

Binding Energy and Stability Calculations on Hydrogenated Forms of Substituted Carbazoles as Hydrogen Storage Materials

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Abstract- The aim of this work is to explore the stable hydrogenated forms of carbazole and 9-methylcarbazole molecules by using M06-2X density functional as computational method. Binding energies per hydrogen atom in these hydrogenated forms were calculated by the counterpoise correction procedure. Relative energies, complexation and binding energies for the conformers of dodecahydrocarbazole were also calculated. Stabilities of all the hydrogenated forms were discussed by the analysis of the frontier molecular orbitals.

Keywords: Hydrogen energy technologies; hydrogenation; M06-2X theory; binding energy.

1. Introduction

Hydrogen is an important energy source that is shield to the global climate changes against the ever-increasing energy demands [1]. Hydrogen technologies relates to development of new methods in areas such as obtain the hydrogen, storage and processing. Also these technologies give very effective results in science to prevent negative environmental impacts and create green energy sources. Hydrogen storage methods are classified as pressurized hydrogen, carbonaceous materials, metal and complexation hydrides, organic liquids according to storage capacity (wt%), safety, stability and transaction costs [2–6].

Carbazole structures in liquid organic hydrides are noteworthy with reversible hydrogen sorption characteristics as hydrogen storage materials [7]. Liquid organic hydrides have significant advantages in hydrogen storage as access to high gravimetric hydrogen storage level, lack of carbon monoxide and carbon dioxide emissions as by-products [7, 8]. Hydrogenation and dehydrogenation techniques are used in the process of hydrogen storage and releasing,

respectively, for the organic liquid hydrides [2, 9–11]. Hydrogenation is the process of adding hydrogen under pressure with the aid of a catalyst. The aim of this procedure is that the hydrogen atoms attend to multiple bonds. In the hydrogenation reaction, alkene is converted to alkane condition by addition of the hydrogen to the unsaturated carbon chemical bond. The dehydrogenation process is the opposite of this. Hydrogenation and dehydrogenation kinetics and catalysis of carbazole derivatives and influences of the reaction temperature and pressure have been experimentally studied in the literature [12–14].

In this study we have theoretically aimed to investigate and interpreted the hydrogen binding energies, complexation energies and energy gaps between frontier (highest occupied and lowest unoccupied) molecular orbitals on the hydrogenated forms of substituted carbazoles as hydrogen storage materials via computational methods. Before anything else, we have determined the optimized molecular forms of carbazole (S1), 9-methylcarbazole (S2) and octahydro-, dodecahydro- structures as their hydrogenated forms. The next phase of our study consists of the

evaluations about the relationship between hydrogen binding energies, frontier molecular orbitals and hardness of all the S1-S2 hydrogenated forms to determine their chemical reactivity and stability.

2. Computational details

All the quantum calculations on the structural optimizing processes and molecular orbitals were performed by using M06-2X theory combined with 6-31+G (d,p) basis set level. Inputs on the atomic coordinates for all the geometry optimizations were created by Gauss View program [15]. Optimizations and computations on the S1, S2 hydrogenated forms and the atomic hydrogen binding energies were obtained by using Gaussian 09W software database [16]. Basis set superposition error (BSSE) corrections,

complexation and binding energies were calculated by the counterpoise correction procedure (CP) [17].

3. Results and discussion

Fig.1 is inclusive the optimized molecular structures of S1, S2 and their hydrogenated forms obtained by the output of quantum computing. In the figure the hydrogens of which the binding energies will be calculated, are located in the green zone. The minimum-energy structures of S1 and S2 have -517.280 and -556.571 a.u. of energies at M06-2X calculation method and 6-31+G (d,p) basis set, respectively. Calculated relative energies and hydrogen binding energies which bind to carbons have been reported in Table 1 for the substituted carbazoles and their hydrogenated forms.

