A Computational Investigation of the Stability of Cyclopropyl Carbenes

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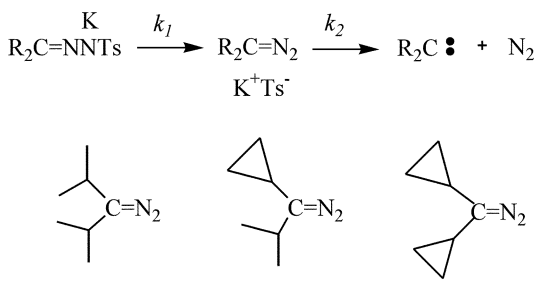
The conformations of dicyclopropyl, isopropyl cyclopropyl, and diisopropylcarbenes were optimized using density functional theory (B3LYP/6-31G(d)). We showed that the optimized geometries of carbenes with cyclopropyl groups are fully in accord with those expected for bisected W-shaped conformations, in which the effective hyperconjugation of a cyclopropyl group with singlet carbene can occur. The stabilization energies were evaluated at the B3LYP/6-311+G(3df, 2p)//B3LYP/6-31G(d) + ZPE level using an isodesmic equation. The relative stability of carbenes is in the order (c-Pr)$_2$C**:** > (i-Pr)(c-Pr)C**:** > (i-Pr)$_2$C**:**, and a cyclopropyl group stabilizes carbene more than an isopropyl group by nearly 9 kcal/mol. Energies for the decomposition of diazo compounds to carbenes increase in the order (c-Pr)$_2$ < (i-Pr)(c-Pr) < (i-Pr)$_2$ by ~9 kcal/mol each. From a singlet-triplet energy gap (E_{ST}) calculation, the singlet level is lower than the triplet level and the E_{ST} shows a trend similar to the stabilization energy calculations. For comparison, the optimized geometries and stabilization energies for the corresponding carbocations were also studied at the same level of calculation. The greater changes in geometries and the higher stabilization energies for carbocations compared to carbenes can explain the greater hyperconjugation effect.

Key Words : Carbene, B3LYP, Conformation, Stabilization energy

Introduction

The effect of a cyclopropyl group in stabilizing the adjacent carbocation,[1] free radical,[2] or carbene[3] has been studied over the past 30 years. Early reports[1g,1h] showed that tricyclopropylcarbinyl benzoate solvolyzes to give the corresponding carbocation more than 10^7 times faster than triisopropylcarbinyl benzoate. The cyclopropyl ring, which is known to have an antisymmetric Walsh orbital, is efficient at delocalizing an empty *p* orbital on an adjacent carbon.[4] The origin of the unusual delocalization of carbocations has been ascribed to the hyperconjugation effect due to the symmetrical bisected conformation of the cyclopropyl group. In term of molecular orbitals, hyperconjugation is the withdrawal of electrons from the bent symmetry orbital of the bisected cyclopropyl group into the vacant *p* orbital on the adjacent carbocation center.[5] The results of a structure analysis of hydroxydicyclopropylmethylium ion by the single-crystal X-ray diffraction technique completely agree with the structure expected for bisected cyclopropylcarbinyl-type cations.[6] Cyclopropyl groups are also effective at stabilizing free radical intermediates. The relative rate enhancement for the decomposition of the dialkyl azo substrates to their free radicals decreases in the order (c-Pr)$_3$ > (c-Pr)$_2$Me > c-PrMe$_2$ and Me$_3$, as with carbocations.[2a] It has also been shown that a carbene with two cyclopropyl groups formed via the consecutive two-step thermal decomposition of tosylhydrazone salt is 15 times more effective than that with two isopropyl groups at stabilizing a carbene (Eq. 1).[3] The rate constant for the second step (k_2) is important, since it governs the rate of carbene formation. This is supported by an experimental evidence that rate enhancement follows the order of dicyclopropyl, isopropyl cyclopropyl, and diisopropyl groups, and by the observed rate enhancements shown in Eq. 1. Based on a product analysis, it seems reasonable to consider the presence of singlet carbene: no evidence was observed for triplet-state hydrogen abstraction or γ-insertion processes.[7] In addition, it has also been shown that a cyclopropyl group significantly stabilizes a singlet carbene via homoconjugative interaction. Although previous experimental kinetic results for the cyclopropyl group show unusually efficient conjugation, there are still some questions regarding the nature of the conformation with a cyclopropyl substituent. There is little theoretical support for the unusual stabilization of carbocation, free radical, or carbenes by cyclopropyl groups.



