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Effect of Angle Strain in Conjugated Cycloalkenylidenes. Singlet−Triplet Splitting of Cyclobutenylidene and Its Ground-State Intramolecular Rearrangements

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The singlet and triplet states of cyclobutenylidene, cyclopenten-3-ylidene, cyclohexen-3-ylidene, and cyclohepten-3-ylidene and some of their isomers (cyclohexen-4-ylidene, cyclohepten-4-ylidene, and cyclohepten-5-ylidene) have been studied computationally (using ab initio and DFT methods) in order to assess the effect of angle strain on the S−T gap of small- and medium-size cyclic alkenylidenes. Ground-state intramolecular rearrangements of the conjugated cycloalkelnylidenes have also been examined with an emphasis on the smaller four-membered ring, which is compared to its higher homologues. It is found that cyclobutenylidene has a singlet ground state and a significant singlet−triplet gap (25 kcal mol^{-1}). This strong preference for the singlet state may be understood if cyclobutenylidene is also viewed as bicyclobut-1(2)-ene. As the size of the ring increases, the singlet state becomes destabilized with respect to the triplet. The break-even point occurs with the six-membered ring where the triplet and singlet states are close in energy. The barrier for the 1,2 hydrogen shift in cyclobutenylidene (50.5 kcal mol^{-1}) is found to be much higher compared to its higher homologues and to other alkylcarbenes. The ring contraction to form methylenecyclopropene (1,2 carbon shift) is energetically more favorable, requiring 34.8 kcal mol^{-1}. However, the lowest isomerization path available for singlet cyclobutenylidene is the formation of vinylacetylene, which is predicted to have a barrier of around 9 kcal mol^{-1}. This small but significant barrier implies that cyclobutenylidene should be observable.

Introduction

The experimental work of Staudinger demonstrated the existence of carbenes as reactive intermediates.[1] Later studies by Meerwein, Hine and Doering established carbenes as a class of molecules with distinct properties and provided ways of generating them.[2] For several years, the main source of information of these short-lived species came from analysis of their reaction products. However, nowadays their direct observation has become possible with sophisticated techniques such as time-resolved spectroscopy[3] and matrix isolation spectroscopy.[4] Despite the availability of these state-of-the-art techniques, the complete characterization of carbenes has not been achieved yet.

The reason for this can be traced to the fact that carbenes can exist both as singlet or triplet states with widely different chemical properties. Therefore, a key parameter in understanding the overall reactivity of a carbene is its singlet−triplet splitting (ΔE_{S-T}), which is closely related to its molecular structure. However, the simultaneous observation and characterization of the two states is often not possible, making the experimental determination of ΔE_{S-T} very difficult.[5] In this respect, computational chemistry methods have become increasingly important in this field. With calculations, it is possible to explore the effect of substituents and geometrical constraints on the ΔE_{S-T} in a systematic and comprehensive way. This is especially true nowadays, since high-level ab initio calculations can predict singlet−triplet gaps with reasonable accuracy.[6]

The relationship between molecular structure and singlet−triplet splitting is usually analyzed in terms of π and σ effects. The π effects refer to the interaction between the carbenic p orbital and the substituents' p or π system, while the σ effects are mainly related to the steric effects on the central bond angle. The π effects have been well-analyzed, but the σ effects have not been examined in a systematic fashion.[7] To better understand these effects, we decided to study a homologous series of cycloalkenylcarbenes at definitive levels of theory.

Cyclopropenylidene has been studied both experimentally and computationally.[8] It is believed to have a singlet

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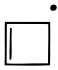
ground state, unlike its acyclic analogue vinylcarbene, which is a triplet ground state.[9−11] This difference is partly due to the small carbenic angle of the former.[8a] The higher homologue cyclobutenylidene (**1**)[12,13] remains elusive. When Shevlin et al.[12] attempted to generate **1** by deoxygenation of cyclobutenone using atomic carbon, the final product was vinylacetylene (**2**). No products that could have resulted from a 1,2 hydrogen shift or from a 1,2 carbon shift were detected, implying that carbene **1** does not rearrange to cyclobutadiene (**3**) or methylenecyclopropene (**4**). This is somewhat surprising, since, in most singlet carbenes with α-hydrogens, the 1,2 H shift is the predominant rearrangement path.[14] In a few cases of sterically constrained carbenes, the 1,2 C shift becomes also important.[15,16] The higher homologues (**5**−**7**) have received less attention, and to the best of our knowledge no experimental data have been reported.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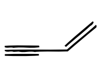
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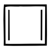
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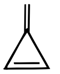
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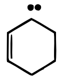
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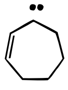
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In this paper, we examine how the angle strain at the carbenic angle affects the geometrical characteristics and the S−T splittings of these cyclic carbenes. The 1,2 H and 1,2 C shifts have also been studied as a function of the ring size. Finally, the ring-opening of cyclobutenylidene to give vinylacetylene is also examined and compared with the experimental results of Shevlin et al.[12]

