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Singlet−Triplet Energy Separation of Cyclobutylidene

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Ab initio (MP2, CCSD(T)) and density functional theory (BLYP, B3LYP) calculations provide insight concerning novel aspects of structure and bonding in cyclobutylidene (**1**). Singlet cyclobutylidene (^{1}**1**) adopts a bicyclobutane-like structure (C_s symmetry) that includes a weak, transannular bonding interaction between the carbene carbon and the opposing CH_2 group. Conformational ring inversion in ^{1}**1** occurs through a transition state of C_{2v} symmetry (**TS^{1}1**) with an enthalpy barrier of approximately 3 kcal/mol. Stabilization afforded the singlet state by the transannular interaction appears to be largely offset by a loss of hyperconjugative stabilization from the adjacent C−H bonds. Triplet cyclobutylidene (^{3}**1**) exhibits a C_{2v} structure and conventional bonding. The triplet state lies 5.9 kcal/mol above the singlet ground state at the CCSD(T)/TZP//CCSD(T)/DZP level of theory. The singlet−triplet energy gap of cyclobutylidene (−5.9 kcal/mol) lies between that of an acyclic analogue, dimethylcarbene (−1.6 kcal/mol), and a highly strained analogue, cyclopropylidene (−13.8 kcal/mol). The magnitude of the energy gap suggests that triplet cyclobutylidene (^{3}**1**) will be thermally accessible under a variety of experimental conditions.

Introduction

The interdependent relationship among geometry, substitution, spin multiplicity, and singlet−triplet energy separation governs the reactivity of organic carbenes.[1] The electron-withdrawing and -donating properties of substituents play an important role in determining the ground-state multiplicity.[2] Carbenes bearing a vinyl[3] or aryl[4] substituent generally display triplet ground states, while carbenes bearing an electron-donating heteroatom substituent, such as $-NR_2$, −OR, and −X, display singlet ground states.[2] In recent years, considerable interest has focused on understanding the structure and reactivity of simple dialkylcarbenes. The absence of strongly stabilizing donor substituents and the existence of low-energy pathways for intramolecular rearrangement render dialkylcarbenes highly reactive intermediates. Recent experimental and computational studies of dimethylcarbene,[5] dicyclopropylcarbene,[6] and 2-adamantylidene[7] reveal that alkyl substituents act as weak electron donors (via hyperconjugation), affording carbenes with singlet ground states and small singlet−triplet energy separations. In systems bearing bulky substituents, such as di-*tert*-butylcarbene[8] and diadamantylcarbene,[9] the larger bond angle favors a triplet ground state.

Cyclobutylidene (**1**) represents an intriguing system in which to study the relationship between geometry and singlet−triplet energy separation.[10] In dimethylcarbene, which may be considered an acyclic, dialkylcarbene analogue of cyclobutylidene (**1**), the triplet state is predicted to lie only 1.64 kcal/mol above the singlet state.[5b] Given this small energy gap, subtle structural effects may play an important role in determining the ground-state multiplicity of **1**. The constrained bond angle at the carbene center of cyclobutylidene will destabilize the triplet relative to the singlet. Conversely,

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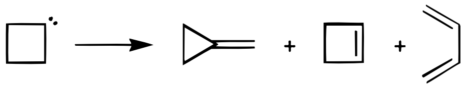
the constrained geometry of the four-membered ring may not allow the optimal geometry to maximize hyperconjugation, thereby destabilizing the singlet relative to the triplet. Computational studies suggest a nonclassical structure for singlet cyclobutylidene, one with significant transannular interaction between C1 and C3.[11-13] This behavior is reminiscent of the unsaturated analogue, cyclobutenylidene, in which the transannular interaction between the divalent carbon and the alkene alters the electronic nature of the molecule so dramatically that it can no longer be considered a true carbene.[14] In light of the current interest in the structure and reactivity of cyclobutylidene[12,13,16] and related alkylcarbenes,[5-7] we sought to probe the crucial issues that remain unanswered concerning cyclobutylidene (**1**): the structure of the triplet state, the magnitude of the singlet−triplet energy gap, and the accessibility of the triplet state to intervene in the chemistry of **1**. In the present paper, we report the results of computational investigations of singlet and triplet cyclobutylidene using a variety of density functional theory and ab initio methods (including coupled cluster theory). These calculations provide the most reliable results to date regarding the geometry and relative energies of singlet and triplet cyclobutylidene. In addition, the results of natural bond orbital (NBO) analyses on both singlet and triplet cyclobutylidene lend further insight into the electronic structure of these molecules.

