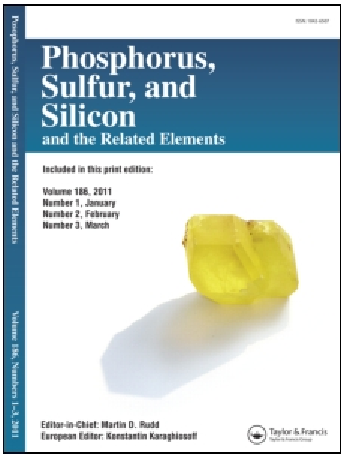

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Mono-Heteroatom Effects on Singlet-Triplet Energy Gaps of Divalent Five-Membered Ring XC_3H_3C (X = CH, N, P, and As)

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Mono-Heteroatom Effects on Singlet–Triplet Energy Gaps of Divalent Five-Membered Ring XC_3H_3C (X = CH, N, P, and As)

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Heteroatom effects were investigated on singlet–triplet energy gaps of divalent five-membered ring XC_3H_3C*,* $\mathbf{1_X}$ *and* $\mathbf{2_X}$ *(X = CH, N, P, and As) at B3LYP/6-311++G** level. All triplet states of* $\mathbf{1_X}$ *and* $\mathbf{2_X}$ *are more stable than the related singlet state.* ΔG_{s-t} *between singlet and triplet states of* $\mathbf{1_X}$ *and* $\mathbf{2_X}$ *were changed in the order (in kcal/mol):* $\mathbf{1_{As}}$ *(14.43) >* $\mathbf{1_P}$ *(10.07) >* $\mathbf{1_{CH}}$ *(9.60) >* $\mathbf{1_N}$ *(8.50) and* $\mathbf{2_N}$ *(11.56) >* $\mathbf{2_{CH}}$ *(9.60) >* $\mathbf{2_P}$ *(3.07) >* $\mathbf{2_{As}}$ *(2.13).*

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

INTRODUCTION

Divalent carbenes and their analogues are strongly reactive.[1] The 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.[4–15] These divalent structures have been described in terms of the Huckel 4n + 2 rule.[5–8] Non-planar conformers have been found at ground state for 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 carbene and their heavy analogues.[4,10–14] As a continuation of our work,[10–14] in this article mono-heteroatom effects are studied on singlet–triplet energy gaps for divalent five-membered ring $\mathbf{XC_3H_3C}$,$\mathbf{1_X}$ and $\mathbf{2_X}$ (X=CH, N, P, and As).

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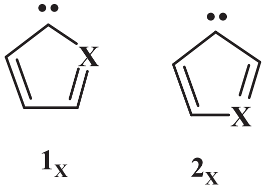


SCHEME 1 Divalent species for singlet states of $\mathbf{1_X}$ and $\mathbf{2_X}$ (X= CH, N, P, and As).

COMPUTATIONAL METHODS

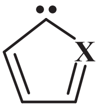
Full geometry optimizations of $\mathbf{XC_3H_3C}$, $\mathbf{1_X}$ and $\mathbf{2_X}$ (X = CH, N, P, and As) were carried out by density functional theory (DFT) model (Scheme 1). Gaussian 98 offers a wide variety of DFT models.[15] The B3LYP method is the best method of DFT model. B3LYP method is formed through a combination of Becke's three-parameter hybrid functional and the LYP non-local correlation functional. 6-311++G** basis set is used with B3LYP method.[16,17]

6-311++G** basis set designates the 6-311G basis set supplemented by diffuse functions (++) and polarization functions (**). The B3LYB/6-311G* optimized geometrical outputs were used as inputs for the B3LYB/6-311++G** basis set. To find a global minimum on a specific surface, all possible conformations of the given species are examined by scanning the specific dihedral angles at the B3LYP/6-311++G** level. For minimum state structures, only real frequency values are accepted. This is for obtaining more accurate values of thermal energies (E), enthalpies (H), and Gibbs free energies (G). In order to find thermochemistry parameters including thermal energy (E), thermal enthalpy (H), and Gibbs free energy (G), keyword "Freq" was used. The calculations exhibit systematic errors and thus benefit from scaling. Thermodynamic functions, obtained through frequency calculations, are multiplied by Hehre et al.[18] scaling factor of 0.89 for HF and by 0.99 scaling factor of Rauhut and Pulay[19] for B3LYP. Nevertheless, scaling factors fitted to observe (anharmonic) frequencies will deviate from unity even for exact calculations. Here, a set of molecules containing similar motifs are treated together, where they benefit from similar scalings.

