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Theoretical Studies of the Structure of the Benzene–Hydrogen Fluoride Complex

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Abstract: We present ab initio quantum-chemical calculations including correlation effects via second-order Møller–Plesset perturbation theory, on the benzene–hydrogen fluoride complex. We describe our results for a number of complex structures. These include symmetric and nonsymmetric configurations in which benzene acts as proton acceptor as well as a coplanar configuration where hydrogen fluoride is the proton acceptor. Calculations are also reported on the interaction of benzene with an extended dipole mimicking the hydrogen fluoride molecule, in order to assess roughly the relative importance of the contributions to the binding energy due, on one hand, to purely electrostatic interactions and, on the other hand, to hydrogen bond formation.

I. Introduction

Since the fifties, many efforts have been devoted to investigating the structure of small molecular clusters. In particular, a number of studies have dealt with complexes that benzene or other π-electron-containing compounds form with small molecules such as halogens,[1-3] halogen halides,[4-11] alkanes,[12,13] water,[14-17] ammonia,[15] hydrogen cyanide,[18-20] or rare gas atoms.[21,22] In recent years, advanced experimental techniques (for instance, infrared spectroscopy of a complex frozen in a solid matrix, microwave molecular beam electric resonance, photoionization time-of-flight mass spectroscopy) have allowed for accurate characterization of the structure of such complexes.

In the early eighties, Flygare and co-workers have used microwave molecular beam techniques to examine the structure of complexes of hydrogen fluoride with acetylene and ethylene.[9,11] In both cases, these authors concluded that the geometric structure of the cluster is T-shaped with the hydrogen fluoride molecular axis pointing toward the midpoint of the carbon–carbon bond. The bonding arises from interaction between the acidic proton with the π-system of the hydrocarbon, a type of interaction that has long been noted.[23] The experimentally derived structures of those two complexes are fully consistent with the results of ab initio calculations including correlation effects, reported by Pople and co-workers.[24,25]

More recently, Baiocchi et al.[6] and Andrews et al.[7] have probed the structure of the benzene–hydrogen fluoride complex, using molecular beam electric resonance and infrared spectroscopy, respectively. Theoretical predictions for the structure of the complex were conflicting. Semiempirical CNDO (complete neglect of differential overlap) calculations lead to an asymmetric structure in which the hydrogen fluoride molecule points at a carbon–carbon bond.[26,27] A simple HOMO–LUMO model also results in the prediction of a nonsymmetric structure, since the symmetries of the benzene HOMO and the hydrogen fluoride LUMO do not favor C_{6v} geometry.[6] However, analysis of the electrostatic potential map of benzene, as obtained from an Hartree–Fock ab initio minimal basis set calculation,[28] indicates that the most favored position for interaction with a positive charge is along the benzene C_6 axis, thus suggesting a symmetric structure for the complex. A similar conclusion is reached by recent Hartree–Fock ab initio extended basis set calculations.[29] Experimental evidence gathered by the works of Baiocchi et al.[6] and Andrews et al.[7] also points to the presence of a C_{6v} equilibrium structure for the benzene–hydrogen fluoride complex.

In this paper, we present results of calculations performed at the ab initio level, going beyond Hartree–Fock by including correlation effects via Møller–Plesset second-order perturbation theory and using extended basis sets with polarization functions on the carbon and fluorine atoms. Our aim is threefold. We would like (i) to check on the ability of our theoretical approach to describe adequately the structure of the benzene–hydrogen fluoride complex; (ii) to investigate the nature of the bonding between the aromatic system and the Lewis acid, an important aspect with respect to chemical reactivity since the attack of a π-system by an electrophilic reagent is a familiar first step in a number of organic reaction mechanisms (we look especially for distinguishing between the contributions of (induced)dipole–(permanent)dipole interactions and hydrogen bond formation); (iii) to estimate the amount of energy required for the hydrogen fluoride molecule to travel on top of the aromatic system. More generally, these studies

