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Structural Studies on the Smallest Unit of Nanocarbons, C_2: DFT and *ab initio* Calculations

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The total energies and the energy differences of 3 states (singlet, triplet and quintet) of C_2 with 19 methods have been calculated. The energy results of triplet and quintet are more or less compatible between old and advanced methods. Surprisingly, the results of energies of singlet and triplet states are contradicted between old and advanced methods. Anyway, the singlet state of C_2 is more stable than triplet state with the advanced methods. The bond hybridization of 3 states is calculated by CBSQ/ 6-311++G** level of theory.

Key Words: Nano, Nanocarbons, C_2, DFT, *ab initio*, Calculations.

INTRODUCTION

The C_2 molecules are generated, along with C_1 and C_5, from a 16-v carbon arc under vacuum (1×10^{-4} mm Hg). Reactions occur in condensed phase at liquid nitrogen temperature[1,2]. It was reported that C_2 reacts with alcohols[1] and carbonyl compounds[2] to produce acetylene as the major product. Two electronic states of C_2, the singlet[3,4] ground state and the long-lived triplet[3,4] state, have been suggested as those responsible for acetylene formation from reaction with acetone[2].

In order to confirm C_2 as the precursor of these products, reactions of propane, isobutane and methyl ether were carried out with carbon-14-enriched carbon vapour[5]. The spin state of the C_2 responsible for this reaction was determined by trapping triplet C_2 and observing the effect on product formation. On this basis, it was concluded that the reactive C_2 species must be a singlet.

One of the topics of current interest in carbene research is the generation of molecules with a large number of carbene 'functional groups'[6-22]. The first dicarbene reported in the literature in 1963, when the generation of *p*-phenylene *bis*(pheny1 carbene) was published by Trozzolo *et al.*[12]. They found that *m*-phenylene *bis*carbenes should have quintet ground states. The zero-field splitting (ZFS) parameters were published after 2 years by Wasserman *et al.*[13] and by Itoh[14].

COMPUTATIONAL METHODS

A quest for higher storage of the solar energy is carried out for silicon atom substituted on double bond on norbornadienes **1** and quadricyclanes **2** system, *via ab initio* (Fig. 1). Geometry optimizations are carried out by HF, PUHF[23], B3LYP[24],

MP2, PMP2[25-30], MP3, PMP3[31], MP4D, MP4DQ, MP4SDQ[32-34], CCSD, CCSD(T)[35-38], QCISD(T), QCISD(T)[39-41], G1[42,43], G2, G2MP2[44,45], CBS-Q[46], CBS-QAPNO[47] methods using 6-311++G** basis set of the Gaussian 98 system of programs[48].

RESULTS AND DISCUSSION

It is previously reported that the carbenes have two states as singlet and triplet states. C_2 is a molecule to be investigate for its structure. It could be proposed three states for C_2 molecules as singlet, triplet and quintet states. Quintet is state in which the all four electrons are directed into same direction. The three states are global minima. In fact the C_2 molecule is a dicarbene (Fig. 1). Diagram of three states of C_2 and electron resonance possibility are presented (Fig. 1). For singlet and triplet states, two forms, ionic and diradical forms could be considered but for quintet form it is not possible to considering more form.

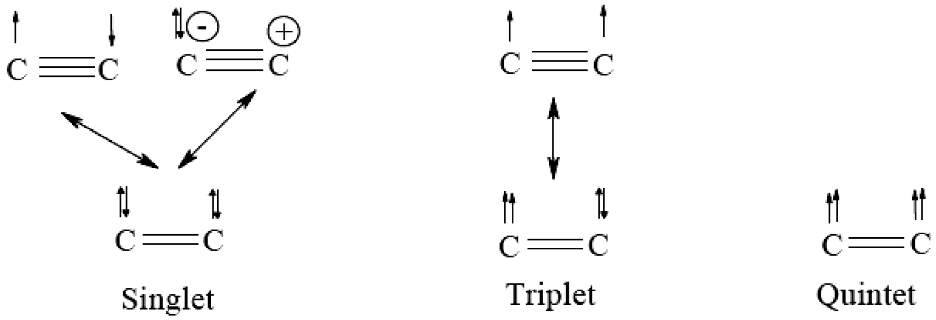


Fig. 1. Possible states of multiplicity for carbon dimer along their likely canonical forms

