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Interconversions of Cyclobutyne, Cyclopentyne, Cyclohexyne, and Their Corresponding Cycloalkylidenecarbenes

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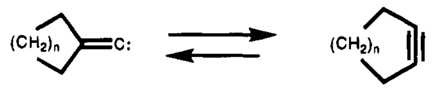
Abstract: C_4 to C_6 cycloalkynes and cycloalkylidenecarbenes have been investigated by MCSCF(4,4)/6-31G* and MP4/6-31G*//MP2/6-31G* calculations. Cyclobutyne (**3**) is predicted to rearrange to cyclopropylidenecarbene (**4**) with a barrier of 0 to 4.6 kcal/mol and a reaction enthalpy of -20 kcal/mol. Cyclobutylidenecarbene (**6**) is predicted to rearrange to cyclopentyne (**7**) with a barrier of 4 to 15 kcal/mol and a reaction enthalpy of -8 kcal/mol. Similarly, cyclopentylidenecarbene (**8**) is predicted to give cyclohexyne (**9**) with a barrier of 11 to 24 kcal/mol and a reaction enthalpy of -17 kcal/mol. The energetics are explained as a balance between the exothermicity of the carbene to alkyne reaction, ring size strain, and strain in the cycloalkyne π bond. An unexpected conclusion is that π bond strain does not increase in large increments with bending about the triple bond, but rather is nearly maximized for cyclopentyne and then increases slowly thereafter. In-plane π bond strain in cyclopropyne (**17**), **3**, **7**, and **9** is estimated from isodesmic reactions to be 75.4, 73.4, 68.1, and 40.7 kcal/mol, respectively. An alternative approach based on homodesmic reactions affords total strain energies of 133, 106, 74, and 41 kcal/mol.

Introduction

1,2-Shifts provide a simple mechanism for interconversion of cycloalkynes (**2**) and cycloalkylidenecarbenes (**1**), with the preferred direction potentially controlled by the balance between the inherent exothermicity of the **1** → **2** transformation and strain in the cycloalkyne.[1] Although these substances have been the subjects of diverse experimental and theoretical studies (*vide infra*), important questions about structure and reactivity remain unanswered. Among the cycloalkynes, experimental evidence for cyclobutyne (**3**) has remained elusive.[2] In 1984, Szeimies reported evidence that a bicyclic cyclobutyne derivative rearranged to a cyclopropylidenemethylene, but the data did not unequivocally support a free cyclobutyne.[3] Tomioka recently described unsuccessful attempts to generate a benzannelated cyclobutyne.[4] Adams has synthesized several metal complexes with **3** as a ligand, although these are not prepared directly from **3**.[5] In a 1992 publication, Schaefer predicted a barrier of ca. 25 kcal/mol for isomerization of **3** to butatriene (**5**) and suggested that **3** should be "makeable".[6] Rearrangement of **3** to **4** was not explored, but this process would be consistent both with Szeimies' results[3] and with Schaefer's earlier prediction that smaller homologue cyclopropyne is only a transition state for degenerate rearrangement of propadienylidene.[6c] To further confuse this field, Dewar and co-workers very recently predicted, based on AM1 calculations, that rearrangement of **4** should yield a cyclobutyne "orbital isomer" rather than "classical cyclobutyne".[7] In an earlier study, Gilbert and Kirschner similarly suggested, again based on AM1 calculations, that cyclobutylidenemethylene (**6**) will rearrange to a higher energy cyclopentyne "lumomer" rather than to cyclopentyne (**7**) itself.[8] For the six carbon series, rearrangement of carbene **8** provides one of several routes to cyclohexyne (**9**).[1,9–11]



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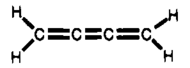

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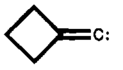

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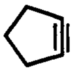

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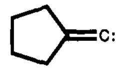

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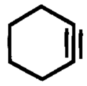

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To address the many questions left unanswered by previous studies, we have carried out a systematic ab initio study of cycloalkyne structures and the interconversions of C_4 to C_6 cycloalkynes with their isomeric cycloalkylidenemethylenes. Our calculations provide predictions for structures and barriers to rearrangements, a much less sanguine prediction for the kinetic

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Table 1. Absolute and Relative Energies for Cyclobutyne (3) and Cyclopropylidenemethylene (4)[a]

