

Relationships between some calculated NMR data and π - π stacking binding energies in complexes involved substituted-coronenes, Benzene, and Hexafluorobenzene

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Abstract

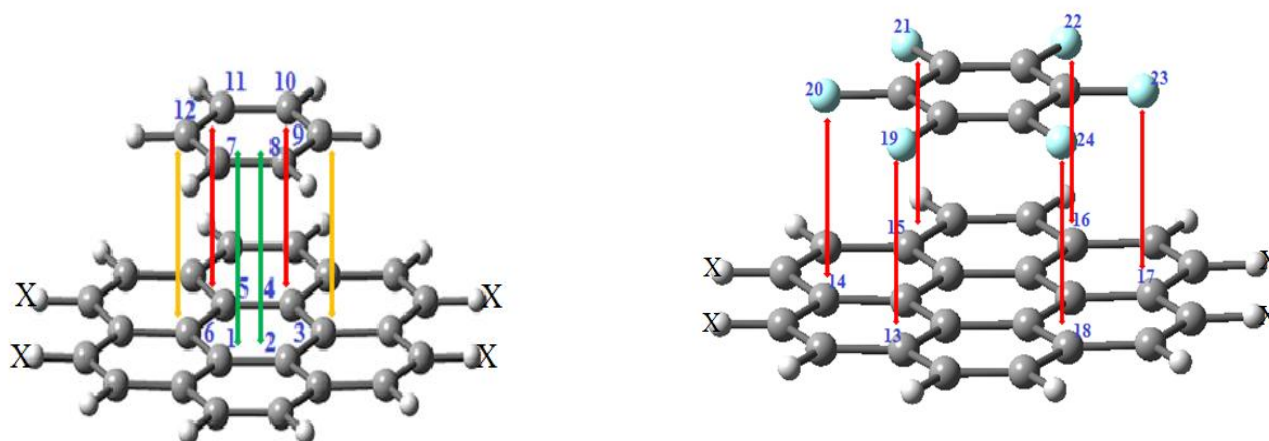
The π - π stacking interactions in the Ben||substituted-coronene and HFBen||substituted-coronene complexes was studied using the computational quantum chemistry methods (where Ben and HFBen are Benzene and Hexafluorobenzene, || denotes π - π stacking interaction, substituted-coronene is coronene molecule which substituted with four X groups, and X= NH₂, CH₃, OH, H, F, CN, and NO). The results reveal effects of substituents and opposite nature of Ben and HFBen on the π - π stacking interactions in complexes which direct electrostatic interactions of substituents on one ring don't manipulate π electron cloud of the other ring. Electron-withdrawing/electron-donating substituents lead to better binding energies in the Ben||substituted-coronene/HFBen||substituted-coronene complexes. Atoms in molecules (AIM) analysis and charge transfer (CT) effects, also relationships between through-space spin-spin coupling constants, J_{C-C} and J_{C-F} , and π - π stacking binding energies were studied in the Ben||substituted-coronene and HFBen||substituted-coronene complexes.

Keywords: coronene; π - π stacking; charge transfer; π electron cloud; coupling constant

1. Introduction

π -stacking" forces or " π - π interactions" describe the interactions between neighboring rings which involved π electron clouds. The π - π stacking interactions along with hydrogen bonds are essential factors which direct stability of the DNA structure. Theoretical and experimental studies have been comprehensively performed on the π - π stacking interactions [1-10]. Some authors have been considered benzene dimer as a prototype of the π - π stacking interactions [11-13]. Moreover, effects of substituent on interactions of aromatic molecules have been studied by theoretical calculations [14-17]. Substituent effects in π - π stacking interactions can be clarified on the basis of polarization of the π -system in substituted ring. Hunter and coworkers [1, 18] and Cozzi et al. [19] confirmed that electron-withdrawing substituents lead to better π - π stacking interactions by decrement of electrostatic repulsion between π clouds of the two interacting rings, but electron-donating ones hold back these interactions. Wheeler and Houk showed that the substituent effects in π -stacked benzene dimers be caused by direct electrostatic interactions between the substituents and the unsubstituted

