

Contribution of the Basal Planes to Carbon Basicity: An Ab Initio Study of the $\text{H}_3\text{O}^+-\pi$ Interaction in Cluster Models

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The contribution to carbon basicity of π -cation interactions in aromatic systems has been investigated in this work by carrying out ab initio calculations on various cluster models. According to various levels of theory, the mono-, bi-, and tridentate H_3O^+ -benzene complexes present a binding enthalpy in the gas phase of about -28 kcal/mol showing intermolecular contact through unconventional hydrogen bonding between H_3O^+ and the π -cloud of benzene. The interaction energies calculated for other cluster models (pyrene-benzene- H_3O^+ , coronene- H_3O^+ , and a $\text{C}_{54}\text{H}_{18}$ - H_3O^+ cluster) indicate that the size of the basal plane has a slight influence on the strength of this π -cation interaction, whereas the presence of the π - π contacts reinforces the electrostatic interaction with the H_3O^+ cation. These theoretical results support experimental data on the ability of the basal planes to contribute to carbon basicity and suggest that π -cation interactions may play an important role in the surface chemistry of carbon materials.

Introduction

The acidic or basic properties of carbon are known to have a profound influence on the effectiveness of these materials when used as catalysts,¹ catalytic supports,² adsorbents,^{3,4} molecular sieves,⁵ etc. Carbon surfaces are, generally, amphoteric in nature with acidic and basic centers coexisting on their surface. Although there is general agreement in attributing acidic groups to oxygen functionalities present on carbon surfaces (such as carboxyl, lactone, and/or phenol groups⁴), the type of sites responsible for the basic properties of carbon surfaces is still subject to debate. Thus, different models have been postulated to account for carbon surface basicity: carbon surfaces behaving as irreversible oxygen electrodes;^{6,7} functional group protonation,^{8,9} reaction with functional groups such as the so-called chromene¹⁰ and/or pyrone-type structures,¹¹ and electron pair donors present on carbon surfaces (i.e., oxygen-free Lewis base sites^{12,13}). Due to the heterogeneous nature of carbon surfaces, several models may be simultaneously operative. However, the latest model has become more important for explaining basic properties of carbons. Indeed, some authors are of the opinion that carbon basicity could not arise from any oxygen-containing group.¹⁴ Despite the exact nature of the oxygen-free base sites being unclear, they are generally expressed according to the following equation:



where C_π is defined as a graphitized carbon surface platelet (i.e., basal plane).¹² Work to date illustrates the potential of basal planes to act as Lewis base centers.^{12,13,15–17}

In recent years π -cation interactions within aromatic systems have received a considerable amount of attention as a new type of binding force¹⁸ important in biological systems since these interactions have been recognized as favorable stabilizing

elements in proteins. In particular, it has been shown in a previous theoretical work^{19,20} that the prototypical ammonium cation forms a strong complex with benzene or toluene where the nitrogen and the center of the aromatic ring are approximately 3.0 \AA apart and the resultant stabilization is interpreted to first order as a directional charge-quadrupole attraction between a positive charge and the π face of the aromatic ring. However, these theoretical studies have also indicated that the π -cation interaction cannot be quantitatively modeled unless additional terms such as induced dipoles, polarizabilities, dispersion forces, and charge transfer are taken into account using ab initio levels of theory.

As a first step in the theoretical investigation of the contribution of the basal plane to carbon basicity, it seems convenient to carry out a study of the $\text{H}_3\text{O}^+-\pi$ interactions in some cluster models, using an appropriate level of theory. Although theoretical results obtained by means of cluster modeling do not often allow a direct comparison with experimental results, truncated models of the H_3O^+ -basal plane complex are aimed at analyzing the adsorption of H_3O^+ on graphite layers throughout π -cation interactions. The H_3O^+ interaction with benzene (which is the prototypical aromatic system) and other cluster models (pyrene-benzene- H_3O^+ , coronene- H_3O^+ , and $\text{C}_{54}\text{H}_{18}$ - H_3O^+) can be considered as the starting point for understanding the intrinsic basicity of the basal plane. The theoretical results reported in this work may be useful for addressing the binding energy and the nature of the H_3O^+ -basal plane interactions. In addition, we intend to gain some insight into the effect of the number of condensed aromatic rings and the presence of π - π interactions throughout the interlayer space on the carbon basicity. Other interesting questions concerning this subject, such as solvent effects, border effects (i.e., the contribution to the total basicity of the oxygen-free carbon atoms at the edges¹⁷), or the variations in the acid/base character when electron-withdrawing or electron-donating functionalities²¹ are combined with carbon atoms at the edges of the basal planes, are beyond the scope of this paper.