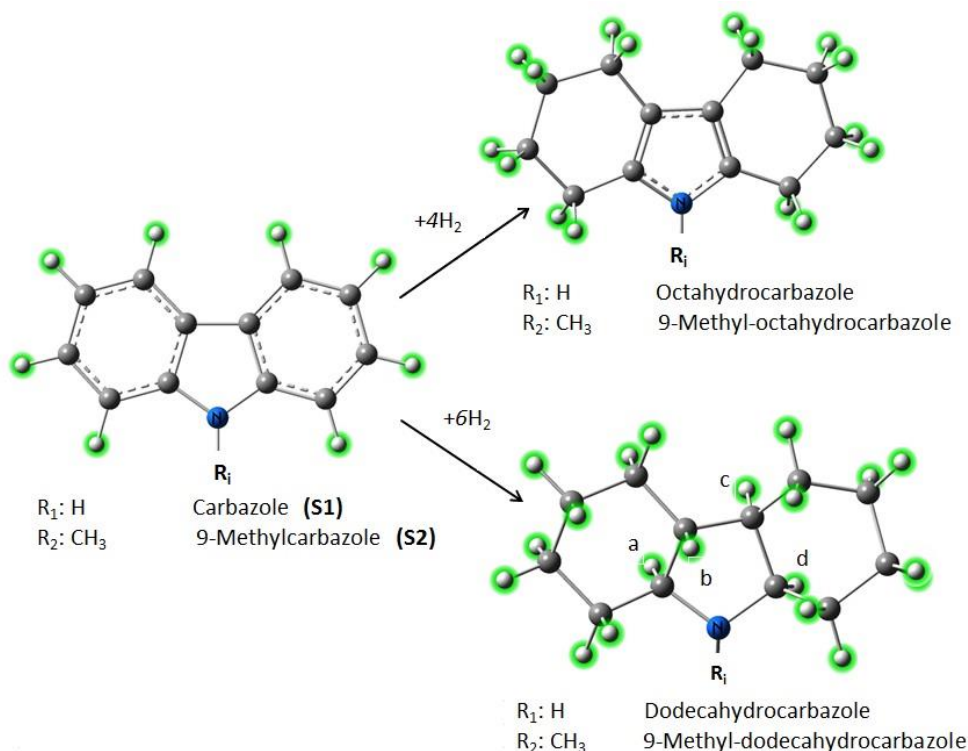


Fig. 1. Optimized structures of S1, S2 and their hydrogenated structures computed at M06-2X theory, 6-31+G (d,p) level

The average values of relative energies per hydrogen atom are 16.24 and 16.28 eV for S1+nH₂ and S2+nH₂ forms, respectively. Total binding energies for the hydrogen atoms attached to carbons have been calculated as -45.815 and -45.744 eV in the S1 and S2 structures, respectively. These values are approximately -82.979 and -82.902 eV in the S1+6H₂ and S2+6H₂ hydrogenated forms, respectively. While the binding energies per hydrogen atom are -5.727 and -5.718 eV in the S1 and S2 structures, these results are -4.149 and -4.145 eV in the S1+6H₂ and S2+6H₂, respectively.

On the other hand, the calculated BSSE energies are increasingly on the rise in hydrogenated forms of S1, S2. This situation can be attributed to positioning where there are involved fragments and of course, to the applied method and

basic set. While the number of functions included in the basic set increases, the BSSE energy is reduced. So, The BSSE energy has a small value in a large basis set. Another factor that affects the BSSE energy value is occupied or unoccupied orbitals. Unoccupied orbital's give greatly an e increasing effect in the BSSE energy.

For the dodecahydrocarbazole structures in Fig. 1, we like to examine the conformers for which the relative values between the ground state energies are many minor by calculation method. The relative energies, complexation and binding energies for the conformers of dodecahydrocarbazoles are given in Table 2. The positioning of the conformers has been identified at the bottom line of Table 2 (see also Fig. 1). Considering the total energies, we say that the most stable optimization is conformer 1 for the

both hydrogenated forms (+6H₂). The calculated energy differences between the various conformations for +nH hydrogenated forms of 9-ethylcarbazole have been calculated by Density Function Theory (DFT) method with the B3LYP hybrid functional including electron correlation in a previous study [7].

Table 1. Calculated relative and hydrogen binding energy values for substituted carbazoles and, their hydrogenated forms.

Organic Liquid Materials	Relative Energy* (eV)	Binding Energy** Per Hydrogen Atom (eV)
S1	0.000	-5.727
+2H ₂	64.822	-4.732
+4H ₂	129.592	-4.242
+6H ₂	195.785	-4.149
S2	0.000	-5.718
+2H ₂	64.783	-7.080
+4H ₂	130.559	-3.994
+6H ₂	195.795	-4.145

* Relative values between the total energy

** obtained by using CP corrected energy.

As seen in Table 2 the minimal corrected complexation energies have been computed as -84.541 (conformer 5) and -84.350 eV (conformer 2), approximately. The lower value of the complexation energy corresponds to the more stable complex [18]. Also, the conformer 5 in the S1+6H₂ and the conformer 2 in S2+6H₂ have minimal values as binding energy per hydrogen atom. In the both hydrogenation structures, the conformers 2 and 5 draw attention with their minimum complexation and binding energies. In here we take into account the conformers 1 for the dodecahydro-structures in the calculations and in the comments relating to binding energy and molecular orbitals since they have the minimum total energies.

