

## Singlet-Triplet Energy Splitting of Divalent Five-Membered Ring $M_2C_2H_2C$ ( $M = N, P, As$ and $Sb$ )

M. M. Hashemi<sup>2,3\*</sup> and M.Mirzaei<sup>1</sup>

<sup>1</sup>Ph.D. Student, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

<sup>2</sup>Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

<sup>3</sup>Department of Chemistry, Sharif University of Technology, Tehran, Iran

### ABSTRACT

In recent work, thermal energy gaps,  $\Delta E_{s,t}$ ; enthalpy gaps,  $\Delta H_{s,t}$ ; Gibbs free energy gaps,  $\Delta G_{s,t}$ , between singlet (s) and triplet (t) states of  $M_2C_2H_2C$ ,  $1_M$  ( $M = N, P, As$  and  $Sb$ ) were calculated and compared with those analogues,  $MC_2H_3C$ ,  $1'_M$  ( $M = CH, N, P, As$  and  $Sb$ ) at B3LYP/6-311++G\*\* level of theory. Our results showed that Gibbs free energy gaps,  $\Delta G_{s,t}$  for  $1_N$  and  $1_P$  are less than  $1'_N$  and  $1'_P$ , respectively. In contrast, the  $\Delta G_{s,t}$  for  $1_{As}$  and  $1_{Sb}$  are more than  $1'_{As}$  and  $1'_{Sb}$ , respectively. The  $\Delta G_{s,t}$  between singlet and triplet states of  $1_M$  and  $1'_M$  were changed in the order:  $1_{Sb} > 1_{As} > 1'_C > 1'_P > 1_N$ ;  $1'_{Sb} > 1'_{As} > 1'_P > 1'_C > 1'_N$ , respectively.

**Keywords:** Carbene; Heteroatom; Five-Membered Ring; Singlet-Triplet Energy Gap

### INTRODUCTION

Divalent carbenes and their analogues are strongly reactive<sup>1</sup>. Carbenes have been found to be useful from fleeting intermediates to powerful reagents<sup>2</sup>. Recently, carbenes have been used as ligands in the preparation of special complexes<sup>3</sup>. The cyclic completely conjugated species have an important role in the chemistry of divalent carbene intermediates<sup>4-12</sup>. These divalent structures have been described in terms of the Hückel  $4n + 2$  rule<sup>9,11</sup>. Non-planar conformers have been used for ground state of the most of these singlet cyclic conjugated carbenes through theoretical studies<sup>4</sup>. The isolation of the stable five membered cyclic conjugated carbene was reported by Arduengo<sup>12</sup>. For the first time Ab initio calculations have been carried out for the determination of the stability and singlet-triplet energy gaps five of membered cyclic conjugated carbene and their analogues<sup>10-12</sup>. In this work, the effects of heteroatoms were studied on singlet-triplet energy gaps for divalent five-membered ring  $M_2C_2H_2C$ ,  $1_M$  ( $M = N, P, As$  and  $Sb$ ).

### COMPUTATIONAL METHODS

Full geometry optimizations of  $M_2C_2H_2C$ ,  $1_M$  ( $M = N, P, As$  and  $Sb$ ) were carried out by density functional theory (DFT) model (Scheme1). Gaussian 03 offers a wide variety of DFT models<sup>13</sup>, one of which is B3LYP method. The B3LYP method is formed through a combination of Becke's three parameter hybrid function and the LYP semi local correlation functional system and 6-311++G\*\* basis set are used with B3LYP method<sup>14, 15</sup>. For Sb atom in the molecule, the calculations was carried out by LANL2DZ basis set. Simultaneously, for other atoms in the molecule, 6-311++G\*\* basis set was used.

Keyword "Freq" was used in order to find thermochemistry parameters including thermal energy (E), enthalpy (H) and Gibbs free energy (G),k.

