Strain Energy of Small Ring Hydrocarbons. Influence of C−H Bond Dissociation Energies

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Abstract: Ab initio calculations at the G2, G3, and CBS-Q levels of theory have been applied to the question of the origin of ring strain in a series of unsaturated hydrocarbons. In addition to the angular ring strain germane to all three-membered ring hydrocarbons, a general trend is in evidence that suggests that the increased ring strain (SE) of unsaturated small ring alkenes may be attributed in part to their relatively weak allylic C−H bonds. The high strain energy of cyclopropene (54.1 kcal/ mol) is attributed largely to angular strain. The anomalously low SE of cyclobutene relative to cyclobutane (ΔSE = 4 kcal/mol) is a consequence of normal C−H bond dissociation energies for cyclobutane (100.6 kcal/mol) and very strong vinyl C−H bonds (111.9 kcal/mol) and a relatively strong π-bond energy (63.5 kcal/mol) for cyclobutene. The greater SE of methylenecyclopropane (39.5 kcal/ mol), relative to methylcyclopropane (29.8 kcal/ mol), can be attributed to the strong ring C−H bonds of methylcyclopropane (110.5 kcal/mol) and relatively weak allylic C−H bonds (99.3 kcal/mol) of methylenecyclopropane. The increased SE of 1-methylcyclo-propene relative to isomeric methylenecyclopropane is ascribed to its weak ring C−H bonds and to angular strain. The relative thermodynamic stability of a series of small ring alkenes is determined by a measure of their hydrogenation enthalpies. Independent confirmation of the SEs of a series of substituted cyclopropenes is provided by their dimerization/combination with cyclopropane to form a six-membered ring reference compound.

Introduction

The assessment of ring strain in small ring compounds has been a topic of major interest to the organic chemist for decades.[1,2] How the magnitude of the strain energy (SE) is measured and the effects that ring strain have upon chemical reactivity continue to be focal points for many researchers even today.[1−5] Cyclopropane is the paradigmatic strained carbocycle, and it has played a unique role in the study of ring strain; it is the "yard stick" by which ring strain is typically measured. Both the C−C and C−H bonds in cyclopropane are shorter than those in a more "normal" carbocycle such as cyclohexane.[4] These two cyclic hydrocarbons comprise the basis of the accepted experimental SE of cyclopropane. One definition of the SE may be taken as the difference between the observed enthalpy of formation (ΔH_f) and that calculated using a strain-free model reference compound. The generally accepted value for the ring strain energy of cyclopropane is derived from its ΔH_f = 12.7 kcal/mol and half of that for cyclohexane (ΔH_f = −14.8 kcal/

mol). This experimental SE = 27.5 kcal/mol is based upon the assumption that cyclohexane is strain-free (SE = 0.0). This does not appear to be completely true as we discuss below.

One of the more intriguing aspects of small ring strain energy is the observed similarity in the SEs of cyclopropane and cyclobutane (27.5 and 26.5 kcal/mol).[4,5] It has been recognized for some time that the C−H bonds of cyclopropane are stronger[6] than those of cyclobutane or larger ring carbocycles. This has led to the suggestion earlier that the weaker C−C bonds in cyclopropane obviously contribute to increased ground state (GS) energy and a greater SE that is compensated in part by stronger C−H bonds.[4a] The calculated C−C intrinsic bond energies (BEs)[7] for cyclopropane, cyclobutane, and cyclohexane (73.2, 79.1, and 87.3 kcal/mol)[7d] are consistent with this precept. We have recently put this suggestion on a more quantitative basis with calculated C−H bond dissociation energies (BDEs) at the G2 level of theory.[3]

This approach, however, is not without its own problems since by convention bond dissociation energies are defined by dissociation of the covalent single bond into two radical

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fragments. The BDE derived in this manner does not necessarily represent the actual energy content of the bond in its molecular ground state. The bond strength, which is usually evaluated in terms of its BDE, has two basic components: the intrinsic BE and the total (geometric and electronic) reorganization energy (R) of the two fragments formed upon bond cleavage.[7] Unfortunately, these two nonobservable contributors (BE and R) are not directly measurable for molecules of the type treated here. Traditionally, the energy of a particular bond in a molecule has been estimated from its atomization energy. Using an adaptation of Bader[7a,b] that relates the bond energy to the integral of the energy density over the interatomic surface, Grimme[7c] parametrized atomization energies in terms of their bond critical points and applied these concepts to the strain energy of fairly simple molecules. A critical evaluation of this scheme to calculate intrinsic bond energies has recently been reported by Exner and Schleyer,[7d] leading to new estimates of the stabilization of cyclopropane due to C−H bond strengthening. Krygowski et al.[7e] have also parametrized C−C bond energies as a single exponential function of experimentally observed bond lengths. More recently, Howard et al.[7f] derived vibrationless atomization energies from molecular total energies (B3LYP/6-311G**) by subtracting the energies of the free ground-state atoms at the same level of theory. The C−C bond energies for a series of linear polyacenes (from anthracene to heptacene and higher) were successfully derived by a model fitting procedure comprising 10 parameters (three Morse functions) reproducing the atomization energies with 0.04% accuracy over the series of 16 test compounds. Extension of this protocol to other types of hydrocarbons should prove useful in further assessing the origins of strain energy. However, partitioning the BE and R for the types of compounds described herein is still quite difficult,[7d] and application of this theory to the rudiments of strain theory remains problematic. This raises the following legitimate question: Can we predict qualitative trends in SE simply on the basis of bond dissociation energies (BDE)? We address this point below.

