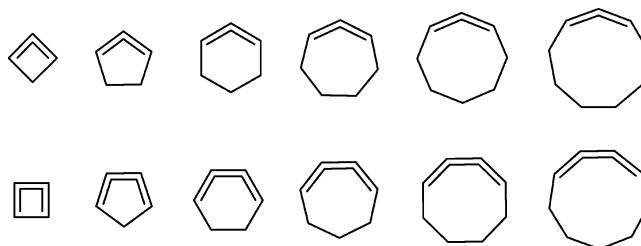# Strain Estimates for Small-Ring Cyclic Allenes and Butatrienes

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Isodesmic and homodesmic equations at the B3LYP/6-311+G(d,p)+ZPVE level of theory have been used to estimate strain for the homologous series of cyclic allenes and cyclic butatrienes. A simple fragment deformation approach also has been applied and appears to work better for the larger rings. For the cyclic allene series, estimates for allene functional group strain (kcal/mol) include: 1,2-cyclobutadiene, 65; 1,2-cyclopentadiene, 51; 1,2-cyclohexadiene, 32; 1,2-cycloheptadiene, 14; 1,2-cyclooctadiene, 5; 1,2-cyclononadiene, 2; 1,2,4-cyclohexatriene, 34; and bicyclo[3.2.1]octa-2,3-diene, 39. For cyclic butatrienes, functional group strain estimates include: 1,2,3-cyclobutatriene, >100; 1,2,3-cyclopentatriene, 80; 1,2,3-cyclohexatriene, 50; 1,2,3-cycloheptatriene, 26; 1,2,3-cyclooctatriene, 17; and 1,2,3-cyclononatriene, 4. Barriers to interconversion of enantiomers in cyclic allenes are reduced with increasing strain. Newly predicted values include: 1,2-cyclopentadiene <1 kcal/mol and bicyclo[3.2.1]octa-2,3-diene, 7.4 kcal/mol. Estimated levels of strain parallel the known reactivity of these substances.

Introduction

One of the oldest structural concepts in organic chemistry is the systematic increase in molecular strain engendered by decreasing ring size in cyclic molecules.[1] Levels of strain usually parallel reactivity, especially for structures with π bonds. Numerous strain estimates have been presented for cycloalkanes and cycloalkenes.[1,2] We have estimated strain in the cycloalkyne series[3] and observed that in-plane bond strain becomes maximized in cyclopentyne at ca. 74 kcal/mol, which is approximately the strength estimated for a single alkyne π bond.[4]

Only crude estimates are available for most of the cyclic allene series.[5a,b] Bachrach used a group equivalent approach to estimate 29.6 kcal/mol of strain in 1,2-cyclohexadiene.[5c] Kamigata and co-workers used geometric deformations relative to 2,3-pentadiene to predict strain in the series of cyclic bisallenes with seven–ten-membered rings.[5d] There have been several recent computational studies on cyclic butatrienes,[6] but the only previous estimate for strain in this homologous series was based on MNDO calculations published by our group.[7] Strain energies were determined by comparison of bending angles to calcula-

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tions on bent planar butatriene. We concluded that strain should approximately double with each successive removal of a carbon from the ring.

Our longstanding interest in structural limitations for cyclic cumulenes[8,9] leads us to present here a more complete analysis for the homologous series of cyclic allenes (**1**−**6**) and cyclic butatrienes (**7**−**12**). These two series present a broad range of chemical behavior, which clearly is linked to increasing strain with decreasing ring size. The smallest members of this series are highly strained transient intermediates, and the largest homologues are isolable compounds.

1   **2**   **3**   **4**   **5**   **6**

7   **8**   **9**   **10**   **11**   **12**
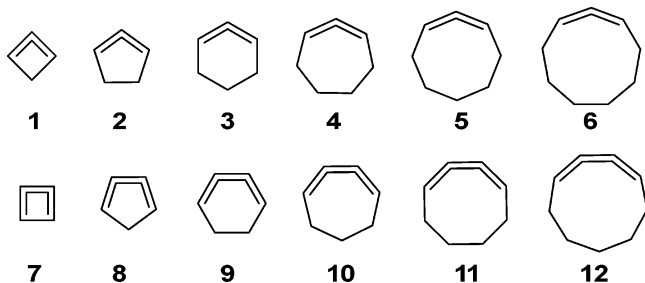
All members of the cyclic allene series (**1**−**6**) appear to be known, at least as transient intermediates. Enyne photorearrangements provide the only experimental evidence for intermediate 1,2-cyclobutadienes.[10] Balci and co-workers have recently reported the synthesis and trapping of several 1,2-cyclopentadienes.[11] We predicted earlier that **2** will prefer a chiral geometry,[12] whereas **1** should be planar.[10b] Cyclic allenes with ring sizes of six carbons are well-known from experiment[8,9] and have been the subject of several theoretical studies.[13,14] Dehydro-Diels−Alder routes to 1,2-cyclohexadienes and 1,2,4-cyclohexatrienes as reactive intermediates are now well documented,[14] as is the Hopf cyclization of 1,3-hexadien-5-ynes.[15]