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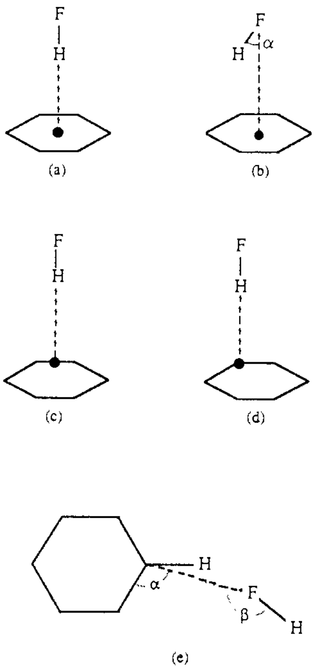

Figure 1. Sketches of the benzene–hydrogen fluoride cluster configurations investigated in this work: (a) C_{6v} configuration, (b–d) nontotally symmetric configurations with the hydrogen fluoride molecule perpendicular to the plane of benzene; (b) fluorine on the C_6 axis with the acid hydrogen pointing toward a benzene carbon–carbon bond; (c) hydrogen fluoride on top of the midpoint of a benzene carbon–carbon bond; (d) hydrogen fluoride on top of a benzene carbon atom; (e) coplanar configuration.

are connected to our general interest in the nature of the interaction between molecular systems and unsaturated carbon surfaces.

Our methodology is described in section II. Results are presented and discussed in section III, first for the individual molecules, then for a totally symmetric configuration of the complex, and finally for less symmetric configurations. Conclusions of our work are given in the last section.

II. Methodology

All the calculations reported in this work have been carried out with the Gaussian-86 IBM/MVS set of programs,[30] as implemented at the IBM Almaden Research Center. We have followed the same basic approach as that successfully used by Pople and co-workers in their studies of the ethylene–hydrogen fluoride and acetylene–hydrogen fluoride complexes.[24,25]

Geometry optimizations are performed on the individual molecules at the Hartree–Fock ab initio level with a split-valence 3-21G basis set.[31] In most of the cases, the molecular geometries are kept frozen in the cluster calculations, where only the intermolecular geometry parameters are fully optimized. This procedure is justified by the fact that the molecular 3-21G bond lengths in ethylene–hydrogen fluoride and acetylene–hydrogen fluoride differ by at most 0.005 Å from their values in the isolated molecules.[24] However, since the C–C–H angle in the acetylene molecule reduces to 179.0° in the cluster, due to the hydrogens moving away from the hydrogen fluoride molecule,[24] we have checked on the possible appearance of a similar phenomenon in the benzene-hydrogen fluoride cluster but did not find any evidence for it.

To make better estimates of complex binding energies, single-point calculations taking account of electron correlation are carried out at the optimized Hartree–Fock 3-21G geometries. These use the 6-31G* basis set (which includes 6 d-polarization functions on all carbon and fluorine atoms but no polarization functions on the hydrogen atoms)[32] and second-order Møller–Plesset theory with single and double substitutions from the Hartree–Fock reference.[33] Such a procedure is usually denoted MP2/6-31G*//Hartree–Fock/3-21G where "//" means "at the geometry of". (We note that each of these single-point calculations requires over 2 h and 30 min of CPU time on an IBM 3081 computer, which explains that it is not possible to go beyond second-order Møller–Plesset perturbation theory in the case of the benzene–hydrogen fluoride complex.) It is important to point out that Pople et al. have examined the influence on the results of also considering polarization functions on the hydrogen atoms (6-31G** basis set).[24] They have found that such an extension of the basis set does not change the complex binding energy in any significant way with respect to the use of the 6-31G* basis set.

Table I. Some of the Molecular Properties of Benzene (D_{6h} Symmetry) and Hydrogen Fluoride as Calculated at the Hartree–Fock 3-21G//3-21G and 6-31G*//3-21G Levels and MP2/6-31G*//Hartree–Fock/3-21G Level

	3-21G//3-21G	6-31G*//3-21G	MP2/ 6-31G*//3-21G
	Benzene		
total energy (au)	−229.41915	−230.70307	−231.45590
r(C–C) (Å)	1.3846		
r(C–H) (Å)	1.0721		
	Hydrogen Fluoride		
total energy (au)	−99.46022	−100.00210	−100.18216
r(F–H) (Å)	0.9374		
dipole moment (D)	2.174	2.019	

We have considered various configurations of the benzene–hydrogen fluoride cluster (see Figure 1): (i) a symmetric configuration where the hydrogen fluoride molecule lies along the C_6 symmetry axis of benzene (Figure 1a) (cases where the acid hydrogen or the fluorine atom points toward benzene have both been investigated); (ii) a situation where the acid hydrogen moves away from the C_6 axis while the fluorine remains on it (Figure 1b) (such a configuration was also proposed by Baiocchi et al.[6]); (iii) configurations where the hydrogen fluoride molecule is perpendicular to the benzene molecular plane and is located on top either of a carbon atom (Figure 1c) or of the midpoint of a carbon–carbon bond (Figure 1d); (iv) a situation where the acid molecule lies in the plane of benzene (Figure 1e). In their earlier work, Sapse and Jain[29] have performed Hartree–Fock 6-31G* calculations on some of these configurations.

