High Level Theoretical Study of Benzene−Halide Adducts: The Importance of C−H−Anion Hydrogen Bonding

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High level ab initio calculations were performed on the interaction of halide anions (F^-, Cl^-, Br^-, and I^-) to benzene. For these systems recent experimental and theoretical data are rather scarce, in spite of their growingly acknowledged importance for binding in complex biological systems. We have thus explored the complete basis set limit and the effect of counterpoise basis set superposition error corrections on the minimum geometries and energies of benzene−halide adducts in their possible interaction modes. The binding energy and enthalpy values (ranging from −15.3 kcal/mol for fluoride to −6.1 kcal/mol for iodide) show that the hydrogen bonding occurring in these complexes cannot be described as a weak interaction. We have furthermore investigated the topology of the minima and of other selected sections of the potential energy surface, so to gain further insight on the nature of the halide−benzene interaction. In particular, the geometry corresponding to the C_{6v} symmetry, although being overall repulsive, has displayed the unprecedented presence of a small flex (a minimum in C_{6v} symmetry) with interaction energy close to zero or slightly attractive.

Introduction

During the last years the study of noncovalent interactions involving aromatic systems has witnessed an intense growth, due to their widespread presence and their importance in complex biological systems. In particular, interactions involving the π electron cloud have been thoroughly investigated. Specific examples include (1) alkaline or alkaline earth metal cation−π interactions, having in some cases a strength comparable to that of chemical bonds,[1−4] (2) interactions between substituted benzenes, or simple heteroaromatic rings, taken as models of aminoacids, with complex cations,[5] and (3) π−π interactions.[6,7] Much less attention, and only more recently, has been devoted to the investigation of the interaction between aromatic systems and anions. However, such interactions, in particular those concerning fluoride and chloride anions, play an important role in organic synthesis,[8] in solvation in heterogeneous media,[9] and in anion recognition processes,[10,11] particularly in connection with the role of anion receptors in many biological systems.[12,13]

The vast majority of recent studies (see ref 14 for a review on arene-anion complexes) has focused on the anion−π interactions between electron deficient aromatic rings with electron-withdrawing groups, presenting a quadrupole moment of opposite sign respect to benzene, and halide anions,[10,15−20] or on the investigation of cooperative effects between cation−π and anion−π interactions.[21,22] Both cases lead to C_{6v} binding geometries similar to those corresponding to metal cation−π adducts. Interactions of unsubstituted benzene with halide anions, where the C−H groups of the benzene ring can act as hydrogen bonding donors toward halide atoms, have in comparison been little studied. Nevertheless, some recent papers[23,37] show that anion−aromatic hydrogen interactions do play an important role[24] and that the resulting hydrogen bond is much less weak than what is generally assumed.

As far as the investigation of benzene−halide complexes is concerned, after the high pressure mass spectrometry (HPMS) experiments by Hiraoka and co-workers[25,26] on the thermodynamics of the whole series of benzene−halide complexes in the late 80s, only in the very last years has there been a renewed attention to the determination of accurate binding energies and the corresponding geometries of these clusters. Recent experimental work consists of IR dissociation spectra[27,28] and photoelectron and photodetachment spectra,[29] whereas theoretical work[23,27,28,30] has mainly been used to support experimental determinations. Most of these studies are, however, limited to benzene−chloride clusters.[23,28−30] Thus, for example, in the case of benzene−fluoride complex, the only available binding energy value dates back to the HPMS determination of ref 25.

All previous theoretical studies point out that in the formation of benzene−halide complexes two minimum geometries are possible, both presenting hydrogen bond interactions in the benzene plane, due, in one case, to the interaction of the halide with a single C−H (linear adduct) and, in the other, to the simultaneous interaction of the halide with two adjacent C−H (bifurcated adduct). The most stable geometry depends on the considered halide. However, although for fluoride, bromide, and iodide ions the old theoretical and experimental data[25,26] qualitatively agree with the recent ones,[27] for the benzene−chloride complex the latest data[23,28,29] indicate the bifurcated complex as the most stable structure, in contrast with the conclusions of the first investigation.[26]

Because of the lack of accurate data for the whole family of benzene−halide adducts, and because the employed levels of theory for the few available theoretical values (although being of a fairly good quality) cannot represent reference values, we decided to undertake a series of high accuracy calculations so to obtain a complete basis set estimate of the strengths of the possible benzene−halide bond and to explore significant sections of the potential energy surfaces (PES). Thus the present study, on the one hand, aims to provide high quality benchmark theoretical data, particularly important because of the absence of recent accurate experimental determinations, and, on the other

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hand, intends to investigate in detail all possible interaction modes arising in these kinds of complexes.

Computational Details

All calculations were performed using MP2 and CCSD(T) levels of theory with Gaussian03[31] to obtain geometrical structures, vibrational frequencies, binding energies and enthalpies, and potential energy scans for the halide−benzene complexes. The basis set superposition error was evaluated following Boys−Bernardi counterpoise (CP) correction method,[32] and BSSE-corrected geometry optimizations were carried out employing the CP corrected PES approach[33] implemented in Gaussian03.

Augmented correlation consistent basis sets up to quadruple-ζ quality, aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ, were used for all atoms to extrapolate the complete basis set limit, with the exception of iodine for which the corresponding aug-cc-pVnZ-PP (n = D, T, Q) small-core relativistic pseudopotential correlation consistent basis sets were employed. In each case the geometry was optimized at MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels of theory on both the CP corrected and uncorrected potential energy surfaces, whereas energies at MP2/aug-cc-pVQZ level were calculated on the MP2/aug-cc-pVTZ optimized geometry. To evaluate CCSD(T) corrections, single point CCSD(T)/aug-cc-pVDZ energy calculations were carried out on the MP2/aug-cc-pVDZ optimized geometry. Harmonic frequencies were also calculated at the MP2/aug-cc-pVDZ level of theory to provide zero point energy and thermal corrections to the electronic energies.

