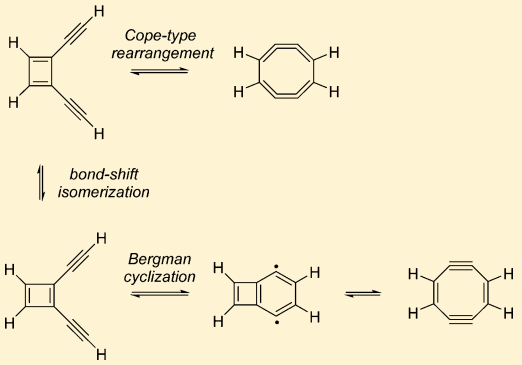
Brian J. Esselman,[†] Frank L. Emmert, III,[‡] Andrew J. Wiederhold,[†] Stephanie J. Thompson,[‡] Lyudmila V. Slipchenko,*[,‡] and Robert J. McMahon*[,†]

[†]Department of Chemistry, University of Wisconsin−Madison, 1101 University Avenue, Madison, Wisconsin 53706-1322, United States

[‡]Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907-2084, United States

Supporting Information

ABSTRACT: The mechanism by which carbon condenses to form PAHs or fullerenes is a problem that has garnered considerable theoretical and experimental attention. The ring-coalescence and annealing model for the formation of C_{60} involves a [2 + 2] cycloaddition reaction of a cyclopolyyne to form a tetraalkynyl cyclobuta-1,3-diene intermediate, followed by a Bergman cycloaromatization reaction of the enediyne moiety. Intramolecular trapping of the incipient *p*-benzyne diradical across a diyne moiety of the macrocyclic ring affords an aromatic ring that must undergo further intramolecular reactions via polyradical intermediates to produce a condensed graphitic structure or fullerene. Computational studies of a model system for the intriguing tetraalkynylcyclobuta-1,3-diene intermediate, however, reveal that the corresponding *p*-benzyne diradical lies in a shallow minimum with a very low barrier to ring opening to cyclooctadienediyne. This pathway has not been previously considered in the mechanism for carbon condensation.



INTRODUCTION

The chemical mechanism by which atomic carbon, or small carbon fragments, create graphitic sheets, fullerenes, and nanotubes is a problem of fundamental importance in science.[1] Considerable experimental and theoretical interest in this problem led to the development of chemical models for carbon condensation and fullerene formation: the *pentagon road*,[2] *fullerene road*,[3] *ring coalescence and annealing*,[4−6] *shrinking hot giant*,[7,8] and *closed network growth*.[9,10] Recent interest in the hexadehydro-Diels−Alder reaction (HDDA)[11,12] invites speculation concerning its possible role in fullerene formation.[13] In addition to these condensation models ("size-up"), pathways to fullerenes are envisioned from degradation of larger carbon molecules ("size-down") such as giant fullerenes,[7,8] carbon nanotubes,[14] graphene nanoflakes,[15] or graphene.[16] Among the various models, the *pentagon road*, *fullerene road*, *shrinking hot giant*, and *closed network growth* are dependent upon a steady supply of C_2 fragments to allow for sufficient carbon accretion. The *ring coalescence and annealing* model accommodates larger mass carbon sources than C_2 to produce C_{60}.

The lowest energy form of carbon changes as a function of size. Carbon exists in linear fragments at a small size (C_3−C_{12}), macrocyclic rings at a medium size (C_{12}−C_{20}), and graphitic or fullerene structures for larger carbon systems.[17−20] In the *ring coalescence and annealing* model, cyclic carbon molecules (cyclopolyynes) combine to form larger macrocyclic rings, which subsequently rearrange and anneal into graphitic structures and fullerenes (Scheme 1).[1] The proposed chemical mechanism involves a [2 + 2] cycloaddition reaction to form a tetraalkynyl cyclobuta-1,3-diene intermediate, followed by a Bergman cycloaromatization reaction of the enediyne moiety. Intramolecular trapping of the incipient *p*-benzyne diradical across a diyne moiety of the macrocyclic ring affords an aromatic ring that must undergo further intramolecular reactions via polyradical intermediates to produce a condensed graphitic structure or fullerene. Intrigued by the expectation of unusual electronic structure and bonding in the tetraalkynyl cyclobuta-1,3-diene moiety, and the manifestation of these factors in modulating the cycloaromatization reaction, we undertook a computational study of 1,2-diethynylcyclobuta-1,3-diene (**1**) as a model system for the intermediate in the *ring coalescence and annealing* model of fullerene formation.

