Structures and Stabilities of Diacetylene-Expanded Polyhedranes by Quantum Mechanics and Molecular Mechanics

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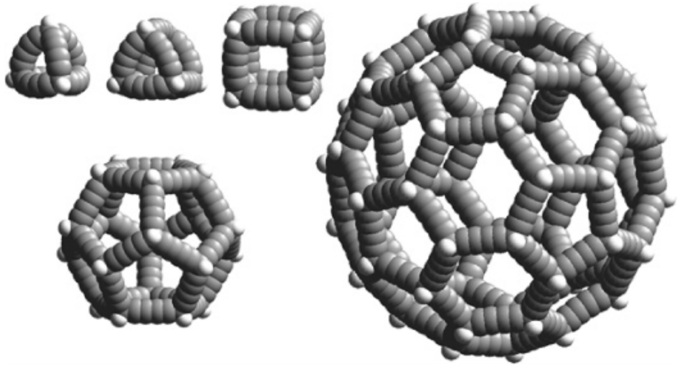
Received November 14, 2004



The structures, heats of formation, and strain energies of diacetylene (buta-1,3-diynediyl) expanded molecules have been computed with ab initio and molecular mechanics calculations. Expanded cubane, prismane, tetrahedrane, and expanded monocyclics and bicyclics were optimized at the HF/6-31G(d) and B3LYP/6-31G(d) levels. The heats of formation of these systems were obtained from isodesmic equations at the HF/6-31G(d) level. Heats of formation were also calculated from Benson group equivalents. The strain energies of these expanded molecules were estimated by several independent methods. An adapted MM3* molecular mechanics force field, specifically parametrized to treat conjugated acetylene units, was employed for one measure of strain energy and as an additional method for structural analysis. Expanded dodecahedrane and icosahedrane were calculated by this method. Expanded molecules were considered structurally in the context of their potential material applications.

Introduction

The synthesis of octamethoxy expanded cubane (Figure 1, left)[1] has demonstrated the feasibility of novel unsaturated versions of familiar saturated molecules, such as cubane, which are topologically analogous to platonic solids. The expansion[2] unit involved in these molecules is the conjugated diacetylene moiety, buta-1,3-diynediyl. The formal insertion of this unit into each C−C single bond of cubane leads to expanded cubane (EC) (Figure 1).

The synthesis of the octamethoxy-EC was accomplished from successive Hay coupling[3] of intermediate building blocks resembling the corners and sides of EC.[1] The methoxy groups are circumstantial and, in principle, may be replaced by a variety of other groups or functionalities early on in the synthesis allowing for a predefined cubic arrangement of substituents in the final product. This could allow access to highly symmetric and rigid templates for the bottom-up design of interesting architectures for use in materials and biological chemistry. For the latter, expanded cubane could serve a function analogous to that being attempted with icosahedral C_{60}.[4] Such molecules may also possess interesting optoelectronic properties.[2]

Like C_{60},[5] the interior of the expanded cubane is also of interest. The inner cavity may be able to complex a number of small molecules or atoms. In particular, the cavities might be hospitable hosts toward cationic guests.[6,7]

Cubane was vigorously pursued in the 1960s as a synthetic target and was also the subject of numerous

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[1] Manini, P.; Amrein, W.; Gramlich, V.; Diederich, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4339.

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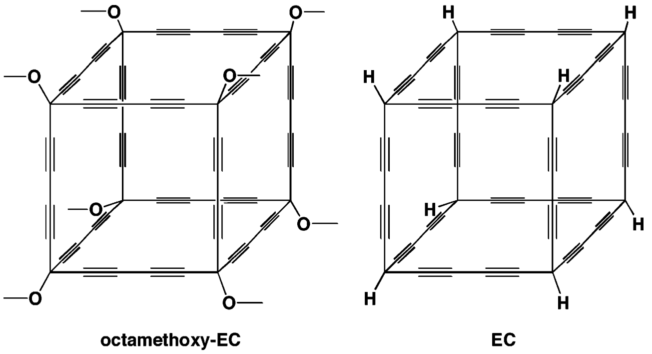

FIGURE 1. Octamethoxy expanded cubane (octamethoxy-EC) (left) and expanded cubane (EC) (right).

theoretical papers.[8] As a high strain target, cubane was sought for the synthetic challenge as well as for the inherent aesthetic appeal found within its symmetry. As a high-energy molecule, cubane is of interest as a combustible fuel source. Expanded cubane maintains all of these aspects. However, unlike cubane, octamethoxy-EC is highly unstable, exploding upon scraping in the presence of oxygen.[1] The highly exothermic decomposition of octamethoxy-EC should be driven, in part, by the release of a considerable amount of strain energy distributed along its bowed buta-1,3-diynediyl units, as well as from the inherently high energy content (high oxidation state) of the acetylene units. The strain energy will be a major focus of the present paper. The instability of EC, however, cannot be rationalized by the release of this strain energy alone. The kinetic instability of EC contrasts sharply with that of cubane; cubane has about 155 kcal mol^{-1} of strain energy[9] but is remarkably stable. Some reasons for this contrast can be proposed. For instance, unstrained diacetylene derivatives are known to polymerize in the solution phase[10] and solid-state[11] forming highly colored linear chromophores through cumulenic diradical intermediates.[12] The already considerable reactivity of the buta-1,3-diynediyl moiety toward polymerization may be enhanced by geometric strain.[13] This geometric distortion may have a similar effect on the ease of oxidation and combustion. An alternate decomposition pathway can be inferred from mass spectral data of octamethoxy-EC. The mass spectrum revealed the successive loss of up to eight methoxy groups in both the positive and negative ion mode.[1] From these data, a polar mechanism of decomposition involving triply propargylic ions was proposed.[1] The deprotonation energy of ethynyl-expanded cubane was recently computed.[6] The anion resulting from deprotonation was calculated to have a free energy roughly 10 kcal mol^{-1} lower in energy than the analogous unstrained 3-ethynylpenta-1,4-diyne model system. Whatever the exact mechanism of decomposition, it is clear that the geometric distortion and the associated strain energy will be important aspects in both the thermodynamic and kinetic stabilities of octamethoxy-EC.

The instability of EC coupled with the exceedingly low synthetic yields (total yield about 1.0% for octamethoxy-EC),[1] make calorimetric experimentation infeasible until a new synthetic method has been worked out; such studies are underway. Furthermore, in general, calorimetric studies of conjugated acetylenes have been problematic.[14] The pursuit of additional expanded polyhedranes or other derivatives of EC will be greatly benefited by understanding their stabilities as a function of structure. Such data, which can be obtained experimentally only after arduous synthetic efforts, are in principle, accessible through computation.