Another point of contention has been the origin of the much greater SE in small ring unsaturated alkenes such as methylenecyclopropane and 1-methylcyclopropene. Initially, Wiberg[4b] measured the heats of formation of these two strained hydrocarbons and suggested that the introduction of *each* trigonal carbon center into a three-membered ring introduces an additional 12−14 kcal/mol of ring strain. For example, the SE of methylenecyclopropane is estimated to be 40.9 kcal/mol, and the heat of formation of isomeric 1-methylcyclopropene is 10.2 kcal/mol higher.[4b] In a recent theoretical study, Borden[6] concurred with the explanation that increased angle strain does result from the presence of additional sp² centers. However, it was suggested that the major source of the additional ring strain that results from the introduction of each trigonal carbon center into methylcyclopropane is not an increase in angle strain but rather the *absence* of the very strong *tert*-C−H bond (107.6 kcal/mol) in methylenecyclopropane

While a number of theoretical methods that have been explored for the assessment of strain energies, the use of homodesmotic[8−10] and group equivalent reactions[11] has been

most extensively employed. Such balanced chemical reactions have played a major role in assessing the overall energetics of a wide variety of such chemical transformations for more than 25 years.[8] Computational efficiency has now progressed to the point where we can also examine such balanced reactions more closely by calculating BDEs at the G2, G3, or CBS-Q level to within 1−2 kcal/mol.[12a] This provides not only the overall energetics of such homodesmotic reactions, but also an explanation of the net change in the reaction energy that is based upon accurate bond energies. Ring strain energy is a delicate balance of stabilization and destabilization effects that manifest themselves in the "measured" strain energy of cyclic molecules. One variable that should remain fairly constant, determining the strain energy of three-membered rings, is angle strain. By definition, a typical three-membered ring has bond angles of approximately 60°, yet the SEs of a wide variety of carbocyclic and heterocyclic three-membered rings exhibit SEs that can vary over a wide range up to 40 kcal/mol. We now extend this computational approach to the calculation of pertinent C−H bond energies and show quite convincingly that the thermodynamic stabilities of small ring compounds are a function of the relative C−H BDEs within a given ring size that is reflected in their ring strain energy.

Computational Methods

Ab initio molecular orbital calculations were performed with the GAUSSIAN 98 system of programs[13] with gradient optimization.[14] The reaction enthalpies and strain energies were calculated using G2, G3, and CBS-Q theory.[15] The G2 method is generally considered to be reliable to about 1.2 kcal/mol. The CBS-Q method[15c] is suggested to be slightly more accurate than the G2 method[15a] over the same test set of 125 compounds, while G3 calculations represent a slight improvement over both earlier methods.[15d] These relatively accurate methods provide an internally consistent set of total energies for the comparison of the strain energies of cyclopropanes with other small ring compounds.

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(10) (b) Skancke, A.; Van Vechten, D.; Liebman, J. F.; Skancke, P. N. *J. Mol. Struct.* **1996**, *376*, 461 and references therein. (c) Liebman, J. F.; Skancke, P. N. *Int. J. Quantum Chem.* **1996**, *58*, 707. (d) Zeiger, D. N.; Liebman, J. F. *J. Mol. Struct.* **2000**, *556*, 83. (e) Skancke, A.; Liebman, J. F. *J. Org. Chem.* **1999**, *64*, 6361.

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(12) (a) In general, the G2 BDEs are about 2 kcal/mol higher in energy than the experimental C−H (99.4 ± 0.5 kcal/mol) and C−C (86.2 ± 0.6 kcal/mol) bond dissociation energies for propane. (b) The C−H BDE in cyclopropane at 298 K is reported to be 106.3 ± 0.3 kcal/mol (Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979** , *101*, 2838), while the secondary C−H BDE in propane was measured to be 98.6 ± 0.4 kcal/mol (Seakins, P. W.; Pilling, M. J.; Niranen, J. T.; Gutman, D.; Kransoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847).

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Zero-point energies (ZPEs) and thermal corrections to obtain reaction enthalpies at 298 K in the G2 series are by convention computed at the HF/6-31G(d) level. Homolytic bond energies (ΔE) quoted in the text are derived from the difference in the total energies of the dissociated radical fragments, while BDEs are derived from ΔH_{298}. Throughout the text, bond lengths are in angstroms and bond angles are in degrees. The bond energy values quoted in the text are at the G2, G3, or CBS-Q level and are considered to be equally accurate for the purposes of discussion. The BDEs calculated by each of the three methods are summarized in Table 1.

For the calculations of inversion barriers ($\Delta E^{\ddagger}$) and reorganization energies (R), B3LYP/6-311+G(3df,2p) optimizations have been performed. The energy differences and rotational barriers reported in the text are calculated with zero-point vibrational energy (ZPVE) corrections.

Results and Discussion

Strain Energy of Cyclopropene versus Cyclobutene. It now seems reasonably certain that the comparable strain energies of cyclopropane and cyclobutane are largely a consequence of the fact that the C—H bonds in the former are strong enough (ΔBDE = 8.4 kcal/mol)[3a] to offset its greater angle strain. The contribution of the C—H bonds to the stabilization energy of cyclopropane is consistent with the shortening of its C—H bond relative to that in ethane.[16a] The reorganization energies, R, defined by the difference between C—H BEs and D°_{298} values are a measure of the stabilization of the corresponding carbon radicals produced on C—H bond cleavage. Fortunately, the R value for cyclopropane is very small ($R = 0.5$).[7d] A correlation of the BEs and the BDEs for its C—H bonds shows that factors determining radical stabilities operate in the GS as well as the radical fragment, although to a lesser extent. By comparison, the R values for cyclobutane, cyclopentane, and cyclohexane have negative values (-7.8, -9.4, and -9.0), which can be traced in part to the inversion barrier at the carbon radical center.[7d] The inversion barrier for cyclopropyl radical is particularly low at $2-3$ kcal/mol.[16b] At the B3LYP/6-311+G(3df,2p)+ZPVE level the calculated inversion barrier is only 0.8 kcal/mol. However, it should be noted that when allylic stabilization comes into play as with propene the reorganization stabilization energy is much greater ($R = -15.0$).[7d] The difference in energy between the planar allyl radical and one constrained to be pyramidal ($\angle$H—C—C=C = 30°) is 11.4 kcal/mol. Both the favored planar and pyramidal radicals are minima at this level of theory. Differences in geometry at the developing carbon radical center can also influence the reorganization energy. For example, the cyclopropyl radical prefers to be pyramidal, while the allyl radical derived from α-C—H bond dissociation in methylenecyclopropane is planar, albeit with a much smaller energy difference ($\Delta E = 4.9$ kcal/mol) between planar and pyramidal structures than the allyl radical. Schleyer et al.[7d] has shown that experimental C—H D°_{298} values can vary widely (80−135 kcal/mol for the test set used) but the calculated intrinsic BEs have a much smaller range (103−110 kcal/mol). Thus, the difference in D°_{298} values is influenced much more than that in intrinsic BEs by geometric and electronic reorganization during bond breaking. Since many of the compounds discussed in the present study have relatively small reorganization energies, we do not

