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Conformational Studies on Aryl-cyclopentadienylidenes: Electronic Effects of Aryl Groups

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The total energy, E_T; zero-point energy, thermal energies (E), enthalpies (H) and Gibbs free energies (G) were calculated for aryl substituted divalent five membered cyclic compounds Ar-C_4H_3G (G = $-NH_2$, –OH, $-CH_3$, –F, –Cl, –Br, –H, $-CF_3$ and $-NO_2$) at B3LYP/6–31+G* and B3LYP/6–311++G** levels of theory. It could be concluded that an allenic character was constructed instead of carbenic character for both singlet and triplet states of Ar-C_4H_3G.

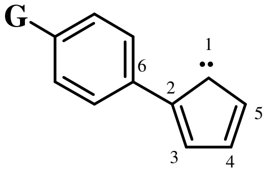
Key Words: Carbene, Cyclopentadienylidenes, Singlet-triplet gap, Electronic effects.

INTRODUCTION

Divalent carbenes and their analogues are strongly reactive[1]. The cyclic completely conjugated species are important in the chemistry of divalent carbene intermediates[2]. These divalent structures were formerly described in terms of the Huckel 4n + 2 rule[3]. However, non-planar isomers are found energy minima for most of these singlet cyclic conjugated carbenes through semi-empirical studies[4]. The isolation of the stable five membered cyclic conjugated carbene is first reported Su and Chu[5] and Arduengo *et al.*[6]. Since most of divalent carbenes and their analogues are unstable, theoretical calculation was required for analysis their properties. As a continuation of our studies[2,7-10], in this manuscript, the conformational studies was carried out on aryl-cyclopentadienylidenes Ar–C_4H_3G (G = $-NH_2$, –OH, $-CH_3$, –F, –Cl, –Br, –H, $-CF_3$ and $-NO_2$).

EXPERIMENTAL

Full geometry optimizations of Ar–C_4H_3G (G = $-NH_2$, -OH, $-CH_3$, -F, -Cl, -Br, -H, $-CF_3$ and $-NO_2$) were carried out by DFT method using 6-311++G** basis set of the GAUSSIAN 98 system of programs[11-13] (**Scheme-I**). To find a global minimum on a specific surface, all possible conformations of the given species were examined through scanning the specific dihedral angles at B3LYP/6-311++G** level. This was for obtaining more accurate values of thermal energies (E) enthalpies (H) and Gibbs free energies (G). Freq keyword was used for obtaining zero-point energies (ZPE), thermal energies (E), enthalpies (H) and Gibbs free energies (G).



G = -NH$_2$, -OH, -CH$_3$, -F, -Cl, -Br, -H, -CF$_3$ and -NO$_2$

Scheme-I: Electron donating substituents (G = –NH$_2$, –OH, –CH$_3$, –F, –Cl and –Br) and electron withdrawing substituents (G = –CF$_3$ and –NO$_2$) of cyclopentadienylidenes

RESULTS AND DISCUSSION

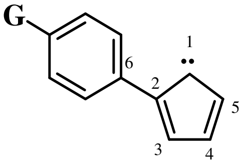
The total energy, E_T; zero-point energy, thermal energies (E), enthalpies (H) and Gibbs free energies (G) were calculated for aryl substituted divalent five membered cyclic compounds Ar-C_4H_3G (G = –NH$_2$, –OH, –CH$_3$, –F, –Cl, –Br, –H, –CF$_3$ and –NO$_2$) at B3LYP/6-31+G* and B3LYP/6-311++G** levels 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 sake of brevity, only the data acquired through B3LYP/6-311++G** level of theory (**Scheme-I** and Table-1). Geometrical parameters including bond lengths (R), bond angle (A) and dihedral angle (D) were calculated at B3LYP/6-311++G** level (Tables 2 and 3). The DFT calculations indicate that all singlet state of Ar–C_4H_3G is ground state with non-planar conformer while all triplet state of Ar–C_4H_3G is ground state with planar conformer (Table-1). DFT calculations specify that all triplet states of Ar-C_4H_3G (G = –NH$_2$, –OH, –CH$_3$, –F, –Cl, –Br, –H, –CF$_3$ and –NO$_2$) is more stable than their corresponding singlet states.