This paper discusses a theoretical study, with quantum mechanics and molecular mechanics methods, of the structures, stabilities, and properties of diyne-expanded polyhedranes. Calculations were performed on expanded cubane (**1**), prismane (**2**), tetrahedrane (**3**), bicyclo[2.2.0]-

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(2) (a) Boldi, A. M.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 468. (b) Nielsen, M.; Schreiber, M.; Baek, Y. G.; Seiler, P.; Lecomte, S.; Boudon, C.; Tykwinski, R.; Gisselbrecht, J.-P.; Gramlich, V.; Skinner, P.; Bosshard, C.; Günter, P.; Gross, M.; Diederich, F. *Chem. Eur. J.* **2001**, *7*, 3263. (c) Schreiber, M.; Anthony, J.; Diederich, F.; Spahr, M. E.; Nesper, R.; Hubrich, M.; Bommeli, F.; DeGiorgi, L.; Bosshard, C.; Gisselbrecht, J.-P.; Gross, M. *Adv. Mater.* **1994**, *6*, 786. (d) Burri, E.; Diederich, F.; Bronsted-Nielsen, M. *Helv. Chim. Acta* **2002**, *85*, 2169. (e) Zhao, Y.; McDonald, R.; Tykwinski, R. R. *J. Org. Chem.* **2002**, *67*, 2805. (f) Scott, L. T.; DeCicco, G. J. *Tetrahedron Lett.* **1976**, *31*, 2663−2666. (g) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546−6555. (h) Houk, K. N.; Scott, L. T.; Rondan, N. G.; Spellmeyer, D. C.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jørgensen, F. S.; Eaton, T. A.; Sarkozi, V.; Petit, C. M.; Ng, L.; Jordan, K. D.; *Ibid.* **1985**, *107*, 6556−6562. (i) Mitzel, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Diederich, F. *Chem. Commun.* **2002**, 2318. (j) Anthony, J.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 406. (k) Anthony, J.; Boldi, A. M. Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Seiler, P.; Knobler, C. B.; Diederich, F. *Helv. Chim. Acta*, **1995**, *78*, 797. (l) Pilling, G. M.; Sondheimer, F. *J. Am. Chem. Soc.* **1971**, *93*, 1970. (m) Diederich, F. *Chem. Commun.* **2001**, 219−227. (n) Wolovsky, R.; Sondheimer, F. *J. Am. Chem. Soc.* **1965**, *87*, 5720.

(3) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320−3321.

(4) Hirsch, A.; Vostrowsky, O. *Eur. J. Org. Chem.* **2001**, 829−848 and references therein.

(5) (a) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843−892. (b) Liu, S. Y.; Sun, S. Q. *J. Organomet. Chem.* **2000**, *599*, 74−86. (c) Eletskii, A. V. *Uspekhi Fizicheskikh Nauk* **2000**, *170*, 113−142. (d) Braun, T. *Ach-Models In Chemistry* **1995**, *132*, 245−263.

(6) Bachrach, S. M.; *J. Phys. Chem A.* **2003**, *107*, 4957−4961.

(7) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests;* The Royal Society of Chemistry: Cambridge, 1994.

(8) (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962. (b) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *104*, 1447. (c) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421.

(9) (a) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312−322. (b) Novak, I. *Chem. Phys. Lett.* **2003**, *380*, 258−262. (c) Carrey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, 4th ed.*; Kluwer Acedemic/Plenum Publishers: New York, 2000.

(10) (a) Cheng, Q.; Yamamoto, M.; Stevens, R. C. *Langmuir* **2000**, *16*, 5333−5342. (b) Iwase, Y.; Kondo, K.; Kamada, K.; Ohta, K. *J. Polym. Sci. Part A.* **2002**, *40*, 3534−3541. (c) Jonas, U.; Shah, K.; Norvez, S.; Charych, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 4580−4588. (d) Reichert, A.; Nagy, J. O.; Spevak, W.; Charych, D. *J. Am. Chem. Soc.* **1995**, *115*, 1146−1147. (e) Charych, D. H.; Nagy, J. O.; Spevak, M.; Bednarski, M. D. *Science* **1993**, *261*, 585−588. Charych, D.; Cheng, Q.; Reichert, A.; Kuziemko, G.; Stroh, M.; Nagy, J. O.; Spevak, W.; Stevens. R. C. *Chem. Biol.* **1996**, *3*, 113−120.

(11) (a) Wegner, G. Z.; *Naturforsch* **1969**, *24b*, 824−832. (b) Wegner, G. *Macromol. Chem.* **1971**, *145*, 85. (c) Wegner, G. *Faraday Discuss. Chem.* **1979**, 68, 495. (d) Bloor, D., Chance, R. R., Eds. *Polydiacetylenes: Synthesis, Structure, and Electronic Properties;* Martinus Jijhoff Pub.: 1985.

(12) (a) Chance, R. R.; Patel, G. N.; Turi, E. A.; Khanna, Y. P. *J. Am. Chem. Soc.* **1977**, *100*, 1407−1309. (b) Cardelino, B. H.; Moore, C. E.; Frazier, D. O.; Musaev, D. G.; Morokuma, K. *J. Quantum Chem.* **1998**, *66*, 189−202.

(13) (a) Guo, L.; Hrabusa, J. M.; Tessier, C. A.; Youngs, W. J.; Lattimer, R.; *J. Organometallic Chem.* **1998**, *578*, 43−54. (b) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1993**, *59*, 1294−1301.

(14) (a) Luk'yanova, V. A.; Pimenova, S. M.; Timofeeva, L. P.; Kozina, M. P.; Kolesov, V. P.; Tarakanova, A. V. *Russ. J. Phys. Chem. (Transl. Of Zh. Fiz. Khim.)* **1992**, *66*, 1083−1085. (b) Mabry, J.; Johnson, R. P.; *J. Am. Chem. Soc.* **2002**, *124*, 6497−6501. (c) Laskoski, M.; Steffen, W.; Morton, J. G. M.; Smith, M. D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 13814−13818.

