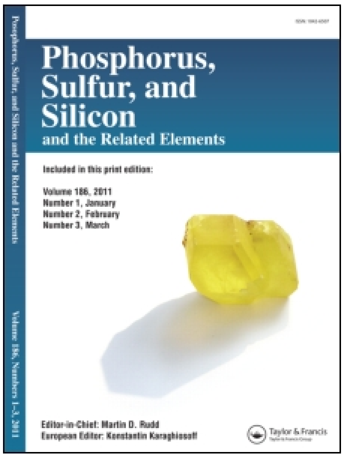


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Heteroatom Effects on Singlet-Triplet Energy Gaps of Divalent Five-Membered Ring $X_2C_2H_2C$ (X = N, P, As, and Sb)

E. Vessally[a]; M. Abbasian[b]; A. Ramazani[c]; A. R. Poor Heravi[d]
[a] Payame Noor University (PNU), Zanjan, Iran [b] Payame Noor University (PNU), Tabriz, Iran [c] Department of Chemistry, University of Zanjan, Zanjan, Iran [d] Payame Noor University (PNU), Zanjan, Abhar, Iran

To cite this Article Vessally, E. , Abbasian, M. , Ramazani, A. and Heravi, A. R. Poor(2010) 'Heteroatom Effects on Singlet-Triplet Energy Gaps of Divalent Five-Membered Ring $X_2C_2H_2C$ (X = N, P, As, and Sb)', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 4, 705 — 708

To link to this Article: DOI: 10.1080/10426500902922925

URL: http://dx.doi.org/10.1080/10426500902922925

Phosphorus, Sulfur, and Silicon, 185:705–708, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902922925

HETEROATOM EFFECTS ON SINGLET–TRIPLET ENERGY GAPS OF DIVALENT FIVE-MEMBERED RING $X_2C_2H_2C$ (X = N, P, As, AND Sb)

E. Vessally,[1] M. Abbasian,[2] A. Ramazani,[3] and A. R. Poor Heravi[4]
[1]*Payame Noor University (PNU), Zanjan, Iran*
[2]*Payame Noor University (PNU), Tabriz, Iran*
[3]*Department of Chemistry, University of Zanjan, Zanjan, Iran*
[4]*Payame Noor University (PNU), Zanjan, Abhar, Iran*

Thermal energy gaps, $\Delta E_{s\text{–}t}$; enthalpy gaps, $\Delta H_{s\text{–}t}$; and Gibbs free energy gaps, $\Delta G_{s\text{–}t}$ between the singlet (s) and triplet (t) states of $X_2C_2H_2C$, 1_X (X = CH, N, P, As, and Sb) were calculated and compared with those analogues, XC_2H_3C, $1'_X$ (X = N, P, As, and Sb) at the B3LYP/6-311++G** level of theory. Density functional theory (DFT) calculations indicated that the $\Delta G_{s\text{-}t}$, for 1_X (X = N and P) should be lower with respect to their monosubstituted $1'_X$. In contrast, the $\Delta G_{s\text{-}t}$ for 1_X (X = As and Sb) should be larger with respect to $1'_X$. The $\Delta G_{s\text{-}t}$ for 1_X and $1'_X$ were increased in the following order: $1_{Sb} > 1_{As} > 1_C > 1_P > 1_N$; $1'_{Sb} > 1'_{As} > 1'_P > 1_C > 1'_N$, respectively.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Carbene; five-membered ring; heteroatom; singlet–triplet energy gap; $X_2C_2H_2C$

INTRODUCTION

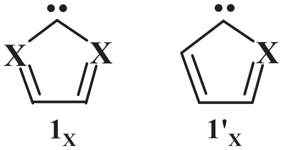
Divalent carbenes and their analogues are strongly reactive.[1] Carbenes have been found to be useful, from fleeting intermediates to powerful reagents.[2] Recently, carbenes have been used as ligands in the preparation of special complexes.[3] The cyclic, completely conjugated species have an important role in the chemistry of divalent carbene intermediates.[4–14] These divalent structures have been described in terms of the Huckel 4n + 2 rule.[5–8] Nonplanar conformers have been found in the ground state for the most of these singlet cyclic conjugated carbenes through theoretical studies.[4] The isolation of the stable five-membered cyclic conjugated carbene was first reported by Arduengo et al.[9] Ab initio calculations have been carried out for the determination of the stability and singlet–triplet energy gaps of five-membered cyclic conjugated carbenes and their heavy analogues.[10–14] In this article, the effects of heteroatoms were studied on singlet–triplet energy gaps for di-substituted divalent five-membered ring $X_2C_2H_2C$, $\mathbf{1_X}$ (X = N, P, As, and Sb).