Computational Procedures

Ab initio molecular orbital calculations[17] were carried out using the GAUSSIAN 94,[18] MOLPRO,[19] and ACES II[20] programs. Optimized geometries were obtained at the HF/6-31G(d), MP2(full)/6-31G(d), and B3-LYP/6-31G(d)[18,21] levels of theory.

Our best results were obtained at the G2, G2(MP2), and G2(MP2,SVP) levels of theory.[22,23] These three methods, which differ in their additivity approximations, represent calculations effectively at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point energies (ZPE) and a so-called higher level correction. While G2 is expected to perform better than its two approximations, its computational cost increases rapidly with the size of the system, and we have applied it only to the smallest homologue and its isomers (C_4 compounds). On the other hand, G2(MP2,SVP), which requires significantly less computational effort, has been used more extensively. A list of total energies at these levels of theory is provided in Table S1 (Supporting Information).

The rather flat potential energy surface in the neighborhood of butadienylidene (**13**) and its *s-cis* and *s-trans* conformers was investigated by carrying out geometry optimizations at the QCISD/6-31G(d) level of theory and characterizing the stationary points by vibrational analyses at the same level.

In all cases we have also applied the B3LYP/6-31G(d) method. Total B3-LYP/6-31G(d) energies at 298 K have been calculated and include zero-point energy corrections (obtained from B3LYP/6-31G(d) frequencies scaled by 0.9806)[24] and thermal corrections to the enthalpy (obtained from B3LYP/6-31G(d) frequencies scaled by 1.0013)[24] (see Table S2 in the Supporting Information).

Heats of formation were obtained with the help of isodesmic reactions (Table 1 and Table S3, Supporting Information) and the atomization reaction (Table S1).

Results and Discussion

Initially, we examine the calculated structures of the title carbenes. Then, from the computed heats of formation, the best estimates of their S−T splittings are derived and the energetics of the interaction between the double bond and the carbenic center is analyzed. At the end, the most important intramolecular rearrangement paths are examined.

Geometries. We begin with a brief description of the essential geometrical features of the higher homologues (**5**−**7**, Table S4, Supporting Information), which are more

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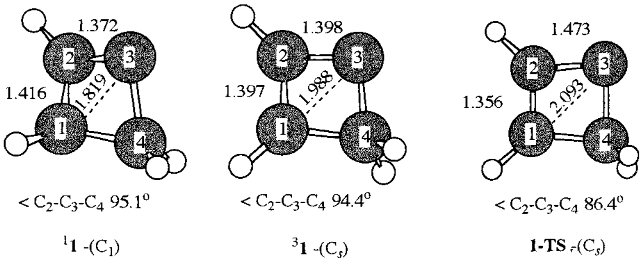


Figure 1. Selected B3LYP/6-31G(d) optimum geometrical parameters (distances in Å, angles in deg).

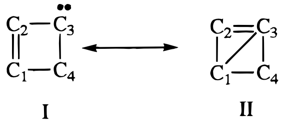
or less as expected, and then we proceed to a more detailed discussion of cyclobutenylidene, which has a rather unusual geometry at its singlet state (**1**, Figure 1 and Table S4, Supporting Information).

Not surprisingly, the angle at the carbenic center ($C_2-C_3-C_4$) increases on going from the five-membered ring to the seven-membered one, and as expected, the carbenic angles of the triplet states are systematically wider than those of the corresponding singlets (by 9−15°). For the singlet states, the widening of the angle is from 103° to 119°, while for the triplet states, it is from 114° to 134°. Also, the triplet states of the higher homologues (^{3}**5**−^{3}**7**) have an allylic-type structure with similar C_1-C_2 and C_2-C_3 bond lengths, whereas in the corresponding singlets the C_2-C_3 bond is systematically longer than the C_1-C_2 by 0.03−0.09 Å.