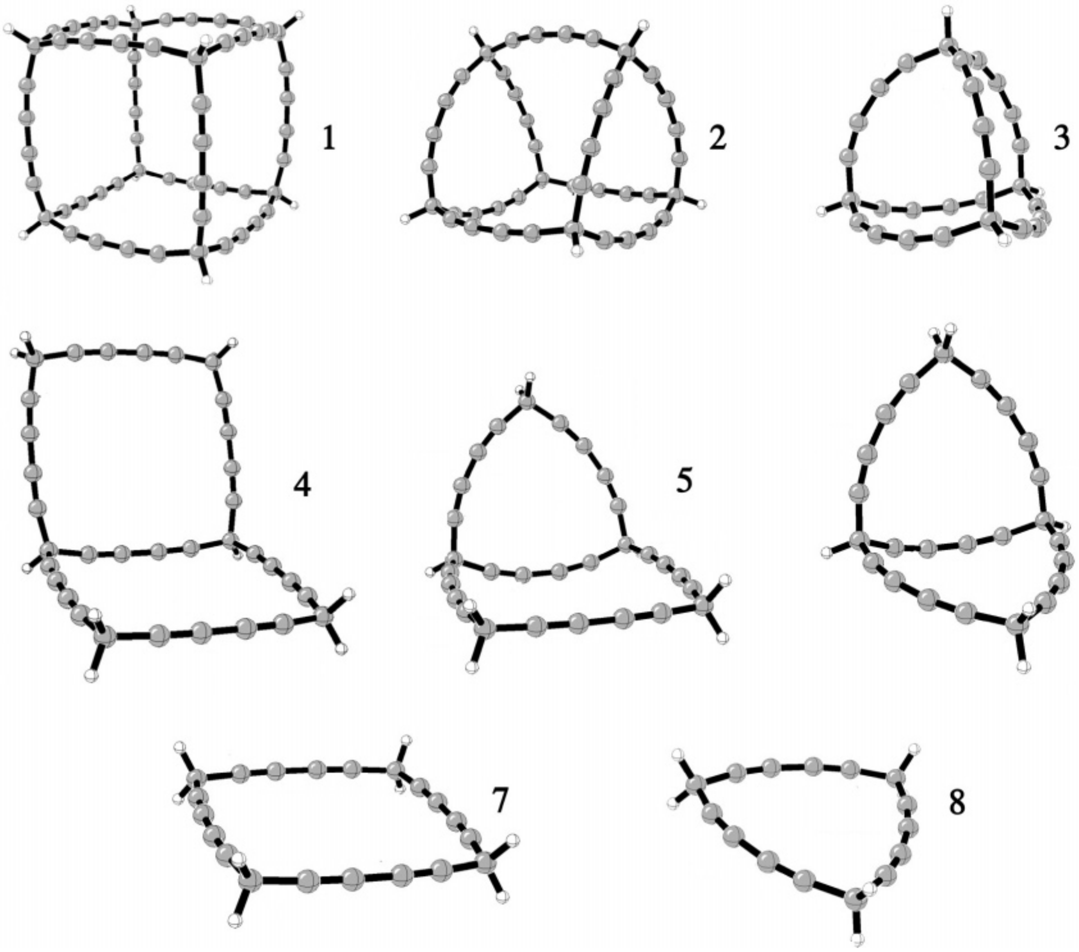

FIGURE 2. Expanded polyhedra, **1**−**3**, and bicyclic and monocyclic structures **4**−**8**.

hexane (**4**), bicyclo[2.1.0]pentane (**5**), bicyclo[1.1.0]butane (**6**), cyclobutane (**7**), and cyclopropane (**8**) (Figure 2).

These expanded molecules have geometries of varying symmetry, and harbor different degrees of strain energy. Molecules **4**−**8** dissect molecules **1**−**3** into their constituent faces and edges, allowing for an analysis of the contributions to the geometry and strain energy from these monocyclic and bicyclic subunits. These molecules were optimized at density functional[15] and Hartree−Fock levels of theory and also by molecular mechanics.

Isodesmic[16] (Supporting Information) and homodesmotic[17] equations were used to arrive at the heats of formation (ΔH_f^{iso}) of **1**−**8**. The hypothetical unstrained heat of formation of these molecules was obtained by group additivity (ΔH_f^{GAV}).[18] Subtracting this heat of formation from the heat of formation obtained from homodesmotic equations gave the conventional strain energy ($\Delta H_f^{GAV} - \Delta H_f^{iso}$).[19a,b] In addition, heats of reaction (ΔH_r^{iso}) considered as additional measures of strain energy. These energies are compared to the strain energy[19c] obtained from molecular mechanics utilizing a modified MM3*[20,21] force field specifically parametrized for these systems.

The molecular mechanics calculations were used to obtain data on much larger structures, expanded dodecahedrane and icosahedrane. The host−guest properties of **1**−**3** as well as these larger structures were investigated.

The electronic properties and probable reactivity characteristics of **1**−**8** were also analyzed from HOMO and LUMO energies (Supporting Information).

Computational Methods

Structures were optimized[22] either at the HF/6-31G(d)[23] or B3LYP/6-31G(d)[23] level of theory. Stationary points were

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(15) (a) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864. (b) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(16) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (c) Dill, J. D.; Greedberg, A.; Liebman, J. *J. Am. Chem. Soc.* **1979**, *101*, 6814.

(17) (a) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500. (b) Blahous, C.; Schaefer, H. F., III. *J. Phys. Chem.* **1988**, *92*, 959. (c) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121. (d) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(18) (a) Benson, S. W.; Garland, L. J. *J. Phys, Chem*. **1991**, *95*, 4915. (b) Cohen, N.; Benson. S. W. *Chem. Rev*. **1993**, *93*, 2419.

(19) (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds,* Academic Press: London, 1970. (b) Lewis, L. L.; Turner, L. L.; Salter, E. A.; Magers, D. H. *J. Mol. Struct. (THEOCHEM)* **2002**, *592*, 161−171. (c) Baeyer, A. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2269.

(20) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H.; *J. Am. Chem. Soc*. **1989**, *111*, 8551.

(21) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C., "MacroModel-An Integrated Software System for Modeling Organic and Bioorganic Molecules using Molecular Mechanics", *J. Comput. Chem.* **1990**, *11*, 440. Version 7.1.

characterized as minima by harmonic vibrational frequency analysis of analytic second derivatives.[24] Energies are reported as enthalpies calculated as the sum of the electronic energy, and thermal correction obtained from these analytical frequencies without scaling at 298 K.[25] Ab initio calculations were performed with the programs Gaussian 03.[23] Single point calculations at the HF/6-311+G(2df,p)//HF/6-31G(d) and B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) levels were also computed (Supporting Information). MM3* structures were calculated with the program Macromodel.[21] The molecular mechanics structures were minimized using the conjugate gradient PRCG method with an RMS convergence threshold of 0.001 Å.[21] Supporting Information provides atomic Cartesian coordinates for HF/6-31G(d) and B3LYP/6-31G(d) optimized structures as well as electronic energies, at the above-mentioned levels, zero-point corrections, and thermal corrections at 298 K.