	3 (C_{2v})	TS **3** to **4** (C_s)	**4** (C_{2v})
TCSCF/3-21G//	−152.734 56	−152.727 21	−152.766 10
TCSCF/3-21G	(0.0)	(4.61)	(−19.8)
MCSCF(4,4)/3-21G//	−152.780 64	−152.773 46	−152.813 92
MCSCF(4,4)/3-21G	(0.0)	(4.50)	(−20.8)
MCSCF(4,4)/6-31G*//	−153.646 84	−153.644 03	−153.678 78
MCSCF(4,4)/6-31G*	(0.0)	(1.76)	(−20.0)
SOCI/6-31G*//	−153.676 33	−153.674 27	−153.712 74
MCSCF(4,4)/6-21G*	(0.0)	(1.29)	(−22.8)
MCSCF/6-31G* ZPVE[b]	41.9	41.0	40.9[c]
(kcal/mol)		($\nu_I = -721.5$)	
MP2/6-31G*//	−154.083 49	−154.079 26	−154.110 54
MP2/6-31G*	(0.0)	(2.65)	(−17.0)
MP2/6-31G* ZPVE[b]	42.0	39.8	39.0
(kcal/mol)		($\nu_I = -912.9$)	
MP4SDTQ/6-31G*	−154.135 86	−154.134 03	−154.170 08
//MP2/6-31G*	(0.0)	(1.15)	(−21.4)
MP4SDTQ/6-311G**	−154.225 44	−154.224 61	−154.257 38
//MP2/6-31G*	(0.0)	(0.52)	(−20.0)

[a] Total energies in hartrees. Relative energies (kcal/mol) for each series are in parentheses. [b] Zero point vibrational energies are unscaled. [c] With constraint to C_{2v} this structure showed a single imaginary frequency of -123.95 cm^{-1}.

Table 2. Absolute and Relative Energies from ab Initio Calculations[a,b]

	MCSCF(4,4)/3-21G	MCSCF(4,4)/6-31G*	MP4SDTQ/6-31G*	ZPVE[c]
6 (C_s)	−191.648 84	−192.722 64	−193.353 27	60.6
	(0.0)	(0.0)	(0.0)	
TS **6** to **7** (C_1)	−191.616 23	−192.698 41	−193.346 77	60.3
($\nu_i = -515.1$)	(20.5)	(15.2)	(4.07)	
7 (C_s)	−191.667 90	−192.735 08	−193.365 99	62.2
	(−12.0)	(−7.81)	(−7.98)	
8 (C_2)	−230.511 19	−231.794 84	−232.572 34	81.0
	(0.0)	(0.0)	(0.0)	
TS **8** to **9** (C_1)	−230.468 36	−231.757 38	−232.554 76	80.0
($\nu_i = -608.9$)	(26.9)	(23.5)	(11.03)	
9 (C_2)	−230.538 28	−231.818 28	−232.598 36	82.1
	(−17.0)	(−14.7)	(−16.7)	

[a] Total energies in hartrees. Relative energies (kcal/mol) for each series are in parentheses. [b] All geometries were optimized at the MCSCF(4,4)/3-21G level. [c] In kcal/mol, calculated at the MCSCF(4,4)/3-21G level.

stability of cyclobutyne, and estimates of relative strain in the cycloalkynes, which result in some very unexpected conclusions about the relationship between ring size and strain.

Computational Methods

Accurate predictions for highly strained structures such as these cycloalkynes require sophisticated ab initio methods. Initial structures were generated with SPARTAN[12], which was also used to visualize SCF molecular orbitals. Two general methodologies based on correlated wavefunctions were then employed.

In one computational approach, a four-orbital/four-electron multiconfiguration SCF (MCSCF) wave function was chosen as a consistent description of electronic structures of the cycloalkyne, transition state, and carbene. The MCSCF orbital space in each case included two in-plane and two out-of-plane orbitals, with full excitation within this orbital space. For the carbenes, optimal correlation for the doubly occupied σ orbital came from a virtual orbital of like symmetry. GAMESS was used for MCSCF studies.[13]

As a complementary method, structures for the cyclobutyne series were optimized using GAUSSIAN 92 at the MP2(FC)/6-31G* level, followed by single point MP4(SDTQ) calculations.[14] All calculations were performed in Cartesian coordinates. Similar optimizations and frequency analyses were performed for cyclopentyne and cyclohexyne. In the C_5 and C_6 series, single point MP4 calculations were performed using the MCSCF/3-21G optimized geometries.

No calculations were undertaken for the corresponding triplet states. Previous studies have shown that both cyclobutyne[6] and this general type of sp-hybridized carbene[15] should have a singlet ground state with a large singlet−triplet gap. As a consequence, we do not expect involvement of the triplet manifold.

Results and Discussion

Total and relative energies are summarized in Tables 1−3, while selected geometrical parameters are given in Figures 1−3. Cartesian coordinates for stationary points are included in the Supplementary Material.

Cyclobutyne (3) and Cyclopropylidenecarbene (4). Cyclobutyne is not an energy minimum at the HF/6-31G* level.[16] Vibrational frequency analysis on the C_{2v} constrained structure affords two negative frequencies, of which the largest (B_1 symmetry, 957 cm^{-1}) corresponds to the reaction coordinate toward **4** described below. MCSCF (or TCSCF[6]) and MP2

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(12) SPARTAN: Versions 2.0 and 3.0; Wavefunction Inc., 1992 and 1993.