In the case of **1** (Figure 1), the triplet (^{3}**1**) is calculated to be planar (C_s), whereas the singlet adopts a puckered conformation of low symmetry (^{1}**1**-(C_1)). Partial optimization of singlet **1** under C_s symmetry leads to a saddle point (**1-TS**), which corresponds to the transition state for the enantiomerization of the two C_1 structures of ^{1}**1**. The barrier for this process is predicted to be 21.3 kcal mol^{-1}. The geometry of the triplet state of **1** displays the allylic feature of its higher homologues. However, in the singlet state the C_2-C_3 bond length is *shorter* than the C_1-C_2 by 0.03 Å, in contrast to the singlets of the larger rings. Another difference between ^{1}**1** and its higher homologues is that its carbenic angle is slightly wider than that of the corresponding triplet.

In the case of the saddle point **1-TS**, the C_2-C_3 bond is longer than the C_1-C_2 (by 0.12 Å) and its $C_2-C_3-C_4$ angle is narrower than that of the triplet state (by 8°). It appears then that **1-TS** displays more of the geometrical characteristics expected for a conjugated cycloalkenylcarbene than the miminum ^{1}**1**. The latter to some extent could also be described as the twisted olefin 1-bicyclobutene due to the rather short C_2-C_3 bond (1.372 Å) and C_1-C_3 distance. From this point of view, **1-TS** can be thought of as a carbene serving as the transition state for the enantiomerization of a twisted olefin. This is reminiscent of homocub-9-ylidene.[25,26] In that case, the carbene is in equilibrium with its isomer homocub-1(9)-ene (a twisted olefin) via a reversible C−C bond insertion mechanism. However, it should be noted that there are few substituted cyclobutenylidenes known add to olefins to give cyclopropane products in a stereospecific fashion, i.e., they exhibit typical singlet carbene reactivity.[27]

Whether ^{1}**1** is better regarded as a strained olefin or as a carbene is debatable, and our studies have not addressed this issue. Nevertheless, the geometrical features of ^{1}**1** strongly suggest that both resonance structures shown below should be important descriptors of its electronic state.



^{1}**1**

Thermochemistry. G2 theory and its approximations have been shown to predict reliably the heats of formation for a variety of systems.[22] However, with large-size systems some caution is needed in applying these methods.[28] Calculated heats of formation based on the atomization reaction can exhibit significant errors for medium- and large-size hydrocarbons, especially those with a high degree of unsaturation (for example, benzene). For that matter, the cyclic alkenylcarbenes examined in the present study have an unsaturation degree of two, and therefore, heats of formation based on the atomization reaction are expected to be somewhat overestimated. In addition, singlet−triplet gaps are notoriously difficult to calculate accurately, even at high levels of theory. For example, at the G2 level of theory the S−T gap of methylene is underestimated by 2.4 kcal mol^{-1}.[22a] For these reasons, heats of formation and the derived S−T splittings have been estimated with the help of isodesmic reactions, such as shown in Table 1.

From reactions 1−5 in Table 1, a range of ΔH_{f298} is obtained for ^{1}**1**. Considering the average of the G2 ΔH_{f298} values as the best estimate, we arrive at our recommended value of 111.3 kcal mol^{-1} for ΔH_{f298} (^{1}**1**). The G2 values are very close to this average (maximum difference of 1.5 kcal mol^{-1}), providing an idea of the associated error. In a similar way, the heats of formation for ^{3}**1** and for the higher homologues were obtained (Table 1 and Table S3, Supporting Information) and the results are summarized in Table 2.

As might have been expected,[7c] the smaller the angle at the carbenic center, the more the singlet state is stabilized relative to the triplet. For the cyclic carbenes considered in this study, the break-even point seems to be the six-membered ring for which triplet and singlet states are calculated to be nearly isoenergetic. The largest cyclic vinylcarbene (**7**) that we examined, like the parent vinylmethylene, has a triplet ground state and a similar T−S gap.[29] It seems, therefore, that for larger rings the carbon skeleton is flexible enough to accommodate the geometrical requirements of both the singlet and the triplet states, and such systems should behave more or less like the open-chain vinylmethylene, i.e., have triplet ground states.

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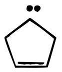
(29) MCSCF calculations predict the T−S gap of the parent vinylmethylene to be 12−13 kcal mol^{-1}.[10c,11] However, at the G2 level of theory (using isodesmic reactions) it is found to be 6.4 kcal mol^{-1}.

