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CH/π Interaction in Benzene and Substituted Derivatives with Halomethane: A Combined Density Functional and Dispersion-Corrected Density Functional Study

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The present work intends to establish the efficiency of dispersion-corrected density functionals in explaining the potential energy curves of benzene−methane, benzene−fluoroform, and 1,3,5-trifluoro benzene−methane complexes. The interaction energies of all of the complexes under investigation have been evaluated using both van der Waals-corrected and normal gradient-corrected Perdew−Burke−Ernzerhof and Becke−Lee−Yang−Parr density functionals. Our analyses suggest that the potential energy curves for both benzene−methane and benzene−fluoroform complexes are in excellent agreement with highly accurate coupled cluster (CCSD(T)) results as well as high-level counterpoise-corrected MP2 results. Remarkably, the interaction energies of the benzene−fluoroform complex are fairly higher than those of the other two complexes. This is primarily attributed to the dispersion correction present in it. Finally, the overall study highlights the importance of halogen substitution in strengthening the CH/π interactions.

1. Introduction

In recent times, one of the major goals of chemistry has been the investigation and understanding of nonbonded or weak interactions because of their ubiquitous role in diverse fields. These cover bimolecular structure, molecular recognition, supramolecular chemistry, condensed matters, crystallography, reaction mechanisms, and so forth.[1−5] Of several nonbonded interactions, the weak attraction between a C−H bond and systems containing π-electrons, better known as CH/π interaction, plays a crucial role in determining the structure(s) of various van der Waals complexes. These interactions attracted broad interest as an important ones for controlling molecular recognition, processes, structures of biological molecules, and crystal packing.[6−9] Many experimental and theoretical studies supporting the existence of CH/π attraction have been reported.[10−20] Statistical analyses of crystal structures[21] and spectroscopic measurements[12b,15a,b] show that the C−H bond prefers to point toward the π system. The nature of the CH/π interaction is found to be significantly different from that of conventional hydrogen bonds.[16,22] Whereas the dispersion force is the major factor responsible in these CH/π systems, the electrostatic contribution is quite small.[12a,13] On the contrary, electrostatic interaction is the major source of attraction in conventional hydrogen bonded systems.[22]

Among various CH/π interacting systems, the interaction of methane and halomethanes with aromatic monocyclic as well as polycyclic compounds is of particular importance. Recently reported high-level ab initio calculations of benzene−hydrocarbon complexes (C_6H_6-X, X = CH_4, C_2H_6, C_2H_4, and C_2H_2) show that dispersion plays the key role in these systems.[12a] The interaction energy between the C−H bond of an alkyne and a π-electron system, often called an "activated" CH/π interaction, is strongly enhanced in comparison with that of the "typical" aliphatic CH/π interaction. The binding energy for the benzene−acetylene complex is 2.7 ± 0.2 kcal/mol.[12a] It has also been observed that halogen substitution in an aliphatic system remarkably enhances the magnitude of aliphatic CH/π interaction, even more than that of alkyne systems.[11,14] The binding energies of benzene with dichloromethane and chloroform (3.8 ± 0.2 and 5.2 ± 0.2 kcal/mol)[11] are found to be quite large relative to that of the benzene−methane complex and benzene−acetylene complex[12a] as well. The interaction of the aliphatic C−H group in haloalkane of types CH_2X_2 and CHX_3 (X = halogen) is thus different from the ordinary C−H bond interaction.

Albeit, there have been a lot of investigations regarding the evaluation of binding energies and equilibrium separation distance for many CH/π complexes; however, most of them are performed at a sophisticated level of theory, that is, using MP2 or CCSD(T). These highly correlated methods are time-consuming and computationally very expensive.[23] Moreover, basis set superposition error (BSSE),[24] which is very laborious, is very essential for performing MP2 or CCSD(T) calculations.[25] The problem can easily be removed if one uses DFT and includes some appropriate vdW-corrected potentials in it.[23,26] At this point, it should be noted that several new functionals such as those developed by Truhlar and his groups (the Minnesota functional) have been designed, which give good results for various kinds of intermolecular interactions.[27] In 2004 and 2006, Grimme[28,29] started using dispersion-corrected density functional theory (DFT-D), which is an enhancement of similar methods developed earlier.[30] The vdW correction in this method is described by pairwise additive R^{-6} potentials.