COMPUTATIONAL METHODS

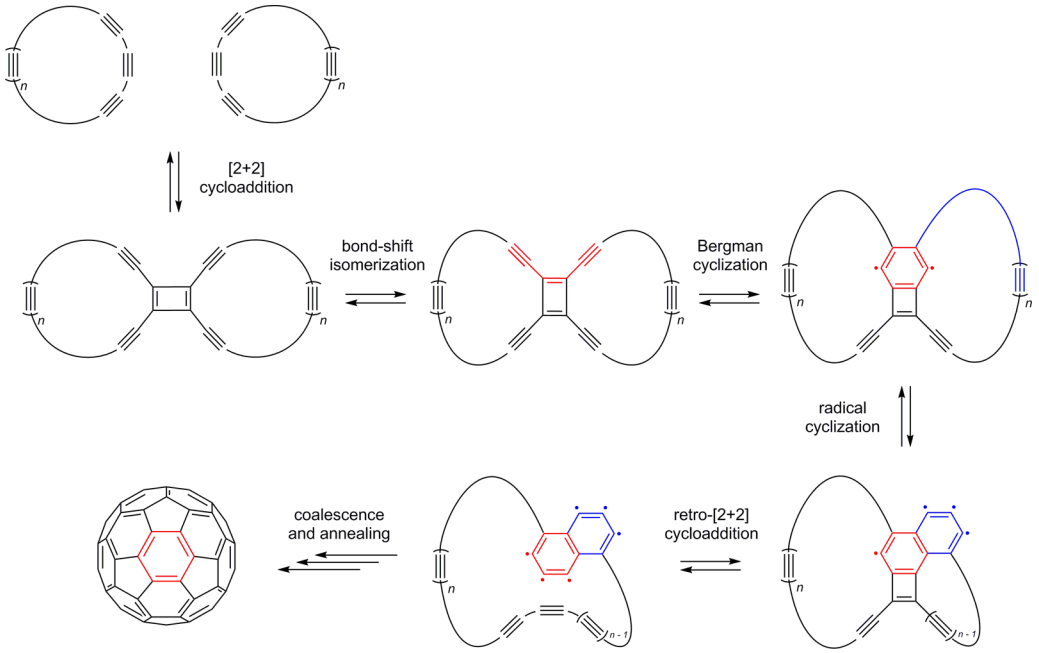
Geometry optimizations, transition-state searches, harmonic vibrational frequency calculations, and intrinsic reaction coordinate (IRC) calculations were performed using restricted second-order Møller−Plesset (MP2) perturbation theory with a correlation consistent basis set of triple-ζ quality (cc-pVTZ)[21] in the GAMESS[22,23] electronic structure package. Single-point energy calculations at the optimized MP2 structures and along the IRC pathway were performed using the

Special Issue: 50 Years and Counting: The Woodward-Hoffmann Rules in the 21st Century

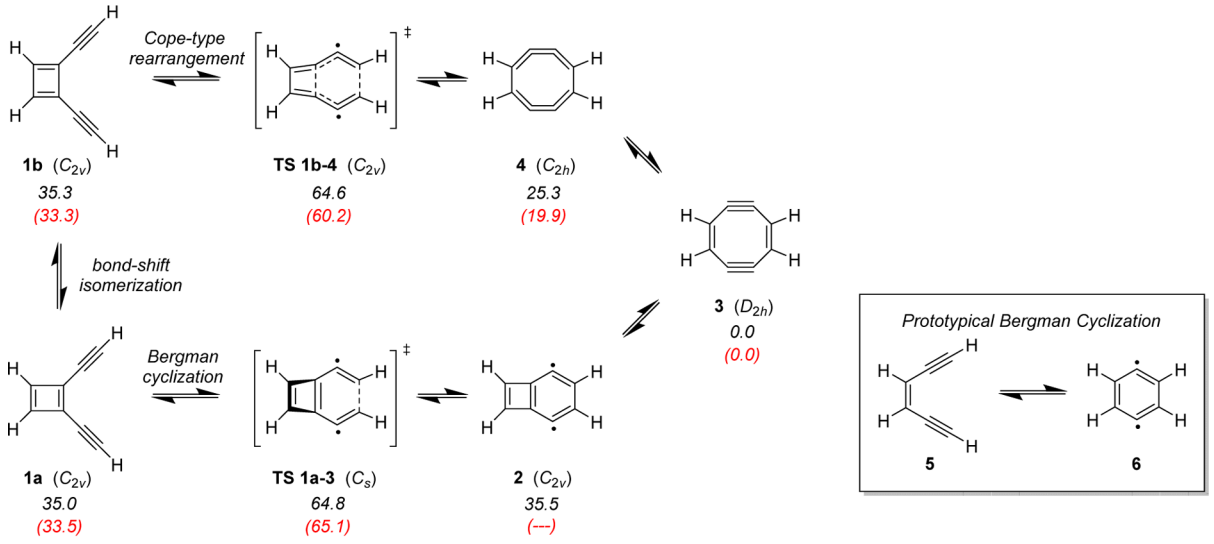
Received: August 11, 2015
Published: October 28, 2015

