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Alkyl Substituted Effects on Carbenes: DFT *ab initio* Calculations

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Full geometry optimizations are carried out on alkyl substituted acyclic carbene by B3LYP method using 6-311++G** basis set of the Gaussian 98 system of program. For methylene (CH_2) and ethylidene (CH_3CH), the triplet state is ground state while for propylidene and other large substituted acyclic carbenes, the singlet state is ground state. By comparing NBO charges on methylenic carbon of CH_2 and other large substituted acyclic carbenes, the role of methyl group is electron withdrawing more than hydrogen atom. Higher electronegatively of methyl group leads to stabilize the singlet respect to triplet state as well as decreasing the singlet-triplet splitting energies.

Key Words: Carbene, Alkyl effects, Singlet-triplet state, DFT, *ab initio* calculations.

INTRODUCTION

Highly reactive intermediates, carbenes, have attracted much attention in organic chemistry[1-10]. The reactivity of carbenes can be understood in terms of their electronic structure; singlet (σ^2 and/or π^2 configurations) and triplet ($\sigma\pi$ configuration) states. The trends in the reactivity of carbenes can be recognized through determination of their singlet-triplet splitting. For both the triplet and the singlet states, the π orbital is essentially a pure *p*-like orbital while the σ orbital is a hybrid of *s*- and *p*-like atomic orbital. Thus, σ orbital with increased *p* character favour a triplet ground state while the σ orbital with increased *s* character favour singlet. The singlet state should be stabilized by substituents that are electronegative and/or have electron pairs that can be donated *via* hyper-conjugation to the empty σ orbital. The triplet state, on the other hand, should be stabilized by substituents that are bulky and/or electroposotive. It is of interest to compare the singlet-triplet splitting in the various carbenes. Our goal in the present work is to obtain quantitative information on the magnitude of singlet-triplet splitting in the simple acyclic carbenes.

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EXPERIMENTAL

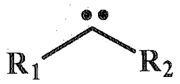
Geometry optimizations are carried out by B3LYP[11,12] method using 6-311++G** basis set of the Gaussian 98 system of program[13]. In order to find energy minima, keyword "FOPT" are used. This keyword requests that a geometry optimization be performed. The geometry will be adjusted until a stationary point on the potential surface is found. Here, the Berny algorithm is employed for all minimizations using reduntant internal coordinates[14]. For minimum state structures, only real frequency values are accepted. For singlet states, the restricted RBecke3LYP is used while the unrestricted UBecke3LYP is used for triplet states.

RESULTS AND DISCUSSION

Full geometry optimizations are carried out by B3LYP method using 6-311++G** basis set of the Gaussian 98 system of program. Our goal in the present work is to obtain quantitative information on the magnitude of singlet-triplet splitting in the simple acyclic carbenes. Since the trends in the reactivity of carbenes are attributed to the singlet-triplet splitting, we calculated the singlet-triplet splitting for simple acyclic carbenes: C_nH_{2n} (n = 1-9). The total energies and energy differences between singlet and their corresponding triplet states, $\Delta E_{(t-s)}$ are calculated using B3LYP/6-311++G** level of theory (**Scheme-1** and Table-1). Since the lowest energy geometry for both singlet and triplet states is found to be the *trans* configuration, we focus our attention on *trans* configurations for all of C_nH_{2n} (n = 1-9) compounds.

TABLE-1
CALCULATED B3LYP/6-311++G** TOTAL ENERGIES AND ENERGY DIFFERENCES BETWEEN SINGLET AND THEIR CORRESPONDING TRIPLET STATES, $\Delta E_{(t-s)}$ FOR ACYCLIC CARBENES, C_nH_{2n} (n = 1-9)