In the present work, we focused our attention on some well-known CH/π interacting complexes, viz. benzene−methane, benzene−fluoroform, and 1,3,5-trifluorobenzene−methane, employing DFT and DFT-D methods to explain the potential energy curves (PECs). The basis set effect has also been studied with the use of Dunning's augmented basis sets. To explicate the role of halogen substituents in influencing the PECs of the benzene−methane system, fluorine is used. The obtained values are then compared with some of the earlier high-level results.

2. Computational Details

All of the monomers, that is, benzene, methane, fluoroform, and 1,3,5-trifluoro benzene, are optimized at the B3LYP[31]/6-

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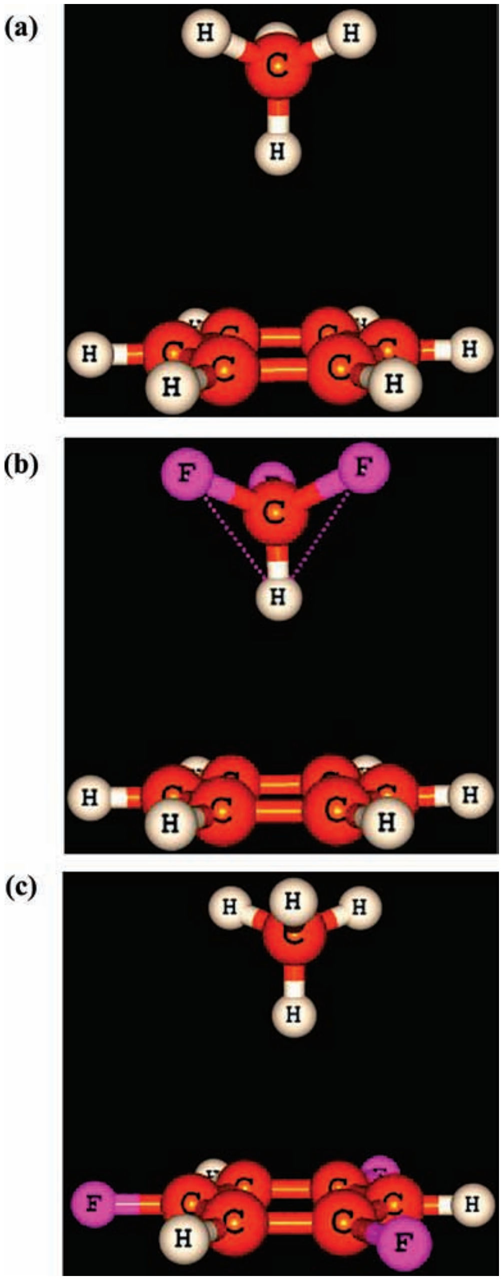

Figure 1. Three vdW complexes, (a) benzene−methane, (b) benzene−fluoroform, and (c) 1,3,5-trifluoro benzene−methane, under investigation.

311G(d,p) level of theory within Gaussian 03.[32] The geometry for the vdW complexes is then constructed by placing the optimized methane and fluoroform molecules in such a way so that the C−H bond makes an angle of 90° with the molecular planes of benzene and 1,3,5-trifluoro benzene. The arrangement leads to a perfect T-shaped geometry for each complex, which will be much more clear from Figure 1.

For calculating the PECs of the aforementioned three vdW complexes, normal gradient-corrected functionals of Perdew−Burke−Ernzerhof (PBE)[33] and Becke−Lee−Yang−Parr (BLYP)[31b,34] have been employed along with their dispersion-corrected counterparts. The basis sets that are used here are the Dunning's correlation-consistent augmented double and triple-ζ basis sets (aug-cc-pVDZ and aug-cc-pVTZ, respectively).[35]

Although dispersion correction was previously incorporated into HF and DFT levels of theory by several groups,[30] in the present study, we adopted the methodology of Grimme (to GGA functionals) where the vdW interaction term is well described by a damped interatomic potential.[29] The interaction potential is applied to account for long-range dispersion effects in nonbonded systems. The total density functional energy can be written as follows

$$E_{\mathrm{DFT-D}} = E_{\mathrm{DFT}} + E_{\mathrm{vdW}} \qquad (1)$$

where E_{DFT} is the normal self-consistent density functional energy and E_{vdW} is the empirical dispersion correction term, which is given by

$$E_{\mathrm{vdW}} = -s_6 \sum_{i=i}^{N-1} \sum_{j=i+1}^{N} \frac{C_6^{ij}}{R_{ij}^6} f_{\mathrm{dmp}}(R_{ij}) \qquad (2)$$