In order to ascertain the relative importance of the induced dipole–permanent dipole interactions in the formation of the benzene–hydrogen fluoride cluster, we have carried out a series of calculations at the 3-21G level. In these calculations, two point charges are used to simulate an extended dipole mimicking the hydrogen fluoride molecule and put in presence of benzene in the C_{6v} symmetric configuration.

III. Results and Discussion

(A) Individual Molecules. Results obtained at Hartree–Fock 3-21G and 6-31G*//3-21G levels and MP2/6-31G*//Hartree–Fock/3-21G level are collected for both benzene and hydrogen fluoride in Table I. In the case of benzene, the 3-21G carbon–carbon and carbon–hydrogen bond lengths are optimized to be slightly too short: 1.385 and 1.072 Å, respectively, to be compared with experimental values of 1.397 and 1.084 Å.[34] For hydrogen fluoride, the tendency is reversed since the hydrogen–fluorine bond is calculated to be 0.937 Å, that is about 0.02 Å longer than the experimental value.[35] The experimental dipole moment in hydrogen fluoride is 1.82 D.[36] The Hartree–Fock calculated values are about 20 and 10% larger at the 3-21G//3-21G and 6-31G*//3-21G levels, respectively. These trends are fully in the line of what is generally obtained with such types of calculations.[31]

(B) Cluster Fully Symmetric Configuration. We have first considered a cluster configuration in which the hydrogen fluoride molecule lies along the C_6 symmetry axis of benzene, the acid hydrogen pointing toward the aromatic moecule. As will be

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Table II. Some of the Molecular Properties of the Benzene–Hydrogen Fluoride Complex, as Calculated at the Hartree–Fock 3-21G//3-21G and 6-31G*//3-21G Levels and MP2/6-31G*//Hartree–Fock/3-21G Level for Four of the Configurations Illustrated in Figure 1[a]

configuration	3-21G//3-21G	6-31G*//3-21G	MP2/6-31G*//3-21G
(a)			
E_B	4.48	3.66	5.17
μ	2.5800	2.5214	
r	3.2811		
(c)			
E_B	4.38	3.46	4.82
μ	2.6965	2.6264	
r	3.2683		
(d)			
E_B	4.14	3.24	4.51
μ	2.6939	2.6200	
r	3.2781		
(e)			
E_B	5.06	0.51	2.06
μ	2.2263	2.0178	
r	3.2264		

[a] The binding energies (E_B) relative to the individual molecules are given in kcal/mol; the dipole moments (μ) are in D; and the intermolecular distances (r) between fluorine and the benzene molecular plane are in Å, except for case e where the intermolecular distance is that between fluorine and the nearest carbon.

Table III. Hartree–Fock Basis Set Superposition Errors (in kcal/mol) for the Hydrogen Fluoride–Benzene Complex[a]

	3-21G// 3-21G	6-31G*// 3-21G
benzene + hydrogen fluoride basis functions	0.71	0.29
hydrogen fluoride + benzene basis functions	0.44	0.49

[a] The optimal geometry of the complex (C_{6v} symmetry) is considered in all cases.

discussed later and can be observed from Table II where the total energies and optimal intermolecular geometries are reported for the different configurations investigated in this paper, this configuration turns out to be the most stable case when electron correlation effects are included, in full agreement with the experimental data of Andrews et al.[7] and Baiocchi et al.[6]

At the Hartree–Fock 3-21G level, the fluorine atom is optimized to be 3.281 Å (and the hydrogen atom therefore 2.344 Å) away from the benzene center of mass. These values compare favorably with experiment; they are both ≈0.1 Å larger than the estimates of Baiocchi et al. (3.18 and 2.25 Å, respectively).[6] The Hartree–Fock 6-31G* results of Sapse and Jain lead to even slightly longer intermolecular distances, 3.36 and 2.45 Å.[29]

