

## Absorption mechanism, structural and electronic properties of MCI9 (M = B and Si) fullerenes with 1-acetylpiperazine

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### Abstract

The interaction mechanisms of undoped, silicon- and boron-doped C<sub>20</sub> fullerenes and 1-acetylpiperazine (1-ap) were investigated. Stability, electronic properties, influence of water on the solubility and stability, molecular parameters, descriptive vibrational bands and nuclear magnetic resonance shielding values are reported. The quantum mechanical calculations were carried out using the M06-2X functional and the 6-31G(d) basis set. It is observed that all the complexes are more stabilized in water compared to the gas phase. The most stable complex was found as silicon-doped fullerene interacting with the carbonyl edge of 1-ap releasing energy of 64.13 kcal/mol in water.

### Keywords

C<sub>20</sub>, density functional theory, binding energy, interaction mechanism

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## Introduction

C20 fullerenes, comprising only pentagons and having the largest mass density among the fullerene family, are the smallest members of fullerenes (Han et al., 2000; Li and Zhang, 2013). They were first experimentally synthesized by Prinzbach et al. (2000). Due to their useful and versatile properties, fullerenes have found a wide range of applications expanding from medical, bio-nano technological research to the drug industry (Beyeh et al., 2010; Hatnapure et al., 2012; Kharb et al., 2012; Kavitha et al., 2013; Zhou et al., 2010).

The development of different types of materials with enhanced physical, chemical and biological properties is of current research interest. Theoretical approaches provide useful insights for studying molecular systems before going into experimental investigations. Density functional theory (DFT) has been widely used as a theoretical approach (Anafcheh et al., 2016; Anafcheh and Ghafouri, 2014; Dheivamalar and Sugi, 2015; Handy et al., 1993; Handy et al., 1996; Hassani and Tavakol, 2014; Helgaker et al., 1999; Lee and Boo, 1996; Li et al., 2015; Stephens et al., 1994). Piperazine and its derivatives have been the target of research in the production of anti-microbial and anti-carcinogenic pharmacological agents, in a series of therapeutic processes and in the synthesis of complexes and clathrates (Beyeh et al., 2010; Hatnapure et al., 2012; Long et al., 2010; Parlak et al., 2009a, 2009b).

The scope of the present research involves the study of the interaction mechanisms of 1-ap and undoped C20 and B-, Si-doped C20 fullerene complexes based on computational methods with the M06-2X functional and 6-31G(d) basis set (Zhao and Truhlar, 2008). We, hereby, report the results obtained, discuss these results and hope that this study catalyses further investigations.

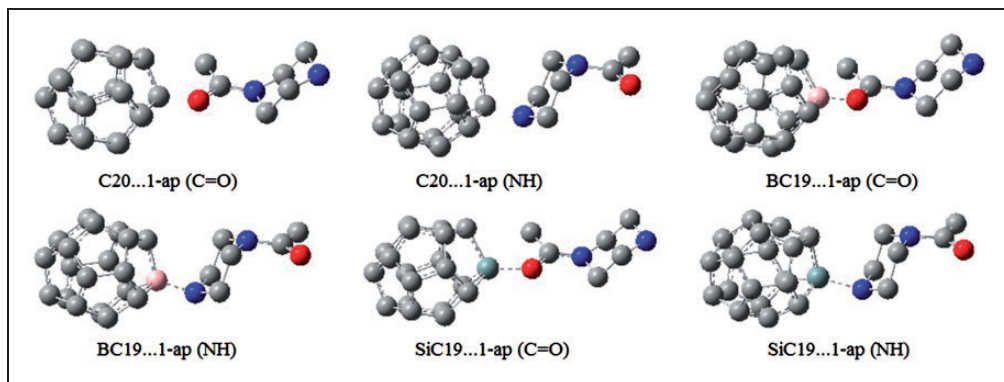
## Computational details

Molecular structures of the complexes were examined using the M06-2X/6-31G(d) method in the gas phase and in the water as the solvent. Vibrational frequency calculations and computations of the chemical shift values for  $^{11}\text{B}$  and  $^{29}\text{Si}$  nuclei were also performed at the same level of theory. The optimization processes were repeated with no geometric constraints until imaginary frequencies were not observed. The optimized structures of the complexes obtained are given in Figure 1. In order to evaluate the stability of the complexes, binding energies ( $E_b$ ) were calculated using equation (1) (Hazrati and Hadipour, 2016):