In the above equation, s_6 is a scaling factor that depends entirely on the density functional/semiempirical method used. For the PBE and BLYP functionals, Grimme determined the scaling factor by least-squares optimization of the deviations observed in the interaction energy values for the various weakly interacting systems.[29] The combined dispersion coefficient for the pair of atoms i and j (calculated from the atomic C_6 coefficients) is denoted by C_6^{ij}. R_{ij} is the interatomic distance between atoms i and j, $f_{\mathrm{dmp}}(R_{ij})$ is the damping function, and N is the number of atoms present in the system. The mathematical expression of the damping function, $f_{\mathrm{dmp}}(R_{ij})$, is given by the following expression

$$f_{\mathrm{dmp}}(R_{ij}) = \frac{1}{1 + \mathrm{e}^{-\alpha(R/R_0 - 1)}} \qquad (3)$$

where α is taken to be 20 in the exponent.[29] This value of α gives larger corrections at intermediate distances. There are several mathematical expressions for C_6^{ij} as well, but the one that produced better results for elements up to xenon is taken here. This expression is the geometric mean of individual atomic C_6 coeffients,[29] that is

$$C_6^{ij} = (C_6^{i} C_6^{j})^{0.5} \qquad (4)$$

The PECs for the three vdW complexes in the present work are obtained by taking the difference in single-point energy values between the complex and the individual moieties (free molecules) at each separation distance, r, between the two moieties. Here r is the distance between the ring center of benzene or 1,3,5-trifluoro benzene moieties and the carbon atom of methane or fluoroform. It is wise to mention that all single-point calculations are performed without disturbing the perfect T-shaped geometry of the vdW complexes. The calculations have been implemented within ORCA suite of programs.[36]

3. Results and Discussions

This section deals with the analysis of the PECs obtained for benzene−methane, benzene−fluoroform, and 1,3,5-trifluorobenzene−methane complexes using both vdW-corrected and normal gradient-corrected density functional methods. A comparison with earlier high-level counterpoise-corrected MP2 and CCSD(T) results has also been made.[14] This is done to see whether DFT or DFT-D can successfully reproduce the high-level results and can be used as a cheaper alternative compared

TABLE 1: Comparison of the Equilibrium Separation Distances and Corresponding Binding Energy Values from the Potential Energy Curves of Benzene/Substituted Benzene and Methane/Halo Methane (CHX_3; X = F) Complexes

			density functionals				
parameters of interest	vdW complexes	basis sets	PBE	PBE-D	BLYP	BLYP-D	earlier results[a]
equilibrium separation distance, r_{eq} (Å)	C_6H_6−CH_4	aug-cc-pVDZ	4.09	3.59		3.59	3.8 (MP2/cc-pVTZ)
		aug-cc-pVTZ	4.29	3.69		3.69	
	C_6H_6−CHF_3	aug-cc-pVDZ	3.59	3.39	3.89	3.39	3.4 (MP2/cc-pVTZ)
		aug-cc-pVTZ	3.69	3.39		3.39	
	$C_6H_3F_3$−CH_4	aug-cc-pVDZ	4.09	3.49		3.69	
		aug-cc-pVTZ		3.59		3.59	
equilibrium binding energy (kcal/mol)	C_6H_6−CH_4	aug-cc-pVDZ	−0.6	−2.1		−3.4	MP2/cc-pVDZ: −0.7 (1.0); MP2/cc-pVTZ: −1.4 (0.4); MP2/cc-pVQZ: −1.6 (0.2); $E_{MP2(limit)}$: −1.7; $E_{CCSD(T)(limit)}$: −1.5
		aug-cc-pVTZ	−0.5	−1.7		−1.4	
	C_6H_6−CHF_3	aug-cc-pVDZ	−2.6	−5.3	−1.1	−5.1	MP2/cc-pVDZ: −2.3 (1.9); MP2/cc-pVTZ: −3.7 (1.2); MP2/cc-pVQZ: −4.3 (0.6); $E_{MP2(limit)}$: −4.6; $E_{CCSD(T)\ (limit)}$: −4.2
		aug-cc-pVTZ	−2.1	−4.8		−4.6	
	$C_6H_3F_3$−CH_4	aug-cc-pVDZ	−0.5	−2.1		−3.7	
		aug-cc-pVTZ		−1.8		−1.5	