benzene ring [20]. In the present work, binding energies, results of atoms in molecules (AIM) analysis, charge transfer (CT) effects, and also NMR calculations have been used to clarify strength of π - π stacking interactions 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 [21]. This point has been verified by some authors who considered the nature of molecular interactions involving these molecules [22]. Coronene (super Benzene) is a polycyclic aromatic hydrocarbon comprising of six peri-fused Benzene rings [23] which has a symmetrical structure. In the past, adsorption of hydrogen on benzene, coronene, and graphene was examined using quantum Monte Carlo calculations [24]. Also, substituent effects in C₆F₆-C₆H₅X stacking interactions have been previously investigated [25]. However, substituents X in C₆F₆-C₆H₅X complexes can lay on top of the π -face of HFBen and interfere in face-to-face π - π stacking interactions of Ben and HFBen. Herein, coronene was substituted with four electron-withdrawing or electron-donating groups (X= NH₂, CH₃, OH, H, F, 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-coronenes. Thus, face-to-face π - π stacking interactions of Ben and HFBen with an aromatic system can be examined. Typical optimized structures of the Ben||substituted-coronene and HFBen||substituted-coronene complexes are depicted in scheme (1). This study aids us to discover effects of substituent and charge transfer, also through-space spin-spin coupling constants on π - π stacking interactions. These simple modeled complexes can be supportive to recognize π -stacked structures in bio-molecular systems, also to propose new drugs.



(a)

(b)

Scheme 1. Presentation of through-space C-C (a), and C-F (b) spin-spin couplings in the Ben||substituted-coronene and HFBen||substituted-coronene complexes (X=NH₂, CH₃, OH, H, F, CN, and NO).

2. Computational Methods

All geometries were fully optimized at the M05-2X/6-311++g(d,p) level of theory with Gaussian09 program package [26]. Truhlar and Zhao developed a new generation of DFT methods to illustrate the π - π stacking interactions in DNA base pairs [27,28]. 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 insertion of an improved treatment of spin kinetic energy density in both the exchange and correlation functional [29]. Moreover, the CCSD(T) calculations are very time-consuming. Therefore, M05-2X functional was 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 the AIM method on the wave functions of optimized geometries using AIM2000 program [30]. Atomic net charges were calculated using ChelpG scheme at the M05-2X/6-311++g(d,p) level of theory [31]. The diamagnetic and paramagnetic effects of ring currents related to aromaticity and anti-aromaticity can be gauged by nucleus independent chemical shift (NICS) [32,33]. criterion. The NMR calculations have been performed at the M05-2X/6-311++g(d,p) level of theory using GIAO method [34]. SPINSPIN keyword was utilized to calculate coupling constants between atoms of the Ben||substituted-coronene and HFBen||substituted-coronene complexes. Total through-space spin-spin coupling constants J_{C-C} and J_{C-F} have been evaluated as the sum of paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC), and spin-dipole (SD) terms.

