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Theoretical study of the effects of substituent and quadrupole moment on π-π stacking interactions with coronene

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ABSTRACT

Stability of the π-π stacking interactions in the Ben||substituted-coronene and HFBen||substituted-coronene complexes was studied using the computational quantum chemistry methods (where Ben and HFBen are benzene and hexaflourobenzene, || denotes π-π stacking interaction, substituted-coronene is coronene molecule which substituted with four X groups, and X= NH_2, CH_3, OH, H, F, CF_3, CN and NO). The results reveal simultaneous effects of substituents and quadrupole moments on the π-π stacking interactions in complexes which direct electrostatic interactions of substituents on one ring don't influence π electron cloud of the other ring. Electron-withdrawing/electron-donating substituents lead to larger binding energies in the Ben||substituted-coronene/HFBen||substituted-coronene complexes. Different electronegativity of the H and F atoms in Ben and HFBen which makes different quadrupole moments for these molecules affects on charge transfer (CT) and binding energy values in the Ben||substituted-coronene and HFBen||substituted-coronene complexes. Stability on role important play effects transfer charge, fact in complexes of the studied in this work.

Keywords: Coronene; Quadrupole moment; π-π stacking; Charge transfer; π electron cloud

INTRODUCTION

The π–π stacking interactions are noncovalent forces that play an important role in chemistry and biology [1,2]. These interactions take part in protein folding [3-6], enzyme-substrate recognition [3,4] and crystal packing [7].

The π–π stacking interactions along with hydrogen bonds are basic factors which manage stability of the DNA structure. Theoretical and experimental studies have been extensively performed on the π–π stacking interactions [8-17].

Among essential noncovalent forces which exist between biomolecules, π–π stacking interactions have been little recognized. Because these interactions are frequently observed in nature [18] it is necessary to discover various factors which handle strength of them.

Computational studies have afforded helpful information about π–π interactions in biological molecules. For example, results of computational calculations on π–π stacking interactions between DNA nucleobases [19-25] or interactions between nucleobases and aromatic systems [26-31] are useful for biochemical or medical applications.

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Some authors have been considered benzene dimer as a prototype of the π–π stacking interactions [32-34]. Moreover, effects of substituent on interactions of aromatic molecules have been studied by theoretical calculations [35-38].

Substituent effects in π–π stacking interactions can be elucidated on the basis of polarization of the π-system in substituted ring. Hunter and coworkers [2, 8] and Cozzi et al. [39] declared that electron-withdrawing substituents get better π–π stacking interactions by decrement of electrostatic repulsion between π clouds of the two rings, but electron-donating ones hold back these interactions.

Wheeler and Houk showed that the substituent effects in π–stacked benzene dimers arise from direct electrostatic interactions between the substituents and the unsubstituted benzene ring [40]. Indeed, local nature of substituent effects in π–π stacking interactions has been descripted by Steven Wheeler [41].

In the present work, simultaneous effects of substituent and quadrupole moment on the strength of π–π stacking interactions have been studied in Ben||substituted-coronene and HFBen||substituted-coronene complexes (where Ben and HFBen are benzene and hexafluorobenzene, and || denote π–π stacking interaction). In these systems, Ben and HFben have similar permanent quadrupole moments, but with opposite signs [42]. Coronene (super benzene) is a polycyclic aromatic hydrocarbon comprising of six peri-fused benzene rings [43]. Because of symmetrical structure of this molecule we considered it for investigation of the simultaneous effects of substituent and quadrupole moment on π–π stacking interactions.

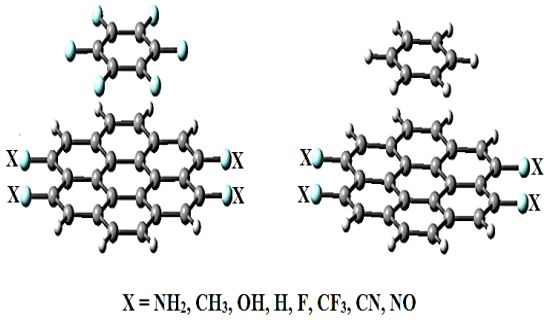
This molecule was substituted with four electron-withdrawing or electron-donating groups (X= NH_2, CH_3, OH, H, F, CF_3, CN and NO) and π–π stacking interactions of Ben and HFben on central ring of each substituted-coronene were considered.

