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Ab Initio Study of the Interaction of CHX_3 (X = H, F, Cl, or Br) with Benzene and Hexafluorobenzene

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In this paper, the results of a study of the interaction of methane, fluoroform, chloroform, and bromoform with benzene and hexafluorobenzene are presented. The benzene complexes were studied at the MP2/6-31G(d) and MP2/6-311++G(2d,p) levels, and the hexafluorobenzene complexes were only studied at the MP2/6-31G(d) level. The optimized geometries, stabilization energies, potential energy surfaces, harmonic frequencies, and vibrational intensities are reported. A net attraction is predicted for all four benzene complexes, whereas for the $CHX_3 \cdot C_6F_6$ complexes, it was found that MP2/6-31G(d) predicts a net attraction for the CH_4, $CHCl_3$, and $CHBr_3$ complexes and does not predict a stable complex for $CHF_3 \cdot C_6F_6$. The three complexes with net attractions all have blue-shifts of the CHX_3 CH stretching wavenumber and a slight contraction (0.001−0.003 Å) of the CH bond in CHX_3. The MP2/6-31G(d) level predicts that the intensity of the CHX_3 CH stretch will vary widely. For $CH_4 \cdot C_6H_6$ and $CHF_3 \cdot C_6H_6$, it is predicted that the intensity will be smaller for the complexes than the free molecules, whereas for the other complexes, anywhere from a 30% increase to an increase of 87 times is predicted. The atoms in molecules analysis showed that only three of the eight criteria for normal hydrogen bonding are satisfied for all eight complexes studied. Criterion 3 (value of the Laplacian at the bond critical point) is not satisfied for any of the eight complexes.

Introduction

In this paper, the results of theoretical calculations on complexes of methane, fluoroform, chloroform, and bromoform with benzene and hexafluorobenzene are presented to examine the interaction between carbon proton donors and aromatic rings. Initially, these interactions were labeled anti-hydrogen bonds,[1] but more recently, they have become known as improper, blue-shifting hydrogen bonds.[2,3]

There have been numerous papers that have examined this type of interaction in complexes involving aromatic molecules and carbon proton donors.[1−7] Most of the literature calculations were performed using the second-order Møller−Plesset method with various basis sets for the complexes of carbon proton donors with both aromatic and nonaromatic molecules.[1−4,6,8−14] Generally, the formation of the complex results in a shortening of the C−H bond of the carbon proton donor and a blue-shift of its stretching frequency. Since these results are opposite (with respect to change in the bond length and frequency shift) to what is seen with normal hydrogen bonding, there has been much debate as to whether the blue-shifting H-bonds are distinct from normal H-bonds.[7−10,13,15] There have been several very extensive reviews of these interactions in recent years,[2,3,7,12,15] and the reader is referred to those articles for a more complete description of the research. Many of the studies that have been completed have found that there is essentially no difference between the normal hydrogen bonds and the blue-shifting hydrogen bonds.[11] A hyperconjugative interaction has been suggested by Alabugin et al.[13] to explain the shortening of the C−H bond with the blue-shifting hydrogen bonds. Hermansson[7] has brought forward the idea that the improper, blue-shifting hydrogen bonds are basically the same as their normal red-shifting counterparts and that molecules such as CH_4, CHF_3, and $CHCl_3$ are also capable of producing the normal types of hydrogen bonds in addition to the blue-shifting hydrogen bonds. Recently, Keefe and Bertie observed[16,17] a similar interaction between benzene molecules in pure liquid benzene and labeled the interaction as a pseudo-hydrogen bond. Blue-shifting hydrogen bonds also have been observed in complexes involving only nonaromatic molecules.[2,3,7,11−14]

Cubero et al.[18] performed an analysis of the electron density topology of hydrogen bonded and anti-hydrogen bonded complexes utilizing the atoms in molecules (AIM) theory.[19,20] Their results suggest that the difference between the two types of interactions is due to changes in electron density that occur upon complex formation. Their analysis of C−H···benzene complexes found there to be six (3,−1) bond critical points (BCP) linking the hydrogen atom of chloroform to each carbon atom in benzene, six (3,+1) ring critical points (RCP) between the BCP, and one (3,+3) cage critical point (CCP). Their analysis of a chloroform-fluorobenzene supermolecule found that a BCP existed between the hydrogen atom of the chloroform and the para carbon of the fluorobenzene.