Received 11 January 2009; accepted 24 March 2009.

Address correspondence to E. Vessally, Payame Noor University (PNU), Zanjan, Iran. E-mail: e_vesali@yahoo.com

COMPUTATIONAL METHODS

Full geometry optimizations of di-substituted $X_2C_2H_2C$, $\mathbf{1_X}$ (X = CH, N, P, As, and Sb) were carried out by the density functional theory (DFT) model (Scheme 1). Gaussian 98 offers a wide variety of DFT models.[15] The B3LYP method is the best method; it is formed through a combination of Becke's three-parameter hybrid functional and the LYP semi-local correlation functional. The 6-311++G** basis set is used with the B3LYP method.[16,17] For the Sb atom in the molecule, the calculations were carried out by a LANL2DZ basis set. Simultaneously, for other atoms in the molecule, the 6-311++G** basis set was used. All calculations were carried out for gas phase at 298 K temperature and 1 atm pressure. All possible conformations of the given species were examined in order to find a global minimum.



$\mathbf{1_X}$ $\mathbf{1'_X}$

X = N, P, As and **Sb**

Scheme 1 Divalent species of $\mathbf{1_X}$ and $\mathbf{1'_X}$ (X = N, P, As, and Sb).

In order to find thermochemical parameters including the thermal energy (E), thermal enthalpy (H), and Gibbs free energy (G), the keyword "Freq" was used.

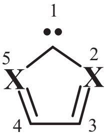
RESULTS AND DISCUSSION

Thermal energies (E), enthalpy energies (H), and Gibbs free energies (G) were calculated for divalent five-membered cyclic di-substituted structures $X_2C_2H_2C$, $\mathbf{1_X}$ (X = CH, N, P, As, and Sb) and compared with those analogues monosubstituted XC_2H_3C, $\mathbf{1'_X}$ (X = N, P, As, and Sb) at the B3LYP/6-311G* and B3LYP/6-311++G** levels of theory (Scheme 1, Table I). Considering the size of the molecules probed and the consistency of the results obtained, these ab initio levels proved to be appropriate. For the sake of brevity, only the data acquired through the highest level of theory (B3LYP/6-311++G**) were reported. Thermal energy gaps, $\Delta E_{s\text{–}t}$; enthalpy gaps, $\Delta H_{s\text{–}t}$; and Gibbs free energy gaps, $\Delta G_{s\text{–}t}$, between singlet (s) and triplet (t) states of $\mathbf{1_X}$ and $\mathbf{1'_X}$ were calculated at B3LYP/6-311++G** (Table I). Geometrical parameters including bond lengths (R), bond angle (A), and dihedral angle (D) of $\mathbf{1_X}$ and $\mathbf{1'_X}$ were calculated at the B3LYP/6-311++G** level (see Table S1 and Figure S1, available online in the Supplemental Materials).

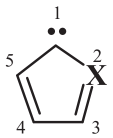
The DFT calculations indicated that the singlet states of $\mathbf{1_P}$, $\mathbf{1_{Sb}}$, and $\mathbf{1'_X}$ (X = N, P, As, and Sb) have nonplanar conformation relative to their corresponding planar triplet states. Both the singlet and triplet states of $\mathbf{1_N}$ and $\mathbf{1_{As}}$ have a planar conformation (Tables I and S1).

