Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 12 (4) 359-368: Winter 2016
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Theoretical study of π-π stacking interactions in substituted-coronene||cyclooctatetraene complexes: A system without direct electrostatic effects of substituents

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Received August 2015; Accepted January 2016

ABSTRACT

Stability of the π-π stacking interactions in the substituted-coronene||cyclooctatetraene complexes was studied using the computational quantum chemistry methods (where || denotes π–π stacking interaction, and substituted-coronene is coronene which substituted with four similar X groups; X = OH, SH, H, F, CN, and NO). There are meaningful correlations between changes of geometrical parameters and topological properties of the electron charge densities at ring critical points due to formation of complexes and π-π stacking binding energies. In these complexes both electron-withdrawing and electron-donating substituents lead to larger binding energies compared to X = H (unsubsitituetted-coronene||cyclooctatetraene complex).This finding was interpreted on the basis of NMR data, especially spin-spin coupling constants between C atoms of cyclooctatetraene and C atoms at central rings of substituted-coronenes. Herein, relationships between the π–π stacking binding energy (-ΔE) values and, through-space C-C spin-spin coupling constants ($J_{C\text{-}C}$) in the substituted-coronene||cyclooctatetraene complexes has been investigated in the complexes without direct electrostatic effects of substituents.

Keywords: Coronene; Cyclooctatetraene; π-π stacking; NMR; Coupling constant

INTRODUCTION

The π–π stacking interactions are weak noncovalent forces that play n necessary 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]. Moreover, these forces are important for intercalation of drugs into the DNA molecule [8].

Characterization of individual π–π interactions experimentally has difficulties, but computational investigations gave useful information about these contacts in biological molecules. For example, computational calculations on π–π stacking interactions between DNA nucleobases [9-15] or interactions between nucleobases and aromatic systems [16-21] provide helpful insight for biochemical or medical researchers.

Hunter and coworkers [2, 22] explained substituent effects in π–π stacking interactions on the basis of polarization of the π-system of substituted ring. In fact, they reported that electron-withdrawing substituents enhance π–π stacking interactions by decrease of electrostatic repulsion between π–clouds of the two interacting rings, but electron-donating ones deter these interactions. Sinnokrotand coworkers [23] show that both electron-

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withdrawing and electron-donating substituents enhance strength of the π–π stacking interactions. On the other hand, Wheeler and Houk pointed out that the substituent effects in π–stacked benzene dimers arise from direct electrostatic interactions between the substituents and unsubstituted benzene ring [24].

Martin N. H. and coworkers studied through-space NMR shielding effects in some aromatic π-stacked complexes. They interpreted their findings in terms of polarization of the π-electron clouds of the substituted benzene rings duo to formation of complexes and NMR data [25].

Ab initio calculations have been previously performed on linear polycyclic aromatic hydrocarbons (acenes) [26]. Results of shielding increments above each ring center can be considered as an extension of aromaticity which correlated to geometric, energetic, and magnetic measurements of aromaticity.

Through-space NMR shielding effects in aromatic ring-cation complexes have been reported which confirm enhanced shielding over the π electron cloud of benzene during complexation with ammonium, lithium, sodium, potassium, magnesium, and calcium ions [27].

Effects of substituents on the through-space shielding of a series of aromatic rings were examined by C. W. Anson and D. M. Thamattoor. They discussed results of their work on the basis of polarization and field effects [28].

Through-space NMR shielding effects have been also computed in small-ring aromatic and anti-aromatic hydrocarbons using a diatomic hydrogen probe which indicate shielding and deshielding effects above the center of aromatic and anti-aromatic rings, respectively [29].