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Table 3. Data from ab Initio Møller–Plesset Calculations[a]

	MP2/6-31G*	MP4SDTQ/ 6-31G*	ν_{stretch}[b]
cyclobutyne (**3**)	−154.083 49	−154.135 86	1693 (1796)
cyclopentyne (**7**)	−193.299 65	−193.367 76	1799 (1908)
cyclohexyne (**9**)	−232.518 75		1953 (2072)
cyclobutene (**13**)	−155.410 18	−155.468 38	
cyclopentene (**14**)	−194.618 15	−194.691 78	
cis-2-butene (**15**, C_2)	−156.623 47	−156.689 04	
2-butyne (**16**, D_{3h})	−155.415 72	−155.473 48	
cyclopropene (**18**)	−116.205 25	−116.247 12	
cyclopropyne[c] (**17**)	−114.868 70	−114.911 46	
hydrogen (H_2)	−1.1441 408	−1.1509 257	
ethane	−79.494 74	−79.532 82	
propane	−118.660 34	−118.714 07	
propyne	−116.241 81	−116.284 10	
acetylene	−77.0667 9	−77.0935 8	

[a] All calculations are at the MP2(FC)/6-31G* optimized geometries. [b] In cm^{-1}. Values given are scaled[31] by 0.9427. Unscaled values are given in parentheses. [c] Restricted to C_{2v}. Structure is actually a transition state. See ref 6c.

calculations do predict the C_{2v} structure to be a true minimum. Stationary points for the C_4 series were located and subjected to frequency analysis at the MCSCF(4,4)/3-21G and MCSCF-(4,4)/6-31G* levels.[17] The MCSCF(4,4)/6-31G* wave function was further utilized as the basis for multireference CI calculation involving all singly and doubly excited configurations generated from the MCSCF reference. Further MP2 optimizations were performed beginning with the MCSCF geometries.

As in the previous study by Schaefer,[6] we found a substantial barrier along the C_2 electrocyclic coordinate toward **5**, which is best described as a conrotatory opening. Our MCSCF(4,4)/6-31G* calculations give a transition state energy of −153.547 99 hartrees, which leads to a predicted barrier to ring opening of 62.0 kcal/mol. Schaefer's calculated barriers ranged from 41 to 71, with a final estimate of ~25 kcal/mol.[6]

We next explored the more likely reaction path toward carbene **4**. Slight elongation of the C2–C3 bond in **3** led to a transition state of C_s symmetry for rearrangement to carbene **4**.[7] In the MCSCF(4,4)/6-31G* or MP2/6-31G* transition state structures (Figure 1), the breaking σ bond has lengthened less than 0.1 Å relative to **3**. To ensure location of the correct saddle point, the intrinsic reaction coordinate[18] was calculated in both directions at the MCSCF/3-21G level; in each case, this led smoothly to either **3** or **4**.

The energetics of the **3** to **4** rearrangement were only modestly dependent on basis set and level of calculation. The predicted enthalpy change (Table 1) proved to be remarkably consistent at ca. −20 cal/mol, independent of the level of calculation. The classical enthalpic barrier for rearrangement of **3** to **4** ranged (Table 1) from 0.52 to 4.6 kcal/mol. Correction for zero point vibrational energy differences lowers this predicted barrier in each case. Using the values from MCSCF zero point calculation, and the MCSCF or SOCI energies, the predicted barrier is either 0.86 or 0.39 kcal/mol. With the MP4//MP2 values, the enthalpic barrier disappears altogether because of the lower transition state zero point energy, and, at this level, cyclobutyne is not predicted to be a minimum! Higher level calculations might once again reverse this, but *the most reasonable conclusion at present is that cyclobutyne must exist in a very shallow minimum and will rearrange with little or no barrier to carbene* ***4***. This minimal barrier is consistent with the "early" transition state geometry, i.e., one which strongly resembles **3**. The predicted facility of this rearrangement is underscored by an earlier prediction that alkyl shifts in vinylidenes should have much larger barriers (ca. 20 kcal/mol)[19] than hydrogen shifts (<10 kcal/mol).[20]

Dewar and co-workers recently suggested that cyclobutyne will exist as an "orbital isomer" rather than "classical cyclobutyne". AM1 calculations predict $\Delta H_{\mathrm{R}} = -45.3$ and $\Delta H^{\ddagger} = 18.0$ kcal/mol for rearrangement of **3** to **4**.[7] Our own analysis of the SCF or MCSCF orbitals of **3** revealed nothing remarkable, and we do not see evidence that this substance is an "orbital isomer". Cyclobutyne is cyclobutyne.