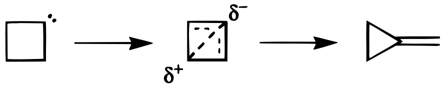
Background

In the first experiments designed to probe the chemistry of cyclobutylidene (**1**), Friedman and Shechter isolated methylenecyclopropane (**2**), cyclobutene (**3**), and 1,3-butadiene (**4**) from the thermal decomposition of the sodium salt of cyclobutanone tosylhydrazone.[15] The formation of methylenecyclopropane (**2**) as the major product represents an intriguing result; most carbenes possessing α-hydrogens preferentially rearrange by 1,2-hydrogen migration. Many years later, Pezacki et al. investigated the photochemical decomposition of diazocyclobutane in solution.[16] Although a significant fraction of the excited-state diazo compound rearranges directly to methylenecyclopropane (**2**) and cyclobutene (**3**), without intervention of cyclobutylidene (**1**), quenching studies establish that free singlet cyclobutylidene (^{1}**1**) rearranges almost exclusively to methylenecyclopropene (**2**) with a first-order rate constant of (5−25) × 10^7 s^{-1} in cyclohexane.



1 **2** **3** **4**
79% 18% 2%

The preference of cyclobutylidene for carbon migration over hydrogen migration represents an unusual departure from the normal reactivity pattern for carbenes. Schoeller investigated the electronic basis for this unusual reactivity using MINDO/3 semiempirical calculations.[11] At this level of theory, singlet cyclobutylidene (**1**) adopts a C_{2v} geometry. Ring contraction of **1** to methylenecyclopropane (**2**) occurs in a two-step process involving a nonclassical bicyclic carbene intermediate. The bicyclobutane-like intermediate, formed by transannular overlap of the empty 2p atomic orbital at the carbene center with the opposing CH_2 group, was estimated to lie 4.8 kcal/mol lower in energy than the C_{2v}-symmetric singlet carbene (**1**). Wang and Deng later investigated the potential energy surface for the rearrangement of singlet cyclobutylidene (**1**) to methylenecyclopropane (**2**), cyclobutene (**3**), and bicyclobutane using HF/3-21G geometries and HF/6-31G** energies.[12] The C_s structure computed for singlet cyclobutylidene (**1**) is reminiscent of the nonclassical bicyclic carbene intermediate calculated by Schoeller. Recently, Sulzbach et al. studied the structure and rearrangements of singlet cyclobutylidene (**1**) and related dialkylcarbenes using coupled cluster, Møller−Plesset perturbation, and hybrid Hartree−Fock/density functional theory methods.[13] These reliable computational methods once again predict a nonclassical bicyclic structure for singlet cyclobutylidene (**1**) (^{1}**1** in Figure 1). Thus, the explanation for the unusual preference for 1,2-carbon migration in cyclobutylidene derives directly from the unusual structure of singlet cyclobutylidene itself. Because of the structural similarity between the ground-state geometry of ^{1}**1** and the transition state for 1,2-carbon migration, the 1,2-carbon rearrangement becomes quite facile with respect to 1,2-hydrogen migration or ring opening to 1,3-butadiene.[17]



1 **2**

The literature contains only a single estimate for the singlet−triplet gap in cyclobutylidene (**1**). Schoeller's calculation (MINDO/2 including 3 × 3 CI) placed the singlet state 8.9 kcal/mol above the triplet state,[11] but this semiempirical result cannot be considered to be reliable.

Computational Methods

Geometry optimizations were performed using Møller−Plesset second-order perturbation theory (MP2),[18] density functional theory (DFT), with the exchange potentials of Becke[19] and the correlation functional of Lee, Yang, and Parr[20] (BLYP and B3LYP), and coupled cluster theory, including single and double excitations iteratively and triple excitations perturbatively (CCSD(T)).[21] Dunning's double-ζ correlation-