Direct electrostatic interactions between substituents in one ring and π electron cloud of the other ring typically manipulate the π–π stacking interactions, but in the present complexes substituents are in far distances from two interacting π systems. Additionally, symmetry of complexes inhibit from horizontal displacements of Ben and HFBen relative to the substituted-coronene molecules.

Typical optimized structures of the Ben||substituted-coronene and HFBen||substituted-coronene complexes are depicted in scheme 1.

Optimized geometrical parameters, binding energies, results of atoms in molecules (AIM) analysis and NMR calculations, also results of charge transfer (CT) between monomers have been used to clarify strength of π–π stacking interactions in these complexes.

This study aids us to discover effects of substituent and quadrupole moment on π–π stacking interactions. These simple modeled complexes can be helpful to recognize π-stacked structures in biomolecular systems, also to design new drugs and supramolecular systems.



Scheme 1. The optimized Ben||substituted-coronene and HFBen||substituted-coronene complexes (The turquoise spheres are X substituents).

COMPUTATIONAL METHODS

All geometries were fully optimized at the M05-2X/6-311++g(d,p) level of theory with Gaussian09 program package [44]. The binding energies of all complexes were calculated with correction for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise technique [45].

The second-order Møller–Plesset perturbational method, MP2, usually overestimate binding energy (-ΔE) values and is not passable for evaluation of the π–π stacking binding energies. The DFT methods are useful for studying the biological systems, but the B3LYP method fails for dispersion interactions and cannot describe the π–π stacking interactions. However, Truhlar and Zhao developed a new generation of DFT methods to describe the π–π stacking interactions in DNA base pairs [46, 47]. They proposed that hybrid meta-GGA functional, M05-2X, has good performance for computing the π-π stacking binding energies. In fact, the M05-2X functional compensated the deficiencies of other hybrid functionals by incorporating an improved treatment of spin kinetic energy density in both the exchange and correlation functionals [48]. On the other hand, the CCSD(T) calculations are very time-consuming. Therefore, M05-2X functional has chosen for evaluation of the π-π stacking binding energies of the complexes studied in this work.

The topological properties of electron charge density have been calculated by AIM method on the wave functions obtained at the M05-2X/6-311++g(d,p) level of theory using AIM2000 [49] program. Atomic net charges were calculated using ChelpG scheme [50] at the M05-2X/6-311++g(d,p) level of theory.

The diamagnetic and paramagnetic effects of ring currents related to aromaticity and anti-aromaticity can be gauged by nucleus independent chemical shift (NICS) [51,52] criterion. The NMR calculations have been performed at the M05-2X/6-311++g(d,p) level of theory using GIAO (gauge independent atomic orbital) method [53].

RESULTS AND DISCUSSION

The binding energies of all complexes are gathered in Table 1. As can be seen, binding energies of the Ben||substituted-coronene complexes decrease by 2.61-2.80 kcal mol^{-1} with BSSE correction at the M05-2X/6-311++g(d,p) level of theory.

The inset of substituents in Table 1 is given on the basis of electron-withdrawing character $NH_2 < CH_3 < OH < H < F < CF_3 < CN < NO$ in terms of the Hammett constants. The order of binding energies for mentioned complexes is $CH_3 < OH < H < NH_2 < F < NO < CF_3 < CN$.

The electron-withdrawing substituents improve the π–π stacking interactions compared to the electron-donating ones.