1,2-Cycloheptadiene (**4**) cannot be made by the Doering−Moore−Skattebol method[16] but has been prepared by several other routes.[17] 1,2-Cyclooctadiene (**5**) has been observed at ambient temperature, but it rapidly dimerizes.[18] We have shown that the 1-*tert*-butyl derivative of **5** is isolable and can even be purified by gas chromatography.[19] Larger ring allenes have minimal strain and are stable.[8,9,16]

The series of cyclic butatrienes has received much less attention. We recently concluded that 1,2,3-cyclobutatriene (**7**) represents a transition state rather than an energy minimum.[20] Our own efforts to prepare derivatives of the parent five-membered ring (**8**) have been unsuccessful,[21] but 5-thia and 5-aza derivatives have been reported by Wong and co-workers.[22] We have shown that 1,2,3-cyclohexatriene (**6**) is easily prepared and trapped in solution[23] and that derivatives can be generated as reactive intermediates by intramolecular [2+4] cycloaddition of an alkene with a 1,3-diyne.[14h,i] The parent seven-ring cumulene (**10**) has been generated and trapped by Szeimies and co-workers through a bicyclobutene rearrangement.[24] Further along this series, we found evidence of a brief lifetime for the eight-ring homologue **11**.[25] Earlier, we had observed that 1,2,3,-cyclononatriene (**12**) can be easily generated and observed in solution.[7]

The ensemble of these results supports a rapid increase in reactivity, presumably driven by strain, with decreasing ring size. In both cyclic allene and butatriene series, the nine-membered homologue (**6** and **12**) is isolable[7,16] and the eight-membered ring (**5** and **11**) shows borderline isolability;[18,25] smaller homologues are best considered reactive intermediates.[8,9,15] In the present work, we have sought to estimate the levels of strain associated with each ring size and experimental behavior.

Methods

Hypothetical homodesmic and isodesmic reactions provide a simple way to estimate strain energies, especially because high-quality structures and energies are readily available from calculations.[26] Isodesmic reactions are schemes in which the number of each type of bond is retained on either side of the equation.

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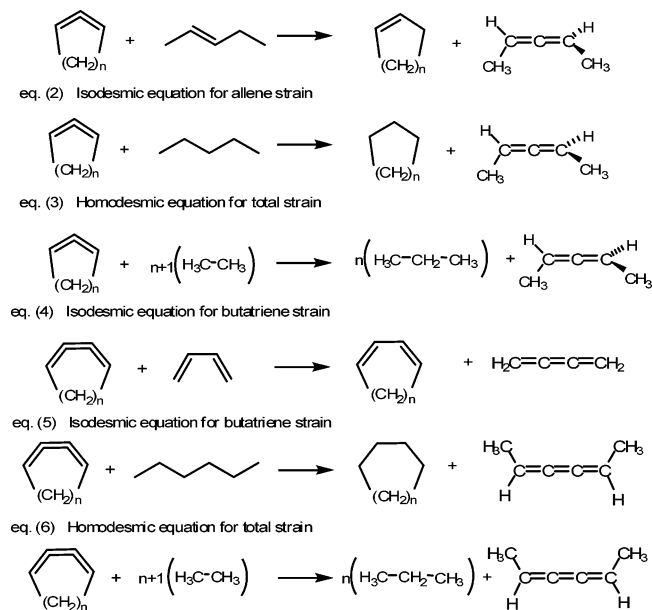
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Homodesmic (or homodesmotic) reactions are a more strictly defined subset which requires that the number of carbon atoms in each hybridization state must be equal in products and reactants. In addition, the number of hydrogens attached to each carbon atom must also be equal on both sides of the equation. This general approach has been widely applied, with many variations.[27] As presently applied, isodesmic reactions should give predictions of functional group strain whereas homodesmic reactions afford accurate predictions of total molecular strain.

Equations 1−6 show the expressions we used to evaluate strain in the cyclic cumulenes. In each case, we apply a simple *isodesmic*

eq. (2) Isodesmic equation for allene strain

eq. (3) Homodesmic equation for total strain

eq. (4) Isodesmic equation for butatriene strain

eq. (5) Isodesmic equation for butatriene strain

eq. (6) Homodesmic equation for total strain

relationship (eqs 1, 2, 4, and 5) to predict strain in the allene or butatriene functional group by comparison to a cycloalkene or cycloalkane of the same ring size. A second *homodesmic* equation (eqs 3 and 6) should yield total molecular strain through comparison to acyclic structures.