Table 1. Calculated Heats of Isodesmic Reactions (ΔH_{298}, kcal mol^{-1}) and Derived Heats of Formation (ΔH_{f298}, kcal mol^{-1})

		ΔH_{298}				
		G2	G2(MP2)	G2(MP2,SVP)	B3LYP^{b}	ΔH_{f298}^{a}
						ΔH_{f298} (^{1}**1**)
(1)	^{1}**1** + 5 CH_4 → $^{1}CH_2$ + C_2H_4 + 3 C_2H_6	31.2	31.0	31.5	33.0	112.8
(2)	^{1}**1** + CH_4 → $^{1}CH_2$ + cyclobutene	46.1	46.2	46.5	49.1	111.9
(3)	^{1}**1** + 6 CH_4 → C_2H_4 + 4 C_2H_6	−72.2	−72.5	−72.1	−76.1	111.2
(4)	^{1}**1** + CH_3CH_3 → C_2H_4 + bicyclobutane	−25.9	−26.0	−26.3	−25.0	110.3
(5)	^{1}**1** + 2 CH_4 → C_2H_6 + cyclobutene	−57.3	−57.3	−57.2	−60.0	110.3
						ΔH_{f298} (^{3}**1**)
(6)	^{3}**1** + 5 CH_4 → $^{3}CH_2$ + C_2H_4 + C_2H_6	−2.0	−2.6	−2.3	1.6	137.0
(7)	^{3}**1** + 4 CH_4 → 2 C_2H_4 + $C_2H_3^{\bullet}$ + $C_2H_5^{\bullet}$	−4.9	−5.2	−5.3	−5.5	135.9
(8)	^{3}**1** + 3 CH_4 → $C_3H_5^{\bullet}$ + $C_2H_5^{\bullet}$ + C_2H_6	−33.7	−33.8	−33.8	−35.2	136.3

[a] Based on the calculated (G2) ΔH_{298} in conjuction with experimental heats of formation[38] for all species involved except the one of interest. [b] With the 6-31G(d) basis set, including ZPE corrections and thermal corrections to the enthalpy.

With **5**−**7**, the possibility of isomerism with respect to the relative positions of the carbenic center and the double bond arises (compounds **8**−**11**). In the case of the triplets ^{3}**8**, ^{3}**9**, and ^{3}**10**, the angle at the carbenic center is essentially the same (within 1°) with the corresponding angles of ^{3}**5**, ^{3}**6**, and ^{3}**7**, respectively, implying that the angle strain at the carbenic center for these three sets of isomers should be more or less the same. Therefore, a direct comparison of their relative energies should be primarily associated with the stabilization effect of the double bond on the carbenic center. Indeed, in all three cases, the most stable isomer is the one in which the double bond can conjugate with the carbenic center and the resulting stabilization energy varies between 10.2 and 13.2 kcal mol^{-1}. A similar stabilization effect of the double bond is also found for the singlets ^{1}**5**, ^{1}**6**, and ^{1}**7** as compared to ^{1}**8**, ^{1}**9**, and ^{1}**10** (or ^{1}**11**), respectively. In the case of the singlets, this stabilization is 5.0−9.1 kcal mol^{-1} or 10−50% less than for the triplets.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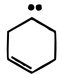
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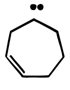
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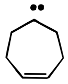
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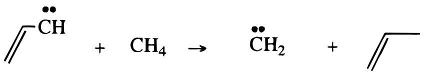
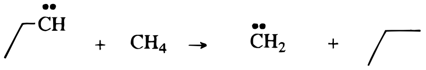
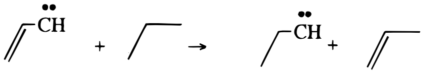
This small difference in the stabilization effect between singlet and triplet states can be understood by considering the computed enthalpies (kcal mol^{-1}) of the following isodesmic reactions for the singlet (S) and triplet (T) states of vinylcarbene and ethylcarbene:


(9) S: 18.2 / T: 17.6


(10) S: 16.5 / T: 5.3


(11) S: 1.7 / T: 12.3

From eq 9, it is seen that a vinyl group stabilizes the singlet (which is isoelectronic to a carbocation) somewhat more than the triplet compared to a hydrogen substituent.[17] However, an ethyl group stabilizes the singlet significantly more than the triplet (eq 10), presumably due to hyperconjugation.[17,30] Equation 11, which is the difference between eqs 9 and 10, shows that a vinyl group stabilizes the triplet more than the singlet, as compared to an alkyl (ethyl) substituent. Thus, in **8**−**11** the singlet is already stabilized by hyperconjugation (of the alkyl group) to a larger extent than the corresponding triplet. Therefore, conjugation of the double bond with the carbenic center in **5**−**7** offers little extra stabilization to the singlet state, but more to the triplet.