Kolandaivel and Nirmala[21] used the AIM theory[19,20] and NBO analysis[22,23] to examine 15 different complexes exhibiting either proper or improper hydrogen bonding. Complexes with X−H···Y (X = N, O, F, or Cl; Y = N or O) interactions were found to result in an elongation of the X−H bond upon complex formation and a decrease of the vibrational stretching frequency. The formation of complexes with C−H···Y (Y = N, O, F, or Cl) interactions were found to result in a contraction of the C−H bond and an increased C−H stretching frequency. However, it was found that all 15 complexes could satisfy the criteria for hydrogen bonding. The change in bond length was found to be based upon the type of charge transfer that occurrs in a given complex.

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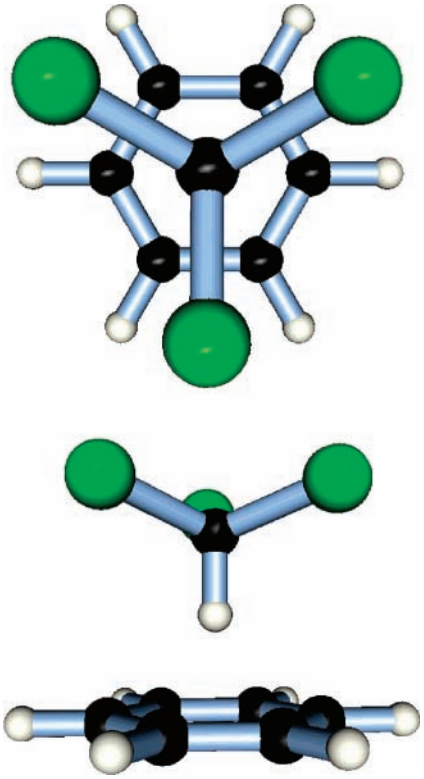

Figure 1. Orientation of $CHX_3 \cdot C_6Y_6$ complexes. Top image is the view from above the plane of the C_6Y_6 ring looking down the CH bond of CHX_3.

A unified theory to explain the cause of X−H···Y (where Y is an electron-rich species) red- and blue-shifted hydrogen bonds was put forward by Joseph and Jemmis.[24] The contraction of the X−H bond that is seen for blue-shifting hydrogen bonds is said to result from less polar, electron-poor X−H bonds due to the electron affinity of X. This causes a gain of electron density in the X−H region of the molecule when it is in the presence of Y. The elongation of the X−H bond seen for normal hydrogen bonding cases is attributed to the attractive interaction between H and Y that occurs with polar X−H bonds.

In this paper, we present a systematic study of the interaction of CHX_3 (X = H, F, Cl, or Br) with benzene and hexafluorobenzene. The $CHBr_3 \cdot C_6H_6$ complex and $CHX_3 \cdot C_6F_6$ complexes are reported for the first time. In addition to the effect on the vibrational frequencies, we also present an analysis of the effect of complex formation on the vibrational intensities, something that has essentially been ignored to this point. We also present an AIM study of these complexes with hopes that this will provide insight into the differences between improper and normal types of hydrogen bonding.

Computational Methods

The ab initio calculations were preformed using Gaussian 03[25] on a Pentium 4 computer, a Dual Processor Pentium Xeon computer, an AMD Opteron cluster, and a multiprocessor SGI Itanium 2 computer. Geometry optimizations, potential energy surface (PES) scans, and frequency calculations were carried out for complexes of methane, trifluoromethane, trichloromethane, and tribromomethane with benzene and hexafluorobenzene. The basis set superposition error (BSSE) was approximated using the counterpoise method.[26,27] For each case, complexes were studied with the CH of the trihalomethane perpendicular to and pointing toward the center of the phenyl ring. The orientation is illustrated in Figure 1. The calculations were performed at the MP2/6-31G(d) and MP2/6-311++G-(2d,p) levels for the benzene complexes and at the MP2/6-31G-(d) level for the hexafluorobenzene complexes.