The order of binding energies for HFBen||substituted-coronene complexes is $NO < CF_3 < CN < F < H < OH < NH_2 < CH_3$. The binding energies of these complexes decrease by 5.41-7.19 kcal mol^{-1} with BSSE correction at the M05-2X/6-311++g(d,p) level of theory. As can be seen, electron-donating substituents enhance the π–π stacking interactions, while electron-withdrawing ones have opposite effect. This result arises from the nature of quadrupole moment in HFBen and highlights the role of electrostatic effects on the π–π stacking interactions.

The binding energy values in the HFBen||substituted-coronene complexes are higher than the Ben||substituted-coronene ones. In fact, interplay between positive quadrupole moment of HFBen and

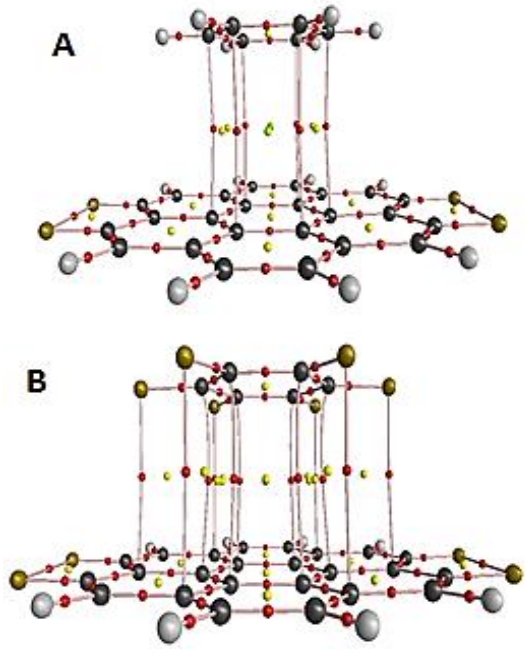
negative quadrupole moment of substituted-coronenes generates high π–π stacking binding energies.

To determine effects of π-resonance on π-π stacking binding energies, structural parameters of the central rings in coronene and substituted-coronenes were considered. Results show that attachment of X substituents to coronene leads to increment of C-C bond lengths at central ring of it. Also, differences between alternative C-C bond lengths at central rings of the substituted-coronenes are larger than coronene. Therefore, π-resonance effects in the central rings of substituted-coronenes are lower than coronene.

However, there aren't good correlations between ΔE values of both Ben||substituted-coronene and HFBen||substituted-coronene complexes and changes made by X substituents in these bonds.

Formation of the Ben||substituted-coronene/HFBen||substituted-coronene complexes leads to a little decrement/increment of C-C bond lengths at the central rings of substituted-coronenes. Thus, different nature of quadrupole moments in Ben and HFBen causes dissimilar changes in structural parameters at central rings of substituted-coronenes. In Fig. 1 ΔE values against these changes in the C-C bond lengths (Δr_{C-C}) are depicted. As can be seen, in both the Ben||substituted-coronene and HFBen||substituted-coronene complexes increment of Δr_{C-C} values is accompanied by increment of binding energies. Indeed, HFB changes these bonds more than Ben and leads to higher π-π stacking binding energies.

The results suggest that π electron cloud properties of central ring in coronene, which is changed by substituents, together with quadrupole moments of Ben and HFBen direct the strength of π-π stacking interactions in the Ben||substituted-coronene and HFBen||substituted-coronene complexes. There is a repulsive quadrupole-quadrupole interaction between Ben and substituted-coronenes in the Ben||substituted-coronene complexes. Thus, electron-withdrawing substituents lead to increment of binding energies by reduction of above repulsion. In contrast, there is an attractive quadrupole-quadrupole interaction between HFBen and substituted-coronenes in the HFBen||substituted-coronene complexes. In this case, complexes which carry electron-donating substituents have more binding energies in comparison with ones which have electron-withdrawing groups. In Fig.2 binding energies of the complexes against quadrupole moments of the substituted-coronenes are depicted. As can be seen, decrement of quadrupole moments of substituted-coronenes lead to increment of binding energies in Ben||substituted-coronene complexes, while reverse is true for HFBen||substituted-coronene complexes.