\*Corresponding author: mhashemi@sharif.edu

## RESULTS AND DISCUSSION

Thermal energies (E), enthalpy energies (H) and Gibbs free energies (G) were calculated for divalent five-membered cyclic di-heteroatom structures  $M_2C_2H_2C$ ,  $1_M$  ( $M = N, P, As$  and  $Sb$ ) and compared with those analogues mono-heteroatom  $MC_2H_3C$ ,  $1'_M$  ( $M = CH, N, P, As$  and  $Sb$ ) at B3LYP/6-311G\* and B3LYP/6-311++G\*\* levels of theory. Considering the size of molecules probed, and the consistency of the results obtained, these *Ab initio* levels proved to be appropriate. For the simplicity, only the data acquired through the highest level of theory (B3LYP/6-311++G\*\*) were reported (Scheme 1 and Table 1). Thermal energy gaps,  $\Delta E_{s,t}$ ; enthalpy gaps,  $\Delta H_{s,t}$ ; Gibbs free energy gaps,  $\Delta G_{s,t}$ , between singlet (s) and triplet (t) states of  $1_M$  and  $1'_M$  were calculated at B3LYP/6-311++G\*\* level (Table 2). Geometrical parameters including bond lengths (R), bond angle (A) and dihedral angle (D) of  $1_M$  and  $1'_M$  were calculated at B3LYP/6-311++G\*\* level (Table 3 and Figure 1). The DFT calculations indicated that the singlet states of  $1_P, 1_{Sb}$  and  $1'_M$  ( $M = CH, N, P, As$  and  $Sb$ ) have a nonplanar conformation relative to their corresponding planar triplet states. Both singlet and triplet states of  $1_N$  and  $1_{As}$  have a planar conformation (Table 2 and 3).

All triplet states of  $1_M$  and  $1'_M$  are more stable than their related singlet states. Therefore, Gibbs free energy gaps,  $\Delta G_{s,t}$  between singlet and triplet states show a positive value. The  $\Delta G_{s,t}$  between singlet and triplet states of  $1_M$  and  $1'_M$  at B3LYP/6-311++G\*\* level were changed in the order of (in kcal/mol) (Table 2):  $1_{Sb}$  (21.90) >  $1_{As}$  (14.95) >  $1'_C$  (9.60) >  $1_P$  (8.22) >  $1_N$  (1.73);  $1'_{Sb}$  (18.88) >  $1'_{As}$  (14.43) >  $1'_P$  (10.07) >  $1'_C$  (9.60) >  $1'_N$  (8.50). Increasing the stability of singlet or triplet states responsible would decrease the  $\Delta G_{s,t}$ , which is explained by comparison relative energies between various singlet and triplet states. With respect to relative energies, one concludes that increased instability for singlet state of  $1_M$  and  $1'_M$  from  $M = N$  to  $M = Sb$  is responsible for obtaining a higher  $\Delta G_{s,t}$  (Figure 2).

Instability for singlet state of  $1_N$  and  $1'_M$  with replacement of heavy heteroatom (from  $M = N$  to  $M = Sb$ ) could reasonably be explained by following factors. The higher atomic radius of a heteroatom (M) increases the bond length :C-M. Therefore, carbenic center prefers to have nonbonding electrons in atomic orbitals with a less

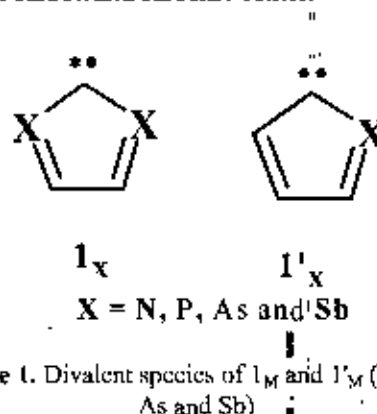
percentage of s-character. The less s-character of nonbonding electrons leads to decrease in stability of singlet state. Another factor is the polarity of the :C-M bond. The :C-C bond in  $1'_C$  is nearly nonpolar, but the :C-M bond at  $1_{Sb}$  is strongly polarized in this direction :C-M<sup>+</sup>. Strongly polarized bond destabilize the singlet state.