Is this belated prediction consistent with experiment? In a much overlooked paper, Baumgart and Szeimies reported in 1984 that reaction of **10** (X = Cl, Br, or I) with lithium diisopropylamide resulted in products which resulted from nucleophilic trapping of both **11** and **12** in a 0.15:1 ratio.[3]

10 **11** **12**

This result implies facile rearrangement of **11** to **12**, with nucleophilic trapping at both stages, in qualitative agreement with our computational results. However, the very small magnitude of our calculated barrier, in conjunction with the expectation of a modest barrier for nucleophilic addition, seems inconsistent with trapping of free **11**.[21a] It is also possible that the observed reactions are characteristic of a β-lithiohaloalkene. Isotopic labeling experiments, which might prove the existence of a symmetrical intermediate, have not yet been completed.[21b]

Cyclopentyne (7) and Cyclobutylidenecarbene (6). In larger rings, a carbene to cycloalkyne rearrangement is observed experimentally. This reversal occurs because the exothermicity[20] of the carbene to alkyne rearrangement now overcomes cycloalkyne ring strain. Cyclopentyne (**7**) is relatively well known and often is prepared by the intermediacy of carbene **6**.[11]

Results for this series are summarized in Figure 2 and Table 2. Our calculations predict a very modest enthalpy change of ca. −8 kcal/mol. The MCSCF enthalpic barrier of 15.2 kcal/mol is decreased to only 4.07 kcal/mol at the MP4/6-31G*//MCSCF/3-21G* level. The lower value is probably the more accurate prediction.

As with a previous ab initio study by Olivella et al.[23], our MCSCF and MP2 calculations predict cyclopentyne to represent a true energy minimum. The structure has C_s symmetry and a slightly puckered ring, much like cyclopentene. Examination

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(19) Goddard, J. D. *Chem. Phys. Lett.* **1981**, *84*, 609.

(20) (a) Schaefer, H. F. *Acc. Chem. Res.* **1979**, *11*, 107. (b) Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *79*, 408. (c) Osamura, Y.; Schaefer, H. F.; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904. (d) Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1990**, *112*, 8714. (e) Smith, B. J.; Smernik, R.; Radom, L. *Chem. Phys. Lett.* **1992**, *188*, 589. (f) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6133. (g) Semprini, E.; Palma, A.; Stefani, F. *THEOCHEM* **1993**, *99*, 133.

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(22) (a) Fitjer, L.; Kliebisch, U.; Wehle, D.; Modaressi, S. *Tetrahedron Lett.* **1982**, *23*, 1661. (b) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 664. See also ref 4.

(23) TCSCF study on cyclopentyne: Olivella, S.; Pericas, M. A.; Riera, A.; Sole, A. *J. Am. Chem. Soc.* **1986**, *108*, 6884.

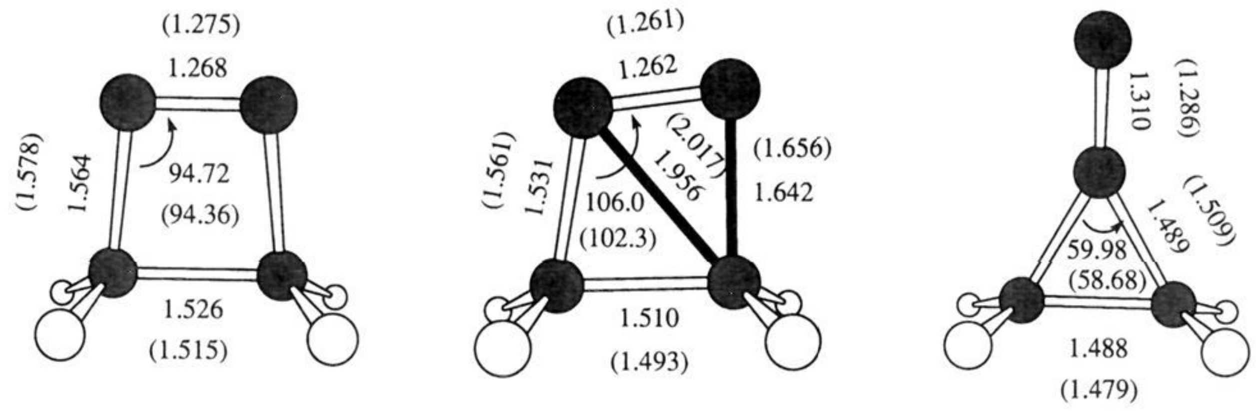


Figure 1. MCSCF(4,4)/6-31G* and MP2/6-31G* (in parentheses) optimized geometries for **3**, TS **3** to **4**, and **4**.