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Table 1. Calculated C—H Bond Energies (ΔE, kcal/mol) and Bond Dissociation Energies (BDE = ΔH°_{298}, kcal/mol) at the G2 (Plain), G3 (Bold), and CBS-Q (Italic) Levels of Theory

bond type	ΔE	BDE, ΔH°_{298}
	Ethylene	
vinyl C—H	110.5, **108.8**	112.0, **110.3**
	Propane	
methyl C—H	101.5	103.3
secondary C—H	98.5	100.3
C—CH$_3$	88.2	90.5
	Cyclopropane	
C—H	108.8, **107.7**, *108.0*	110.3, **109.2**, *109.5*
	Methylcyclopropane	
ring C—H	109.0, *107.9*	110.5, *109.5*
methyl C—H	98.1	99.7
tert-C—H	106.0,[a] **104.9**	107.6, **106.5**
C—CH$_3$	98.5[a]	
	1,1-Dimethylcyclopropane	
C—CH$_3$	97.1[a]	
	Methylenecyclopropane	
C—H (ring)	97.5, **95.9**, *94.8*	99.3, **97.6**, *96.5*
vinyl C—H	108.2	109.7
	Cyclopropene	
ring C—H	**98.8**	**100.4**
vinyl C—H	**108.1**	**109.6**
	1-Methylcyclopropene	
ring C—H	99.3	100.8
vinyl C—H	108.3	109.8
methyl C—H	86.7	88. 1
	3-Methylcyclopropene	
tert ring C—H	98.7	100.3
vinyl C—H	107.7	109.2
methyl C—H	96.8	98.4
	3,3-Dimethylcyclopropene	
vinyl C—H	**105.0**	**106.5**
C—CH$_3$	**87.4**	**89.3**
	Cyclobutane	
C—H	100.2, **98.9**	101.9, **100.6**
	Methylcyclobutane	
C—CH$_3$	90.8[a]	92.9[a]
	Methylenecyclobutane	
α-C—H	*83.5*	*85.0*
β-C—H	*99.7*	*101.4*
vinyl C—H	*108.7*	*110.2*
	Cyclobutene	
ring C—H	**88.9**	**90.6**
vinyl C—H	**110.4**	**111.9**
	1-Butene	
α-C—H	*81.5*, **82.6**	*83.1*, **84.2**
	Cyclopentane	
C—H	96.2, **94.9**	97.8, **96.3**
	Cyclohexane	
C—H	99.2, *98.2*	100.8, *100.0*
	Methylenecyclopentane	
α-C—H	*81.1*	*82.7*
β-C—H	*97.6*	*99.4*
vinyl C—H	*109.3*	*110.6*
	Cyclopentene	
α-C—H	**82.6**	**84.2**
β-C—H	**95.1**	**97.0**
vinyl C—H	**112.5**	**113.9**
	Isobutane	
methyl C—H	101.9	103.6
tert-C—H	96.9	98.8
	Isobutylene	
methyl C—H	88.8	89.8
vinyl C—H	112.1	113.6

[a] From ref 3.

feel that this potential error will impact the qualitative discussion presented.

The long-standing controversy concerning the fact that three- and four-membered ring hydrocarbons have comparable SEs can now be more easily rationalized. Decomposition of the total strain into individual C−C and C−H BE contributions shows that while the total C−C bond strain of cyclopropane is 10.1 kcal/mol higher than that of cyclobutane, this difference is largely compensated for by the stronger C−H bonds in cyclopropane (8.0 kcal/mol).[7d] The G2 BDEs ($\Delta H°_{298}$) for the C−H bonds in C3, C4, C5, and C6 cyclic saturated hydrocarbons are 110.3, 101.9, 97.8, and 100.8 kcal/mol, suggesting that the greater C−C−C angular strain in cyclopropane is offset by its greatly increased C−H bond energies. This more quantitative approach recently led to the suggestion that the SE of the parent dioxirane (DO) is reduced from ca. 18 to ca. 11 kcal/mol for dimethyldioxirane (DMDO).[3b] The unusual thermodynamic stability of DMDO is partly a consequence of its relatively strong C−H (BDE = 102.7 kcal/mol) and C−CH₃ (BDE = 98.9 kcal/mol) bonds. The effect of relatively strong C−H bonds has been shown to be particularly important for cyclopropanes.[6] The C−H BDE in cyclopropane has been measured to be about 8 kcal/mol stronger than the secondary C−H bond in propane (ΔBDE = 7.7 kcal/mol).[12b] By comparison, the calculated primary methyl C−H and C−CH₃ G2 bond dissociation energies in propane are 103.3 and 90.5 kcal/mol. *gem*-Dimethyl substitution on a cyclopropane ring also imparts an additional thermodynamic stability of about 7−9 kcal/mol, *relative to that of a linear reference molecule*.[3a] This not only is due to the strong bond energies of the C−H bonds of the cyclopropane ring (BDE = 110.3 kcal/mol) but is also a consequence of relatively strong methylcyclopropane C−CH₃ bonds (97.1 kcal/mol). In this particular case, the stability of dimethylcyclopropane is *not* due to especially strong methyl C−H bonds, as above, since the methyl C−H BDE of methylcyclopropane is only 99.7 kcal/mol, a value lower than the primary methyl C−H BDE (103.3 kcal/mol) of the above reference compound, propane. Thus, the cyclopropyl ring has a definite influence on the C−H BDE of a methyl substituent due to its interaction with the Walsh orbitals of cyclopropane (see below).