The  $\Delta G_{s,t}$  between  $1_M$  and  $1'_M$  were compared with replacement of heavy heteroatoms from  $M = N$  to  $M = Sb$ . The  $\Delta G_{s,t}$  for  $1_N$  and  $1_P$  is less than for  $1'_N$  and  $1'_P$ , respectively. In contrast, the  $\Delta G_{s,t}$  for  $1_{As}$  and  $1_{Sb}$  are more than for  $1'_{As}$  and  $1'_{Sb}$ .

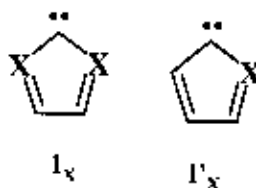
Bond lengths (R) in  $1_M$  and  $1'_M$  indicated that all bonds :C-M ( $M = P, As$  and  $Sb$ ) tend to have a single bond (Table 3). Heavy atoms with single bonds are more stable than at double bonds. The stability of heavy atoms at single bonds of  $1_M$  and  $1'_M$  were reported by Kutzelnigg<sup>16</sup>. "Single bonds between first row elements are weak and multiple bonds are strong, whereas the second or higher row elements single bonds are strong and multiple bonds are weak." Therefore, P and As atoms construct a weak double bond and make a single bond between  $1_M$  and  $1'_M$ .

Singlet state of  $1_N$  has an allenic (N=C=N) form while singlet state of  $1_{As}$  as well as  $1_{Sb}$  tends to have carbenic form (As-C-As and Sb-C-Sb) (FIGURE 1). However, singlet state of  $1_P$  tends to have an intermediate between allenic and carbonic form (P=C=P). Therefore, it is concluded that electronegative and electropositive substituents at a position of  $1_M$  tend to have allenic and carbonic form.

Singlet state of  $1'_M$  tends to have an olefinic form. However, double bond in  $1'_N$  was formed between nitrogen and carbenic center while double bond in  $1'_M$  ( $M = P, As$  and  $Sb$ ) was formed between carbon and carbenic center.

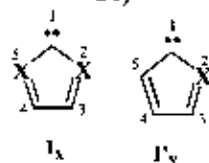


Scheme 1. Divalent species of  $1_M$  and  $1'_M$  ( $M = N, P, As$  and  $Sb$ )

Table 1. Thermal energy (E), enthalpy (H), Gibbs free energy (G), in kcal/mol, at B3LYP/6-311++G\*\* for the singlet (s) and triplet (t) states of  $1_X$  and  $1'_X$  (X= N, P, As and Sb).

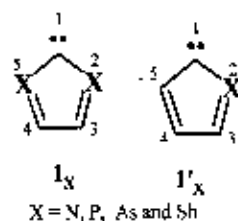
X = N, P, As and Sb

Compound	ZPE	E	H	G
Singlet state				
$1_N$	27.39	-141083.11	-141082.52	-141102.19
$1_P$	22.81	-500788.72	-500788.13	-500809.94
$1_{As}$	21.20	-2878384.80	-2878384.21	-2878407.17
$1_{Sb}$	20.27	-79123.35	-79122.76	-79147.24
$1'_C$	41.53	-120903.60	-120903.00	-120922.94
$1'_N$	34.41	-130994.45	-130993.86	-131013.43
$1'_P$	32.29	-310847.12	-310846.52	-310867.17
$1'_{As}$	31.53	-1499646.22	-1499645.63	-1499667.32
$1'_{Sb}$	31.10	-100018.11	-100017.51	-100039.96
Triplet state				
$1_N$	27.78	-141084.69	-141084.10	-141103.92
$1_P$	23.12	-500796.40	-500795.80	-500818.16
$1_{As}$	21.99	-2878398.61	-2878398.01	-2878422.12
$1_{Sb}$	21.24	-79144.36	-79143.76	-79169.14
$1'_C$	41.86	-120912.85	-120912.25	-120932.54
$1'_N$	34.90	-131002.46	-131001.86	-131021.92
$1'_P$	32.45	-310856.5	-310855.91	-310877.24
$1'_{As}$	32.08	-1499660.1	-1499659.5	-1499681.8
$1'_{Sb}$	31.83	-100036.56	-100035.96	-100058.85