(1)

k_2^{rel} 1 5.8 15.4

Previous theoretical studies of the geometry of cyclopropylcarbenes mainly focused on the optimized conformation.[8] The theoretical (MP2/6-31G*) equilibrium geometry for dicyclopropyl carbene clearly shows that the expected W-shaped bisected conformation is favored over the sickle-shaped bisected conformation.[8a] However, it is not clear whether any significant stabilization of dicyclopropylcarbene compared to other carbenes can satisfactorily explain previous experimental results. In particular, the observed kinetic data for carbenes **1-3** appear to require further theoretical calculations. The goal of our investigation was to determine the effect of a cyclopropyl group on the rate enhancement and stability with respect to the optimized conformation by theoretical calculations.[9]

Results and Discussion

The lowest-energy conformation of dicyclopropylcarbene **3** is the W-shaped conformation (Figure 1). The sickle-shaped conformation for **3** is 4.1 kcal/mol higher in energy at the B3LYP/6-31G(d) level,[10] correcting for the zero-point energy differences.[11] It is known that density functional methods, and BLYP in particular, can provide reliable geometry optimizations and relative energies for carbene systems.[12] Table 1 lists the calculated and relative energies of diisopropyl, cyclopropylisopropyl, and dicyclopropyl carbenes by RHF/6-31G(d) and B3LYP/6-31G(d) calculations. The structures of carbenes are shown in Figure 1.

The optimized geometry for **3** is the W-shape as well as bisected conformations:[13] the dihedral angles are $\varphi_{1,2,8,11} = 148.5^o$ and $\varphi_{1,2,8,12} = -148.5^o$. Even though the sickle-shaped dicyclopropyl carbene adopts a bisected geometry, the W-shape represents an energy minimum on the B3LYP/6-31G(d) potential surface and therefore may be considered the most stable geometry. In addition, the W-shape preference can be explained in terms of hyperconjugation effects: the empty *p* orbital on the singlet carbene is expected to efficiently participate in delocalization with the cyclopropyl ring located in the W-shape.

The calculated geometry for cyclopropylisopropylcarbene **2** closely resembles the W-shaped bisected conformation: $\varphi_{1,2,6,13} = 150.3^o$ and $\varphi_{1,2,6,14} = -146.7^o$. The isopropyl group is twisted slightly from the bisected conformation by 18.7^o ($\varphi_{H(4),1,2,6,}$). On the other hand, in the case of diisopropylcarbene **1**, one isopropyl group is twisted from the W-shape by 60^o. Thus, the energy difference between the W- and sickle-shapes is smaller to 1.9 kcal/mol.

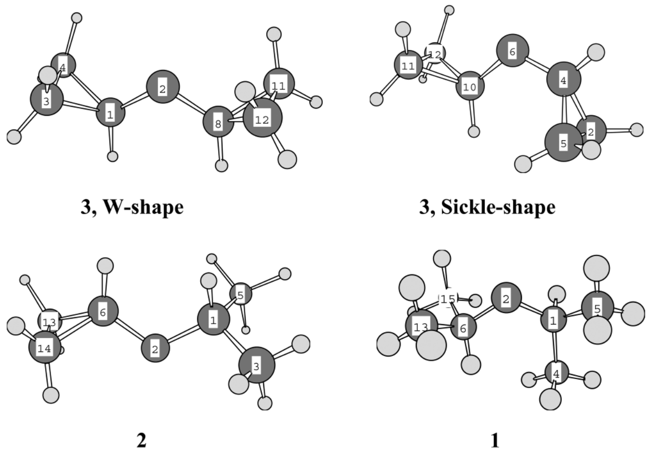


Figure 1. Optimized geometries for singlet carbenes **1**, **2**, and **3** at the B3LYP/6-31G(d) level.

Table 1. Calculated Energies (au) and Relative Energies (kcal/mol, in Parentheses) of carbenes **1-3** by RHF/6-31G(d) and B3LYP/6-31G(d) Methods

Carbenes 1-3	RHF/6-31G(d)	B3LYP/6-31G(d)[a]	
	W-Shape	W-Shape	Sickel-Shape
(*i*-Pr)$_2$C: **1**	-273.105128	-274.862455 (0)	-274.859447 (1.9)
(*i*-Pr)(*c*-Pr)C: **2**	-271.921586	-273.658957 (0)	-273.651328 (4.8)
(*c*-Pr)$_2$C: **3**	-270.731804	-272.448714 (0)	-272.442141 (4.1)