Molecular Mechanics Method. To our knowledge, there are no specific parameters for the conjugated diyne moiety in any standard force field.[20,21,26] The force constant for the central single bond ($C_{sp}-C_{sp}$) stretch and, parameters for the bending terms, $C_{sp}-C_{sp}\equiv C_{sp}$, $C_{sp}\equiv C_{sp}-C_{sp^3}$ and $C_{sp}-C_{sp^3}-C_{sp}$ are unknown. These force constants are imperative for a proper description of **1**−**8**. Although generalized parameters (taken from nonconjugated acetylene units) can give reasonable geometries,[2h] energies obtained from these parameters would not be reliable. The parametization of the buta-1,3-diynediyl moiety was carried out at the B3LYP/6-31G(d) level to afford the missing terms. A more thorough presentation of the parametrization including curve-fitting data[27] is supplied in the Supporting Information.

Isodesmic Method for Heat of Formation Estimates. An isodesmic equation[16,17] is a hypothetical reaction where the number and type of bonds on the reactant side equal the number and type on the product side. The change in energy of an isodesmic reaction is a measure of changes in strain or resonance that are not accounted for in standard bond energies. The energy of an isodesmic reaction, ΔH_r^{iso}, can be computed from quantum mechanics. If the heats of formation of all but one component, a molecule of interest, are known, one may solve for the heat of formation of this unknown component, ΔH_f^{iso}. Isodesmic equations generally yield more accurate heats of formation than atomization energies,[28] since they benefit from significant cancellations of error. This is particularly important when considering the theoretical treatment of large molecular systems. The calculation of heats of formation from atomization energies becomes increasingly inaccurate very quickly for large molecules; thermodynamic data computed from isodesmic equations can continue to perform well for these large systems.[16,17,28,29]

In the present study both isodesmic and homodesmotic equations have been considered. Homodesmotic equations "same-bond" are a type of isodesmic equation "equal-bond." Homodesmotic equations not only balance the type of bonds, *i.e.* $C\equiv C$, $C-C$, and $C-H$, but also account for the specific hybridization of each atom that makes up the bond. For example, while an acetylenic $C_{sp}-H$ bond might be balanced with an aliphatic $C_{sp^3}-H$ bond in an isodesmic equation, the acetylenic $C_{sp}-H$ bond is expressly balanced with another acetylenic $C_{sp}-H$ in a homodesmotic process. Homodesmotic equations give more accurate results when compared to isodesmic equations since the structural similarity between products and reactants is greater leading to better error cancellation. Homodesmotic equations are used for the calculation of heats of formation in the present study. All heats of formation presented for molecules **1**−**8** are calculated at the HF/6-31G(d) level, which was found to be most accurate for the treatment of the model system 2,4-hexadiyne after extensive computational investigation employing multiple levels of theory and using multiple isodesmic equations (Supporting Information).

Heats of formation for small hydrocarbons in this study were taken from the NIST database[30] and have experimental heats of formation reported to at least ±0.1 kcal mol^{-1} accuracy. Errors of this magnitude will not contribute significantly to the final total error. Table 1 lists the experimental heats of formation used.

The NIST values for 1,3-butadiyne and 2,4-hexadiyne are not of high quality. Both values were derived indirectly by group additivity methods and experimental heats of hydrogenation.[14a,31] A better value for both can be obtained, in principle, from ab initio calculations. At the highly accurate G3[32a] level of theory, using the isodesmic method described above, a heat of formation of 108.9 kcal mol^{-1} is calculated for 1,3-butadiyne[33] and 87.3 kcal mol^{-1} is calculated for 2,4-hexadiyne (Supporting Information). The NIST values are 111 and 90.2 kcal mol^{-1} for 1,3-butadiyne and 2,4-hexadiyne, respectively.[30] The G3 values, rather than those obtained from the NIST database, will be used throughout this study (Table 1).

Strain Energy Determinations. Benson group equivalents can be used to predict the heats of formation of many types of organic molecules.[18a] For alkynes, including conjugated ones, the Group Additivity Values (GAV) predict the known experimental heat of formation to within 1 kcal mol^{-1}.[18b] In our present study, two experimentally derived Benson groups are used, $C_{sp}-(C_{sp^3})$ for the terminal buta-1,3-diyndiyl carbon, and $C_{sp}-(C_{sp})$ for the central buta-1,3-diynediyl carbon.[18b] Two additional groups are required for treating substituted meth-

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[22] H. B. Schlegel, *J. Comput. Chem.* **1982**, *3*, 214.

[23] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Revision A.9, B.01; Gaussian, Inc.: Pittsburgh, PA, 2003.

[24] Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 325.

[25] D. A. McQuarrie, *Statistical Thermodynamics* Harper and Row: New York, 1973.

[26] Nevins, N.; Chen, K.; Allinger, N. L. *J. Comput. Chem.* **1996**, *17*, 695−729.

[27] *Pro Fit*, version 5.6.4; trial version; Quantumsoft: http://www.quantumsoft.com.

[28] Redfern, P. C.; Zapol, P.; Curtiss, L. A.; Raghavachari, K. *J. Phys. Chem. A* **2000**, *104*, 5850−5854.

[29] Cioslowski, J., Ed. *Quantum-Mechanical Prediction of Thermochemical Data;* Klumer Academic Publishers: Dordrecht, 2001.

[30] H. Y. Afeefy, J. F. Liebman, and S. E. Stein, "Neutral Thermochemical Data" in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

[31] (a) Cowperthwaite, M.; Bauer, S. H.; *J. Chem. Phys.* **1962**, *36*, 1743−1753. (b) Flitcroft, T. L.; Skinner, H. A.; Whiting, M. C.; *Trans. Faraday Soc.* **1957**, *53*, 784. (c) Stein, S. E.; Fahr, A.; *J. Phys. Chem.* **1985**, *89*, 3714−3725.

[32] (a) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764−7776. (b) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (c) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703−4709.