The Hartree–Fock 6-31G*//3-21G binding energy of the cluster is calculated to be 3.7 kcal/mol. A direct and significant comparison between our results and those of Pople et al.[24] can be made at this level of calculation. The comparison indicates that the benzene–hydrogen fluoride cluster is slightly less stable than the complexes that hydrogen fluoride forms with acetylene (4.0 kcal/mol) and ethylene (4.1 kcal/mol). A similar conclusion has been drawn experimentally by Andrews et al. on the basis of shorter intermolecular bond lengths and larger displacements of the ν_s hydrogen fluoride modes in the acetylene and ethylene complexes.[7] It is interesting to notice that an opposite order of stability is experimentally observed in the case of complexation of those three π-systems with hydrogen chloride.[5]

In order to estimate the basis set superposition error at the Hartree–Fock level, we have carried out 3-21G//3-21G and 6-31G*//3-21G calculations for benzene in the presence of the hydrogen fluoride basis functions and vice versa. We have used the Boys–Bernardi counterpoise technique[37] and considered the optimal cluster configuration in order to locate all extra basis functions. Results are given in Table III and indicate superposition errors that are at most of the order of 1.2 kcal/mol with the 3-21G basis set and 0.8 kcal/mol with the extended basis set. As shown, for instance, by Bagus et al.,[38] such values for the superposition errors are upper bounds and are likely to be high overestimates since the occupied orbitals of the other unit and not only the virtual orbitals are used.

Inclusion of electron correlation effects via second-order Møller–Plesset perturbation theory leads to a significant stabilization of the benzene–hydrogen fluoride cluster, up to 5.2 kcal/mol from the 3.7-kcal/mol binding energy calculated with the Hartree–Fock 6-31G*//3-21G approach. If we compare our result with those obtained by Pople et al.[24] for the ethylene and acetylene complexes, we anticipate that, upon increasing the correlation contributions and taking account of zero-point energy corrections, the actual binding energy of the benzene–hydrogen fluoride complex should be on the order of 2.5–3.0 kcal/mol. The binding energy estimated in this way for benzene–hydrogen fluoride is larger than the 2.1-kcal/mol binding energy experimentally measured by Read et al.[5] for the benzene–hydrogen chloride complex. If we follow the arguments of Andrews et al.[7] mentioned above, this result is in agreement with the fact that the intermolecular bond lengths are observed to be larger for benzene–hydrogen chloride than for benzene–hydrogen fluoride.[6]

The molecular properties that we calculate at the Hartree–Fock 6-31G*//3-21G level indicate that, upon complex formation, the dipole moment increases by 0.50 D (2.52 D with respect to 2.02 D calculated for isolated hydrogen fluoride). This result is in nice agreement with the 0.59-D increase found experimentally by Klemperer and co-workers.[6] If, with all caution required, we refer to the Mulliken population analysis, we observe that cluster formation leads to a charge transfer of 0.013 e from the benzene molecule toward the Lewis acid, the transferred charge being actually mostly picked up by the fluorine atom. Such a charge transfer is qualitatively consistent with the concept of hydrogen bond formation, benzene playing the role of electron donor/proton acceptor. (Note that, despite their larger intermolecular distance, Sapse and Jain[29] report a surprisingly five times larger charge transfer, on the order of 0.069 e.)

We have also considered the situation in which the hydrogen fluoride molecule points with the fluorine atom down toward benzene. This situation is antibonding throughout the range of benzene plane–fluorine distances that have been considered, that is, between 3 and 5 Å. (We have not tried to look for a possible very small bonding at larger distances, possibly corresponding to a physisorption process.) For the 3-Å distance, the Hartree–Fock 3-21G total energy of the complex is 2.4 kcal/mol larger than the total energy of the individual molecules; the dipole moment is 2.26 D and the charge transfer is 0.002 e toward benzene. This nonbonding situation is easily understood since in this case, it is the electron-rich part of the hydrogen halide molecule that is directed toward the π-electron system of benzene.

