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## SHORT COMMUNICATION

# ELECTRONIC EFFECTS AT α-POSITION OF DIVALENT FIVE-MEMBERED RING CARBENES: SINGLET-TRIPLET ENERGIES THROUGH DFT CALCULATIONS

E. Vessally*

Payame Noor University (PNU), Zanjan, Iran

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**ABSTRACT.** 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 G–$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$, –$NO_2$) were calculated at B3LYP/6-311++G** level of theory. DFT calculations indicated that electron donating substituents (G = –$NH_2$, –OH and –$CH_3$) at α position cause to decrease $\Delta G_{s-t}$ and electron withdrawing substituents (G = –F, –Cl, –Br, –$CF_3$ and –$NO_2$) lead to increase the $\Delta G_{s-t}$ of G-$C_4H_3C$. Nuclear independent chemical shifts (NICS) calculations were carried out to determine the aromatic character.

**KEY WORDS:** DFT calculations, Electronic effects, Singlet-triplet energies, Carbene, Five-membered, NICS

## INTRODUCTION

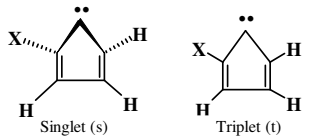
Divalent carbenes and their analogues are strongly reactive [1]. The carbenes have played important roles as transient intermediates and powerful reagents [2]. Recently, carbenes have been used as ligand in the preparation of special complexes [3]. The cyclic completely conjugated species have important 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]. However, non-planar conformers have been obtained for the most of these singlet cyclic conjugated carbenes through theoretical studies [4]. The isolation of the stable five membered cyclic conjugated carbene has firstly been reported by Arduengo [9]. *Ab initio* calculations have been carried out for determination of the stability and singlet-triplet energy gaps five membered cyclic conjugated carbene and their heavy analogues [4,10]. Follow up on our works [10], in this manuscript, the singlet-triplet gaps of divalent five-membered ring G-$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$, –$NO_2$) was discussed. The aromatic character of G–$C_4H_3C$ was determined through NICS calculations [11]. The concept of NICS was introduced by Schleyer *et al.* in 1996 as a measure of aromaticity and antiaromaticity (or non-aromaticity) [11a]. It is based on a probe with no basis functions (bq) which is placed at or above the geometrical center of a conjugated ring. Its calculated isotropic NMR chemical shift indicates the aromatic properties of the ring, either as an individual moiety in a polycyclic compound or as a molecule. Initially the probe was placed at the geometrical center of the molecules, but after realizing that in some systems the chemical shifts are influenced by the σ-system (e.g. cyclopropane) it was placed 0.5 Å above the center (denoted as NICS (0.5)). The method has been used for the assignment of aromatic character in many systems, generally very successfully.

The correlation between the aromatic character and the stability was investigated for G–$C_4H_3C$.

*Corresponding author. E-mail: e_vesali@yahoo.com

## COMPUTATIONAL METHODS

Full geometry optimizations of G–$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$, –$NO_2$) were carried out by Density Functional Theory (DFT) method using 6-311++G** basis set at GAUSSIAN 98 program [12-14] (Figure 1). All calculations were carried out for gas phase at 298 Kº temperature and 1atm pressure. All possible conformations of the given species were examined to find a global minimum. This is for obtaining more accurate values of thermal energies (E) enthalpies (H) and Gibbs free energies (G).




**X = -$NH_2$, -OH, -$CH_3$, -H, -F, -Cl, -Br, -$CF_3$, -$NO_2$**

Figure 1. Singlet and triplet states of G–$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$ and –$NO_2$).

## RESULTS AND DISCUSSION

The thermal energies (E), enthalpies (H) and Gibbs free energies (G) were calculated for divalent five membered cyclic conjugated structures G–$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$, –$NO_2$) at HF/6-311G**, HF/6-311++G** and B3LYP/6-311++G** levels of theory. 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 G-$C_4H_3C$ were calculated (Table 1). Geometrical parameters including bond lengths (R), bond angle (A) and dihedral angle (D) were calculated (Figure 2). Considering the size of molecules probed, and the consistency of the results obtained, the mentioned *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**) are reported.

Table 1. Thermal energy gaps between singlet (s) and triplet (t) states, $\Delta E_{s-t}$; thermal enthalpy gaps, $\Delta H_{s-t}$; Gibbs free energy gap, $\Delta G_{s-t}$, in kcal/mol, at B3LYP/6-311++G** for G–$C_4H_3C$ (in where G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$, –$NO_2$).

| G–$C_4H_3C$ | $\Delta E_{s-t}$ | $\Delta H_{s-t}$ | $\Delta G_{s-t}$ |
|---|---|---|---|
| G = –$NH_2$ | 5.09 | 5.09 | 6.07 |
| G = –OH | 8.44 | 8.44 | 9.12 |
| G = –$CH_3$ | 9.09 | 9.09 | 9.47 |
| G = –H | 9.15 | 9.15 | 9.50 |
| G = –F | 12.71 | 12.71 | 13.34 |
| G = –Cl | 11.74 | 11.74 | 12.21 |
| G = –Br | 11.23 | 11.23 | 11.75 |
| G = –$CF_3$ | 9.86 | 9.86 | 10.26 |
| G = –$NO_2$ | 10.20 | 10.20 | 10.59 |

DFT calculations indicated that all singlet states of G–$C_4H_3C$ are ground state with non-planar conformer relative to its corresponding planar triplet state (Figure 1 and 2).