TABLE 1: Optimized Geometries, Stabilization Energies, and Frequency Shifts of Trihalomethane Complexes with Benzene and CH Bond Lengths and Dipole Moments of Isolated Trihalomethane Compounds Calculated at MP2/6-311++G(2d,p)

variable	CH_4/C_6H_6	CHF_3/C_6H_6	$CHCl_3/C_6H_6$	$CHBr_3/C_6H_6$
R_{CC} (Å)	1.396	1.397	1.397	1.398
R_{CH} (C_6H_6) (Å)	1.086	1.085	1.085	1.085
R_{H-ring} (Å)	2.72	2.40	2.25	2.24
R_{CH} (CHX_3) (Å)	1.089	1.086	1.083	1.083
R_{CX} (Å)	1.089	1.349	1.776	1.937
∠HCX (deg)	109.56	110.73	107.83	107.28
ΔE (kJ mol^{-1})	5.4	15.7	24.2	27.2
$\tilde{\nu}$ shift[a] (cm^{-1})	1	28	18	*b*
		Free CHX_3		
R_{CH} (CHX_3) (Å)	1.090	1.089	1.086	1.086

[a] Reported as the wavenumber of the CH stretch of $CHCl_3$ in the complex minus the wavenumber of the CH stretch of free $CHCl_3$; thus, a positive value indicates a blue-shift. [b] Frequency calculation is too large to be carried out on the system available for this study.

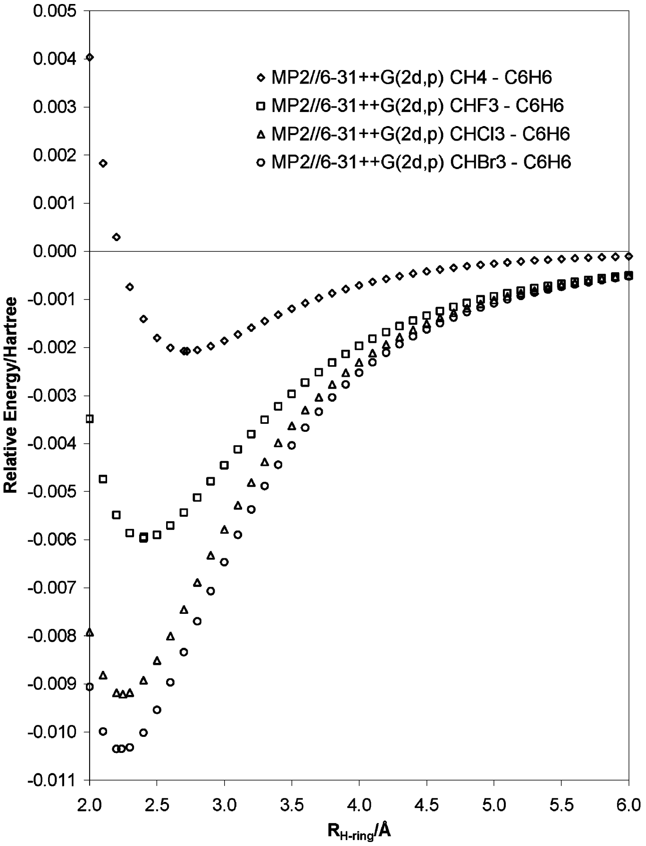

Figure 2. PES calculated at the MP2/6-311++G(2d,p) level along R_{H-ring} for complexes of C_6H_6 with CH_4, CHF_3, $CHCl_3$, and $CHBr_3$. Energies were corrected for basis set superposition error using the counterpoise estimation.

Results and Discussion

Methane and Trihalomethane Complexes with Benzene. The optimized geometric parameters of the various benzene complexes studied are given at the MP2/6-311++G(2d,p) level in Table 1 along with the stabilization energies, the distances between the phenyl plane and the H of the trihalomethane compounds at the energy minimum, and the wavenumber shifts

TABLE 2: Results of the MP2/6-31G(d) Level Calculations for CHX_3 Complexes with Benzene and Hexafluorobenzene

