

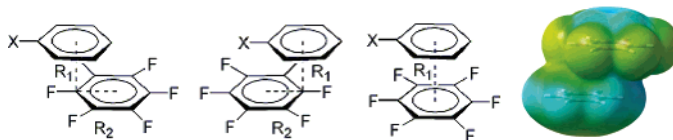
Substituent Effects in C₆F₆–C₆H₅X Stacking Interactions

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Parallel displaced and sandwich configurations of hexafluorobenzene-substituted benzene dimers are studied by ab initio molecular orbital methods up to the MP2(full)/aug-cc-pVDZ level of theory to reveal how substituents influence π – π interactions. Two minimum energy configurations are found, one with the substituent group away from the π -face of the hexafluorobenzene ring (**2a–f**) and the other with the substituent group on top of the π -face of the hexafluorobenzene (**3a–f**). Higher binding energies are predicted for dimers with the substituent on the π -face (**3a–f**). All sandwich dimers (**4a–e**) are found to be saddle points on the potential energy surfaces. A parallel-displaced minimum energy configuration is also predicted for the parent complex, C₆F₆–C₆H₆, which is in contrast to predictions based on quadrupole moments of benzene and hexafluorobenzene. The preference for the parallel displaced, rather than the sandwich configuration, is rationalized based on the smaller interplanar distance in the former. The closeness of contact in the parallel-displaced dimers leads to greater binding energies. The shape of the electron density isosurface of the monomers is suggested to provide a guide for the prediction of how arenes stack with one another. A large difference in binding energy between the C₆F₆ complex of aniline (**3e**) and N,N-dimethylaniline (**3f**) is calculated, and charge-transfer interactions are suggested to play a role in the latter.

Introduction

Weak noncovalent forces such as π – π stacking are important in biomolecular recognition and in crystal engineering.^{1–6} π – π Stacking interactions also play a significant role in the outcomes of stereoselectivity in synthetic organic reactions.^{7–10} Not surprisingly, there has been widespread interest in the magnitude

and origin of π – π interactions.^{2–5,11–14} Recently we reported experimental studies aimed at an energetic quantification and an improved understanding of noncovalent interactions involving aromatic rings.^{13,14} Our experimental studies using triptycene-derived models measure arene–arene interactions in the parallel-

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displaced configuration. Opposite trends of substituent effects were observed for strongly perturbed vs mildly perturbed arenes.¹³ Furthermore, charge-transfer bands were observed in the interactions that involved perfluorinated arenes and an N,N-dimethylaminobenzyl group, which also exhibited greater than normal binding energy based on the Hammett plot.^{13,15} To better understand our experimental results and to examine the relative importance of electrostatic, dispersion, and charge-transfer interactions, we initiated a study of substituent effects in C₆F₆-C₆H₅X interactions by ab initio molecular orbital methods. Although computational studies of benzene dimers have been performed extensively,^{16–22} studies of substituted benzene dimers are relatively limited.^{11,23,24} Theoretical studies on C₆F₆-C₆H₆ interactions found that the edge-to-face or T-shaped configurations, with either a C–H bond pointed toward the C₆F₆-π cloud or a C–F bond pointed toward the C₆H₆-π cloud, were approximately 3–5 kcal/mol less stable than the sandwich and the parallel-displaced arrangements.^{12,25,26} These results are consistent with experimental observations of equimolar mixtures of hexafluorobenzene and benzene, which show the nearly parallel-stacking configuration of C₆F₆-C₆H₆.^{27,28} To our knowledge, theoretical studies of substituted benzene-hexafluorobenzene interactions have not been reported.

Stacking arrangements have been identified both in gas phase and in solid-state studies of C₆F₆-C₆H₆ dimers.^{28–30} The advantage of recognizing the role played by the quadrupole moments of benzene and hexafluorobenzene has been convincingly demonstrated.^{31–33} Many have depicted these aromatic molecules topologically as a d₂^z orbital with opposite charges labeled for the center belt region and the top and bottom lobes.^{2–4} It appears that the consideration of quadrupole moments provides an easy way to visualize the charge distribution of aromatics and correctly predicts the preferred geometry of π–π interactions. However, this study shows that the

importance of the quadrupole moments may have been over-emphasized and erroneous conclusions may be reached if one considers the electrostatic force alone. The implied conclusion from the exclusive consideration of two opposite quadrupoles is that the face-to-face dimer of C₆F₆-C₆H₆ should be the energy minimum.^{2–4} From the popular sketches of the quadrupole moments of benzene and hexafluorobenzene, the C₆F₆-C₆H₆ dimer has already been depicted as a representative of the sandwich configuration.³ However, this and another recent study show that the sandwich configuration of the C₆F₆-C₆H₆ dimer is a saddle point, rather than an energy minimum.¹²

This study demonstrates that the magnitude of the attractive interactions of C₆F₆-C₆H₅X dimers depends on the closeness of contact between the arenes and on the donor ability of the benzene substituent (X). Similar to our experimental observations,¹³ the results from this theoretical study are also consistent with an electron donor-acceptor relationship in addition to electrostatic considerations. The optimized minimum configurations of C₆F₆-C₆H₅X dimers have a parallel displacement, rather than a sandwich configuration, indicating that more complex interactions are involved than a simple Coulombic attraction. Important factors such as dispersion and charge transfer are demonstrated by considering the shape of the electron density surface and the Hammett free-energy relationship.

Computational Methods

Theoretical calculations were carried out using the Gaussian 98 and 03 suite of programs.³⁴ All of the monomers were fully optimized at the MP2(full) level using Dunning's augmented correlation-consistent polarized valence triple-ζ basis set (aug-cc-pVTZ), except for the N,N-dimethylaniline monomer which was optimized using Dunning's correlation-consistent polarized valence triple-ζ basis set (cc-pVTZ).^{35–37} Interaction energies were calculated for parallel-displaced dimers of hexafluorobenzene with several monosubstituted benzenes (C₆F₆-C₆H₅X) at the MP2(full) level using four different basis sets (6-31+G**, 6-311+G**, 6-311++G(2d,2p), and aug-cc-pVDZ).^{35–37} The substituents in the monosubstituted benzenes are F, CN, CH₃, NH₂, and N(CH₃)₂. During the dimer energy calculations, the monomer geometries were not allowed to vary. However, for the dimers, the energies of the geometric configurations were examined for the parallel-displaced orientation and the intermonomer center-of-mass distances were varied to determine the largest interaction energy. Both the vertical, R₁, and the horizontal, R₂, center-of-mass distances were systematically varied starting from the values of 3.4 and 1.6 Å, respectively, which are the optimal values determined by Sherrill and co-workers for the parallel-displaced benzene dimer.^{20,38} R₂ values are denoted

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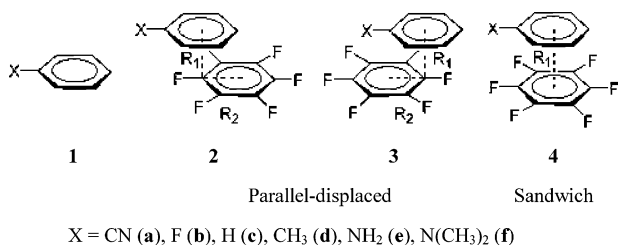
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as positive for dimers (2) with the phenyl substituent away from the hexafluorobenzene face while denoted as negative for dimers (3) with the phenyl substituent on top of the hexafluorobenzene. Basis set superposition error (BSSE) was accounted for using the counterpoise correction method.^{39,40} Electrostatic potential surfaces of the aromatic rings are generated by mapping the HF/6-31+G** electrostatic potentials onto surfaces of molecular electron density (isosurface of 0.0004 electrons au⁻³) and by color coding, using the program GaussView.⁴¹ In all surfaces shown, the electrostatic potential values range from +0.04 to -0.04 hartree/mol (+25 kcal/mol to -25 kcal/mol), with red signifying a value greater than or equal to the maximum in negative potential and blue signifying a value greater than or equal to the maximum in positive potential.