In the present work, π–π stacking interactions in thesubstituted-coronene||cyclooctatetraene complexes have been investigated using the computational quantum chemistry methods (where || denotes π–π stacking interaction, and substituted-coronene is coronene which substituted with four similar X groups; X = OH, SH, H, F, CN, and NO). Coronene or super benzeneis a polycyclic aromatic hydrocarbon (PAH) and provides a symmetric scheme of six fused benzene rings [30].Substitutions of four hydrogens of coronene with four X groups result in substituted-coronenes which have C2v symmetry and substituents are far from reaction centers (central rings of substituted-coronenes). Thus, π–π stacking interactions of planar cyclooctatetraene with the central rings of substituted-coronenes can be studied without direct electrostatic effects of substituents. In fact, the substituted-coronene||cyclooctatetraene complexes represent anti-aromatic||aromatic systems which aromatic rings of these systems have different π–electron clouds and anisotropic surroundings. Results of this study indicate that both electron-withdrawing and electron-donating substituents increase the π–π stacking interactions in the substituted-coronene||cyclooctatetraene complexes. Relationships between NMR and energy data were considered to investigate role of through-space spin-spin couplings in the observed behavior of the mentioned complexes.

COMPUTATIONAL METHODS

All geometries were fully optimized at the M05-2X/6-311++g (d, p) level of theory with Gaussian09 program package [31]. Truhlar and Zhao developed a new generation of DFT methods to illustrate the π–π stacking interactions in DNA base pairs [32, 33]. 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 inclusion of an improved treatment of spin kinetic energy density in both the exchange and correlation functionals [34]. On the other hand, the CCSD (T) calculations are very time-consuming. Therefore, M05-2X functional has 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 method on the wave functions of optimized geometries using AIM2000 [35] program.

The diamagnetic and paramagnetic effects of ring currents related to aromaticity and anti-aromaticity can be gauged by nucleus independent chemical shift (NICS) [36, 37] criterion.The NMR calculations have been performed at the M05-2X/6-311++g (d, p) level of theory using GIAO method [38]. SPINSPIN keyword was utilized to calculate coupling constants between atoms of the Substituted-coronene||cyclooctatetraene complexes. Total through-space spin-spin coupling constants JC-C have been evaluated as the sum of paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC), and spin-dipole (SD) terms.

RESULTS AND DISCUSSION

Energy data and geometrical parameters

The binding energies, most important geometrical parameters, and topological properties of electron charge densities of all complexes are gathered in Table 1.

Table 1. The binding energies, -ΔE, (in kcal mol^{-1}), most important geometrical parameters (in Å), and topological properties of the electron charge density (in au) for the substituted-coronene||cyclooctatetraene complexes calculated at the M05-2X/6-311++G(d,p) level of theory

X	-ΔE	$^{a}r_{C1\text{-}C2}$	$^{a}r_{C2\text{-}C3}$	$^{b}r_{C1\text{-}C2}$	$^{b}r_{C2\text{-}C3}$	$^{c}r_{C7\text{-}C8}$	$^{c}r_{C8\text{-}C9}$	$^{c}r_{C9\text{-}C10}$	$\Delta\rho_{RCP}\times10^{2}$	$\rho_{CCP}\times10^{3}$
OH	10.10	1.4262	1.4262	1.4248	1.4256	1.4759	1.3396	1.4755	0.206	1.154
SH	11.25	1.4287	1.4257	1.4271	1.4247	1.4763	1.3399	1.4757	0.269	1.165
H	9.57	1.4240	1.4240	1.4232	1.4233	1.4758	1.3362	1.4743	0.185	1.120
F	10.54	1.4243	1.4248	1.4231	1.4240	1.4762	1.3397	1.4756	0.269	1.128
CN	12.08	1.4254	1.4258	1.4242	1.4249	1.4756	1.3492	1.4760	0.290	1.121
NO	11.26	1.4268	1.4270	1.4256	1.4260	1.4764	1.3401	1.4759	0.305	1.132

^{a} refers to central rings of the substituted-coronene monomers, ^{b} refers to central rings of the substituted-coronenes in the Substituted-coronene||cyclooctatetraene complexes, and ^{c} refers to the cyclooctatetraene in the substituted-coronene||cyclooctatetraene complexes. The $r_{C7\text{-}C8}$, $r_{C8\text{-}C9}$, and $r_{C9\text{-}C10}$ bond lengths in monomer cyclooctatetraene are 1.4743, 1.3361, and 1.4743 Å, respectively.