Table 2. Thermal energy differences  $\Delta E_{s-t}$ ; enthalpy differences,  $\Delta H_{s-t}$ ; and Gibbs energy differences,  $\Delta G_{s-t}$ , between singlet (s) and triplet (t) states, in kcal/mol, at B3LYP/6-311++G\*\* for  $1_M$  and  $1'_M$  (M= N, P, As and Sb)

X = N, P, As and Sb

Compound	$\Delta E_{s-t}$	$\Delta H_{s-t}$	$\Delta G_{s-t}$
$1_N$	1.58	1.58	1.73
$1_P$	7.68	7.68	8.22
$1_{As}$	13.81	13.81	14.95
$1_{Sb}$	21.00	21.00	21.90
$1'_C$	9.25	9.25	9.60
$1'_N$	8.00	8.00	8.50
$1'_P$	9.39	9.39	10.07
$1'_{As}$	13.90	13.90	14.43
$1'_{Sb}$	18.45	18.45	18.88

**Table 3.** Bond lengths (Å), bond angle (degree) and dihedral angles (degree) at B3LYP/6-311++G\*\* for  $1_M$  and  $1'_M$  (M= N, P, As and Sb)

Compound	R <sub>1,2</sub>	R <sub>2,3</sub>	R <sub>3,4</sub>	R <sub>4,5</sub>	R <sub>5,1</sub>	A <sub>2,1,3</sub>	D <sub>3,2,1,5</sub>	D <sub>4,5,1,2</sub>
Singlet state								
$1_N$	1.24	1.46	1.38	1.46	1.24	143.1	0.1	0.1
$1_P$	1.70	1.80	1.40	1.80	1.70	141.9	29.1	-29.1
$1_{As}$	1.82	1.95	1.37	1.95	1.82	146.9	0.2	0.2
$1_{Sb}$	2.04	2.14	1.37	2.14	2.04	141.6	27.9	-27.9
$1'_C$	1.39	1.40	1.47	1.37	1.43	116.7	31.2	30.2
$1'_N$	1.29	1.37	1.44	1.41	1.40	122.6	29.7	30.3
$1'_P$	1.70	1.81	1.43	1.39	1.38	131.9	27.4	30.6
$1'_{As}$	1.94	1.84	1.42	1.43	1.30	123.6	28.1	32.2
$1'_{Sb}$	2.19	2.06	1.40	1.45	1.33	120.3	-23.4	28.2
Triplet state								
$1_N$	1.35	1.32	1.48	1.32	1.35	119.3	0.0	0.0
$1_P$	1.71	1.85	1.35	1.85	1.71	124.3	0.0	0.0
$1_{As}$	1.83	1.97	1.34	1.97	1.83	124.2	0.0	0.0
$1_{Sb}$	2.03	2.18	1.34	2.18	2.03	124.7	0.0	0.0
$1'_C$	1.43	1.37	1.48	1.37	1.43	112.9	0.0	0.0
$1'_N$	1.30	1.37	1.45	1.37	1.47	114.6	0.0	0.0
$1'_P$	1.83	1.77	1.38	1.47	1.34	115.3	0.0	0.0
$1'_{As}$	1.95	1.92	1.36	1.47	1.34	114.6	0.0	0.0
$1'_{Sb}$	2.16	2.14	1.35	1.48	1.33	113.9	0.0	0.0

