

Hybrid density functional theory study of low reactivity of imidazol-2-ylidene toward insertion and addition reactions

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A hybrid functional theory study was performed with the target being to evaluate reasons for the exceptional stability of imidazol-2-ylidene. Computed structural properties for this carbene were compared with its chlorinated analog, as well as with unsaturated analogues for both of these carbenes. The aromaticity was evaluated through the enthalpy of hydrogenation of the carbenes and their reactivity through activation barriers for the hydrogen insertion and ethylene addition reactions. Activation barriers for saturated carbenes were compared with the activation barriers for unsaturated carbenes to assess their aromatic character and the influence of electron-withdrawing substituents on their reactivity.

Introduction

Carbenes are very important reactive intermediates in organic syntheses.¹ They have very short lifetimes. In many cases, carbenes have been isolated by matrix isolation at low temperatures. First in the series of carbenes, CH₂, methylene as all other carbenes can exist as a singlet. One of the methods to distinguish the singlet from triplet starts with the Skell² approach, which is based on one evaluation of the carbene cycloadduct to unsaturated compounds. For instance, if the singlet species adds to *cis*-but-2-ene, the resulting cyclopropane should be the *cis* isomer, since the formation of both CC bonds should be simultaneous and the geometry is preserved. In the case of the triplet carbene addition to *cis*-but-2-ene the product is *trans*-dimethylcyclopropane. The CH₂ carbene is usually prepared as a singlet, although spectroscopic and some computational studies determine that the triplet CH₂ carbene is more stable than the singlet CH₂ carbene. The evaluated energy difference is around 8–10 kcal mol⁻¹.^{3,4} In fact, we have used the triplet–singlet energy difference for fluorinated carbenes to determine their stability–reactivity behavior.⁴

One of the carbenes shows exceptionally high stability and it was able to be characterized with conventional spectroscopic techniques, including X-ray structural analysis. These compounds are imidazol-2-ylidenes.⁵ These carbenes are stable at room temperature under a nitrogen atmosphere for a long time, but they are sensitive to moisture and air. There have been many computational studies with regard to their high stabilities.⁶ A very large singlet–triplet gap (~80 kcal mol⁻¹) along with π -conjugation and steric effects were used to explain why these carbenes are exceptionally stable. Considering the geometric properties of substituted imidazol-2-ylidenes, the steric effect should not be an important factor for their stabilization. Here we would like to perform further computational studies of this interesting molecular system through the evaluation of its aromatic character and activation barrier to the addition to hydrogen and acetylene. The hybrid density functional theory method was selected because in many cases it has been demonstrated that a reliable assessment of the reaction barriers,⁷ as well as aromaticity⁸ can be performed using this method.

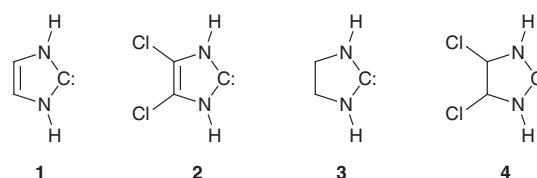
Computational methods

All computational studies were performed with the hybrid B3LYP⁹ density functional theory method with the 6-31G(d,p)

basis set, as implemented in the GAUSSIAN94¹⁰ computational package. For a full explanation of the hybrid density functional theory method and selected basis sets, see ref. 11. The transition state structures are optimized by the procedure explained elsewhere.¹² All stationary points were characterized by performing vibrational analysis and all positive frequencies are obtained for the minimum on the potential energy surface, while the transition state structures have one imaginary frequency. When analyzed, this imaginary frequency had atomic motions that connect reactants and products on the potential energy surface.

Results and discussion

To determine the influence of electron-withdrawing substituents, as well as the presence of double bonds on the carbene stability, derivatives of imidazol-2-ylidene presented in Scheme 1 were selected for this study. One can argue that the singlet



Scheme 1 Structures of carbenes derived from imidazol-2-ylidenes.