Table 2. Best Estimates of Heats of Formation (ΔH_{f298}, kcal mol^{-1}) and Derived S−T Splittings (ΔE_{S-T}, kcal mol^{-1}) for Small- and Medium-Size Cyclic Carbenes^{a}

	ΔH_{f298}		ΔH_{f298}		ΔE_{S-T}
^{1}**1**	111.3	^{3}**1**	136.4	**1**	−25
^{1}**5**	95.7	^{3}**5**	101.9	**5**	−6
^{1}**6**	88.8	^{3}**6**	88.7	**6**	∼0
^{1}**7**	88.9	^{3}**7**	85.2	**7**	4
^{1}**8**	104.8	^{3}**8**	112.1	**8**	−7
^{1}**9**	96.6	^{3}**9**	101.9	**9**	−5
^{1}**10**	95.0	^{3}**10**	96.8	**10**	−2
^{1}**11**	93.9	^{3}**11**	96.8	**11**	−3

[a] Based on the isogyric reactions of Table 1 and Table S3 (Supporting Information).

As mentioned above, the smaller the angle at the carbenic center, the more stable the singlet state with respect to the triplet. While this argument is compatible with the rather small S−T splitting (6 kcal mol^{-1}) predicted for **5**, it can hardly explain the significant S−T gap of 25 kcal mol^{-1} calculated for **1**. This is supported by the finding that if the carbenic angles in methylene and vinylmethylene are restricted to be the same as in **1**, then the S−T gap is calculated to be only 4.1 and 10.6 kcal mol^{-1}, respectively.[31]

The energy of isodesmic reaction 12 provides a measure of the stabilization of the carbenic center due to the double bond, which is 2.6 kcal mol^{-1} for ^{3}**1**. On the basis of the above discussion for the higher homologues, one would expect that for ^{1}**1** this stabilization would be less, since singlet cyclobutylidene (^{1}**12**) should be stabilized by hyperconjugation more than its triplet state (^{3}**12**). In contrast to this expectation, reaction 13 predicts a stabilization of 20.4 kcal mol^{-1} for the interaction with the double bond in ^{1}**1**. We also note that the difference between reactions 12 and 13 represents the difference in the S−T gaps between **1** and its saturated analogue **12**. Despite the formal similarity of the two compounds, the S−T gap of the former is calculated to be 17.8 kcal mol^{-1} larger (in absolute value) than that of the latter.

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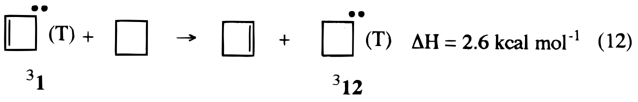
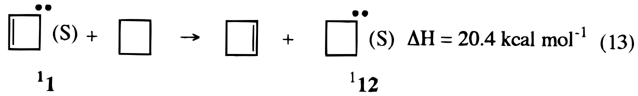
(30) Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. v. R.; Schaefer, H. F.; Hadad, C. M. *J. Am. Chem. Soc.* **1996**, *118*, 9908.

(31) At the G2 level of theory (using isodesmic reactions) and ignoring differences in ZPEs.



(12)



(13)

Both from the S−T gap and the exothermicity of reaction 13, it appears that ^{1}**1** is approximately 15−20 kcal mol^{-1} more stable than expected. Again, the contribution of resonance structure II provides a possible rationalization. This resonance structure has an extra formal bond (at the carbene carbon) compared to the "carbenic" resonance structure (I). This diagonal (C_1−C_3) bonding interaction could in principle provide the extra stabilization. The bond dissociation energy of the "diagonal" C−C bond of bicyclobutane is calculated to be 51.8 kcal mol^{-1}.[32] The fact that the "extra" stabilization energy of ^{1}**1** is 30−40% of this quantity may be taken as a qualitative indication of the relative importance of resonance structure II.