In order to enable us to distinguish at least qualitatively between the contributions to the complex binding energy coming, on one hand, from the permanent dipole-induced-dipole interactions and, on the other hand, from hydrogen bond formation, we have carried out Hartree–Fock 3-21G calculations where the hydrogen fluoride molecule is simulated by two point charges forming an extended dipole. The two charges are located along the C_6 symmetry axis of benzene and separated by 0.9374 Å, as for the two atoms of the hydrogen fluoride molecule. The values of the point charges are chosen to be ±0.4825 e in such a way as to reproduce the 3-21G dipole of the isolated hydrogen fluoride molecule (2.17 D). This approach actually closely follows that designed by Broughton and Bagus in their investigations of the rubidium–hydrogen fluoride complex.[39]

The results for this extended dipole approach are illustrated in Figure 2, for the positive charge as well as for the negative

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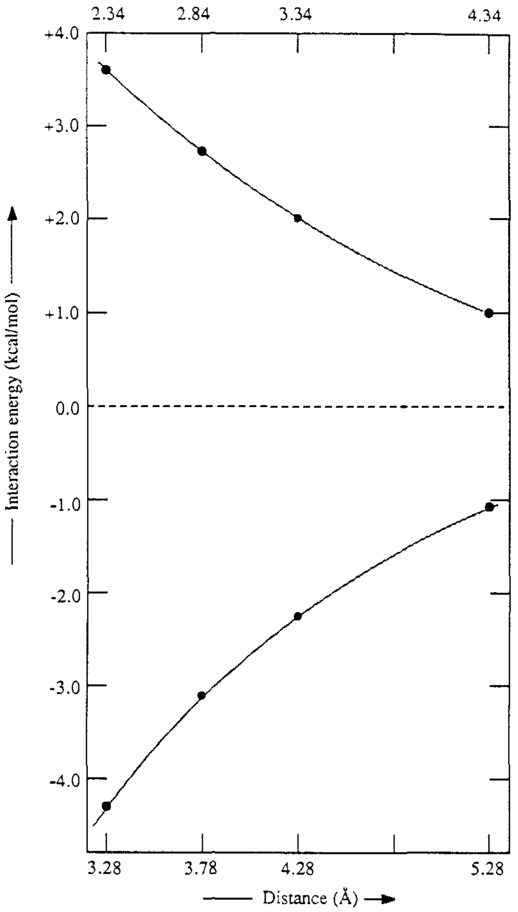

Figure 2. Hartree–Fock 3-21G binding energies (in kcal/mol) for the interaction between benzene and an extended dipole mimicking the hydrogen fluoride molecule, in the C_{6v} symmetry configuration, as a function of the distance between the fluorine atom and the benzene center of mass. The lower curve is for the case where the positive end of the dipole is directed toward benzene, the upper curve for the negative end directed toward benzene.

charge directed toward benzene. Broughton and Bagus have shown that, at the equilibrium distance of the Rb–hydrogen fluoride complex, the binding energies calculated with the extended dipole approach are about 1.5–2.0 kcal/mol too large, because the repulsive interaction resulting from the overlap between the rubidium and hydrogen fluoride wave functions are neglected.[39] Therefore, considering a similar overestimation in our case, we obtain that, for the optimal cluster geometry, the contribution to the binding energy coming from the interaction between the permanent dipole of hydrogen fluoride and the dipole induced in benzene is on the order of 4.2 minus 1.5–2.0 kcal/mol, that is ≈2.5 kcal/mol. This value is to be compared with the 3-21G 4.5-kcal/mol binding energy calculated for the full benzene–hydrogen fluoride complex (Table II). This result suggests that the contributions to the total binding energy due to electrostatic interactions roughly constitute about half of the total contributions and that the other half comes from hydrogen bond formation.

This conclusion is further substantiated by examining the evolution of the dipole moment. At the 3-21G level, the total increase in dipole moment when going from isolated hydrogen fluoride (2.17 D) to the complex (2.58 D) is 0.41 D. For the optimal geometry, the calculation performed with the extended dipole approach leads to a dipole moment increase of 0.18 D whereas a 0.21-D increase is found if we perform a simple point charge electrostatic calculation taking into account the 3-21G 0.010-e intermolecular charge transfer toward hydrogen fluoride. The sum of these two increases is thus 0.39 D, very close to the 0.41-D value mentioned above. The total dipole moment increase of the complex can therefore also be seen as originating in, on one hand, the induced intramolecular polarization of the benzene electronic cloud and, on the other hand, the intermolecular charge transfer related to hydrogen bond formation.