Our primary interest in this study is in the relative energetics of the parallel-displaced C₆F₆-C₆H₅X dimers, and our choices of theoretical methods enabled us to perform calculations at a practical pace with our computational resources (average ~24 h/structure). Several other studies have shown that in order to obtain accurate absolute interaction energies of π - π systems, very large basis sets, such as the aug-cc-pVTZ and the aug-cc-pVQZ basis sets and electron correlation methods beyond MP2, such as the CCSD(T) method, are needed (which are beyond our computational resources).^{11,12,23,42} To assess whether the relative energies of the substituted complex C₆F₆-C₆H₅X remain relatively constant with different basis sets, we have performed calculations with four different basis sets at the MP2(full) level of theory for both complex series 2 and 3. A greater binding energy is found with a larger basis set. However, the relative energies do remain relatively constant. In general, all complexes have the same proportional increase in energy as basis set increases in size. For complex series (2), the relative strength of the complexes follows the same order according to substituents for all basis sets employed. For complex series (3) where the substituent X is on top of the C₆F₆ ring, all complexes follow the same relative energetic order except for complex 3a (X = CN), which exhibits a slight disproportional increase in binding energy with a larger basis set. The results performed at the highest level of theory indicate a diminished difference in interaction energies between X = CN, F, and H. This is consistent with our experimental observations.¹³

Computational Results

The interplanar (R_1) and the center-of-mass separation (R_2) of the parallel-displaced C₆F₆-C₆H₅X (X = H, F, CN, CH₃, NH₂, N(CH₃)₂) dimers were calculated at the MP2(full)/6-31+G** level by systematically optimizing the R_1 and R_2 distances, with the starting values being 3.4 and 1.6 Å, respectively. The R_1 distance was optimized first using a fixed R_2 value of 1.6 Å and was varied from 2.9 to 3.6 Å. For all C₆F₆-C₆H₅X dimers, the optimal R_1 distance was determined

TABLE 1. Parallel-Displaced C₆F₆-C₆H₅X (2a-f) BSSE Corrected Interaction Energies (in kcal/mol) at the MP2(full)/6-31+G Optimized R_1 and Fixed $R_2 = 1.6$ Å**

	X = CN (2a)	X = F (2b)	X = H (2c)	X = CH ₃ (2d)	X = NH ₂ (2e)	X = N(CH ₃) ₂ (2f)
R_1 (Å)	3.4	3.4	3.4	3.4	3.4	3.4
ΔE_{int}	-4.29	-4.60	-4.87	-5.36 ^a	-5.79 ^a	-6.29 ^a
				-5.43 ^b	-5.44 ^b	-5.95 ^b

^a Energy with CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair pointing away from the lower hexafluorobenzene ring. ^b Energy with CH₃ hydrogen, and NH₂ lone pair, and N(CH₃)₂ lone pair pointing toward the lower hexafluorobenzene ring.

to be 3.4 Å and the BSSE corrected interaction energies calculated using this R_1 value and $R_2 = 1.6$ Å are given in Table 1.

With the use of the optimized R_1 value of 3.4 Å, the R_2 values were varied from -2.0 to 2.0 Å and the BSSE corrected energy was calculated at each distance. Positive values of R_2 (2) indicate that the functional group is moving away from the center of the hexafluorobenzene ring, and negative values of R_2 (3) indicate that the functional group is moving toward the center of the hexafluorobenzene ring. A distance of 0.0 Å is, therefore, for a sandwich complex (4). For positive R_2 distances, the optimal values were determined to be between 0.9 and 1.1 Å for all dimers, and for negative R_2 distances, the optimal values were determined to be between -0.8 and -1.3 Å for all dimers. The BSSE corrected interaction energies at the optimum positive and negative R_2 distances are listed in Table 2 at four different levels of theory. The optimized structures are shown in Figures 1 and 2, respectively. As can be seen in Table 2, the magnitudes of the interaction energies at both the positive and negative R_2 distances are larger than the values at $R_2 = 1.6$ Å (Table 1). By the comparison of the interaction energies for a given dimer at the optimal positive and negative R_2 distances with each other, it can be seen that the energies for the negative R_2 distances are generally larger than those for positive R_2 values, indicating a significant interaction between the substituent X and the C₆F₆ ring. The general trend in the interaction energies for complex series 2 at the optimal R_1 distances is N,N-dimethylaniline > aniline > toluene > benzene > fluorobenzene > cyanobenzene, although the magnitudes of the N,N-dimethylaniline, aniline, and toluene dimers depend to a small extent on whether the lone pair or the hydrogen is pointing toward or away from the hexafluorobenzene ring. The general trend in the interaction energies for complex series 3 follows the same order except where X = CN. With the larger basis set aug-cc-pVDZ, complex 3a (X = CN) exhibits a slightly larger interaction energy than complexes 3b (X = F) and 3c (X = H). This is consistent with our recent experimental observations which we will discuss further in later sections.

Sandwich C₆F₆-C₆H₅X Dimers (4a-e). The BSSE corrected interaction energies of the sandwich C₆F₆-C₆H₅X (X = H, F, CN, CH₃, NH₂, N(CH₃)₂) dimers were calculated at the MP2 (full)/6-31+G** level by systematically varying the interplanar distance from 3.0 to 4.0 Å. For all C₆F₆-C₆H₅X sandwich dimers, the optimal distance was determined to be either 3.5 or 3.6 Å, and the interaction energies calculated at these distances are given in Table 3. The optimized sandwich structures are shown in Figure 3. Similar to that of the parallel-displaced C₆F₆-C₆H₅X dimers, the trend in the interaction energies for the sandwich dimers is predicted to be N,N-dimethylaniline > aniline > toluene > benzene > fluorobenzene > cyanobenzene. The sandwich dimers are determined to be