[a]Energies of the individual species were calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level, and were corrected for zero-point energy differences at the B3LYP/6-31G(d) level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1-6**

Carbenes	Length (Å)	Angle (deg)	Cations	Length (Å)	Angle (deg)
3			**6**		
:C-(*c*-Pr)	C1-C2 = 1.438	C1-C2-C8 = 114.0	$^+$C-(*c*-Pr)	C1-C2 = 1.406	C1-C2-C8 = 125.5
(*c*-Pr)	C1-C4 = 1.553	C3-C1-C4 = 56.4	(*c*-Pr)	C1-C4 = 1.584	C3-C1-C4 = 54.6
	C3-C4 = 1.469	C1-C3-C4 = 61.8		C3-C4 = 1.451	C1-C3-C4 = 62.7
2			**5**		
:C-(*c*-Pr)	C2-C6 = 1.428	C1-C2-C6 = 114.4	$^+$C-(*c*-Pr)	C2-C3 = 1.383	C3-C2-C4 = 126.3
(*c*-Pr)	C6-C14 = 1.558	C13-C6-C14 = 55.8	(*c*-Pr)	C3-C8 = 1.616	C8-C3-C9 = 52.8
	C13-C14 = 1.434	C6-C13-C14 = 61.8		C8-C9 = 1.436	C3-C8-C9 = 63.6
(*i*-Pr)	C1-C2 = 1.495	C5-C1-C3 = 110.3	(*i*-Pr)	C2-C4 = 1.472	C5-C4-C6 = 110.5
	C1-C3 = 1.537			C4-C5 = 1.557	
1			**4**		
:C-(*i*-Pr)	C2-C1 = 1.488	C1-C2-C6 = 117.2	$^+$C-(*i*-Pr)	C8-C2 = 1.445	C2-C8-C10 = 126.9
	C2-C6 = 1.489			C8-C10 = 1.444	
(*i*-Pr)	C1-C5 = 1.543	C5-C1-C4 = 111.6	(*i*-Pr)	C2-C1 = 1.534	C1-C2-C7 = 110.8
	C1-C4 = 1.544			C2-C7 = 1.605	
	C6-C13 = 1.540	C13-C6-C15 = 109.8		C10-C16 = 1.534	C14-C10-C16 = 110.8
	C6-C15 = 1.559			C10-C14 = 1.604	

Optimized geometry of the individual species calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level + ZPE at B3LYP/6-31G(d).

It is important to examine the bond lengths and bond angles for these carbenes. We can calculate both substantial shortening of the C(2)-cyclopropyl ring bonds and lengthening of two vicinal bonds in the cyclopropyl ring for the optimized geometry. These changes result from the effective hyperconjugation of a cyclopropyl group with singlet carbene. The bond lengths between C(2) and rings are the same distance 1.438 Å in carbene **3** and are slightly shorter (1.428 Å) in carbene **2** (Table 2 and Figure 1). Meanwhile, the bond distance between the C(2)-(*i*-Pr) group in carbene **2** is elongated to 1.495 Å compared to 1.488 Å for the corresponding bond length in carbene **1** (the other bond length C2-C6 in **1** is 1.489 Å). The vicinal bonds of the two cyclopropyl groups in **3** have the same internuclear distance of 1.553 Å. This is 0.045 Å longer than that found in cyclopropane at the B3LYP/6-31G(d) level.[14] Furthermore, the two vicinal bonds of the cyclopropane ring in carbene **2** are longer, at 1.558 Å and 1.568 Å. Meanwhile, the distal bonds in the cyclopropyl rings in carbenes **3** and **2** are shorter, at 1.469 Å and 1.434 Å, respectively. In the case of carbene **2**, the average elongation (0.005 Å) of the two vicinal bonds compared to carbene **3** is matched by a decrease (0.010 Å) in the C(2)-ring bond distance. The bond angles for ∠3,1,4 in **3** and for ∠13,6,14 in **2** are 56.4° and 55.8° whereas for ∠1,3,4 in **3** and ∠6,13,14 in **2**, they are the same (61.8°). The bond angles at the carbene center for **2** and **3** are similar (114.0° and 114.4°), while for **1** this value is 117.2°. It is worth noting that the bond angle at the carbene center is affected by steric hindrance: 125.5° for singlet di-*tert*-butylcarbene and 110.8° for singlet dimethylcarbene at the B3LYP/6-31G(d) level.[15] Thus, isopropyl groups, which are more sterically demanding than cyclopropyl groups, increase the bond angles at the carbene center.