			CHX_3 R_{CH} (Å)		CHX_3 $\tilde{\nu}_{CH}$ (cm^{-1})			intensity (km mol^{-1})		
complex	R_{H-ring} (Å)	ΔE (kJ mol^{-1})	free molecule	complex	free molecule	complex	shift	free molecule	complex	ratio
CH_4 C_6H_6	3.08	2.1	1.091	1.090	3245	3254	9 (blue)	19.8	9.1	0.5
CHF_3 C_6H_6	2.51	11.8	1.089	1.086	3233	3283	50 (blue)	47.5	12.3	0.3
$CHCl_3$ C_6H_6	2.44	15.7	1.086	1.086	3241	3267	26 (blue)	0.03	26.1	87
$CHBr_3$ C_6H_6	2.38	18.6	1.086	1.085	3247	3272	25 (blue)	3.5	58.1	17
					H···ring[a]					
CH_4 C_6F_6	3.28	1.5	1.091	1.090	3245	3247	2 (blue)	19.8	26.4	1.3
CHF_3 C_6F_6[b]	3.13	−1.1	1.089	1.089	3233	3228	−5 (red)	47.5	60.1	1.3
$CHCl_3$ C_6F_6	2.65	1.5	1.086	1.085	3241	3255	14 (blue)	0.03	0.3	10
$CHBr_3$ C_6F_6	2.56	5.1	1.086	1.084	3247	3274	27 (blue)	3.5	10.3	2.9

H···F[c]

			CHX_3 R_{CH} (Å)	
complex	R_{H}-F (Å)	ΔE (kJ mol^{-1})	free molecule	complex
CH_4 C_6F_6	2.92	0.8	1.091	1.090
CHF_3 C_6F_6	2.59	2.4	1.089	1.088
$CHCl_3$ C_6F_6	2.46	3.5	1.086	1.085
$CHBr_3$ C_6F_6	2.41	4.2	1.086	1.085

[a] Values in these rows are for the complex with the H of CHX_3 perpendicular to and pointing toward the plane of C_6F_6. [b] This complex optimized to a stable complex, but the frequency calculation gave three imaginary frequencies, and the energy was slightly higher than the sum of the free molecules. [c] Values in these rows are for the complex with the H of the CHX_3 pointing toward one of the F atoms of C_6F_6.

of the CH stretch of the trihalomethane compounds. It is clear from these values that there is very little change in the benzene geometry in the four different complexes. The R_{CC} and R_{CH} values of the benzene portion of the complexes vary by only 0.001 Å. The R_{CH} values of the CHX_3 portion of the complexes also vary only slightly both between the different complexes as well as between the complex and the free CHX_3 molecule. For example, at the MP2/6-311++G(2d,p) level, the R_{CH} values vary from a maximum of 1.089 Å in the $CH_4{\cdot}C_6H_6$ complex to a minimum of 1.083 Å in both $CHCl_3{\cdot}C_6H_6$ and $CHBr_3{\cdot}C_6H_6$ complexes. Also, at the MP2/6-311++G(2d,p) level, the R_{CH} value is 1.086 Å in free $CHCl_3$ and 1.083 Å in $CHCl_3{\cdot}C_6H_6$. Although the variations are small, all of the complexes are consistent at the MP2/6-311++G(2d,p) level in that a slight shortening of the CH bond length in CHX_3 is predicted upon complex formation.

The shifts in the CHX_3 CH stretching wavenumber also are given in Table 1. In the cases given, blue-shifts are predicted, although it is only a slight shift for $CH_4{\cdot}C_6H_6$. The wavenumber shifts as well as changes in intensity are discussed in more detail in the next section along with the results for the C_6F_6 complexes.

The relaxed PES calculated at the MP2/6-311++G(2d,p) level along the R_{H-ring} coordinate are plotted in Figure 2 for the four different benzene complexes. In Figure 2, the diamonds are for $CH_4{\cdot}C_6H_6$, the squares are for $CHF_3{\cdot}C_6H_6$, the triangles are for $CHCl_3{\cdot}C_6H_6$, and the circles are for $CHBr_3{\cdot}C_6H_6$. The PES calculations predict a net attraction between all the benzene complexes.

Methane/Hexafluorobenzene and Trihalomethane/Hexafluorobenzene Complexes. Attempts were made to study these complexes with the 6-311++G(2d,p) basis set at the MP2 level, but the computers available for this work could not handle these systems. The 6-31G(d) basis set was the largest basis set that could successfully be used to study the complexes at the MP2 level with the computers available to this group. The results for the $CHX_3{\cdot}C_6H_6$ and $CHX_3{\cdot}C_6F_6$ complexes at the MP2/6-31G(d) level are summarized in Table 2.