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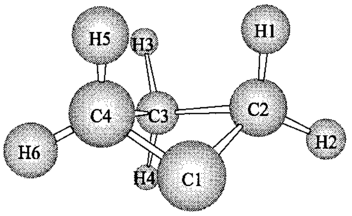
Dihedral C1-C2-C3-C4		Distance C1-C3	
MP2	39.9°	MP2	1.723 Å
BLYP	38.6°	BLYP	1.760 Å
B3LYP	38.3°	B3LYP	1.770 Å
CCSD(T)	38.5°	CCSD(T)	1.842 Å

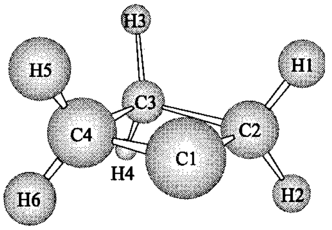
Dihedral H1-C2-C1-C4		Angle C4-C1-C2	
MP2	47.4°	MP2	101.3°
BLYP	49.7°	BLYP	101.5°
B3LYP	51.8°	B3LYP	100.1°
CCSD(T)	55.4°	CCSD(T)	96.1°



^{1}**1**

Dihedral C1-C2-C3-C4		Distance C1-C3	
MP2	0.0°	MP2	2.078 Å
BLYP	0.0°	BLYP	2.079 Å
B3LYP	0.0°	B3LYP	2.067 Å
CCSD(T)	0.0°	CCSD(T)	2.092 Å

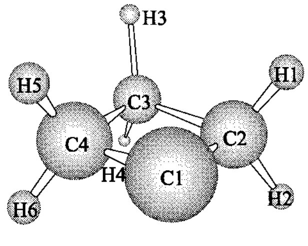
Dihedral H1-C2-C1-C4		Angle C4-C1-C2	
MP2	115.3°	MP2	97.6°
BLYP	115.4°	BLYP	98.5°
B3LYP	115.4°	B3LYP	98.3°
CCSD(T)	115.2°	CCSD(T)	97.3°



^{3}**1**

Dihedral C1-C2-C3-C4		Distance C1-C3	
MP2	0.0°	MP2	2.250 Å
BLYP	0.0°	BLYP	2.262 Å
B3LYP	0.0°	B3LYP	2.242 Å
CCSD(T)	0.0°	CCSD(T)	2.257 Å

Dihedral H1-C2-C1-C4		Angle C4-C1-C2	
MP2	121.5°	MP2	87.1°
BLYP	121.8°	BLYP	87.1°
B3LYP	121.6°	B3LYP	87.3°
CCSD(T)	120.8°	CCSD(T)	87.1°



TS^{1}1

Figure 1. Structures of ^{1}**1**, ^{3}**1**, and **TS^{1}1** obtained by optimization with CCSD(T)/DZP. Geometric parameters obtained using four optimization methods are included.

consistent basis set, cc-pVDZ,[22] was used for optimizations with BLYP, B3LYP, and MP2 and for single-point calculations on these geometries using CCSD(T). Double- and triple-ζ Dunning−Huzinaga basis sets, with added polarization functions suggested by Bartlett and co-workers (DZP and TZP),[23] were used for CCSD(T) optimizations and single-point calculations on DZP geometries, respectively. The geometries obtained with all methods were verified as minima or transition states by calculation of their harmonic vibrational frequencies. All calculations were performed using the Gaussian 94[24] and ACESII[25] computational packages. NBO analyses were performed using Weinhold's program[26] as implemented in Gaussian 94.

Results and Discussion

Structures and Bonding. The geometries of singlet and triplet cyclobutylidene (^{1}**1** and ^{3}**1**) obtained via optimization with CCSD(T)/DZP are shown in Figure 1, along with a transition-state structure for the ring inversion of the singlet (**TS^{1}1**). Figure 1 displays the C1−C2−C3−C4 dihedral angles, H1−C2−C1−C4 dihedral angles, C1−C3 distances, and carbene (C4−C1−C2) bond angles obtained at the MP2/cc-pVDZ, BLYP/cc-pVDZ, B3LYP/cc-pVDZ, and CCSD(T)/DZP levels of theory. Absolute energies and zero-point vibrational energies for ^{1}**1**, ^{3}**1**, and **TS^{1}1**, the barrier to ring inversion in singlet cyclobutylidene ($\Delta E_{\mathrm{inversion}}$), and the singlet−triplet en-