All triplet states of $\mathbf{1_X}$ and $\mathbf{1'_X}$ are more stable than their related singlet states. Therefore, the $\Delta G_{s\text{–}t}$ has a positive value. The $\Delta G_{s\text{–}t}$ between singlet and triplet states of $\mathbf{1_X}$ and $\mathbf{1'_X}$ at B3LYP/6-311++G** level were increased in the following order (in kcal/mol)

Table I Thermal energy differences, $\Delta E_{s\text{–}t}$; enthalpy differences, $\Delta H_{s\text{–}t}$; and Gibbs energy differences, $\Delta G_{s\text{–}t}$, between singlet (s) and triplet (t) states at B3LYP/6-311++G** for $\mathbf{1_X}$ and $\mathbf{1'_X}$ (X = N, P, As, and Sb)



$\mathbf{1_X}$



$\mathbf{1'_X}$

X = N, P, As and Sb

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

(Table I): $\mathbf{1_{Sb}}$ (21.90) > $\mathbf{1_{As}}$ (14.95) > $\mathbf{1_C}$ (9.60) > $\mathbf{1_P}$ (8.22) > $\mathbf{1_N}$ (1.73); $\mathbf{1'_{Sb}}$ (18.88) > $\mathbf{1'_{As}}$ (14.43) > $\mathbf{1'_P}$ (10.07) > $\mathbf{1_C}$ (9.60) > $\mathbf{1'_N}$ (8.50).

The lower $\Delta G_{s\text{–}t}$ could be related to decrease the stabilization of the singlet or to increase the instabilization of the triplet state. The lower $\Delta G_{s\text{–}t}$ could be explained by comparison of the relative energies between various singlet and triplet states. With respect to relative energies, we can conclude that increased instability for singlet state of $\mathbf{1_X}$ and $\mathbf{1'_X}$ from X=N to X=Sb is responsible to obtain a higher $\Delta G_{s\text{–}t}$.

Instability for singlet state of $\mathbf{1_X}$ and $\mathbf{1'_X}$ with replacement of heavy heteroatom (from X = N to X = Sb) could reasonably be explained by the following factors: The higher atomic radius of a heteroatom (X) increases the bond length :C—X. Therefore, the carbenic center prefers to have nonbonding electrons in atomic orbitals with a lesser percentage of *s*-character. The less *s*-character of nonbonding electrons leads to a decrease in the stability of the singlet state. Another factor is the polarity of the :C—X bond. The :C-C bond in $\mathbf{1_C}$ is nearly nonpolar, but the :C—X bond at $\mathbf{1_{Sb}}$ is strongly polarized in the direction $:C^-—X^+$. Strongly polarized bonds lead to destabilization of the singlet state.

The $\Delta G_{s\text{–}t}$ between $\mathbf{1_X}$ and $\mathbf{1'_X}$ were compared with replacement of heavy heteroatoms from X = N to X=Sb. DFT calculations indicated that the $\Delta G_{s\text{–}t}$ for $\mathbf{1_X}$ (X=N and P) should be lower with respect to their mono-substituted $\mathbf{1'_X}$. In contrast, the $\Delta G_{s\text{–}t}$ for $\mathbf{1_X}$ (X = As and Sb) should be larger with respect to $\mathbf{1'_X}$.

Bond lengths (R) in $\mathbf{1_X}$ and $\mathbf{1'_X}$ indicated all bonds :C—X (X = P, As, and Sb) tend to have a single bond (Table S1). Heavy atoms in the single bond are more stable than in the double bond. The stability of heavy atoms at single bonds of $\mathbf{1_X}$ and $\mathbf{1'_X}$ has been reported by Kutzelnigg: "Single bonds between the first row elements are weak and multiple bonds are strong, whereas for the second or higher row elements single bonds are strong and multiple bonds weak."[18] Therefore, P and As atoms construct weak double bonds and lead to construction of a single bond at $\mathbf{1}_\mathbf{X}$ and $\mathbf{1'}_\mathbf{X}$.

The singlet state of $\mathbf{1}_\mathbf{N}$ tends to have an allenic (N=C=N) form, while the singlet states of $\mathbf{1}_\mathbf{As}$ as well as $\mathbf{1}_\mathbf{Sb}$ tend to have a carbenic form (As—C—As and Sb—C—Sb) (Figure S1). However, the singlet state of $\mathbf{1}_\mathbf{P}$ tends to have an intermediate between allenic and carbenic form (P=P). Therefore, it could be concluded that higher and lesser bond distance of :C—X in $\mathbf{1}_\mathbf{X}$ leads to a carbenic and allenic form, respectively.