The stabilization energies, interaction distances, and wavenumber shifts calculated with the 6-31G(d) basis set for the C_6H_6 complexes are slightly different than those calculated with the 6-311++G(2d,p) level. The stabilization energies are smaller with the 6-31G(d) basis set, and as a result, the interaction distances are slightly larger. The wavenumber shifts predicted with the 6-31G(d) basis set are larger than those predicted with the 6-311++G(2d,p) basis set. However, the orders for all three properties for the four benzene complexes are the same with both basis sets. It is also probable that the stabilization energies, interaction distances, and wavenumber shifts will vary accordingly between the 6-31G(d) and the 6-311++G(2d,p) basis sets for the hexafluorobenzene complexes.

At the MP2/6-31G(d) level, there were found to be net attractions between hexafluorobenzene and methane, chloroform, and bromoform. No net attraction was found to exist between hexafluorobenzene and fluoroform. The predicted stabilization energies are very small for the CH_4, CHF_3, and $CHCl_3$ complexes. The stabilization energy for the $CHBr_3{\cdot}C_6F_6$ complex is a little larger but still very small. In all cases, the stabilization energies are much smaller for the hexafluorobenzene complexes than for the benzene complexes. As a consequence, the interaction distances are larger. Both of these results can be attributed to the high electronegativity of fluorine; thus, the electron density above the ring is reduced, and the interaction is weakened.

For all the benzene and hexafluorbenzene complexes, there are no major changes in the C−H bond of the CHX_3 molecules upon complex formation; however, contractions of 0.001−0.003 Å are predicted for the complexes with a net attraction. Apart from the $CHF_3{\cdot}C_6F_6$ complex, all the CH stretch wavenumber shifts are blue-shifts. While the changes in the CH stretch wavenumber are consistent, the predicted changes in intensity vary significantly, from approximately only 30% as strong for the $CHF_3{\cdot}C_6H_6$ complex to 87 times as strong for the $CHCl_3{\cdot}C_6H_6$ complex. It is clear that the changes in intensity are not systematic for the different complexes.

Since fluorine is so electronegative, complexes where the H on CHX_3 was pointed toward one of the F atoms of C_6F_6 were also explored. This orientation is shown in Figure 3, and the results are summarized in Table 2 with the other complexes. It is interesting to note that in all four cases, the H at the PE minima is a little closer to the F than the H is to the ring in the corresponding complexes with the CH perpendicular to the ring. The stabilization energies for the CHF_3 and $CHCl_3$ complexes

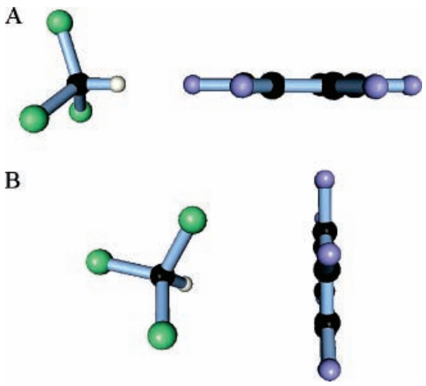

Figure 3. Alternate orientations of CHX_3•C_6F_6 complexes.

are greater for the CH···F interactions than for the CH···ring interactions, while for the CH_4 and $CHBr_3$ complexes, the stabilization energies are less in the CH···F arrangement. However, there is only a small difference in energy between the complexes having CH···F and CH···ring interactions, and both types of C_6F_6 arrangements have weaker interactions than what is seen for the C_6H_6 complexes.