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Table 1. Absolute Energies,^{a} Zero-Point Vibrational Energies (ZPVE),^{b,c} Inversion Barriers in ^{1}1 ($\Delta E_{\mathrm{inversion}}$),^{b,d} and Singlet–Triplet Energy Gaps ($\Delta E_{\mathrm{S-T}}$)^{b,d,e}

method and basis set	^{1}**1** abs energy	^{1}**1** ZPVE	^{3}**1** abs energy	^{3}**1** ZPVE	**TS^{1}1** abs energy	**TS^{1}1** ZPVE	$\Delta E_{\mathrm{inversion}}$	$\Delta E_{\mathrm{S-T}}$
MP2/cc-pVDZ	−155.354 22	53.4	−155.346 01	53.8	−155.337 44	51.5	8.6	−5.6
BLYP/cc-pVDZ	−155.787 10	50.6	−155.777 84	51.0	−155.779 62	49.0	3.1	−6.2
B3LYP/cc-pVDZ	−155.879 30	52.4	−155.872 77	52.7	−155.872 77	50.8	2.5	−4.4
CCSD(T)/DZP	−155.492 62	53.4	−155.486 35	53.7	−155.485 96	52.4	3.1	−4.2
CCSD(T)/cc-pVDZ//MP2/cc-pVDZ	−155.419 61	53.4	−155.413 67	53.8	−155.412 08	51.5	2.8	−4.1
CCSD(T)/cc-pVDZ//BLYP/cc-pVDZ	−155.420 01	50.6	−155.413 60	51.0	−155.412 17	49.0	3.3	−4.4
CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ	−155.420 16	52.4	−155.413 43	52.7	−155.411 89	50.8	3.6	−4.5
CCSD(T)/TZP//CCSD(T)/DZP	−155.546 98	53.4	−155.538 01	53.7		52.4		−5.9

^{a} In Hartrees. ^{b} In kcal/mol. ^{c} Frequencies are unscaled. ^{d} Corrected for zero-point vibrational energy. ^{e} A negative value means the singlet is lower in energy than the triplet.

Table 2. Natural Bond Orbital Analysis^a

	^{1}**1**		**TS^{1}1**		^{3}**1**	
orbital	occupancy	π_{C1} deletion^b	occupancy	π_{C1} deletion^b	occupancy α spin	occupancy β spin
σ_{C1}	1.892		1.981		0.995	0.098
π_{C1}	0.315	−0.315	0.154	−0.154	0.917	0.052
$\sigma_{\mathrm{C1-C2}}$	1.978		1.986		0.994	0.994
$\sigma_{\mathrm{C1-C4}}$	1.978		1.986		0.994	0.994
$\sigma_{\mathrm{C2-C3}}$	1.870	+0.122	1.992		0.997	0.952
$\sigma_{\mathrm{C3-C4}}$	1.870	+0.122	1.992		0.997	0.952
$\sigma_{\mathrm{C2-H1}}$	1.978	+0.013	1.955	+0.038	0.997	0.983
$\sigma_{\mathrm{C2-H2}}$	1.991		1.955	+0.038	0.997	0.983
$\sigma_{\mathrm{C4-H5}}$	1.978	+0.013	1.955	+0.038	0.997	0.983
$\sigma_{\mathrm{C4-H6}}$	1.991		1.955	+0.038	0.997	0.983
$\sigma_{\mathrm{C3-H3}}$	1.947	+0.047	1.989		0.996	0.987
$\sigma_{\mathrm{C3-H4}}$	1.989		1.989		0.996	0.987

^{a} BLYP/6-31G* calculation at CCSD(T)/DZP geometries. ^{b} Occupancy change upon deletion of the π_{C1} orbital from the NBO analysis. Changes of <0.004 are not reported.

ergy gap ($\Delta E_{\mathrm{S-T}}$) are given in Table 1. Cartesian coordinates (MP2, BLYP, B3LYP, CCSD(T)/DZP) and harmonic vibrational frequencies (CCSD(T)/DZP) calculated for ^{1}**1**, ^{3}**1**, and **TS^{1}1** are available as Supporting Information.