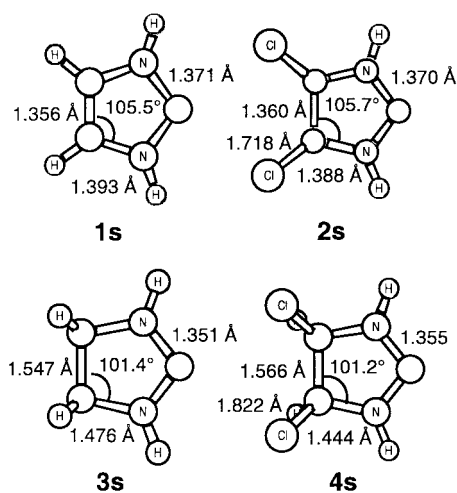
carbene **1** should be aromatic and, therefore, more stable than the saturated carbene **3**. One can easily envision its aromaticity if the two electrons of the singlet carbene **1** are placed in the plane of the molecule and two nitrogen electron pairs are added to the two electrons of the π -bond, which results in the six electron cyclic system required by the Hückel rule for aromaticity. This is also present for carbene **2** but of course, not in their saturated analogues **3** and **4** (Scheme 1). It is well established that by putting electron-withdrawing substituents on the CH₂ carbene, a higher stability of the carbene can be achieved.¹³ This might also be true for imidazol-2-ylidene, therefore the reactivity of **2** will be compared with the reactivity of the other three carbenes in Scheme 1 in the search for the chlorine stabilization effect of the imidazole carbene.

It is well established that the structural properties of cyclic conjugated compounds can be used to determine the compound's aromatic character.¹⁴ For chemical systems built only

Table 1 Computed energies of hydrogenation for two singlet unsaturated carbenes

	$E(\text{unsaturated})$	$E(\text{saturated})$	ΔH
Ethene	-78.593806	-79.838739	41.7
(0 K)	-78.542675	-79.763801	33.1
<i>cis</i> -1,2-Dichloroethane	-997.781672	-999.024175	40.1
(0 K)	-997.747452	-998.965820	31.4
1s-3s	-226.177074	-227.383745	17.7
(0 K)	-226.105732	-227.290261	10.1
2s-4s	-1145.353863	-1146.570512	23.9
(0 K)	-1145.301231	-1146.495233	16.1
H ₂	-1.178539		
H ₂ (0 K)	-1.168366		

(0 K) = Sum of electronic and zero-point energies; $E(\text{unsaturated})$ = total energy (arbitrary units) for carbenes **1s** and **2s**; $E(\text{saturated})$ = total energy (arbitrary units) for carbenes **3s** and **4s**; ΔH = energy of hydrogenation in kcal mol⁻¹.

**Fig. 1** The B3LYP/6-31G(d,p) computed structures for singlet carbenes.

from carbon and hydrogen it is relatively easy from either the experimental or the computed structures to determine the aromatic or antiaromatic character of the investigated chemical system. In aromatic systems, all cyclic CC bond distances are the same, such as in benzene, or there is full localization of the ring's double CC bond, as in the case of cyclobutadiene. This is not so easy a task if the molecule is not symmetric and there are some heteroatoms in the ring, such as in the case of imidazol-2-ylidene **1s**. Structures of those carbenes optimized at the B3LYP/6-31G(d,p) theory level are presented in Fig. 1. If we examine the structural properties of these carbenes separately, it is obvious that the aromatic character of these compounds cannot be determined by the examination of its bond distances. However, if we compare the unsaturated and the corresponding saturated carbenes, then certain π -bond delocalization can be observed. Considering that in the Kékulé presentation of carbenes in Scheme 1, in both **1s** and **3s** cases these are two identical C–N single bonds. If delocalization of the π -bond and nitrogen's lone pair is not present then the two C–N bond distances in **1s** and **3s** should be similar. This is not the case. Those two bond distances are substantially shorter in **1s** than in its saturated analogue **3s**. This indicates that carbene **1s** has considerable aromatic character. Similarly, by comparison of structural properties of carbenes **2s** and **4s**, the aromatic character of the unsaturated carbene **2s** can be demonstrated by its shorter C–N bond distance than in **4s** (Table 1). One can further investigate those four structures and from the C–N bond distance changes determine which of the two unsaturated carbenes has higher aromatic character. This can be assessed by the change of their C–N bond distances in the course of

hydrogenation. In the case of **1s** this change is 0.083 Å (1.476–1.393) and in **2s** this change is 0.056 Å (1.444–1.388), therefore the non-chlorinated carbene **1s** should have higher aromatic character than the chlorinated **2s**.