$$E_b = E_{\text{complex}} - (E_{\text{C20 or MC19}} - E_{1\text{-ap}}) \quad (1)$$

In equation (1),  $E_{\text{complex}}$ ,  $E_{\text{C20 or MC19}}$  and  $E_{1\text{-ap}}$  represent the total electronic energies of the ligand interacted complex system, undoped and B-, Si-doped fullerene complex and 1-ap molecule, respectively.

When dealing with the minimization of energy of the systems with multiple components, basis set superposition error (BSSE) appears as an important factor affecting the results of  $E_b$  values (Liu and McLean, 1973). In this work, BSSE was taken into account using the counterpoise correction method (Boys and Bernardi, 1970; Gutowski and Chałasinski, 1993; Simon et al., 1996). Charge transfer direction and electrophilic character assessments of the



**Figure 1.** Optimized molecular structures for the investigated systems.

complexes were examined by calculating electrophilicity indexes ( $\omega$ ) and chemical hardness ( $\eta$ ) as given by equations (2) and (3), respectively (Parr et al., 1991; Pearson, 1986):

$$\omega = \mu^2/2\eta \quad (2)$$

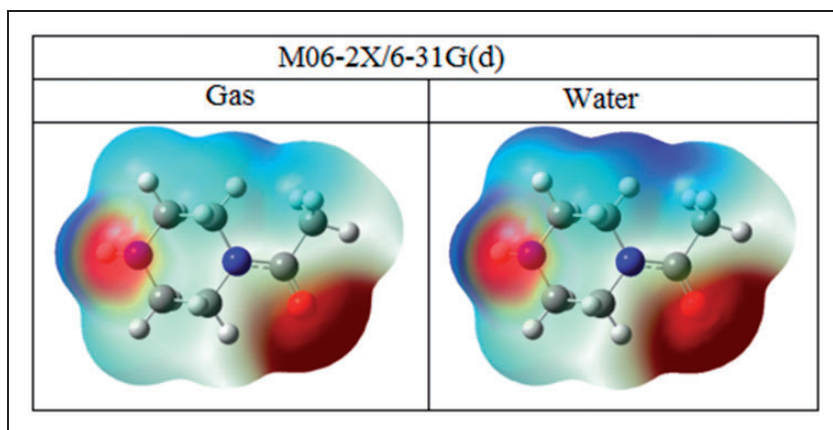
$$\eta = [-E_{\text{HOMO}} - (-E_{\text{LUMO}})]/2 \quad (3)$$

In order to have insights of the solvent effect, all the calculations were conducted both in the gas phase and water as the solvent. Gaussian 09 was used for all calculations (Frisch et al., 2009). The optimized molecular structures were viewed with the GaussView program (Dennington et al., 2008).

## Results and discussion

Firstly, electrostatic potential surfaces (EPSs) were obtained for 1-ap ligand molecule and they are illustrated in Figure 2. Two possible interaction edges, C=O and NH, were located based on the EPS findings. As for undoped C20+1-ap interaction, the complex system was analysed as different structures and the lowest energy configurations for the complex systems are shown in Figure 1. Interaction sites for doped fullerene systems were chosen as the boron and silicon atoms similar to the earlier reports (Hazrati and Hadipour, 2016; Mitschker and Kluner, 2012). Binding energy can be described as the difference between total energy of the optimized complex and the total energy of the each fragment, which are free 1-ap and undoped C20 or B-, Si-doped C20 (Ivanov et al., 2011).