Compound	Singlet state			Triplet state			Singlet-triplet splitting (kcal/mol)
	Zero point energy (kcal/mol)	Total energy (Hartree)	Total energy (kcal/mol)	Zero point energy (kcal/mol)	Total energy (Hartree)	Total energy (kcal/mol)	
CH_2	10.356	-39.147	-24554.330	10.754	-39.166	-24566.092	-11.762
C_2H_4	29.169	-78.495	-49226.439	29.407	-78.502	-49231.107	-4.668
C_3H_6	47.093	-117.838	-73896.856	47.482	-117.838	-73896.109	0.747
C_4H_8	64.944	-157.164	-98556.128	65.619	-157.161	-98553.858	2.270
C_5H_{10}	82.795	-196.490	-123215.258	83.617	-196.485	-123211.855	3.403
C_6H_{12}	100.646	-235.814	-147873.698	101.439	-235.810	-147870.393	3.305
C_7H_{14}	118.361	-275.139	-172532.243	119.220	-275.135	-172528.889	3.354
C_8H_{16}	136.079	-314.463	-197190.718	136.995	-314.459	-197187.309	3.409
C_9H_{18}	153.864	-353.787	-221849.137	154.754	-353.783	-221845.740	3.397



Scheme-I: Alkyl substituted simple acyclic carbenes

Methylene (CH_2) is a ground state triplet with the singlet lying -11.762 kcal/mol higher in energy while substituting of a methyl group (CH_3CH) reduce the singlet-triplet splitting (-4.668 kcal/mol). Nevertheless, the triplet state is ground state for ethylidene (CH_3CH). Substituting of two methyl groups on methylenic center leads to reducing the singlet-triplet splitting (0.747 kcal/mol) where the singlet state is ground state. Substituting of three and four methyl groups on methylenic center (C_4H_8 and C_5H_{10}) leads to rising the singlet-triplet splitting (2.270 and 3.403 kcal/mol), respectively) with singlet ground state. The singlet-triplet splitting does not significantly change with substituting of more methyl groups on methylenic center (from C_6H_{12} to C_9H_{18}).

The geometrical parameters including bond lengths (R_1-R_3) and bond angle (A_1) of singlet and triplet states for C_nH_{2n} (n = 1-9) is presented (Table-2). By compare CH_3CH with CH_2, the substitution of a methyl group has only a small effect on the bond angle (4-5°) and that the C–H bond length *ca.* 0.00 Å, suggesting that CH_3 does not be exert much steric repulsion. This is inconsistent to the other homologues C_nH_{2n} (n = 3-9).

TABLE-2
CALCULATED B3LYP/6-311++G** BOND LENGTHS (R_1-R_3) AND BOND ANGLE (A_1) OF SINGLET AND TRIPLET STATES FOR ACYCLIC CARBENES, C_nH_{2n} (n = 1-9)

Compound	Singlet state			Triplet state		
	$R_{1,2}$	$R_{1,3}$	A_{213}	$R_{1,2}$	$R_{1,3}$	A_{213}
CH_2	1.114	1.114	101.502	1.080	1.080	135.375
C_2H_4	1.455	1.110	106.323	1.464	1.083	134.888
C_3H_6	1.471	1.471	112.641	1.468	1.468	133.731
C_4H_8	1.467	1.473	112.928	1.472	1.470	134.063
C_5H_{10}	1.469	1.469	113.265	1.472	1.472	134.532
C_6H_{12}	1.468	1.468	113.265	1.471	1.473	134.587
C_7H_{14}	1.468	1.468	113.265	1.471	1.471	134.725
C_8H_{16}	1.468	1.468	113.265	1.471	1.472	134.615
C_9H_{18}	1.469	1.469	113.214	1.472	1.472	134.560

In particular, singlet CH_2 exhibits larger bond lengths than triplet CH_2. It is obvious that the singlet states of carbenes generally utilize more *p* character in their bonds, which results in smaller H–C–H bond angles. Decreased bond angles produce greater repulsion between the substituents, which is in turn reduced by lengthening the bonds. For ethylidene, the bond length (CH_3C–H) of singlet exhibits larger than triplet state while the bond length (CH_3–CH) of triplet is larger than singlet state. Substituting of more methyl groups on methylenic center C_nH_{2n} (n = 3-9) reveal that the bond length (CH_2–C) of triplet is larger than singlet state.