To test our assumptions based on structural properties, it is appropriate to evaluate carbenes **1s** and **2s** hydrogenation energies. This approach was used by many to evaluate the aromatic character of cyclic conjugated systems.¹⁵ The B3LYP/6-31G(d,p) computes the enthalpy of hydrogenation for ethylene to be -41.7 kcal mol⁻¹. If the double bond in carbene **1s** is conjugated, then the enthalpy of hydrogenation should be substantially less exothermic than in the case of ethene. The enthalpy of hydrogenation of **1s** is estimated to be -17.7 kcal mol⁻¹ or with zero-point energy correction -10.1 kcal mol⁻¹. This value strongly indicates the high aromatic character of carbene **1s**, as was also determined through the comparison of structural changes. The question that remains to be answered is whether the carbene **2s** is less or more aromatic in comparison to the carbene **1s**. Considering the heat of its hydrogenation, it should be less aromatic than non-chlorinated carbene **1s** because its enthalpy of hydrogenation is more exothermic (-23.9 kcal mol⁻¹, Table 1). This can be considered an even more accurate approach if we consider the fact that the enthalpy of hydrogenation for *cis*-1,2-dichloroethane is almost identical to the enthalpy of ethene hydrogenation (Table 1). In this way we have confirmed our finding based on the structural properties of imidazol-2-ylidene, which is that they have aromatic character and that by introducing an electron-withdrawing substituent, such as a chlorine atom, their aromatic character is diminished.

We have performed an exhaustive computational study for stable cyclic conjugated molecules and transition state structures in their ground (singlet) and excited (triplet) states.¹⁶ In general, it can be stated that cyclic molecular systems that are aromatic in the ground state are antiaromatic in their excited states, and the reverse is true. Systems that are antiaromatic in the ground states are aromatic in their excited (triplet) states. The same approach can be applied for the study of the stability of conjugated carbenes such as imidazol-2-ylidenes. Computed structural properties of some of those carbenes in their triplet states are presented in Fig. 2. When the geometries of the excited (triplet) states are compared by their structural properties, aromatic stabilization can be deduced. In the case of the triplet state the orbitals should be arranged in the Möbius array. That must be reflected in the position of the substituents bound to the carbene ring. In the case of triplet **1t** all atoms are in one plane, indicating that this arrangement is not accommodated. That is not true for the chlorinated **2t** carbene. This indicates that carbene **2t** actually has higher aromaticity than **1t**. Structural changes in the course of the hydrogenation of triplet unsaturated carbenes, such as the two C–N bond distances also indicates the higher aromaticity of **2t** in comparison to **1t**. For instance, there is a higher change going from **1t** to **3t** than from **2t** to **4t** (Fig. 2). Because the triplet state is higher in energy than the singlet state, more structural changes should reflect more exothermicity and therefore less aromaticity.

To evaluate our conclusion of aromatic character for triplet imidazol-2-ylidenes we have also computed the enthalpy of hydrogenation (Table 2). Lower exothermicity is evaluated for the hydrogenation reaction carbene that has higher aromatic character. Considering our computational study, the **2t** has higher aromaticity because the exothermicity of the hydrogenation for this carbene is lower by 15.4 kcal mol⁻¹ (Table 2). In this way, we have demonstrated that in terms of their aromaticity, cyclic carbenes are behaving in a similar manner to other conjugated cyclic compounds.¹⁵

Stability of chemical systems is best assessed through the evaluation of reaction barriers for some chemical reactions. Two chemical reactions that are characteristic for carbenes are the insertion of the carbene into a single bond and the addition

Table 2 Computed energies of hydrogenation for two triplet unsaturated carbenes

	$E(\text{unsaturated})$	$E(\text{saturated})$	ΔH
Ethene	-78.491982		
(0 K)	-78.446429		
<i>cis</i> -1,2-Dichloroethane	-997.693856		
(0 K)	-997.663627		
1t–3t	-226.032550	-227.272456	-38.5
(0 K)	-225.966489	-227.180624	-28.7
2t–4t	-1145.248136	-1146.460655	-21.3
(0 K)	-1145.198802	-1146.388395	-13.3

(0 K) = Sum of electronic and zero-point energies; $E(\text{unsaturated})$ = total energy (arbitrary units) for carbenes **1t** and **2t**; $E(\text{saturated})$ = total energy (arbitrary units) for carbenes **3t** and **4t**; ΔH = energy of hydrogenation in kcal mol⁻¹.