We have also applied a simple-minded approach in which the allene or butatriene molecular fragment (C_3H_4 or C_4H_4) is isolated by deleting ring atoms but maintaining bond angles. A single-point DFT calculation at this excised geometry is then compared to the energy of the optimized functional group. This is referred to as fragment deformation strain.[28]

Structures for cyclic cumulenes and reference compounds were optimized at the B3LYP/6-311+G(d,p) level of theory with

FIGURE 1. B3LYP/6-311+G(d,p) optimized structures for cyclic allenes.

FIGURE 2. B3LYP/6-311+G(d,p) optimized structures for cyclic butatrienes.

Gaussian 03[29] or Spartan 04[30] followed by vibrational frequency analysis. Optimized structures are shown in Figures 1 and 2. Our geometries agree well with previous calculations at different levels of theory.[6,13,14] Unless otherwise indicated, strain is predicted with B3LYP+ZPVE energies. Selected structures were evaluated at other

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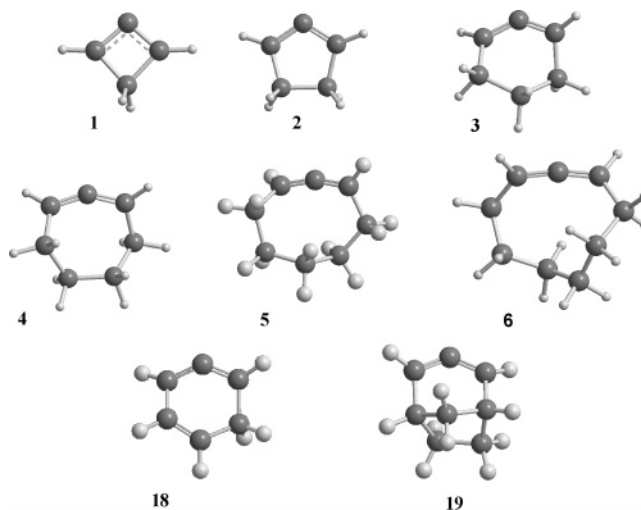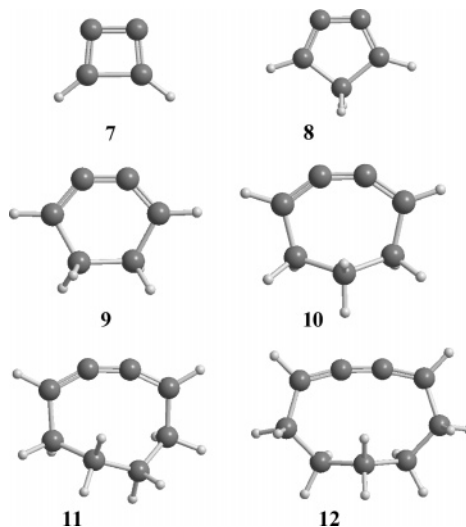
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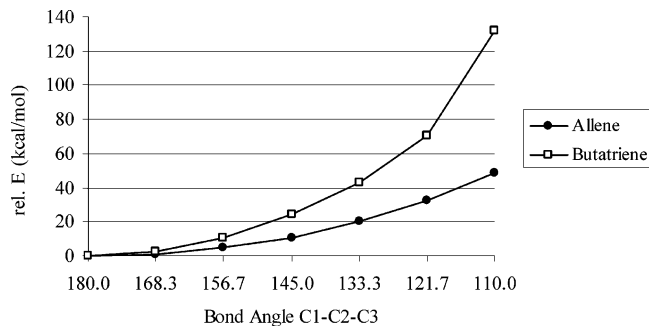(30) *Spartan 04*; Wavefunction, Inc.: Irvine, CA, 2005.

FIGURE 3. Energy (kcal/mol) vs bending angle for allene and butatriene.

levels of theory; in general, use of smaller basis sets or failure to include ZPVE corrections affords only slight differences in strain estimates. For the most strained members of the series, where some degree of diradical character seems likely, care was taken to test the stability of the wave function.

Several structures in these series are unusual and bear comment. First, we have previously reported a planar C_{2v} diradical structure for **1** based on UMP2 optimization.[10b] In the present study, unrestricted DFT calculations find a similar diradical energy minimum ($S^2 = 1.04$) which is 67.1 kcal/mol above vinylacetylene. The wave function for 1,2-cyclobutadiene is of $^1A_2$ electronic symmetry, with one electron in-plane and three out-of-plane in the π system; this is best represented by **13**. We have also located an unusual chiral structure **14** with a short C2−C4 distance at slightly higher energy, but we believe the allene is better represented by **13**; our strain estimates use this energy. The structure for **2** also showed significant diradical character, with $S^2 = 0.804$, even though the geometry remains chiral. Larger cyclic allenes converged to a closed-shell wave function.
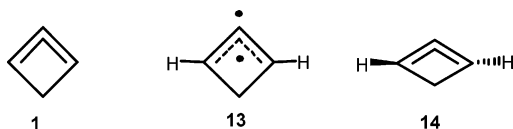
In the cyclic butatriene series, we had found earlier that C_{2v} 1,2,3-cyclobutatriene (**7**) is a transition state.[20] This structure may also be considered antiaromatic and hence has multiple sources of instability. Butatriene **7** and higher homologue **8** might be expected to have diradical character, but our DFT calculations instead supported a closed-shell description with $S^2 = 0$.