[a] All data are taken from ref 14. The MP2 and CCSD values of the binding energies are the BSSE-corrected energies, whereas in the parentheses, the corresponding BSSEs are given.

to the time-consuming methods. In their work, Tsuzuki and coworkers[13] found that for the methane−benzene complex, the preferred configuration has the methane molecule residing directly above the center of the benzene with one hydrogen atom pointed at the center of the ring and the rest of the three atoms directed away. On the basis of this result, the PECs are obtained by calculating the single-point energies at a series of separation distances, r, keeping the geometry of monomers unchanged as well as maintaining the perfect T-shaped structure of the vdW complexes for each r values.

Before proceeding further, we would like to provide a brief overview of some of the recent investigations related to CH/π interactions. Of particular relevance, we will mention different works from the group of Tsuzuki and Sherrill. Tsuzuki et al.[13] performed some high-level ab initio calculations (MP2 and CCSD(T) including basis set limit) to evaluate the CH/π interaction energies for various model systems. Their findings emphasized the fact that careful estimation of the interaction energies by computational techniques is very informative and is quite essential in exploring the origin of CH/π interactions. In a later work, the group of Tsuzuki studied the effect of halogenation on CH/π interactions by taking benzene and chloro- and fluoromethanes as model systems.[14] Their results suggest that halogen substitution in methane increases attractive electrostatic and dispersion interactions to a significant extent. However, short-range interactions remain unaffected. In a review article, Tsuzuki highlighted some recent progress in the quantitative analysis of intermolecular interactions of several aromatic molecules including CH/π interacting systems.[19] Very recently, Ringer et al.[18] presented PECs for three CH/π complexes, viz. methane−benzene, methane−phenol, and methane−indole complexes, using sophisticated methods. These systems are the prototypes for interactions between CH bonds and aromatic units of amino acids. Very recently, the group of Tsuzuki and Fujii reported back-to-back works on these CH/π interacting systems. One deals with the application of mass-selected two-color ionization spectroscopy for the accurate determination of CH/π interaction energies in some model clusters,[11] whereas the other relates to the study of CH/π interactions between methane and some polycyclic hydrocarbons.[20]

Table 1 depicts the equilibrium separation distance, r_{eq} (in angstroms), as well as binding energy (in kilocalories per mole) of the corresponding equilibrium geometry for each vdW complex using different density functional methods and basis sets. We calculated the binding energies for the equilibrium geometry of all of the vdW complexes by subtracting the energies of the constituent monomers from that of the complex, all calculated at the same level of theory. The mathematical expression is as follows

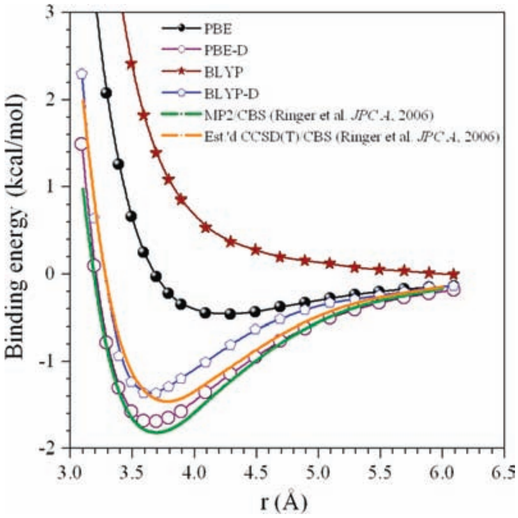

Figure 2. Energy curves for the benzene−methane complex in PBE/PBE-D and BLYP/BLYP-D methods plotted against separation distance, r, between the complexes. The basis set used is aug-cc-pVTZ. For comparison, the MP2 and Estd. CCSD(T) results of Ringer et al. (ref 18) obtained at complete basis set (CBS) limit are also plotted.

$$E_{\text{Binding Energy}} = E_{\text{vdW complex}} - E_{\text{One monomeric unit}} - E_{\text{Another monomeric unit}} \qquad (5)$$