For bromine and iodine correlation consistent basis sets were used according to their formulation, i.e., including only the outer s and p electrons in the active space for correlation treatment.[34,35] Due to technical limitations in the software, whose default excludes $(n-1)$d electrons in the definition of the frozen core, optimizations on the CP-corrected PES with the simultaneous use of a nondefault frozen core and pseudopotentials could not be performed. Thus, for benzene−I^- we calculated CP corrected minima geometries using the default Gaussian03 core. Energy values were then obtained for such geometries employing the correct frozen core. Tests performed on benzene−Br^-, where the use of all electron basis sets makes both approaches feasible, showed that differences in the corresponding geometries amount to less than 0.009 Å for distances and 0.04° for angles.

The binding energy corresponding to the MP2 complete basis set limit, $E_{\mathrm{CBS}}^{\mathrm{MP2}}$, was extrapolated by means of the mixed exponential/Gaussian function:[36]

$$E(n) = E_{\mathrm{CBS}} + B\exp[-(n-1)] + C\exp[-(n-1)^2] \quad (1)$$

where $n = 2$ (aug-cc-pVDZ), 3 (aug-cc-pVTZ), and 4 (aug-cc-pVQZ). This expression is reported to be slightly superior to other extrapolation formulas when correlation consistent basis set energies up to quadruple-ζ quality are available.[35,37,38]

The CCSD(T) complete basis set limit energy for the complexes, $E_{\mathrm{CBS}}^{\mathrm{CCSD(T)}}$, has then been estimated through the MP2 complete basis set limit, $E_{\mathrm{CBS}}^{\mathrm{MP2}}$, using the following expression:

$$E_{\mathrm{CBS}}^{\mathrm{CCSD(T)}} \approx E_{\mathrm{CBS}}^{\mathrm{MP2}} + \Delta\mathrm{CCSD(T)}$$

$$\Delta\mathrm{CCSD(T)} = E_{\text{aug-cc-pVDZ}}^{\mathrm{CCSD(T)}} - E_{\text{aug-cc-pVDZ}}^{\mathrm{MP2}} \quad (2)$$

where ΔCCSD(T) is the CCSD(T) correction to the MP2 energy calculated with the aug-cc-pVDZ basis set. Indeed, it has been noted that for many weakly bound complexes, for example, for benzene dimers[6] or when hydrogen bonds are involved,[39] the higher order correlation effects are quite insensitive to the size of the basis set (provided that a minimum size, with the inclusion of diffuse functions, is reached), thus allowing the correction calculated with a small basis set to be used for the infinite basis set limit.

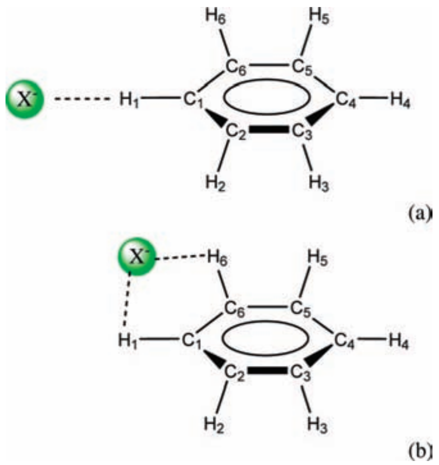

Figure 1. In-plane minimum geometries for benzene−halide complexes: (a) linear adduct, with the halide ion hydrogen bonded to one aromatic hydrogen; (b) bifurcated adduct, with the halide ion hydrogen bonded to two adjacent aromatic hydrogens.

We have also investigated the ability of basis sets of Pople-type to accurately reproduce the minimum geometry and energy: two basis sets of medium and large size, 6-311++G(d,p) and 6-311++G(3df,2pd) respectively, were employed, both at the MP2 level of theory. The first of these sets is widely used in quantum mechanical calculations, and the second was chosen so to have a basis set slightly smaller than aug-cc-pVTZ, yet with a large number of multiple polarization functions to allow a good description of electron correlation, particularly important for binding in these kinds of systems. The 6-311++G(3df,2pd) set, which proved to be a good compromise between quality of results and computational load (see the following), was also used to scan significant sections of the potential energy surface.

The basis sets employed in this work were all taken from Gaussian03 internal library, with the exception of the aug-cc-pVnZ-PP ECP and valence basis sets,[34] taken from the EMLS basis set library,[40] and the 6-311++G(3df,2pd) basis set, taken from ref 41 for iodine.

Results and Discussion

Geometries and Binding Energies. It is well-known that two different minimum geometries can be found in the complex formed between halide ions and benzene: a *linear* complex, with the halide ion lying in the benzene plane, interacting with one hydrogen (Figure 1a) and a *bifurcated* complex, with the halide again in the benzene plane, but interacting simultaneously with two hydrogens (Figure 1b). Both geometries present a C_{2v} symmetry. The relative strength of the two binding modes depends on the considered halide.

Tables 1 and 2 report the main geometrical parameters for the optimized structures of the linear and bifurcated geometries from fluoride to iodide complexes, obtained with the augmented correlation consistent basis sets of double- and triple-ζ quality and with Pople-type basis sets. In each case, we included values calculated both on the CP-corrected and on the uncorrected potential energy surfaces. Indeed, the problem of the evaluation of basis set error remains an open question for this kind of accurate calculation. It is known that, although uncorrected approaches lead to overbound complexes (large interaction

TABLE 1: Geometrical Parameters for $\mathrm{X^-{-}}$Benzene Linear Complexes (Distances in Å and Angles in Degrees)

