Structure and Binding Energy of Anion−π and Cation−π Complexes: A Comparison of MP2, RI-MP2, DFT, and DF-DFT Methods

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Several complexes of benzene with cations, hexafluorobenzene with anions, 1,3,5-trifluorobenzene with cations and anions, and *s*-triazine with cations and anions have been evaluated and compared at the MP2 and resolution of the identity MP2 (RI-MP2) levels. The RI-MP2 method is considerably faster than the MP2 and the interaction energies and equilibrium distances are almost identical for both methods. A similar result is found when comparing DFT and density fitting DFT (DF-DFT) levels. Therefore RI-MP2 and DF-DFT methods are well suited for the study of ion−π interactions.

1. Introduction

Meyer et al.[1] have recently reviewed interactions involving aromatic rings, which are important binding forces in both chemical and biological systems. For instance arene−arene interactions play an essential role in the structure of DNA and proteins, as well as in their interaction with small molecules.[2,3] The interactions of cation and π-electrons, namely cation−π interactions,[4] are strong noncovalent forces of great importance in many systems, including cation receptors and biomolecules.[5] The cation−π interaction is in general dominated by electrostatic and cation-induced polarization.[6] The nature of the electrostatic component has been rationalized emphasizing the function of the permanent quadrupole moment of benzene.[7] The interaction of anions with electron-deficient aromatic rings, namely anion−π interactions,[8−10] has attracted considerable attention in the past few years.[11−13] Experimentally, anion−π interactions have been recently observed, first in the solid state in a $Cl^-\cdots$*s*-triazine complex[14] and second in solution in anion-binding studies of *N*-confused porphyrins as a secondary interaction.[15] It has been speculated that electron-deficient aromatic rings can be used as new binding units for the molecular recognition of anions,[16,17] and recently two receptors based on anion−π interactions have been reported.[18,19]

Computational methods are widely used to rationalize and understand the noncovalent interactions that are present in any host−guest system and to design improved receptors for a given guest. High-level ab initio calculations are usually required to obtain accurate results, especially when π-interactions are present. In such systems, the use of a theoretical treatment that takes into account the electron correlation is mandatory. The MP2 method is the least expensive post HF procedure that takes into account dispersion forces, which are neglected in currently popular DFT approaches. Nevertheless, the main obstacle to a more widespread use of the MP2 method continues to be its high computational requirement, principally in medium to large systems. Because of the time-consuming nature of the MP2 calculations on these systems, we have explored the reliability of two computationally faster treatments than traditional MP2 and DFT methods. We have applied them to study the interaction of aromatic rings with cations and anions. Anion−π complexes are, in general, computationally more costly than cation−π complexes since they have a major number of heavy atoms as a consequence of the electron-withdrawing groups attached to the aromatic ring. The first selected method is the resolution of the identity MP2 (RI-MP2),[20,21] which uses an auxiliary fitting basis to avoid treating the complete set of two-electron repulsion integrals. The second is the density-fitting DFT (DF-DFT) approach,[22,23] which expands the density in a set of atom-centered functions when computing the Coulomb interaction instead of computing all of the two-electron integrals. It should be mentioned that the DFT method does not take into account dispersion effects, which can be non-negligible in cation−π[24] and anion−π interactions[17,25] and, particularly, in arene−arene stacking interactions.[26]

In this article, we report a comparative analysis to explore the reliability of the above-mentioned methods for the study of cation−π and anion−π interactions. We have tested the methods by performing calculations on a series of π-complexes of benzene (BEN) with cations and hexafluorobenzene (HFB) with anions, and additionally we have performed calculations on complexes of 1,3,5-trifluorobenzene (TFB) and *s*-triazine (TAZ), which present dual binding mode,[27] with cations and anions (see Figure 1). First, we compared the results at the MP2/6-31++G** and RI-MP2/6-31++G** levels of theory. Second, we have compared the results at the BLYP/6-31++G** and DF−BLYP/6-31++G** levels of theory in order to check the validity and performance of the density fitting treatment. Third, we have also compared the results at the MP2 level with the corresponding results at the BLYP and DF-BLYP levels to evaluate the importance of considering the dispersion effects when studying these interactions. To the best of our knowledge, previous calculations on anion−π complexes at the RI-MP2 level of theory to evaluate its reliability are not present in the literature. There is a previous study on $N-H\cdots\pi$ interactions[28] at the RI-MP2/TZVPP level of theory and, more recently,