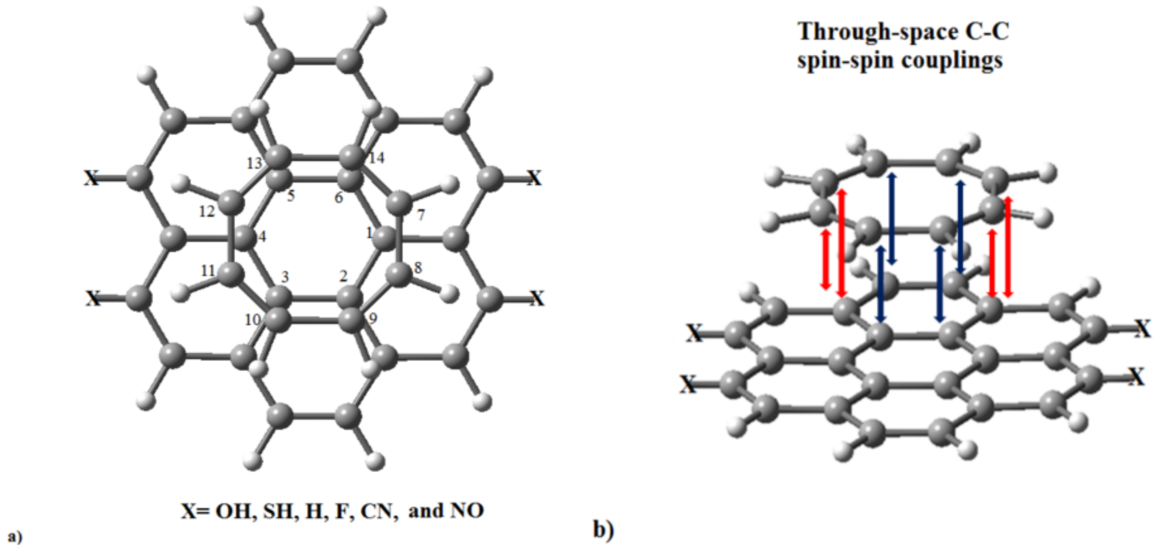
As can be seen, binding energiesof the substituted-coronene||cyclooctatetraene complexes are in the range of 9.57-12.08 kcal mol-1 at the M05-2X/6-311++g (d, p) level of theory. The order of binding energies for mentioned complexes is H <OH< F <SH <NO < CN.

In the Substituted-coronene||cyclooctatetraene complexes, four substituents (electron-withdrawing or electron-donating) were added tocoronene. These substituents are far from central ring of coronene and arrange in a symmetrical scheme. In this study, planar 8π-electron cyclooctatetraene was considered as an anti-aromatic molecule. This planar anti-aromatic molecule can interact with central rings of the substituted-coronenes without direct electrostatic effects of substituents.

Therefore, effects of substituents and aromaticity on π–π stacking interactionscan be gauged in anti-aromatic||aromatic complexes without direct hindrance of substituents (see scheme 1). Results show that the binding energies of all complexes are higher than the unsubstituted-coronene||cyclooctatetraene complex (X=H), and electron-withdrawing substituents improve the π–π stacking interactions more than the electron-donating ones.

As can be seen in Table 1, substituents lead to increase of C-C bond lengths at the central rings of substituted-coronenes. Results indicate that there is no direct relationship between this change in C-C bond lengths (${}^{1}\Delta r_{C\text{-}C}$) and binding energies. In fact, substituents aren't alone control π–π stacking binding energies in the Substituted-coronene||cyclooctatetraene complexes. Moreover, complex formation leads to decrement of the above mentioned C-C bond lengths. To connect theπ–π stacking binding energies with these changes in C-C bond lengths (${}^{2}\Delta r_{C\text{-}C}$) correlation between -ΔE and ${}^{2}\Delta r_{C\text{-}C}$ values was considered. As can be observed in Fig. 1, increment of ${}^{2}\Delta r_{C\text{-}C}$ values is relatively accompanied by increase of -ΔE values. On the other hand, complex formation leads to alternative increment and decrement of C-C bond lengths of the cyclooctatetraene monomer.