method	no. of basis functions	CP-uncorrected PES[a]			CP-corrected PES[b]		
		$\mathrm{X^-{-}H_1}$	$\mathrm{C_1{-}H_1}$	$\mathrm{C_2\hat{C}_1C_6}$	$\mathrm{X^-{-}H_1}$	$\mathrm{C_1{-}H_1}$	$\mathrm{C_2\hat{C}_1C_6}$
		$\mathrm{F^-{-}}$Benzene					
MP2/aug-cc-pVDZ	215	1.6452	1.1340	117.28	1.6872	1.1305	117.47
MP2/aug-cc-pVTZ	460	1.6453	1.1229	117.55	1.6693	1.1213	117.57
MP2/6-311++G(d,p)	196	1.6676	1.1241	117.50	1.7552	1.1164	117.76
MP2/6-311++G(3df,2pd)	363	1.6177	1.1257	116.99	1.6785	1.1196	117.17
		$\mathrm{Cl^-{-}}$Benzene					
MP2/aug-cc-pVDZ	219	2.3879	1.1028	118.69	2.4528	1.1021	118.81
MP2/aug-cc-pVTZ	464	2.3537	1.0924	118.81	2.4000	1.0920	118.84
MP2/6-311++G(d,p)	204	2.4009	1.0939	118.73	2.5394	1.0923	118.05
MP2/6-311++G(3df,2pd)	371	2.3587	1.0913	118.45	2.4204	1.0905	118.48
		$\mathrm{Br^-{-}}$Benzene					
MP2/aug-cc-pVDZ	228	2.5656	1.1007	118.91	2.6653	1.0998	119.00
MP2/aug-cc-pVTZ	473	2.5491	1.0899	119.02	2.6146	1.0890	119.06
MP2/6-311++G(d,p)	222	2.6127	1.0916	118.96	2.7309	1.0914	119.08
MP2/6-311++G(3df,2pd)	389	2.5746	1.0879	118.66	2.6298	1.0882	118.70
		$\mathrm{I^-{-}}$Benzene					
MP2/aug-cc-pVDZ-PP	224	2.7946	1.0988	119.06	2.9437	1.0980	119.21
MP2/aug-cc-pVTZ-PP	469	2.7981	1.0879	119.22	2.8840	1.0870	119.26
MP2/6-311++G(d,p)	240	2.9107	1.0894	119.17	3.0343	1.0896	119.28
MP2/6-311++G(3df,2pd)	407	2.8299	1.0860	118.86	2.9281	1.0856	118.95

[a] Minima calculated on the potential energy surface with no BSSE corrections. [b] Minima calculated on the counterpoise corrected potential energy surface.

TABLE 2: Geometrical Parameters for $\mathrm{X^-{-}}$Benzene Bifurcated Complex (Distances in Å and Angles in Degrees)

method	CP-uncorrected PES[a]					CP-corrected PES[b]				
	$\mathrm{X^-{-}C_1}$	$\mathrm{X^-{-}H_1}$	$\mathrm{C_1{-}H_1}$	$\mathrm{C_1{-}C_6}$	$\mathrm{H_1\hat{C}_1C_6}$	$\mathrm{X^-{-}C_1}$	$\mathrm{X^-{-}H_1}$	$\mathrm{C_1{-}H_1}$	$\mathrm{C_1{-}C_6}$	$\mathrm{H_1\hat{C}_1C_6}$
						$\mathrm{F^-{-}}$Benzene				
MP2/aug-cc-pVDZ	2.8969	2.1535	1.0983	1.4106	114.69	2.9243	2.1807	1.0984	1.4106	114.90
MP2/aug-cc-pVTZ	2.8790	2.1427	1.0870	1.3968	114.74	2.8977	2.1595	1.0871	1.3970	114.77
MP2/6-311++G(d,p)	2.9276	2.1893	1.0899	1.4028	115.05	2.9917	2.2499	1.0897	1.4027	115.32
MP2/6-311++G(3df,2pd)	2.8591	2.1221	1.0870	1.3963	114.54	2.9071	2.1684	1.0868	1.3959	114.82
						$\mathrm{Cl^-{-}}$Benzene				
MP2/aug-cc-pVDZ	3.4932	2.7267	1.0957	1.4092	117.14	3.5540	2.7873	1.0957	1.4094	117.45
MP2/aug-cc-pVTZ	3.4516	2.6908	1.0846	1.3956	116.96	3.4716	2.7124	1.0845	1.3959	117.17
MP2/6-311++G(d,p)	3.5163	2.7531	1.0874	1.4012	117.22	3.6685	2.9009	1.0875	1.4014	117.71
MP2/6-311++G(3df,2pd)	3.4735	2.7172	1.0838	1.3950	117.35	3.5245	2.7647	1.0839	1.3955	117.40
						$\mathrm{Br^-{-}}$Benzene				
MP2/aug-cc-pVDZ	3.6651	2.8901	1.0954	1.4091	117.46	3.7536	2.9777	1.0955	1.4091	117.83
MP2/aug-cc-pVTZ	3.6333	2.8650	1.0842	1.3953	117.40	3.6915	2.9228	1.0841	1.3954	117.66
MP2/6-311++G**	3.7143	2.9437	1.0873	1.4010	117.72	3.8394	3.0641	1.0874	1.4012	117.99
MP2/6-311++G(3df,2pd)	3.6720	2.9073	1.0834	1.3946	117.81	3.7215	2.9529	1.0836	1.3948	117.79
						$\mathrm{I^-{-}}$Benzene				
MP2/aug-cc-pVDZ-PP	3.8972	3.1103	1.0952	1.4089	117.74	4.0279	3.2405	1.0952	1.4089	118.24
MP2/aug-cc-pVTZ-PP	3.8743	3.0958	1.0840	1.3950	117.82	3.9475	3.1688	1.0838	1.3951	118.11
MP2/6-311++G(d,p)	3.9942	3.2128	1.0871	1.4007	118.22	4.1230	3.3365	1.0872	1.4010	118.38
MP2/6-311++G(3df,2pd)	3.9014	3.1276	1.0830	1.3942	118.22	3.9976	3.2180	1.0833	1.3945	118.23

[a] Minima calculated on the potential energy surface with no BSSE corrections. [b] Minima calculated on the counterpoise corrected potential energy surface.

energies and short interaction distances), CP correction techniques tend to overcorrect energy values. The debate over the extent of these effects and whether it is worth applying CP corrections to BSSE is still quite heated.[42] In any case, because BSSE corrections to the whole potential energy surface have important consequences on the minima position and on its topology,[43] BSSE corrections calculated on the uncorrected potential energy surface minima should be avoided: they are, in fact, too large and lead to too weak interaction energies. Moreover, the inclusion of BSSE corrections during optimization seems to be very important when hydrogen bonds[44] or anion−π interactions[45] are involved. We have thus calculated minima on both surfaces, so that the range of the corresponding values can serve as an indication of the uncertainty related to the two approaches.

For all complexes, as mentioned above, the relevant distances involved in the interaction of the two fragments are always correspondingly larger on the CP-corrected PES, the differences becoming more conspicuous for heavier halides (at most 0.08 Å for F^- to about 0.24 Å for I^-). As expected, due to the nature of BSSE, differences within each set (Pople's and Dunning's correlation consistent) become less marked as the size of the basis set increases.

