Singlet-triplet Splitting and Stability of Saturated Acyclic and Cyclic Carbenes: DFT Calculations

ESMAIL VESSALLY
Payame Noor University (PNU), Zanjan, Iran.

(Received 14th May 2008, accepted in revised form 12th September 2008)

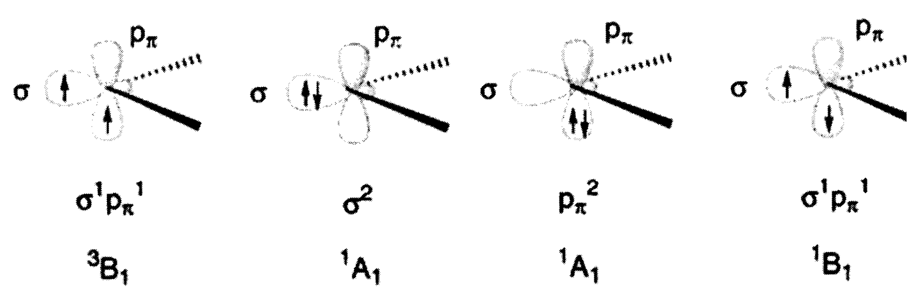
Summary: DFT calculations were carried out on the singlet-triplet splitting for $C_nH_{2n+2}C$: (n = 0-7) and $C_nH_{2n}C$: (n = 2-7) at B3LYP/6-311++G (3df,2p) level of theory. For the estimation of stabilization energies (SE), the isodesmic reactions were applied. The results of the isodesmic reaction show a high stability for singlet state relative to the corresponding triplet state by substitution of methyl or methylene groups at the both sides of methylenic center in $C_nH_{2n+2}C$:. Substitution of methylene groups at the both sides of cyclopropenylidene ($C_nH_{2n}C$:) leads to reduce the instability of triplet state; decreasing the singlet-triplet splitting.

Introduction

Highly reactive carbenes intermediates have attracted much attention in organic chemistry [1-5]. The reactivity of carbenes can be understood in terms of their electronic structure; triplet state ($\sigma\pi$ configuration) and singlet states (σ^2, π^2 and $\sigma\pi$ configurations) (Scheme-1). The trends in the reactivity of carbenes can be recognized through determination of their singlet-triplet splitting. For both the triplet and the singlet states, the π-orbital is essentially a pure *p*-like orbital while the σ-orbital is a hybrid of *s*- and *p*-like atomic orbital. Thus, σ-orbital with increased *p*-character favor a triplet ground state while the σ-orbital with increased *s*-character favor singlet state. The hybridization of the σ-orbital is in turn determined by the following factors [6]. First, the bulky substituents favor a large bond angle. This leads to decreasing *s*-character in the nonbonding σ- orbital, thus favoring the triplet state. Secondly, the substituents with high electronegativity respect to the carbon form a polar bond. The polar bond increases the *p*-orbital contributions, which in turn decreases the *p*-character in the nonbonding carbon σ-orbital. As a result, the σ-orbital increases the *s* character and stabilized the singlet state. In contrast, the electropositive substituents favor the triplet state. Thirdly, hyperconjugation also increase the singlet-triplet splitting with stabilizing the singlet state while destabilizing the triplet state. Valence electron pairs on the substituent may donate electron density to the nonbonding σ-orbital of the central carbon. Thus, the singlet state should be stabilized by substituents that are electronegative and/or have electron pairs that can be donated *via* hyperconjugation to the empty σ-orbital. Our goal in the present work is to obtain quantitative information on the magnitude of the relative stability and singlet-triplet splitting of the simple saturated acyclic $\mathbf{C_nH_{2n+2}C}$**:** and cyclic $\mathbf{C_nH_{2n}C}$**:** carbenes.