Allene or butatriene functional group strain should arise through deviation from the ideal linear geometry. As a point of reference, we have also calculated the potential energy curve associated with bending allene and butatriene at the B3LYP/6-311+G(d,p) level of theory. These results are shown in Figure 3. In both cases, the first 10−15° of bending has minimal energetic cost. For the same bending angle, the strain energy associated with bending allene is about half that of butatriene.

Results and Discussion: Strain in Cyclic Allenes

Isodesmic and homodesmic results for the allene series are presented in Tables 1 and 2, respectively. Table 3 summarizes homodesmic results and also includes bending and twisting angles, fragment deformation estimates, and a column labeled "best estimate" which endeavors to balance these results. Twist angles show a steady progression in planarization of the allene from 90° (orthogonal) to 180° (planar) as ring size decreases.

To evaluate our methodology, we first focus on results for 1,2-cyclohexadiene (**3**), where ring strain should play a minor role. Jones and co-workers first used MMX calculations to

estimate strain of 36.5 kcal/mol for **3**.[5b] In the present work, both isodesmic equations give predictions for strain of ca. 32 kcal/mol. For comparison, the MP4SDQ/6-31G*//MP2/6-31G* theory predicted an allene strain of 32.6 kcal/mol according to eq 1. We next applied the fragment deformation approach in which the bent allene unit in **3** was removed from the cyclic structure and compared to the optimized functional group; the B3LYP/6-311+G(d,p) stabilization was 32.3 kcal/mol, in excellent agreement with other methods. Analysis of the optimized geometry for **3** shows a variety of geometric changes. The allene group is bent from 180 to 133.3°, twisted toward planarity, and slightly pyramidalized at the sp^2 carbons. Plotting the bending angle on the curve in Figure 1 gives a strain energy of 19.7 kcal/mol. This is underestimated because it does not include the full range of ring-enforced geometric changes.

The total strain in this structure (Table 2) is nearly identical to allene strain, as might be expected for an essentially unstrained ring. On the basis of these consistent data, we assign 1,2-cyclohexadiene both allene strain and total strain energies of 32 kcal/mol. This is similar to the value predicted earlier by Bachrach.[5c]

Strain in the smaller cyclic allenes predictably increases at a rapid rate. For 1,2-cyclobutadiene (**1**), we use the planar diradical structure **13** as a reference. The total strain (89.9 kcal/mol) is seen as a composite of allene strain (61−67 kcal/mol) and the typical ring strain (ca. 27 kcal/mol) in a four-membered ring. 1,2-Cyclopentadiene (**2**) has a predicted allene strain of 50−51 kcal/mol and a total strain of 55.3; in this case, there is expected to be only a modest contribution to total strain from the five-membered ring. For the seven-membered ring allene (**4**), the predicted total strain also seems to be a good composite of the allene strain (13.5−14.3) and the typical strain (ca. 7 cal/mol) assigned to this ring size. The fragment strain estimate for **2** is higher than other estimates, and this method was not applied to **1** because of H−H repulsion in the fragment structure.

For eight- and nine-ring cyclic allenes, the isodesmic schemes do not appear to be reliable; indeed, both methods assign a *negative* strain energy to **6**. This occurs because the allene functional group strain is small, and ring strain is unbalanced in this equation. In particular, the lowest-energy conformation for reference cyclononane[32] still shows considerable torsional strain, not all of which would be present in the cyclic allene. Homodesmic figures also support this conclusion because the total strain is similar to that usually attributed to eight- or nine-membered rings (9.6 and 12 kcal/mol, respectively[2]). In this case, we believe the fragment deformation approach should provide a more accurate description of strain in the allene unit.
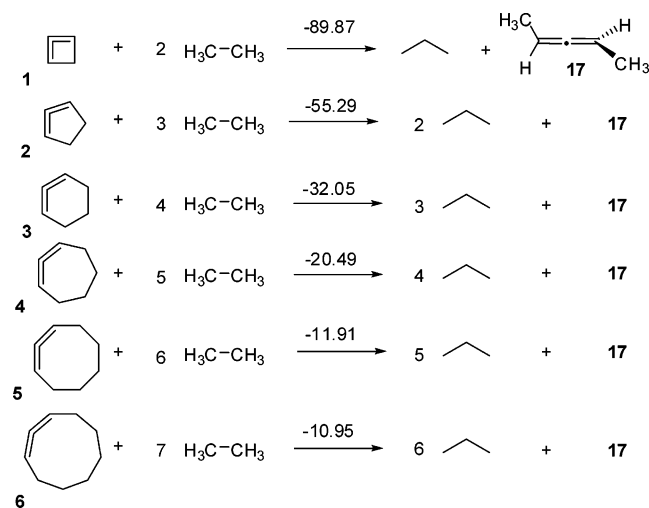
We have estimated strain for two additional cyclic allenes. 1,2,4-Cyclohexatriene (**18**) is well-known as a reactive intermediate,[13b,15] and we have applied the same isodesmic approach to estimate strain in this benzene isomer. All methods yield allene strain values which are slightly greater than those for parent