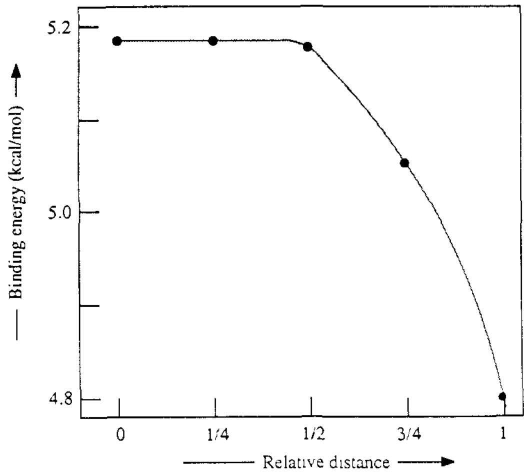

Figure 3. Evolution of the MP2/6-31G//Hartree–Fock/3-21G binding energy (in kcal/mol) as the hydrogen fluoride molecule leaves the C_6 symmetry axis and moves toward the top of a benzene carbon–carbon bond, as a function of the distance between the benzene center of mass and the midpoint of a carbon–carbon bond taken as unity.

We now consider the situation where the extended dipole simulating hydrogen fluoride is oriented with the negative end toward benzene. In this case, as for the full calculations, the interaction is calculated to be repulsive (top of Figure 2). For a distance of 3 Å between the negative point charge and the benzene plane, we calculate a dipole moment of 2.29 D. This value is very similar to that given before for the corresponding full calculation, 2.26 D. We infer that in this situation the interaction is primarily electrostatic and the antibonding character is due to the repulsion between the π-electron system of benzene and the negative end of the extended dipole.

(C) Cluster Nonfully Symmetric Configurations. We have first considered the case where the fluorine atom remains on the benzene C_6 axis and the hydrogen atom points toward a carbon–carbon bond (Figure 1b). Such a situation was left as possible from the data collected by Baiocchi et al.[6] At the 3-21G level, we do not find any stable value for the α angle (illustrated in Figure 1b) other than 0°, which indicates that the hydrogen atom tends at equilibrium to be also located on the C_6 axis. This finding is in full agreement with the results of Andrews et al.[7] The potential barrier is, however, not very high since it is on the order of 0.15 kcal/mol for α equal to 20° and 0.04 kcal/mol for α equal to 11°.

We have then studied the configuration in which the hydrogen fluoride molecule is located on top of the middle of a carbon–carbon bond and is perpendicular to the benzene plane (Figure 1c). This situation corresponds to the one found as the most stable by CNDO calculations.[26,27] The 3-21G geometry optimization results in a very slight decrease of the fluorine–benzene plane distance with respect to the fully symmetric case (as is also found at the Hartree–Fock 6-31G* level by Sapse and Jain[29]). This distance becomes 3.268 Å, down from 3.281 Å. The MP2/6-31G*//Hartree–Fock/3-21G binding energy is 4.8 kcal/mol, that is, 0.4 kcal/mol smaller than in the fully symmetric configuration. When hydrogen fluoride is located on top of a carbon atom (Figure 1d), the binding energy decreases further to 4.5 kcal/mol and the 3-21G optimized distance between fluorine and the benzene molecular plane is 3.278 Å, a value intermediate between what is optimally found in the cases illustrated in Figure 1a and c.

We have followed the MP2/6-31G*//Hartree–Fock/3-21G potential surface when the hydrogen fluoride molecule leaves the C_6 axis toward the top of a carbon–carbon bond. We have kept the hydrogen fluoride molecule perpendicular to benzene and a fluorine–benzene plane distance of 3.2811 Å. Such a choice for the intermolecular distance is justified by the fact that it is the

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[39] Broughton, J. Q.; Bagus, P. S. *J. Chem. Phys.* **1982**, *77*, 3627.

optimal distance for the C_{6v} symmetry of the complex and it merely provokes a 0.002-kcal/mol increase in total energy for the on-bond situation. The results are displayed in Figure 3 and indicate that the total energy remains almost constant as the hydrogen fluoride molecule starts moving away from the C_6 axis. The total energy significantly increases only past the midpoint between the center of mass of benzene and the bond. Such an evolution is consistent with the electrostatic potential due to the π-electrons varying smoothly around the middle of the benzene ring. Although we should remain cautious when comparing such small binding energy differences, an important aspect is that this series of results indicates that the motion of an hydrogen fluoride molecule on top of an aromatic system is facile and the mobility should even increase as the size of the aromatic compound gets larger.