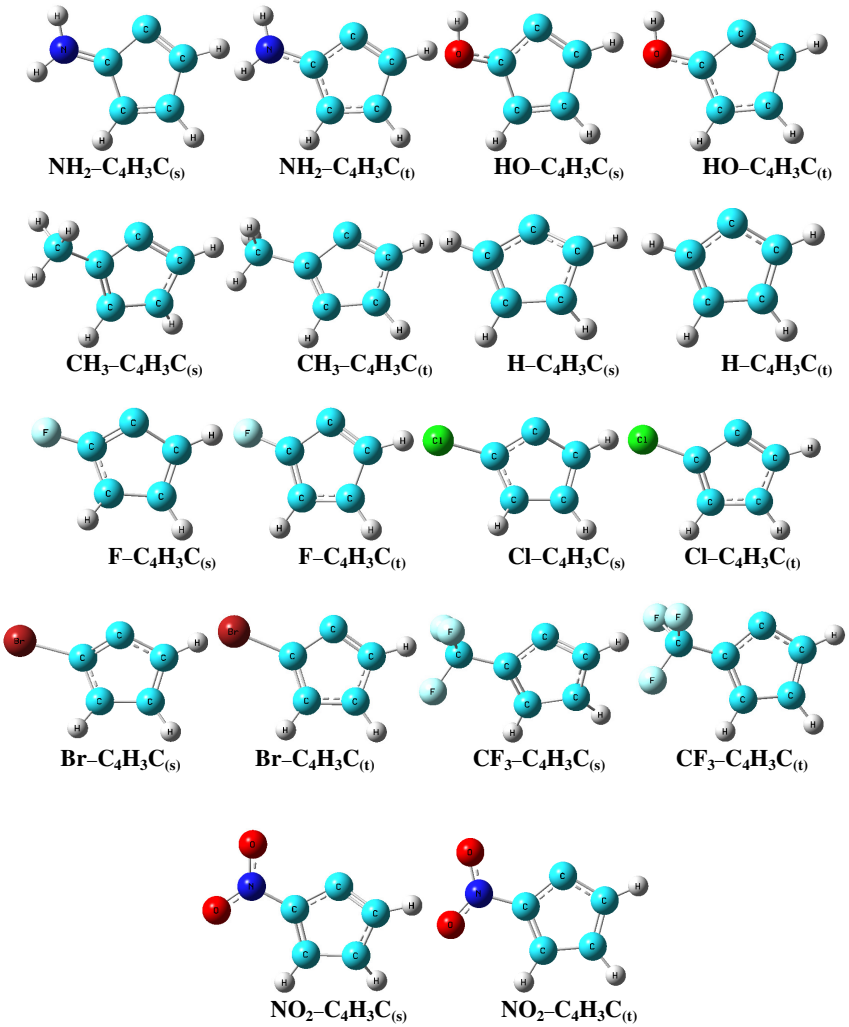


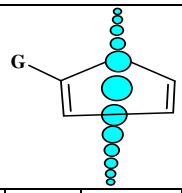

Figure 2. Bond length types of singlet and triplet states of G–$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$ and –$NO_2$).

DFT calculations specified that all triplet states of G–$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$ and –$NO_2$) are more stable than their corresponding singlet states. DFT calculations indicated that the electron donating substituents (G = –$NH_2$, –OH and –$CH_3$) at α-position of G–$C_4H_3C$ cause to decrease $\Delta G_{s-t}$ and electron withdrawing substituents (G = –F, –Cl, –Br, –$CF_3$ and –$NO_2$) lead to increase $\Delta G_{s-t}$. Therefore, replacement of substituents (G) at α-position of G–$C_4H_3C$ from electron donating toward electron withdrawing groups lead to increase the $\Delta G_{s-t}$. $\Delta G_{s-t}$ of G–$C_4H_3C$ was changed, in kcal/mol, in the order: –F (13.34) > –Cl (12.21) > –Br (11.75) > –$NO_2$ (10.59) > –$CF_3$ (10.26) > –H (9.50) > –$CH_3$ (9.47) > –OH (9.12) > –$NH_2$ (6.07). Whether increase the stability of singlet or the instability of triplet state is responsible to decrease the $\Delta G_{s-t}$, could be explained by comparison of the relative energies

between various singlet and triplet states. Relative energy analysis reveals that substitution of electron donating groups at α-position of G–$C_4H_3C$ leads to stability of singlet state (respect to their corresponding triplet state) while substitution of electron withdrawing groups leads to instability of singlet state (respect to their corresponding triplet state).