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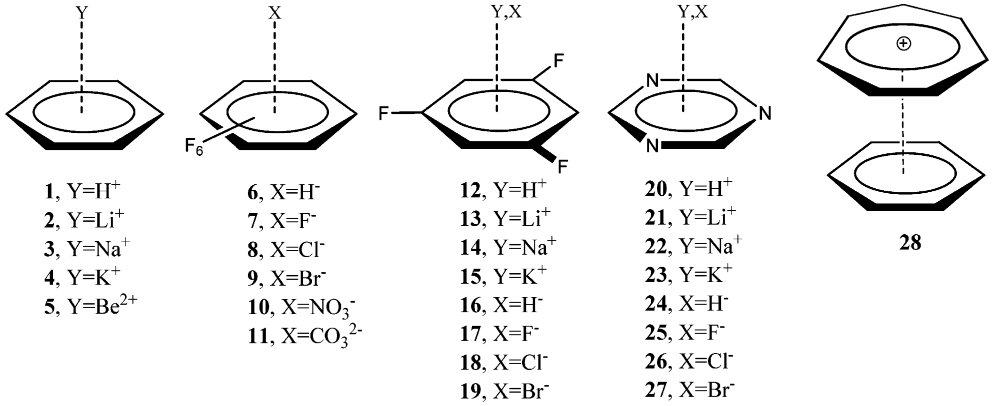

Figure 1. Cation−π and anion−π complexes (**1**−**28**) studied in this work.

another study at the same level on the interaction of dihydrogen with aromatic systems.[29] Additionally, there is a previous comparative study where both MP2 and RI-MP2 methods are used to evaluate the stacking behavior of DNA base pairs.[30] Moreover, there are several works that have successfully used RI-MP2 calculation to study several issues regarding nucleic acid bases, i.e., stacking,[31] hydrogen bonding,[32] tautomers,[33] and complexation with metal ions.[34] Similarly to RI-MP2, there are no previous calculations on anion−π interactions using the DF-DFT methodology in the literature. However, there are several works where fast DFT methods[35] are used to evaluate cationic complexes of transition metals with aromatic ligands.[36]

2. Computational Methods

The geometry of all the complexes included in this study was fully optimized at the MP2/6-31++G**, BLYP/6-31++G**, DF-BLYP/6-31++G**, and B3LYP/6-31++G** levels of theory with use of the Gaussian 98[37] and Gaussian 03 programs.[38] No symmetry constrains have been imposed in the optimizations except for complexes **7** (HFB⋯F^-), **17** (TFB⋯F^-), **24** (TAZ⋯H^-), and **25** (TAZ⋯F^-) where C_{6v} (**7**) and C_{3v} (**17**, **24**, and **25**) symmetry was used at all levels of theory. The minima correspond to the nucleophilic attack of the fluoride/hydride to one carbon atom of the ring. In addition, complex **11** (HFB⋯CO_3^{2-}) has been optimized only at the MP2 and RI-MP2 levels of theory since they do not converge at the density functional methods used in this paper. The binding energies were calculated at the same level with and without correction for the basis set superposition error (BSSE), using the Boys−Bernardi counterpoise technique.[39] The geometry optimization of the complexes at the RI-MP2/6-31++G** level of theory was performed with the program TURBOMOLE version 5.7.[40] Since the TURBOMOLE program does not include an auxiliary basis set for the 6-31++G** basis, we used Ahlrichs VDZ[41] (SVP in TURBOMOLE notation) as the auxiliary basis set. To examine a system where the dispersion effect is expected to be very important, thus being a good test for the RI-MP2 method, we have optimized complex **28** where the cation is a large π-system (see Figure 1). This complex has been optimized at the RI-MP2/6-31++G** and MP2/6-31++G** levels of theory without symmetry constrains. The geometry of the minimum corresponds to the parallel-displaced stacked structure.