Results and Discussion

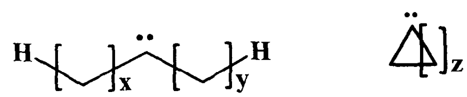
As the continuation of our previous works, our goal of investigation is to obtain quantitative



Scheme-1: Electronic structures of triplet ($\sigma\pi$ configuration) state and singlet states (σ^2, π^2 and $\sigma\pi$ configurations).

information on the magnitude of singlet-triplet splitting in the simple saturated acyclic and cyclic carbenes. Since the trends in the reactivity of carbenes are attributed to the singlet-triplet splitting, we calculated and compared the singlet-triplet splitting for $\mathbf{C_nH_{2n+2}C:}$ (n = 0-7) $\mathbf{C_nH_{2n}C:}$ (n = 2-7) at HF/6-311+G*, B3LYP/6-311+G* and B3LYP/6-311++G(3df,2p) levels of theory (Scheme-2 and Table-1). Considering the size of molecules probed and the consistency of the results obtained, this *ab initio* level proved to be appropriate. For the sake of brevity, only the data acquired through the highest level of theory (B3LYP/6-311++G(3df,2p)) was reported.

Since the lowest energy geometry for both singlet and triplet states of $\mathbf{C_nH_{2n+2}C:}$ (n = 0-7) was found to be the *trans* configuration, we focused our attention on *trans* configurations. For the estimation of stabilization energies (SE), suitable isodesmic



x+y=0-7 z=1-6

$C_nH_{2n+2}C:$ $C_nH_{2n}C:$

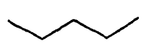
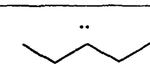
(a) (b)

Scheme-2: The molecular structure of singlet and triplet states for $\mathbf{C_nH_{2n+2}C:}$ (n = 0-7) $\mathbf{C_nH_{2n}C:}$ (n = 2-7).

Table-1: The total energy, E_T and singlet-triplet splitting of $\mathbf{C_nH_{2n+2}C:}$ (n = 0-7) and $\mathbf{C_nH_{2n}C:}$ (n = 2-7) at B3LYP/6-311++G (3df,2p) level of theory.

Compound	Total Energy, E_T of $C_nH_{2n+2}C:$	Singlet-triplet Splitting of $C_nH_{2n+2}C:$	Total Energy, E_T of $C_nH_{2n}C:$	Singlet-triplet Splitting of $C_nH_{2n}C:$
	Singlet State		Singlet State	
n = 0	-24554.330	-11.762	---	---
n = 1	-49226.439	-4.668	---	---
n = 2	-73896.856	0.747	-73123.588	14.239
n = 3	-98556.128	2.270	-97783.876	3.468
n = 4	-123215.258	3.403	-122466.611	15.743
n = 5	-147873.698	3.305	-147123.753	9.718
n = 6	-172532.243	3.354	-171775.961	9.396
n = 7	-197190.718	3.409	-196428.855	9.206
	Triplet State		Triplet State	
n = 0	-24566.092		---	
n = 1	-49231.107		---	
n = 2	-73896.109		-73109.349	
n = 3	-98553.858		-97780.408	
n = 4	-123211.855		-122450.867	
n = 5	-147870.393		-147114.035	
n = 6	-172528.889		-171766.565	
n = 7	-197187.309		-196419.649	

Table-2: The isodesmic reaction and relative stabilization energies (SE) of singlet and triplet states for $\mathbf{C_nH_{2n+2}C:}$ (n = 0-7) at B3LYP/6-311++G (3df,2p) level of theory.

Compound	$C_nH_{2n+2}C:$	+ 	⟶ $C_nH_{2n+2}CH_2$	+ 	
		Singlet State			SE
n = 0	-24554.330		-25407.392		-29.295
n = 1	-49226.439		-50063.837		-13.632
n = 2	-73896.856		-74722.241		-1.619
n = 3	-98556.128	-124039.024	-99380.670	-123215.258	-0.775
n = 4	-123215.258		-124039.024		0.000
n = 5	-147873.698		-148697.460		0.005
n = 6	-172532.243		-173355.826		0.184
n = 7	-197190.718		-198014.296		0.189
		Triplet State			SE
n = 0	-24566.092		-25407.392		-14.130
n = 1	-49231.107		-50063.837		-5.561
n = 2	-73896.109		-74722.241		1.037
n = 3	-98553.858	-124039.024	-99380.670	-123211.855	0.358
n = 4	-123211.855		-124039.024		0.000
n = 5	-147870.393		-148697.460		0.103
n = 6	-172528.889		-173355.826		0.233
n = 7	-197187.309		-198014.296		0.183