As far as the linear halide−benzene complexes are concerned, the interaction distance between the halide ion and the hydrogen becomes larger as the halide becomes heavier. The benzene, in all these complexes, shows a distortion from the original geometry, connected to the strength of the binding, which is more significant for lighter halides: C_1-H_1 bond length tends to become longer and the $C_2-C_1-C_6$ angle is smaller than 120°. The same behavior is found in bifurcated complexes, which present a lengthening of the X^--H distances as the halide becomes heavier and also show a significant deviation of the $H_1-C_1-C_6$ angle from 120°. Deviations in the C_1-H_1 bond lengths are instead less marked. It can be noted that, although the differences between the values of the geometrical parameters calculated with various basis sets onto each of the two surfaces can be rather large and do not generally follow a specific pattern, they become much smaller for the values calculated with the two largest sets of each kind: less than 0.05 Å for X^--H_1 distances and less than 0.4° for benzene angles. Differences are generally smaller for minima calculated on the CP-corrected PES.

Furthermore, in many cases the values obtained with the smallest basis set (6-311++G(d,p)) calculated on the uncorrected PES are quite close to those calculated with the aug-cc-pVTZ set on the CP-corrected PES. This issue, which has been noted to often occur, is not due to a better performance of the uncorrected approaches, as misleadingly suggested in some cases, but rather to a fortuitous cancelation of error between BSSE and basis set incompleteness error, as pointed out by some recent studies.[44,46,47]

In Tables 3 and 4 we have reported the electronic binding energies, ΔE, of the linear and bifurcated complexes, respectively, calculated on both the uncorrected and the CP-corrected PES. For the minima obtained with the uncorrected approach we added in parentheses the corresponding basis set superposition error calculated by the counterpoise technique. These values, when summed to the uncorrected ΔE results, indeed lead to binding energies weaker than the CP-corrected ones, as mentioned before. The importance of BSSE corrections grows with the mass of the halide. This is related to the minimum geometry of the complexes: the distance of the ion from the benzene ring is larger for heavier halides, thus resulting in more significant BSSE corrections. When basis sets of similar size are compared, BSSE corrections calculated with correlation consistent basis sets, specifically designed to systematically converge to the complete basis set limit, present a basis set superposition error always smaller than Pople's type basis functions.

The MP2/CBS energies calculated by eq 1 and the CCSD(T)/CBS energies calculated with eq 2 are also reported in the tables. To further investigate the effect of the CP corrections to BSSE, we have evaluated the CBS limit for both the CP corrected and uncorrected energies, calculated on the corresponding potential energy surfaces. Indeed, for the reasons underlined above, as the basis set size increases, the two values should approach the correct CBS limit from above (CP corrected values) and from below (uncorrected values). The interval between the two values thus represents the range of reliability of the method and the related uncertainty.

Figure 2 displays the convergence of the uncorrected/CP-corrected approaches to the MP2/CBS limit. A few noteworthy points emerge from the analysis of this figure: as expected the two approaches converge to the CBS limit respectively from below and from above. The convergence is smooth with both approaches; however, the curve corresponding to minima calculated on the CP-corrected surface is always less steep than that obtained on the uncorrected surface (i.e., differences between the energy values obtained with the smallest basis set of the series and the CBS limit are smaller). The uncertainty related to the use of the two procedures is, in any case, very small (less than 0.40 kcal/mol), showing that both methods lead to satisfactory results.

TABLE 3: Binding Energies (kcal/mol) of X^-−Benzene Linear Complexes

method	CP-uncorrected PE[a] ΔE[c]	CP-corrected PES[b] ΔE^{CP}
	X = F	
MP2/aug-cc-pVDZ	−15.42 (1.52)	−13.93
MP2/aug-cc-pVTZ	−15.05 (0.98)	−14.09
MP2/aug-cc-pVQZ[d]	−14.90 (0.59)	−14.32
MP2/CBS	−14.83	−14.47
CCSD(T)/CBS	−15.36	−15.00
MP2/6-311++G(d,p)	−14.87 (2.85)	−12.16
MP2/6-311++G(3df,2pd)	−16.51 (2.51)	−14.07
	X = Cl	
MP2/aug-cc-pVDZ	−8.77 (1.35)	−7.46
MP2/aug-cc-pVTZ	−8.62 (0.84)	−7.80
MP2/aug-cc-pVQZ[d]	−8.37 (0.42)	−7.93
MP2/CBS	−8.21	−8.01
CCSD(T)/CBS	−8.17	−7.97
MP2/6-311++G(d,p)	−9.33 (3.30)	−6.22
MP2/6-311++G(3df,2pd)	−8.46 (1.05)	−7.44
	X = Br	
MP2/aug-cc-pVDZ	−8.02 (1.68)	−6.43
MP2/aug-cc-pVTZ	−7.51 (0.85)	−6.70
MP2/aug-cc-pVQZ[d]	−7.23 (0.43)	−6.82
MP2/CBS	−7.06	−6.90
CCSD(T)/CBS	−7.08	−6.92
MP2/6-311++G(d,p)	−8.00 (2.57)	−5.53
MP2/6-311++G(3df,2pd)	−7.03 (0.66)	−6.40
	X = I	
MP2/aug-cc-pVDZ-PP	−6.89 (1.72)	−5.33
MP2/aug-cc-pVTZ-PP	−6.41 (0.92)	−5.53
MP2/aug-cc-pVQZ-PP[d]	−6.06 (0.43)	−5.68
MP2/CBS	−5.84	−5.78
CCSD(T)/CBS	−5.73	−5.67
MP2/6-311++G(d,p)	−6.63 (2.09)	−4.63
MP2/6-311++G(3df,2pd)	−6.49 (1.24)	−5.34

[a] Minima calculated on the potential energy surface with no BSSE corrections. [b] Minima calculated on the counterpoise corrected potential energy surface. [c] The counterpoise correction calculated for the minimum structure on the uncorrected surface is reported in parentheses. Adding this value to ΔE leads to weaker binding than ΔE^{CP}. [d] MP2/aug-cc-pVQZ//MP2/aug-cc-pVTZ.