3. Results and Discussion

TABLE 1: Interaction Energies (kcal/mol) at MP2/6-31++G and RI-MP2/6-31++G** Levels of Theory with (E_{BSSE}) and without (E) the BSSE Correction, and Equilibrium Distances (R_e, Å) for Complexes 1−28**

	E		E_{BSSE}		R_e	
compd	MP2	RI-MP2	MP2	RI-MP2	MP2	RI-MP2
BEN⋯H^+ (**1**)	−130.6	−130.7	−126.0	−126.0	0.865	0.866
BEN⋯Li^+ (**2**)	−37.4	−37.5	−33.2	−33.7	1.899	1.914
BEN⋯Na^+ (**3**)	−24.6	−26.1	−21.0	−21.4	2.429	2.393
BEN⋯K^+ (**4**)	−17.7	−18.0	−15.0	−14.9	2.894	2.904
BEN⋯Be^{2+} (**5**)	−228.8	−229.9	−220.2	−220.7	1.279	1.271
HFB⋯H^- (**6**)	−17.5	−17.5	−14.3	−14.6	2.706	2.705
HFB⋯F^- (**7**)	−21.3	−21.9	−18.1	−18.8	2.570	2.566
HFB⋯Cl^- (**8**)	−18.0	−18.4	−13.2	−13.1	3.155	3.154
HFB⋯Br^- (**9**)	−20.7	−17.7	−12.4	−12.7	3.214	3.282
HFB⋯NO_3^- (**10**)	−18.7	−19.1	−12.4	−12.7	2.922	2.927
HFB⋯CO_3^{2-} (**11**)	−41.2	−40.8	−32.9	−32.1	2.734	2.750
TFB⋯H^+ (**12**)	−104.2	−105.5	−100.2	−101.4	0.948	0.955
TFB⋯Li^+ (**13**)	−19.1	−20.3	−15.9	−16.1	2.056	2.020
TFB⋯Na^+ (**14**)	−12.2	−11.9	−8.2	−8.0	2.552	2.503
TFB⋯K^+ (**15**)	−7.8	−7.6	−4.9	−4.6	3.044	3.038
TFB⋯H^- (**16**)	−6.9	−6.7	−4.4	−4.4	3.021	3.031
TFB⋯F^- (**17**)	−10.0	−10.2	−7.7	−7.7	2.748	2.755
TFB⋯Cl^- (**18**)	−8.8	−9.0	−4.8	−4.8	3.323	3.336
TFB⋯Br^- (**19**)	−11.6	−8.9	−4.4	−4.9	3.359	3.468
TAZ⋯H^+ (**20**)	−84.8	−84.6	−79.7	−79.5	0.782	0.783
TAZ⋯Li^+ (**21**)	−8.7	−9.1	−6.2	−6.1	2.195	2.166
TAZ⋯Na^+ (**22**)	−4.5	−5.4	−2.6	−2.6	2.696	2.634
TAZ⋯K^+ (**23**)	−3.5	−3.4	−1.6	−1.3	3.124	3.131
TAZ⋯H^- (**24**)	−7.1	−7.0	−4.8	−4.8	2.982	2.887
TAZ⋯F^- (**25**)	−12.7	−12.8	−9.7	−9.8	2.592	2.584
TAZ⋯Cl^- (**26**)	−8.8	−9.0	−5.2	−5.3	3.223	3.220
TAZ⋯Br^- (**27**)	−10.2	−8.4	−5.0	−5.0	3.339	3.338
28	−15.2	−8.8	−14.5	−8.7	3.564[a]	3.565[a]

[a] Ring centroid to ring centroid distance.