B3LYP/6-311++G** calculations indicated that bond length C_1–C_2 for singlet states of Ar-C_4H_3G increase with substitution of electron donating groups while decrease with substitution of electron withdrawing groups at phenyl group (Table-2). The bond length of C_1–C_2 is higher with respect to C_1–C_5 for both singlet and triplet states of Ar–C_4H_3G. Comparison between C_1–C_2 and C_1–C_5 show that a double bond was formed between C_1 and C_5. Therefore, it could be concluded that an allenic character was constructed instead of carbenic character for both singlet and triplet states of Ar–C_4H_3G. Allenic character was not significantly affected by substitution of electron withdrawing or electron donating groups at phenyl group.

Bond angle $\angle A_{2,1,5}$ for singlet states of Ar–C_4H_3G is more than for triplet state (Table-3). This is inconsistent for acyclic carbenes. DFT calculations indicated that bond angle $\angle A_{2,1,5}$ for both singlet and triplet states of Ar–C_4H_3G was increased through replacement of electron withdrawing groups at phenyl group.

DFT calculations specified that dihedral angle $\angle D_{2,1,5,4}$ for singlet states of Ar–C_4H_3G decrease with substitution of electron donating groups while increase with substitution of electron withdrawing groups at phenyl group (Table-3). Therefore, TABLE-1

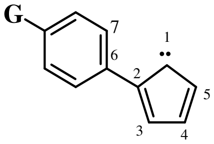
SUM OF TOTAL ENERGY (E_T), ZERO POINT ENERGY (ZPE), THERMAL ENERGY (E), THERMAL ENTHALPY (H), THERMAL FREE ENERGY (G) AT B3LYP/6-311++G** FOR BOTH SINGLET (s) AND TRIPLET (t) STATES of Ar-C_4H_3G



Compound	Singlet state				
	E_T kcal/mol	ZPE kcal/mol	E kcal/mol	H kcal/mol	G kcal/mol
G=-NH_2	-300664.770	-300561.822	-300555.492	-300554.899	-300584.125
G=-OH	-313140.845	-313045.675	-313039.531	-313038.939	-313067.886
G=-CH_3	-290586.575	-290467.262	-290460.681	-290460.089	-290490.863
G=-F	-328221.282	-328133.808	-328127.919	-328127.327	-328155.915
G=-Cl	-554344.482	-554257.854	-554251.723	-554251.130	-554280.541
G=-Br	-1880829.451	-1880743.234	-1880736.933	-1880736.340	-1880766.608
G=-H	-265925.150	-265832.531	-265827.162	-265826.569	-265853.839
G=-CF_3	-477483.876	-477379.765	-477372.091	-477371.498	-477405.345
G=-NO_2	-394287.832	-394185.263	-394178.270	-394177.677	-394209.309
Compound	Triplet state				
	E_T kcal/mol	ZPE kcal/mol	E kcal/mol	H kcal/mol	G kcal/mol
G=-NH_2	-300675.569	-300572.565	-300566.270	-300565.677	-300595.460
G=-OH	-313150.951	-313055.897	-313049.753	-313049.160	-313078.771
G=-CH_3	-290596.375	-290476.962	-290470.381	-290469.789	-290500.462
G=-F	-328230.926	-328143.661	-328137.763	-328137.171	-328166.433
G=-Cl	-554353.987	-554267.501	-554261.384	-554260.792	-554290.812
G=-Br	-1880838.953	-1880752.911	-1880746.614	-1880746.021	-1880776.929
G=-H	-265934.631	-265842.168	-265836.809	-265836.216	-265864.107
G=-CF_3	-477492.728	-477388.518	-477380.844	-477380.251	-477414.098
G=-NO_2	-394296.463	-394193.795	-394186.802	-394186.209	-394217.842