3. Results and discussion

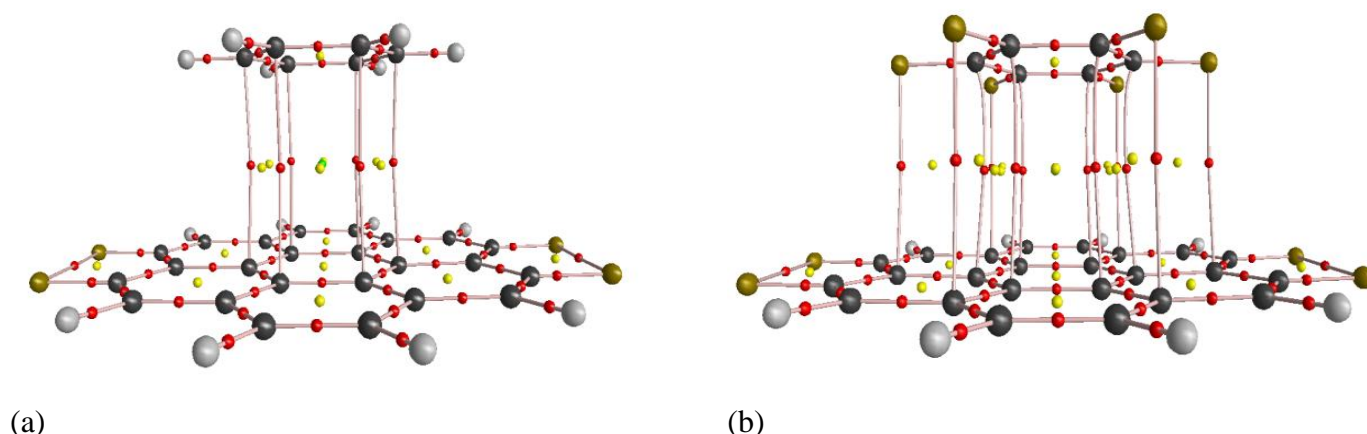
3.1. Energy data

The BSSE corrected binding energies, $-\Delta E$, of the Ben||substituted-coronene complexes calculated at the M05-2X/6-311++G(d,p) level of theory are in the range of 5.39 – 6.85 kcal mol⁻¹. The order of binding energies for these complexes is OH (5.39) < H (5.42) < NH₂ (5.55) < CH₃ (5.91) < F (5.75) < NO (6.09) < CN (6.85). As can be seen, the electron-withdrawing substituents improve the π - π stacking interactions compared to the electron-donating ones. The order of BSSE corrected binding energies of the HFBen||substituted-coronene complexes is NO (169.32) < CN (171.08) < F (171.35) < H (172.30) < OH (172.31) < NH₂ (172.53) < CH₃ (173.01). As can be seen, electron-donating substituents enhance the π - π stacking interactions, while electron-withdrawing ones have opposite effect in these complexes. 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 the substituted-coronene molecules makes large 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 mentioned 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.

3.2. 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) [35]. 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.



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

As can be seen in scheme 2, there are no BCPs between hydrogen atoms of Ben and carbon atoms of substituted-coronenes in the Ben||substituted-coronene complexes, while BCPs are observed between fluorine atoms of HFBen and carbon atoms of substituted-coronenes in the HFBen||substituted-coronene complexes. This finding indicates that electronegative fluorine atoms of HFBen tend to interplay with carbon atoms of the substituted-coronene molecules in the HFBen||substituted-coronene complexes, but there are no such interactions between hydrogen atoms of Ben and carbon atoms of the substituted-coronenes. To connect properties of the electron charge density at BCPs of C-F, ρ_{C-F} , in the HFBen||substituted-coronene complexes, correlations between π - π stacking binding energies and $\rho_{C14-F20}$ values were considered (atom numbering of the complexes are presented in scheme 1). As can be observed in Fig. 1, complexes with higher binding energies have relatively lower $\rho_{C14-F20}$ values. Therefore, although it seems that existence of BCPs between Fluorine atoms of HFBen and carbon atoms of substituted-coronenes has direct effect on π - π stacking binding energies in the HFBen||substituted-coronene complexes, but there is opposite effect. In fact, lower values of $\rho_{C14-F20}$ in complexes with larger π - π stacking binding energies shows the higher C14-F20 distances in these complexes than those have lower π - π stacking binding energies. However, all C-F distances have lower values than C-C ones in the HFBen||substituted-coronene complexes.