Table 1 reports the energies and equilibrium distances corresponding to the interaction of BEN with a series of cations (complexes **1**−**5**), HFB with a series of anions (complexes **6**−**11**), TFB with a series of cations and anions (complexes **12**−**19**), and TAZ with a series of cations and anions (complexes **20**−**27**) at the MP2 and RI-MP2 levels of theory. The results indicate that the interaction energies obtained at both levels of theory are in excellent agreement. The largest difference found is only 1.2 kcal/mol (E_{BSSE}), very small considering that the range of binding energies is large (from −13 to −220 kcal/mol) and the different nature of the complexes. A similar behavior is observed when examining the equilibrium distances computed at both levels. The largest difference is 0.109 Å, obtained for complex **19**. The average for all complexes is only 0.022 Å. The performance of the RI-MP2 method can be examined from the correlation analysis given in Figure 2, which shows an $R^2 = 1.0000$ for the correlation between the binding energies (E_{BSSE}) computed at both levels of theory, and it also shows a strong correlation $R^2 = 0.9998$ for the relationship between the equilibrium distances (R_e) computed at both levels.

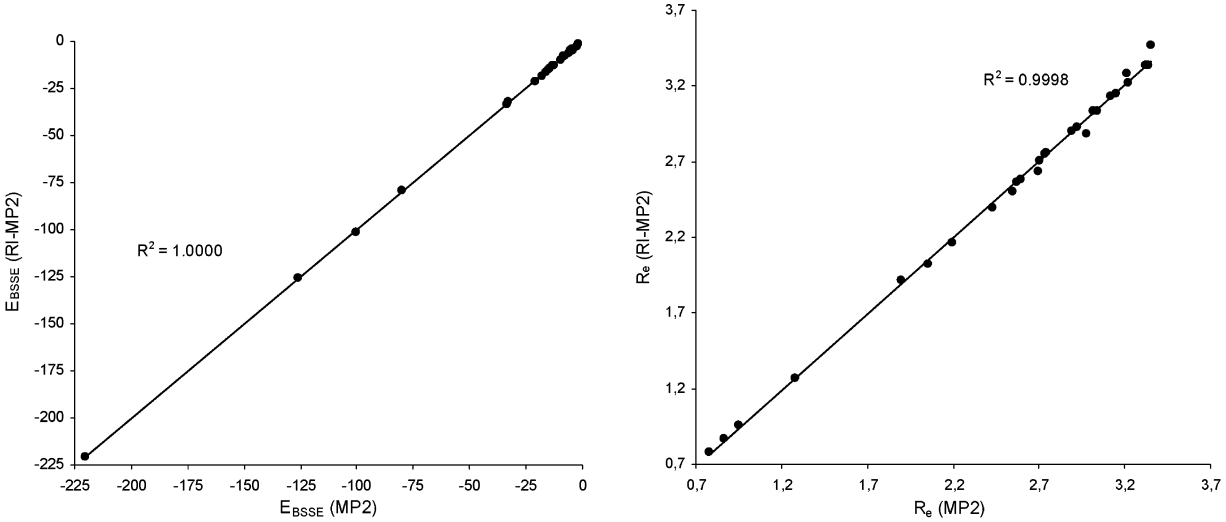

Figure 2. Plot of the regressions between the E_{BSSE} (left) and between the R_e (right) computed values at MP2 and RI-MP2 levels of theory, using the 6-31++G** basis set.

TABLE 2: Interaction Energies (kcal/mol) at MP2/6-31++G, MP4/6-31++G**, and CCSD/6-31++G** Levels of Theory with (E_{BSSE}) and without (E) the BSSE Correction, and Equilibrium Distances (R_e, Å) for Selected Cation−π and Anion−π Complexes**

	E			E_{BSSE}			R_e		
compd	MP2	MP4	CCSD	MP2	MP4[a]	CCSD[a]	MP2	MP4	CCSD
BEN···Li$^+$ (**2**)	−37.4	−37.2	−37.0	−33.2			1.899	1.899	1.899
HFB···H$^-$ (**6**)	−17.5	*b*	−16.3	−14.3	*b*	−13.0	2.706	*b*	2.789
TFB···Li$^+$ (**13**)	−19.1	−18.6	−18.3	−15.9			2.056	2.056	2.056
TFB···H$^-$ (**16**)	−6.9	−6.1	−5.9	−4.4	−3.5	−3.2	3.021	3.110	3.145
TAZ···Li$^+$ (**21**)	−8.7	−8.3	−8.1	−6.2			2.195	2.194	2.195
TAZ···H$^-$ (**24**)	−7.1	−6.2	5.9	−4.8	−3.8	−3.4	2.982	2.952	3.042

[a] The BSSE correction calculation unexpectedly fails for all the cation−π complexes at MP4 and CCSD levels, using either Gaussian-98 or Gaussian-03 programs. [b] The optimization of **6** stops with an unsolvable error message at the MP4/6-31++G** level of theory.