Scheme 2. Typical molecular graphs of the Ben||substituted-coronene (a) and HFBen||substituted-coronene (b) complexes.

AIM analysis

AIM analysis has been employed to illustrate π-π stacking interactions in terms of topological properties of electron charge densities at the critical points (CPs). Typical molecular graphs of the complexes studied in this work are presented in scheme 2. From these graphs, positions of bond critical points (BCPs), ring critical points (RCPs) and cage critical points (CCPs) can recognize. The wave functions obtained at the M05-2X/6-311++G(d,p) level were used for the AIM analysis.

Results of AIM analysis are consistent with structural parameters of the complexes. Formation of the Ben‖substituted-coronene and HFBen‖substituted-coronene complexes leads to increment of the electron charge densities at ring critical points (ρ_{RCPs}) of central rings of substituted-coronenes. Magnitude of this increment ($\Delta\rho_{RCP}$) in HFBen‖substituted-coronene complexes is more than Ben‖substituted-coronene ones. There aren't good correlations between binding energies of these complexes and corresponding $\Delta\rho_{RCP}$ values.

As can be seen in scheme 2, there are no BCPs between hydrogen atoms of Ben and carbon atoms of substituted-coronenes, while BCPs are observed between fluorine atoms of HFBen and carbon atoms of substituted-coronenes. This dissimilarity affects on the π-π stacking interactions in above mentioned complexes.

Charge transfer analysis

Atomic net charges were calculated using ChelpG scheme [50] on the optimized geometries obtained at the M05-2X/6-311++G(d,p) level of theory.

Results show that the negative charge on Ben in the Ben‖substituted-coronene complexes increases in comparison with the isolated monomer. Thus, CT occurs from substituted - coronene to Ben (substituted–coronene → Ben). The magnitude of this CT is in the range of -0.003− -0.051 e. The order of CT in these complexes is CN < NO < F < CF_3 < OH < H < NH_2 < CH_3. Also, the negative charge on HFBen in the HFBen‖substituted-coronene complexes show an enhancement compared to the free HFBen molecule. Accordingly, CT occurs from substituted-coronene to HFBen (substituted-coronene→HFBen). The magnitude of this CT is in the range of -0.034− -0.153 e. The order of CT in these complexes is CN < NO < CF_3 < F < OH < H < CH_3 < NH_2. As can be seen, the magnitude of CT in the HFB‖substituted-coronene complexes is higher than the Ben‖substituted-coronene ones. Indeed, electron-donating character of substituents in both complexes helps to CT happen from substituted-coronenes to Ben and HFBen.

The binding energy values against CT occurred between fragments for both Ben‖substituted-coronene and HFBen‖substituted-coronene complexes are depicted in Fig. 3. As can be observed, larger binding energy values in the Ben‖substituted-coronene complexes correspond to the cases with lower CT. In contrast, increment of CT in the HFBen‖substituted-coronene complexes leads to increase of binding energy values. The higher CT in the HFBen‖substituted-coronene complexes can be attributed to highly electronegative F atoms of HFBen. Results show that sum of negative atomic charges on these atoms in the HFBen‖substituted-coronene complexes is larger than the free HFBen molecule. On the other hand, H atoms of the isolated benzene molecule have positive atomic charges. Duo to CT, these atoms bears less positive charges in the Ben‖substituted-coronene complexes compared to the isolated Ben molecule. Complex formation indicate that decrement of positive charges

of H atoms in Ben is more than increment of negative charges of F atoms in HFBen. Indeed, C atoms have negative and positive charge in the isolated Ben and HFBen molecules, respectively. Complex formation leads to decrement of negative charge of C atoms in Ben.