The C_s structure for singlet cyclobutylidene (^{1}**1**) displays a carbene angle of 96.1°, a C1−C2−C3−C4 dihedral angle of 38.5°, and a C1−C3 distance of 1.84 Å at the CCSD(T)/DZP level of theory (Figure 1). Structures obtained via optimization at lower levels of theory tend to have somewhat larger carbene angles and smaller C1−C3 distances. Although the structures for ^{1}**1** obtained using various computational methods display reasonably good agreement, it is apparent that the results are not fully converged with respect to basis set size (see below). BLYP/6-31G* optimizations afforded a second structure with an energy 3.9 kcal/mol higher than that of singlet cyclobutylidene (^{1}**1**). This structure exhibited a less pronounced ring puckering (C1−C2−C3−C4 dihedral angle of 18.8°) and a longer C1−C3 distance (2.21 Å). At higher levels of theory, however, this structure does not exist as a minimum on the potential energy surface, in agreement with the results of Sulzbach et al.[13]

The C_{2v} structure for triplet cyclobutylidene (^{3}**1**) displays a carbene bond angle of 97.3° and a C1−C3 distance of 2.09 Å at the CCSD(T)/DZP level of theory (Figure 1). The structures for ^{3}**1** obtained using various computational methods display excellent agreement with one another.

The short distance between C1 and C3 in ^{1}**1** reflects a nonclassical structure with a bonding interaction between C1 and a pentacoordinate C3. NBO analysis of this carbene shows a p-type lone pair orbital at C1 (π_{C1}, 0.315 electron occupancy; Table 2) with an orientation that reveals electron density between C1 and C3 (Figure 2).

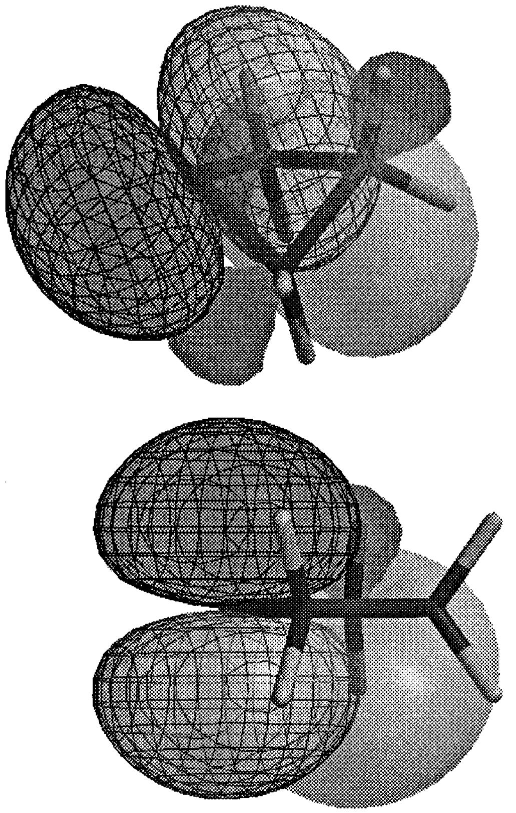


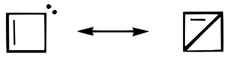
Figure 2. Natural bond orbital representations of the orbital interactions involving π_{C1}: (top) overlap with $\sigma_{\mathrm{C2-C3}}$ leading to transannular interaction in ^{1}**1** ($\sigma_{\mathrm{C3-C4}}$ omitted for clarity), (bottom) overlap with $\sigma_{\mathrm{C2-H1}}$ affording hyperconjugative stabilization in **TS^{1}1** (other vicinal C−H bonds omitted for clarity).