1,2-Hydrogen Migration. (For the 1,2 H-shifts calculated barriers are reported in Table 3 and transition state structures (HTS) in Table S4, Supporting Information). 1,2 Hydrogen-shifts in alkyl carbenes are believed to occur rather easily.[14] Indeed, for **5**−**7**, the calculated barriers for these H shifts vary between 5.6 and 9.7 kcal mol^{-1}. Also the barrier for ^{1}**12**, which is closely related to ^{1}**1**, is 9.9 kcal mol^{-1}.[16b] On the other hand, a significantly larger barrier of 50.4 kcal mol^{-1} is predicted for ^{1}**1**. This large difference can be attributed in part to the requirement for the migrating hydrogen to be well aligned with the empty p orbital of the carbenic center. A measure of this orbital alignment is provided by the dihedral angle C_2−C_3−C_4−H_5 (H_5 is the migrating H) of the transition state (**1-HTS**),[16b] which in the case of ^{1}**1** is 110.9° (Table S4, Supporting Information), somewhat different from the ideal value of 97° predicted for the 1,2-hydrogen shift in methylcarbene. However, this deviation is expected to have a rather small energetic cost of around 5 kcal mol^{-1}.[16b] Energetically more important is that alignment of orbitals in **1-HTS** is accompanied by planarization of the ring, which as discussed above requires approximately 21 kcal mol^{-1}. Another factor that may be also contributing to the high 1,2-H barrier for ^{1}**1** is the formation of the antiaromatic cyclobutadiene. As Table 3 shows, there is a reasonable correlation between the barrier height and the exothermicity of the 1,2 H-shift. This is also reflected at the geometries of the transition states, since the migrating hydrogen is closer to the methylenic carbon than to the carbene center. On the other hand, in the case of ^{1}**1**, the difference between the two distances is the smallest, implying a later transition state.[33]

Table 3. Calculated Barriers ($\Delta H^{\ddagger}$, kcal mol^{-1}) and Reaction Enthalpies (ΔH, kcal mol^{-1}) at 298 K for 1,2 Hydrogen and 1,2 Carbon Shifts at the G2(MP2,SVP) and B3LYP/6-31G(d) Levels of Theory

	$\Delta H^{\ddagger}$		ΔH	
	G2(MP2, SVP)	B3LYP/ 6-31G(d)	G2(MP2, SVP)	B3LYP/ 6-31G(d)
1,2 H shift				
1	50.4[a]	52.6	−9.9[b]	−7.1
5	7.6[c]	11.5	−63.4[d]	−61.4
6	9.7	12.1	−62.8	−61.7
7	5.6	8.6		−65.3
cyclohex-1,3dien-5-ylidene	<0.2	2.3	−91.3	−90.6
1,2 C-Shift				
1	34.3[e]	34.4	−19.3[f]	−23.3
5	55.6[g]	55.2	−36.3[h]	−35.5
6	38.7	39.8	−61.9	−61.6
7	11.8	13.6		−73.3

[a] 50.5 kcal mol^{-1} (G2). [b] −9.4 kcal mol^{-1} (G2). [c] 8.1 kcal mol^{-1} (G2(MP2)). [d] −62.8 kcal mol^{-1} (G2(MP2)). [e] 34.8 kcal mol^{-1} (G2). [f] −19.3 kcal mol^{-1} (G2). [g] 56.0 kcal mol^{-1} (G2(MP2)). [h] −35.9 kcal mol^{-1} (G2(MP2)).

1,2 Carbon Migration. (For the 1,2 C shifts calculated barriers are reported in Table 3 and transition-state structures (CTS) in Table S4, Supporting Information). 1,2 C shifts are much less common than 1,2 H shifts, but they have been reported in a few cases of conformationally rigid systems.[15] A recent example is cyclobutylidene (**12**), where C migration is preferred over H migration.[16] The same preference but more pronounced is found for cyclobutenylidene ^{1}**1**. In contrast, the higher homologues (^{1}**5**−^{1}**7**) have C−C insertion barriers larger than for C−H insertion. A common geometrical feature of these rearrangements is the cleavage of the C_4−C_5 bond, with little development of the new bond (C_3−C_5). These transition states (**5-CTS**, **6-CTS**, **7-CTS**) to some extent resemble bicyclic systems made from a three-membered ring with "elongated" bonds and a fused 4-, 5- or 6-membered cycloalkene. As the size of the cycloalkene ring increases, the strain in the transition state should be reduced in agreement with the lower barriers predicted on going from **5** to **7**.[34] An exception to this trend is cyclobutenylidene, which has a smaller 1,2 C shift barrier than ^{1}**5**, but this is most likely due to the close proximity of the diagonal C_1 and C_3 carbons, which makes the structure of ^{1}**1** somewhat similar to that of **1-CTS**.

Formation of Vinylacetylene (2) from Singlet 1. The formation of vinylacetylene is predicted to be the lowest energy path available for the intermolecular rearrangement of **1** (Figure 2a), in agreement with the experimental observations of Shevlin et al.[12] This isomerization proceeds via rupture of the C_3−C_4 bond of ^{1}**1** to form the intermediate 1,3-butadienylidene (**13**, Figure 2a).