(31) (a) Sevin, F.; Duz, B. *NATO Sci. Ser., II* **2003**, *122*, 303. (b) Bottini, A. T.; Hilton, L. L. *Tetrahedron* **1975**, *31*, 2003. (c) Mohanakrishnan, P.; Tayal, S. R.; Vaidyanathaswamy, R.; Devaprabhakara, D. *Tetrahedron Lett.* **1972**, 2871. (d) Tümer, F.; Taşkesenligil, Y.; Daştan, A.; Balci, M. *Aust. J. Chem.* **1996**, *49*, 599.

(32) The conformational surface for cyclononane is complex, with the two lowest structures nearly isoenergetic. For the most detailed study, see: Suvire, F. D.; Santagata, L. N.; Bombasaro, J. A.; Enriz, R. D. *J. Comput. Chem.* **2006**, *27*, 188. At the B3LYP/6-311+G(d,p)+ZPVE level of theory, we find the order inverted relative to the above report but the energy difference is only 0.02 kcal/mol. Thus, our reference structure corresponds to M2 in the above study.

TABLE 1. Isodesmic Reaction Energies for Cyclic Allenes[a,b]
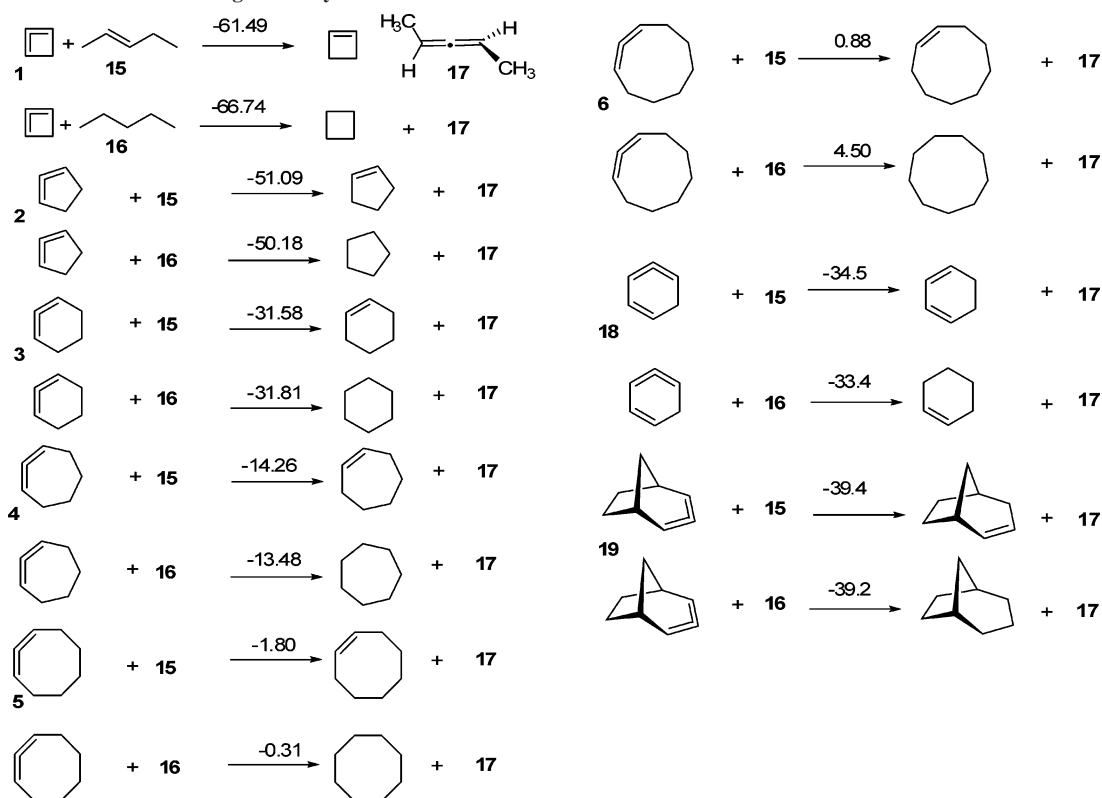
TABLE 2. Homodesmic Reaction Energies (kcal/mol) for Cyclic Allenes[a,b]

[a] Calculated from B3LYP/6-311+G(d,p) + ZPVE energetics. [b] Energies in kcal/mol.