reactions were applied (Tables-2 and 3) [7]. Geometrical parameters including bond lengths (R), bond angle (A) and dihedral angle (D) were calculated at B3LYP/6-311++G (3df,2p) level.

For $\mathbf{C_nH_{2n+2}C}$:, the methylene ($:CH_2$) has triplet ground state while substitution of one methyl group (CH_4C:) reduced the singlet-triplet splitting. The singlet-triplet splitting was decreased with replacement of two methyl groups at methylenic center. The singlet-triplet splitting was increased with replacement of three and four methyl groups at methylenic center (C_3H_8C: and $C_4H_{10}C$:). The singlet-triplet splitting does not significantly change with substitution of more methyl groups at methylenic center (from $C_5H_{12}C$: to $C_7H_{16}C$:). Comparison of NBO charges at methylenic carbon for singlet states of CH_2 and CH_3CH indicated that the methyl groups donate less electrons than does H to the methylenic carbon, consistent with more electronegativity of methyl group as compared to hydrogen atom. Polar bond leads to increase the *p*-character in the nonbonding carbon σ-orbital; stabilizing singlet state and rise the singlet-triplet gap.

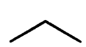
For $\mathbf{C_nH_{2n}C}$:, the cyclopropenylidene (C_2H_4C:) have a singlet ground state (Table-1). Substitution of a methylene group on cyclopropenylidene (C_3H_6C:) leads to reduce the singlet-triplet splitting. Substitution of two methylene groups on cyclopropenylidene (C_4H_8C:) rise the singlet-triplet splitting. At all, for $\mathbf{C_nH_{2n}C}$: the singlet states are ground state. However, the slope of singlet-triplet splitting is not harmonized.

Whether increase in the stability of singlet state or instability of triplet state is responsible to raise the ΔG_{s-t}, is not clearly known. Therefore, the various isodesmic reactions were applied to determination of the stability for singlet state and/or instability for triplet states of $\mathbf{C_nH_{2n+2}C}$: and $\mathbf{C_nH_{2n}C}$: [11]. System with negative SE, are stabilized but with positive SE are destabilized.

For $\mathbf{C_nH_{2n+2}C}$:, the isodesmic reaction and relative SE energies were presented at B3LYP/6-311++G (3df,2p) level (Table-2). The base of an isodesmic reaction is *n*-pentane and its corresponding carbenic structure. The results of the isodesmic reaction show more stability of the singlet state (SE with negative sign) relative to the triplet state by substitution of more methyl groups on methylenic center for $\mathbf{C_nH_{2n+2}C}$:. Thus, the high stability of the singlet state relative to the triplet state leads to raise the singlet-triplet splitting.

The isodesmic reaction and relative SE energies for $\mathbf{C_nH_{2n}C}$: are presented at B3LYP/6-311++G (3df,2p) level (Table-3). For $\mathbf{C_nH_{2n}C}$:, the base of isodesmic reaction is *n*-propane and its corresponding carbenic structure. The results of the isodesmic reaction show that the cyclopropenylidene is less stable than propeneylidene. Moreover, the results of the isodesmic reaction show that the triplet state (SE with negative sign) is stabilized more than singlet state by the substitution of more methylene groups at methylenic center in the ring of $\mathbf{C_nH_{2n}C}$:. Another word, exchanging of cyclic carbenic compounds to acyclic carbenic compounds release strain energy for triplet states more than their corresponding singlet states. Therefore, it could be concluded that the triplet state of cyclic carbenic compounds occurred under more strain and/or was more unstable than singlet state. Substitution of

Table-3: The isodesmic reaction and relative stabilization energies (SE) of singlet and triplet states for $\mathbf{C_nH_{2n}C}$: (n = 0-7) at B3LYP/6-311++G (3df,2p) level of theory.