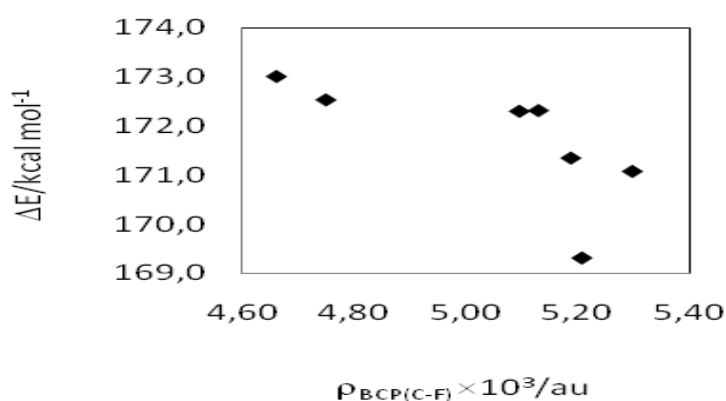


Figure 1. The π - π stacking binding energies, $-\Delta E$, against electron charge density values at BCPs of the C14-F20 contacts in the HFBen||substituted-coronene complexes.

3.3. CT analysis

Atomic net charges were calculated using ChelpG scheme [31] 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 < OH < H < NH₂ < CH₃. 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 < F < OH < H < CH₃ < NH₂. As can be seen, the magnitude of CT in the HFBen||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. 2. As can be observed, larger binding energy values in the Ben||substituted-coronene complexes correspond to the ones 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 compared to the Ben||substituted-coronene ones can be attributed to highly electronegative F atoms of HFBen which interplay with carbon atoms of substituted-coronenes. Also, different nature of quadrupole moments in HFBen and substituted-coronenes affects on magnitude of CT in these complexes (see scheme 2). 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. Because of CT, these atoms bears less positive charges in the Ben||substituted-coronene complexes compared to isolated Benzene. 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 charges in the isolated Ben and HFBen molecules, respectively. Complex formation leads to decrement of negative charges of C atoms in Ben. 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 that 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.

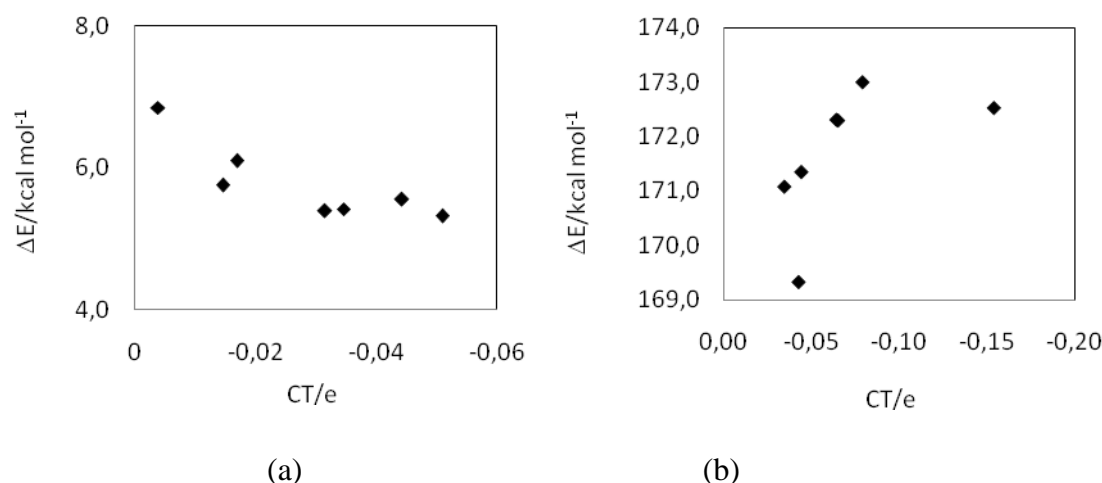


Figure 2. Correlations between the π - π stacking binding energies and charge transfer occurred in the Ben||substituted-coronene (a), and HFBen||substituted-coronene (b) complexes.