[33] (a) Raghavachari, K. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related materials, Vol. 3,* Proceedings − Electrochemical Society, Los Angeles, USA, May 96−10, 1996; Kadish, K. M.; Ruoff, R. S., Eds.; The Electrochemical Society, Inc.: Pennington, 1996. (b) Rogers, D. W.; Matsunaga, N.; Zavitsas, A. A.; McLafferty, F. J.; Liebman, J. F.; *Org. Lett.* **2003**, *5*, 2373−2375.

TABLE 1. Calculated and Experimental Thermochemical Data. Heats of Formation Derived from Homodesmotic Equations (ΔH_f^{iso}) HF/6-31G(d) (column 2), Group Additivity Derived Heat of Formation (ΔH_f^{GAV}) (column 3), Heat of Reaction of Homodesmotic Equation (ΔH_r^{iso}) HF/6-31G(d) (column 4), and Experimental Heats of Formation (ΔH_f^{exp}) Are Given (kcal mol^{-1})

compound	ΔH_f^{iso}	ΔH_f^{GAV}	ΔH_r^{iso}	$\Delta H_f^{GAV} - \Delta H_f^{iso}$	$\Delta H_f^{exp\ a}$	ΔH_f^{exp} unexpanded^b
methane					−17.89	
ethane					−20.04 ± 0.07	
ethyne					54.190	
propyne					44.32 ± 0.21	
2-butyne					34.68 ± 0.24	
1,3-butadiyne	108.9^c				111	
2,4-hexadiyne	87.3^c				90.20	
expanded cubane **1**	1451.1	1343.3	−117.3	107.8		154.7
expanded prismane **2**	1120.6	1007.5	−120.2	113.1		150.0^d
expanded tetrahedrane **3**	783.4	671.7	−116.5	111.8		136.6^d
expanded bicyclo[2.2.0]hexane **4**	799.6	753.4	−45.4	46.3		51.8
expanded bicyclo[2.1.0]pentane **5**	706.7	649.1	−57.6	57.7		54.7
expanded bicyclo[1.1.0]butane **6**	615.3	544.7	−71.5	70.7		63.9
expanded cyclobutane **7**	439.9	417.6	−19.1	22.4		26.5
expanded cyclopropane **8**	345.8	313.2	−30.2	32.7		27.5

[a] Values taken from the NIST database, see ref 28. [b] Values taken from ref 9a unless otherwise noted. [c] Values derived at the G3 level of theory (Supporting Information). [d] Calculated values taken from ref 9b.

ylene and methyne groups attached to diynes, $C(C_{sp})_2(H)_2$, and $C(C_{sp})_3(H)$ carbons, respectively. These were taken as the high quality values calculated at the G2[34] level by Green and coworkers.[33] From these values, the heat of formation, ΔH_f^{GAV}, for **1**−**8** (Table 1) were calculated. The difference between ΔH_f and the ΔH_f^{GAV} provides one estimate of the strain energy ($\Delta H_f^{GAV} - \Delta H_f^{iso}$).[19b,c]

Quality estimates of strain energy can also be obtained from heats of reaction of appropriate isodesmic equations (ΔH_r^{iso}) (Table 1). Here, the molecule of interest is fragmented into structurally related molecules that are presumed to harbor only limited degrees of strain. Thus, these heats of reaction can be equated directly to the strain energy.

Results and Discussion

Hartree−Fock and Density Functional Geometries. Bond distances and angles for molecules **1**−**8** were optimized at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory. The calculated bond lengths, $C_{sp}-C_{sp}$, $C_{sp}\equiv C_{sp}$, and $C_{sp}-C_{sp^3}$ do not vary significantly across the set **1**−**8** using either method. These lengths are nearly identical to the corresponding values for 2,4-hexadiyne (Table 2) calculated at the same level.

The average values for $C_{sp}-C_{sp}$, $C_{sp}\equiv C_{sp}$, and $C_{sp}-C_{sp^3}$ are 1.39, 1.19, and 1.48 Å, respectively, according to the HF/6-31G(d) calculations and 1.37, 1.22, and 1.48 Å, respectively, at the B3LYP/6-31G(d) level. The SD for bond lengths $C_{sp}-C_{sp}$ and $C_{sp}\equiv C_{sp}$ are both 0 Å, at both levels, while there are small deviations in $C_{sp}-C_{sp^3}$ that correspond to elongation of this bond. Both levels of theory predict bond lengths that are in good agreement with tabulated experimental and calculated values for diacetylenes.[35] Note the short central $C_{sp}-C_{sp}$ bond length of the buta-1,3-diynediyl unit in both 1,3-butadiyne and 2,4-hexadiyne which is a result of strong conjugative effects between acetylenes.[33b,36] Structural parameters from X-ray data for octamethoxy-EC were not obtainable due to its instability.[1] However, the calculated values for **1**−**8** compare well to the X-ray crystallographic parameters obtained for a precursor of EC[1] with $C_{sp}-C_{sp}$, $C_{sp}\equiv C_{sp}$, and $C_{sp}-C_{sp^3}$ bond lengths of 1.373, 1.188, and 1.476 Å, respectively.

The average, maximum, and minimum values at the B3LYP/6-31G(d) and HF/6-31G(d) levels of theory are shown in Table 2. All unique bond angles for **1**−**8** are presented in Supporting Information.

Bond angles for expanded cyclobutane (**7**) compare well to the X-ray crystallographic data reported for the precursor mentioned previously.[1] Average crystallographic parameters, $C_{sp}-C_{sp}\equiv C_{sp}$, $C_{sp}\equiv C_{sp}-C_{sp^3}$, and $C_{sp}-C_{sp^3}-C_{sp}$, are 176.8, 174.1, and 107.1°, respectively. These values are all within two degrees of the calculated HF/6-31G(d) angles. The largest discrepancy is three degrees at the B3LYP/6-31G(d) level.

The buta-1,3-diyndiyl moiety prefers to be linear according to prior experiment[35a] and computation,[35b] and the methods used in this study. However, acetylenes and conjugated polyynes are known to be flexible,[37] resulting in the highly bowed structures of **1**−**8**. Maximum distortions of 18 and 22° are calculated at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory, respectively. These occur within molecules **3** and **6**. Molecules **4** and **7** contain the minimum distortions. The geometric distortion is not distributed evenly across the buta-1,3-diynediyl moiety. The average distortion of the $C_{sp}\equiv C_{sp}-C_{sp^3}$ bond angle is slightly greater than the average distortion for the $C_{sp}-C_{sp}\equiv C_{sp}$ bond angle. This uneven distribution occurs to a greater extent at the B3LYP/6-31G(d) level than the HF/6-31G(d) level. The $C_{sp}-C_{sp^3}-C_{sp}$ bond angle of 2,4,7,9-undecatetrayne is calculated to be 113°, and the average bond angle, at both levels of theory, is 108°.