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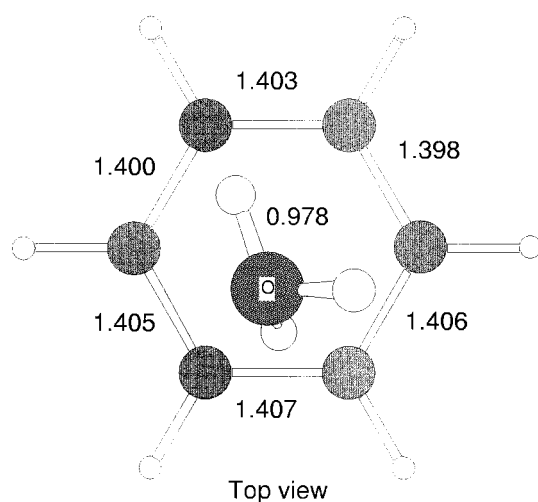
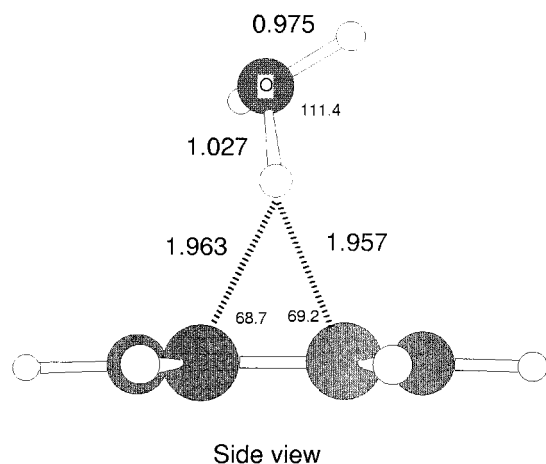
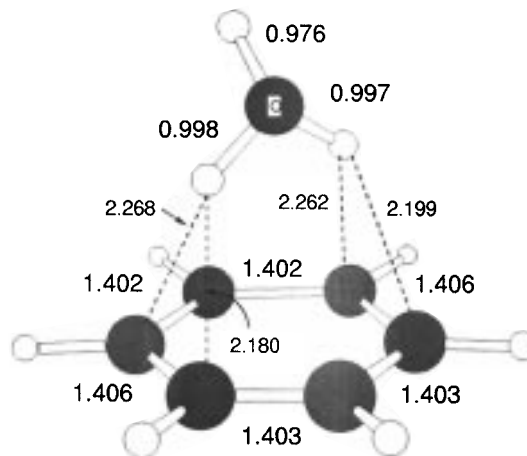
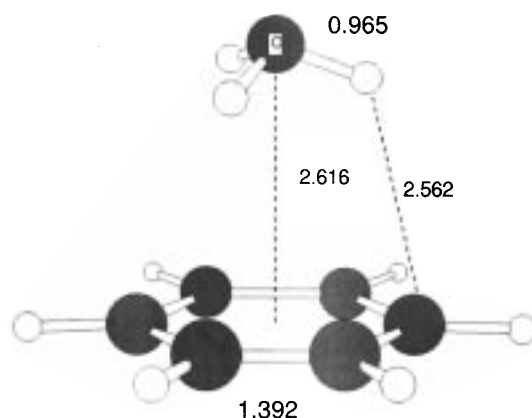
**C1 Monodentate Complex****C2 Bidentate Complex****C3 Tridentate Complex**

Figure 1. MP2/6-31G(d) optimized structure of the mono-, bi-, and tridentate benzene- H_3O^+ complexes (distances in angstroms and angles in degrees).

Methods

Quantum chemical calculations were carried out with the Gaussian 94 system of programs.²² Most of the calculations were performed using the MP2 method with a standard 6-31G(d) basis set²³ augmented with an extra set of p polarization functions centered on the hydrogen atoms of the H_3O^+ cation. The full counterpoise (CP) method²⁴ was used in order to eliminate the basis set superposition error²⁵ (BSSE) in interaction energies at the MP2/6-31G(d) level. The frozen core approximation, in which 1s electrons are not considered in the calculation of correlation energy, was used in all the correlation energy calculations.