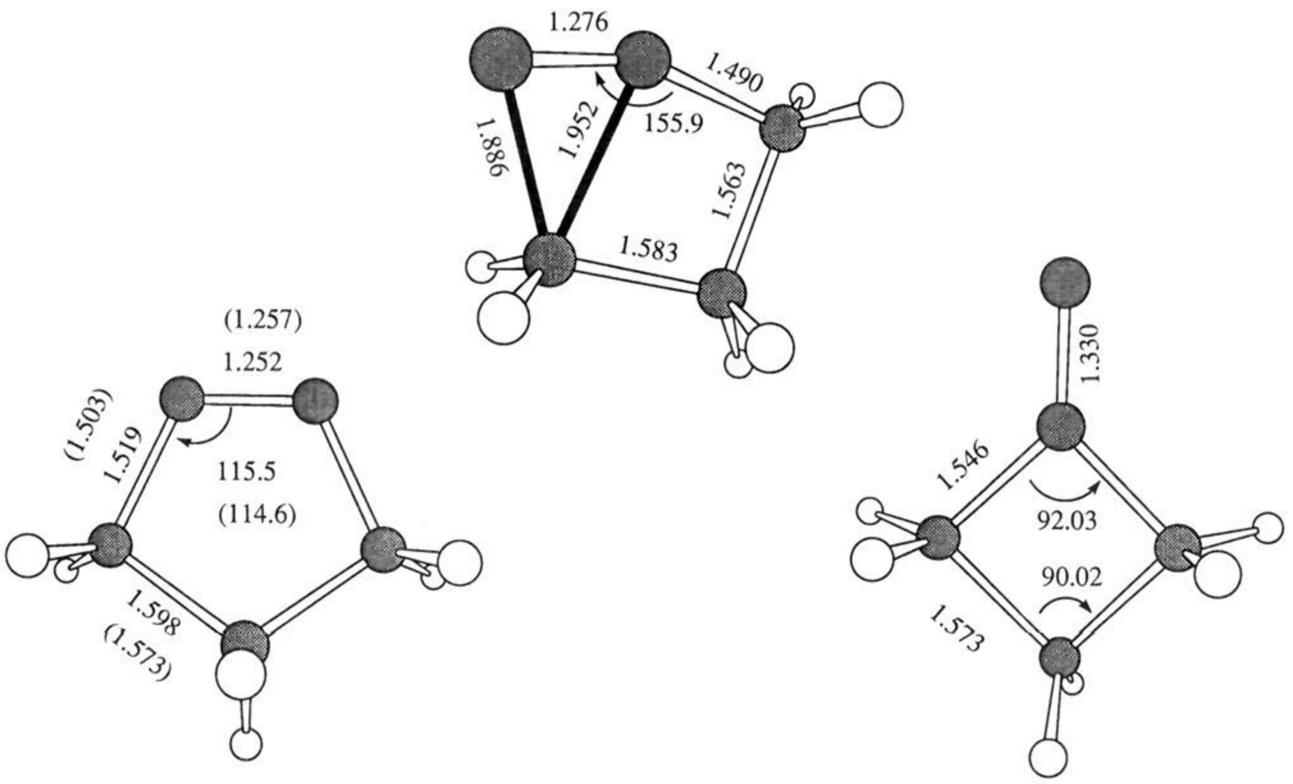


Figure 2. MCSCF(4,4)/3-21G optimized geometries for **6**, TS **6** to **7**, and **7**. MP2/6-31G* values are in parentheses.