DOI: 10.1021/acs.joc.5b01864
J. Org. Chem. 2015, 80, 11863−11868

Scheme 1. Ring Coalescence and Annealing Model of Fullerene Formation



Scheme 2. Thermal Isomerization Pathways of 1,2-Diethynylcyclobuta-1,3-diene (1)[a]



[a]Relative energy (kcal/mol; ZPVE not included) CCSD(T)/cc-pVTZ//MP2/cc-pVTZ (B3LYP/6-31G(d) in parentheses).

spin-flip version[24−27] of the equation-of-motion coupled-cluster with single and double excitations method[28−31] (EOM-SF-CCSD) in the cc-pVDZ basis set (in the Q-Chem[32] electronic structure package) and using CCSD with perturbative triples[33] (CCSD(T)) in cc-pVTZ basis in GAMESS. Density Functional Theory calculations employed the B3LYP density functional[34,35] with the 6-31G(d)[36] basis set as implemented in Gaussian 09.[37]

RESULTS AND DISCUSSION

In the current investigation, we focus our attention on early steps in the *ring coalescence and annealing* model. Although strained alkynes are known to undergo [2 + 2] and [2 + 2 + 2] cycloaddition reactions,[38−44] the manifestation of these reactions in highly conjugated systems merits further scrutiny. The putative [2 + 2] dimerization product of a polyyne−a tetraalkynyl cyclobutadiene intermediate−represents an intriguing structure that may be expected to exhibit unusual characteristics with respect to both electronic structure and reactivity.[38,40,43] Organometallic complexes of alkynyl cyclobutadienes have been described,[45,46] but the free ligand has not been studied experimentally. We recently described computational studies concerning thermodynamic effects of ethynyl[47,48] and cyano[49] substitution of cyclobutadiene. We now describe theoretical studies of 1,2-diethynylcyclobuta-1,3-diene (**1**) and its thermal isomerization pathways (Scheme 2).[50,51] One pathway involves Bergman cyclization[52] and represents a model system for a key step in the *ring coalescence and annealing* model (Scheme 1). The second pathway involves a [3,3]-sigmatropic (Cope-type) rearrangement.[53−55] The activation barriers for these two pathways are remarkably similar.

DOI: 10.1021/acs.joc.5b01864
J. Org. Chem. 2015, 80, 11863−11868

The Bergman cyclization reaction poses a significant challenge to theory because of the involvement of a singlet diradical intermediate (*p*-benzyne). Computational methods based on density functional theory typically encompass sufficient electron correlation to provide qualitatively reliable predictions, although these predictions often suffer, quantitatively, from the common tendency of DFT methods to overemphasize delocalization in conjugated systems.[56−60] Multireference ab initio methods provide the best theoretical framework for treating singlet diradicals, but the calculations are technically challenging because of the need to incorporate a sufficiently large active space to recover adequate electron correlation. Although single-reference ab initio calculations appear less well-suited to handle singlet diradicals, it has been empirically determined that high-level coupled-cluster methods are valuable tools for investigating cycloaromatization reactions.[61]