Finally, we have studied a fully coplanar configuration (Figure 1e) for which the hydrogen fluoride molecule lies in the plane of benzene. The electrostatic potential of benzene being in this case electron attractive, the fluorine atom points here toward a benzene hydrogen, and hydrogen fluoride acts as the electron donor/proton acceptor. The fluorine is optimized to be 3.226 Å away from a carbon atom, the C–H···F bond deviating only slightly from linearity (the angle α of Figure 1e is optimized to be 118.8°). The hydrogen fluoride molecule makes an angle (β in Figure 1e) of 101.1° with the carbon–fluorine axis. This cluster geometry is analogous to that theoretically obtained by Frisch et al. for acetylene–hydrogen fluoride.[25] (Note that there is a misprint in the paper of Frisch et al., the C···F distance published in Scheme I of ref 25 actually corresponding to the H···F distance).

It is interesting to note that the Hartree–Fock 3-21G total energies would predict that this complex configuration for which the fluorine acts as proton acceptor is the most stable structure ($\approx$0.6 kcal/mol more stable than the C_{6v} geometry). However, improving the basis set to include polarization functions, as with the 6-31G* basis set, results in the coplanar configuration to be significantly (by at least $\approx$2 kcal/mol) less favorable than any of the other configurations investigated in this work where benzene is the proton acceptor. A similar artifact of Hartree–Fock 3-21G//3-21G calculations has been obtained by Pople et al. in the case of the acetylene–hydrogen fluoride complex.[24] As mentioned by these authors, poor Hartree–Fock 3-21G//3-21G results are obtained in the configuration where hydrogen fluoride acts as proton acceptor because of very large basis set superposition errors occurring in this configuration (indeed, the presence of neighboring acetylene hydrogen basis functions close to the fluorine compensates for some of the deficiency of the limited (21) basis functions used for the (7) valence electrons of fluorine). Note that, in the configurations where benzene acts as proton acceptor, the 3-21G basis set is more satisfactory, as can be inferred from Table II and the results of Pople et al.;[24] this justifies our use of this basis set in section III.B to examine qualitatively the different contributions to the complex binding energy.

IV. Conclusions

In summary, we can draw the following conclusions from our theoretical investigations of the benzene–hydrogen fluoride complex.

(i) In full agreement with the experimental data, MP2/6-31G*/Hartree–Fock/3-21G calculations indicate that the most stable structure is the symmetric C_{6v} configuration with the π-electron system of benzene acting as proton acceptor. The binding energy is calculated to be 5.2 kcal/mol. From a comparison with the experimental data and the theoretical results gathered on smaller complexes of hydrogen fluoride with acetylene and ethylene, the actual binding energy can be estimated to be on the order of 2.5–3.0 kcal/mol. The fluorine atom is optimized to be 3.28 Å away from the benzene center of mass, to be compared with an experimental value of 3.18 Å.

(ii) On the basis of calculations of the interaction of a benzene ring with an extended dipole simulating the hydrogen fluoride molecule, we estimate that the contributions to the total binding energy are roughly coming for one-half from electrostatic (induced dipole–permanent dipole) interactions and, for the other half, from charge-transfer hydrogen bond formation.

(iii) Calculations on nonfully symmetric configurations indicate that the hydrogen fluoride molecule should move rather easily on top of the aromatic ring. Going from the C_{6v} configuration to a situation where the molecule lies on top of the middle of a benzene carbon–carbon bond is calculated to cost a total energy of about 0.4 kcal/mol (that is, on the low side of room-temperature thermal energy).

(iv) The overall quality of our results support the adequacy of our approach based on MP2/6-31G*//Hartree–Fock/3-21G calculations to investigate the structure of benzene complexes. In a forthcoming paper, we intend to report on calculations performed for the complexes of benzene or pyrene with water, formic acid, ammonia, and methane.

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