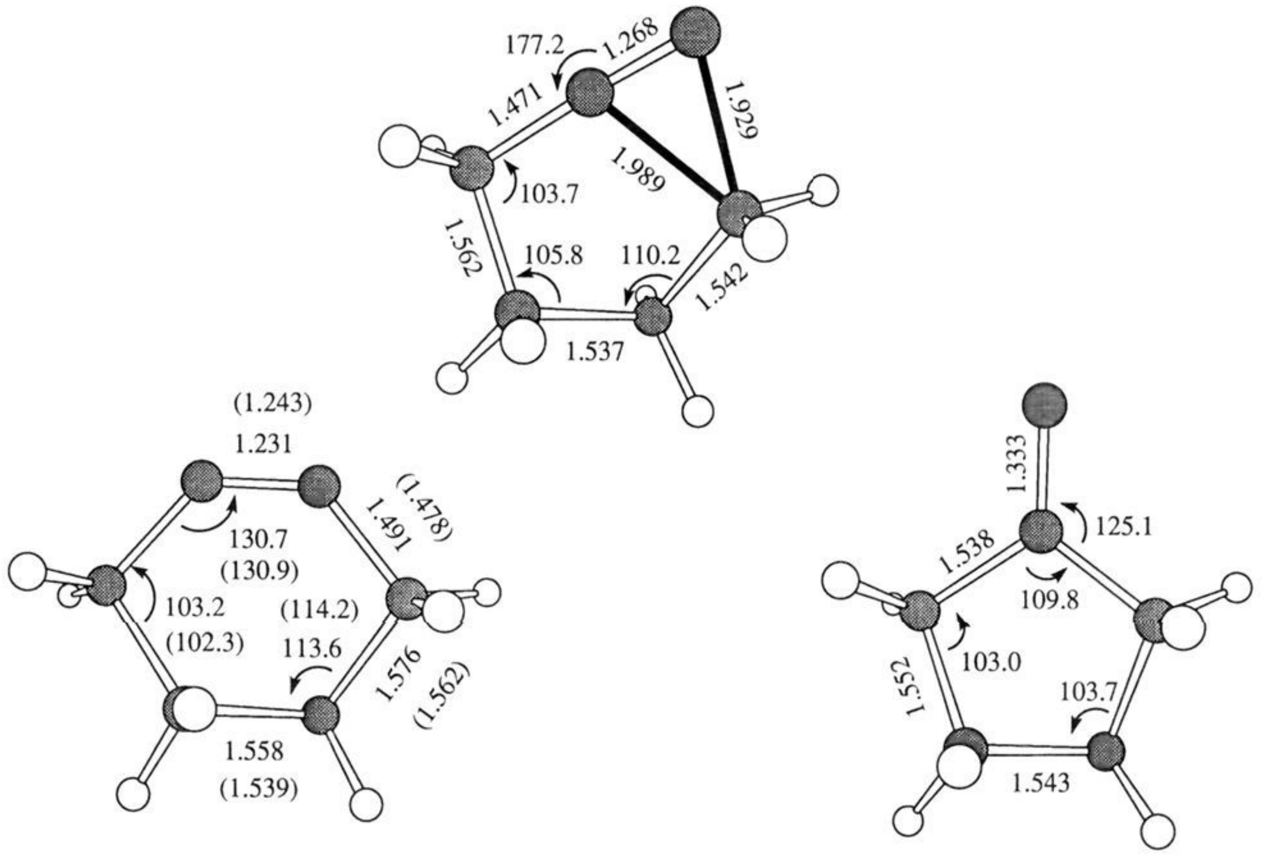
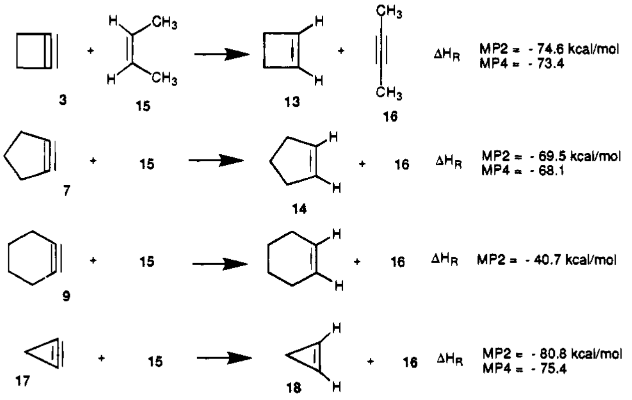


Figure 3. MCSCF(4,4)/3-21G optimized geometries for **8**, TS **8** to **9**, and **9**. MP2/6-31G* values are in parentheses.

of the molecular orbitals along the reaction path shows smooth correlation of occupied orbitals, with an apparent crossing of the in-plane HOMO and LUMO rendered "avoided" by the multiconfiguration wave function. Gilbert and Kirschner recently predicted an unsymmetrical "lumomer" structure for cyclopentyne.[8] We believe this "lumomer" is most likely an artifact of the AM1 methodology, which also incorrectly predicts that rearrangement of **6** to **7** would be *endothermic* by 25.6 kcal/mol.

Cyclohexyne (9) and Cyclopentylidenecarbene (8). For the six carbon series, one previous MP2/6-31G*//HF/3-21G study has been described by McKee and co-workers.[10] A TCSCF study on cyclohexyne also has been reported.[24] Cyclohexyne is relatively well known and often is prepared by rearrangement

Scheme 1. Isodesmic Reactions to Estimate Cycloalkyne π Bond Strain[a,b]



[a] Data are taken from Tables 1 and 3. [b] MP2 = MP2/6-31G*//MP2/6-31G*; MP4 = MP4SDTQ/6-31G*//MP2/6-31G*.

of carbene **8**.[9-11] Our structures were optimized at the MCSCF(4,4)/3-21G level, followed by single point MCSCF(4,4)/6-31G* and MP4/6-31G* calculations. Both MP2 and MCSCF methods yield a structure of C_2 symmetry for **9**, which resembles the well-known half-chair structure of cyclohexene. Once again, the MP4//MCSCF barrier of 11.0 kcal/mol is much smaller than that predicted by MCSCF//MCSCF calculations and is probably the more accurate of the two predictions. The predicted enthalpy change is consistently -14 to -17 kcal/mol.