Singlet carbenes are isoelectronic with carbocations. Thus, we would expect that effects that stabilized carbocations would also stabilize singlet carbenes. It would be interesting to compare the optimized geometries for the corresponding cyclopropylcarbinyl cations at the same B3LYP/6-31G(d) level (Figure 2).

The bisected W-conformation of dicyclopropylcarbinyl cation **6** has the lowest energy, as expected by Olah.[1i] The sickle-shaped conformations for **6** and **5** are 2.5 and 2.2 kcal/mol higher in energy at the same level of calculation. Based on a comparison of the geometry of carbene **3** with that of **6**, the bond length between the α-carbon and cyclopropyl group is shortened to 1.406 Å (0.032 Å shorter than in **3**) and the two vicinal bonds are lengthened to 1.584 Å (0.031 Å longer than in **3**), as shown in Table 2. The isopropyl cyclopropylcarbinyl cation **5** also has a W-shaped conformation in which both the isopropyl and cyclopropyl groups are located at the bisected geometry without distortion ($\varphi_{3,2,4,5}$ = -119.7° and $\varphi_{3,2,4,6}$ = +119.7°). Meanwhile, in the case of diisopropylcarbinyl cation **4**, the two isopropyl groups are twisted from the W-shape bisected conformation by +36.18° and -36.29°, respectively. The bond angles at the carbocation center for **6**, **5**, and **4** are 125.5°, 126.3°, and 126.8°, whereas, the corresponding angles in sickle-shaped **6** and sickle-shaped **5** are 128.2°, and 129.4°. The bond angles of the sickle-shape are 2.7-3.9° wider than those of the W shape. Significant bond shortening between the carbocation and cyclopropyl ring (1.383 Å) and bond lengthening between the two vicinal bonds (1.616 Å) is seen in **6**. Consequently, greater changes are seen in the bond lengths in carbocations compared to carbenes. Considering these changes, it is understandable that the rate constant for a carbocation with two dicyclopropyl rings (× 10^7) relative to that with two isopropyl groups is much greater than that for a carbene (× 14). Overall, with regard to the optimized geometries for carbenes and carbocations, a cyclopropyl group is more effective at stabilizing an empty p orbital on an adjacent carbon than an isopropyl group. As shown in Figure 3 and Table 3, the bond lengths between cyclopropyl groups and C2 for dicyclopropyl methane **9** and cyclopropylisopropylmethane **8** are the same at 1.519 Å, which is 0.081 Å longer than that of carbene **3** and 0.113 Å longer than that

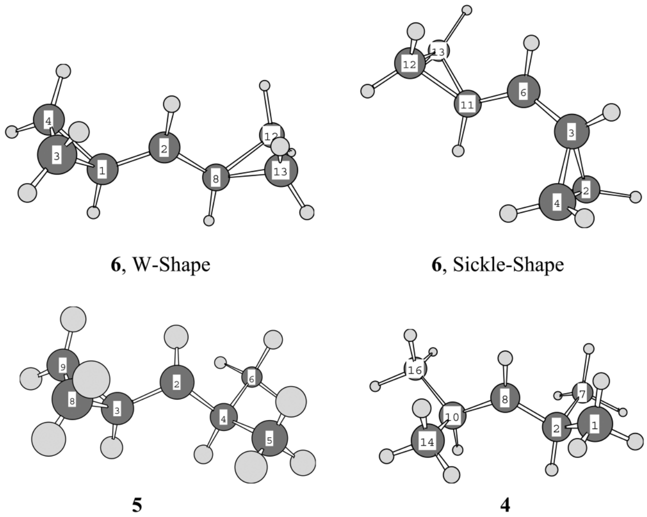


Figure 2. Optimized geometries for carbocations **4**, **5**, and **6** at the B3LYP/6-31G(d) level.

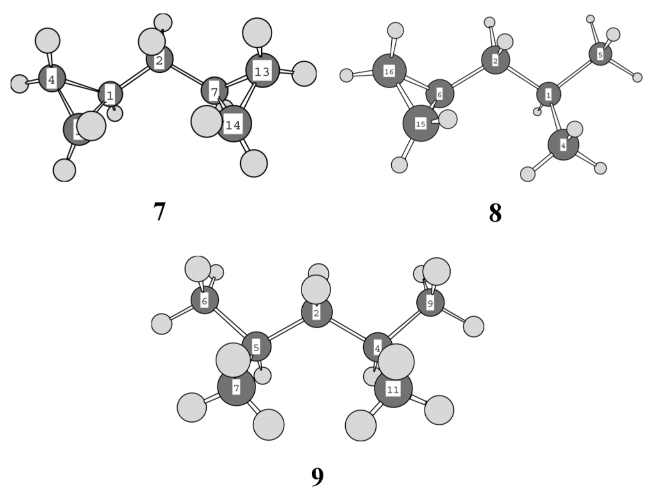


Figure 3. Optimized geometries for alkanes **7**, **8**, and **9** at the B3LYP/6-31G(d) level.