In the case of the benzene−methane system, distinct minima are observed using dispersion-corrected PBE and BLYP functionals. On the contrary, no minima are obtained in the BLYP method using both aug-cc-pVDZ and aug-cc-pVTZ bases, and the same are very shallow using normal PBE functional. This is clear from Figure 2, where the energy curves for the normal and vdW-corrected density functionals are plotted using the aug-cc-pVTZ basis set. The relevant curves using the aug-cc-pVDZ basis set are given in Figure F1 of the Supporting Information. The figures illustrate the importance of dispersion forces in these weakly bound systems. For a comparison, we have also plotted the MP2 and Estd. CCSD(T) results reported by Sherrill and coworkers[18] obtained at the complete basis set (CBS) limit. From Figure 2, it is quite clear that the *r* value obtained by using the aug-cc-pVTZ basis set corroborates well with the earlier high-level results. However, for the other basis set, that is, aug-cc-pVDZ, the dispersion-corrected results are overestimated for the binding energies, in particular, that of BLYP-D. Table 1 also reveals the fact that the obtained r_{eq} value is in accordance with the MP2/cc-pVTZ results of Tsuzuki et al.[14] in both PBE-D and BLYP-D methods. Double-ζ basis sets slightly underestimate the equilibrium distance. The observation that normal density functional highly overestimates the separation distances in benzene−methane complex is interesting. When it comes to explaining the binding energies for this weakly interacting complex, a remarkable basis set effect is seen to occur. Using the augmented triple-ζ basis set, the energy values in PBE-D and BLYP-D methods match very well the earlier MP2/cc-pVQZ results as well as the MP2 and CCSD(T) results obtained at the CBS limit.[14] However, when the basis set is changed to aug-cc-pVDZ, the corresponding energy values are greatly overestimated compared with the earlier results.[14] The normal gradient-corrected PBE functional underestimates the binding energies in both of the basis sets used. The basis set dependency is more prominent for the BLYP-D method and seems to be quite unusual because the size of the basis set is not very essential for the evaluation of the correlation in DFT-D methods. It has been observed that for the PBE-D and B97-D functionals, there is a very negligible difference in the energy values using augmented double- and triple-ζ basis sets. Therefore, the BLYP-D functional needs to be reformulated, particularly in dealing with such systems. This dependency might be attributed to the BSSE factor as well, which is actually much smaller for a more complete basis such as aug-cc-pVTZ than for the double-ζ counterpart. The difference in the energy values using two basis sets might also result from the near-linear dependencies in the basis in case of large systems.

The second system that we have studied is the benzene−fluoroform complex, where three H atoms of methane are replaced by three F groups, as is obvious in Figure 1b. A close look at the table indicates that the equilibrium separation distances obtained using dispersion-corrected PBE and BLYP functionals irrespective of the basis sets used are exactly equal to the MP2 results.[14] The distances obtained by normal density functionals deviate by 0.2 to 0.5 Å from the high-level MP2 results. As far as binding energies are concerned, unlike benzene−methane, here the energy values of the PBE(BLYP)-D/aug-cc-pVTZ method only concur with the data obtained at the MP2 level of theory performed at the CBS limit.[14] All other data obtained deviate appreciably from the previous works, particularly that of PBE and BLYP methods. Distinct minima in the PECs are observed in each case except that of BLYP method. Just like the previous system, a remarkable basis set effect is also observed here. The variation of the binding energies is plotted against *r* and is depicted in Figure 3 using the aug-cc-pVTZ basis, whereas the same using the aug-cc-pVDZ basis set is presented in the Supporting Information (Figure F2). Here the role of vdW interactions is also clearly illustrated through these plots.

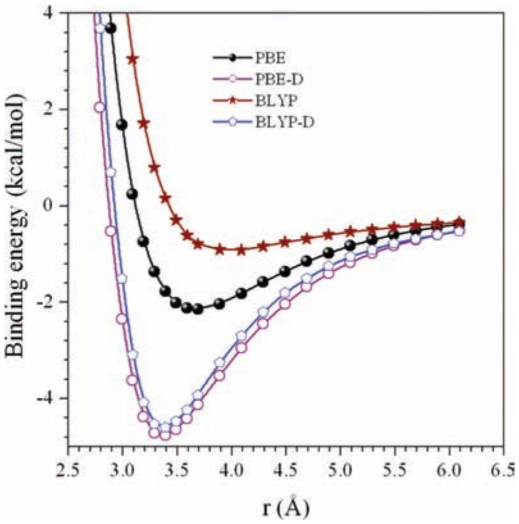

Figure 3. Energy curves for the benzene−fluoroform complex in PBE/PBE-D and BLYP/BLYP-D methods plotted against the separation distance, *r*, between the complexes. The basis set used is aug-cc-pVTZ.