At any level of theory the linear complex is more stable for fluoride, whereas for chloride, bromide, and iodide the bifurcated complex corresponds to the lowest minimum, in agreement with ref 27 although the energy differences between the two geometries only amount to ca. 0.5 kcal/mol. For benzene−chloride this result supports the recent theoretical and experimental data,[27−29] against the conclusion of ref 26 - mainly based on small 3-21G basis calculations, which gave the linear complex as the most stable structure.

A comparison of the CCSD(T)/CBS energies and enthalpies with the very limited experimental data and previous theoretical works on these complexes is given in Table 5. The agreement between the only experimental enthalpy value of refs 25 and 26 for benzene−F^- and benzene−I^- is excellent. Benzene−Cl^- is the only system for which, along with the HPMS enthalpy value of Hiraoka et al.,[26] there is a more recent experimental dissociation energy estimate obtained by photoelectron and photodetachment spectra.[29] The latter work gives an upper limit

TABLE 4: Binding Energies (kcal/mol) of X^-−Benzene Bifurcated Complexes

method	CP-uncorrected PES[a] ΔE[c]	CP-corrected PES[b] ΔE^{CP}
	X = F	
MP2/aug-cc-pVDZ	−13.51 (1.21)	−12.32
MP2/aug-cc-pVTZ	−13.40 (0.82)	−12.59
MP2/aug-cc-pVQZ[d]	−13.22 (0.46)	−12.76
MP2/CBS	−13.10	−12.87
CCSD(T)/CBS	−13.71	−13.48
MP2/6-311++G(d,p)	−13.12 (2.50)	−10.68
MP2/6-311++G(3df,2pd)	−14.63 (2.20)	−12.48
	X = Cl	
MP2/aug-cc-pVDZ	−9.17 (1.34)	−7.90
MP2/aug-cc-pVTZ	−9.05 (0.79)	−8.27
MP2/aug-cc-pVQZ[d]	−8.84 (0.40)	−8.44
MP2/CBS	−8.70	−8.54
CCSD(T)/CBS	−8.58	−8.42
MP2/6-311++G(d,p)	−9.31 (3.18)	−6.34
MP2/6-311++G(3df,2pd)	−8.91 (1.12)	−7.82
	X = Br	
MP2/aug-cc-pVDZ	−8.55 (1.67)	−6.95
MP2/aug-cc-pVTZ	−8.06 (0.82)	−7.27
MP2/aug-cc-pVQZ[d]	−7.81 (0.40)	−7.43
MP2/CBS	−7.66	−7.53
CCSD(T)/CBS	−7.55	−7.42
MP2/6-311++G(d,p)	−8.21 (2.58)	−5.75
MP2/6-311++G(3df,2pd)	−7.57 (0.71)	−6.88
	X = I	
MP2/aug-cc-pVDZ-PP	−7.42 (1.70)	−5.85
MP2/aug-cc-pVTZ-PP	−7.02 (0.92)	−6.16
MP2/aug-cc-pVQZ-PP[d]	−6.70 (0.42)	−6.30
MP2/CBS	−6.50	−6.38
CCSD(T)/CBS	−6.47	−6.35
MP2/6-311++G(d,p)	−7.05 (2.19)	−4.95
MP2/6-311++G(3df,2pd)	−7.30 (1.49)	−5.87

[a] Minima calculated on the potential energy surface with no BSSE corrections. [b] Minima calculated on the counterpoise corrected potential energy surface. [c] The counterpoise correction calculated for the minimum structure on the uncorrected surface is reported in parentheses. Adding this value to ΔE leads to weaker binding than ΔE^{CP}. [d] MP2/aug-cc-pVQZ//MP2/aug-cc-pVTZ.

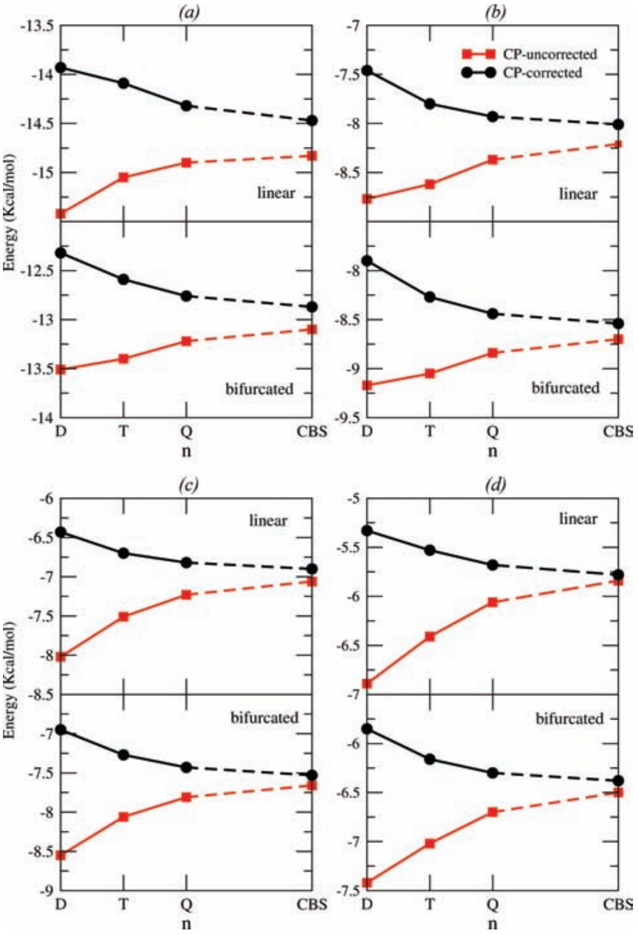

Figure 2. ΔE values calculated at MP2/aug-cc-pVnZ level (n = D, T and Q) and their corresponding CBS limit, obtained with eq 1 for the whole family of benzene−halide complexes: (a) fluoride, (b) chloride, (c) bromide, and (d) iodide, both for linear (upper part) and for bifurcated (lower part) adducts. The energy values and their convergence to the CBS limit were calculated on the CP corrected (full circles) and on the uncorrected (full squares) potential energy surfaces. The difference in the corresponding CBS values can be taken as an estimate of the uncertainty of the approach.

for D_0 of 8.1 kcal/mol against a HPMS value of 9.5 kcal/mol. Our CCSD(T)/CBS result, 8.3 kcal/mol, lies in between the two experimental data, very close to the more recent limit obtained in ref 29. For benzene−Br^- the difference with the binding enthalpy of ref 26 amounts to ca. 1.5 kcal/mol, with the calculated value smaller than the experimental one. However, the latter value (9.0 kcal/mol) is the least homogeneous in the set of HPMS data, being only 0.4 kcal/mol weaker than bonding in benzene−Cl^- and nearly 3 kcal/mol stronger than in benzene−I^-. This, also in the light of the more recent photodetachment data for benzene−Cl^-, would suggest that the experimental estimate in this case gives too strong binding energies.