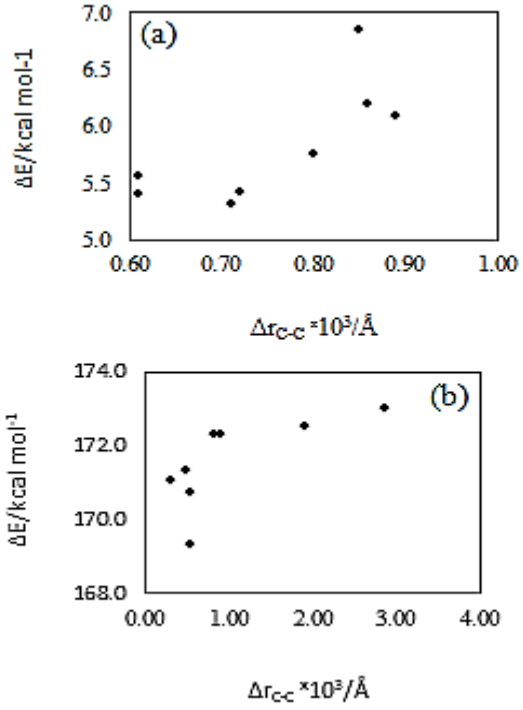


Fig. 1. The binding energies versus changes made by X groups in C-C bond lengths of the central ring of coronene for the Ben||substituted-coronene (a) and HFBen||substituted-coronene (b) complexes.

However, there isn't observed a regular behavior for changes of atomic charges of C atoms in HFBen during complex formation. Additionally, sums of atomic charges of the central rings of substituted-coronenes change during complex formation. Results reveal that these changes are more outstanding in the HFBen||substituted-coronene complexes than the Ben||substituted-coronene ones. Whereas in this study π-π stacking interactions were considered above central rings of substituted-coronenes it seems that more changes in the atomic charges at central rings of substituted-coronenes in the HFBen||substituted-coronene complexes affects on the π-π stacking binding energies. For that reason, increment of CT in the HFBen||substituted-coronene complexes is accompanied by increment of binding energy values. Thus, different electronegativity of the H and F atoms in Ben and HFBen which makes different quadrupole moments for these molecules affects on CT and binding energy values in the Ben||substituted-coronene and HFBen||substituted-coronene complexes. Consequently, these results reveal simultaneous effects of substituents and quadrupole moments on the π-π stacking interactions in complexes which direct electrostatic interactions of substituents on one ring don't influence π electron cloud of the other ring.

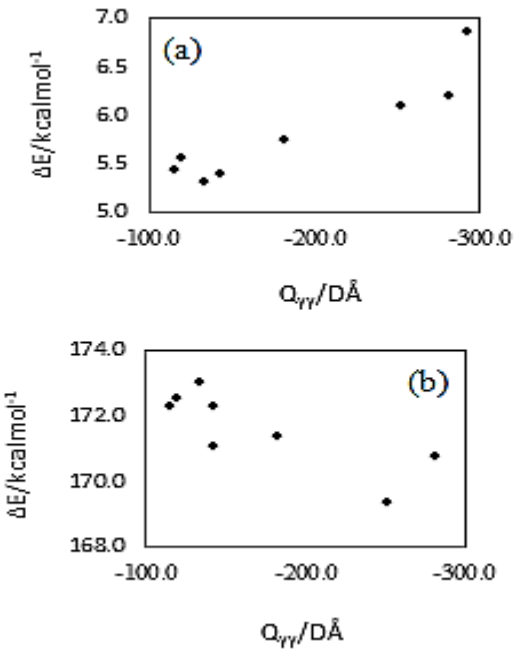


Fig. 2. The binding energies versus quadrupole moments of the substituted-coronenes for the Ben||substituted-coronene (a) and HFBen||substituted-coronene (b) complexes.

NMR calculations

Aromaticity has been judged on the basis of magnetic criterion and Scheyer et al.

suggested NICS as an index of aromaticity [51,52]. The NMR calculations have been performed at the M05-2X/6-311++g(d,p) level of theory using GIAO method [53] to understand effects of aromaticity of the substituted-coronenes on binding energies of the complexes. Because NICS at the 1 Å above the center of ring, NICS(1), is recommended as a better aromaticity diagnostic than the NICS(0) [51,52], this index was considered.