Figure 1 depicts a relevant portion of the C_8H_4 singlet potential energy surface computed at the MP2/cc-pVTZ, CCSD(T)/cc-pVTZ, and EOM-SF-CCSD/cc-pVDZ levels of theory. Most striking, to us, was the difficulty in obtaining an optimized structure for the *p*-benzyne diradical (**2**). At the B3LYP/6-31G(d) level, all attempts to optimize the structure of diradical **2** led directly to cycloocta-1,5-dien-3,7-diyne (**3**). Although the *p*-benzyne diradical (**2**) is a true minimum on the potential energy surface at the EOM-SF-CCSD/cc-pVDZ level of theory, the surface is exceedingly flat. The barrier to ring opening to cycloocta-1,5-dien-3,7-diyne (**3**) must lie no more than 1 kcal/mol higher in energy than diradical **2**. We consider the MP2 prediction of a relatively stabilized *p*-benzyne diradical (**2**) and a distinct barrier to ring opening of **2** to **3** (Figure 1) to be a spurious result arising from the well-documented problems of spin contamination in MP2 calculations of open-shell species. The MP2 prediction (Figure 1, red ■) is not supported by either coupled-cluster or density functional theory calculations.

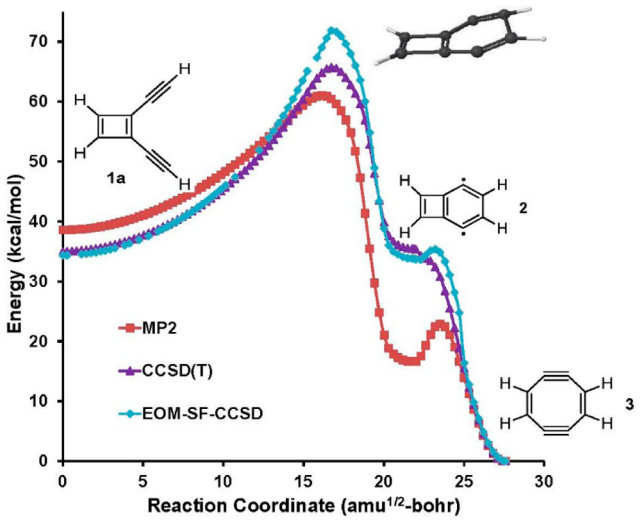


Figure 1. C_8H_4 singlet potential energy surface along intrinsic reaction coordinate (IRC) calculated at the MP2/cc-pVTZ level. Relative energies (kcal/mol) calculated by MP2/cc-pVTZ (red ■), CCSD(T)/cc-pVTZ (purple ▲), and EOM-SF-CCSD/cc-pVDZ (cyan ◆).

The electronic structure of singlet C_8H_4 undergoes dramatic changes along the reaction coordinate from 1,2-diethynylcyclobuta-1,3-diene (**1a**) to cycloocta-1,5-dien-3,7-diyne (**3**). 1,2-Diethynylcyclobutadiene (**1a**) is a diradical of $\pi-\pi$ character that is typical of cyclobutadienes.[26] The transition state (**TS 1a-3**) between cyclobutadiene **1a** and *p*-benzyne (**2**) is the highest point along the intrinsic reaction coordinate (IRC) path. This structure has a complicated electron distribution, which, in addition to $\pi-\pi$ diradical character of the cyclobutadiene moiety, reveals weakening of the triple bonds and partial bond formation in the six-membered ring. At all levels of theory employed, **TS 1a-3** exhibits an unusual, nonplanar (C_s) geometry—a feature that is not characteristic of the Bergman cyclization[52,59,62] but does represent a typical mode of distortion (pyramidalization) in strained alkenes.[63] The dihedral angle between the planes of the 4- and 6-membered rings is 162° (B3LYP/6-31G(d)); the barrier to planarization in systems of this type is expected to be of the order of a few kilocalories per mole.[63,64]

Another interesting structure along the IRC path is *p*-benzyne (**2**), in which both the cyclobutadiene ring and the fully formed *p*-benzyne moiety coexist. Formally, structure **2** is a tetraradical, combining two diradical π orbitals of cyclobutadiene with two σ-type orbitals of *p*-benzyne. Because of this complicated electronic structure, various computational methods disagree whether *p*-benzyne (**2**) is a true minimum on the potential energy surface. *p*-Benzyne (**2**), if real, has a very low barrier toward formation of cycloocta-1,5-dien-3,7-diyne (**3**). Structure **3** is a well-defined closed-shell molecule, for which the energy is the lowest along the IRC path.