A direct comparison of the C−H bond strengths in cyclopropane with cyclopropene is also instructive. The energies of two of the strong C−H bonds lost from cyclopropane (109.2 kcal/mol) are offset by the equally strong vinyl C−H bonds (109.6 kcal/mol) gained in cyclopropene. The two ring C−H bonds of cyclopropene are admittedly much weaker (100.4 kcal/mol), but this alone cannot account for the fact that the SE of cyclopropene (55.2 kcal/mol) is essentially double that of cyclopropane (27.5 kcal/mol)! One can argue that cyclopropene is still missing two strong C−H bonds; however, this cannot account for the magnitude of its SE. We are left with the conclusion that angular strain[4] makes a major contribution to the SE of this highly strained alkene.
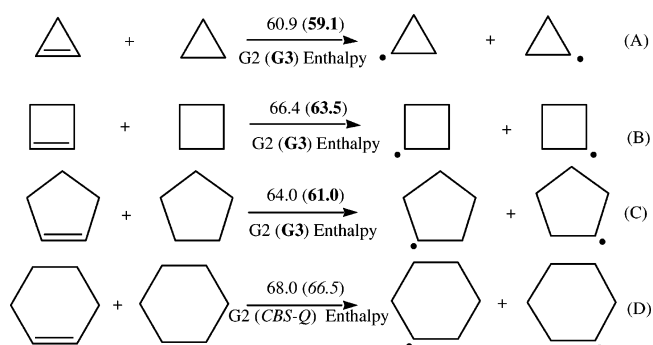
The widely differing SEs of cyclopropene (55.2 kcal/mol)[4a] and cyclobutene (28.4 kcal/mol)[4a] represent a much truer reflection of the impact of angular strain on these two cyclic alkenes. Examination of the ring C−H BDE at the G3 level (Table 1) shows that cyclopropane has much stronger ring C−H bonds than either cyclopropene (100.4 kcal/mol) or cyclobutene (90.6 kcal/mol). The vinyl C−H BDEs of cyclopropene and

cyclobutene (109.6 and 111.9 kcal/mol) are not sufficiently different to account for the very large difference in strain energy. To place these vinyl C−H BDEs in perspective, the C−H BDE for ethylene is right between these two values at 110.3 kcal/mol. The *R* value for ethylene is also positive (5.2 kcal/mol),[7b] and we find comparatively little difference in geometry reorganization upon forming vinylic radicals from ethylene or cyclopropene. Thus, it would appear that within this series of cyclic hydrocarbons cyclopropene exhibits significant angular strain while it is *the SE of cyclopropane that is anomalous*, and this energetic consequence may be attributed largely to its very strong C−H bonds (109.2 kcal/mol) that account for its thermodynamic stability and hence its relatively *low* strain energy.
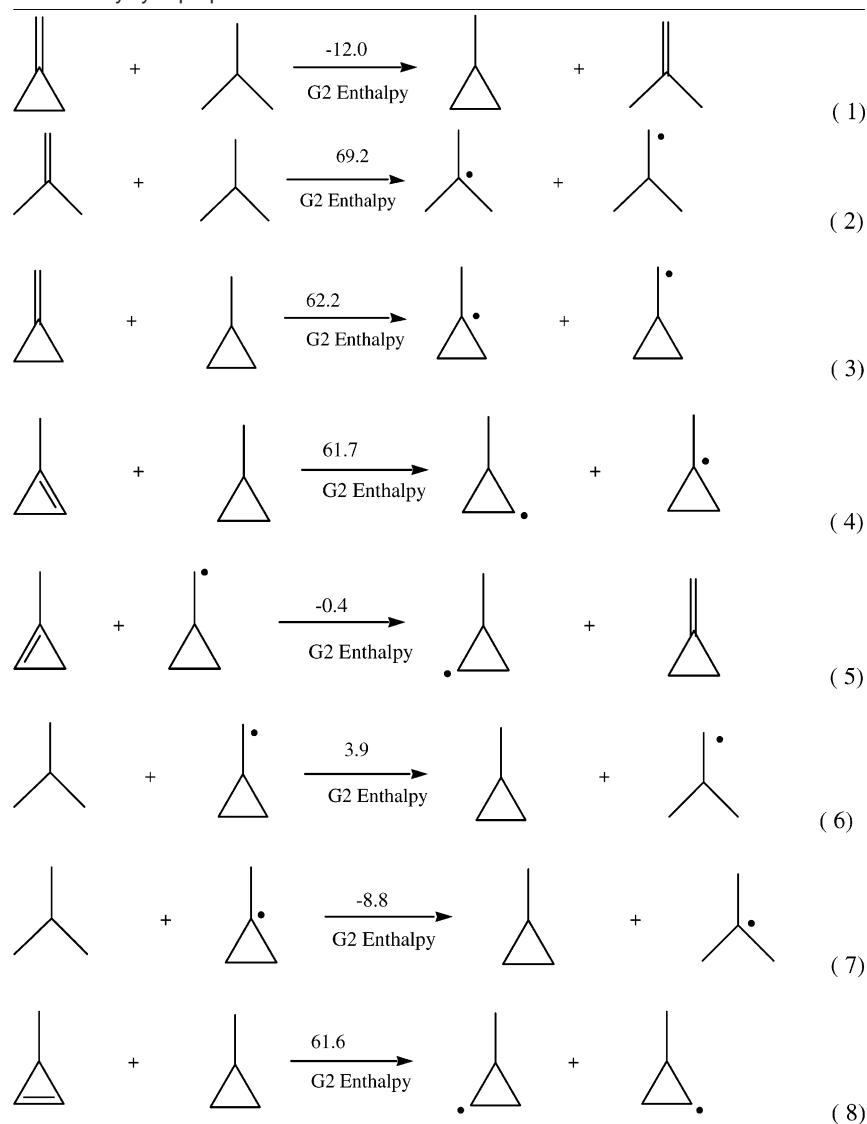
The angle strain induced by the two sp² centers in cyclobutene has only a modest effect upon its strain energy. Experimental estimates suggest that cyclobutene is only 1.9 kcal/mol more strained than cyclobutane.[4a] The C−H BDEs for cyclobutane (100.6 kcal/mol, G3) are much lower than the vinyl BDEs of cyclobutene (111.9 kcal/mol). Moreover, the relatively low (90.6 kcal/mol) bond strengths of the allylic ring hydrogens of cyclobutene also impact the observed strain energy. While we again see offsetting BDEs, augmented strain due to the introduction of sp² carbon centers in a four-membered ring is not in evidence, and in fact, it is the strength of the vinyl C−H bonds that serves to stabilize cyclobutene relative to cyclobutane. The contribution made by relatively strong vinyl C−H bonds to the thermodynamic stability of strained alkenes has been largely overlooked. We also note that ethylene, cyclopropene, cyclobutene, and cyclopentene all have vinyl C−H BDEs of a comparable magnitude that range from 109.6 to 113.9 kcal/mol (Table 1). Surprisingly, vinyl C−H BDEs are not influenced by angle strain.