The electron density in π_{C1} arises from donation by the C2−C3 and C3−C4 bonding orbitals (0.244 e$^-$) and the three C−H bonding orbitals on the concave face of the bicyclobutane skeleton (0.073 e$^-$). This analysis is consistent with Schoeller's interpretation of the charge densities in the nonclassical carbene intermediate.[11] In all other respects, classical bonding patterns are observed, with a carbene lone pair orbital at C1 with sp$^{1.06}$ hybridization and an electron occupancy of 1.892. Singlet cyclobutylidene (^{1}**1**), according to CCSD(T)/DZP calculations, undergoes a conformational ring inversion process through a planar, C_{2v}-symmetric transition state (**TS^{1}1**, Figure 1) which lies only ca. 3 kcal/mol higher in energy than ^{1}**1** and has a C1−C3 distance of 2.26 Å. NBO analysis does not reveal a C1−C3 bonding interaction in **TS^{1}1**. Because the π_{C1} orbital in **TS^{1}1** is nearly perpendicular to its orientation in ^{1}**1**, this orbital is not suitably disposed to accept electron density from the C2−C3 and C3−C4 bonding orbitals. Rather, the π_{C1} orbital (0.154 e$^-$) in **TS^{1}1** accepts electron density from the four vicinal C−H bonding orbitals via a hyperconjugative interaction (Table 2). This transition-state structure is similar in geometry to triplet cyclobutylidene (^{3}**1**), although the carbene angle is somewhat smaller in **TS^{1}1** (87.1°) than in ^{3}**1** (97.3°). The NBO analysis points to an interesting bonding pattern for the triplet, with the carbene electrons occupying a p orbital and an sp$^{1.24}$ orbital at C1. The low occupancy of the singly-occupied π_{C1} orbital (α spin $=$ 0.917 e$^-$) arises because of donation to the four vicinal C−H antibonding orbitals. Nevertheless, the carbene center in ^{3}**1**, with a total electron occupancy of 2.062 e$^-$ at C1, is slightly electron *rich* because of the donation of electron density into the two vacant carbene orbitals of β spin. Interaction between the formally vacant σ_{C1} orbital (β spin $= 0.098$ e$^-$) and the occupied C2−C3 and C3−C4 bonding orbitals affords a very weak transannular bonding interaction. In addition, hyperconjugation between the formally vacant π_{C1} orbital (β spin $= 0.052$ e$^-$) and the occupied vicinal C−H bonding orbitals yields an additional increment of electron density at C1.

Singlet−Triplet Gap. The energies of singlet and triplet cyclobutylidene obtained by the various computational methods, along with singlet−triplet energy separations corrected for zero-point vibrational energy, are listed in Table 1. In general, the methods display good agreement in predicting that singlet cyclobutylidene (^{1}**1**) lies ca. 4−6 kcal/mol lower in energy than triplet cyclobutylidene (^{3}**1**). The highest level of theory (CCSD(T)/TZP//CCSD(T)/DZP) predicts a singlet−triplet energy gap of −5.9 kcal/mol in favor of the singlet ground state. The computational methods used in this study are single-configuration methods and do not account for nondynamic electron correlation (near-degeneracy effects). Consideration of the T1 diagnostic values obtained from the CCSD(T) calculations suggests that a single-configuration calculation is adequate for this system. The T1 diagnostic values for singlet cyclobutylidene (0.011) and triplet cyclobutylidene (0.012) both fall well below the commonly accepted threshold values that reveal the influence of multireference character (T1 > 0.02 and 0.04 for closed- and open-shell species, respectively).[27]

The singlet−triplet gap ($\Delta E_{S-T} = -5.9$ kcal/mol) for cyclobutylidene appears reasonable in comparison to the recent multireference configuration interaction (MRCI) result obtained for dimethylcarbene ($\Delta E_{S-T} = -1.6$ kcal/mol).[5b] The larger (more negative) value for cyclobutylidene may be attributed, at least in part, to the constraint on the carbene angle that is imposed by the ring. In dimethylcarbene, the carbene angle is predicted to be significantly larger in the triplet (130.4°) than in the singlet (110.3°).[5b] The enforced bond angle of ca. 100° in cyclobutylidene will therefore destabilize the triplet more than the singlet, leading to a larger singlet−triplet energy gap. A similar, but more pronounced, effect is predicted by Cramer and Worthington for cyclopropylidene ($\Delta E_{S-T} = -13.8$ kcal/mol, based on MCSCF and DFT calculations), a much more constrained system with carbene angles of 66.1° for the triplet and 58.6° for the singlet.[28] Not surprisingly, the earlier prediction of a triplet ground state for cyclobutylidene ($\Delta E_{S-T} = +8.9$ kcal/mol), obtained using semiempirical calculations,[11] appears to be seriously in error.