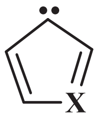
RESULTS AND DISCUSSION

Zero-point energies (ZPE), thermal energies (E), enthalpy energies (H), and Gibbs free energies (G) were calculated for divalent five-membered cyclic conjugated structures **XC_3H_3C**, **1_X** and **2_X** (X = CH, N, P and As) at B3LYP/6-311G* and B3LYP/6-311++G** levels of theory (Scheme 1 and Table I). Names **1_X** and **2_X** are related to replacement of a heteroatom (X) at the α and β positions of the carbenic center, respectively. 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 (Table I). Zero-point energy gaps, ΔZPE; thermal energy gaps, ΔE_{t-s}; enthalpy gaps, ΔH_{t-s}; Gibbs

TABLE I Sum of Electronic and Thermal Energy, (E); Sum of Electronic and Thermal Enthalpy (H); Sum of Electronic and Thermal Free Energy (G) at B3LYP/6-311++G for Singlet (s) and Triplet (t) States of 1_X and 2_X (X = N, P, and As)**



1_X

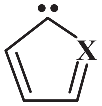


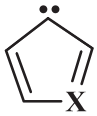
2_X

X = N, P and As

Compound	ZPE	E	H	G
		Singlet state		
1_C	−120906.30	−120903.60	−120903.00	−120922.94
1_N	−130996.96	−130994.45	−130993.86	−131013.43
1_P	−310849.95	−310847.12	−310846.52	−310867.17
1_{As}	−1499649.28	−1499646.22	−1499645.63	−1499667.32
2_N	−130987.60	−130984.84	−130984.25	−131004.47
2_P	−310860.95	−310857.79	−310857.20	−310878.56
2_{As}	−1499666.21	−1499662.81	−1499662.21	−1499684.68
		Triplet state		
1_C	−120915.37	−120912.85	−120912.25	−120932.54
1_N	−131004.84	−131002.46	−131001.86	−131021.92
1_P	−310859.33	−310856.5	−310855.91	−310877.24
1_{As}	−1499663.1	−1499660.1	−1499659.5	−1499681.8
2_N	−130998.94	−130996.52	−130995.93	−131016.03
2_P	−310863.79	−310861.05	−310860.45	−310881.62
2_{As}	−1499668.2	−1499665.3	−1499664.7	−1499686.8

TABLE II Sum of Electronic and Thermal Energy Differences Between Singlet (s) and Triplet (t) states, ΔE_{s-t}; Electronic and Thermal Enthalpy Differences, ΔH_{s-t}; Electronic and Thermal Free Energy Differences, ΔG_{s-t}, at B3LYP/6-311++G for 1_X and 2_X (X = N, P, and As)**





$\mathbf{1_X}$ $\mathbf{2_X}$

X = N, P and As

Compound	ΔZPE_{s-t}	ΔE_{s-t}	ΔH_{s-t}	ΔG_{s-t}
$\mathbf{1_C}$	9.08	9.25	9.25	9.60
$\mathbf{1_N}$	7.88	8.00	8.00	8.50
$\mathbf{1_P}$	9.38	9.39	9.39	10.07
$\mathbf{1_{As}}$	13.82	13.90	13.90	14.43
$\mathbf{2_N}$	11.34	11.68	11.68	11.56
$\mathbf{2_P}$	2.84	3.26	3.26	3.07
$\mathbf{2_{As}}$	2.02	2.51	2.51	2.13

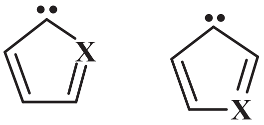
free energy gaps, ΔG_{t-s}, between singlet and triplet states of $\mathbf{1_X}$ and $\mathbf{2_X}$ were calculated at B3LYP/6-311++G** (Table II). Geometrical parameters including bond lengths (R), bond angle (A), and dihedral angle (D) were calculated at the B3LYP/6-311++G** level (Table III).