3.4. NMR calculations

Aromaticity has been judged on the basis of magnetic criterion and Scheyer et al. suggested NICS as an index of aromaticity [32,33]. The NMR calculations have been performed at the M05-2X/6-311++g(d,p) level of theory using GIAO method [34] 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 NICS(0) [32,33], this index was considered in this work. 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 in ppm is NO (-3.23) < CH₃ (-3.40) < H (-3.53) < NH₂ (-3.54) < CN (-3.82) < OH (-3.86) < F (-4.05). Thus, substituents change the aromaticity of the substituted-coronenes. However, as a result 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 doesn't control magnitude of the binding energies in the mentioned complexes. As was said, quadrupole moment and CT effects have key roles in these complexes.

Moreover, NMR calculations were performed using SPINSPIN keyword to understand relationships between π - π stacking binding energies and coupling constants J_{C-C} and J_{C-F} in the Ben||substituted-coronene and HFBen||substituted-coronene complexes. Thus, C-C couplings between carbon atoms at the central rings of substituted-coronenes (C1, C2, C3, C4, C5, and C6) and carbon atoms of Ben and HFBen (C7, C8, C9, C10, C11, and C12) were studied. Also, C-F couplings between carbon atoms of substituted-coronenes and Fluorine atoms of HFB in the HFBen||substituted-coronene complexes were calculated. As can be seen in scheme 1, 6 C-C couplings (C1-C7, C2-C8, C3-C9, C4-C10, C5-C11, and C6-C12) can be considered. The Ben||substituted-coronene and HFBen||substituted-coronene complexes have C_{2v} symmetry. Thus, C1-C7, C3-C9, C4-C10, and C6-C12 couplings are the same. Also, C2-C8, and C5-C11 couplings have the same values of coupling constants. Therefore, C1-C7 and C2-C8 couplings were chosen and values of total coupling constants J_{C-C} and components of them for these couplings are presented in the Tables 1 and 2 at the Ben||substituted-coronene and HFBen||substituted-coronene complexes, respectively. Moreover, there is 6 C-F couplings (C13-F19, C14-F20, C15-F21, C16-F22, C17-F23, and C18-F24) between carbon atoms of substituted-coronenes and Fluorine atoms of HFB in the HFBen||substituted-coronene complexes which

because of symmetry of the complexes two C13-F19 and C14-F20 couplings were selected and values of total coupling constants J_{C-F} and components of them for these couplings are presented in the Table 3.

The total coupling constants J_{C-C} and J_{C-F} have been evaluated as the sum of PSO, DSO, FC, and SD terms. Results indicate that the most important components of J_{C-C} in both the Ben||substituted-coronene and HFBen||substituted-coronene complexes are FC component. The total coupling constants J_{C-C} in the above mentioned complexes have the negative values and as can be observed in Fig. 3, complexes with higher binding energies have relatively the more negative J_{C1-C7} values. The most important components of J_{C-F} in the HFBen||substituted-coronene complexes are DSO components. Results show that increment of $J_{C14-F20}$ is accompanied by relatively increase of π - π stacking binding energies in the HFBen||substituted-coronene complexes (see Fig. 4). Also, absolute values of total coupling constants $J_{C14-F20}$ and all components of them in the HFBen||substituted-coronene complexes are greater than J_{C1-C7} ones. Therefore, through-space spin-spin couplings between C and F atoms, together with CT effects and quadrupole moment of HFBen, are important factors which make larger π - π stacking binding energies for the HFBen||substituted-coronene complexes in comparison with the Ben||substituted-coronene ones. These results highlight the role of Fluorine atoms of HFBen which contribute to through-space spin-spin couplings in π - π stacked systems and affect on magnitude of π - π stacking binding energies.