Upon comparing the binding energies of the benzene−fluoroform complex with those of benzene−methane, the interaction energy of the fluoroform complex is found to be about three times larger in magnitude than that of the benzene−methane when the aug-cc-pVTZ basis set is used. This in turn indicates the presence of large interaction in the benzene−fluoroform complex, thereby signifying that the strength of the CH/π interaction strongly depends on the system used. A previous study on the interactions of $C_6H_6-C_2H_4$ and $C_6H_6-C_2H_2$ complexes also shows that the size of the CH/π interaction is not constant and varies considerably. The calculated bonding energies of those alkenyl and alkynyl systems (−2.1 and −2.8 kcal/mol, respectively) are considerably larger, that is, more negative than that of the $C_6H_6-CH_4$ complex (−1.5 kcal/mol).[13] The origin of the enhancement of the CH/π interaction in alkynes is attributed to the larger contribution of the electrostatic interactions. Here the calculated PECs of the complexes suggest that the driving force behind large interactions in the fluoroform complex is mainly due to dispersion energy. The same conclusion was obtained for the benzene−halomethane clusters reported by Tsuzuki and coworkers.[11,14] In the present investigation, the energy values given in Table 1 for both benzene−methane and benzene−fluoroform complexes clearly indicate that the dispersion energy lies within −1.1 to −1.5 kcal/mol for the former complex, whereas the latter one has a dispersion value of greater than −2.6 kcal/mol. The binding energy values plotted against *r* clearly highlight the role of vdW interactions in benzene−halomethane complexes. In this context, it is wise to mention that the increase in interaction energies obtained because of halogen substitution was first examined by Tamres way back in 1952 by the observation of exothermic dissolution of benzene into chloroform.[37] After few years, the group of Huggins and Pimentel[38] concluded the H-bond nature of the interaction between benzene and chloroform via IR spectroscopic measurements.

The last system that we have chosen in this work is the 1,3,5-trifluorobenzene−methane complex. Very recently, investigations on the noncovalent interactions have been reported for similar substituted benzene systems.[39] The aromatic system in the present investigation is symmetric in nature. To the best of our knowledge, no such investigations regarding the evaluation of the PECs for this complex have been carried out yet. The only reason for choosing this sample is to see the effect of the change in interaction energies as well as equilibrium separation distance by replacing the H atoms in an aromatic system rather than in methane. Because there are no earlier results, we are unable to compare our data; instead, we compare the results

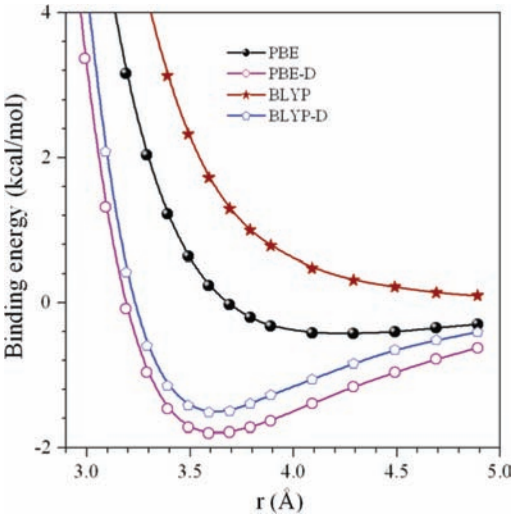

Figure 4. Energy curves for the 1,3,5-trifluorobenzene−methane complex in PBE/PBE-D and BLYP/BLYP-D methods plotted against separation distance, *r*, between the complexes. The basis set used is aug-cc-pVTZ.

with those of the other two complexes studied. A look at the table will reveal the fact that the r_{eq} values are hardly affected by the F substitution in the aromatic ring, and the results are more or less consistent with that of benzene−methane complex, with only 0.1 Å difference using dispersion-corrected functionals. In the case of binding energy, all values of the 1,3,5-trifluorobenzene−methane system are slightly larger in magnitude than those of benzene−methane. This is mainly attributed to the presence of the halogen substituent in benzene. Figure 4 presents the binding energy curves for this vdW complex using the aug-cc-pVTZ basis set, whereas the corresponding curves using the double-ζ basis are provided in Figure F3 of the Supporting Information. The minima observed for the PBE-D and BLYP-D functionals are not as sharp and distinct as those that we noticed for the first two complexes.