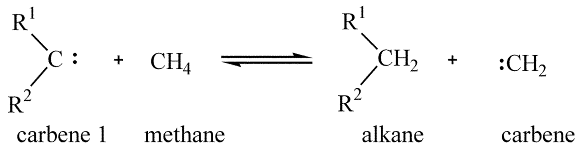
Table 3. Selected Bond Lengths (Å) and Angles (deg) for **7-9**

	7	**8**	**9**
Length (Å)	C2-C5 = C2-C4 = 1.548	C2-C6 = 1.519 C2-C1 = 1.543	C2-C1 = C2-C7 = 1.519
	C5-C6 = C4-C9 = 1.540	C6-C16 = C15-C16 = 1.510	C1-C4 = C7-C13 = 1.509
	C5-C7 = C4-C11 = 1.537	C6-C15 = 1.511	C1-C3 = C7-C14 = 1.509
		C1-C5 = C1-C4 = 1.536	C3-C4 = C13-C14 = 1.511
Angle (deg)	C5-C2-C4 = 118.3	C1-C2-C6 = 115.1	C1-C2-C7 = 113.6
	C6-C5-C7 = 109.4	C15-C6-C16 = 60.0	C4-C1-C3 = C13-C7-C14 = 60.1
	C9-C4-C11 = 109.4	C6-C15-C16 = 60.0	C1-C4-C3 = C7-C14-C13 = 60.0
		C6-C16-C15 = 60.1	C1-C3-C4 = C7-C13-C14 = 59.9

Optimized geometry of the individual species calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level + ZPE at B3LYP/6-31G(d).

of carbocation **6**. Furthermore, the bond lengths and angles of cyclopropyl groups for **9** and **8** are not significantly different than those of cyclopropane,[14] even though all of the cyclopropyl groups are located in the bisected conformation; for example, the dihedral angle for H (on C2)-C2-C1-H (on C1) is 180.0°. Consequently, the optimized geometry of the cyclopropyl group is influenced by the electronic environment of the adjacent carbon atom.

To predict the relative stabilities, isodesmic equations such as that shown in Eq. 2 were calculated at both the B3LYP/6-31G(d) and B3LYP/6-311+G(3df,2p) levels, while correcting for zero-point energy differences. The B3LYP/6-311+G(3df,2p) energies will be used in our discussion.



(2)

The stabilization energies for singlet carbenes **1**, **2**, and **3** are 26.81, 36.44, and 45.10 kcal/mol (Table 4). A cyclopropyl group can stabilize carbene more than an isopropyl group by 9.63 kcal/mol: thus, two cyclopropyl groups provide nearly twice (18.29 kcal/mol) the effective stabilization.

Although the calculated stabilization energies for carbenes are in reasonable agreement with experimental values, they need to be evaluated by calculating the isodesmic equation for carbocation. As expected, the results provide a clear explanation for the additional stability of carbocations compared to carbenes. The stabilization energies are 81.95 kcal/mol for diisopropylcarbinyl cation **6**, 92.30 kcal/mol for cyclopropylisopropylcarbinyl cation **5**, and 104.16 kcal/mol for dicyclopropylcarbinyl cation **4** (Table 5). A cyclopropyl group can stabilize carbocation more than an isopropyl group by 10.35 kcal/mol, and two cyclopropyl groups provide more than twice (22.21 kcal/mol) the effective

Table 4. Stabilization Energies of carbenes 1, 2, and 3 calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) and B3LYP/6-31G(d)//B3LYP/6-31G(d) level[a]

R^1/R^2	carbene1		alkane		**SE**[b]	
	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)
i-Pr/*i*-Pr	-274.862455	-274.960663	-276.179989	-276.275731	27.39	26.81
i-Pr/*c*-Pr	-273.658957	-273.756139	-274.960862	-275.055817	37.20	36.44
c-Pr/*c*-Pr	-272.448714	-272.545424	-273.736688	-273.831353	45.94	45.10