Comparing the thermochemistry of the cycloaromatization reaction of 1,2-diethynylcyclobuta-1,3-diene (**1a**) with that of the *cis*-hex-3-ene-1,5-diyne (**5**; the parent system for the Bergman cyclization) is instructive. The cyclization of 1,2-diethynylcyclobutadiene (**1a**) is thermoneutral, in contrast to the cyclization of *cis*-hex-3-ene-1,5-diyne (**5**), which is endothermic by 8.5 kcal/mol.[65,66] The computed barrier to cyclization of 1,2-diethynylcyclobutadiene (**1a**) of 30 kcal/mol is quite similar to the experimental (28.2 ± 0.5 kcal/mol)[65] and computed (28.5 kcal/mol using CCSD(T)/6-31G(d,p))[66] values for the prototypical *cis*-hex-3-ene-1,5-diyne (**5**). The basis for the difference in thermochemistry between these two systems is not immediately apparent.[67] We initially hypothesized that incorporation of the cyclobutadienyl ring would destabilize the enediyne moiety, relative to the *p*-benzyne moiety, thereby decreasing the endothermicity of the cyclization. Two factors, however, suggest that this is not the case. First, as depicted in Figure 1, the transition state for cyclization of 1,2-diethynylcyclobuta-1,3-diene (**1a**) is late and thus relatively unaffected by factors that stabilize or destabilize the reactant, relative to product. Second, the computed barrier to cyclization of **1a** is very similar to the computed barrier to cyclization of **5**. An alternative explanation—that the cyclobutadienyl ring would "stabilize" the *p*-benzyne moiety, relative to the enediyne moiety—seemed counterintuitive to us, but we now believe we understand the matter. The presence of the cyclobutadienyl ring in **2** introduces an alternate reaction pathway that is not available in the parent *p*-benzyne (**6**), namely, ring opening to the eight-membered ring (**3**). This reaction is highly exothermic (−35 kcal/mol), exhibits an early transition state, and occurs with a very low barrier. These factors pull the *p*-benzyne derivative **2** down in energy, thereby decreasing the endothermicity of the cycloaromatization step. The singlet potential energy surface in the vicinity of the structure **2** displays significant energy gradients. The entrance channel exhibits a high barrier and late transition state, and the

DOI: 10.1021/acs.joc.5b01864
J. Org. Chem. 2015, 80, 11863−11868

exit channel exhibits a low barrier and early transition state. Structure **2** is poised, precariously, between the transition state of the entrance channel and the ring-expanded product (**3**), which differ in energy by 70 kcal/mol. The structure and energy of **2** are strongly influenced by this topology, which also accounts for the sensitivity of the computational results to the level of theory employed. Returning to the matter of thermochemistry: to say that *p*-benzyne derivative **2** is "stabilized" by the cyclobutadienyl ring does not really convey the appropriate context of the situation. A somewhat better description may be to say that partial relief of strain in the cyclobutadienyl ring of **2** lowers the energy of **2** relative to enediyne **1a**.

Considerable attention has been paid to the distance between terminal carbons of the enediyne moiety (*c-d* distance) and the barrier to Bergman cyclization.[68−72] The computed distance between the terminal acetylenic carbons in 1,2-diethynylcyclobutadiene (**1a**) is 0.9 Å longer than *cis*-hex-3-ene-1,5-diyne (**5**) (5.2 Å vs 4.3 Å), owing to the significantly larger exocyclic bond angle (135° vs 124°) imposed by the cyclobutadiene ring (Figure 2). The energy required to distort 1,2-diethynylcyclobutadiene (**1b**) to the equivalent *c-d* distance as in enediyne **5** (4.3 Å) will be small; the low frequency, in-plane C−C−C bending vibration (ca. 100 cm^{-1}) in **1a** will involve excursions that approach this distance. This vibrational mode is, in effect, the reaction coordinate for cycloaromatization, which is relatively insensitive to the *c-d* distance at early points along the reaction coordinate (Figure 1). Thus, the larger *c-d* distance in **1a** does not translate into a larger activation energy for cyclization.