The energies and enthalpies of ref 27 obtained with a lower level of theory and smaller basis sets are all smaller than the CCSD(T)/CBS values, the discrepancy being larger for heavier halides, consistent with the growing importance of the basis set size with the mass of the halide for a correct description of the binding, as pointed out above.

The binding data obtained in the present work show that noncovalent bonding between aromatic hydrogens and halide anions cannot be described as a weak hydrogen bond. Indeed, according to the classification of ref 48 the strength of the hydrogen bond in benzene−fluoride is between a moderate and a strong interaction, whereas the hydrogen bond for all the other complexes should be considered moderately strong.

This also explains why the benzene−fluoride adduct is the only complex for which the linear geometry—with a single, rather strong, hydrogen bond—corresponds to the lowest minimum, whereas in all the other complexes two moderate hydrogen bonds work cooperatively to give the most stable configuration.

Potential Energy Curves. To further investigate bonding in halide−benzene systems, we calculated potential energy curves at a few significant selected geometries for the whole family of the considered halides.

The results of the preceding section have shown that the MP2/6-311++G(3df,2pd) level of theory, with the inclusion of counterpoise BSSE corrections, is able to quite accurately reproduce the experimental data, yet remaining manageable in size and, as a consequence, in computational load. Potential energy scans at this level of theory were thus performed by initially optimizing the geometry of benzene assuming a D_{6h} symmetry. The center of mass of the optimized structure was then taken as the center of a polar coordinate system placing the halide anion at given radius R and polar angles θ and ϕ (see Figure 3).

TABLE 5: Binding Energies and Enthalpies (kcal/mol) for X^-−Benzene Complexes

geometry	method	ΔE^{CP}	ΔH_0	ΔH_{298}	ref
		X = F			
linear	CCSD(T)/CBS	−15.0	−15.2	−15.3	this work
bifurcated	CCSD(T)/CBS	−13.5	−13.8	−14.4	this work
expt	HPMS			−15.3	25
		X = Cl			
linear	CCSD(T)/CBS	−8.0	−7.9	−7.7	this work
linear	MP2/aug-cc-pVDZ	−7.4	−7.3	−7.2	27
linear	MP2/SDD	−6.7	−7.4	−7.3	27
bifurcated	CCSD(T)/CBS	−8.4	−8.3	−8.3	this work
bifurcated	MP2/aug-cc-pVDZ	−7.9	−7.9	−7.9	27
bifurcated	MP2/SDD	−7.0	−7.4	−7.2	27
expt	HPMS			−9.4	26
expt	Photoelectron Spectrum		−8.1		29
		X = Br			
linear	CCSD(T)/CBS	−6.9	−6.7	−7.2	this work
linear	MP2/SDD	−6.3	−6.3	−6.2	27
bifurcated	CCSD(T)/CBS	−7.4	−7.3	−7.3	this work
bifurcated	MP2/SDD	−6.6	−6.6	−6.2	27
expt	HPMS			−9.0	26
		X = I			
linear	CCSD(T)/CBS	−5.7	−5.4	−5.9	this work
linear	MP2/SDD	−4.7	−4.7	−4.5	27
bifurcated	CCSD(T)/CBS	−6.3	−6.1	−6.1	this work
bifurcated	MP2/SDD	−5.3	−5.3	−5.1	27
expt	HPMS			−6.1	26

Figures 4−7 show the intermolecular potential as a function of R or of the angle θ under four significant conditions: when the halide anion approaches in the benzene plane along the C−H bond direction (panel *a*, $\theta = 90°$ and $\phi = 0°$), toward the center of the C−C bond (panel *b*, $\theta = 90°$ and $\phi = 30°$), along the benzene symmetry axis (panel *c*, $\theta = 0°$), at a fixed R value as a function of θ at $\phi = 0°$ or 30°, according to the most stable geometry of the complex (panel *d*).

The qualitative behavior of all systems is very similar; nonetheless they present interesting features, some of which have already emerged from the analysis of the minimum structures, smoothly varying with the mass of the halide. The depth of both minima (panels a and b) decreases as the halide becomes heavier; however, their relative size gradually changes from F^- to I^-: for benzene−F^- the linear complex corresponds to the most stable configuration; for benzene−Cl^- the two minima are very similar in size, with only a slight preference for the bifurcated over the linear complex. This preference becomes more marked for benzene−Br^- and for benzene−I^-. In all cases (Figures 4−7), the minimum depicted in panel *b*, corresponding to the halide approaching toward the C−C bond, is wider than that corresponding to the halide approaching toward the C−H bond (panel *a*), probably due to the large repulsion exerted by the short-range interaction between the hydrogen and the halide atoms, stronger in the linear interaction mode.

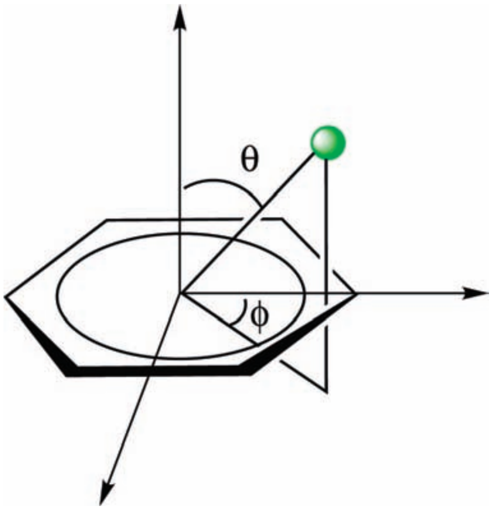

Figure 3. Polar coordinates R, θ, ϕ, defining the halide ion orientation with respect to the center of the benzene ring.