Correlations between binding energy values andthese changes in the C-C bond lengths, (${}^{3}\Delta r_{C\text{-}C}$) and (${}^{4}\Delta r_{C\text{-}C}$),were also examined.



Scheme 1. Typical structure of the substituted-coronene||cyclooctatetraene complexes (a); Manifestation of the through-space C-C spin-spin couplings in the substituted-coronene||cyclooctatetraene complexes (b).

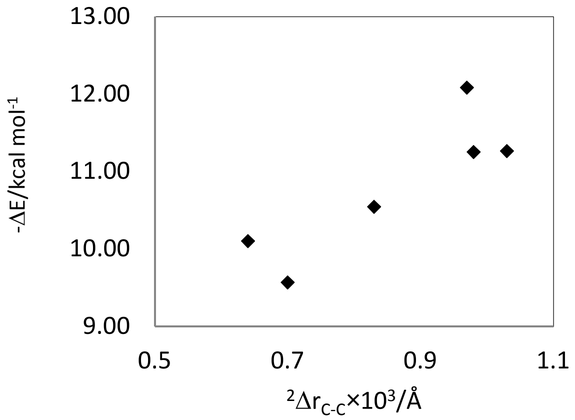
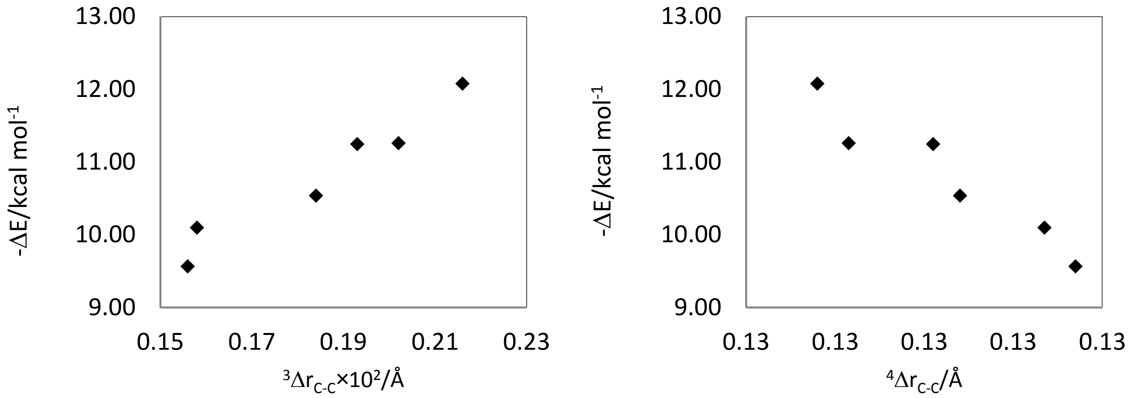


Fig. 1. The binding energies versus changes accrued in the C-C bond lengths at the central rings of substituted-coronenes duo to formation of the Substituted-coronene||cyclooctatetraene complexes.



(a) **(b)**

Fig. 2. The binding energies versus increment (a) and decrement (b) accrued in the C-C bond lengths of cyclooctatetraene duo to formation of the substituted-coronene||cyclooctatetraene complexes.

As demonstrated in Fig. 2, higher $^{3}\Delta r_{C\text{-}C}$ and lower $^{4}\Delta r_{C\text{-}C}$ values connect with higher π–π stacking binding energies. In fact, changes occurred in geometrical parameters of cyclooctatetraene during π–π stacking interaction with substituted-coronenes are important factors which show good correlations with ΔE values.