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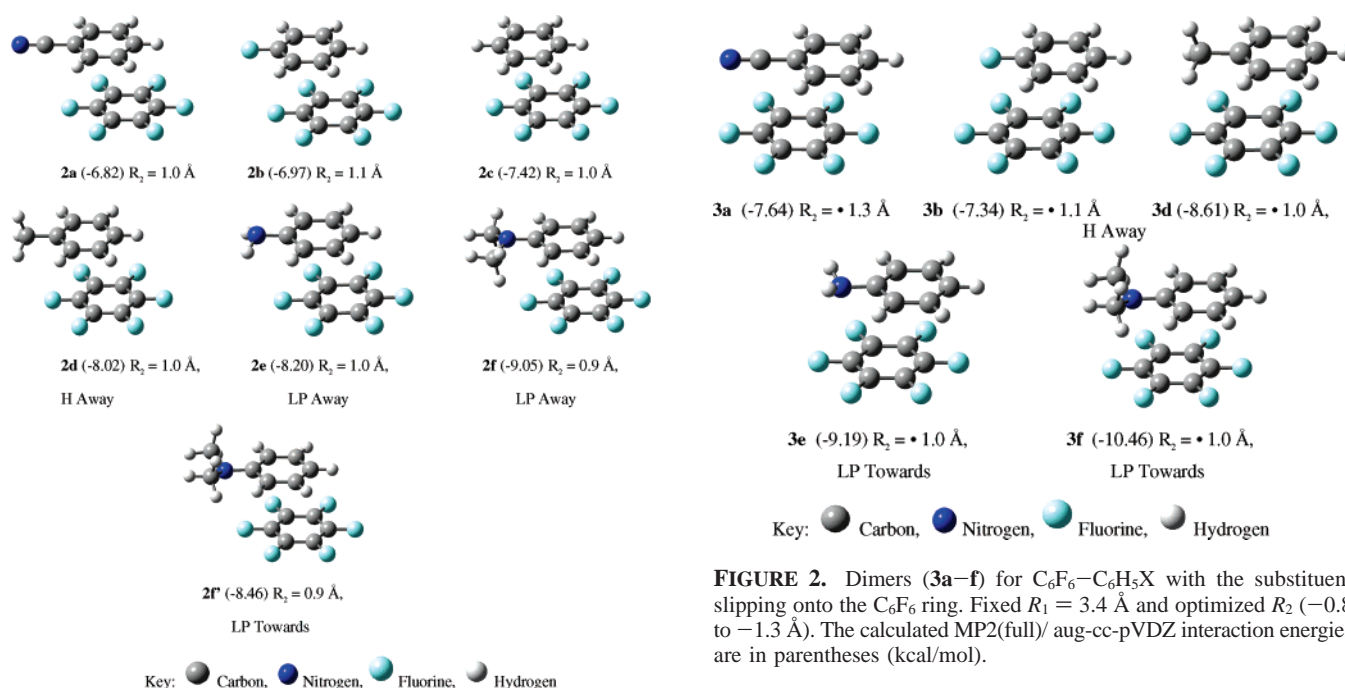
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TABLE 2. Parallel-Displaced C₆F₆-C₆H₅X (2a-f and 3a-f) MP2(full) BSSE Corrected Interaction Energies (in kcal/mol) at the MP2(full)/6-31+G** Optimized R₂ and Fixed R₁ = 3.4 Å^a

	X = CN (a)	X = F (b)	X = H (c)	X = CH ₃ (d)	X = NH ₂ (e)	X = N(CH ₃) ₂ (f)
(2) positive R ₂ (Å)	1.0	1.1	1.0	1.0, ^b 1.0 ^c	1.0, ^b 1.0 ^c	0.9, ^b 0.9 ^c
6-31+G**	-4.83	-5.05	-5.39	-6.12, ^d -6.13 ^e	-6.34, ^d -5.88 ^e	-7.05, ^d -6.54 ^e
6-311+G**	-5.23	-5.42	-5.97	-6.53 ^d	-6.73 ^d	-7.43, ^d -6.94 ^e
6-311++G(2d,2p)	-6.42	-6.57	-7.05	-7.63 ^d	-7.82 ^d	-8.63, ^d -8.06 ^e
aug-cc-pVDZ ^f	-6.82	-6.97	-7.42	-8.02 ^d	-8.20 ^d	-9.05, ^d -8.46 ^e
(3) negative R ₂ (Å)	-1.3	-1.1	-1.0	-1.0, ^b -0.8 ^c	-0.8, ^b -1.0 ^c	-1.0 ^g
6-31+G**	-5.30	-5.41	-5.39	-6.45, ^d -5.55 ^e	-6.54, ^d -7.30 ^e	-8.41 ^g
6-311+G**	-5.77	-5.68	-5.97	-6.90 ^d	-7.64 ^e	-8.74 ^g
6-311++G(2d,2p)	-7.15	-6.90	-7.05	-8.16 ^d	-8.77 ^e	-10.00 ^g
aug-cc-pVDZ ^f	-7.64	-7.34	-7.42	-8.61 ^d	-9.19 ^e	-10.46 ^g

^a The R₁ = 3.4 Å distance was the optimized distance found when R₂ was fixed at 1.6 Å. ^b Optimized distance when the CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair are pointing away from the lower hexafluorobenzene ring. ^c Optimized distance when the CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair are pointing toward the lower hexafluorobenzene ring. ^d Energy with the CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair pointing away from the lower hexafluorobenzene ring. ^e Energy with the CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair pointing toward the lower hexafluorobenzene ring. ^f Calculations performed at the MP2/aug-cc-pVDZ level. ^g Optimized distance when the N(CH₃)₂ lone pair is pointing toward the lower hexafluorobenzene ring. A minimum was not found for negative R₂ values with the lone pair pointing away from the lower hexafluorobenzene ring.

**FIGURE 1.** Dimers (2a–f) for C₆F₆-C₆H₅X with the substituent slipping away from C₆F₆. R₁ = 3.4 Å and optimized R₂ (0.9–1.1 Å). The calculated MP2(full)/aug-cc-pVDZ interaction energies are listed in parentheses (kcal/mol).

saddle points, and the parallel-displaced orientation is the minimum energy configuration for these complexes (see Figures 4 and 5).

Discussion

A. General Trend in Interaction Energies. In accordance with our recent experimental results,¹³ both the parallel displaced and sandwich C₆F₆-C₆H₅X dimers are predicted to have the general trend in that the electron-donating substituent enhances the interaction energies (Tables 1, 2, and 3). The overall order of interaction energies is found to be N,N-dimethylaniline > aniline > toluene > benzene > fluorobenzene > cyanobenzene in complex series 2. This is in contrast to interactions between benzene-substituted benzenes, which exhibit the opposite trends;

FIGURE 2. Dimers (3a–f) for C₆F₆-C₆H₅X with the substituent slipping onto the C₆F₆ ring. Fixed R₁ = 3.4 Å and optimized R₂ (−0.8 to −1.3 Å). The calculated MP2(full)/aug-cc-pVDZ interaction energies are in parentheses (kcal/mol).

i.e., electron-withdrawing substituents lead to stronger binding energies.^{11,13,14,43} This reversal in trend is consistent with the opposite signs of the quadrupole moments of hexafluorobenzene and benzene, which suggests that electrostatic forces play a prominent role in the interactions of the C₆F₆-C₆H₅X dimers, at least for the complex series 2. However, this does not mean the interactions are entirely due to electrostatic forces. Consistent with Sherrill's results,¹¹ dispersion forces are found to be important and, in addition, donor–acceptor interactions also play an important role as we will demonstrate.