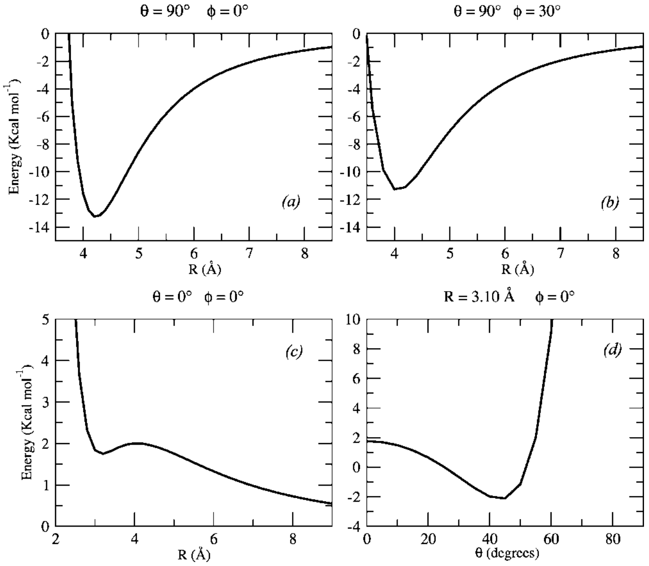

Figure 4. Potential energy curves at selected geometries for F^-−benzene.

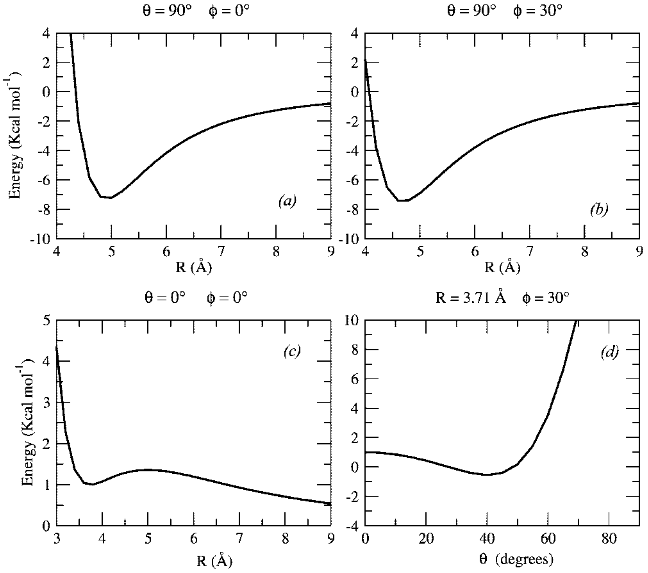

Figure 5. Potential energy curves at selected geometries for Cl^-−benzene.

Panel c, corresponding to the halide approaching along the D_{6h} symmetry axis of benzene, shows a peculiar behavior, again shared by all systems: it is expected that along this axis the potential energy curve is repulsive (i.e., with interaction energy ΔE always positive); however, our calculations highlight the presence of a small metastable minimum, with an interaction energy between 0 and 2 kcal/mol, according to the system, and a depth less than 1 kcal/mol. To shed some light on the nature of this minimum, we performed a series of optimizations, with the inclusion of CP corrections to BSSE, at the same levels of theory we used to characterize the linear and bifurcated

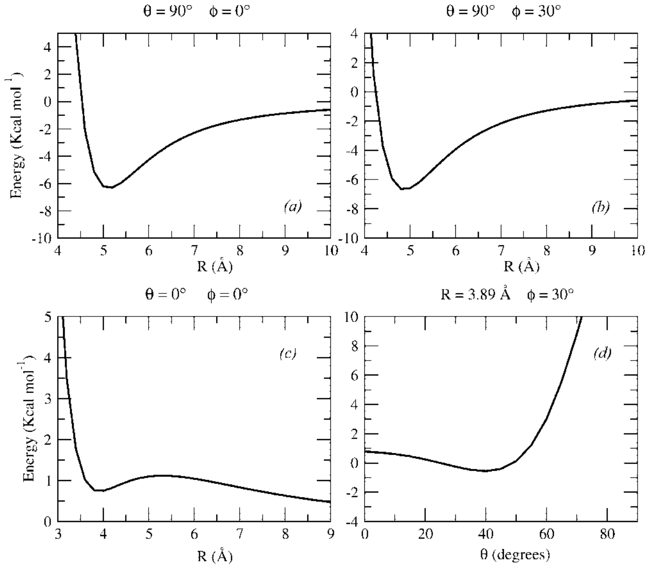

Figure 6. Potential energy curves at selected geometries for Br$^-$−benzene.

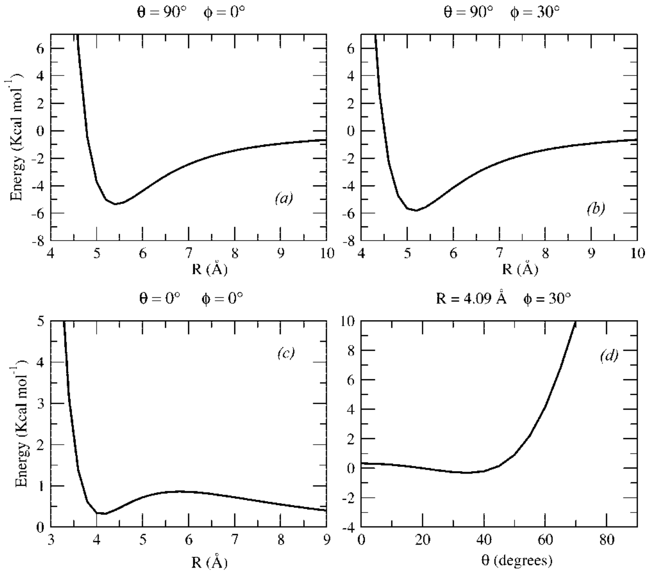

Figure 7. Potential energy curves at selected geometries for I$^-$−benzene.

minimum geometries and, because of the sensitivity of the results to the basis set size, frequency calculations also at the larger MP2/aug-cc-pVTZ level, and not only at the MP2/aug-cc-pVDZ level.

