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Effects of structure and number of heteroatom on the π-π stacking interactions of benzene with *N*-substituted coronenes: A theoretical study

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Abstract

Stability of the π-π stacking interactions in the Ben||*N*-substituted-coronene complexes was studied using the computational quantum chemistry methods (where Ben is benzene and || denotes π-π stacking interaction, and *N*-substituted-coronene is coronene molecule which substituted with different number of N atoms). The results reveal simultaneous effects of structure and number of Heteroatom on the π-π stacking interactions with *N*-substituted-coronenes. Changing the number of Heteroatom N in *N*-substituted-coronenes and substitution of 8*N*-coronene with electron-withdrawing or electron-donating X groups alter the electron charge density at rings of this molecule and leads to different binding energies in the Ben||X-8N-substituted-coronene complexes. Results indicate that electron-withdrawing groups lead to higher π–π stacking binding energies compared to electron-donating ones in the Ben||X-8N-substituted-coronene complexes.

Keywords: π-π Stacking interaction, benzene, *N*-substituted-coronene, electron charge density, binding energy.

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Introduction

The noncovalent π–π stacking interactions play vital role in chemistry and biology [1,2]. These interactions contribute in protein folding [3-6], enzyme-substrate recognition [3,4] and crystal packing [7].

Computational studies give helpful information about π–π interactions in biological molecules. For example, results of computational calculations on π–π stacking interactions between DNA nucleobases [8-14] or interactions between nucleobases and aromatic systems [15,16] are useful for biochemical or medical applications.

Some authors have considered benzene dimer as a prototype of the π–π stacking interactions [17,18]. In the π-π stacking interactions involving phenyl rings, such as benzene dimer, the p orbitals do not function as in usual covalent bonds and overlapping between orbitals occurs [19-22]. The long-range dispersion interactions play a major role in the interaction energy of the benzene dimer [23]. The preferred geometries of the benzene dimer are sandwich, parallel-displaced, and T-shaped configurations and relative binding energies of these configurations can be explained by quadrupole-quadrupole and dispersion forces [24].

The nature of π-π stacking interactions has been illustrated by Hunters and Sanders using a model on the basis of electrostatic quadrupole-quadrupole interactions between fragments [25]. However, results of experimental and theoretical work of Rashkin and Waters on π-π stacking interactions emphasize on direct interactions of substituents on one ring with hydrogens on the other ring [26]. Also, Houk and Wheeler provide computational evidence for the importance of direct interactions of substituents on one ring with other aromatic ring in the π-π stacking interactions [27].

Coronene (superbenzene) is a polycyclic aromatic hydrocarbon (PAH) comprising six peri-fused benzene rings [28] with $C_{24}H_{12}$ chemical formula. It is a yellow material that dissolves in solvents such as benzene, toluene, and dichloromethane. Coronene has higher resonance energy per pi electron than benzene [29]. This symmetrical aromatic molecule is a good choice for theoretical investigations. In this work, π–π stacking interactions of benzene with central rings of coronene and *N*-substituted-coronenes have been investigated using computational quantum chemistry methods. We replaced outer C atoms of coronene with 1 to 8 N atoms to create *N*-substituted coronenes in order to study the effects of inclusion of heteroatom N in carbon structures on the π-π stacking interactions.

Computational methods

All geometries were fully optimized at the M05-2X/6-31g (**d**) level of theory with Gaussian09 program package [30]. The second-order Møller–Plessetperturbational method, MP2, usually overestimatesbinding 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 [31,32]. They proposed that hybrid meta-GGA functional, M05-2X, has good performance for computing the π-πstacking binding energies. On the other hand, the CCSD(T) calculations are very time-consuming. Therefore, M05-2X functional has been chosen for evaluation of the π-πstacking binding energies of the complexes studied in this work. The topological properties of electron charge density have been calculated by the AIM (atoms in molecules) method using AIM2000 [33] program.

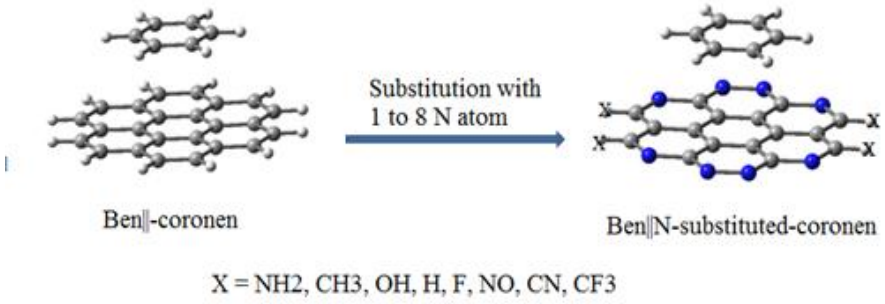
Results and discussion

The energy of monomers and binding energies of all complexes are gathered in Table 1. As can be seen, binding energies of the Ben||N-substituted-coronene complexes increase by increment of the number of Heteroatom N with the exception of complex **4a** at the M05-2X/6-31g (d) level of theory.

Table 1. The energy of monomers and complexes (in HartreeFock), binding energies (in kcal mol^{-1}) and lowest frequency (in cm^{-1}) of the Ben||N-substituted-coronene complexes.