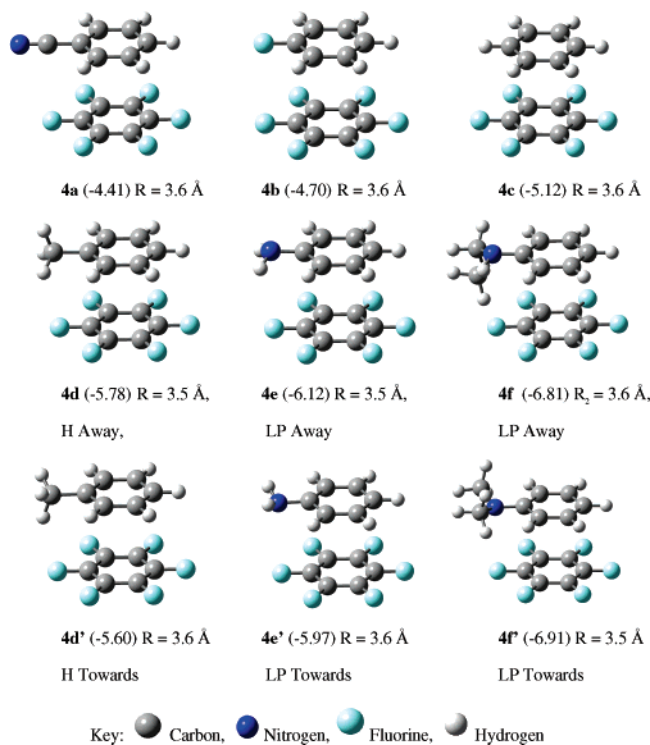
The first indication of the importance of dispersion forces is the general stronger interactions displayed by complex series 3 than by series 2. The substituent X is in contact with the C₆F₆ ring in complex 3, which increases the contact surface area between the two aromatic rings, a requirement for dispersion interactions. The second indication is the gradual leveling off and slight reversal of the substituent effect in complex series 3.

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TABLE 3. Sandwich C₆F₆-C₆H₅X (4a-e) BSSE Corrected Interaction Energies (in kcal/mol) at the MP2(full)/6-31+G** Optimized Intermonomer Distances

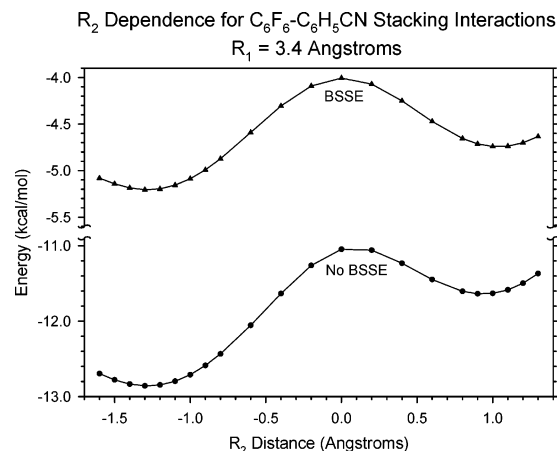
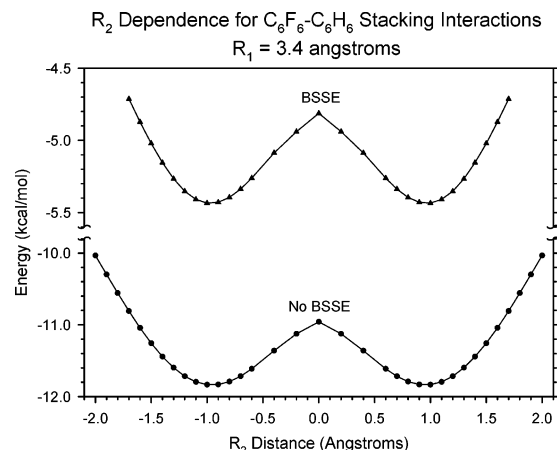
	X = CN (a)	X = F (b)	X = H (c)	X = CH ₃ (d)	X = NH ₂ (e)	X = N(CH ₃) ₂ (f)
R (Å)	3.6	3.6	3.6	3.5 ^a , 3.6 ^b	3.5, ^a 3.6 ^b	3.6, ^a 3.5 ^b
ΔE _{int}	-4.41	-4.70	-5.12	-5.78, ^c -5.60 ^d	-6.12, ^c -5.97 ^d	-6.81, ^c -6.91 ^d

^a Optimized distance when the CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair are pointing away from the lower hexafluorobenzene ring. ^b Optimized distance when the CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair are pointing toward the lower hexafluorobenzene ring. ^c Energy with CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair pointing away from the lower hexafluorobenzene ring. ^d Energy with CH₃ hydrogen, NH₂ lone pair, and N(CH₃)₂ lone pair pointing toward the lower hexafluorobenzene ring.

**FIGURE 3.** Sandwich dimers (4a-f) of C₆F₆-C₆H₅X with optimized vertical separation distance ($R = 3.5\text{--}3.6$ Å). The calculated MP2-(full)/6-31+G** interaction energies are listed in parentheses (kcal/mol).

At the highest level of theory (MP2/aug-cc-pVDZ) performed in this study, the substituent effect in **3** is calculated as N,N-dimethylaniline > aniline > toluene > cyanobenzene > benzene ~ fluorobenzene. This is interesting in that the electrostatic potential is no longer the dominant factor when the substituent is an electron-withdrawing group. Since a CN group has a larger surface area than a fluorine or a hydrogen atom, the results indicate the importance of dispersion forces. Our recent experimental results, which employ a model mimicking complex series **3**, have demonstrated that the interactions between a pentafluorobenzoate and a substituted benzyl group are attractive and that the trend observed for enhancing attractive interactions was 4-N,N-dimethylanilinyll > 4-methoxyphenyl > 4-methylphenyl > phenyl ~ 4-fluorophenyl ~ 4-trifluoromethylphenyl.¹³ Our experimental results showed that in the interactions with a strongly electron-deficient arene, electron-rich arenes gave rise to larger interaction energies whereas electron-poor arenes displayed similar interaction energies. Thus, the computational results agree with the experimental observations within system and experimental errors.