TABLE 3: Interaction Energies (kcal/mol) at BLYP/6-31++G, DF−BLYP/6-31++G** and B3LYP/6-31++G** Levels of Theory with (E_{BSSE}) and without (E) the BSSE Correction, and Equilibrium Distances (R_e, Å) for Complexes 1-27**

	E			E_{BSSE}			R_e		
compd	BLYP	DF-BLYP	B3LYP	BLYP	DF-BLYP	B3LYP	BLYP	DF-BLYP	B3LYP
BEN···H$^+$ (**1**)	−132.9	−132.9	−130.7	−132.4	−132.4	−130.3	0.935	0.934	0.917
BEN···Li$^+$ (**2**)	−36.2	−36.2	−37.8	−35.5	−35.5	−37.2	1.936	1.936	1.835
BEN···Na$^+$ (**3**)	−23.2	−23.2	−24.6	−22.6	−22.6	−24.1	2.422	2.416	2.395
BEN···K$^+$ (**4**)	−14.3	−14.3	−15.9	−13.9	−13.9	−15.5	2.907	2.907	2.943
BEN···Be^{2+} (**5**)	−231.2	−231.2	−232.8	−230.3	−230.4	−231.9	1.288	1.289	1.291
HFB···H$^-$ (**6**)	−17.5	−18.4	−15.3	−16.6	−17.6	−14.8	2.640	2.894	2.802
HFB···F$^-$ (**7**)	−18.4	−18.9	−18.9	−14.8	−16.9	−17.5	2.726	2.725	2.656
HFB···Cl$^-$ (**8**)	−11.2	−11.0	−11.2	−10.2	−10.7	−11.0	3.376	3.357	3.310
HFB···Br$^-$ (**9**)	−12.9	−13.3	−13.7	−8.6	−9.1	−9.4	3.416	3.396	3.367
HFB···NO$_3^-$ (**10**)	−8.4	−8.8	−9.4	−7.2	−7.7	−8.4	3.272	3.269	3.226
TFB···H$^+$ (**12**)	−112.6	−112.5	−107.9	−108.8	−108.7	−106.9	1.042	1.042	1.011
TFB···Li$^+$ (**13**)	−19.6	−19.5	−19.7	−18.8	−18.8	−19.1	2.019	2.019	1.990
TFB···Na$^+$ (**14**)	−10.5	−10.5	−10.7	−9.6	−9.7	−10.0	2.518	2.520	2.531
TFB···K$^+$ (**15**)	−4.7	−4.6	−5.10	−4.2	−4.2	−4.7	3.122	3.125	3.118
TFB···H$^-$ (**16**)	−4.1	−4.1	−3.8	−3.0	−3.0	−3.2	3.212	3.217	3.363
TFB···F$^-$ (**17**)	−8.0	−7.9	−7.9	−6.0	−6.0	−6.6	2.922	2.922	2.854
TFB···Cl$^-$ (**18**)	−3.1	−3.1	−3.5	−2.9	−2.9	−3.3	3.730	3.730	3.626
TFB···Br$^-$ (**19**)	−5.4	−5.3	−3.6	−1.6	−1.6	−0.4	3.625	3.627	3.639
TAZ···H$^+$ (**20**)	−88.6	−88.5	−83.3	−86.7	−86.5	−82.0	0.850	0.850	0.849
TAZ···Li$^+$ (**21**)	−8.1	−8.1	−8.2	−7.6	−7.6	−7.7	2.168	2.169	2.153
TAZ···Na$^+$ (**22**)	−3.7	−3.7	−4.0	−3.2	−3.3	−3.6	2.647	2.648	2.678
TAZ···K$^+$ (**23**)	−1.1	−1.2	−1.4	−0.8	−0.9	−1.2	3.359	3.361	3.234
TAZ···H$^-$ (**24**)	−4.4	−4.4	−4.3	−3.4	−3.4	−3.7	3.275	3.275	3.193
TAZ···F$^-$ (**25**)	−10.5	−10.4	−10.4	−8.3	−8.3	−8.9	2.708	2.708	2.659
TAZ···Cl$^-$ (**26**)	−3.8	−3.7	−4.2	−3.6	−3.5	−4.0	3.589	3.588	3.475
TAZ···Br$^-$ (**27**)	−5.0	−5.0	−5.6	−2.6	−2.6	−3.0	3.668	3.668	3.582