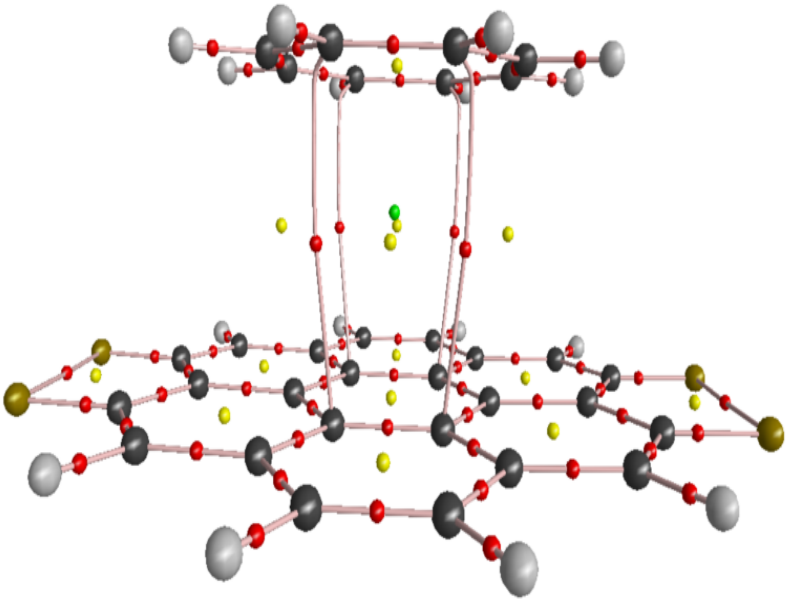
AIM analysis

AIM analysis has been employed to exemplify π-π stacking interactions in terms of topological properties of electron charge densities at the critical points (CPs) [39]. Typical molecular graphs of the complexes studied in this work are presented in scheme 2.

From these graphs, ring critical points (RCPs), positions of bond critical points (BCPs) and cage critical points (CCPs) can distinguish. Results explain that values of the electron charge densities at BCPs of all structures (ρ_{BCP}) are in accord with geometrical parameters. In fact, substituents lead to decrease of ρ_{BCP} at the central rings of substituted-coronenes.

Also, ρ_{BCP} values at the central rings of substituted-coronenes are higher than that in the substituted-coronene||cyclooctatetraene complexes.

Results indicate that complex formation is accompanied by increment of the electron charge densities at RCPs of central rings of substituted-coronenes. The π–π stacking binding energies against changes occurred in the electron charge densities of above mentioned RCPs, $\Delta\rho_{RCP}$,is shown in Fig. 3. As can be seen, increment of $\Delta\rho_{RCP}$ values is relatively associated with increase of -ΔE values.



Scheme 2. Typical molecular graph of the substituted-coronene||cyclooctatetraene complexes (red, yellow, and green spheres are bond, ring and cage critical points, respectively).

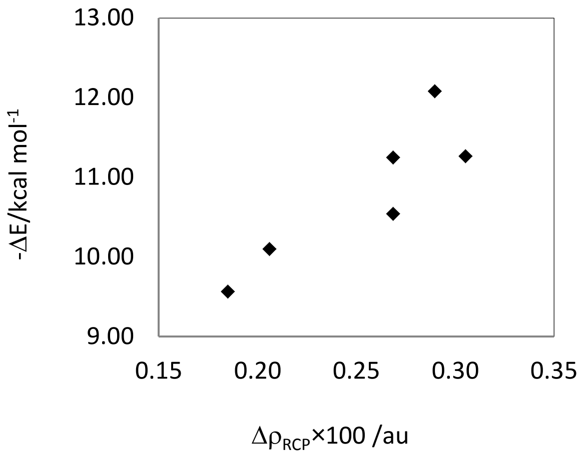


Fig. 3. The relationship between the binding energies and changes accrued in the ring critical points at the central rings of substituted-coronenes duo to formation of the substituted-coronene||cyclooctatetraene complexes.