The potential surface is quite complicated for butadienylidene, and several different minima can be found depending on the level of theory and basis set used. Butadienylidene, by analogy to butadiene, is expected to have two types of minima: A planar *s-trans* structure (*s-trans*-**13**) and a twisted one (C_2 symmetry for butadiene, but C_1 for **13**). The planar *s-cis* structure should be a transition state connecting the two C_1 conformers of

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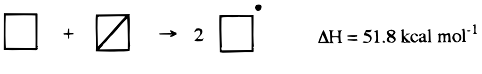
(32) From the energy of the following reaction:



This chemical equation represents the difference between the C−H BDE in cyclobutane and the C_3−H BDE of cyclobutyl radical. The implicit assumption is that the latter BDE is smaller than the former by an amount that is equal to the "diagonal" C−C BDE of bicyclobutane.

(33) Similarly, cyclohex-1,3-dien-5-ylidene, which has the most exothermic 1,2 H-shift (due to the formation of the aromatic benzene), has the smallest barrier and the earliest TS.

(34) In the case of ^{1}**5**, the TS for the formation of vinylallene (which also involves rupture of the C_4−C_5 bond) lies 16.9 kcal mol^{-1} (B3LYP/6-31G(d)) higher in energy than the singlet carbene.

Table 4. B3-LYP/6-31G(d) Harmonic Vibrational Frequencies[a] (ν, cm^{-1}) and Intensities (I, km mol^{-1}) for Singlet 1

ν	*I*	approximate description	ν	*I*	approximate description
3159	1.1	C−H str	1073	5.2	C−H bend + CH_2 wag
3069	8.1	C−H sym str	1038	2.8	C−H bend + C−C str
2997	25.5	C−H asym str	1003	1.4	CH_2 twist + ring def
2969	37.4	C−H str	987	6.5	CH_2 rock
1472	0.7	CH_2 scissoring	912	44.3	ring def
1423	0.8	C−C str + CH_2 scissoring	757	34.4	ring def
1279	4.5	C−C str + CH_2 wag	650	14.2	ring def + CH_2 twist
1216	2.6	C−H bend	597	64.8	ring breathing
1121	0.7	CH_2 wag	503	9.3	ring puckering

[a] Scaled by 0.9614.[24]

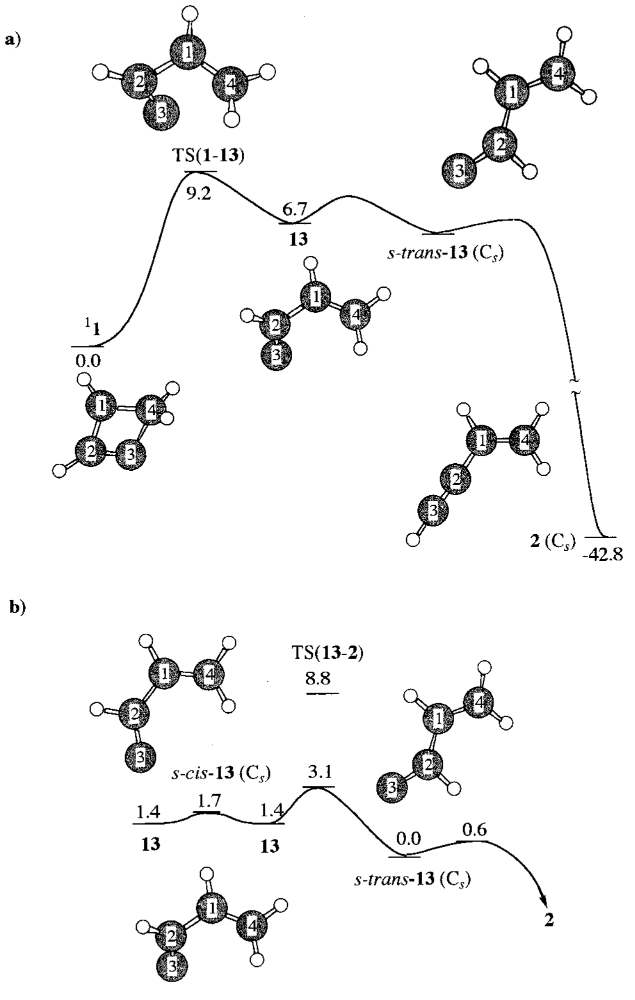


Figure 2. (a) Lowest energy rearrangement path of ^{1}**1** leading to the formation of vinylacetylene (G2 energies (kcal mol^{-1}) relative to ^{1}**1**). (b) QCISD(T) relative energies (kcal mol^{-1}) of butadienylidene conformers (including ZPE corrections using QCISD/6-31G(d) frequencies scaled by 1.0147[24]).