Taking into consideration that the RI-MP2 is significantly faster than the MP2 method for systems of the size of the complexes present in Figure 1, we deduce that the RI-MP2 method is well suited for the theoretical treatment of these systems. Finally, we have tested the RI-MP2 method in complex **28**, where the cation is a large aromatic system, because in this complex the dispersion effect is expected to be very important and the use of electron correlation in the calculations is mandatory. The results are present at the end of Table 1 (last entry) and they indicate that the RI-MP2 gives good results even in systems

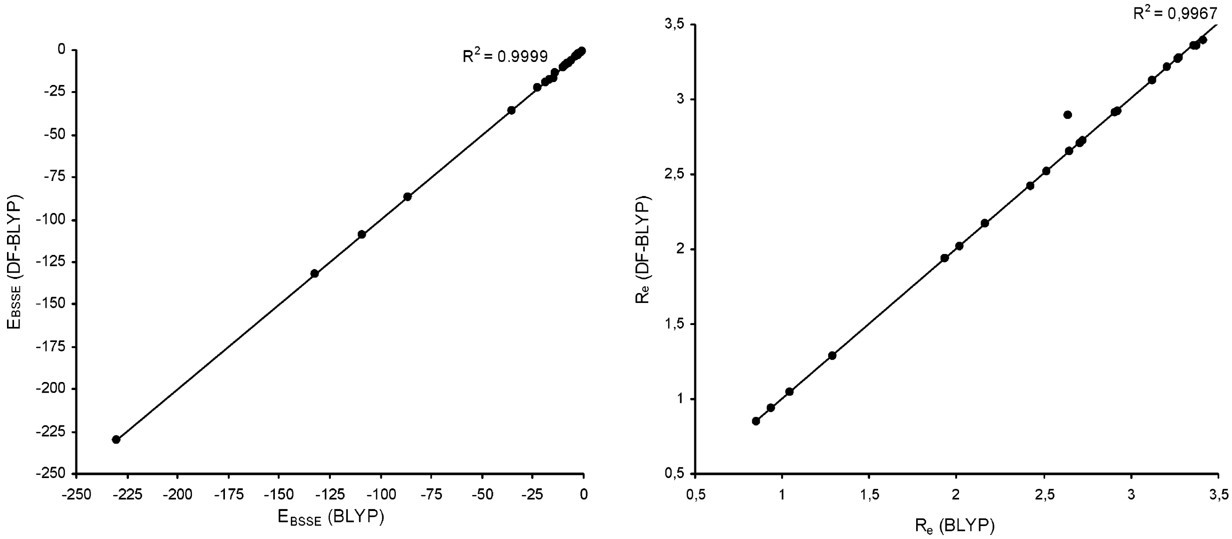

Figure 3. Plot of the regressions between the E_{BSSE} (left) and between the R_e (right) computed values at BLYP and DF-BLYP levels of theory, using the 6-31++G** basis set.