Monomer	**Energy**	**Complex**	**Energy**	**-ΔE**	**Frequency**
coronene	-921.842	**a**	-1154.066	4.65	-20.49
1*N*-coronene	-937.877	**1a**	-1170.103	5.46	-49.16
2*N*-coronene	-953.875	**2a**	-1186.102	6.09	-75.06

3*N*-coronene	-969.908	**3a**	-1202.135	6.50	-44.21
4*N*-coronene	-985.903	**4a**	-1218.130	5.87	-42.42
5*N*-coronene	-1001.929	**5a**	-1234.158	7.38	-31.81
6*N*-coronene	-1017.954	**6a**	-1250.182	7.45	-12.83
7*N*-coronene	-1033.977	**7a**	-1266.207	8.29	-48.20
8*N*-coronene	-1049.999	**8a**	-1282.230	8.43	93.27



Scheme 1. Substitution of complex **a** with 1 to 8 N atom gives **1a** to **8a** complexes.

Results indicate that thedifference between C-C bond lengths at central ring of 3*N*-coronene is lower than 4*N*-coronene. Therefore, bond equivalent (which reflects delocalization effects) in 3*N*-coronene is higher than 4*N*-coronene and complex **4a** has lower π–π stacking interaction energy in comparison with complex **3a**.

The Ben||*N*-substituted-coronene complexes were optimized without the effects of

charge transfer (CT) in order to understand the effects of purely electrostatic interactions on the binding energies. Results reveal that binding energies of the complexes change from 6.54 to 10.32 kcal mol^{-1} in the absence of CT. Therefore, CT has an important contribution in the binding energies of the Ben||N-substituted-coronene complexes. Also, the effect of quadrupole moments of coronene and N-substituted coronenes (Qzz) on the binding energies of the Ben||N-substituted-coronene complexes was considered. Results show that increment of the number of N in the *N*-substituted-coronenemonomers is accompanied by increment of Qzz values. The Qzz values are in the range of -129.75 to -143.53 Debye Å. As stated in the manuscript, binding energies of the Ben||N-substituted-coronene complexes increase by increment of the number of Heteroatom N. Thus, quadrupole moments of the monomers influence on the binding energies of the mentioned complexes.

Increment of the number of Heteroatom N in the aromatic molecule coronene alters the electron charge densities at the rings of *N*-substituted-coronenes. Therefore, the π–π stacking interactions of the benzene molecule on central rings of *N*-substituted-coronenes can be affected by this phenomenon. Results of AIM analysis reveal that increment of the number of N atoms in the *N*-coronenes leads to increment of electron charge density at ring critical points (ρ_{RCP}) of central rings of *N*-coronenes. The ρ_{RCP} values are in the range of 1.971×10^{-2} to 2.165×10^{-2} au inwhich the lowest and highest values correspond to coroneneand **8*N*-coronene**, respectively. On the other hand, the ρ_{RCP} values for the X-8 *N*-substituted-coronenes are in the range of 2.006×10^{-2} to 2.165×10^{-2} au and order of ρ_{RCP} values is F < CN < NO ≈ OH < CH_3 < NH_2< H. Thus, decrement of the ρ_{RCP} values at central rings of X-8N-substituted-coronenes caused by electron-withdrawing substituents is accompanied by increment of binding energies in the above mentioned complexes.

It should be noted that substituent F has inductive electron-withdrawing and resonance electron-donating character. However, electron-withdrawing character of F overcomes its electron-donating character in the Ben||X-8N-substituted-coronene complexes and leads to decrement of ρ_{RCP} value.

Complex **8a** was considered to inquire the effects of substituents on the π–π stacking interactions in the Ben||N-substituted-coronene complexes. For this purpose, four electron-withdrawing or electron-donating X substituents (X = OH, NH_2, CH_3, F, NO, and CN) were attached to **8N-coronene**. Results

show that the binding energies increase in the order of CH_3 (7.43) < OH (7.89) < NH_2 (8.34) < H (8.43) < F (9.33) < NO (9.49) < CN (9.70).). Data shownin parentheses are binding energies in kcal mol^{-1}. As can be observed, It should be noted that X = H refersto the complex **8a** in the table 1. As can be observed, electron-withdrawing substituents improve the π–π stacking interactions compared to the electron-donating ones. In fact, the π–π stacking interaction of the benzene molecule with X-8N-coronene is affected by substituents X. Electron-withdrawing groups alter the electron charge density and quadruple moment of **8N-coronene** in such a way that they lead to more binding energies than electron-donating ones. Consequently, increments of thenumber of Heteroatom N in the coronene molecule and its substitution with electron-withdrawing groups give rise to the high π–π stacking binding energies.

Conclusion

Changing the number of Heteroatom N in N-substituted-coronenes alters the electron charge density at rings of these molecules and leads to different binding energies in the Ben||N-substituted-coronene complexes. Indeed, Charge transfer has an important contribution in the binding energies of the Ben||N-substituted-coronene complexes. Also, substitution of N-substituted-coronenes with electron-withdrawing groups leads to the high π–π stacking binding energies.

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