Consistent with this argument, the SE of cyclopentene (4.1 kcal/mol)[4a] is actually *lower* than that of cyclopentane (6.2 kcal/mol). The C−H BDEs of cyclopentane (96.3 kcal/mol) are quite typical, so the relatively low SE of cyclopentene is a consequence of two strong vinyl C−H BDEs of 113.9 kcal/mol. The α- and β-C−H BDEs of the CH₂ groups of cyclopentene are normal at 84.2 and 97.0 kcal/mol (G3). For example, the allylic C−H BDE of 1-butene is 83.1 kcal/mol (CBS-Q).

We can also show that the relative energy of the π-bonds of this homologous series of cyclic alkenes makes a surprising contribution to the difference in their SEs. The thermodynamic π-BDEs can be estimated by the enthalpies of the balanced equations given in reactions A−D.

The thermodynamic π-BDEs of cyclopropene and cyclobutene differ by 5.5 and 4.4 kcal/mol at the G2 and G3 levels

Table 2. Isodesmic Reactions Providing π-Bond Dissociation Energies and Selected C−H Bond Energies for Isobutylene, Methylenecyclopropane, and 1-Methylcyclopropene

of theory. The π-BDE of cyclobutene is calculated to be 2.4 and 2.5 kcal/mol *greater* than that of cyclopentene, and this surprisingly strong π-bond obviously contributes to the relatively low SE of cyclobutene. As expected, cyclohexene, an essentially strain free alkene, has the most stable π-bond dissociation energy of the four alkenes.

Strain Energies of Methylenecyclopropane and 1-Methylcyclopropene. The introduction of a nominally trigonal carbon center into a three-membered ring results in an increase in ring strain.[4b] Several reasons have been offered in explanation of this experimental observation. The typical SE assigned to cyclopropane is 27.5 kcal/mol, while that for methylenecyclopropane is 40.9 kcal/mol. Wiberg[4] suggested that each additional sp[2] center in a three-membered ring increases the SE by 12−14 kcal/mol and identified part of the cause as the increased strain associated with the sp[2] carbon center. Borden,[6] using a series of isodesmic reactions, arrived at the conclusion that the loss of a very strong *tert*-C−H bond upon introduction of the sp[2] carbon in methylenecyclopropane was the major source of the additional strain energy. We reexamine this intriguing question using a series of related isodesmic reactions[6] augmented

with the BDE approach (Table 2). This is a particularly unique case since the energy differences between these isomeric alkenes can be expressed precisely as the difference between two C−H bond energies.

The difference between the heats of hydrogenation (ΔH_{hyd}) of methylenecyclopropane and isobutylene can be calculated (G2) from the exothermicity exhibited by reaction 1 to be −12.0 kcal/mol (Table 2). On the basis of experimental heats of formation, the difference in the heats of hydrogenation of these isomeric disubstituted alkenes is estimated to be 14.3 kcal/mol.[4,6] A direct measure of ΔH_{hyd} comes from the calculated enthalpies of hydrogenation of these alkenes (39.2 and 27.7 kcal/mol, Table 3); a $\Delta\Delta H_{hyd}$ in reasonable agreement with the above $\Delta H_{298} = 14.3$ kcal/mol[4b] when consideration is given to the uncertainty in the four experimental heats of formation (reaction 1). Borden[6] also convincingly demonstrated that relief of angle strain has only a modest effect (ca. 5 kcal/mol, CASPT2N) upon the exothermicity of reaction 1. The differences in the alkene π-bond energies can also be determined with reasonable accuracy at this level of theory. The relative thermodynamic π-BDEs of isobutylene and methylenecyclopropane can be estimated from

Table 3. Heat of Hydrogenation of Alkenes (ΔH_{hyd}) at the G2, G3, and CBS-Q Levels of Theory

	G2	G3	CBS-Q
ethylene	32.3		*31.9*
1-butene			*29.6*
(*E*)-2-butene	27.5		
(*Z*)-2-butene	28.8		
isobutylene	27.9		*27.7*
(*E*)-3-hexene			*27.2*
cyclopropene	54.4	**54.6**	*54.3*
cyclobutene	32.2	**32.3**	*31.4*
cyclopentene	26.4	**26.3**	
cyclohexene	28.3		*27.9*
cycloheptene	25.8		
3,3-dimethylcyclohexene			*27.9*
methylenecyclopropane	39.9	**39.7**	*39.2*
methylenecyclobutane			*29.6*
methylenecyclopentane			*26.7*
methylenecyclohexane			*29.4*
3-methylcyclopropene	54.1		*54.3*
3,3-dimethylcyclopropene			*54.5*
1-methylcyclopropene	51.1		*50.6*
trimethylethylene	26.3		
1-methylcyclohexene			*25.5*
(*E*)-3-methyl-3-hexene			*27.0*

reactions 2 and 3. At the G2 level the π-bond energies (69.2 and 62.2 kcal/mol, G2) differ by 7 kcal/mol. However, the π-BDEs of methylenecyclopropane and 1-methylcyclopropene are virtually indistinguishable (reactions 3 and 4). This assertion is confirmed by isodesmic reaction 5, which estimates the difference in their π-bond energies ($\Delta H_{298} = -0.4$ kcal/mol) by an effective cancellation of the p-orbital at C1 of both alkenes.