TABLE 3. Geometry and Functional Group Strain Estimates (kcal/mol) for Cyclic Allenes

structure	bending angle[a]	twist angle[b]	isodesmic strain	fragment strain[c]	best estimate
1	97.9	180.0	61.5, 66.7		65
2	114.2	164.6	51.1, 50.2	62.8	51
3	133.3	142.2	31.6, 31.8	33.2	32
4	149.3	138.1	14.3, 13.5	14.9	14
5	161.5	128.3	1.8, −0.3	5.0	5
6	169.3	125.3	−0.9, −4.5	1.7	2
18	131.3	145.5, 145.2	34.5, 33.4	38.9	34
19	131.3	144.3, 141.0	39.4, 39.2	43.1	39

[a] Bending angle $C_1-C_2-C_3$ in degrees. [b] Twist angle $H-C_1-C_2-C_3$ in degrees. [c] Energy difference between the excised C_3H_4 fragment and the optimized structure.

structure **3**. Bicyclo[3.2.1]octa-2,3-diene (**19**) is representative of bicyclic allenes.[31] Results for this structure are summarized in Table 1 and Figure 1. Following the same isodesmic methodology used above, we estimated the allene strain in **19** to be 39 kcal/mol. Molecular fragment strain is 43.1 kcal/mol. Thus, the additional ring constraints in **19** lead only to a modest increase in strain.

In principle, the maximum strain energy in an allene may be equated to the energy required for allene π bond rotation, co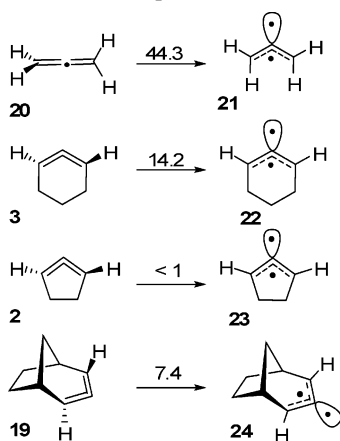mbined with destabilization due to additional bending. From the UV resonance Raman spectrum, Brudzynski and Hudson determined the torsional barrier for allene to be 43 kcal/mol.[33] This is in good agreement with the measured barrier of 46.2 kcal/mol for 2,3-pentadiene.[34] The transition state for rotation in allene (**20**, Table 4) is best described as a planar diradical (**21**).[35] With B3LYP/6-311+G(d,p) theory, we find that this structure is bent to 142.8°, with a predicted barrier of 44.3 kcal/mol, in excellent agreement with experimental results and previous estimates.[33,35]

For small ring allenes, the inversion barrier should be diminished substantially and in proportion to increasing strain. In an earlier study, we estimated inversion barriers for **2** and **3**

(33) Brudzynski, R. J.; Hudson, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 4963.
(34) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48.
(35) Bettinger, H. F.; Schreiner, P. R.; Schleyer, P. v R.; Shaefer, H. F., III. *J. Phys. Chem.* **1996**, *100*, 16147.

TABLE 4. B3LYP/6-311+G(d,p) Allene Inversion Barriers[a,b]

[a] Calculated from B3LYP/6-311+G(d,p) + ZPVE energetics. [b] Energies in kcal/mol.

TABLE 5. Isodesmic Reaction Energies for Cyclic Butatrienes[a,b]

[a] Calculated from B3LYP/6-311+G(d,p) + ZPVE energetics. [b] Energies in kcal/mol.

TABLE 6. Homodesmic Reaction Energies for Cyclic Butatrienes[a,b]

[a] Calculated from B3LYP/6-311+G(d,p) + ZPVE energetics. [b] Energies in kcal/mol.

of 2−5 and 15 kcal/mol, respectively, on the basis of MCSCF calculations.[12] A more recent high-level study[13b] predicts 15.4 kcal/mol for the barrier in **3**, consistent with our earlier number. We find that B3LYP/6-311+G(d,p)+ZPVE gives an inversion barrier of 14.2 kcal/mol for 1,2-cyclohexadiene (**3**) in good agreement with other predictions. To complete this series, we calculated the inversion barrier in **2**. As with **3** and the parent allene,[13a,35] the transition state (**23**) is best described as a diradical ($S^2 = 1.04$). With B3LYP/6-311+G(d,p) theory, the barrier is 0.47 kcal/mol. Zero-point corrections place **23** slightly *below* the chiral structure for **2**, and it seems safe to estimate this inversion barrier as <1 kcal/mol. This substantial change may be expected from the 18 kcal/mol difference in predicted allene strain between **3** and **2**. For bicyclo[3.2.1]octa-2,3-diene (**19**), we calculate a racemization barrier of 7.4 kcal/mol.