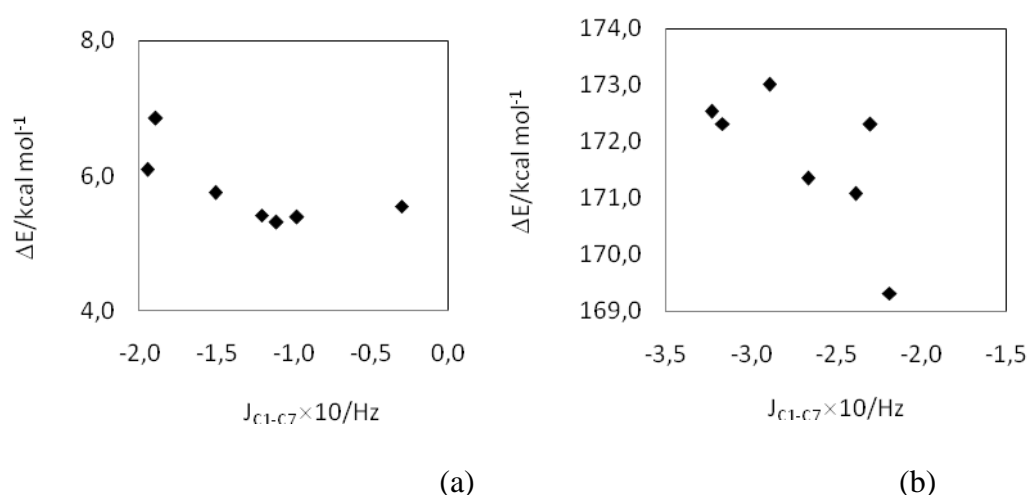


Figure 3. Relationships between the π - π stacking binding energies and total through-space C1-C7 spin-spin coupling constants in the Ben||substituted-coronene (a), and HFBen||substituted-coronene (b) complexes.

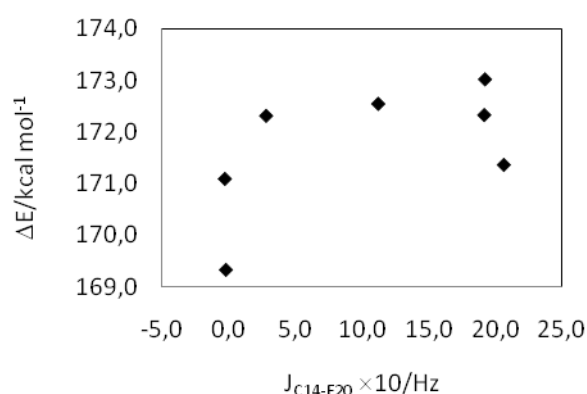


Figure 4. Relationships between the π - π stacking binding energies and total through-space C14-F20 spin-spin coupling constants in the HFBen||substituted-coronene complexes.

4. Conclusions

The order of binding energies in the Ben||substituted-coronene complexes is $\text{OH} < \text{H} < \text{NH}_2 < \text{CH}_3 < \text{F} < \text{NO} < \text{CN}$, while this order in the HFBen||substituted-coronene ones is $\text{NO} < \text{CN} < \text{F} < \text{H} < \text{OH} < \text{NH}_2 < \text{CH}_3$.

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

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 $\text{CN} < \text{NO} < \text{F} < \text{OH} < \text{H} < \text{NH}_2 < \text{CH}_3$, and in the HFBen||substituted-coronene complexes is $\text{CN} < \text{NO} < \text{F} < \text{OH} < \text{H} < \text{CH}_3 < \text{NH}_2$.

The magnitude of CT in the HFBen||substituted-coronene complexes is higher than the Ben||substituted-coronene ones and increment of CT in the HFBen||substituted-coronene complexes is accompanied by increase of π - π stacking binding energies.

The most important components of $J_{\text{C-C}}$ in the Ben||substituted-coronene and HFBen||substituted-coronene complexes are FC. Also, the most important components of $J_{\text{C-F}}$ in the HFBen||substituted-coronene complexes are DSO.

Fluorine atoms of HFBen which contribute to through-space spin-spin couplings in π - π stacked systems affect on magnitude of π - π stacking binding energies.

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