The plot in Figure 4 illustrates the dependence of interaction energy on the center-of-mass separation distance R_2 for the C₆F₆-C₆H₅CN dimer and is representative of the R_2 dependence

**FIGURE 4.** Plot of interaction energy (MP2(full)/6-31+G**) vs center-of-mass separation distance (R_2) for C₆F₆-C₆H₅CN: top, with BSSE correction; bottom, without BSSE correction. Complex **2a** is located at the minimum position on the right with positive R_2 , and complex **3a** is located at the minimum position on the left with negative R_2 . Sandwich **4a** is located at the saddle point where $R_2 = 0.0$ Å.**FIGURE 5.** Plot of interaction energy (MP2(full)/6-31+G**) vs center-of-mass separation distance (R_2) for C₆F₆-C₆H₆: top, with BSSE correction; bottom, without BSSE correction. The sandwich configuration is at the saddle point where $R_2 = 0.0$ Å.

for all dimers studied (see Supporting Information). Two types of minimum configurations (**2** and **3**) and a saddle point (**4**) are found for the stacking C₆F₆-C₆H₅X dimers. Stronger interaction energies are found for dimers **3a-f** where the substituent X is in contact with the π -face of the C₆F₆ ring (see graphics in Figure 2). The energy difference between the two minimum configurations **2a-f** and **3a-f** depends on the substituent group. In other words, the energy differences between $R_2 =$ positive and $R_2 =$ negative are computed to be (kcal/mol): 0.82 (CN), 0.37 (F), 0.59 (CH₃), 0.99 (NH₂), and 1.41 (N(CH₃)₂) at the

MP2/aug-cc-pVDZ level of theory. The most negative interaction energy for each configuration was chosen to be compared in consideration of the lone pair inversion and methyl group rotation under normal conditions. The difference in contacting surface area between complex **2** and **3** seems to be consistent with the difference of the magnitude in interaction energies. For example, the difference between **2a** and **3a** ($X = \text{CN}$) in contacting surface area is greater than that between **2b** and **3b** ($X = \text{F}$) and the interaction energy difference follows the same order. The large preference displayed by the *N,N*-dimethylamino group suggests the involvement of charge-transfer interactions.

A finer structural difference of the dimers involves the relative orientation of the substituent group *X*. With symmetrical substituents such as CN and F (**a** and **b**), there is only one minimum configuration for either dimers **2a–c** or **3a–c** (Figures 1 and 2). However, the magnitudes of the *N,N*-dimethylaniline, aniline, and toluene interaction energies with C_6F_6 depend to a small extent on whether the *N,N*-dimethylaniline and aniline lone pairs or the toluene methyl hydrogen are pointing at or away from the lower hexafluorobenzene ring (for example, see **3d**, **3d'** and **3e**, **3e'**). With the substituent *not* in contact with the π -face of C_6F_6 (**2a–f**, Figure 1), there is essentially no difference for the toluene dimer (-6.12 kcal/mol, **2d** and -6.13 kcal/mol, **2d'**) whether the hydrogen is pointing at or away from the C_6F_6 ring. For the aniline (-6.34 kcal/mol, **2e**, and -5.88 kcal/mol, **2e'**) and *N,N*-dimethylaniline (-7.05 kcal/mol, **2f**, and -6.54 kcal/mol, **2f'**) dimers, the more stable configuration (**2e** and **2f**) is predicted when the lone pair is pointing away from the hexafluorobenzene ring. This is likely due to a repulsive interaction in **2e'** and **2f'** between the lone pair on nitrogen and a nearby fluorine atom from C_6F_6 when the lone pair is pointing at the hexafluorobenzene ring.

With the substituent *in* contact with the π -face of C_6F_6 (**3a–f**, Figure 2), there are differences for the toluene, aniline, and *N,N*-dimethylaniline dimers (**3d–f** and **3d'–f'**) with regard to which direction the hydrogen or the lone pair is pointing. For the toluene–hexafluorobenzene dimer, the more stable configuration is predicted when the hydrogen atom is pointing away from the C_6F_6 ring (-6.45 kcal/mol for **3d** vs -5.55 for **3d'**, Figure 2). This is most likely due to a repulsive interaction between the methyl hydrogen atom and the nearest fluorine atom of the C_6F_6 ring in **3d'**. The distance between the hydrogen atom and the fluorine atom in contact in **3d** is 2.35 Å, which is shorter than the sum of the van der Waals radii for the two atoms in question.⁴⁴ For the complexes of aniline (-6.54 kcal/mol, **3e**, and -7.30 kcal/mol, **3e'**) and *N,N*-dimethylaniline (-8.41 kcal/mol, **3f'**), the more stable configuration (**3e'** and **3f'**) is predicted when the lone pair is pointing at the hexafluorobenzene ring. When the lone pair is pointing away, the potential energy surface is flat for *N,N*-dimethylaniline complex and no minimum energy conformation corresponding to **3f** was located. The preference for the nitrogen lone pair to point at the C_6F_6 ring is likely due to a combination of electrostatic, charge-transfer, and dispersion effects. More discussion on the origin of the enhanced attraction when $R_2 = \text{negative}$ will be presented later.

B. Closeness of Contact and the Minimum Stacking Configuration. By definition set forth in this study, when the center-of-mass separation $R_2 = 0.0$ Å, the dimer assumes the sandwich configuration. The sandwich configuration is computed to be a saddle point, rather than a minimum along the

parallel-displaced coordinate, and this saddle point exists even for the symmetrical dimer $\text{C}_6\text{F}_6\text{--C}_6\text{H}_6$ (Figure 5). The energy barriers along this coordinate generally range from 0.62 kcal/mol for the $\text{C}_6\text{F}_6\text{--C}_6\text{H}_6$ dimer to 1.98 kcal/mol for the $\text{C}_6\text{F}_6\text{--C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ dimer. At the sandwich configuration, minima are found along the symmetrical coordinate (R in Table 3) at slightly larger distances ($3.5\text{--}3.6$ Å) and the energy differences between the parallel-displaced minima and the sandwich minima range from 0.27 kcal/mol for the $\text{C}_6\text{F}_6\text{--C}_6\text{H}_6$ dimer to 1.50 kcal/mol for the $\text{C}_6\text{F}_6\text{--C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ dimer.

As described earlier, the $\text{C}_6\text{F}_6\text{--C}_6\text{H}_6$ dimer has been depicted in the literature as a representative of a face-to-face aromatic dimer. The face-to-face graphical depiction suggests that the interactions between hexafluorobenzene and benzene are dominated by electrostatic attractions. However, the fact that the sandwich configuration is not the energy minimum is at odds with this simple picture. As pointed out by both Reisse and Dougherty, the representation of the electronic distribution of a molecule as a multipole expansion is valid only at large interaction distances.^{32,33} Because of the distance requirement, the cation– π interaction cannot be quantitatively modeled as just an ion–quadrupole interaction when van der Waals contact distance is involved.³³ For the same reason, neither can the benzene–hexafluorobenzene interaction be quantitatively modeled as just a quadrupole–quadrupole interaction. The argument should be even more important here since there are two quadrupoles involved. In $\text{C}_6\text{F}_6\text{--C}_6\text{H}_6$ stacking interactions, the dimensions of the quadrupole (e.g., the distance between the two centers of negative charge in hexafluorobenzene) are greater than the separation distance between the arenes. It is clearly inappropriate to make any quantitative argument based on a multipole expansion. Similar to cation– π interactions,⁴⁵ the structures of hexafluorobenzene and benzene dimer cannot be rationalized unless other terms such as dispersion and charge transfer are also considered. In other words, the interactions between hexafluorobenzene and benzene cannot be treated as two simple quadrupoles with opposite signs.