One might expect that the expanded polyhedranes, **1**−**3**, would be more geometrically distorted than open

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(34) Sumathi, R.; Green, W. H., Jr. *J. Phys. Chem. A.* **2002**, *106*, 11141−11149.

(35) (a) Smith, M.; March, J. *March's Advanced Organic Chemistry, 5th ed.;* John Wiley & Sons: New York, 2001. (b) Plattner, D. A.; Li, Y.; Houk, K. Modern Computational and Theoretical Aspects of Acetylene Chemistry. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; pp 1−32.

(36) (a) Jarowski, P. D.; Wodrich, M. D.; Wannere, C. S.; Schleyer, P. v. R.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 15036−15037. b) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832−4840.

(37) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175−4205.

TABLE 2. Maximum, Minimum, and Average Bond Angles (deg) for $C_{sp}-C_{sp}\equiv C_{sp}$, $C_{sp}\equiv C_{sp}-C_{sp^3}$, and $C_{sp}-C_{sp^3}-C_{sp}$ of Molecules 1–8 Are Given along with the Calculated Bond Lengths (Bonds Defined in Figure 3) of 2,4-Hexadiyne (Å)

	Bond Length								
	HF/6-31G(d)			B3LYP/6-31G(d)			MM3*		
item	$C_{sp}-C_{sp}$	$C_{sp}\equiv C_{sp}$	$C_{sp}-C_{sp^3}$	$C_{sp}-C_{sp}$	$C_{sp}\equiv C_{sp}$	$C_{sp}-C_{sp^3}$			
2,4-hexadiyne	1.39	1.19	1.47	1.37	1.22	1.46			
	Bond Angle								
item	$C_{sp}-C_{sp}\equiv C_{sp}$	$C_{sp}\equiv C_{sp}-C_{sp^3}$	$C_{sp}-C_{sp}-C_{sp}$	$C_{sp}-C_{sp}\equiv C_{sp}$	$C_{sp}\equiv C_{sp}-C_{sp^3}$	$C_{sp}-C_{sp^3}-C_{sp}$	$C_{sp}-C_{sp}\equiv C_{sp}$	$C_{sp}\equiv C_{sp}-C_{sp^3}$	$C_{sp}-C_{sp^3}-C_{sp}$
2,4,7,9-undecatetrayne			113			113			
maximum distortion	163	162	105	169	158	105	164	162	107
minimum distortion	177	175	112	177	175	112	175	175	112
average	172	170	108	174	167	108	171	169	110

expanded structures, **4**–**6**. However, the differences are small as is clear upon comparison of analogous edges contained within these structures (Figure 3). Figure 3 defines types of ring edges, depending on which ring or rings to which they belong.

Angles $C_{sp}-C_{sp}\equiv C_{sp}$ and $C_{sp}\equiv C_{sp}-C_{sp^3}$, for expanded cubane (**1**) are 173 and 172°, respectively, and are contained within a 4–4 edge. Molecule **4** has angles of 176 and 170° for the 4–4 edge. For expanded cyclobutane (**7**), these angles are both 175°. Expanded tetrahedrane and prismane experience a similar trend. The expanded tetrahedrane angles of the 3–3 edge are both 163°, while these angles are 165 and 162°in expanded bicyclo[1.1.0]-butane. In expanded cyclopropane (**8**), these angles are 169 and 168°. Expanded prismane has both 4–4 and 4–3 edges, and these are similar to these edges in molecules **4** and **5**. Fused edges (4–4, 4–3, and 3–3) are significantly more distorted than the monocyclic (4–0 and 3–0) edges, but the polyhedra do not experience considerably more distortion than **4**–**6**. The energetic contribution from these distortions will be discussed in terms of the calculated molecular mechanics force constants below.

MM3* Geometries and Energies. Bond angles calculated by molecular mechanics are presented in Table 2. The bond lengths, as expected, show only small deviation from equilibrium values. The total bond stretching energies, in all cases, represent a comparatively small energetic contribution and are not presented. The $C_{sp^3}-H$ stretching and bending terms were, likewise, minor contributors to the total strain energy; these are also not presented. The MM3* geometries agree well (within a few degrees) with the HF/6-31G(d) and B3LYP/6-31G(d) optimized structures.

The energetic contributions from the bending terms, $C_{sp}-C_{sp}\equiv C_{sp}$, $C_{sp}\equiv C_{sp}-C_{sp^3}$, and $C_{sp}-C_{sp^3}-C_{sp}$ are presented in Table 3 along with the total bending energy (E_{bend}).

The $C_{sp}-C_{sp}\equiv C_{sp}$, $C_{sp}\equiv C_{sp}-C_{sp^3}$, and $C_{sp}-C_{sp^3}-C_{sp}$ bending energies constitute 41, 46, and 13% of the total bending strain energy on average. Thus, the majority of the strain energy occurs internal to the diacetylene moiety. The contributions from each term are related to the magnitudes of the bending force constants (Supporting Information). The force constant for bending about the sp^3 center, $C_{sp}-C_{sp^3}-C_{sp}$, is three times greater than the force constant for bending about the adjacent bond, $C_{sp}\equiv C_{sp}-C_{sp^3}$. The central force constant, $C_{sp}-C_{sp}\equiv C_{sp}$, is slightly larger than the latter. The geometric strain is borne by the more flexible acetylene units, in particular $C_{sp}\equiv C_{sp}-C_{sp^3}$, and less by the more rigid corner sp^3 center. As the geometric distortion of the expanded molecule becomes greater the more flexible bond angles contain more strain energy. This is best exemplified in the series **1**–**3** where the total bending energies are 31, 51, and 67 kcal mol^{-1}, and the contributions from the $C_{sp}-C_{sp^3}-C_{sp}$ term are only 20, 15, and 13% of these totals, respectively.

Very large systems can be treated using this modified molecular mechanics force field to obtain reliable geometries. Estimates of strain energies are also available. Two large systems, expanded dodecahedrane and icosahedrane are shown in Figure 4. These are $C_{100}H_{20}$ and $C_{300}H_{60}$, respectively!