[a]Energies were corrected for zero-point energy from B3LYP/6-31G(d) frequency calculations on B3LYP/6-31G(d) optimized geometries. [b]The stabilization energy SE=$E_{alkane}+E_{carbene}-E_{carbene1}-E_{methane}$ in kcal/mol. Energies for methane at the B3LYP/6-311+G(3df,2p)+ZPE and B3LYP/6-31G(d)+ZPE are -40.491550 and -40.473179. Energies for methylene(carbene) at the B3LYP/6-311+G3df,2p) +ZPE and B3LYP/6-31G(d) +ZPE are -39.133754 and -39.111990.

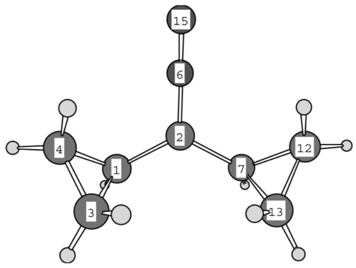
Table 5. Stabilization Energy of carbocations **4**, **5**, and **6** calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) and B3LYP/6-31G(d)//B3LYP/6-31G(d) level[a]

$$R^1R^2\overset{+}{C}H + CH_4 \rightleftharpoons R^1R^2CH_2 + {}^{+}CH_3$$

carbocation1 methane alkane carbocation

R^1/R^2	Carbocation1		alkane		**SE**[b]	
	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)
i-Pr/*i*-Pr	-275.287915	-275.378530	-276.179989	-276.275731	82.63	81.95
i-Pr/*c*-Pr	-274.088532	-274.173556	-274.960862	-275.055817	95.02	92.30
c-Pr/*c*-Pr	-272.882339	-272.969535	-273.736688	-273.831353	106.30	104.16

[a]Energy was corrected for zero-point energy from B3LYP/6-31G(d) frequency calculations on B3LYP/6-31G(d) optimized geometries. [b]The stabilization energy SE=$E_{alkane}+E_{carbocation}-E_{carbocation1}-E_{methane}$ in kcal/mol. Energies for methyl carbocation at the B3LYP/6-311+G(3df,2p)+ZPE and B3LYP/6-31G(d)+ZPE are -39.463747 and -39.449427. Energies for methane at the B3LYP/6-311+G(3df,2p) +ZPE and B3LYP/6-31G(d) +ZPE are -40.491550 and -40.473179.



N15-N6=1.150Δ N6-C2= 1.300Δ C2-C1=1.492Δ
C1-C4=1.510Δ C1-C3=1.519Δ C3-C4=1.505Δ
∠C1,C3,C4=59.9° ∠C4,C1,C3=59.6° ∠C1,C4,C3=60.5°
$\varphi_{6,2,1,5}$=112.2°

Figure 4. Optimized geometries for the dicyclopropyl diazo compound at the B3LYP/6-31G(d) level.

stabilization. The higher stabilization energies for carbocations **4-6** compared to carbenes **1-3** can explain the greater hyperconjugation effects: 1) shortening of the C^+-ring bond and lengthening of the vicinal bonds in the ring, 2) in particular, in the case of isopropylcyclopropyl species, **5** displays the bisected W-geometry without distortion, and thus gives an unusually higher SE than **2**, and 3) the carbocation angles (125.0° for 1,2,8 in **4** and 126.3° for 3,2,4 in **5**) are greater than the carbene angles by ~10°.

To evaluate the factors that stabilize carbenes, we computed the stabilization energies of diazo compounds for dicyclopropyl, isopropyl cyclopropyl, and dicyclopropyl groups (Table 6). The calculated stabilization energies revealed that the cyclopropyl group does not participate in the stabilization of diazo compounds. In addition, the optimized geometry for the cyclopropyl group in diazo compounds is very similar to that for cyclopropane (Figure 3), which is an indication of no hyperconjugation effect. This also suggests that for the thermal decomposition of diazo compounds (Eq. 1), the stability of singlet carbene intermediates must govern the relative rate and products.

Energies for the decomposition of diazo compounds are shown in Table 7 for the same theoretical calculations. The positive E for **1-3** can be understood in terms of endothermic reactions. The relative E increases in the order $(c\text{-Cy})_2$ < (i-Pr)(c-Cy) < $(i\text{-Pr})_2$, and the stabilization energies of diazo compounds are similar, as shown in Table 6, which means that the rate constant k_2 (in Eq. 1) is mainly influenced by the effective stabilization of singlet carbene by a cyclopropyl group.