B3LYP/6-311++G** NBO charges on methylenic center (C_1) is calculated for singlet and triplet states of C_nH_{2n} (Table-3). By comparing NBO charges on methylenic carbon of CH_2 and CH_3CH for singlet state, the methyl groups donates less electrons than does H to the methylenic carbon, consistent with most electronegativity of methyl group compared to hydrogen atom. This is in contrast to the conventional concept that the methyl group is more electron rich and has electron donating nature. Substituting of more methyl groups on methylenic center C_nH_{2n} (n = 2-7) show the increasing charge on C_1. The dipole moments also decrease with substituting of CH_3 groups on methylenic center suggesting an electron withdrawing character for CH_3 group with respect to hydrogen atoms. For triplet state, substituting of methyl groups on methylenic center C_nH_{2n} (n = 1-9) slightly increase charge on the C_1 atom with respect to singlet state.

TABLE-3
CALCULATED B3LYP/6-311++G** NBO CHARGES ON ATOMS AND DIPOLE MOMENT OF SINGLET AND TRIPLET STATES FOR ACYCLIC CARBENES, C_nH_{2n} (n = 1-9)

Compound	Singlet state				Triplet state			
	Charge on C1	Charge on C2 (H2)	Charge on C3 (H3)	Dipole	Charge on C1	Charge on C2 (H2)	Charge on C3 (H3)	Dipole
CH_2	-0.1118	0.0559	0.0559	2.0620	0.9071	0.0464	0.0464	0.6899
C_2H_4	-0.0398	-0.7303	0.0810	2.5757	0.9410	-0.4071	0.0548	1.0029
C_3H_6	0.1174	-0.7310	-0.7310	2.1082	0.9817	-0.3928	-0.3928	0.8221
C_4H_8	0.1213	-0.5434	-0.7262	2.0329	0.9873	-0.2934	-0.3936	0.8182
C_5H_{10}	0.1262	-0.5390	-0.5390	1.9726	0.9906	-0.2927	-0.2910	0.7883
C_6H_{12}	0.1333	-0.5377	-0.5383	1.8969	0.9928	-0.2928	-0.2906	0.8359
C_7H_{14}	0.1408	-0.5372	-0.5372	1.8198	0.9955	-0.2926	-0.2907	0.7301
C_8H_{16}	0.1402	-0.5347	-0.5368	1.8714	0.9956	-0.2913	-0.2905	0.7379
C_9H_{18}	0.1405	-0.5346	-0.5346	1.9257	0.9958	-0.2911	-0.2892	0.8038

TABLE-4
CALCULATED B3LYP/6-311++G** HOMO, LUMO (eV) AND HOMO, LUMO SPLITTING OF SINGLET AND TRIPLET STATES FOR ACYCLIC CARBENES, C_nH_{2n} (n = 1-9)

Compound	Singlet state		Triplet state		HOMOs-LUMOs splitting
	HOMO	LUMO	HOMO	LUMO	
CH_2	-0.2610	-0.1424	-0.2499	-0.0013	0.2597
C_2H_4	-0.2253	-0.0930	-0.2127	-0.0048	0.2205
C_3H_6	-0.2072	-0.0734	-0.1870	-0.0077	0.1995
C_4H_8	-0.2070	-0.0727	-0.1870	-0.0085	0.1985
C_5H_{10}	-0.2068	-0.0720	-0.1860	-0.0068	0.2000
C_6H_{12}	-0.2063	-0.0716	-0.1850	-0.0068	0.1995
C_7H_{14}	-0.2057	-0.0712	-0.1844	-0.0073	0.1984
C_8H_{16}	-0.2054	-0.0707	-0.1838	-0.0076	0.1978
C_9H_{18}	-0.2051	-0.0704	-0.1836	-0.0073	0.1978

The amount of singlet-triplet splitting is rationalized in terms of simple qualitative arguments based on the HOMO-LUMO gap and in *s* and *p* orbital occupancy (Table-4)[15]. A higher HOMO-LUMO gap makes a larger singlet-triplet splitting. Substituting of methyl groups on methylenic center C_nH_{2n} (n = 1-4) decrease HOMO-LUMO gap as well as singlet-triplet splitting.

Conclusion

It is explained that substitution of methyl groups lowers the energy gap between the singlet and the triplet. In particular, the factor that decrease the singlet-triplet splitting is charge transfer to the methylenic carbon and responsible for the decrease in the singlet triplet splitting of alkyl substituted carbenes relative to CH_2.

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