TABLE 3. Total Molecular Mechanics Bending Energy (E_{Bend}) (kcal mol^{-1}) is the Sum of the Individual Bending Terms $C_{sp}-C_{sp}\equiv C_{sp}$, $C_{sp}\equiv C_{sp}-C_{sp^3}$, and $C_{sp}-C_{sp^3}-C_{sp}$ Bending Terms[a]

compound	E_{bend}	$C_{sp}-C_{sp}\equiv C_{sp}$	$C_{sp}\equiv C_{sp}-C_{sp^3}$	$C_{sp}-C_{sp^3}-C_{sp}$
expanded cubane **1**	30.6	11.4	13.1	6.1
expanded prismane **2**	50.7	20.3	22.9	7.5
expanded tetrahedrane **3**	66.6	27.3	30.5	8.8
expanded bicyclo[2.2.0]hexane **4**	8.9	3.5	4.0	1.4
expanded bicyclo[2.1.0]pentane **5**	22.8	9.2	10.3	2.9
expanded bicyclo[1.1.0]butane **6**	37.6	15.6	17.5	4.5
expanded cyclobutane **7**	3.7	1.6	1.8	0.3
expanded cyclopropane **8**	15.9	6.8	7.7	1.4
average percentage		40.7	45.9	13.2

[a] The average percentage is the average contribution from the bending term to the total strain energy.

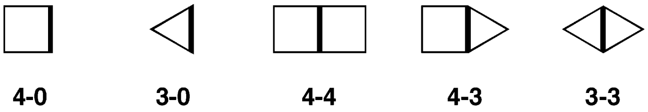


FIGURE 3. Definition of edges in molecules **1**−**8**. Acetylene bonds not shown.

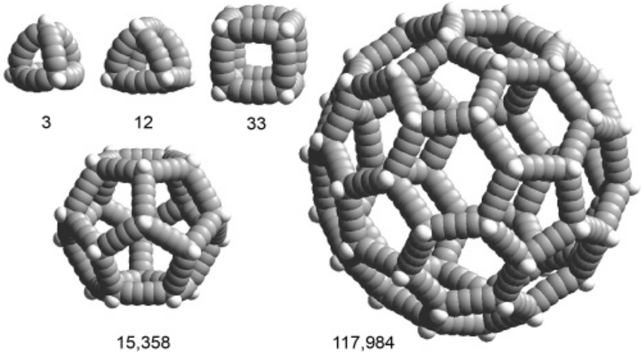
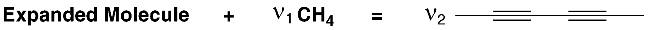


FIGURE 4. MM3* CPK space filling models of molecules **1**−**3**, expanded dodecahedrane, and icosahedrane. Interior volumes are given (Å^3) under each structure.

SCHEME 1. Homodesmotic Equation Used to Calculate the Heats of Formation of Molecules are Balanced by Appropriate Choice of Coefficients ν_1 and ν_2 for 1−8[a]



[a] Results are presented in Table 1.

Expanded dodecahedrane is constructed of expanded cyclopentane faces, while expanded icosahedrane is made-up of both expanded cyclopentane and cyclohexane faces. Expanded cyclohexane and cyclopentane were found to be essentially unstrained according to our parameters. Expanded dodecahedrane is calculated to have only 10.9 kcal mol^{-1} of bending energy. Expanded icosahedrane has a bending energy of 47.6 kcal mol^{-1}, but this is only 0.2 kcal mol^{-1} per diyne unit. Angles $C_{sp}-C_{sp}\equiv C_{sp}$, $C_{sp}\equiv C_{sp}-C_{sp^3}$, and $C_{sp}-C_{sp^3}-C_{sp}$ are very close to their respective equilibrium values in both cases.

Host Properties of Expanded Polyhedranes. Bachrach has predicted that ethynyl-expanded cubane and ethynyl-expanded cyclobutane both bind lithium and sodium cations (from gas-phase calculations) with considerable binding affinities (50−60 kcal mol^{-1}).[6] The structures and binding affinities of these complexes were highly sensitive to the size of the cation. Lithium forms the most stable complex at the center of one face, while sodium complexes at the center of the cube.

The volume of the inner cavity for expanded cubane, prismane, tetrahedrane, dodecahedrane, and icosahedrane were estimated by calculating the distance between sp^3 carbons, according to MM3* geometries, minus twice the van der Waals radius of carbon (1.70 Å).[6,38] Space filling CPK[21] models show these interior spaces along with the estimated volumes (Figure 4). The interior volumes of expanded cubane (33 Å^3) and expanded prismane (12 Å^3) are estimated from simple geometric treatments. The volume of expanded tetrahedrane (3 Å^3) was calculated from the equation $V = 1/12\sqrt{2}\,a^3$, where a is the edge length. The interior volumes of expanded dodecahedrane (15,358 Å^3) and expanded icosahedrane (117,984 Å^3) are approximated as spheres. These volumes are expected to be underestimates since the space created by the bowing of the buta-1,3-diyndyl moieties is truncated using this approximation. Expanded tetrahedrane has essentially no interior volume and would make a poor host, while expanded dodecahedrane and icosahedrane have exceedingly large interior volumes, making them possible host for all kinds of guests. The atomic or molecular van der Waals volumes of a number of species of interest have been previously calculated.[38] Expanded prismane has an interior volume compatible for binding to small atomic cations such as lithium or sodium. Expanded cubane should be able to accommodate up to fourth row cationic alkali and alkaline earth metals, as well as some small neutral molecules. For example, H_2S (30 Å^3), CO_2 (33 Å^3), NH_3 (23 Å^3), and PH_3 (33 Å^3) are all of the right shape and size. The van der Waals volumes of CH_4 (28 Å^3) and HCCH (38 Å^3) make these small organic molecules suitable guests as well.

The size of the orifice leading to the center of expanded polyhedranes is also of interest. The area of the opening has been calculated for molecules **7** (11 Å^2) and **8** (4 Å^2). Interestingly, the area of the cylindrical cross section of diacetylene can be approximated as 9 Å^2; for expanded molecules constructed of expanded cyclobutane faces, a linear polyacetylene could be fed through the center making possible concatenated rings and rotaxanes.

Heats of Formation and Strain Energies. Homodesmotic equations (Scheme 1) calculated at the HF/6-31G(d) level were used to arrive at heats of formation for **1**−**8**. After extensive study, employing multiple isodesmic equations at multiple levels of theory, the above methodology was found to be most reliable. These data can be found in Supporting Information.