The difference between the strengths of the primary methyl C−H bonds (3.9 kcal/mol) and the tertiary C−H bonds (−8.8 kcal/mol) of methylcyclopropane and isobutane can be estimated from reactions 6 and 7. A direct comparison of homolytic bond dissociation energies at the G2 level (Table 1) gives quite comparable results. The primary methyl C−H bonds of isobutane are 3.8 kcal/mol stronger than those of methylcyclopropane, while the tertiary C−H bond of the latter is 8.8 kcal/mol stronger. These offsetting BDEs are also partly responsible for the exothermicity of reaction 7. Comparable data, at the CASPT2N-MP2 level, led Borden[6] to conclude that the biggest contributor to the larger heat of hydrogenation of methylenecyclopropane was the greater strength of the tertiary C−H bond in hydrogenation product methylcyclopropane than in isobutane (107.6 versus 98.8 kcal/mol, G2).

The question of the stabilizing influence of a cyclopropyl group on the stability of an adjacent free radical center is also relevant. The singly occupied molecular orbital of the CH_2 group of a cyclopropylcarbinyl radical can effectively overlap with the Walsh orbitals of the cyclopropane ring and stabilize the adjacent free radical. The rotational barrier for C−CH$_2$ rotation in cyclopropylcarbinyl radical is calculated to be 3.2 kcal/mol [B3LYP/6-311+G(3df,2p)+ZPVE]. There is a modest preference for the bisected versus planar conformation due to this type of "homoallylic" or cyclopropylcarbinyl stabilization, which is far less than the allylic stabilization in the allyl radical (CH$_2$= CH−CH$_2$•). The comparable C−C rotational barrier in the allyl radical that takes the C=C out of conjugation with the adjacent radical center is $\Delta E^{\ddagger} = 16.0$ kcal/mol. However, the two relatively strong vinyl C−H bonds in methylenecyclopropane (109.7 kcal/mol, G2) more than offset the loss of this single

tertiary C−H bond. Thus, we must look for additional sources of *destabilization* of methylenecyclopropane.

While we often tend to rationalize the stability of a molecule on the basis of its electron delocalization, the weakening of an allylic C−H bond by delocalization with its adjacent π-bond also has thermodynamic consequences. The C−H BDEs of the respective cyclopropane rings also exert a dominant effect upon the thermodynamic stability of methylenecyclopropane; the ring C−H BDEs are reduced from 109.5 kcal/mol (CBS-Q) in methylcyclopropane to 96.5 kcal/mol in methylenecyclopropane. The energetic consequences of two of these weaker C−H bonds can be offset by the two relatively strong vinyl C−H bonds, but the ΔBDE = 13 kcal/mol for *each of* the remaining C−H bonds can readily account for the increase in the SE of methylenecyclopropane of 12−14 kcal/mol proposed by Wiberg[4b] Thus, methylcyclopropane unquestionably has a relatively strong *tert*-C−H bond that exerts a stabilizing influence,[6] while methylenecyclopropane has *four* weak allylic C−H bonds (relative to those of a cyclopropyl system) that account for its instability. By comparison, the methyl C−H bonds in isobutane are reduced to 89.8 kcal/mol in isobutylene (ΔBDE = 13.8 kcal/mol).

Many opposing forces are obviously at work in the determination of the relative thermodynamic stability of these isomeric hydrocarbons. The source of the difference in the SEs of methylenecyclopropane and 1-methylcyclopropene can also be traced back to the same basic difference in the ring C−H BDEs. Wiberg[4b] reported that 1-methylcyclopropene was less stable by 10.2 kcal/mol on the basis of experimental heats of formation of these isomeric alkenes. We calculate a total energy difference of 10.9 and 11.0 kcal/mol and an enthalpy difference of 11.2 and 11.4 kcal/mol at the G2 and CBS-Q levels. Both the ring C−H and vinyl C−H BDEs of 1-methylcyclopropene are slightly stronger than those in methylenecyclopropane. It is the relatively weak allylic methyl C−H BDEs in 1-methylcyclopropene (88.1 kcal/mol) compared to those in methylcyclopropane (99.7 kcal/mol) that are at the root of its higher energy. Presumably, the weakening of these C−H bonds is due to delocalization of the π-bond by its $\sigma-\pi$ hyperconjugative interaction with the stabilization of the allylic radical. However, the comparable ring C−H bond distances of methylcyclopropane and methylenecyclopropane (1.0856 and 1.0869 Å) are not indicative of GS delocalization, an effect that manifests itself *after* bond dissociation and geometry relaxation.

At the CBS-Q level the energies of hydrogenation of 1-methylcyclopropene (50.6 kcal/mol) and methylenecyclopropane (39.2 kcal/mol) differ by 11.4 kcal/mol. The relative thermodynamic stabilities and the relationship between the π-BDEs can be estimated from reaction 5. Thus, it would appear that the two π-bonds are of comparable energy ($\Delta E = -0.4$ kcal/mol) and that the π-BDEs of 1-methyl- and 3-methylcyclopropene are essentially identical (reactions 4 and 8) and only slightly higher than that of cyclopropene itself (60.9 kcal/mol, reaction A). Thus, the energy difference (11 kcal/mol) between these highly strained isomeric alkenes is reduced largely to the thermodynamic influence of their respective C−H BDEs.

The BDEs for the next higher cyclic homologues of methylenecyclopropane also support the hypothesis that the differences in C−H bond strengths play a role in determining the SEs of three-membered rings. The α-allylic ring C−H BDE of

methylenecyclobutane (85.0 kcal/mol, CBS-Q) is actually 11.5 kcal/mol weaker than that of the corresponding C−H bond in methylenecyclopropane but comparable to that of the corresponding C−H bond in isobutylene (89.8 kcal/mol). Recall that it is the weakness of this particular allylic C−H bond that is partly responsible for the higher energy of 1-methylcyclopropene versus methylenecyclopropane. While the greatly increased s character of the bonding orbitals of three-membered rings gives rise to stronger C−H bonds,[6] in a four-membered ring the allylic C−H BDE is more typical of that in an acyclic alkene such as 1-butene (83.1 kcal/mol). The β-C−H (101.4 kcal/mol) and vinyl C−H (110.2 kcal/mol) BDEs in methylenecyclobutane are also normal (Table 1). The C−H BDEs in methylenecyclopentane are also quite similar to those in unstrained alkenes.