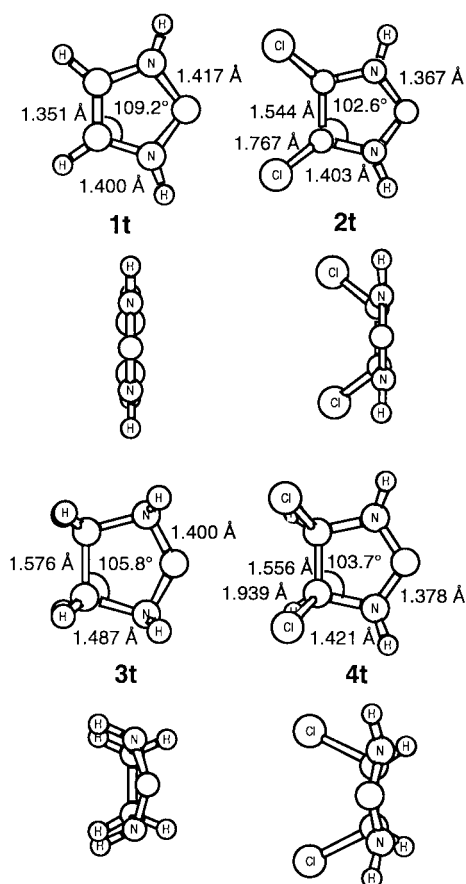


Fig. 2 The B3LYP/6-31G(d,p) structural properties for some triplet imidazol-2-ylidenes.

of the carbene to a multiple bond. Recently, we have explored the insertion reaction of fluorinated carbenes to hydrogen, hydrogen fluoride, and fluorine.¹⁷ The computational study was performed with the complete basis set *ab initio* method, which is known to produce exceptionally reliable energies for small chemical systems. The transition state structure for the singlet CH₂ insertion reaction into the hydrogen molecule was not possible to find due to the fact that the activation barrier is too small (1–2 kcal mol⁻¹), but the transition state structures were optimized for the CHF and CF₂ carbene insertion reaction into hydrogen molecules. The CBSQ (0 K) computed reaction barriers are 8.1 and 34.0 kcal mol⁻¹, indicating a very high stability of fluorinated carbenes.

In the case of the imidazol-2-ylidene insertion reaction into the hydrogen molecule there was not a problem in generating the corresponding transition state structure (Fig. 3). Their geometries in many instances resemble the classical transition state structures of any carbene hydrogen insertion reaction. In

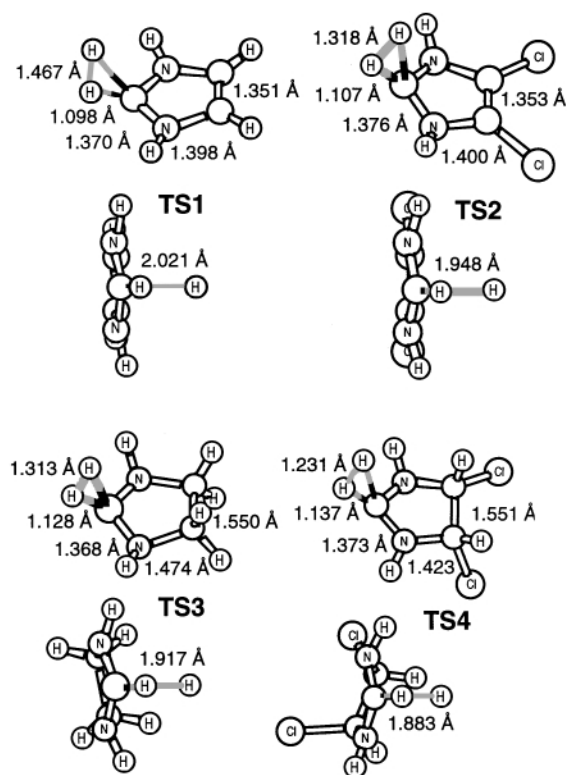


Fig. 3 The B3LYP/6-31G(d,p) computed transition state structures for carbenes **1–4** insertion into hydrogen molecule.