Orientation Dependence of CHX_3•C_6F_6 Complexes. It is well-known that the CH bond of CHX_3 in the CHX_3•C_6H_6 complexes is preferentially oriented perpendicular to the plane of the benzene ring. However, as introduced previously, C_6F_6 offers a second electron density that can attract the H, namely, the fluorine atoms that to date have not been studied. To study these interactions, relaxed PES scans were performed. The CHX_3 was tilted from perpendicular and centered over the ring at one extreme (see Figure 1) to the CH bond being collinear with the CF bond at the other extreme (see Figure 3A). In these relaxed PES scans, the CCC angle of C_6F_6 was constrained to 120°, and the XXCC dihedrals angles were held fixed at 120°. All other variables were allowed to vary, although there was negligible change throughout the scans. The results of these PES scans are shown in Figure 4. It is interesting to note that there is significant variation in the PES for the three different complexes. As indicated previously, the CHF_3•C_6F_6 complex does not form a stable complex in the perpendicular orientation, but rather, this is a transition state between the two linear (0 and 180°) orientations with a very small barrier (~1 kJ mol^{-1}). For both $CHCl_3$•C_6F_6 and $CHBr_3$•C_6F_6 complexes, the 90° orientation is a PE minimum as are the interactions with the electron density surrounding the F (close to 180°). However, the relative position with respect to the 90° orientation is opposite for the two complexes, being slightly lower for the $CHCl_3$•C_6F_6 complex and slightly higher for the $CHBr_3$•C_6F_6 complex. In both cases, there is a transition state between the two interactions at around 130°. Note that the minima for the attractions with F are not exactly at 180°. To ensure that this was not due to the fact that the ring was constrained to be a perfect hexagon, another optimization was carried out at the 180° orientation for the $CHCl_3$•C_6F_6 complex. In this case, no constraints were placed on the geometry, and the structure was reoptimized at the 180° orientation. This made only a ~0.04 kJ mol^{-1} difference in the energy. Although the interactions are all fairly weak, the fact that the orientation dependence of the CHX_3 is different for the three complexes is intriguing and needs further study, which is beyond the scope of this paper.

The second relaxed PES scan that was carried out is that the H was held fixed above the center of the ring, but the CH bond was tilted. This orientation is depicted in Figure 3B. This scan was only carried out for the $CHCl_3$•C_6F_6 complex between 90 and 106° and is shown with the open diamonds in Figure 4. It is interesting to note that the initial tilting gives rise to a stronger interaction by about 1.5 kJ mol^{-1} through the interactions of the chlorines with the carbons. However, after ~12° rotation to 102°, further rotation causes significant repulsion between the chlorines and the flourines, causing the energy to rise sharply.

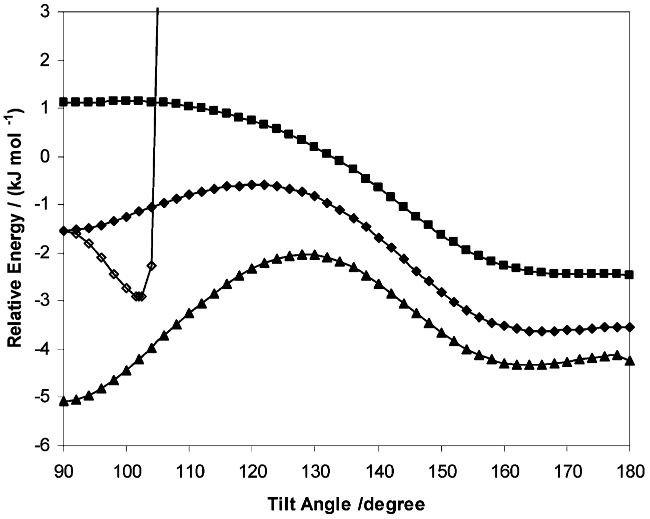

Figure 4. Relaxed PES scans for the tilting of CHX_3 from 90 to 180° with respect to the plane of C_6F_6. The energies given are relative to the total energies of the free molecules and were corrected for basis set superposition error using the counterpoise estimation. The solid systems are for rotating CHX_3 about the center of the C_6F_6 ring from having the C−H bond perpendicular to the ring (Figure 1) to parallel to the CF bond as depicted in Figure 3A. The squares are for CHF_3, the diamonds for $CHCl_3$, and the triangles for $CHBr_3$. The open diamonds are for rotating the CCl_3 portion and keeping the H centered over the C_6F_6 ring.