Theoretical studies from this work and others are consistent with experimental observations concerning the $\text{C}_6\text{F}_6\text{--C}_6\text{H}_6$ dimer.^{12,25,26} A low-temperature crystal structure of an equimolar mixture of hexafluorobenzene and benzene shows that nearly parallel molecules stack alternately in infinite columns with an interplanar distance of about 3.4 Å and an intercentroid distance of 3.7 Å.²⁸ The difference between the interplanar and intercentroid distances clearly shows a parallel-displaced structure.

The optimized interplanar distance between hexafluorobenzene and benzene in a sandwich configuration is 3.6 Å (Figure 3). This distance is decreased to 3.4 Å when the center-of-mass separation (R_2) is allowed to change from 0.0 to 1.0 Å (Figure 1 and 5). When the interplanar distance is fixed at 3.4 Å and R_2 is allowed to change between -2.0 and 2.0 Å, a saddle point appears at $R_2 = 0.0$ Å (Figure 5). The sandwich configuration does not allow as close contact between the two arenes as the parallel-displaced configuration. An examination of the electron density isosurface of hexafluorobenzene and benzene prompts us to suggest a new application of the 3D pictures for the understanding of the slightly displaced (-1.0 Å) dimer configuration.

Electrostatic potential surfaces of the aromatic monomers were generated by mapping the electrostatic potential onto the surfaces of the total electron density isosurface (0.0004 electrons au^{-3}) for each monomer using the program GaussView and are

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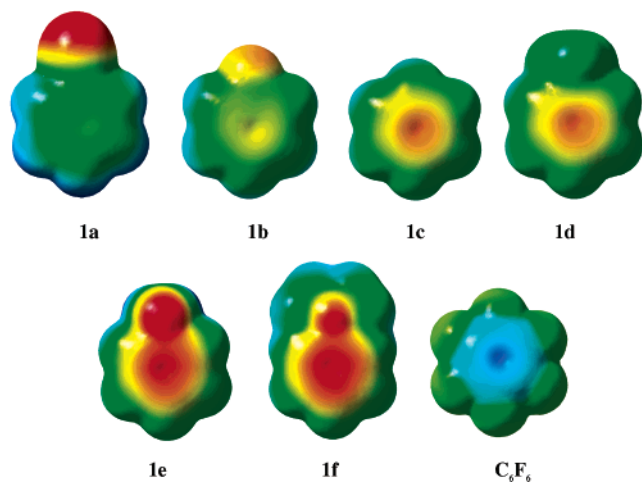


FIGURE 6. Calculated HF/6-31+G** electrostatic potential surfaces of substituted benzenes (**1a–f**) and hexafluorobenzene. From left to right: (first row) C_6H_5CN , C_6H_5F , C_6H_6 , and $C_6H_5CH_3$; (second row) $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, and hexafluorobenzene.

shown in Figure 6.⁴¹ Dougherty has shown that electrostatic potential surfaces of aromatic compounds can serve as a useful qualitative guide in the prediction of cation- π interaction strengths.⁴⁶ It is shown here that the increasing negative electrostatic potential (more red) on the substituted benzenes also follows qualitatively the order of increasing strength for the $C_6F_6-C_6H_5X$ dimers. A proposal to use the shape of the electron density surface to understand the preferred minimum energy configuration is presented.

We propose to use the shape and boundaries of the 3D molecular surface to predict arene-arene stacking arrangement. First, we will use the arene electron density surface to understand why the perfectly symmetrical sandwich configuration is not an energy minimum even for the $C_6F_6-C_6H_6$ dimer. As expected, the total electron density isosurfaces reveal that the aromatic- π system has a doughnut-shaped surface, Figure 7 (parts a and b).

The six aromatic ring carbon atoms, which provide their p orbitals to make up the circular- π system, are directly under the torus- π orbital. In a sandwich configuration, the carbon atoms and hence the ridge of the circular- π system from one arene are directly on top of those from the other arene. The arenes are prevented from getting any closer than their allowed density surfaces in the sandwich configuration by the disallowance of electrons from nonbonded atoms to occupy the same space. The interactions would become sharply repulsive if electrons of the same spin from nonbonded atoms were to occupy the same space (steric effect). Thus the steric repulsion from the circular- π system in the sandwich configuration causes the arenes to be separated at a greater distance ($R = 3.6 \text{ \AA}$). In the center of the circular- π system, a bowl-shaped empty space is present in benzene and an even deeper void is present in hexafluorobenzene. As shown in Figure 7d, the arenes can achieve a closer contact distance by sliding away slightly from the sandwich configuration so that the empty space in the center of the circular- π system of one arene is on top of a carbon atom from the other arene. By avoiding the direct contact of the ridges from the two π systems, a shorter vertical separation distance

between the two arenes is achieved ($3.3-3.4 \text{ \AA}$ vs $3.5-3.6 \text{ \AA}$ for the sandwich configuration), which allows a better mesh of more atoms at their optimal van der Waals distances.

The closeness of contact of electron density surfaces between the arenes can also be seen from the positions of the fluorine atoms relative to the benzene ring. The fluorine atoms have distinct spherical surfaces, and by situating between two hydrogen atoms of the benzene ring, rather than on top of them, maximum contact of the surface area is achieved. Since dispersion forces are proportional to contacting surface area,⁴⁷ a greater contact area leads to a greater stability. The parallel-displaced configuration was also found to be more stable by Tsuzuki.¹² He showed that both the sandwich and the parallel-displaced configurations are stabilized by electrostatic and dispersion forces. We propose here that by matching the empty space in the circular- π system of one arene with a carbon atom from the other arene, a smaller interplanar separation is achieved, which allows a greater contact area and hence a greater stabilization from dispersion interactions. A smaller interplanar separation would also allow charge-transfer interactions to occur. In the case of $C_6F_6-C_6H_5N(CH_3)_2$ dimer, the next section argues for a case of charge-transfer interactions.

Stacking interactions play an important role in the stabilization of DNA structures.⁴⁷ The base pairs in double-helical DNA structures arrange like a spiral stair case stacking on top of one another in a parallel-displaced fashion. No sandwich stacking of any aromatic residues exists in natural protein structures.^{48,49} The known structures of stacked octafluoronaphthalene with arenes and the bifunctional hexafluorophenyl phenylbutadiyne also show structure motifs that are remarkably similar to the feature described above for $C_6F_6-C_6H_6$.^{2,4,6} These facts are consistent with our analysis using the electron-density isosurface of the arenes to achieve a maximum closeness of contact.

C. A Threshold for Charge-Transfer Interactions. A monotonic relationship between the binding energy and the Hammett constants has been interpreted to indicate a polar/ π (or electrostatic) interaction between the arenes.⁴³ Hunter and co-workers have also used Hammett plots to illustrate the dominance of electrostatic forces in aromatic interactions.^{50,51} Although the Hammett constants do not necessarily correlate with ground state arene π -electron density,^{11,46} they do give some information about possible correlations between the calculated binding energies ($-\Delta E_{in}$) and classical substituent effects. The calculated binding energies vs the Hammett σ_{para} constants are plotted in Figure 8 for complex series **2** $C_6F_6-C_6H_5X$ (\blacklozenge). Again the values with the largest magnitude are chosen for all complexes. This plot looks remarkably like the published results from our recent experimental studies conducted in $CDCl_3$ less the aniline complex.¹³ Namely, the binding energy of the complex of $C_6F_6-C_6H_5N(CH_3)_2$ is much higher than that expected from the substituent constant.