Results and Discussion: Strain in Cyclic Butatrienes

Tables 5 and 6 present isodesmic and homodesmic data for the cyclic butatriene series. Optimized geometries were presented in Figure 2. Bending angles and fragment deformation energies are collected in Table 7. In all structures, the butatriene functional group remained within 5° of planarity.

Symmetrical bending of a butatriene primarily weakens the in-plane π bond. The strength of this bond can be estimated from the disproportionation reaction shown in eq 7. With
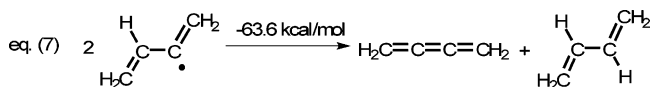

B3LYP theory, and assuming a planar radical as the best model,[36] the π bond strength is estimated as 63.6 kcal/mol, nearly identical to that for ethylene.

To be comprehensive, 1,2,3-cyclobutatriene (**7**) is included in this series, even though this structure displays one imaginary mode at this level of theory;[20] however, we believe the synergestic effects of antiaromaticity, allene strain, and ring strain render results for **7** unreliable. Estimates for butatriene strain in 1,2,3-cyclopentatriene (**8**) are remarkably consistent at 79 kcal/mol; this number is larger than the π bond strength

(36) Without geometric restriction, this structure optimizes to the α-allenyl radical. The planar radical model better preserves the diene in this structure.
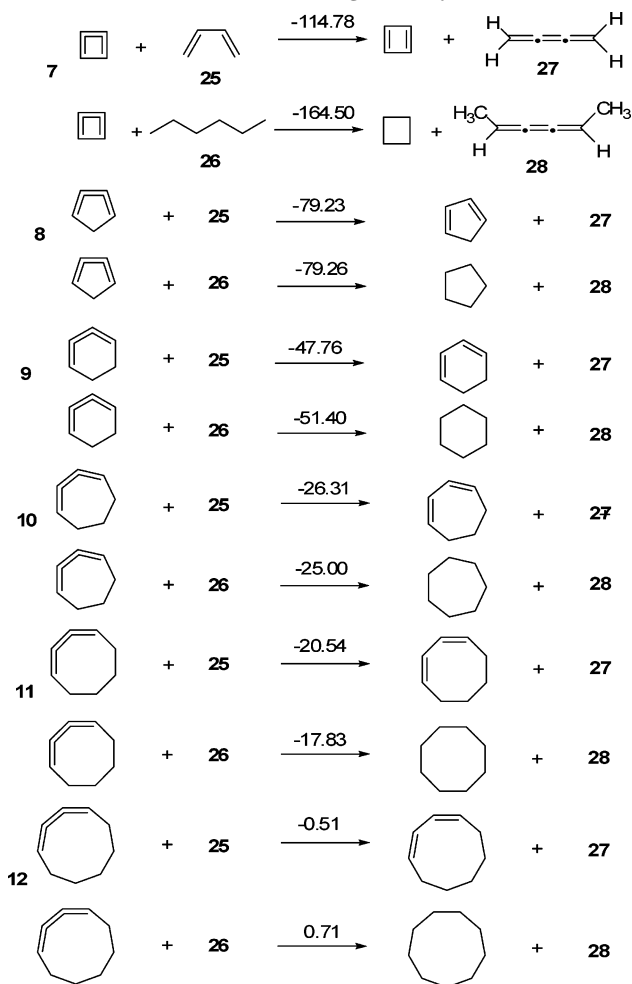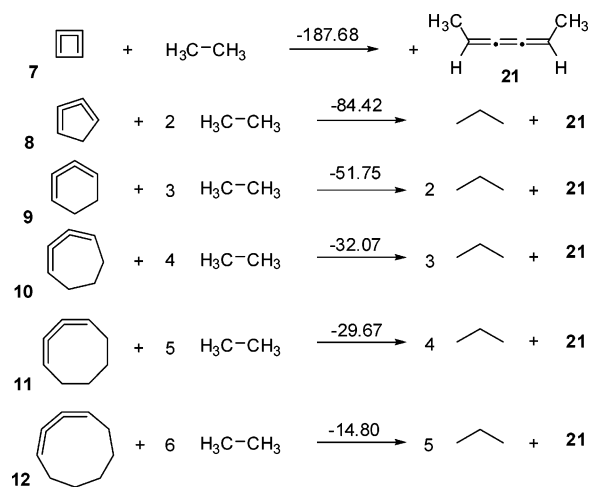
estimated above. The total strain of 84.4 in **8** includes a modest contribution from ring strain, assigned as 4.1 kcal/mol in cyclopentene. With the six-membered ring homologue **9**, isodesmic and homodesmic estimates are nearly identical at ca.