Table 1 collects the calculated binding and solvent energies ( $E_b$  and  $E_s$ ). For all the complexes, interactions with NH edge of 1-ap with C20 and B-, Si-doped fullerenes have larger binding energies in the gas phase compared to interaction with C=O edge. This is also observed in water except for the Si-doped fullerene complex. As for SiC19, interaction with C=O edge gives slightly larger binding energy in magnitude (0.71 kcal/mol) when compared to interaction with NH site in water media. It is reported that  $E_b$  values, which is less than 10 kcal/mol, can be considered as physisorption while the  $E_b$  energies larger than 10 kcal/mol can be chemisorption (Ameta and Penoni, 2015; Bhushan, 1999). Therefore,  $E_b$  energies obtained for all the complexes except C20+1-ap (C=O) in gas phase lie in the range of chemisorption. However, calculations in water of C20+1-ap (C=O) complex resulted



**Figure 2.** Electrostatic potentials on 1-ap. Surfaces are defined by the  $0.0004 \text{ e}/\text{\AA}^3$  contour of the electronic density. Color ranges (a.u.): blue, more positive than 0.03 and red, more negative than  $-0.03$ .

**Table 1.** BSSE-corrected binding and solvent energies (kcal/mol) of the investigated structures.

Structure	$E_b$ (gas)	$E_b$ (water)	$E_s$
C20 + 1-ap (C=O)	-1.77	-10.49	-15.71
C20 + 1-ap (NH)	-19.42	-28.09	-8.68
BC19 + 1-ap (C=O)	-36.02	-41.65	-12.77
BC19 + 1-ap (NH)	-45.39	-50.58	-12.32
SiC19 + 1-ap (C=O)	-53.65	-64.13	-20.93
SiC19 + 1-ap (NH)	-54.42	-63.42	-19.30

$E_b$ : binding energy;  $E_s$ : solvent energy.

in  $-10.49 \text{ kcal/mol}$  as the  $E_b$  energy, which is also close to the possible non-covalent interaction range and the non-covalent adsorptions, that can be considered to occur via charge-induced dipole interactions. It is to be noted that introduction of water as the solvent increases the stability of the all complexes.

$E_s$  energies reflect the degree of the solubilities of the examined complexes (Hazrati and Hadipour, 2016). Therefore, higher solubilities are expected for the complexes of SiC19+1-ap (C=O) and SiC19+1-ap (NH) with  $E_s$  energies of  $-20.93$  and  $-19.30 \text{ kcal/mol}$ , respectively. It is observed that electrophilic behaviour of all the complexes shows an increase from gas phase to calculations in water (Table 2). In addition, it is observed that electrophilic indexes of all the complexes show larger changes if the interaction with the ligand occurs with C=O edge when compared to NH edge (Table 2). It is also observed that the values of chemical hardness, which reflects the resistance of a given molecular system to any possible change in its electronic configurations, depend on the interaction site and the medium in which the optimizations and calculations were carried out (Table 2) (Makov, 1995). Interatomic distances of Si...O, Si...N, B...O and B...N were

**Table 2.** Some energetic parameters (eV) of the investigated structures.

System	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$E_g$	$\eta$	$\omega$
Gas					
C20 + 1-ap (C=O)	-4.838	-0.875	3.953	1.977	2.057
C20 + 1-ap (NH)	-5.261	-1.384	3.877	1.939	2.847
BC19 + 1-ap (C=O)	-4.780	-0.971	3.809	1.905	2.171
BC19 + 1-ap (NH)	-5.266	-1.484	3.782	1.891	3.012
SiC19 + 1-ap (C=O)	-4.719	-0.990	3.729	1.865	2.185
SiC19 + 1-ap (NH)	-5.240	-1.469	3.775	1.888	2.984
Water					
C20 + 1-ap (C=O)	-5.366	-1.327	4.039	2.020	2.773
C20 + 1-ap (NH)	-5.454	-1.479	3.975	1.989	3.023
BC19 + 1-ap (C=O)	-5.305	-1.512	3.793	1.897	3.063
BC19 + 1-ap (NH)	-5.410	-1.620	3.790	1.895	3.260
SiC19 + 1-ap (C=O)	-5.356	-1.497	3.859	1.930	3.042
SiC19 + 1-ap (NH)	-5.493	-1.660	3.833	1.917	3.337