Table 1. The binding energies, -ΔE (in kcal mol^{-1}), equilibrium distances (in Å), changes of the electron charge densities at RCPs of the central rings of substituted-coronenes (in au) for all of the complexes calculated at the M05-2X/6-311++G(d,p) level of theory.

X	[a]ΔE	[a]$\Delta\rho_{RCP}\times10^{6}$	[a]$R_{cen-cen}$	[b]ΔE	[b]$\Delta\rho_{RCP}\times10^{3}$	[b]$R_{cen-cen}$	X	[a]ΔE
NH_2	8.26(5.55)	6.858	3.463	179.01(172.53)	1.260	3.311	NH_2	8.26(5.55)
OH	8.08(5.39)	6.146	3.486	177.78(172.31)	1.250	3.307	OH	8.08(5.39)
CH_3	7.92(5.91)	11.210	3.490	178.42(173.01)	1.290	3.303	CH_3	7.92(5.91)
H	7.94(5.42)	5.698	3.491	177.40(172.30)	1.286	3.319	H	7.94(5.42)
F	8.51(5.75)	10.810	3.495	176.90(171.35)	1.282	3.312	F	8.51(5.75)
CF_3	9.27(6.20)	13.610	3.496	177.21(170.77)	1.255	3.305	CF_3	9.27(6.20)

[a] Correspond to the Ben||substituted-coronene complexes.
[b] Correspond to the HFB||substituted-coronene complexes.
The data in parentheses are BSSE corrected binding energies calculated at the M05-2X/6-311++G(d,p) level of theory.
$\Delta\rho_{RC}$ indicates ($\rho_{RCP,\ complex}$ - $\rho_{RCP,\ monomer}$).

Results show that central rings of the substituted-coronenes are aromatic. The trend of aromaticity, on the basis of the NICS (1) values, for substituted-coronenes is NO < CH_3 < CF_3 < H < NH_2 < CN < OH < F. Thus, substituents change the aromaticity of the substituted-coronenes. However, on account of electron-withdrawing and electron-donating nature of substituents there is no reasonable relation between aromaticity of the central rings of the substituted-coronenes and binding energies of the Ben||substituted-coronene and HFBen||substituted-coronene complexes. Consequently, aromaticity of the central rings of the substituted-coronenes dosn't control magnitude of the binding energies in the mentioned complexes. As was said, quadrupole moment and CT effects have major roles in these complexes.

CONCLUSIONS

The order of binding energies in the Ben||substituted-coronene complexes is NH_2 < CH_3 < OH < H < F < CF_3 < CN < NO, while this order in the HFBen||substituted-coronene ones is NO < CF_3 < CN < F < H < OH < NH_2 < CH_3.

The binding energy values in the HFBen||substituted-coronene complexes are higher than the Ben||substituted-coronene ones.

The π-resonance effects in the central rings of substituted-coronenes are lower than coronene.

Formation of the Ben||substituted-coronene/HFBen||substituted-coronene complexes leads to a little decrement/increment of C-C bond lengths at the central rings of substituted-coronenes. HFB changes these bonds more

than Ben and leads to higher π-π stacking binding energies.

Decrement of quadrupole moments of substituted-coronenes lead to increment of binding energies in the Ben||substituted-coronene complexes, while reverse is true for the HFBen||substituted-coronene complexes.

Electron-donating character of substituents in both complexes helps to CT happen from substituted-coronenes to Ben and HFBen.

The order of CT in the Ben||substituted-coronene complexes is CN < NO < F < CF_3 < OH < H < NH_2 < CH_3, and in the HFBen||substituted-coronene complexes is CN < NO < CF_3 < F < OH < H < CH_3 < NH_2. The magnitude of CT in the HFB||substituted-coronene complexes is higher than the Ben||substituted-coronene ones.

The CT effects in the HFBen||substituted-coronene complexes are more than the Ben||substituted-coronene ones and increment of CT in the HFBen||substituted-coronene complexes is accompanied by increment of binding energies.

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