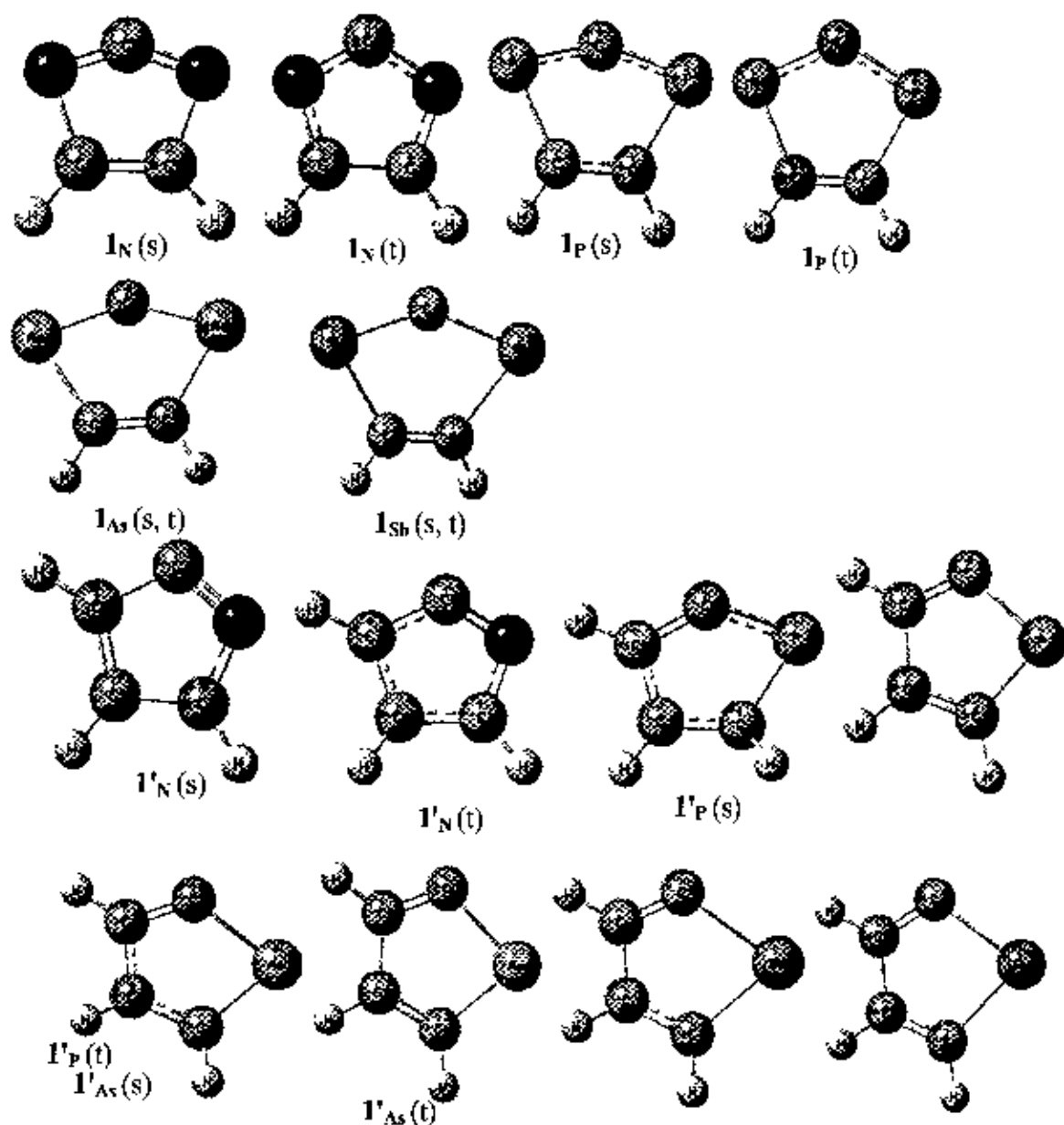


Fig. 1. Bond types for singlet and triplet states of  $1_M$  and  $1'_M$  ( $M=N, P, As$  and  $Sb$ ).