All singlet states of $\mathbf{1'}_\mathbf{X}$ tend to have an olefinic form. However, the double bond in $\mathbf{1'}_\mathbf{N}$ was formed between nitrogen and carbenic center, while the double bond in $\mathbf{1'}_\mathbf{X}$ (X = P, As, and Sb) was formed between carbon and carbenic center.

CONCLUSIONS

Heteroatom effects were investigated on singlet–triplet energy gaps for divalent five-membered cyclic diheteroatom structures, $X_2C_2H_2C$, $\mathbf{1}_\mathbf{X}$ (X = N, P, As). The $\Delta G_{s\text{–}t}$ between singlet and triplet states of $\mathbf{1}_\mathbf{X}$ and $\mathbf{1'}_\mathbf{X}$ at B3LYP/6-311++G** level were increased in the following order (in kcal/mol): $\mathbf{1}_\mathbf{Sb} > \mathbf{1}_\mathbf{As} > \mathbf{1}_\mathbf{C} > \mathbf{1}_\mathbf{P} > \mathbf{1}_\mathbf{N}$; $\mathbf{1'}_\mathbf{Sb} > \mathbf{1'}_\mathbf{As} > \mathbf{1'}_\mathbf{P} > \mathbf{1}_\mathbf{C} > \mathbf{1'}_\mathbf{N}$. The $\Delta G_{s\text{–}t}$ for $\mathbf{1}_\mathbf{N}$ and $\mathbf{1}_\mathbf{P}$ is less than for $\mathbf{1'}_\mathbf{N}$ and $\mathbf{1'}_\mathbf{P}$, respectively. In contrast, the $\Delta G_{s\text{–}t}$ for $\mathbf{1}_\mathbf{As}$ and $\mathbf{1}_\mathbf{Sb}$ is more than for $\mathbf{1'}_\mathbf{As}$ and $\mathbf{1'}_\mathbf{Sb}$, respectively.

REFERENCES

1. P. P. Gaspar and R. West, In *Chemistry of Organic Silicon Compounds*, Z. Rappoport and Y. Apeloig, eds., vol. 2 (Wiley, Chichester, UK, 1997), p. 2436.
2. G. Bertrand, *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents* (Taylor & Francis, New York, 2002).
3. C. M. Crudden and J. M. Praetorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis* (Springer, Berlin, 2007).
4. M. Z. Kassaee, S. Arshadi, M. Acedy, and E. Vessally, *J. Organomet. Chem.*, **690,** 3427 (2005).
5. R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90,** 5457 (1968).
6. H. Kollmar, *J. Am. Chem. Soc.*, **100,** 2660 (1978).
7. L. Radom, H. F. Schaefer, and M. A. Vincent, *Nouv. J. Chim.*, **4,** 411 (1980).
8. M. Kausch and H. Durr, *J. Chem. Res.*, 2 (1982).
9. A. J. Arduengo, R. L. Harlow, and M. Kline, *J. Am. Chem. Soc.*, **113,** 361 (1991).
10. E. Vessally, *Heteroatom Chem.*, **19,** 245 (2008).
11. E. Vessally, M. Nikoorazm, and A. Ramazani, *Chin. J. Inorg. Chem.*, **24,** 631 (2008).
12. E. Vessally, A. Rezaei, N. Chaliyavi, and M. Nikoorazm, *Russ. J. Phys. Chem.*, **81,** 1821 (2007).
13. E. Vessally, A. Rezaei, N. Chaliyavi, and M. Nikoorazm, *J. Chin. Chem. Soc.*, **54,** 1583 (2007).
14. E. Vessally, N. Chaliyavi, A. Rezaei, and M. Nikoorazm, *Asian J. Chem.*, **19,** 5000 (2007).
15. M. J. Frisch, et. al., Gaussian 98, Revision A. 6, Gaussian, Inc., Pittsburgh, PA (1998).
16. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37,** 785 (1988).
17. A. D. Becke, *J. Chem. Phys.*, **98,** 5648 (1993).
18. W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, **84,** 1578 (1984).