The DFT calculations indicated that the singlet states of $\mathbf{1_X}$ and $\mathbf{2_X}$ (except $\mathbf{2_{As}}$) are ground state with nonplanar conformation relative to their corresponding planar triplet states (Tables I–III). The ground state of $\mathbf{2_{As}}$ has a planar conformation.

Gibbs free energy, G, was selected for discussion. Gibbs free energy values, G, were compared between $\mathbf{1_X}$ and $\mathbf{2_X}$ (Table I). The stability of both singlet and triplet states of $\mathbf{1_N}$ (–8.95 and –5.89 kcal/mol, respectively) is more than $\mathbf{2_N}$, while the stability of both singlet and triplet states of $\mathbf{2_P}$ (–11.39 and –4.39) and $\mathbf{2_{As}}$ (–17.35 and –5.05) is more than corresponding $\mathbf{1_P}$ and $\mathbf{1_{As}}$ at the B3LYP/6-311++G** level, respectively. The stability slope for the singlet states of $\mathbf{1_N}$, $\mathbf{2_P}$, and $\mathbf{2_{As}}$ is more than their corresponding triplet states.

All triplet states of $\mathbf{1_X}$ and $\mathbf{2_X}$ are more stable than the related singlet state. ΔG_{s-t} between singlet and triplet states of $\mathbf{1_X}$ at the B3LYP/6-311++G** level were changed in the following order (in kcal/mol):

TABLE III Bond Lengths (Å), Bond Angles (degree), and Dihedral Angles (degree) at B3LYP/6-311++G for $\mathbf{1_X}$ and $\mathbf{2_X}$ (X = N, P, and As)**



$\mathbf{1_X}$ $\mathbf{2_X}$

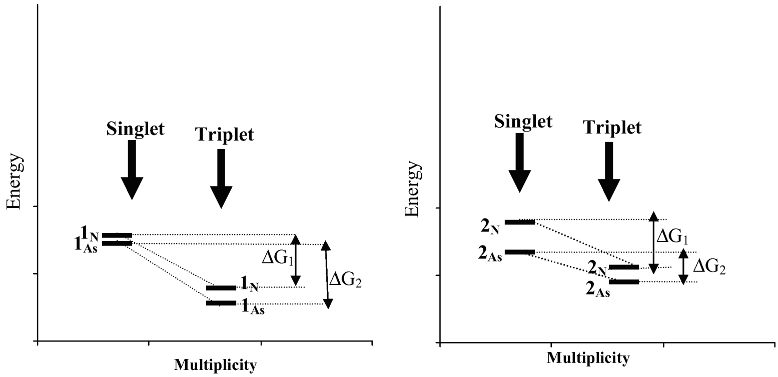
X = N, P and As

Compound	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	$R_{4,5}$	$R_{5,1}$	$A_{2,1,3}$	$D_{3,2,1,5}$	$D_{4,5,1,2}$
				Singlet state				
$\mathbf{1_C}$	1.39	1.40	1.47	1.37	1.43	116.7	31.2	30.2
$\mathbf{1_N}$	1.29	1.37	1.44	1.41	1.40	122.6	29.7	30.3
$\mathbf{1_P}$	1.70	1.81	1.43	1.39	1.38	131.9	27.4	30.6
$\mathbf{1_{As}}$	1.94	1.84	1.42	1.43	1.30	123.6	28.1	32.2
$\mathbf{2_N}$	1.34	1.37	1.38	1.38	1.39	127.7	10.5	9.0
$\mathbf{2_P}$	1.29	1.87	1.77	1.39	1.38	141.1	12.2	11.2
$\mathbf{2_{As}}$	1.27	2.06	1.90	1.38	1.39	146.5	0.1	0.1
				Triplet state				
$\mathbf{1_C}$	1.43	1.37	1.48	1.37	1.43	112.9	0.0	0.0
$\mathbf{1_N}$	1.30	1.37	1.45	1.37	1.47	114.6	0.0	0.0
$\mathbf{1_P}$	1.83	1.77	1.38	1.47	1.34	115.3	0.0	0.0
$\mathbf{1_{As}}$	1.95	1.92	1.36	1.47	1.34	114.6	0.0	0.0
$\mathbf{2_N}$	1.47	1.31	1.40	1.42	1/37	109.0	0.0	0.0
$\mathbf{2_P}$	1.35	1.80	1.82	1.35	1.46	119.3	0.0	0.0
$\mathbf{2_{As}}$	1.33	1.94	1.95	1.35	1.47	122.0	0.0	0.0