Strain Estimates. How strained are these cycloalkynes? No more fundamental question exists for a homologous series such as this. In principle, reliable estimates of strain may be derived by comparison to appropriate reference molecules.

We first consider the series of isodesmic reactions[14b] shown in Scheme 1. All structures were optimized at the MP2(FC)/6-31G* level; data are summarized in Table 3. MP4//MP2 or MP2//MP2 total energies are used because these are the most consistent in application to all relevant structures.[25] Data for cyclopropyne (**17**) also are included. This structure is actually a transition state,[6c] but our strain analysis as a cycloalkyne should still be valid. The isodesmic reactions in Scheme 1 effectively trade the highly strained cycloalkyne triple bond for a similar unstrained bond in butyne, while leaving the orthogonal π bond minimally changed. As a consequence, ΔH_R should be a measure of strain in the in-plane π bond. According to these calculations, the series of homologous cycloalkynes **17**, **3**, **7**, and **9** have in-plane π bond strain energies of 75.4, 73.4, 68.1, and 40.7 kcal/mol, respectively. If we add the strain energy of the respective cycloalkenes[26] as an approximation for other strain components, total strain energies of 130.6, 101.8, 68.1, and 40.7 kcal/mol are predicted. For comparison, we note that a similar calculation for *o*-benzyne using experimental heats of formation[27,28] gives a π bond strain energy of 50.1 kcal/mol. The same trends are reflected in MP4//MP2 heats of hydrogenation (alkyne to alkene), calculated to be -115.9, -114.0, and -108.6 kcal/mol for **17**, **3**, and **7**, respectively. Nicolaides and Borden recently ascribed a strength of 76.0 kcal/mol to each of the π bonds in acetylene.[29] Our results thus suggest that the in-plane π bond in cyclobutyne should have a strength of only ca. 3 kcal/mol, while the π bond in cyclopropyne is effectively broken! The same simple arithmetic yields in-plane π bond energies of 7.9 and 35.3 kcal/mol for **7** and **9**.

An alternative approach is based on the homodesmic reactions[30] shown in Scheme 2. These equations relate the cycloalkyne with completely unstrained acyclic structures and thus yield estimates for total molecular strain. The predicted total strain energies of 133, 106, 74, and 41 kcal/mol for **17**, **3**, **7**, and **9**, respectively, are in good agreement with the estimates above.

In principle, both π bond strain and total strain in this homologous series should increase steeply with the internal ring angle (ϕ) about the triple bond. Inspection of the data in Figures 1–3 suggests that cyclobutyne ($\phi = 94.9°$ at the MP2 level) should be much more strained than cyclopentyne ($\phi = 114.6°$), with cyclohexyne ($\phi = 130.9°$) a distant third. The corresponding MP2/6-31G* value for cyclopropyne is 65.3°. Total strain (Scheme 2) seems to increase in large increments as expected. However, π bond strain (Scheme 1), a critical component in this analysis, rises steeply from **9** to **7** and then increases slowly thereafter. Thus, *quite unexpectedly, we find that cyclobutyne and cyclopropyne have π bond strain energies only slightly greater then cyclopentyne*!

This apparent anomaly may have a simple explanation. If a double bond is twisted, the limit of strain should be the rotational barrier (ca. 65 kcal/mol) in which the π bond is completely broken. By analogy, *there should also be a limit to the strain possible for in-plane bending in alkynes, i.e., the π bond strength of 76 kcal/mol.*[30] Our data suggest that, in cyclopentyne, the structure is already approaching the maximum strain available in the π bond, and so with **3** and **17**, only modest additional increases in strain are possible. The predicted increase in total strain then comes primarily from other components which correspond to those present in cycloalkenes.

Vibrational Frequencies. Triple bond vibrational frequencies for these strained alkynes might provide further correlation with experiment. Some earlier predictions have been made at the TCSCF level.[6,23,24] Scaled and unscaled MP2 values are given in Table 3.[31] The predicted MP2 vibrational frequency of cyclobutyne, 1693 cm^{-1}, is only marginally above that for a double bond! Sander and Chapman have reported the matrix IR spectrum for 3,3,6,6-tetramethylcyclohexyne[32] but were unable to assign a band for the triple bond. Our calculations predict a very weak band (IR intensity = 0.33) at ca. 1953 cm^{-1}, but the published spectrum shows nothing identifiable near this frequency.

Reaction Energetics. The relative energetics of cyclobutyne on the C_4H_4 potential energy surface are also of inherent interest. It is thus pertinent to note that the MP4//MP2 total energies of cyclobutyne are 6.0, 12.5, and 77.6 kcal/mol, respectively, above energies for isomers 1,2-cyclobutadiene,[33] tetrahedrane, and vinylacetylene. This latter isomer is believed to be the global

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(27) The heat of formation of *o*-benzyne has been reported to be 106.6 ± 3 kcal/mol: Wenthold, P.G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.