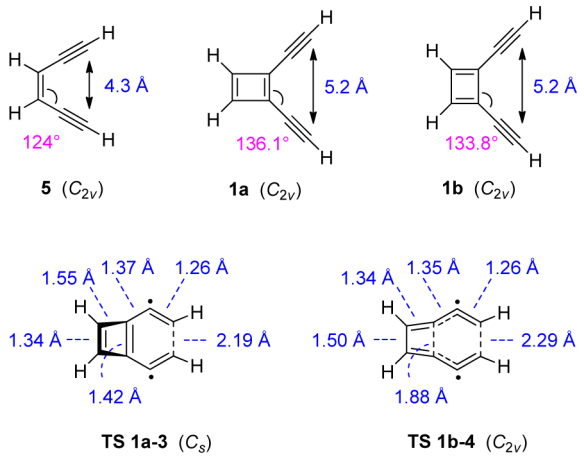
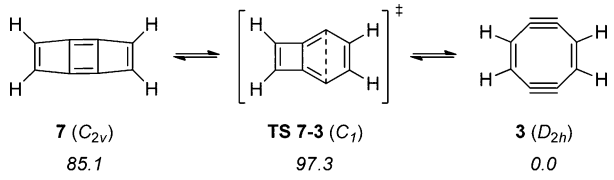


Figure 2. Geometric parameters of selected structures. Experimental values for *cis*-hex-3-ene-1,5-diyne (**5**);[72] computed values for **1a**, **1b**, **TS 1a-3**, and **TS 1b-4** (B3LYP/6-31G(d)). Distance in angstroms and angles in degrees.

During our efforts to understand the nonplanar transition state for the Bergman cyclization reaction (**TS 1a-3**), we discovered a different, planar transition state (**TS 1b-4**) (Scheme 2). IRC analysis establishes that **TS 1b-4** is derived from 1,4-diethynylcyclobuta-1,3-diene (**1b**), the bond shift isomer of **1** in which the alkyne substituents are formally bonded across the long C−C bond of the cyclobutadiene moiety, and leads to cycloocta-1,2,3,5,6,7-hexaene (**4**), the bond-shift isomer of cycloocta-1,5-dien-3,7-diyne (**3**). Thus, **TS 1b-4** represents the transition state for a Cope-type [3,3]-sigmatropic rearrangement.[53−55] That the system maintains planarity along the reaction coordinate for the rearrangement of **1b** to **4** apparently reflects the lengthening of the C1−C4 bond and the relief of strain in the cyclobutadiene ring in **TS 1b-4** (Figure 2).

Despite their intriguing structural differences, the transition states for Bergman cyclization (**TS 1a-3**) and Cope-type rearrangement (**TS 1b-4**) are computed to be of nearly equal energy (Scheme 2). Since the cyclobutadiene bond-shift isomers **1a** and **1b** are very similar in energy and will equilibrate rapidly under thermal conditions, the Cope-type rearrangement pathway may well be relevant to the thermal chemistry of alkynylcyclobutadienes. It is also interesting to note that **TS 1a-3** and **TS 1b-4** are not too dissimilar in geometry from **TS 7−3**, the transition state for thermal ring-opening of the butalene derivative **7** to cycloocta-1,5-diene-3,7-diyne (**3**) (Scheme 3).[64] **TS 1a-3** and **TS 1b-4** are, however, considerably lower in energy (ca. 30−40 kcal/mol) than **TS 7−3**.

Scheme 3. Ring Opening of Butalene Derivative 7[a]



[a]Relative energy (kcal/mol; ZPVE included; B3LYP/6-31G(d)).

CONCLUSIONS

Our current findings raise questions concerning the *ring coalescence and annealing* model for carbon condensation and fullerene formation (Scheme 1). Computational studies suggest that a dialkynylcyclobuta-1,3-diene derivative may undergo thermal ring expansion to afford an eight-membered ring via either Cope-type [3,3]-sigmatropic rearrangement or Bergman cyclization followed by ring opening. The model for carbon condensation does not include either of these reaction pathways. The singlet *p*-benzyne diradical structure proposed in the model lies in an extremely shallow portion of the potential energy surface, and its very existence as an intermediate remains in question. Interestingly, a recent ab initio molecular dynamics simulation of fullerene formation suggests the involvement of a number of unanticipated 4-, 5-, and 8-membered ring intermediates.[15] In that study, one structure appears to be a dialkynyl cyclooctadiendiyne, and another appears to be a dialkynyl cyclobutadiene (Figure 1, panel d of ref 15); these structures are directly analogous to those in the current investigation (Scheme 2).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01864.

Computed energies, Cartesian coordinates, harmonic vibrational frequencies and infrared intensities of all species studied at all levels of theory (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: lslipchenko@purdue.edu.