many of our instances we have used the transition state structure's characteristics to assess the relative activation barriers.¹⁸ One of the approaches is based on the bond distance of the bond in formation in combination with the Hammond postulate.¹⁹ Knowing that the reactions with carbene are exothermic, then the transition state structure that is closest to the product should have the lowest activation barrier. This approach has many problems and only very similar transition state structures, such as **TS1** and **TS2** as well as **TS3** and **TS4** can be compared. Transition state **TS1** has longer H–H bond distances, (1.467 Å in comparison with 1.318 Å in **TS2**, Fig. 3), therefore it is more advanced in the potential energy surface and should have a lower activation barrier than **TS2**. The same is true when **TS3** is compared to **TS4**.

Of course, it is very hard to assess the actual reaction barriers on the basis of the transition state structural properties. On the other hand, through the comparison of the carbene structural properties there is an indication that these carbenes are relatively stable due to the nitrogen lone pair as well as the double bond stabilization. For unsaturated carbenes, we have evaluated their aromatic character through the computed enthalpy of hydrogenation (Table 1). In the structures of saturated carbenes **3s** and **4s**, shortening of nitrogen–carbene carbon bond distance, in comparison with their unsaturated analogues **1s** and **2s**, indicates a strong overlap of empty singlet carbene orbital overlap with two neighbouring nitrogens (Fig. 1). This separated moiety (NCN) of **3s** and **4s** carbenes is in some way isoelectronic to the allyl anion and is therefore stabilized. Although this stabilization is not as strong as the aromatic stabilization observed in carbenes **1s** and **2s**, these compounds should have substantial activation barriers for the hydrogen insertion reaction. Due to the fact that chlorine atoms are relatively far from the reaction center and can influence the carbene reactivity only through the inductive effect, little difference in activation energy for **3s** and **4s** hydrogen insertion reaction is expected.

In the course of reaction, interactions between the highest occupied orbital of one reactant and the empty orbital of the

Table 3 Total energies for transition state structures and activation barriers for singlet carbenes **1–4** insertion into hydrogen molecule

Transition state	$E(\text{TS})$	ΔE	$\Delta\Delta E$
TS1	-227.288136	42.3	8.3
(0 K)	-227.203162	44.5	7.5
TS2	-1146.461901	44.2	9.7
(0 K)	-1146.395683	46.4	9.2
TS3	-228.508161	34.0	
(0 K)	-228.399689	37.0	
TS4	-1147.694083	34.5	
(0 K)	-1147.604378	37.2	

(0 K) = Sum of electronic and zero-point energies; $E(\text{TS})$ = total energy for corresponding transition state structure in Hartrees; ΔE = activation barrier in kcal mol⁻¹; $\Delta\Delta E$ = activation barrier difference in kcal mol⁻¹ for the reaction with unsaturated and saturated carbene.

other occur. In the reaction of the carbene with hydrogen, the carbene's lowest energy orbital interacts with the highest energy orbital of the hydrogen molecule. Considering that electron-withdrawing substituents generally stabilize carbenes, it is expected that both **TS2** and **TS4** will have relatively higher activation barriers than **TS1** and **TS3**, respectively. This finding should not be misused in connection with the aromaticity discussed above. In the evaluation of aromaticity, the carbene center was not directly involved in the reaction. The reaction was performed on the double bond of **1s** and **3s**, and the energy of the double bond was used as a measure of aromaticity.

The computed activation barrier for the hydrogen insertion reaction reflects exactly our discussion of the carbene stability. The activation barriers for the **1s** and **2s** insertion reactions are very high, indicating their solubility. By elimination of the double bond, the reactivity of carbenes increases, which is demonstrated by a substantial drop in the activation barrier. The presence of chlorine atoms increases reaction barriers in both cases but the effect is higher in the unsaturated carbene (Table 3).