A comparison of the thermodynamic stabilities of 1-methylcyclopropene and isomeric 3-methylcyclopropene is also instructive. The BDE for the allylic tertiary hydrogen in 3-methylcyclopropene is quite high at 100.3 kcal/mol as are the vinyl (109.2 kcal/mol) and the methyl (98.4 kcal/mol) C−H bond strengths.

Alkene Thermodynamic Stability Derived from Energies of Hydrogenation. The thermodynamic stability of *isomeric alkenes* can also be estimated by comparison of their relative energies of hydrogenation. It is essential that the comparison be made with a suitably substituted acyclic reference alkene that provides the same number and types of C−H bonds on both sides of the equation.[3] For example, a trisubstituted cyclic alkene should have a strain-free trisubstituted (*E*)-alkene as a reference molecule since the product of hydrogenation will have a tertiary C−H with a lower BDE than a secondary C−H. On the basis of the relative enthalpy of hydrogenation (Table 3) of (*E*)-3-hexene (27.2 kcal/mol) and cyclohexene (27.9 kcal/mol), we suggest a *relative* SE for cyclohexene of 0.7 kcal/mol. The same exercise with the hydrogenation of (*E*)-3-methyl-3-hexene (27.0 kcal/ mol) and 1-methylcyclohexene (25.5 kcal/mol) suggests that this methyl-substituted cyclohexene is 1.5 kcal/mol *less strained than its acyclic reference alkene*. On the basis of the relative energies of hydrogenation of (*E*)-2-butene (27.5 kcal/mol) and cyclobutene (32.2 kcal/mol, G2), the SE of cyclobutene is predicted to be 4.7 kcal/mol higher than its saturated analogue; the experimental estimate is 1.9 kcal/mol.[4] These data also suggest that both cyclopentene ($\Delta\Delta H_{hyd}$ = 1.9 kcal/mol) and cycloheptene ($\Delta\Delta H_{hyd}$ = 2.8 kcal/mol) are less strained than cyclohexene (G2).

The generally accepted SEs of cyclopropene, cyclobutene, and cyclopentene are 55.2, 28.4, and 4.1 kcal/mol.[4] Their calculated G3 heats of hydrogenation (54.6, 32.3, and 26.3 kcal/mol, Table 3) give an indication of their relative strain energy but more closely parallel the relief of ring strain upon reduction of carbon−carbon double bonds.

It is well-known that alkyl substitution on a carbon−carbon double bond has a stabilizing influence. Thus, on the basis of their total energies, trisubstituted 1-methylcyclopropene is 3.1 kcal/mol (G2) more stable than disubstituted 3-methylcyclopropene. The difference in the heat of hydrogenation (3.7 kcal/mol) for 1-methylcyclopropene (50.6 kcal/mol, CBS-Q) and 3-methylcyclopropene (54.3 kcal/mol, CBS-Q) is also in accord with this relative stability. The heat of hydrogenation of 3,3-dimethylcyclopropene (54.5 kcal/mol) also suggests that it has

a greater SE than 1-methylcyclopropene. A similar conclusion is found in Table 4 (ΔSE = 1.4 kcal/mol).

Strain Energies Based upon Dimerization/Combination with Cyclopropane. We recently reported an extension of the dimerization (diagonal) protocol of Liebman et al.[10] that has proven quite effective in estimating the SEs for a series of different cyclic molecules including dioxiranes.[3b] For example, the dimerization of cyclopropane affords a larger ostensibly strain free molecule, cyclohexane, that differs only in the bond angles of the fragments and the number of gauche interactions (reaction 9). On the basis of the differences in computed total energies, which include zero-point energy corrections, the dimerization of cyclopropane, where SE = $(2E_{cyclopropane} - E_{cyclohexane})/2$, gives an SE = 27.2 kcal/mol at the G2 level of theory[3] and 27.8 kcal/mol at the CBS-Q level (Table 4), in excellent agreement with experiment (27.5 kcal/mol).[4a]
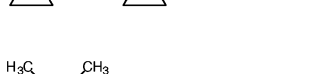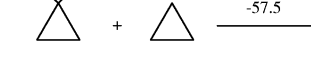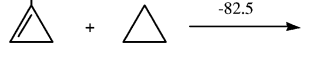
Surprisingly, on the basis of this protocol, the SE of methylcyclopropane is 2.0 kcal (29.8 kcal/mol, reaction 10) greater than that of cyclopropane but comparable to that of 1,1-dimethylcyclopropane (29.7 kcal/mol, reaction 11). Recall that neopentane is 5.2 kcal/mol more stable than *n*-pentane due to its stronger methyl C−H bonds.[3a] These SE values, however, are based upon their six-membered ring saturated reference compounds. Disproportionation of two methylcyclohexanes into 1,1-dimethylcyclohexane and cyclohexane is endothermic by 1.0 kcal/mol. This reaction, however, is complicated by the fact that one of the methyl groups is axial. We have argued previously that the SE of cyclohexane is not zero.[3] Cyclization of *n*-hexane to cyclohexane suggests an SE ≈ 2 kcal/mol relative to that of an all-anti *n*-hexane reference compound. The energy of all-gauche *n*-hexane is 1.3 kcal/mol higher than that of strain-free *n*-hexane, and therefore, one should anticipate a nonzero SE for cyclohexane. If we assign an SE to cyclohexane of 1−2 kcal/mol relative to that of the traditional all-anti linear hydrocarbon reference compound, then these SEs should be increased by 1−2 kcal/mol. The thermodynamic stabilities of cyclohexene and 3,3-dimethylcyclohexene based upon the above hydrogenation data do not differ measurably.

On the basis of this combination protocol,[3] the difference in estimated strain energies between methylenecyclopropane (reaction 12) and methylcyclopropane (reaction 10) of 9.7 kcal/mol is in excellent accord with the difference in experimental heats of formation of 10.2 kcal/mol.[4b] The SE of methylenecyclopropane is predicted to be 11.7 kcal/mol greater than that of cyclopropane, consistent with the 12−14 kcal/mol increase in angular strain estimated by Wiberg.[4b]

We also estimate the SE of cyclopropene as 54.1 kcal/mol on the basis of its combination with cyclopropane to form cyclohexene (reaction 13). This prediction is in excellent agreement with earlier assessments of 55.2 kcal/mol.[4] In a similar fashion (reaction 14) the SE of 1-methylcyclopropene is predicted to be 54.7 kcal/mol (CBS-Q). The SEs of 3-methyl- and 3,3-dimethylcyclopropene exhibit the same relatively high SE that we attribute largely to angular ring strain.