Almost 40 years ago, charge-transfer bands were observed for 1:1 complexes of C_6F_6 and N,N-dimethylaniline and N,N-dimethyltoluidine and N,N-diethylaniline.⁵² No charge-transfer

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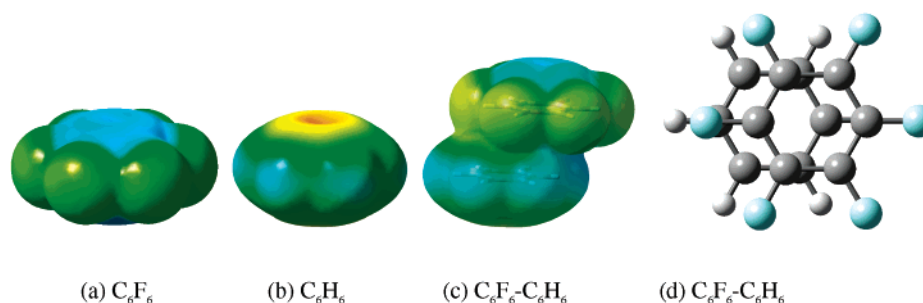


FIGURE 7. Sections a, b, and c show ab initio electron density (HF/6-31+G**) isosurfaces color mapped with electrostatic potential for C_6F_6 , C_6H_6 , and their complex. The isosurfaces show circular- π systems with bowl-shaped centers. (d) Ball & stick models for the optimized $C_6F_6-C_6H_6$ complex. A carbon atom from each arene is located near the center of the other arene to achieve a shorter vertical separation.

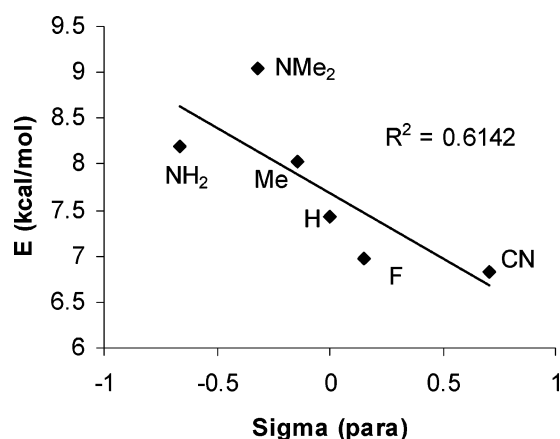


FIGURE 8. Plot of binding energy ($-\Delta E_{int}$, MP2(full)/6-31+G**) vs σ_{para} for complex series 2 $C_6F_6-C_6H_5X$ (\blacklozenge). Note that the binding energy of $C_6F_6-C_6H_5N(CH_3)_2$ deviates from that predicted by the Hammett parameter by a significant amount, which we suggest is indicative of the presence of charge-transfer interactions.

complex has been reported for aniline–hexafluorobenzene.⁵³ A charge-transfer band was observed for the model compound that we used to study the interaction between C_6F_6 and $C_6H_5N(CH_3)_2$.¹³ The large difference in binding energy between **3e** and **3f** is likely due to the difference in the ionization potentials of aniline (7.7 eV) and N,N-dimethylaniline (7.1 eV).^{54,55} By examination of the structures of **3e** and **3f** (Figure 2), $CH\cdots F$ hydrogen bonding in **3f** should be negligible. The distance between the nearest hydrogen atom of N,N-dimethylaniline and the fluorine atom in hexafluorobenzene is 3.2 Å while possible $CH\cdots F$ hydrogen bonds are reported anywhere between 2.36 and 2.86 Å.⁴⁴ Thus, the relatively “normal” position of aniline complex (**3e**) on the Hammett plot is most likely due to the relatively higher ionization potential of aniline and associated lack of charge-transfer interactions. Since the contributions from electrostatic and dispersive effects should be comparable for aniline and N,N-dimethylaniline, we attribute the higher binding energy of **3f** to charge-transfer interactions arising from the lower ionization potential of N,N-dimethylaniline. The evidence

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that supports this proposal includes the observation of charge-transfer bands for the complexes involving hexafluorobenzene and N,N-dimethylaniline,⁵² our recent experimental results,¹³ and this theoretical study. Since aniline does not seem to, but N,N-dimethylaniline does show a charge-transfer interaction with hexafluorobenzene, it seems reasonable to suggest a threshold for charge-transfer interactions between arenes with different characteristics. The intensity of charge-transfer interactions is inversely proportional to the difference between the ionization potential (IP) of the donor and the electron affinity (EA) of the acceptor.⁵⁶ The electron affinity of hexafluorobenzene is relatively small (0.53 eV) compared with typical π -acceptors such as *p*-benzoquinone (1.9 eV), chloranil (2.54 eV), and TCNE (3.17 eV), which explains why a strong donor is required to form a charge-transfer complex with C_6F_6 .

D. Distance Dependence of Interaction Energy at Short Contacting Range. Plot of interaction energy (MP2(full)/6-31+G**) vs interplanar distance (R_1) for complexes $C_6F_6-C_6H_5CN$ (\blacksquare), $C_6F_6-C_6H_6$ (\bullet), and $C_6F_6-C_6H_5N(CH_3)_2$ (\blacktriangle) are shown in Figure 9. The interaction energy of $C_6F_6-C_6H_5N(CH_3)_2$ is more than 3 kcal/mol larger than that of the other two complexes at $R_1 = 3.3$ Å but levels off to less than 1 kcal/mol when $R_1 \geq 4$ Å. Assuming electrostatic and dispersion forces play major roles in these dimers and in light of the evidence presented in the previous section, we hypothesize that the exceedingly high attraction of $C_6F_6-C_6H_5N(CH_3)_2$ at close distance is due to the presence of charge-transfer interactions. To assess this hypothesis, we examined several model potential energy curves.