NMR analysis

NMR calculations have been performed at the M05-2X/6-311++g (d, p) level of theory to relate binding energies of the Substituted-coronene||cyclooctatetraene complexes to diamagnetic or paramagnetic effects of ring currents and also to coupling constant values between atoms of the above mentioned complexes. Results indicate that on the basis of the NICS(1) values, which represents effects of ring currents 1Å above center of the central rings of substituted-coronenes, substitutedcoronene monomers are aromatic. However, there is no direct relation between NICS (1) values and electron-donating or electron-withdrawing nature of substituents. The order of aromaticity on the basis of NICS (1) values in ppm at the central ringsofsubstituted-coronene monomers is NO (-3.23) < H (-3.64) < OH (-3.86) < CN (-3.89) < F (-4.05) < SH (-4.38).

To find relationship between the π–π stacking binding energies and total through-space spin-spin coupling constants J_{C-C}in the substituted-coronene||cyclooctatetraene complexes, C-C couplings between carbon atoms at the central rings of substituted-coronenes(C1, C2, C3, C4, C5, and C6) and carbon atoms of cyclooctatetraene (C7, C8, C9, C10, C11, C12, C13, and C14) were studied. As can be seen in scheme 1, four C2-C9, C3-C10, C5-C13, and C6-C14 couplings can be considered (blue two-sided arrows). Also, C1-C7, C1-C8, C4-C11, and C4-C12 couplings were measured (red two-sided arrows). The total coupling constants J_{C-C} have been evaluated as the sum of PSO, DSO, FC, and SD terms. Results indicate that SD and PSO components of J_{C-C} better correlate with the π–π stacking binding energies in the Substituted-coronene||cyclooctatetraene complexes. In fact, increment of SD and PSO components of coupling constants J_{C-C} in these complexes accompanied by relatively increase of -ΔE values. The π–π stacking binding energies versus SD and PSO components of J_{C2-C9} coupling constants in the substituted-coronene||cyclooctatetraene complexes are shown in Fig. 4.

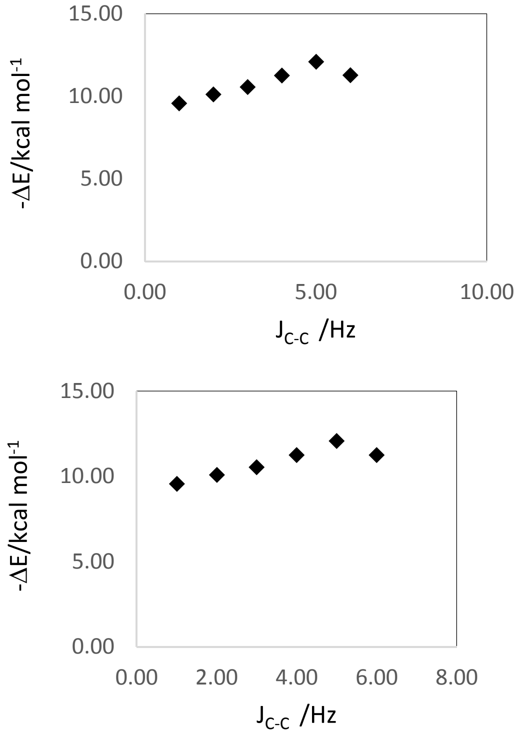


Fig. 4. Correlation between the π–π stacking binding energies and, SD (a) and PSO (b) components of J_{C2-C9} coupling constants in the substituted-coronene||cyclooctatetraene complexes.