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(38) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

In this equation the central single bond, C_{sp}—C_{sp}, of 2,4-hexadiyne balances the central single bond of the buta-1,3-diyndiyl moiety of the expanded molecule. The C_{sp}—C_{sp^3} and C_{sp^3}—H bonds are also balanced homodesmotically. The stoichiometric coefficients, ν_1, and ν_2 vary for each expanded molecule. The calculated heats of formation (ΔH_f^{iso}), strain energy ($\Delta H_f^{iso}-\Delta H_f^{GAV}$), and heat of reaction (ΔH_r^{iso}) are given in Table 1. The latter value can be equated to the strain energy since 2,4-hexadiyne and methane are unstrained. The $\Delta H_f^{iso}-\Delta H_f^{GAV}$ and ΔH_r^{iso} values agree well for the open structures **4**−**8**. The ΔH_r^{iso} tends to give slightly lower strain energies compared to $\Delta H_f^{iso}-\Delta H_f^{GAV}$. For **1**−**3** ΔH_r^{iso} estimates the strain energy to be larger than $\Delta H_f^{iso}-\Delta H_f^{GAV}$. All estimates predict considerable strain energies for the expanded polyhedra.

The stabilities of **1**−**8** follow the same basic order as the corresponding unexpanded analogues. The unexpanded analogues of **1**−**3** have strain energies greater or equal to the sum of their constituent faces. For example, cubane has roughly six times the strain energy of cyclobutane[9a] while prismane and tetrahedrane are considerably more strained than the sum of their respective faces. Expanded cyclobutane (22.4 kcal mol^{-1}) has a ring strain energy of about half of that calculated for expanded bicyclo[2.2.0]hexane (46.3 kcal mol^{-1}). Likewise, the strain energy of expanded cyclopropane is close to half of the strain energy for expanded bicyclo[1.1.0]-butane. The strain energy of expanded bicyclo[2.1.0]-pentane (57.7 kcal mol^{-1}) compares well to the sum of the strain energies of expanded cyclopropane and cyclobutane (55.1 kcal mol^{-1}). In great contrast to unexpanded analogues, the strain energies of expanded polyhedranes are substantially less than the sum of their constituent faces according to Benson group equivalent derived strain energies ($\Delta H_f^{iso}-\Delta H_f^{GAV}$) and roughly equal according to estimates from the heat of reaction (ΔH_r^{iso}). Considering the former, the strain energies for expanded cubane, prismane, and tetrahedrane are, 107.8, 113.1, and 111.8 kcal mol^{-1}, respectively. Six times the strain energy of expanded cyclobutane (134.4 kcal mol^{-1}) is almost 30 kcal mol^{-1} larger than the calculated value for expanded cubane. The sum of the strain energies of the faces for expanded prismane and tetrahedrane are 132.6, and 130.4 kcal mol^{-1}, respectively. Both of these values are substantially overestimated. Expanded polyhedra can similarly be deconstructed into constituent expanded bicyclic hydrocarbons. These likewise overestimate the strain energies of **1**−**3**. Polyhedranes would be expected to carry more strain energy than the sum of the strain energies of their constituent faces, since the buta-1,3-diyndiyl units in expanded polyhedranes are calculated to be much more geometrically distorted as compared to the structures of expanded cyclobutane and propane. Presumably, the great flexibility of the diyne unit accounts for the lack of this degree of strain energy.

Conclusion

Optimized structures of expanded molecules at the HF/6-31G(d) and B3LYP/6-31G(d) levels show good agreement to available experimental geometric parameters. Structures obtained from molecular mechanics calculations using specifically parametrized force constants for the buta-1,3-diynediyl moiety are also able to reproduce experiment. Analysis of these geometries suggests that the distortions of expanded three-dimensional polyhedranes are similar to those of analogous open bicyclic expanded structures. Both the bicyclic expanded hydrocarbons and the expanded polyhedranes are significantly distorted relative to monocyclic expanded molecules. Ring-fusion to form expanded bicycles results in the largest geometrical distortions.

The stabilities of these compounds have been investigated by a combination of isodesmic, group additivity, and molecular mechanics methods. Molecular mechanics results reveal that the great majority of strain in these systems is contained within the bowed buta-1,3-diyndiyl units; only a small portion of this strain rest about the corners sp^3 centers. Expanded dodecahedrane and icosahedrane have minimal distortion of their diyne units.

Homodesmotic equations were used to arrive at the most reliable heats of formation and strain energies. The polyhedranes have large heats of formation, far greater than C_{60} and even some small carbon nanotubes.[39] The expanded molecules were found to follow a similar strain energy trend to that of their unexpanded counterparts. However, the flexibility of the diyne unit makes expanded polyhedranes less strained than expected.

There are a number of potential applications for expanded polyhedranes. They may serve as hosts for atomic cations and small organic molecules having dynamic access to their interior cavities. They have potential as templates for rigid functional structures with optoelectronic and biological applications. In addition, the tending of the diacetylene unit to undergo polymerization, although currently a possible detriment to their synthesis, may allow for future three-dimensional polymer networks. The applications for these molecules are broad, and further synthetic and theoretical investigations are underway. These results will have a fertilizing effect on further experimental studies aimed at the synthesis of additional expanded polyhedranes.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research. This work was partially supported by National Computational Science Alliance under MCA93S015N and utilized the IBM pSeries 690 supercomputing system. P.D.J. is grateful for the support of the American Chemical Society Organic Division Fellowship sponsored by Organic Reactions, Inc. We thank N. L. Allinger for helpful advice.

Supporting Information Available: Full discussion of methodology including, curve fitting data for molecular mechanics force field parametrization, complete isodesmic and homodesmotic results at all levels of theory employed for the model system 2,4-hexadiyne, 1−3,butadiyne, and for molecule **1**−**8**. Electronic energies, zero-point energies, and thermal corrections at 298 K at these levels are also presented. HOMO−LUMO energies and gaps for **1**−**8** are provided as well as the HF/6-31G(d) and B3LYP/6-31G(d) optimized coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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[39] (a) Kolesov, V. P.; Pimenova, S. M.; Pavlovich, V. K.; Tamm, N. B.; Kurskaya, A. A. *J. Chem. Thermodynamics* **1996**, *28*, 1121−1125. (b) Cioslowski, J.; Rao, N.; Moncrieff, D. *J. Am. Chem. Soc.* **2000**, *122*, 8265−8270. (c) Cioslowski, J.; Rao, N.; Moncrieff, D. *J. Am. Chem. Soc.* **2002**, *124*, 8485−8489.