The total energies of C_2 with 19 methods are calculated (Table-1). The energy differences of three states are also presented (Table-2). The energy results of triplet and quintet are more or less compatible between old and advanced methods. Surprisingly, the results of energies of singlet and triplet are contradicted between old and advanced methods. With the old methods triplet states is more stable than singlet state. This is consistent with the results that the triplet state of simple carbenes is more stable than singlet state with even advanced methods. However, the singlet state of C_2 is more stable than triplet state with the advanced methods. Thus it is important that the singlet, triplet and/or quintet states are calculated with advanced methods.

The bond hybridizations, bond orders and bond lengths of C_2 are calculated with CBSQ method (Table-3). Four, three and two bond hybridization type is formed for singlet, triplet and quintet states, respectively. NBO calculations show two π-bonds for singlet and one π-bond for triplet states, but there is no π-bond for quintet states. There is not any bond hybridization for quintet state of C_2 since two carbons attached each other with *p* and/or *s*-orbitals.

TABLE-1
TOTAL ELECTRONIC ENERGY (kcal mol^{-1}), FOR OPTIMIZED SINGLET (s), TRIPLET (t) AND QUINTET (q) STATES OF CARBON DIMER BY 19 METHODS [Ref. 1-19], USING 6-311++G** BASIS SET. FOR THE SAKE OF BREVITY, THE SUM OF THERMAL AND ELECTRONIC ENERGIES (E), ENTHALPIES [H] AND GIBBS FREE ENERGIES {G} ARE SPECIFIED ONLY FOR HIGHER METHODS: CCSD(T), QCISD(T), G2, CBS-Q AND CBS-APNO

	HF[1]	B3LYP[1]	MP2[1]	MP3[1]	MP4D[1]	MP4DQ[1]
s	-47307.492	-47625.602	-47512.268	-47488.549	-47509.828	-47503.215
t	-47366.314	-47648.775	-47507.158	-47514.551	-47520.388	-47515.064
q	-47321.848	-47569.061	-47424.714	-47441.343	-47446.706	-47443.076
	PUHF[1]	PMP2[1]	PMP3[1]	MP4SDQ[1]	CCSD[1]	CCSD(T)[1]
s	–	–	–	-47513.627	-47510.623	-47529.650
t	-47368.377	-47508.387	-47515.068	-47518.725	-47518.682	-47528.058
q	-47322.895	-47425.395	-47441.696	-47444.639	-47445.231	-47451.051
	QCISD [1]	QCISD(T)	G1[1]	G2MP2 [1]	G2 [1]	CBS-Q[1]
s	-47513.979	-47530.639	-47564.740	-47563.316	-47563.919	-47562.315
t	-47519.739	-47528.598	-47557.979	-47556.921	-47557.636	-47558.233
q	-47445.647	-47451.269	-47474.339	-47474.405	-47474.589	-47476.798
	CBS-APNO	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)		
s	-47633.842	-47302.894	-47302.301	-47315.864		
t	-47630.517	-47362.374	-47361.782	-47376.039		
q	-47548.651	-47318.044	-47317.451	-47332.263		

	CCSD(T)			QCISD(T)		
	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)
s	-47525.377	-47524.784	-47538.361	-47526.389	47525.797	-47539.377
t	-47524.102	-47523.509	-47537.802	-47524.657	47524.065	-47538.359
q	-47448.033	-47447.441	-47462.266	-47448.260	47447.668	-47462.495
	G2			CBS-Q		
s	–	–	–	-47293.335	-47292.742	-47306.310
t	–	–	–	-47352.984	-47352.392	-47366.654
q	–	–	–	-47309.469	-47308.876	-47323.689