The first and second frontier molecular orbitals and energy diagrams of S2+6H₂ hydrogenated form have been displayed in Fig. 2. The claret red and green tones represent the positive and negative wave functions, respectively, for the orbitals. The visual for the highest occupied molecular orbital is scattered over the nitrogen and the carbons close to the nitrogen. The positive wave functions for the lowest unoccupied orbitals are focused in the C-H bonds. Frontier molecular orbitals (HOMO and LUMO), act as the electron donor and acceptor, respectively, and these orbital energy values explain the optical and electrical properties of the molecules in quantum computations [19-21].

HOMO-LUMO energy gaps and chemical hardness in hydrogenated carbazoles are given in Table 3. The type of bonding interaction can be explained by the topic of the

highest occupied and lowest unoccupied orbital energies and also molecules with high HOMO energies are more reactive and of course unstable [22].

Table 2. Calculated relative, complexation and hydrogen binding energy values for conformers of dodecahydrocarbazole formed according to positions of hydrogens attached to carbons.

Conformers	Relative Energy (eV)	Complexation Energy [corrected] (eV)	Binding Energy Per Hydrogen Atom (eV)
S1+6H₂			
1	0.000	-82.975	-4.149
2	0.2060	-84.312	-4.216
3	0.2062	-83.627	-4.182
4	0.3389	-84.219	-4.211
5	0.4403	-84.541	-4.227
6	0.5453	-83.828	-4.191
S2+6H₂			
1	0.000	-82.897	-4.145
2	0.1690	-84.350	-4.218
3	0.2039	-83.862	-4.193
4	0.3860	-84.090	-4.205
5	0.5478	-84.252	-4.213
6	0.4972	-83.773	-4.189

Conformer 1= b(front),acd(back); 2= abcd(front); 3=ab(front),cd(back); 4=abc(front),d(back); 5=ac(front),bd(back); 6=bc(front),ad(back)

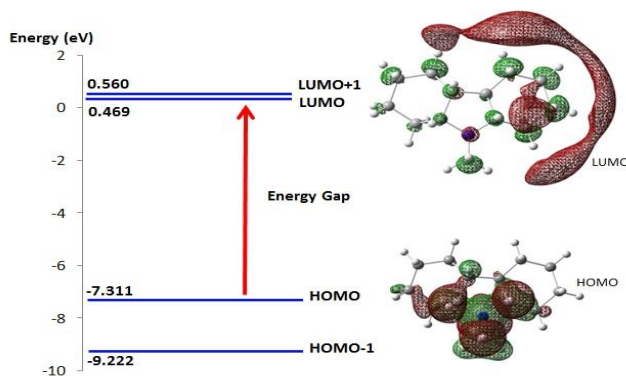


Fig. 2. Highest and lowest energy levels of occupied and unoccupied orbitals for S2+6H₂ hydrogenated forms

As seen in Table 3, the HOMO energies have been computed at the highest values in the octahydro- structures. The energy gaps in FMO's comment the intramolecular charge transfer interactions and, its lower value means a

more reactive molecule, chemically [23]. On the other hand, the higher values of hardness are directly related to the stability [23-26]. The octahydro- structures have smaller energy gaps relative to the others in this study. Conversely, the maximal energy gaps have been computed in the S1+6H₂ and S2+6H₂ hydrogenated forms. The calculation results for the chemical hardness support that the stabilities of S1+6H₂ and S2+6H₂ hydrogenated forms are highest.

Table 3. HOMO energies, energy gaps and chemical hardnesses for substituted carbazoles and their hydrogenated forms

Organic Liquid Materials	HOMO energy (eV)	Energy Gap (eV)	Chemical Hardness (eV)
S1	-6.978	6.724	3.362
+2H ₂	-6.616	6.850	3.425
+4H ₂	-6.286	6.638	3.319
+6H ₂	-7.565	7.902	3.951
S2			
	-6.811	6.571	3.286
+2H ₂	-6.480	6.773	3.386
+4H ₂	-6.270	6.572	3.286
+6H ₂	-7.311	7.780	3.890

4. Conclusion

In present study, the hydrogenated forms of substituted carbazoles have been achieved by the output of quantum computing at M06-2X theory, 6-31+G (d,p) level. Considering the total energies, the most stable optimization is conformer 1 for the S1+6H₂ and S2+6H₂ structures. But the conformers 2 and 5 have drawn our attention with their minimum complexation (corrected) and binding energies per hydrogen atom. As for the hydrogenated forms, S1+4H₂ and S2+4H₂ are more reactive than the other forms according to the highest occupied molecular orbitals. Conversely, the stabilities of the S1+6H₂ and S2+6H₂ hydrogenated forms are highest since of their maximal energy gaps.

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