Also, total coupling constants $J_{C-C}$and components of them in the above mentioned complexes are gathered in Table 2. The substituted-coronene||cyclooctatetraene complexes have C_{2v} symmetry. Thus, C2-C9, C3-C10, C5-C13, and C6-C14 couplings are the same. Also, C1-C7, C1-C8, C4-C11, and C4-C12 couplings have the same values of coupling constants. Therefore, C2-C9 and C1-C7 couplings were chosen and values oftotal coupling constants J_{C-C} and components of them are presented in the Table 2. As can be observed, the most important components of $J_{C2\text{-}C9}$ and $J_{C1\text{-}C7}$ are FC and DSO, respectively. Moreover, total coupling constants $J_{C2\text{-}C9}$ andall components of them in the substituted-coronene||cyclooctatetraene complexes are greater than $J_{C1\text{-}C7}$ ones (with the exception of PSO components). Therefore, C2-C9, C3-C10, C5-C13, and C6-C14 couplings have higher through-space effects than C1-C7, C1-C8, C4-C11, and C4-C12 ones and may have important contributions in increment of π–π stacking binding energies in the Substituted-coronene||cyclooctatetraene complexes. These results emphasize on major role of total through-space spin-spin coupling constants $J_{C\text{-}C}$, which are criterions of couplings between C atoms of two interacting rings, on the strength of π–π stacking interactions.

Table 2. The coupling constant $J_{C\text{-}C}$ and its components (in Hz) for the substituted-coronene||cyclooctatetraene complexes calculated at the M05-2X/6-311++G** level of theory.

X	^{a}FC	^{a}SD×10	^{a}PSO×10	^{a}DSO	$^{a}J_{C\text{-}C}$	^{b}FC×10	^{b}SD×10	^{b}PSO×10	^{b}DSO	$^{b}J_{C\text{-}C}$
OH	0.390	0.019	-0.470	0.126	0.471	-0.817	-0.182	-0.461	0.123	-0.023
SH	0.434	0.110	-0.459	0.127	0.530	-0.146	-0.190	-0.469	0.127	-0.084
H	0.407	0.135	-0.426	0.121	0.498	-0.204	-0.188	-0.424	0.116	0.034
F	0.397	0.048	-0.468	0.125	0.480	-0.123	-0.173	-0.465	0.122	0.046
CN	0.563	0.198	-0.459	0.125	0.662	-0.323	-0.158	-0.474	0.122	0.055
NO	0.698	0.440	-0.478	0.126	0.821	-0.416	-0.160	-0.488	0.124	0.017

^{a}and ^{b} refer to C2-C9 and C1-C7 couplings, respectively.

Also, substituents X can impact on reaction centers (central rings of substituted-coronenes) and influence the strength of π–π stacking interactions in the substituted-coronene||cyclooctatetraenecomplexes.Finally, these results highlight the role of total through-space C-C spin-spin coupling constants as important NMR data and substituents on strength of the π–π stacking interactions.

CONCLUSIONS

The order of binding energies calculated at the M05-2X/6-311++G (d, p) level of theory for the substituted-coronene||cyclooctatetraene complexes is H < OH< F < SH < NO < CN. The binding energies of all complexes are higher than the unsubstituted-coronene||cyclooctatetraene complex (X=H). Electron-withdrawing substituents improve the π–π stacking interactions more than the electron-donating ones in the substituted-coronene||cyclooctatetraene complexes.

Complex formation leads to decrement of the C-C bond lengths at the central rings of substituted-coronenes and higher changes occurred in the mentioned bond lengths relatively accompanied by increase of ΔE values. Indeed, complex formation leads to alternative increment and decrement of C-C bond lengths of the cyclooctatetraene monomer. There are good correlations between the π–π stacking binding energy values and these changes occurred in the C-C bond lengths.

Increment of $\Delta\rho_{RCP}$ values at central rings of substituted-coronenes is relatively associated with increase of ΔE values. The order of aromaticity at the central rings of substituted-coronene monomers is NO < H < OH < CN < F < SH.

Increment of SD and PSO components of coupling constants J_{C-C} in the substituted-coronene||cyclooctatetraene complexes accompanied by relatively increase of ΔE values. Total through-space spin-spin coupling constants J_{C-C} have major role on the strength of π–π stacking interactions.

Substituents X can effect on reaction centers (central rings of substituted-coronenes) and influence the strength of π–π stacking interactions in the substituted-coronene||cyclooctatetraene complexes.

ACKNOWLEDGEMENT

I thank research consul of university of Zabol for the financial supports.

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