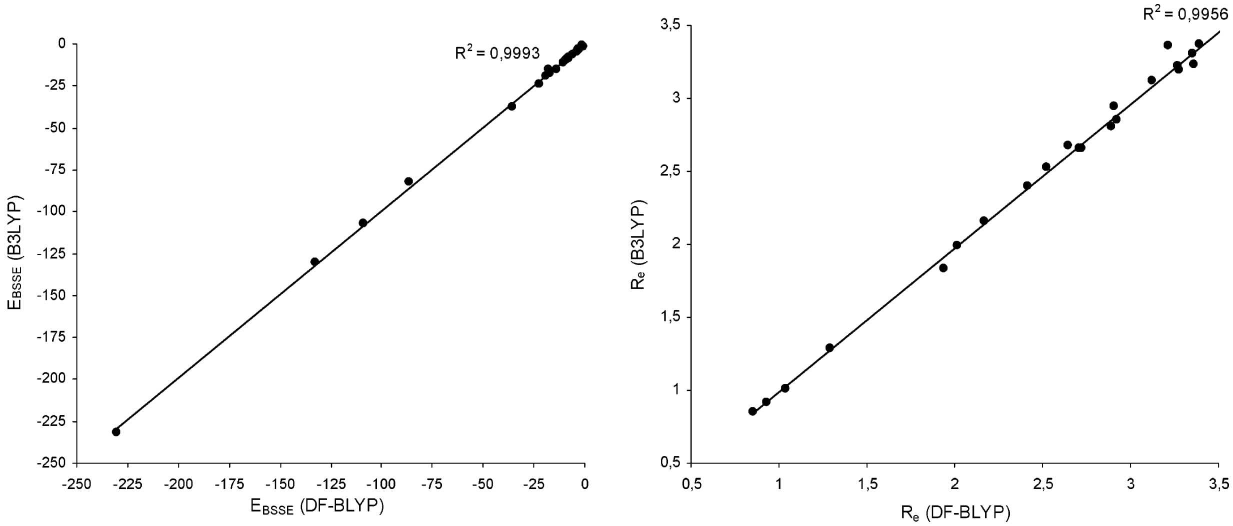

Figure 4. Plot of the regressions between the E_{BSSE} (left) and between the R_e (right) computed values at B3LYP and DF-BLYP levels of theory, using the 6-31++G** basis set.

which are very dependent on electron correlation. Both methods predict a very similar geometry that consists of a parallel-displaced stacked arrangement.

Suggested by one referee, we have optimized some complexes representative of the four kinds of complexes shown in Figure 1 using higher order correlation effects. In particular, we have computed complexes **2**, **6**, **13**, **16**, **21**, and **24** at the MP4/6-31++G** and CCSD/6-31++G** levels of theory. The results are summarized in Table 2. For the cation−π complexes the binding energies (E) are comparable and the equilibrium distances (R_e) are almost identical at the three levels of theory. For the anion−π complexes the differences between the three methods are small, but more considerable than those for the cation−π complexes. The equilibrium distances are larger and the binding energies are more positive (about 1 kcal/mol, E and E_{BSSE}) at the MP4 and CCSD levels than at the MP2 level of theory.

The interaction energies and equilibrium distances calculated with B3LYP, BLYP, and DF-BLYP methods are compared in Table 3. From the inspection of the results several considerations arise. First, the results indicate that there is a good agreement between the interaction energies calculated with the BLYP and DF-BLYP methods. For cation−π complexes (**1**−**5**, **12**−**15**, and **21**−**23**) and anion−π complexes (**16**−**19** and **24**−**27**), the interaction energies are almost identical and the main differences are found in the results computed for the anion−π complexes of HFB (**6**−**10**). In particular, complex **7** has the largest difference, which is about 2 kcal/mol. Second, a similar behavior is observed for the computed equilibrium distances. The agreement is good, especially in all cation−π complexes studied and the anion−π complexes of TFB and TAZ, where the R_e differences are very small and the main ones are observed in the anion−π complexes **6**−**10**, see Table 2. The correlation analyses given in Figure 3 confirm the agreement between both methods. We have found excellent correlations for the relationships between either the interaction energies (E_{BSSE}) or the equilibrium distances (R_e) computed at DF-BLYP level with the corresponding values computed at the BLYP level of theory.