The stability for singlet and triplet states of G–$C_4H_3C$ may be related to the aromatic character of carbenic ring. Therefore, the aromatic character for both singlet and triplet states of G–$C_4H_3C$ determined through magnetic criterion (Table 2). Nuclear independent chemical shifts (NICS) calculation procedure is the most important magnetic criterion for the determination of the aromatic character. The NICS calculations were carried out for both singlet and triplet states of G–$C_4H_3C$. NICS with negative and positive signs have aromatic and anti-aromatic character, respectively. It has been reported that NICS (0.5) give more reliable results [11]. NICS (0.5) calculations reveal that singlet state of $NH_2$–$C_4H_3C$ and OH–$C_4H_3C$ have an anti-aromatic character while singlet state of $NO_2$–$C_4H_3C$ have an aromatic character in the carbenic ring. Furthermore, NICS (0.5) calculations indicate that triplet state of G–$C_4H_3C$ (except for $NH_2$–$C_4H_3C$) have more or less anti-aromatic character in the carbenic ring. Therefore, it can be concluded that the aromatic and/or anti-aromatic character can not play a significant role on the stability of singlet states or on the singlet-triplet gaps.

Table 2. NICS calculations for aromatic character determination of singlet (s) and triplet (t) states of G–$C_4H_3C$ (where G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$, –$NO_2$) at B3LYP/6-311++G** level.




| G–$C_4H_3C$ | NICS (0) | NICS (0.5) | NICS (1.0) | NICS (1.5) | NICS (2.0) | NICS (2.5) |
|---|---|---|---|---|---|---|
| G = –$NH_2$(s) | 19.51 | 20.01 | 12.74 | 5.78 | 2.49 | 1.08 |
| G = –OH(s) | 24.64 | 25.21 | 16.58 | 7.98 | 3.70 | 1.79 |
| G = –$CH_3$(s) | -0.53 | 1.32 | 0.81 | -0.14 | -0.34 | -0.52 |
| G = –H(s) | -0.92 | 1.03 | 0.29 | -0.29 | -0.31 | -0.23 |
| G = –F(s) | 2.74 | 3.86 | 2.00 | 0.66 | 0.21 | 0.08 |
| G = –Cl(s) | 2.62 | 3.72 | 1.89 | 0.57 | 0.15 | 0.04 |
| G = –Br(s) | 2.48 | 3.27 | 1.48 | 0.33 | 0.01 | -0.05 |
| G = –$CF_3$(s) | -3.06 | -0.07 | -0.31 | -0.83 | -0.68 | -0.45 |
| G = –$NO_2$(s) | -7.33 | -7.86 | -4.46 | -2.81 | -1.76 | -1.10 |
| | | | | | | |
| G = –$NH_2$(t) | -0.80 | 0.90 | 0.94 | 0.02 | -0.26 | -0.28 |
| G = –OH(t) | 2.04 | 4.48 | 3.87 | 1.68 | 0.62 | 0.20 |
| G = –$CH_3$(t) | 8.74 | 10.13 | 7.29 | 3.42 | 1.52 | 0.69 |
| G = –H(t) | 9.12 | 10.49 | 7.58 | 3.60 | 1.60 | 0.71 |
| G = –F(t) | 5.78 | 8.34 | 6.73 | 3.28 | 1.47 | 0.67 |
| G = –Cl(t) | 7.97 | 9.76 | 7.32 | 3.52 | 1.58 | 0.71 |
| G = –Br(t) | 8.56 | 10.27 | 7.63 | 3.67 | 1.63 | 0.73 |
| G = –$CF_3$(t) | 6.84 | 8.02 | 5.53 | 2.39 | 0.97 | 0.39 |
| G = –$NO_2$(t) | 5.73 | 7.35 | 5.44 | 2.42 | 0.97 | 0.35 |
| Benzene | -8.05 | -9.87 | -10.23 | -7.61 | -4.87 | -3.04 |

## CONCLUSIONS

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 G–$C_4H_3C$ (G = –$NH_2$, –OH, –$CH_3$, –F, –Cl, –Br, –H, –$CF_3$, –$NO_2$) were calculated at B3LYP/6-311++G** level of theory. DFT calculations indicated that electron donating substituents (G = –$NH_2$, –OH and –$CH_3$) at α-position cause to decrease $\Delta G_{s-t}$ and electron withdrawing substituents (G = –F, –Cl, –Br, –$CF_3$ and –$NO_2$) lead to increase the $\Delta G_{s-t}$ of G–$C_4H_3C$. NICS (0.5) calculations reveal that singlet state of $NH_2$–$C_4H_3C$ and OH–$C_4H_3C$ have an antiaromatic character while singlet state of $NO_2$–$C_4H_3C$ have aromatic character in the carbenic ring. NICS (0.5) calculations indicate that triplet state of G–$C_4H_3C$ (except for $NH_2$–$C_4H_3C$) have more or less antiaromatic character in the carbenic ring. Therefore, it can be concluded that the aromatic and/or antiaromatic character can not play a significant role on the stability of singlet states or on the singlet-triplet gaps.

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