$\mathbf{1_{As}}$ (14.43) > $\mathbf{1_P}$ (10.07) > $\mathbf{1_{CH}}$ (9.60) > $\mathbf{1_N}$ (8.50). ΔG_{s-t} of $\mathbf{2_X}$ at the B3LYP/6-311++G** level were changed in the following order (in kcal/mol): $\mathbf{2_N}$ (11.56) > $\mathbf{2_{CH}}$ (9.60) > $\mathbf{2_P}$ (3.07) > $\mathbf{2_{As}}$ (2.13) (Table II).

Whether increasing the stability of the singlet or increasing the instability of the triplet state is responsible for decreasing the ΔG_{s-t}, it could be explained by comparing relative energies between various singlet and triplet states (Figure 1). With respect to relative energies, one concludes that increased instability for singlet state of $\mathbf{1_X}$ from X = N to X = As is responsible to obtain a higher ΔG_{s-t} (Figure 1a). In contrast, the increased stability for singlet state of $\mathbf{2_X}$ from X = N to X = As is responsible to gain a lower ΔG_{s-t} (Figure 1b).

Instability for the singlet state of $\mathbf{1_X}$ with replacement of heavy heteroatom (from X = N to X = As) could reasonably be explained by the following factors. A lower electronegativity of X increases the bond



(a) (b)

Figure 1 a) Diagram of energy vs. multiplicity of $\mathbf{1_X}$. b) Diagram of energy vs. multiplicity of $\mathbf{2_X}$.

length :C—X. Therefore, the 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 the stability of the singlet state. Another factor is the polarity of the : C—X bond. The :C–C bond in $\mathbf{1_{CH}}$ is nearly nonpolar, but the :C—X bond at $\mathbf{1_{As}}$ is strongly polarized in the direction $:C^-–X^+$. A strongly polarized bond leads to destabilization of the singlet state.

Stability for the singlet state of $\mathbf{2_X}$ with replacement of the heavy heteroatom (from X = N to X = As) could be explained by ring electron resonance. Ring electron resonance for both the singlet and triplet states of $\mathbf{2_N}$ are similar, while for the singlet state of $\mathbf{2_{As}}$ is more than triplet state. Therefore, $\Delta G_{s\text{–}t}$ of $\mathbf{2_X}$ decreases from X = N to X = As.

Bond lengths (R) at $\mathbf{1_X}$ and $\mathbf{2_X}$ indicates that all bonds :C-X (X=P and As) tend to have a single bond (Table III). Heavy atoms at single bond are more stable than at the double bond. The stability of heavy atoms at single bonds of $\mathbf{1_X}$ and $\mathbf{2_X}$ has been reported by Kutzelnigg[2]: "Single bonds between 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." Therefore, P and As atoms construct a weak double bonds and leads to construct a single bond at $\mathbf{1_X}$ and $\mathbf{2_X}$.

CONCLUSION

Heteroatom effects were investigated on singlet–triplet energy gaps of divalent five-membered ring XC_3H_3C, $\mathbf{1_X}$ and $\mathbf{2_X}$ (X=CH, N, P and As) at the B3LYP/6-311++G** level. All triplet states of $\mathbf{1_X}$ and $\mathbf{2_X}$ are more stable than the related singlet state. ΔG_{s-t} between singlet and triplet states of $\mathbf{1_X}$ were changed in the following order (in kcal/mol): $\mathbf{1_{As}}$ (14.43) > $\mathbf{1_P}$ (10.07) > $\mathbf{1_{CH}}$ (9.60) > $\mathbf{1_N}$ (8.50). While, ΔG_{s-t} of $\mathbf{2_X}$ were changed in the order: $\mathbf{2_N}$ (11.56) > $\mathbf{2_{CH}}$ (9.60) > $\mathbf{2_P}$ (3.07) > $\mathbf{2_{As}}$ (2.13). With respect to relative energies, one concludes that increased instability for singlet state of $\mathbf{1_X}$ from X = N to X = As is responsible to obtain a higher ΔG_{s-t}. In contrast, the increased stability for singlet state of $\mathbf{2_X}$ from X = N to X = As is responsible to gain a lower ΔG_{s-t}.

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