The ΔE_{S-T} values computed at the CCSD(T) level of theory display a modest basis set dependence. The energy gap obtained with the double-ζ basis ($\Delta E_{S-T} = -4.2$ kcal/mol) increases by 1.7 kcal/mol with the triple-ζ basis ($\Delta E_{S-T} = -5.9$ kcal/mol). Thus, the use of even larger basis sets might be expected to give slightly larger values for the singlet−triplet gap (at a given geometry). Of equal importance, however, will be the influence of a larger basis set on the optimized structure. It is interesting to note that the magnitude of the singlet−triplet gap in cyclobutylidene (**1**), as computed at the CCSD(T)/cc-pVDZ level, correlates with both the C1−C3 transannular distance and the H1−C2−C1−C4 dihedral angle: as the C1−C3 distance and the dihedral angle decrease, the singlet−triplet gap decreases (Figure 1, entries 5−7 in Table 1). In the different optimized geometries of ^{1}**1** shown in Figure 1, the deviation of the H1−C2−C1−C4 dihedral angle from 90° increases as the C1−C3 transannular distance decreases, thereby reducing the hyperconjugative stabilization afforded the carbene by the vicinal C−H bonds. Thus, the true optimum geometry for singlet cyclobutylidene (^{1}**1**) reflects a delicate balance between transannular bonding and hyperconjugative stabilization. As transannular bonding decreases, hyperconjugative stabilization increases, and vice versa. These opposing factors contribute to a low inversion barrier in singlet cyclobutylidene (^{1}**1**) ($\Delta E_{\text{inversion}} =$ ca. 3 kcal/mol, Table 1). This behavior contrasts sharply with that of the unsaturated analogue, singlet cyclobutenylidene (**5**), in



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which strong transannular bonding dominates. As the C1−C3 distance in **5** decreases, the singlet−triplet gap increases substantially because of the stabilization afforded the singlet state by transannular interaction between the carbene and the alkene.[14] This interaction leads to a large inversion barrier for singlet cyclobutenylidene (^{1}**5**) ($\Delta E_{\text{inversion}} = 21.3$ kcal/mol).[14d]

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(27) The T1 diagnostic provides an estimate of the adequacy of a single-reference calculation for a particular system. For details, see: (a) Lee, R. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199−207. (b) Taylor, P. R. In *Lecture Notes in Quantum Chemistry II*; Roos, B. O., Ed.; Springer-Verlag: Berlin, 1994; pp 125−202.

(28) Cramer, C. J.; Worthington, S. E. *J. Phys. Chem.* **1995**, *99*, 1462−1465.

Both the barrier to inversion ($\Delta E_{\mathrm{inversion}}$ = ca. 3 kcal/mol) and the singlet−triplet energy separation ($\Delta E_{\mathrm{S-T}} = -5.9$ kcal/mol) are smaller than the barriers to ring contraction and 1,2-hydrogen migration calculated by Sulzbach et al. (10.5 and 9.7 kcal/mol, respectively, at CCSD(T)/DZP).[13] Thus, the triplet state of cyclobutylidene will be thermally accessible under a variety of experimental conditions.

Summary

Computational investigations of singlet cyclobutylidene (^{1}**1**) predict a bicyclobutane-like structure (C_s symmetry) that includes a weak, transannular bonding interaction between the carbene carbon and the opposing CH_2 group, as first suggested by Schoeller.[11] Conformational ring inversion in ^{1}**1** occurs through a transition state of C_{2v} symmetry with an enthalpy barrier of approximately 3 kcal/mol. Stabilization afforded the singlet state by the transannular interaction appears to be largely offset by a loss of hyperconjugative stabilization from the adjacent C−H bonds. Triplet cyclobutylidene (^{3}**1**) exhibits a C_{2v} structure and conventional bonding. The triplet state lies 5.9 kcal/mol above the singlet ground state at the CCSD(T)/TZP//CCSD(T)/DZP level of theory. Comparison of the singlet−triplet energy gap of cyclobutylidene (−5.9 kcal/mol) with that of an acyclic analogue, dimethylcarbene (−1.6 kcal/mol), suggests that the triplet state in **1** is destabilized relative to the singlet because of the constraint imposed on the bond angle at the carbene center by inclusion in a four-membered ring. Nevertheless, the triplet state lies at lower energy than the transition states for 1,2-carbon or 1,2-hydrogen migration, implying that the chemistry of triplet cyclobutylidene might be revealed under the appropriate reaction conditions.

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Supporting Information Available: Tables giving the Cartesian coordinates for ^{1}**1**, ^{3}**1**, and **TS**^{1}**1** at the MP2/cc-pVDZ, BLYP/cc-pVDZ, B3LYP/cc-pVDZ, and CCSD(T)/DZP levels of theory and harmonic vibrational frequencies and intensities for ^{1}**1**, ^{3}**1**, and **TS**^{1}**1** at the CCSD(T)/DZP level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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