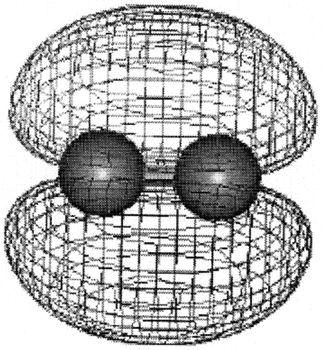
TABLE-2
RELATIVE ENERGIES OF SINGLET (s), TRIPLET (t) AND QUINTET (q) STATES OF CARBON DIMMER, CALCULATED BY 19 METHODS [Ref. 1-19], USING THE 6-311++G** BASIS SET

	HF[1]	B3LYP[1]	MP2[1]	MP3[1]	MP4D[1]	MP4DQ[1]
s	58.822	23.173	0.000	26.002	10.560	11.849
t	0.000	0.000	-5.111	0.000	0.000	0.000
q	44.465	79.714	87.555	73.208	73.682	71.989
	PUHF[1]	PMP2[1]	PMP3[1]	MP4SDQ[1]	CCSD[1]	CCSD(T)[1]
s	–	–	–	5.097	8.059	0.000
t	0.000	0.000	0.000	0.000	0.000	-1.592
q	45.482	82.992	73.372	74.085	73.451	78.599
	QCISD [1]	QCISD(T)	G1[1]	G2MP2 [1]	G2 [1]	CBS-Q[1]
s	5.761	0.000	-6.761	-6.396	-6.284	-4.081
t	0.000	-2.041	0.000	0.000	0.000	0.000
q	74.093	79.369	83.641	82.516	83.046	81.436
	CBS-APNO					
s	-3.325					
t	0.000					
q	81.866					

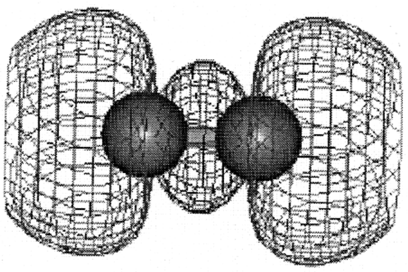
TABLE-3
HYBRIDIZATION, BOND ORDER AND BOND LENGTH FOR SINGLET (s), TRIPLET (t) AND QUINTET (q) STATES OF CARBON DIMMER (C1–C2), CALCULATED AT CBSQ/ 6-311++G** LEVEL OF THEORY

Multiplicity	Hybridization (C_1–C_2)			
s	$sp^{0.19}$–$sp^{1.71}$	p^1–p^1	p^1–p^1	$sp^{5.39}$–$sp^{0.59}$
t	$sp^{0.31}$– $sp^{1.71}$	p^1–p^1	$sp^{3.26}$–$sp^{0.59}$	–
q	$sp^{0.01}$–$sp^{99.99d1.76}$	$sp^{99.99d1.71}$–$sp^{0.01}$	--	–

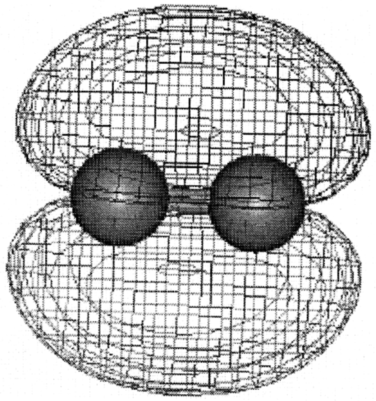
Multiplicity	Bond order (C_1–C_2)	Bond length (C_1–C_2)	HOMO	LUMO	$\Delta_{LUMO-HOMO}$
s	2.795	1.250	-0.452	-0.117	0.335
t	2.604	1.330	-0.398	0.054	0.451
q	1.580	1.561	-0.360	0.031	0.391