Based on previous experimental results, we propose the existence of singlet-state carbene **1-3**. Even though direct experimental evidence demonstrates the existence of singlet-state carbene, it will be further considered in a computational study on the singlet-triplet energy gap.[16] The E_{ST} values are 17.56, 10.38 and 0.46 kcal/mol for **3**, **2**, and **1**, respectively, and the positive numbers correspond to a singlet level below the triplet state (Table 8). The E_{ST} shows a trend similar to the stabilization energy calculations: the greater the stabilization of singlet carbenes, the greater the calculated gap. Based on both the stabilization energy and E_{ST}, it can be assumed that two cyclopropyl groups stabilize

Table 6. Stabilization Energies of diazo compounds calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) and B3LYP/6-31G(d)//B3LYP/6-31G(d) level[a]

$$\underset{\text{diazoalkane}}{R^1R^2CN_2} + \underset{\text{methane}}{CH_4} \rightleftharpoons \underset{\text{alkane}}{R^1R^2CH_2} + \underset{\text{diazomethane}}{CH_2N_2}$$

R¹/R²	diazoalkane		Alkane		SE[b]	
	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)
i-Pr/*i*-Pr	-384.428584	-384.560904	-276.179989	-276.275731	+8.69	+6.89
i-Pr/*c*-Pr	-383.206643	-383.338413	-274.960862	-275.055817	+6.93	+5.28
c-Pr/*c*-Pr	-381.983675	-382.114643	-273.736688	-273.831353	+7.68	+5.71

[a]Energies were corrected for zero-point energy from B3LYP/6-31G(d) frequency calculations on B3LYP/6-31G(d) optimized geometries. [b]The stabilization energy $SE=E_{alkane}+E_{diazomethane}-E_{diazoalkane}-E_{methane}$ in kcal/mol. Energies for diazomethane at the B3LYP/6-311+G(3df,2p) +ZPE and B3LYP/6-31G(d) +ZPE are -148.765740 and -148.707922. Energies for methane at the B3LYP/6-311+G(3df,2p) +ZPE and B3LYP/6-31G(d) +ZPE are -40.491550 and -40.473179.

Table 7. Calculated Reaction Energies for the decomposition of azo compounds to their corresponding carbenes **1-3** using a B3LYP theory[a]

$$R^1R^2C{=}N_2 \xrightarrow{k_2} R^1R^2C\!: + N_2$$

R¹/R²	Azo		Carbene		E[b]	
	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)
i-Pr/*i*-Pr	-384.428584	-384.560904	-274.862455	-274.960663	+29.8	+24.4
i-Pr/*c*-Pr	-383.206643	-383.338413	-273.658957	-273.756139	+18.2	+13.2
c-Pr/*c*-Pr	-381.983675	-382.114643	-272.448714	-272.545424	+10.2	+5.0

[a]Corrected for the zero-point energies. [b]$E=E_{carbene}+E_{nitrogen}-E_{azo}$ in kcal/mol. Energies for nitrogen at the B3LYP/6-311+G(3df,2p) + ZPE and B3LYP/6-31G(d) + ZPE are -109.561326 and -109.518642.

Table 8. Singlet-Triplet Energy Differences for carbenes calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) and B3LYP/6-31G(d)//B3LYP/6-31G(d) level

carbene	E_T		E_S		E_{ST}	
	6-31G(d)	6-311+G(3df,2p)	6-31G(d)	6-311+G(3df,2p)	6-31G(d)[a]	6-311+G(3df,2p)[b]
i-Pr/*i*-Pr	-274.868101	-274.962613	-274.862455	-274.960663	0.55	0.46
i-Pr/*c*-Pr	-273.648463	-273.742270	-273.658957	-273.756139	10.68	10.38
c-Pr/*c*-Pr	-272.427103	-272.520115	-272.448714	-272.545424	17.65	17.56

[a] $E_{ST} = E_T - E_S$ + ZPE + 4.09 (correction factor for the overestimation of methylene is 4.09 kcal/mol at the B3LYP/6-31G*//B3LYP/6-31G(d) level). [b] $E_{ST} = E_T - E_S$ + ZPE + 1.68 (correction factor for the overestimation of methylene is 1.68 kcal/mol at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level). E_T: the unrestricted value.