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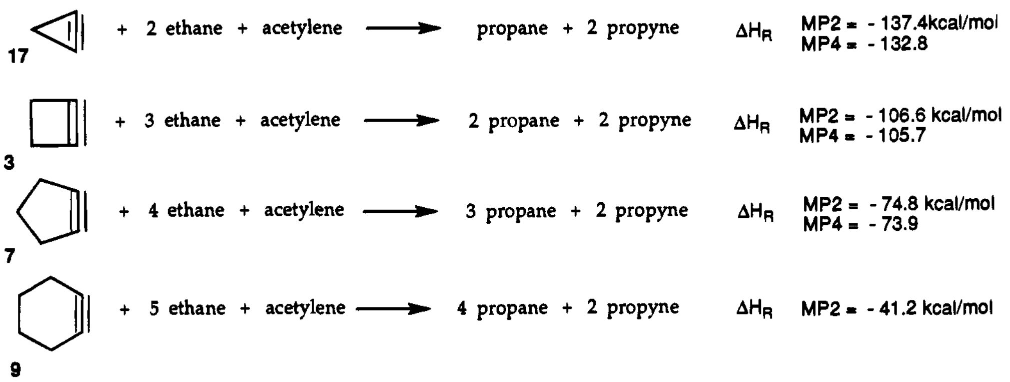
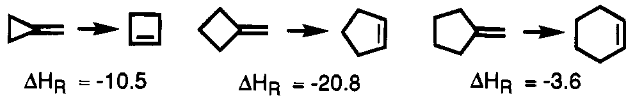
Scheme 2. Homodesmic Reactions to Estimate Cycloalkyne Total Strain[a,b]



[a] Data are taken from Tables 1 and 3. [b] MP2 = MP2/6-31G*//MP2/6-31G*; MP4 = MP4SDTQ/6-31G*//MP2/6-31G*.

C_4H_4 minimum.[16] At the MCSCF(4,4)/6-31G* level, **3** is 39.2 kcal/mol less stable than 1,3-cyclobutadiene.[34]

Thermal interconversion between acetylene and vinylidene has been the subject of numerous investigations.[20] For the cyclic structures described here, overall energetics for the **1** → **2** interconversion must derive principally from a combination of inherent exothermicity of the carbene to alkyne reaction (ca. 45 kcal/mol[20]), strain in the alkyne in-plane π bond, and ring size differences. Simple analysis permits insights into the directionality of the observed reactions. As models for the ring size differences, experimental heats of formation for appropriate endocyclic and exocyclic cycloalkenes give the energy changes shown below.[28] In the C_4 isomers, the exothermicity of ring expansion (−10.5 kcal/mol) and carbene to alkyne rearrangment (−45 kcal/mol) are overwhelmed by alkyne strain (73.4 kcal/mol). Not surprisingly, the resultant energy difference (−17.9 kcal/mol) is nearly identical with our predicted reaction exothermicity. In the cyclopentyne series, the larger ring size difference and diminished cycloalkyne strain serve to reverse the energetics. This trend would continue for larger rings as cycloalkyne strain diminishes.



Conclusions

These calculations predict that cyclobutyne (**3**) should rearrange to cyclopropylidenemethylene (**4**) with little or no barrier. As a consequence, we believe that direct observation of cyclobutyne should be difficult or impossible. Previous exploration of the electrocyclic ring opening of **3** to butatriene shows a substantial barrier in this direction;[6] hence, rearrangement of **3** to **5** should not be observed. In larger rings, the balance of strain and reaction energetics favors the cycloalkyne, and modest barriers are predicted for the **6** → **7** and **8** → **9** rearrangements, in qualitative agreement with experiment. Isodesmic or homodesmic reactions have provided what should be reliable estimates for strain in the cycloalkynes. Unexpectedly, we find that π bond strain does not increase in large increments with bending about the triple bond, but rather is nearly maximized for cyclopentyne and then increases slowly thereafter.

Finally, we believe it should be possible to computationally *design* a more stable cyclobutyne derivative by application of some geometric constraint or electronic substituent effects. Efforts to realize this prediction are in progress.[35] Remarkably, Maier has recently reported evidence for matrix isolation of 3-silacyclopropyne.[36] In this case, the energetics of cycloalkyne−alkylidenecarbene interconversion are dramatically changed by the presence of silicon.

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Supplementary Material Available: Cartesian coordinates for most stationary points calculated in this research (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(35) Bradley, A. Z.; Johnson, R. P. Unpublished results. MCSCF(4,4)/3-21G calculations indicate that perfluorocyclobutyne will have relatively large barriers both for electrocyclic ring opening and rearrangement to a carbene. Higher level calculations and experiments designed to detect this species are in progress.

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