The question that remains, however, is where can we substitute F to get better and more stable CH/π interacting systems? To provide a better explanation, an analysis of the results obtained for the benzene−fluoroform and 1,3,5-trifluorobenzene−methane complexes is essential. In general, the CH/π interaction is found to be weak in nature relative to that of other types of nonbonded interactions. The data related to equilibrium separation distances exemplify that in each case, r_{eq} values are overestimated for the trifluorobenzene complex by an amount of 0.1 to 0.3 Å relative to that of the fluoroform complex. The observation for the PBE/aug-cc-pVDZ method, where it overestimates the separation distance by an amount as high as 0.5 Å, is interesting. A remarkable effect is noticed in the case of binding energies, in particular, for both gradient- and dispersion-corrected PBE functionals. The difference in equilibrium binding energies obtained for the fluoroform and fluorobenzene complex lies in the range of 2.1 to 3.2 kcal/mol, where the latter complex underestimates the energy values. The BLYP-D functional also shows energy differences of 1.4 and 3.1 kcal/mol in favor of the benzene−fluoroform complex using aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. Not only are these large differences dominated by dispersion effects, but electrostatic effects might also play a vital role. Therefore, it has been observed that the CH/π interaction is greatly enhanced when the halogen substituent (F atom) is attached to the carbon atom in the aliphatic compound, methane, instead of attaching to the aromatic nucleus.

In the present investigation, the BSSE energy is also calculated for each complexes studied at the PBE/aug-cc-pVTZ level of theory. It has been observed that the correction value is much lower and amounts to only 0.08 kcal/mol for the benzene−methane complex, 0.23 kcal/mol for the benzene−fluoroform complex, and 0.14 kcal/mol for the 1,3,5-trifluorobenzene−methane complex. (See the Supporting Information.) Therefore, BSSE has a negligible effect in influencing the equilibrium binding energy values. Finally, there is another important issue, which is the performance of DFT-D methods. In all cases, this technique satisfactorily explains the PECs, and we can think of a much cheaper alternative. In this perspective, it is instructive to mention that Chakrabarti and coworkers[23] recently reported that DFT and DFT-D can be used as a much cheaper alternative relative to the high-level time-consuming methods for certain vdW complexes.

4. Conclusions

In the present study, we investigate whether DFT and DFT-D methods are suitable in explaining the PECs for three weakly bound systems, benzene−methane, benzene−fluoroform, and 1,3,5-trifluoro benzene−methane complexes. The results are also compared with the earlier MP2 and CCSD(T) values. Our investigation suggests that the DFT-D method quite satisfactorily explains the separation distances as well as the equilibrium binding energies and reproduces the high-level results for the above-mentioned complexes using the aug-cc-pVTZ basis. Calculated potentials of the complexes also suggest that the major source of attraction in the complexes is long-range interactions. Remarkably, the interaction energies of the benzene−fluoroform complex are found to be much higher than the other two, which is primarily attributed to the dispersion correction present in it, and the electrostatic effects might also play a crucial role. Finally, the overall study emphasizes the importance of halogen substitution in strengthening the CH/π interactions and also invokes the question as to where one can substitute the halogen in these types of CH/π interacting complexes. The suitability of recently developed double-hybrid density functionals in explaining the PECs of these three CH/π systems still remains an unresolved issue and will be communicated in the near future.

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Supporting Information Available: Binding energy curves for benzene−methane, benzene−fluoroform, and 1,3,5-trifluorobenzene−methane complexes in PBE/PBE-D and BLYP/BLYP-D methods plotted against separation distance, *r*, between the complexes using the aug-cc-pVDZ basis set and BSSE energies for each of the complexes studied at the PBE/aug-cc-pVTZ level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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