TABLE 7. Geometry and Functional Group Strain Estimates for Cyclic Butatrienes (kcal/mol)

structure	isodesmic strain	bending[a] angle	fragment[b] strain	best estimate
7	114.8, 164.5	95.4		
8	79.2, 79.3	115.0		80
9	47.8, 51.4	130.9	50.3	50
10	26.3, 25.0	144.2	26.9	26
11	20.5, 17.8	154.8	16.4	18
12	0.5, −0.7	165.4	4.5	4

[a] Bending angle $C_1-C_2-C_3$. [b] Energy difference between the excised butatriene fragment and the optimized structure.

50 kcal/mol. A substantial decrease in both bending angle and strain is expected and observed for 1,2,3-cycloheptatriene (**10**). Ring strain adds only a few kilocalories/mole to the homodesmic estimates. The two larger members of this series **11** and **12** again show the interplay of butatriene strain and ring strain; the fragment strain approach seems to provide more reasonable strain estimates.

Conclusions

Strain in the series of four- to nine-membered ring cyclic allenes and butatrienes has been estimated on the basis of isodesmic and homodesmic relationships and from the deformation energy of isolated functional groups. The latter fragment deformation approach seems more reliable for larger homologues because it is difficult to write an isodesmic equation that balances ring strain in eight- and nine-membered rings which carry different levels of unsaturation. Predicted levels of strain correlate well with known experimental results. 1,2-Cyclobutadiene (**1**) stands out as a highly strained substance (ca. 90 kcal/mol) that may be an intermediate only in high-energy photochemical reactions. The corresponding four-membered ring cyclic butatriene (**7**) does not represent an energy minimum and seems too high in energy to play a role in C_4H_2 chemistry, even as a transition state.[20] The parent 1,2,3-cyclopentatriene (**8**) remains unknown, presumably because of its 84 kcal/mol of total strain; however, several heterocyclic derivatives have been generated and trapped.[22] Derivatives of 1,2-cyclopentadienes (**2**)[12] and the parent 1,2,3-cyclohexatriene (**9**),[23] both with strain estimates of ca. 50 kcal/mol, have been generated in the solution phase as reactive intermediates. It is noteworthy that structures with this level of strain can be so readily prepared. There are numerous routes to 1,2-cyclohexadiene (**3**), despite its estimated 32 kcal/mol of strain.[8,9,15,23] 1,2,4-Cyclohexatriene (**18**)[13b,15] is predicted to have only a few kilocalories/mole more strain than **3**. At a similar level of strain, 1,2,3-cycloheptatriene (**4**) has been easily prepared and trapped.[24] Bicyclo[3.2.1]octa-2,3-diene (**19**) is predicted to have 39 kcal/mol of allene strain; this structure and a number of derivatives have been generated and trapped.[8,9,31] The remaining members of this series have all been generated under fairly ordinary conditions.[8,9] It is easy to understand why butatriene **12** (estimated strain of 4 kcal/mol) is isolable[7] whereas **11** (strain of 17 kcal/mol) is not.[25] One noteworthy observation is that 1,2-cyclooctadiene (**5**) is not isolable, despite its minimal (5 kcal/mol) allene strain.[18] This is attributed to the facile dimerization of the allene group, which proceeds through a bisallyl radical; thus, destabilization of **5** probably is due more to kinetics than to thermodynamics. We have shown that blocking this process with a single *tert*-butyl group renders this ring size isolable.[19]

The fragment deformation approach succeeds surprisingly well, predicting functional group strain values that are generally within a few kilocalories/mole of those derived from isodesmic relationships. For cases where it is difficult to define a balanced isodesmic relationship, this may be the method of choice. Of course, this works because strain is localized in the cumulene functional group. Kamigata and co-workers have assigned a similar strain for eight- and nine-membered bisallenes by using unstrained 2,3-pentadiene as a reference.[5d]

Strained cyclic cumulenes are recognized as intermediates in an increasing array of chemical reactions.[9,14,37] As this field develops, strain estimates will be essential to understand the reactivity and even the existence of these extraordinary substances.

Supporting Information Available: Cartesian coordinates and summary energetics for cyclic allenes and butatrienes and reference compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060698K

(37) Recent examples: (a) Sajimon, M. C.; Lewis, F. D. *Photochem. Photobiol. Sci.* **2005**, *4*, 629. (b) Nikitina, A. F.; Sheridan, R. S. *Org. Lett.* **2005**, *7*, 4467. (c) Hayes, M. E.; Shinokubo, H.; Danheiser, R. L. *Org. Lett.* **2005**, *7*, 3917. (d) Lu, X.; Zhu, M. P.; Wang, X. L.; Zhang, Q. N. *J. Phys. Chem. B* **2004**, *108*, 4478. (e) Azizoğlu, A.; Öezen, R.; Höekelek, T.; Balci, M. *J. Org. Chem.* **2004**, *69*, 1202.