Assuming the interactions between C_6F_6 and C_6H_6 are limited to electrostatic and dispersion forces, we start with a simple Lennard-Jones (12-6) type potential function,⁵⁷ eq 1, where $E(r)$ is the distance dependent potential energy, r is the interplanar distance, and a and b are adjustable constants.

$$E(r) = a/r^{12} + b/r^6 \quad (1)$$

The two parameters (a and b) in eq 1 were varied until a curve was obtained in which the minimum was at 3.4 Å and the potential energy was close to -5.43 kcal/mol, which is the interaction energy for the $C_6F_6-C_6H_6$ dimer at the MP2(full)/6-31+G** level. This was found to be when $a = 1.33 \times 10^7$ and $b = -1.70 \times 10^4$ and is represented as the solid blue curve in Figure 10. To model the distance dependence of the charge-

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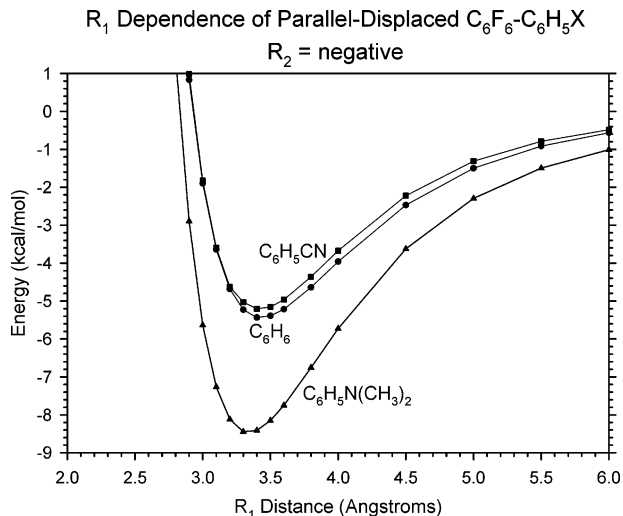


FIGURE 9. Plot of interaction energy (MP2(full)/6-31+G**) vs vertical separation distance for complexes C₆F₆-C₆H₅CN (■), C₆F₆-C₆H₆ (●), and C₆F₆-C₆H₅N(CH₃)₂ (▲). Note that the interaction energy of C₆F₆-C₆H₅N(CH₃)₂ is more than 3 kcal/mol greater than that of the other two complexes at R₁ = 3.3 Å but levels off to less than 1 kcal/mol when R₁ ≥ 4 Å. We suggest that the extra attraction at close distance is indicative of the presence of charge-transfer interactions.

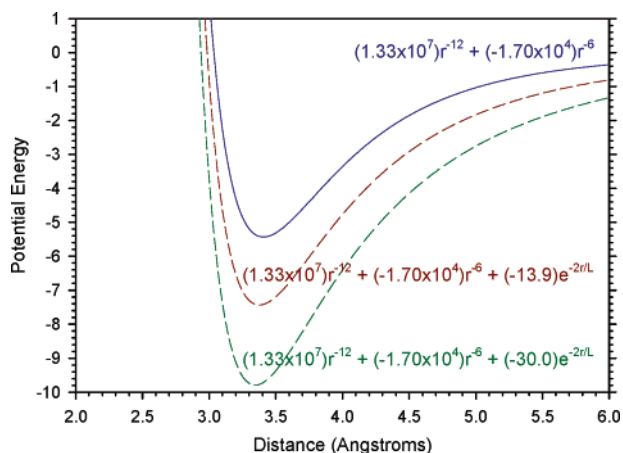


FIGURE 10. Potential energy vs distance plots for (1) Lennard-Jones (solid line); (2) same as (1) except with an additional charge-transfer term (red dash line); and (3) same as (2) except giving a greater weight to the charge-transfer term (green dash line).

transfer interaction, we use an inverse exponential function ($e^{-2r/L}$, where L is the sum of the van der Waals radii of the donor and acceptor) proposed by Dexter to model the distance dependence of the rate constant for excited-state energy transfer via an electron-transfer mechanism.^{58,59} In the current model, we use a value of $L = 3.50$ Å, which is the sum of the van der Waals radii of two carbon atoms. With the inclusion of this charge-transfer term, the overall potential function is represented by eq 2, where a , b , and c are adjustable constants and L is the van der Waals contact distance between the two arenes.

$$E(r) = a/r^{12} + b/r^6 + c/e^{(-2r/L)} \quad (2)$$

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Thus the new functional model includes a term for charge-transfer interaction in addition to the repulsive and the London force terms in the Lennard-Jones equation.

Two different constraints for the parameter c led to two plots, and both are shown in Figure 10. The first was to adjust the value of c until the difference between the simple Lennard-Jones potential and the modified functional curve at 6.0 Å was equal to 0.45 kcal/mol, which is the calculated energy difference between the C₆F₆-C₆H₅N(CH₃)₂ and C₆F₆-C₆H₆ dimers at 6.0 Å. This gives a value of $c = -13.9$ and is given as the dashed red curve in Figure 10. At 3.4 Å, this gives a difference of 2.0 kcal/mol between the simple Lennard-Jones potential and the modified functional curve. As a reminder, the MP2(full)/6-31+G** energy difference at 3.4 Å for the C₆F₆-C₆H₅N(CH₃)₂ and C₆F₆-C₆H₆ dimers is 2.98 kcal/mol. Therefore, the energy difference at the minima between the two initial models is slightly lower than the calculated value; however, the relative shape of the model potential curves is similar to the calculated R₁ dependences shown in Figure 9. The next constraint was to adjust the c value until the difference between the simple Lennard-Jones potential and the modified functional curves at 10.0 Å is equal to 0.1 kcal/mol, which is the calculated energy difference between the C₆F₆-C₆H₅N(CH₃)₂ and C₆F₆-C₆H₆ dimers at 10.0 Å. This gives a value of $c = -30.0$ and is given as the dashed green curve in Figure 10. At 3.4 Å, this gives a difference of 4.3 kcal/mol between the simple Lennard-Jones potential and the modified functional curves. This is now slightly larger than the calculated difference of 2.98 kcal/mol, but again the relative shapes of the model potential curves are similar to the calculated R₁ dependences shown in Figure 9. These models suggest that the addition of a charge-transfer interaction has the effect of increasing the strength of the interaction energy (lowering the well depth) when compared with a simple Lennard-Jones potential. These plots and the Hammett plot for the calculated binding energies are both consistent with our previous experimental studies in CDCl₃ and lend support for the hypothesis that a charge-transfer interaction contributes to the unusually strong interaction energy of the N,N-dimethylamino-hexafluorobenzene dimer.¹³

Conclusions

Perfluoroarene interactions have a rich history in both bioorganic chemistry and crystal engineering.^{6,60} A better understanding of the substituent effects in perfluoroarene interactions will help the rational design efforts in these areas. Three-dimensional molecular electron density surfaces are calculated at the HF/6-31+G** level of theory. The calculated molecular shapes are proposed to be useful in the prediction of the stacking arrangement of perfluoroarenes. The proposal involves the staggering of the two arenes to avoid a head on overlap of the π systems. Interaction energies for the parallel displaced and sandwich C₆F₆-C₆H₅X dimers were calculated up to the MP2/aug-cc-pVDZ level of theory. Electron-donating groups increase and electron-withdrawing groups decrease the interaction energies. N,N-dimethylamino group has by far the largest effect, increasing the interaction energy by nearly 3 kcal/mol relative to the unsubstituted benzene-hexafluorobenzene dimer. This substituent is even capable of increasing the interaction energy by 1 kcal/mol greater than that of the amino group itself, despite the latter having a stronger electron-donating effect according to the classical Hammett constant.¹⁵ This anomaly is attributed to a charge-transfer effect for the N,N-

dimethylamino complex, which is consistent with our previous experimental results.¹³

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Supporting Information Available: Plots of interaction energy vs center-of-mass separation distance and Cartesian coordinates of all the dimers examined. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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