TABLE 6: Binding Energies and Enthalpies (kcal/mol) and R_{Bz-X^-} Distance (Å) for Benzene−X$^-$ Minima in C_{6v} Symmetry

method	R_{Bz-X^-}	ΔE^{CP}	ΔH_0	ΔH_{298}
	X = F			
MP2/aug-cc-pVDZ	3.27	1.72	1.33	0.42
MP2/aug-cc-pVTZ	3.22	1.03	0.64	−0.27
MP2/aug-cc-pVQZ[a]	3.22	0.94	0.55	−0.36
CBS		0.90	0.51	−0.40
CCSD(T)/CBS		0.52	0.13	−0.78
MP2/6-311++G(3df,2pd)	3.11	1.53		
	X = Cl			
MP2/aug-cc-pVDZ	3.81	1.01	0.61	−0.26
MP2/aug-cc-pVTZ	3.67	0.36	−0.04	−0.95
MP2/aug-cc-pVQZ[a]	3.67	0.24	−0.16	−1.03
CBS		0.18	−0.22	−1.09
CCSD(T)/CBS		0.59	0.19	−0.68
MP2/6-311++G(3df,2pd)	3.71	0.81		
	X = Br			
MP2/aug-cc-pVDZ	4.00	0.84	0.40	−0.46
MP2/aug-cc-pVTZ	3.83	0.19	−0.25	−1.11
MP2/aug-cc-pVQZ[a]	3.83	0.06	−0.38	−1.25
CBS		−0.01	−0.45	−1.32
CCSD(T)/CBS		0.48	0.04	−0.83
MP2/6-311++G(3df,2pd)	3.89	0.63		
	X = I			
MP2/aug-cc-pVDZ-PP	4.26	0.59	0.20	−0.66
MP2/aug-cc-pVTZ-PP	4.03	−0.04	−0.43	−1.29
MP2/aug-cc-pVQZ-PP[a]	4.03	−0.19	−0.58	−1.44
CBS		−0.27	−1.66	−1.52
CCSD(T)/CBS		0.22	−0.17	−1.03
MP2/6-311++G(3df,2pd)	4.09	0.27		

[a] MP2/aug-cc-pVQZ//MP2/aug-cc-pVTZ.

The distance R_{Bz-X^-} between the halide ion and the ring center, together with the energy and enthalpy values corresponding to such minima, are summarized in Table 6, and the corresponding Cartesian coordinates are given in the Supporting Information. The examination of the resulting geometries shows that in all complexes there is a deformation of the benzene ring, with the plane of hydrogen atoms closer to the halide anion by ca. 0.04 Å with respect to the plane of carbon atoms, so to maximize the interaction with the partially positively charged atoms and to minimize repulsion with the π electron cloud. As expected, the distance between the halide anion and the ring center increases with the mass of the halide. The binding energy ΔE^{CP} of the minima lowers upon optimization with the size of the basis set, becoming negative for Br$^-$ and I$^-$ (CBS energies −0.01 and −0.27 kcal/mol, respectively). The inclusion of corrections for CCSD(T) effect tends to level the results to a binding energy of ca. 0.5 kcal/mol for all systems, whereas ZPE and thermal corrections lead to negative ΔH_{298} values of approximately −1 kcal/mol.

The examination of the results of the frequency calculations becomes thus crucial to disentangle the nature of such minima. Indeed for all complexes two degenerate small negative frequency values are found with both MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ, corresponding to two mutually perpendicular rocking motions of the benzene molecule on the halide (−63 cm^{-1} for F$^-$, −41 cm^{-1} for Cl$^-$, −32 cm^{-1} for Br$^-$, and −25 cm^{-1} for I$^-$ at the MP2/aug-cc-pVTZ level), indicating that these points are minima only within the constraint of C_{6v} symmetry. Such small frequency values, however, indicate that the potential energy surface around these points is almost flat. This is confirmed by panel d (Figures 4−7), which reports the variation of the interaction energy between benzene and the halide anion as a function of θ at a fixed R value chosen so to correspond to the C_{6v} minima and shows that for small deviations of the angle θ from the starting value of 0° there is very little variation of the energy; only at larger angles is there a sensible decrease in the interaction energy, which then grows much larger when the distance between the halide ion and the carbon and hydrogen atoms becomes too small.

Conclusions

In the present study, we carried out high level ab initio calculations on the binding of halide ions (F$^-$, Cl$^-$, Br$^-$, I$^-$) to benzene. The complete basis set limit interaction energy was explored, using augmented correlation consistent basis sets from double to quadruple-ζ quality, together with the performance of two basis sets of Pople type of different size. The effect of the inclusion of counterpoise corrections to the basis set superposition error on the convergence and accuracy of the results was also investigated. Optimization on the CP-corrected and uncorrected potential energy surface using correlation consistent basis sets leads to CBS limits differing by 0.36 kcal/mol at most. Convergence on the CP-corrected energy surface is only slighlty smoother than on the uncorrected one.

Because of the scarceness of recent experimental and/or high level theoretical data for these complexes (excepting benzene–chloride), we have calculated energies and enthalpies for the in-plane minimum geometries, corresponding to the halide single or double hydrogen bonded to the aromatic hydrogens. For benzene–fluoride the interaction is fairly strong, leading to the linear single bonded geometry as the most stable structure ($\Delta H_{298} = -15.3$ kcal/mol), whereas for chloride, bromide, and iodide adducts the simultaneous interaction of the halide ion with two adjacent aromatic hydrogens results in a more stable bifurcated complex of moderate strength (with ΔH_{298} values ranging from -8.3 to -6.1 kcal/mol). The magnitude of these interactions (in particular those involving fluoride and chloride) suggests that they can indeed significantly contribute to the overall binding in complex systems and in recognition processes, thus playing an important role in biological environments.

We have then investigated the topology of these minima and of other selected sections of the potential energy surface, so to gain further insight on the nature of the halide–benzene interaction. In particular, the geometry corresponding to the C_{6v} symmetry, i.e., the halide approaching the center of the benzene ring, although being overall repulsive, has displayed the unprecedented presence of a small flex (a minimum in C_{6v} symmetry) with interaction energy close to zero or slightly attractive.

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Supporting Information Available: Cartesian coordinates of the optimized geometries (MP2/aug-cc-pVTZ) of benzene–halide complexes in C_{6v} symmetry. This material is available free of charge via the Internet at http://pubs.acs.org.

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