TABLE-2

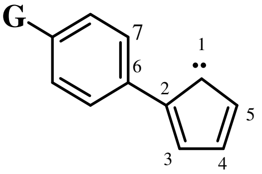
BOND LENGTHS (Å), AT B3LYP/6-311++G** FOR Ar–C_4H_3C



Compound	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	$R_{4,5}$	$R_{5,1}$	$R_{2,6}$
G = –NH_2	1.466	1.378	1.443	1.422	1.375	1.442
G = –OH	1.462	1.375	1.449	1.419	1.376	1.446
G = –CH_3	1.458	1.375	1.450	1.418	1.376	1.448
G = –F	1.457	1.373	1.453	1.416	1.376	1.450
G = –Cl	1.456	1.374	1.453	1.416	1.375	1.449
G = –Br	1.456	1.374	1.453	1.416	1.376	1.449
G = –H	1.456	1.374	1.453	1.416	1.376	1.450
G = –CF_3	1.454	1.374	1.455	1.414	1.375	1.449
G = –NO_2	1.453	1.3755	1.454	1.414	1.374	1.446

G = $-NH_2$	1.460	1.427	1.387	1.467	1.348	1.428
G = –OH	1.468	1.420	1.391	1.466	1.347	1.433
G = $-CH_3$	1.473	1.414	1.396	1.463	1.347	1.436
G = –F	1.475	1.410	1.400	1.461	1.348	1.438
G = –Cl	1.476	1.408	1.401	1.460	1.348	1.437
G = –Br	1.476	1.408	1.402	1.460	1.348	1.438
G = –H	1.476	1.408	1.401	1.460	1.348	1.439
G = $-CF_3$	1.481	1.396	1.414	1.450	1.352	1.442
G = $-NO_2$	1.483	1.390	1.423	1.441	1.356	1.442

TABLE-3
BOND ANGLE (DEGREE) AND DIHEDRAL ANGLE (DEGREE)
AT B3LYP/6-311++G (3df, 2p) FOR Ar-C_4H_3G



Compound	$A_{2,1,5}$	$D_{2,1,5,4}$	$D_{1,2,6,7}$
G = $-NH_2$	113.352	29.353	15.486
G = –OH	114.263	30.310	15.884
G = $-CH_3$	115.002	30.846	15.801
G = –F	115.140	31.056	16.178
G = –Cl	115.298	31.127	15.756
G = –Br	115.333	31.168	15.818
G = –H	115.380	31.170	15.997
G = $-CF_3$	115.848	31.471	15.746
G = $-NO_2$	116.102	31.605	14.510
G = $-NH_2$	112.330	–0.010	–0.142
G = –OH	112.331	–0.013	0.030
G = $-CH_3$	112.352	–179.989	–0.139
G = –F	112.357	0.006	0.000
G = –Cl	112.346	0.041	–0.027
G = –Br	112.351	0.057	–0.036
G = –H	112.380	0.010	0.054
G = $-CF_3$	112.460	–0.005	–0.007
G = $-NO_2$	112.520	0.003	0.000

for singlet states of Ar–C_4H_3G, the electron donating groups lead to less puckered conformer. Dihedral angle $\angle D_{1,2,6,7}$ for singlet states of Ar–C_4H_3G decrease more or less with both electron donating and electron withdrawing groups at phenyl group.

Conclusion

B3LYP/6-311++G** calculations indicated that bond length C_1–C_2 for singlet states of Ar–C_4H_3G increase with substitution of electron donating groups while decrease with substitution of electron withdrawing groups at phenyl group.

Comparison between C_1–C_2 and C_1–C_5 show that a double bond was formed between C_1 and C_5. Therefore, it could be concluded that an allenic character was constructed instead of carbenic character for both singlet and triplet states of Ar–C_4H_3G. Allenic character was not significantly affected by substitution of electron withdrawing or electron donating groups at phenyl group.

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