We have also compared the results at the DF-BLYP level with those of the more popular hybrid density functional B3LYP. It should be mentioned that the density fitting approximation is not applicable to hybrid DFT. The results present in Table 3 show a good agreement between both methods regarding interaction energies and equilibrium distances, as confirmed by the relationships present in Figure 4. Finally, the comparison of the results obtained at the MP2 and RI-MP2

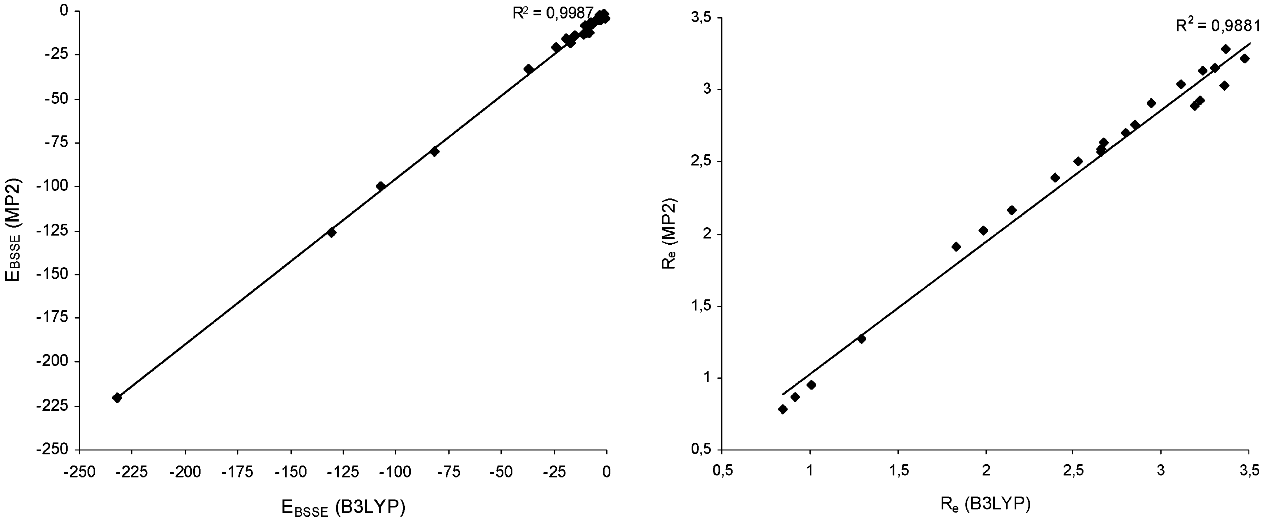

Figure 5. Plot of the regressions between the E_{BSSE} (left) and between the R_e (right) computed values at MP2 and B3LYP levels of theory, using the 6-31++G** basis set.

levels with those obtained at the DFT levels reveals an unexpected result. For cation−π complexes the interaction energies are, in general, more favorable at the DFT than at the MP2 levels of theory. Since dispersion effects are not considered at DFT, a common expectation is that the computed MP2 interaction energies should be more negative than those computed at the DFT level.[42] Therefore, from the inspection of the results present in Tables 1 and 3, we can conclude that the three DFT methods used here overestimate the cation−π interaction. The overestimation is important in complex **5**, where the binding energy is approximately 10 kcal/mol more positive at the MP2 level of theory. In Figure 5, the regression plots of the results obtained at the MP2 and the B3LYP methods regarding the interaction energies and equilibrium distances are shown. The regression coefficients are acceptable for the E_{BSSE} values, and modest for the equilibrium distances ($R^2 = 0.9881$). The main differences are observed for the complexes that present larger R_e values (anion−π complexes).

4. Conclusions

The RI-MP2 method is able to give an accurate description of anion−π and cation−π interactions. The results obtained with the RI-MP2 methodology differ only slightly from those evaluated with the exact MP2, while the saving is very important in terms of computational time and system requirements as, for instance, disk space for scratch files.

Similar behavior is observed regarding the results obtained with the DF-BLYP and BLYP methods, though in this case the agreement is better in cation−π than in anion−π interactions. Moreover, the DFT methods tend to overestimate the cation−π interaction. The results computed at the more affordable DF-BLYP method are comparable to those of the widely used B3LYP level.

The present calculations indicate that the RI-MP2 method is appropriate for the theoretical treatment of ion−π interactions and it will allow the study of larger systems such as extended π-systems or receptors based on these interactions. Finally, the DF-BLYP and the hybrid B3LYP methods give comparable results. Since the former is considerably more inexpensive than the latter, it can be considered as a good alternative to B3LYP for the study of large systems.

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