DOI: 10.1021/acs.joc.5b01864
J. Org. Chem. 2015, 80, 11863−11868

*E-mail: mcmahon@chem.wisc.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the National Science Foundation (CHE-0362264, CHE-1011959 (R.J.M.); CHE-0955419 (L.V.S.)). We also acknowledge NSF support for departmental computing facilities at the University of Wisconsin (CHE-0840494) and support from Purdue University.

■ REFERENCES

(1) Goroff, N. S. *Acc. Chem. Res.* **1996**, *29*, 77−83.
(2) Smalley, R. E. *Acc. Chem. Res.* **1992**, *25*, 98−105.
(3) Heath, J. R. *ACS Symp. Ser.* **1992**, *481*, 1−23.
(4) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 495−500.
(5) McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993**, *259*, 1594−1596.
(6) Hunter, J. M.; Fye, J. L.; Roskamp, E. J.; Jarrold, M. F. *J. Phys. Chem.* **1994**, *98*, 1810−1818.
(7) Irle, S.; Zheng, G.; Wang, Z.; Morokuma, K. *J. Phys. Chem. B* **2006**, *110*, 14531−14545.
(8) Huang, J. Y.; Ding, F.; Jiao, K.; Yakobson, B. I. *Phys. Rev. Lett.* **2007**, *99*, 175503.
(9) Dunk, P. W.; Kaiser, N. K.; Hendrickson, C. L.; Quinn, J. P.; Ewels, C. P.; Nakanishi, Y.; Sasaki, Y.; Sinohara, H.; Marshall, A. G.; Kroto, H. W. *Nat. Commun.* **2012**, *3*, 855.
(10) Dunk, P. W.; Mulet-Gas, M.; Rodriguez-Fortea, A.; Poblet, J. M.; Marshall, A. G.; Kroto, H. W. *AIP Conf. Proc.* **2014**, *1628*, 862−869.
(11) Bradley, A. Z.; Johnson, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 9917−9918.
(12) Hoye, T. R.; Baire, B.; Niu, D.; Willoughby, P. H.; Woods, B. P. *Nature* **2012**, *490*, 208−212.
(13) Weiderhold, A. J.; Esselman, B. J.; Bates, D. M.; McMahon, R. J. Unpublished results.
(14) Neng, W.; Lei, S.-y.; Xu, J.; Matteo, M.; Zhou, Y.-l.; Wan, S.; Sun, L.-t.; Huang, Q.-a. *Nanoscale* **2014**, *6*, 11213−11218.
(15) Pietrucci, F.; Andreoni, W. *J. Chem. Theory Comput.* **2014**, *10*, 913−917.
(16) Chuvilin, A.; Kaiser, U.; Bichoutskaia, E.; Besley, N. A.; Khlobystov, A. N. *Nat. Chem.* **2010**, *2*, 450−453.
(17) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713−1747.
(18) Van Orden, A.; Saykally, R. J. *Chem. Rev.* **1998**, *98*, 2313−2357.
(19) Kosimov, D. P.; Dzhurakhalov, A. A.; Peeters, F. M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *78*, 235433.
(20) Kosimov, D. P.; Dzhurakhalov, A. A.; Peeters, F. M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 195414.
(21) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.
(22) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347−1363.
(23) Gordon, M. S.; Schmidt, M. W. In *Theory and Applications of Computational Chemistry*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier, 2005; pp 1167−1189.
(24) Krylov, A. I. *Chem. Phys. Lett.* **2001**, *338*, 375−384.
(25) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2002**, *117*, 4694−4708.
(26) Levchenko, S. V.; Krylov, A. I. *J. Chem. Phys.* **2004**, *120*, 175−185.
(27) Krylov, A. I. *Acc. Chem. Res.* **2006**, *39*, 83−91.
(28) Krylov, A. I. *Annu. Rev. Phys. Chem.* **2008**, *59*, 433−462.
(29) Sekino, H.; Bartlett, R. J. *Int. J. Quantum Chem.* **1984**, *26* (Suppl 18), 255−265.
(30) Koch, H.; Jensen, H. J. A.; Jørgensen, P.; Helgaker, T. *J. Chem. Phys.* **1990**, *93*, 3345−3350.
(31) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029−7039.
(32) Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; DiStasio, R. A., Jr.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Voorhis, T. V.; Chien, S. H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, R. D.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C.-P.; Kedziora, G.; Khalliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W.; Lotan, I.; Nair, N.; Peters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock, H. L., III; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F., III; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3172−3191.
(33) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483.
(34) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.
(35) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(36) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.
(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09; Revision B.1*; Gaussian, Inc., 2009.
(38) Wittig, G.; Mayer, U. *Chem. Ber.* **1963**, *96*, 342−348.
(39) Krebs, A.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509−510.
(40) Hopf, H.; Witulski, B. *Nachr. Chem., Tech. Lab.* **1991**, *39*, 286−290.
(41) Hopf, H.; Witulski, B.; Jones, P. G.; Schomburg, D. *Liebigs Annalen* **1995**, *1995*, 609−612.
(42) Peña, D.; Pérez, D.; Guitián, E. *Chem. Rec.* **2007**, *7*, 326−333.
(43) Kornmayer, S. C.; Rominger, F.; Gleiter, R. *Synthesis* **2009**, *2009*, 2547−2552.
(44) Hopf, H.; Grunenberg, J. In *Strained Hydrocarbons: Beyond the van't Hoff and Le Bel Hypothesis*; Dodziuk, H., Ed.; Wiley-VCH: Weinheim, 2009; pp 375−397.
(45) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590−602.
(46) Bunz, U. H. F. *Top. Curr. Chem.* **1999**, *201*, 131−161.
(47) Esselman, B. J.; McMahon, R. J. *J. Phys. Chem. A* **2012**, *116*, 483−490.
(48) Thompson, S. J.; Emmert, F. L., III; Slipchenko, L. V. *J. Phys. Chem. A* **2012**, *116*, 3194−3201.
(49) Menke, J. L.; Patterson, E. V.; McMahon, R. J. *J. Phys. Chem. A* **2010**, *114*, 6431−6437.
(50) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie International: Deerfield Beach, FL, 1970.