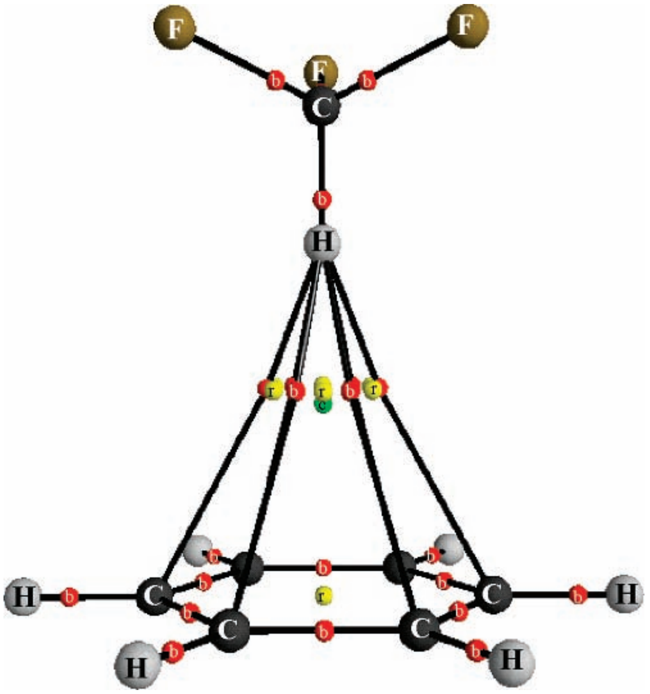

Figure 5. AIM analysis of fluoroform-benzene complex at the MP2/6-31G(d) level. The BCP are labeled with a “b”, the RCP are labeled with an “r”, and the CCP is labeled with a “c”. The solid black lines are the bond paths. There is a BCP between the H on CHF_3 and each of the Cs of the C_6H_6 ring. There are seven RCP, one in the middle of the C_6H_6 ring and six between the H on CHF_3 and the C_6H_6 ring. There is one CCP.

TABLE 3: Eight Criteria for Hydrogen Bonding Proposed by Popelier and Koch[20,29] Applied to the CHX_3 Complexes with Benzene and Hexafluorobenzene

	1	2	3	4	5	6	7	8
complex	BCP[a]	electron density at BCP (au)[b]	Laplacian at BCP (au)[b]	penetration of H and acceptor?	H atom electron loss?	H atom destabilized?	dipolar polarization decrease?	H atom volume decrease?
CH_4 C_6H_6	6[c]	0.002 (yes)	−0.002 (no)	yes	yes	yes	yes	yes
CHF_3 C_6H_6	6	0.003 (yes)	−0.003 (no)	yes	yes	yes	no	no
$CHCl_3$ C_6H_6	6[c]	0.006 (yes)	−0.005 (no)	yes	yes	yes	yes	yes
$CHBr_3$ C_6H_6	6[c]	0.007 (yes)	−0.005 (no)	yes	yes	yes	yes	yes
CH_4 C_6F_6	6	0.002 (yes)	−0.001 (no)	no	yes	no	no	no
CHF_3 C_6F_6[d]	6	0.002 (yes)	−0.002 (no)	no	yes	yes	no	no
$CHCl_3$ C_6F_6	6[c]	0.005 (yes)	−0.004 (no)	yes	yes	yes	yes	yes
$CHBr_3$ C_6F_6	6[c]	0.005 (yes)	−0.004 (no)	yes	yes	yes	yes	yes

[a] Number of BCP between the H of CHX_3 and the ring. [b] Whether or not the condition for H bondinaccg is met is indicated in parentheses. [c] Gaussian 03 found six BCP using the AIM option; however, AIM2000 only found one. [d] While this complex converged to a stable arrangement, it is a little higher in energy than the free molecules.

AIM Analysis. Each of the perpendicular benzene and hexafluorobenzene complexes with CHX_3 (X = H, F, Cl, or Br) were examined using the AIM theory[19] using the AIM2000 software[28] and the AIM option of Gaussian 03.[25] The topology of $CHF_3\cdot C_6H_6$ is shown in Figure 5. Note that the $CHF_3\cdot C_6F_6$ complex was examined with AIM in spite of the fact that the calculated energy of the optimized complex is slightly higher than that of the free molecules. Eight different criteria for hydrogen bonding have been proposed by Popelier and Koch.[20,29] They are as follows: (1) A BCP must be present to classify an attraction as a hydrogen bond. (2) The electron density at the BCP must be within the range of 0.002−0.04 au. (3) The Laplacian at the BCP must be between 0.006 and 0.130 au. (4) There must be penetration of the hydrogen atom and acceptor atom. An electron density value of 0.001 au is taken as being the edge of a molecule. If the electron density at the position of the BCP in the free molecules is greater than 0.001 au, then penetration has occurred. (5) The hydrogen atom must lose electrons when the formation of the hydrogen bond occurs. (6) The hydrogen atom must become destabilized. (7) The dipolar polarization of the hydrogen atom must decrease when a hydrogen bond forms. (8) The hydrogen atom's volume must decrease when the hydrogen bond forms.