Compound	$C_nH_{2n}C$: +	 ⟶	$C_nH_{2n}CH_2$ +		
		Singlet State			SE
n = 2	-73123.588	-74722.241	-73951.431	-73896.856	-2.457
n = 3	-97783.876	-99380.670	-98609.864	-98556.128	-1.446
n = 4	-122466.611	-124039.024	-123286.912	-123215.258	3.465
n = 5	-147123.753	-148697.460	-147950.129	-147873.698	-2.615
n = 6	-171775.961	-173355.826	-172598.222	-172532.243	1.322
n = 7	-196428.855	-198014.296	-197254.001	-197190.718	-1.569
		Triplet State			SE
n = 2	-73109.349	-74722.241	-73951.431	-73896.109	-15.950
n = 3	-97780.408	-99380.670	-98609.864	-98553.858	-2.644
n = 4	-122450.867	-124039.024	-123286.912	-123211.855	-8.875
n = 5	-147114.035	-148697.460	-147950.129	-147870.393	-9.028
n = 6	-171766.565	-173355.826	-172598.222	-172528.889	-4.720
n = 7	-196419.649	-198014.296	-197254.001	-197187.309	-7.366

methylene groups at the both sides of cyclopropenylidene (**$C_nH_{2n}C$**) leads to reduce the instability of triplet state; decreasing the singlet-triplet splitting.

Experimental

Full geometry optimizations were carried out by B3LYP [8, 9] methods using 6-311++G(3df,2p) basis set of the *Gaussian* 98 system of programs [10]. The geometry will be adjusted until a stationary point on the potential surface was found. Here, the Berny algorithm was employed for all minimizations using redundant internal coordinates [11]. For minimum state structures, only real frequency values were considered.

Conclusion

For **$C_nH_{2n+2}C$:**, the methylene (:CH_2) was a ground state triplet while substitution of one or two methyl groups at methylenic center leads to reduce the singlet-triplet splitting with the singlet ground state. Substitution of three and four methyl groups on methylenic center leads to raising the singlet-triplet splitting. The results of the isodesmic reaction show more stability of the singlet state relative to triplet state by substitution of more methyl groups at methylenic center for **$C_nH_{2n+2}C$:**. For **$C_nH_{2n}C$:**, the cyclopropenylidene have a ground state singlet. Substitution of a methylene group on cyclopropenylidene (C_3H_6C:) leads to reduce the singlet-triplet splitting. Substitution of methylene groups at the both sides of cyclopropenylidene (**$C_nH_{2n}C$:**) leads to reduce the instability of triplet state; decreasing the singlet-triplet splitting.

References

1. P. P. Gaspar, M. Xiao, D. H. Pae, D. J. Berger, T. Haile, T. Chen, D. Lei, W. R. Winchester and P. Jiang, *J. Organomet. Chem.*, **646**, 68 (2002).
2. H. Wang and K. Brezinsky, *J. Phys. Chem. A*, **102**, 1530 (1998).
3. M. Z. Kassaee, B. N. Haerizade and S. Arshadi, *J. Mol. Struct. (Theochem.)*, **639**, 187 (2003).
4. K. Klinkhammer, *Polyhedron*, **21**, 587 (2002).
5. M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, **116**, 2691 (1994).
6. E. A. Carter and W. A. Goddard III, *J. Chem. Phys.*, **88**, 1752 (1988).
7. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
8. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
9. GAUSSIAN 98, Revision A.6, M. J. Frisch, *et. al.*, Gaussian Inc., Pittsburgh, PA, (1998).
10. C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comput. Chem.*, **17**, 49 (1996).
11. M. K. Cyranski, P. V. R. Schleyer, T. M. Krygowski, H. Jiao and G. Hohlneicher, *Tetrahedron*, **59**, 1657 (2003).