**Table 3.** C=O and NH stretching vibrations ( $\text{cm}^{-1}$ ) for the investigated structures.

Structure	C=O stretching		NH stretching	
	Gas	Water	Gas	Water
1-ap	1825	1770	3547	3540
BC19 + 1-ap (NH)	1831	1781	3460	3459
SiC19 + 1-ap (NH)	1833	1781	3444	3430
BC19 + 1-ap (C=O)	1689	1703	3563	3555
SiC19 + 1-ap (C=O)	1708	1738	3557	3557

calculated as 1.77, 1.90, 1.52 and 1.60 in the gas phase and 1.72, 1.87, 1.49 and 1.59 Å in water, respectively. It is noted that introduction of water as the solvent leads to the shortening of interatomic distances and larger  $E_b$  energies. This allows the formation of more stable complexes. When the energy gap values from Table 2 are examined, it is observed that the energy value of the gap decreases for the BC19+1-ap (C=O) complex and for the other complexes it increases from the gas to water media. This implies that unlike the other complexes, the reactivity of BC19+1-ap (C=O) complex is expected to increase from the gas phase to water media calculations.

In order to provide further evidence for the possible of 1-ap molecule on the Si- and B-doped fullerenes, C=O and NH stretching vibrational bands were identified and they are given in Table 3. In the gas phase and water, C=O stretching vibrations were found as 1825 and 1770  $\text{cm}^{-1}$  and NH stretching frequencies were found as 3547 and 3540  $\text{cm}^{-1}$  for free 1-ap. Upon the interaction between 1-ap and doped fullerene systems, different band shifts were observed in these vibrational modes. For example, the C=O stretching value of SiC19+1-ap (C=O) was found as 1708  $\text{cm}^{-1}$ , which means a shift of 117  $\text{cm}^{-1}$ , when compared to C=O vibration of 1-ap in the gas phase suggesting an evidence for possible interaction between 1-ap and SiC19 fullerene system.

The nuclear magnetic resonance chemical shifts of boron and silicon atoms were also identified to support the results of structural findings. It was observed that the resonance frequencies of  $^{11}\text{B}$  and  $^{29}\text{Si}$  nuclei in water changed around 71/68 ppm from BC19 to BC19+1-ap (NH)/BC19+1-ap (C=O) and 301/322 ppm from SiC19 to SiC19+1-ap (NH)/SiC19+1-ap (C=O) upon adsorption and these reflect the possible interaction.

## Conclusions

In the current theoretical search, based on the DFT calculation using the M06-2X/6-31G(d) method, the interaction mechanisms of undoped, B- and Si-doped C20 fullerenes and 1-ap were investigated both in the gas phase and water as the solvent. For the calculations conducted in the gas phase, within fullerene system, the complex SiC19+1-ap (NH) with a binding energy of  $-54.42$  kcal/mol was found the most stable, while C20+1-ap (C=O) was found as the least stable with a binding energy of  $-1.77$  kcal/mol. In water, SiC19+1-ap (C=O) complex appears as the most stable with a binding energy of  $-64.13$  kcal/mol and C20+1-ap (C=O) is the least stable with a releasing energy of  $10.49$  kcal/mol. In the gas phase, the interaction of C20 with C=O edge of 1-ap released was around  $1.8$  kcal/mol energy, the value of which lies in the range of physisorption. On the other hand, if the interaction occurs at NH edge, approximately  $20$  kcal/mol is released and this indicates the possibility of a chemisorption.

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## Declaration of Conflicting Interests

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