Table 9. Calculated Dipole Moments (debye) of Singlet Carbenes **1-3**

carbene	RHF		B3LYP			QCISD
	STO-3G[a]	6-31G*	STO-3G[a]	6-31G*	6-31G*[b]	6-31G*[a]
i-Pr/*i*-Pr	1.40	1.71	1.48	1.65	1.75	1.66
i-Pr/*c*-Pr	1.43	1.73	1.57	1.79	2.53	1.75
c-Pr/*c*-Pr	1.07	1.35	1.17	1.26	2.17	1.27

[a]B3LYP/6-31G* optimized geometry used. QCISD=Quadratic Configuration Interaction with Singles & Doubles. [b]Calculations for triplet carbenes.

carbene nearly twice as much as one cyclopropyl group.

To gain more insight into the electronic structure of carbenes, the dipole moments were determined at the different levels of theory. The values are given in Table 9, and they show a remarkable difference depending upon the basis set used. Use of the 6-31G(d) basis set increases the dipole moment by ~10 % compared to the STO-3G basis set at the B3LYP level. The single-point energy calculation of the quadratic configuration interaction (QCI) theory[17] with the 6-31G(d) basis set was performed using B3LYP/6-31G(d) optimized geometries. This was done because it is known that QCI methods are reliable for calculating dipole moments.[18] The QCISD dipole moment is very similar to the B3LYP value at the same level with the 6-31G(d) basis set. The dipole moments calculated for carbenes **1-3** followed the order $(c\text{-Pr})_2 < (i\text{-Pr})_2 < (i\text{-Pr})(c\text{-Pr})$, independent of the basis set used. The slightly larger dipole moment for carbene **2** compared to **1** may indicate that it is a relatively polar molecule. This view can generally be explained on the basis of a significant contribution from two different substituents in which asymmetrical hyperconjugation effects are transferred to the empty *p* orbital. It is worth noting that the B3LYP dipole moment for the triplet carbene is greater than that for the singlet carbene by 0.91 Å for **3**, 0.74 Å for **2** and 0.10 Å for **1**. This trend is consistent with the view that the cyclopropyl group stabilizes singlet carbenes more than the isopropyl group.

Conclusion

The fact that diazo dicyclopropyl compounds decompose faster than the corresponding diazo compounds to carbene clearly shows that a cyclopropyl group is a better participating group than an isopropyl group. The effective hyperconjugation of a cyclopropyl group in the bisected W-shaped conformation may facilitate this reaction. The optimized geometry of singlet dicyclopropylcarbene **3** is fully consistent with that expected for the bisected W-shaped conformation at the B3LYP/6-31G(d) level. The cyclopropyl groups in carbenes **3** and **2** help stabilize the empty p orbital by hyperconjugation and in each case the elongation of the two vicinal bonds is matched by a corresponding decrease in the distal bond of twice the magnitude. The bond between the carbenic center and cyclopropyl ring is also calculated to shorten. When the optimized geometries of diazo compounds of dicyclopropyl and dicyclopropyl methane become available, it will be interesting to see whether the bond lengths and angles of cyclopropyl groups remain similar to those of cyclopropane itself. The changes seen in carbocations are similar but substantially greater than those in carbenes, and this reflected by the fact that the rate constants for carbocations are greater than those for the corresponding carbenes. The computed stabilization energy for the cyclopropyl group of isopropyl cyclopropylcarbene **2** is 9.63 kcal/mol larger than that for the isopropyl group of diisopropylcarbene **1**. Thus, the stabilization energy of dicyclopropylcarbene **3** is nearly twice as large as that of **1**. Very similar trends were computed for the stabilization energies of the isoelectronic dicyclopropyl, cyclopropylisopropyl, and dicyclopropyl carbocations, but these were also greater than those of the corresponding carbenes. The singlet-triplet gap E_{ST} values of carbenes **1**, **2**, and **3** are 0.46, 10.38, and 17.56 kcal/mol, respectively, in favor of the singlet: the stabilization by cyclopropyl groups for singlet carbene increases the energy gap. These calculated results provide a possible explanation for the rate constant and stability of cyclopropylcarbenes.

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16. The experimental Singlet-Triplet (S-T) splitting of methylene is 9.05 ± 0.06 kcal/mol, while at the B3LYP/6-31G* level the S-T for methylene is 13.56 kcal/mol, 4.09 kcal/mol more than the experimental result. Thus, the computed S-T splittings of carbenes **1**-**3** in Table 5 are corrected by 4.09 kcal/mol to account for the overestimation. This analysis followed the approach used by Sulzbach *et al.* See: Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. v. R.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1996**, *118*, 9908.
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