The SE of methylenecyclopropane based upon this protocol (39.5 kcal/mol) is also in good agreement with previous estimates (40.9 kcal/mol).[4a] The incremental increase in the SEs of cyclopropane, methylenecyclopropane (ΔSE = 12 kcal/mol), and 1-methylcyclopropene (ΔSE = 15 kcal/mol) corroborates the much earlier suggestion of Wiberg of a 12−14 kcal/mol

Table 4. Reaction Energies (kcal/mol, CBS-Q) for the Dimerization/Combination of Substituted Cyclopropanes and Cyclopropenes[a]

Reaction	SE, kcal/mol	Reaction
−55.6	27.8	9
−57.6	29.8	10
−57.5	29.7	11
−67.3	39.5	12
−81.9	54.1	13
−82.5	54.7	14
−82.6	54.8	15
−83.9	56.1	16

[a] SEs are relative to that of cyclopropane (27.8 kcal/mol).

increment for each additional sp^2 carbon center. These estimates of strain energy are, of course, predicated upon the assumption that the SE of the reference compound is zero. We provide evidence, based upon the relative energies of hydrogenation of the C=C in the reference alkenes to their saturated hydrocarbons, that the SEs of cyclohexene and 3,3-dimethylcyclohexene are identical. However, on the basis of the ΔH_{hyd} of (*E*)-3-methyl-3-hexene versus 1-methylcyclohexene, the latter is less strained by 1.5 kcal/mol.

Conclusions

Examination of the ring C−H BDEs at the G3 level shows that cyclopropane possesses very strong C−H bonds (109.2 kcal/mol). The ring C−H bond strengths of cyclopropene (100.4 kcal/mol) are also stronger than those of cyclobutene (90.6 kcal/mol). The vinyl C−H BDEs of cyclopropene and cyclobutene (109.6 and 111.9 kcal/mol) are not sufficiently different to account for the very large difference in strain energies (ΔSE = 26.8 kcal/mol). While the BDEs of vinyl C−H bonds are quite high and contribute to the thermodynamic stability of alkenes, vinyl C−H BDEs are not affected by angular strain.

Angular strain[4] makes a major contribution to the relative thermodynamic stability of *both* cyclopropane and cyclopropene

(SE = 54.1 kcal/mol). However, cyclopropane enjoys the luxury of 6 exceptionally strong C−H BDEs, and that is the major source of its anomalously low SE (27.8 kcal/mol). The angle strain induced by the sp^2 centers in cyclobutene has only a modest effect upon its strain energy, and it is only 4.7 kcal/mol more strained than cyclobutane. The π-BDE of cyclobutene is calculated (G3) to be 4.1 kcal/mol less than that of cyclopropene but is 2.5 kcal/mol *greater* than that of cyclopentene. This surprisingly strong π-bond contributes to the relatively low SE of cyclobutene (28.4 kcal/mol).

The C−H BDEs of cyclopentane (96.3 kcal/mol) are quite typical, so the relatively low SE of cyclopentene is a consequence of relatively strong vinyl C−H BDEs of 113.9 kcal/mol (G3).

We calculate an enthalpy difference between methylenecyclopropane and 1-methylcyclopropene of 11.22, 11.44, and 11.37 kcal/mol at the G2, G3, and CBS-Q levels. Despite this, the π-BDEs of methylenecyclopropane and 1-methylcyclopropene are virtually indistinguishable ($\Delta H_{298} = -0.4$ kcal/mol). The C−H BDEs of the respective cyclopropane rings exert a very important destabilizing influence upon the thermodynamic stability of methylenecyclopropane; the ring C−H BDEs are

reduced from 109.5 kcal/mol (CBS-Q) in methylcyclopropane to 96.5 kcal/mol in methylenecyclopropane. The energetic consequences of two of these weaker C–H bonds are offset by the two relatively strong vinyl C–H bonds of methylenecyclopropane. While methylcyclopropane has a relatively strong *tert*-C–H bond (107.6 kcal/mol) that exerts a stabilizing influence, the introduction of an sp^2 carbon center into methylenecyclopropane results in *four* relatively weak allylic C–H bonds that contribute to its instability. In addition to the angular strain attending the introduction of two sp^2 carbon centers in 1-methylcyclopropene, both its ring C–H bonds (ΔBDE = 9.7 kcal/mol) and its methyl C–H bonds (ΔBDE = 11.6 kcal/mol) are significantly weakened relative to those in methylcyclopropane.

Both the ring C–H and vinyl C–H BDEs of 1-methylcyclopropene are slightly stronger than those in methylenecyclopropane. It is the relatively weak allylic methyl C–H BDEs in 1-methylcyclopropene (88.1 kcal/mol) compared to those in methylcyclopropane (99.7 kcal/mol) that are at the root of its higher energy.

The dimerization/combination of three-membered alkenes with cyclopropane to produce a six-membered ring reference alkene has proven quite effective in estimating the SEs for a series of different alkenes, in excellent agreement with experiment.

While angular strain exerts a major influence upon the ring strain of three-membered ring hydrocarbons, it is the subtle changes in C–H bond dissociation energies that provide the most consistent rationale for their widely differing strain energies. The interaction of allylic hydrogens in a σ–π fashion apparently exerts a marked influence upon the thermodynamic stability of strained alkenes.

Since cyclopropane itself has a very small positive *R* value, the use of BDEs to estimate trends in SE for these small ring compounds does not introduce a large error. In general, we see an excellent correlation between diminished BDE and increased SE for this entire series of saturated and unsaturated hydrocarbons.

Supporting Information Available: Tables S1–S8 [G2, G3, and CBS-Q total energies (au) and enthalpies (au)] and Cartesian coordinates of selected compounds and their corresponding CBS-Q energies, enthalpies, and free energies (Appendix) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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