These eight criteria are presented for the eight different complexes in Table 3. Gaussian 03 found six BCP between CHX_3 and benzene or hexafluorobenzene for all eight complexes. Note that AIM2000 only located one BCP for five of the complexes despite trying several starting points and several conditions for the convergence in the iteration algorithm. This may well be due to the fact that the electron density is small and very flat in this region, thus making the BCP difficult to locate. In any case, all of the benzene and fluorobenzene complexes each have at least one BCP between the aromatic ring and the CHX_3. The value of the electron density at the BCP is found to be within the range of 0.002−0.04 au for the benzene and hexafluorobenzene complexes, although the electron density at the BCP is close to the cutoff for three of the complexes. For all the complexes, the value of the Laplacian at the BCP is outside of the range of 0.006−0.130 au. There is penetration between the CHX_3 hydrogen atom and the aromatic ring for all of the benzene complexes, but this is only the case for the hexafluorobenzene complexes with $CHCl_3$ and $CHBr_3$. In all cases, there is a loss of electrons in the CHX_3 hydrogen atom when the complexes form. The CHX_3 hydrogen atom is destabilized upon complex formation for all complexes with the exception of the $CH_4\cdot C_6F_6$ complex. Both the dipolar polarization and the volume of the hydrogen atom are decreased in the complexes with the exception of $CHF_3\cdot C_6H_6$, $CHF_3\cdot C_6F_6$, and $CH_4\cdot C_6F_6$.

It is clear from Table 3 that not all eight criteria are satisfied for these interactions. Only criteria 1, 2, and 5 are satisfied for all eight complexes. It is interesting to note that criterion 3 is not satisfied for any of the eight complexes; thus, it is possible that this may serve as a means of distinguishing blue-shifting hydrogen bonds from normal hydrogen bonds. This will need to be pursued in more detail and is the subject of current work in this lab and will be presented in a future paper.

Conclusion

In this paper, the results of a systematic study of CHX_3 (X = H, F, Cl, or Br) with benzene and hexafluorobenzene were presented. The optimized geometries and PES of the various complexes and the changes in the wavenumbers and intensities of the CHX_3 CH stretch upon complex formation were determined. For the $CHX_3\cdot C_6H_6$ complexes, the MP2 method predicted very little change in the C_6H_6 portion of the complexes. The CH bonds of CHX_3 contracted by up to 0.003 Å from that of the free molecules, and a slight blue-shift was predicted for all the complexes of the CHX_3 CH stretching wavenumber, with the largest shift for $CHF_3\cdot C_6H_6$.

For the $CHX_3\cdot C_6F_6$ complexes, it was found that MP2/6-31G(d) predicted a net attraction for the CH_4, $CHCl_3$, and $CHBr_3$ complexes and did not predict a stable complex for $CHF_3\cdot C_6F_6$. The three complexes with net attractions all had blue-shifts of the CHX_3 CH stretching wavenumber and a slight contraction (0.001−0.003 Å) of the CH bond in CHX_3. It was found that CHF_3, $CHCl_3$, and $CHBr_3$ form stronger attractions with the F of C_6F_6 than with the electron density above the ring. It also was found that slight tilting of the $CHCl_3$ resulted in a stronger attraction to the electron density above the ring through an interaction with the C atoms. However, this attraction was quickly replaced by a net repulsion upon further tilting of $CHCl_3$ above the ring.

The MP2/6-31G(d) level predicted that the intensity of the CHX_3 CH stretch varies widely. For $CH_4\cdot C_6H_6$ and $CHF_3\cdot C_6H_6$, it predicted that the intensity is smaller for the complexes than the free molecules, whereas for the other complexes, anywhere from a 30% increase to an increase of 87 times was predicted.

The AIM analysis showed that only three of the eight criteria for normal hydrogen bonding are satisfied for all eight complexes studied. Criterion 3 (value of the Laplacian at the BCP) was not satisfied for any of the eight complexes.

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