DOI: 10.1021/acs.joc.5b01864
J. Org. Chem. 2015, 80, 11863−11868

(51) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry* ; University Science Books: Mill Valley, CA, 2006; Chapter 15 and references cited therein.
(52) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660−661.
(53) Black, K. A.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 5622−5627.
(54) Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 732.
(55) Huntsman, W. D.; Wristers, H. J. *J. Am. Chem. Soc.* **1967**, *89*, 342−347.
(56) Schreiner, P. R. *J. Am. Chem. Soc.* **1998**, *120*, 4184−4190.
(57) Santos, J. C.; Andres, J.; Aizman, A.; Fuentealba, P.; Polo, V. *J. Phys. Chem. A* **2005**, *109*, 3687−3693.
(58) Chen, W.-C.; Chang, N.-y.; Yu, C.-h. *J. Phys. Chem. A* **1998**, *102*, 2584−2593.
(59) Cramer, C. J. *J. Am. Chem. Soc.* **1998**, *120*, 6261−6269.
(60) Prall, M.; Wittkopp, A.; Fokin, A. A.; Schreiner, P. R. *J. Comput. Chem.* **2001**, *22*, 1605−1614.
(61) Crawford, T. D.; Kraka, E.; Stanton, J. F.; Cremer, D. *J. Chem. Phys.* **2001**, *114*, 10638−10650.
(62) Koseki, S.; Fujimura, Y.; Hirama, M. *J. Phys. Chem. A* **1999**, *103*, 7672−7675.
(63) Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, pp 299−366.
(64) Warner, P. M.; Jones, G. B. *J. Am. Chem. Soc.* **2001**, *123*, 10322−10328.
(65) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765−1779.
(66) Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1994**, *116*, 4929−2936.
(67) Jones, G. B.; Warner, P. M. *J. Am. Chem. Soc.* **2001**, *123*, 2134−2145.
(68) Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 5367−5369.
(69) Magnus, P.; Fortt, S.; Pitterna, T.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 4986−4987.
(70) Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387−1416.
(71) Nicolaou, K. C.; Smith, A. L. *Acc. Chem. Res.* **1992**, *25*, 497−503.
(72) McMahon, R. J.; Halter, R. J.; Fimmen, R. L.; Wilson, R. J.; Peebles, S. A.; Kuczkowski, R. L.; Stanton, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 939−949.

DOI: 10.1021/acs.joc.5b01864
J. Org. Chem. 2015, 80, 11863−11868