On the basis of the hydrogen insertion reaction we have demonstrated that imidazolylidenes are exceptionally stable carbenes due to the presence of two nitrogen lone pairs that overlap with an empty singlet carbene carbon orbital. The stability will be further increased by putting electron-withdrawing substituents in the 3 and 5 positions, as well as by making cyclic systems conjugated. The major reaction for carbene is not the hydrogen insertion reaction, but the cycloaddition reaction with alkenes. We do not expect that the ratio of reactivity of carbenes **1–4** should be different, but the activation barriers for cycloaddition reactions in general should be lower than for the insertion reactions. The transition state structures for the ethylene addition reaction are presented in Fig. 4. The transition states are very similar to those of many other carbene cycloaddition reactions with ethylene. Activation barriers are by ~20 kcal mol⁻¹ lower (Table 4) than the barriers for the hydrogen insertion reaction. The order of reactivity is the same and supports experimental findings that these carbenes are exceptionally stable.

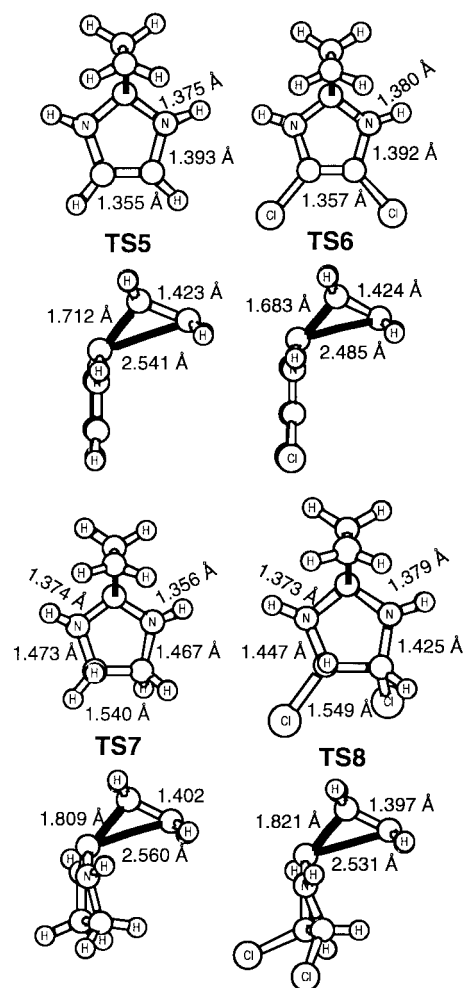
Conclusion

From computational studies presented in this paper, it can be concluded that imidazol-2-ylidenes are exceptionally stable carbenes. It was determined that these compounds are aromatic. Aromaticity is indicated through their structural characteristics, as well as the enthalpy of hydrogenation. The stabilization of singlet carbene comes from the fact that two nitrogens are bound to the carbene carbon, which enables favorable molecular orbital overlap between the empty carbene orbital and the nitrogen lone pairs, making this carbene iso-electronic with very stable allyl anions. Adding π -electrons of

Table 4 Total energies for transition state structures and activation barriers for singlet carbenes **1–4** insertion into ethylene

Transition state	$E(\text{TS})$	ΔE	$\Delta\Delta E$
TS5	-304.732557	24.0	5.5
(0 K)	-304.609143	24.6	3.5
TS6	-1223.907707	25.1	7.2
(0 K)	-1223.803505	25.4	6.3
TS7	-305.948026	18.5	
(0 K)	-305.800865	20.1	
TS8	-1225.135843	17.9	
(0 K)	-1225.007400	19.1	

(0 K) = Sum of electronic and zero-point energies; $E(\text{TS})$ = total energy for corresponding transition state structure in Hartrees; ΔE = activation barrier in kcal mol⁻¹; $\Delta\Delta E$ = activation barrier difference in kcal mol⁻¹ for the reaction with unsaturated and saturated carbene.

**Fig. 4** The B3LYP/6-31G(d,p) computed transition state structures for carbenes **1–4** addition reaction to ethylene.

the ring double bond makes this carbene even more stable, due to its aromatic character. All of that suggests the imidazol-2-ylidene has a lower reactivity in classical carbene reactions, such as the insertion and cycloaddition reaction, for which relatively high activation barriers were computed.

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