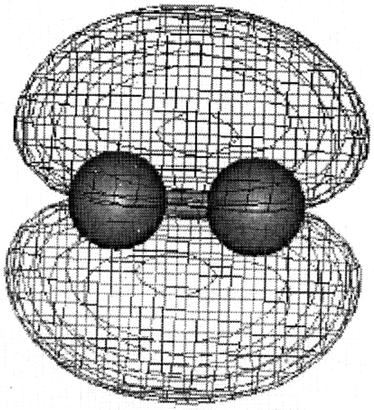
HOMO-CC-s (-8.94 ev)



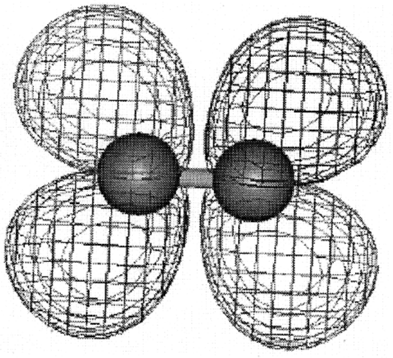
LUMO-CC-s (-7.24)



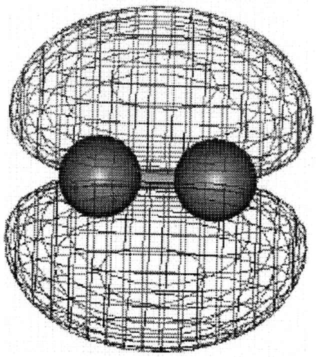
HOMO-CC-t a(-9.11)



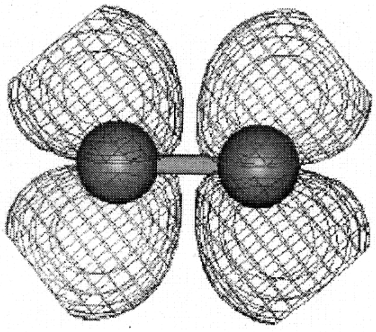
HOMO-CC-t b(-8.58)



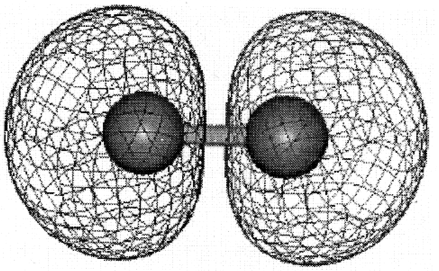
LUMO-CC-t a(-1.53)



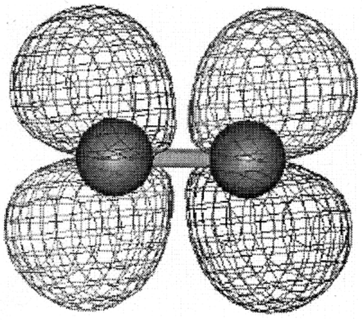
LUMO-CC-t (-6.02)



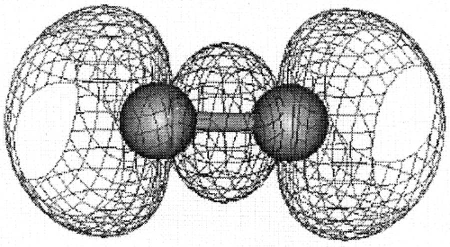
HOMO-CC-q a(-5.48)



HOMO-CC-q b(-10.23)



LUMO-CC-q a(-3.21)



LUMO-CC-q b(-4.99)

Bond order in contrast to bond length of C_2 is reasonably decreased from singlet to quintet states.

Conclusion

The total energies and the energy differences of singlet, triplet and quintet of C_2 with 19 methods using 6-311++G** basis set are calculated. The energy results of triplet and quintet are more or less compatible between old and advanced methods. The results of energies of singlet and triplet states are contradicted between old and advanced methods.

Anyway, the singlet state of C_2 is more stable than triplet state with the advanced methods. With the old methods triplet states is more stable than singlet state. However, the singlet state of C_2 is more stable than triplet state with the advanced methods.

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