13. However, DFT and MP2 methods (with the 6-31G(d) basis set) find *cis*-**13** to be a minimum,[35] but at the QCISD/6-31G(d) level of theory the *s-cis* conformer is correctly predicted to be a first-order saddle point for the enantiomerization of **13**. Therefore, this part of the PES was explored at the QCISD level (Figure 2b).[36] The enantiomerization of **13** via *s-cis* **13** is very facile, requiring only 0.3 kcal mol^{-1} (Figure 2b). The rotational barrier of **13**, toward the more stable *s-trans* conformer, is slightly higher (1.7 kcal mol^{-1}). The latter easily isomerizes to vinylacetylene via a 1,2 H-shift, with a barrier of 0.6 kcal mol^{-1}. This is comparable to the barrier reported for the isomerization of the parent vinylidene to acetylene (1−1.5 kcal mol^{-1}).[37] Attempts to find a direct 1,2 H shift from **13** to **2** led to the same TS for the 1,2 H shift from *s-trans*-**13** to **2**. A direct path between **13** and **2** is via TS(**13**-**2**), which corresponds to a 1,2 C-shift. But this path is 5.7 kcal mol^{-1} higher in energy than the isomerization path via *s-trans*-**13** and, therefore, not likely to be competitive at low temperatures.

Overall, it appears that the bottleneck for the **1** → **2** rearrangement is the cleavage of the C_3−C_4 bond. The intermediate butadienylidenes (**13** and *s-trans*-**13**) lie in shallow potential minima (of less than a couple of kcal mol^{-1} in depth). Based on this, one may conclude that the detection of butadienylidene would be difficult. On the other hand, singlet cyclobutenylidene (^{1}**1**) appears to be in an energy well of around 9 kcal mol^{-1} in depth. Presumably, under Shevlin's conditions the deoxygenation of cyclobutenone by atomic carbon leaves behind a hot carbene that has enough energy to overcome this barrier. However, generation of cyclobutenylidene under suitable conditions should make it experimentally accessible. With this in mind, the calculated harmonic vibrational frequencies and their intensities of ^{1}**1** are presented in Table 4.

Concluding Remarks

Angle strain causes small-ring vinylcarbenes to prefer a singlet ground state, in contrast to the parent (acyclic) vinylcarbene. However, as the angle at the carbenic center is allowed to widen with increasing ring size, the triplet becomes the ground state. The break-even point occurs with the six-membered ring for which singlet and triplet states are close in energy. For five-membered and larger rings, the singlet states are expected to isomerize quite readily to the corresponding olefins via a 1,2 H migration of the neighboring methylenic hydrogen. On the other hand, in cyclobutenylidene (^{1}**1**), there is a much stronger interaction between the double bond and the carbenic center as compared to its higher homologues. This gives rise to a larger than expected S−T gap (of 25

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(35) However, with a larger basis set (6-311++G(d,p)) *cis*-**13** collapses to vinylacetylene (**2**).

(36) QCISD(T)/6-31G(d) energies at QCISD/6-31G(d) optimized geometries and including ZPE corrections at the latter level (scale factor: 1.015).[24]

(37) (a) Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 8714. (b) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 5974.

(38) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem Ref. Data Suppl. 1* **1988**, 17. (b) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; Aug 1997; National Institute of Standards and Technology: Gaithersburg MD, 20899 (http://webbook.nist.gov).

kcal mol^{-1}) and a distinctly different preference for the various intramolecular rearrangement paths. Unlike its higher homologues, ^{1}**1** requires significantly more energy for the 1,2 H than for the 1,2 C shift. But even the latter isomerization path cannot compete with ring opening to butadienylidene and eventually vinylacetylene. The overall barrier for this process, which appears to be the lowest energy path for the rearrangement of ^{1}**1**, is predicted to be around 9 kcal mol^{-1}. Therefore, under suitable experimental conditions cyclobutenylidene should be observable.

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Supporting Information Available: Total G2, and G2(MP2), G2(MP2,SVP) energies and heats of formation based on the standard atomization reaction (Table S1), total B3LYP/6-31G(d) energies (Table S2), calculated heats of isodesmic reactions (Table S3), and selected B3LYP/6-31G(d) geometrical parameters (Table S4). See any current masthead page for ordering and Internet access instructions. This material is available free of charge via the Internet at http://pubs.acs.org.

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