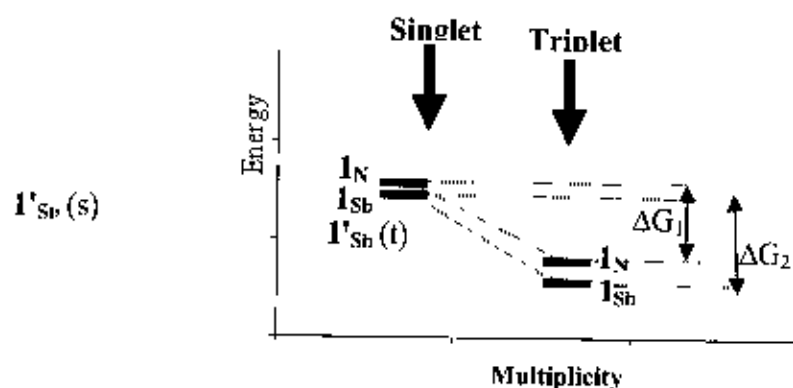


Fig. 2. Diagram of energy vs. multiplicity of  $1_x$ .

## CONCLUSION

Heteroatom effects were investigated on singlet-triplet energy gaps for divalent five-membered cyclic di-heteroatom structures,  $M_2C_2H_2C$ ,  $1_M$  ( $M = N, P, As$ ). The  $\Delta G_{s-t}$  between singlet and triplet states at  $1_M$  and  $1'_M$  at B3LYP/6-311++G\*\* level were changed in the order (in kcal/mol):  $1_{Sb} > 1_{As} > 1'_C > 1_P > 1_N$ ;  $1'_{Sb} > 1'_{As} > 1'_P > 1'_C > 1'_N$ . The  $\Delta G_{s-t}$  for  $1_N$  and  $1_P$  is less than for  $1'_N$  and  $1'_P$ . In contrast,

the  $\Delta G_{s-t}$  for  $1_{As}$  and  $1_{Sb}$  is more than for  $1'_{As}$  and  $1'_{Sb}$ , respectively.

## ACKNOWLEDGMENT

The financial support of Science and Research Branch of Islamic Azad University is gratefully acknowledged.

## REFERENCES

- [1] P. P. Gaspar, R. West, Z. Rappoport and Y. Apeloig, Editors, *Chemistry of Organic silicon compounds* vol. 2, Wiley, Chichester New York(1997), p. 2436.
- [2] S. A Fontismedia. *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*, New York. Basel 2002.
- [3] C. M. Crudden and J. M. Praetorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis*. Topics in Organometallic Chemistry 21, Springer: Berlin, Heidelberg, New York. 2007.
- [4] S.P. Lathrop and T. Rovis, *J. Am. Chem. Soc.*, 131, 13628 (2009).
- [5] N. Luo and Z. Yu, *J. Organometal. Chem.* 694, 3058 (2009).
- [6] (a) M. Z. Kassaei, S. Arshadi, M. Acedy and E. Vessally, *J. Organometal. Chem.* 690, 3427 (2005); (b) E. Vessally, *Heteroatom Chem.* 19, 245 (2008); (c) E. Vessally, M. Nikoorazm and A. Ramazani, *Chin. J. Inorg. Chem.* 24, 631 (2008); (d) E. Vessally, A. Rezaei, N. Chaliyavi and M. Nikoorazm, *Russian J. Phys. Chem.*, 81, 1821 (2007); (e) E. Vessally, A. Rezaei, N. Chaliyavi and M. Nikoorazm. *J. Chin Chem. Soc.*, 54, 1583 (2007).
- [7] R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.* 90, 5457 (1968).
- [8] H. Kollmar, *J. Am. Chem. Soc.* 100, 2660 (1978).
- [9] L. Radom, H. F. Schaefer and M. A. Vincent, *Nouv. J. Chim.* 4, 411 (1980).
- [10] M. Kausch and H. Durr, *J. Chem. Res.* 2 (1982).
- [11] A. J. Arduengo, R.L. Harlow and M. Kline. *J. Am. Chem. Soc.* 113, 361 (1991).
- [12] M. J. Frisch, et. al., Gaussian 98, Revision A. 6, Gaussian Inc., Pittsburgh PA (1998).
- [13] C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B* 37, 785 (1988).
- [14] A. D. Becke, *J. Chem. Phys.* 98, 5648 (1993).
- [15] W. Kutzelnigg, *Angewandte*, 84, 1578 (1984).