The benzene- H_3O^+ complexes were fully optimized by means of the Schlegel algorithm²⁶ at the MP2/6-31G(d) level. Analytical computations of harmonic frequencies were carried out in order to further characterize the critical points and calculate the zero point vibrational energy (ZPVE) and the thermodynamic gas-phase quantities (298.15 K, 1 bar) within the ideal gas, rigid rotor, and harmonic oscillator approximations.²⁷ In addition, single point MP4SDTQ/6-31G(d) and MP2/6-311+G(3df,2p) calculations were performed on the MP2/6-

31G(d) geometries. A topological analysis of the interfragment (+3,-1) bond critical points (BCP) in MP2/6-31G(d) electron density was carried out for the benzene- H_3O^+ monodentate complex. According to the theory of atoms in molecules developed by Bader,²⁸ the values of the electron density $\rho(\bar{r})$ and the Laplacian of the electron density $\nabla^2\rho(\bar{r})$ and of the ellipticity ϵ of the charge density (defined as $\epsilon = (\lambda_1/\lambda_2) - 1$, where λ_1 and λ_2 are the eigenvalues of the Hessian matrix of $\rho(\bar{r})$ corresponding to the eigenvectors perpendicular to the bond path) at the BCPs make it possible to characterize the interatomic interactions.

Results

Figure 1 shows the mono-, bi-, and tridentate optimized H_3O^+ -benzene complexes at the MP2/6-31G(d) level in which the H_3O^+ cation is located above the π cloud near the 6-fold symmetry axis of benzene.²⁹ According to the analytical MP2/6-31G(d) harmonic frequencies, the mono-, bi-, and tridentate complexes correspond with a local minima, a first-order saddle point (transition structure), and a second-order saddle point, respectively. The relative energies of these structures are collected in Table 1.

TABLE 1: Relative Energies (kcal/mol) of the Various Benzene–H₃O⁺ Complexes Studied in This Work (Geometries Optimized at the MP2/6-31G(d) Level)

structure	MP2/6-31G(d) ^a	ZPVE ^b	MP4/6-31G(d) ^c	MP2/6-311+G(3df,2p) ^c
benzene + H ₃ O ⁺	0.0	0.0	0.0	0.0
monodentate complex (minimum) (C1)	−27.4 (3.0)	0.8	−26.5	−28.6
bidentate complex (first-order saddle point) (C2)	−27.2 (2.8)	0.8	−26.4	−28.3
tridentate complex (second-order saddle point) (C3)	−24.7 (2.9)	0.8	−24.2	−25.7

^a CP corrections to the MP2/6-31G(d) binding energies are in parentheses. ^b From MP2/6-31G(d) analytical frequencies. ^c Single point calculations on the MP2/6-31G(d) geometries.

The monodentate complex (**C1** in Figure 1) presents a close contact between both fragments given that the oxygen–carbon plane distance is 2.748 Å and the two H(H₃O⁺)–C(C₆H₆) bond distances amount to 1.963 and 1.957 Å, respectively. A topological analysis of the MP2/6-31G(d) electron density confirms that the most favorable equilibrium structure of this benzene–H₃O⁺ complex involves the formation of an unconventional hydrogen bond directed to the midpoint of a C–C bond. The existence of the corresponding BCP in the electron density located on a plane defined by the H(H₃O⁺) and C–C(benzene) atoms indicates that the binding between the π cloud of benzene and H₃O⁺ may be interpreted in terms of a σ – π complex between the two fragments (the observed Mulliken charge transference from benzene to H₃O⁺ is 0.18 e). Nevertheless, the resultant BCP properties ($\rho = 0.029$ au, $\nabla^2\rho = 0.068$ au, and $\epsilon = 1.164$) show that this hydrogen bond indicates a bonding interaction between closed-shell systems with an asymmetric distribution of the charge density around the corresponding bond path.²⁸

At the MP2/6-31G(d) level, the calculated binding energy of the monodentate complex is −27.4 kcal/mol which is close to some typical stabilization energies for donor–acceptor intermolecular complexes.³⁰ The MP2/6-31G(d) ZPVE correction amounts to only 0.8 kcal/mol. According to the single point MP4/6-31G(d) and MP2/6-311+G(3df,2p) calculations, the binding energies of the **C1** complex are −26.5 and −28.6 kcal/mol, respectively, indicating that the effects on this π –cation complex of higher theoretical methods and larger basis sets are quite moderate. The predicted binding enthalpy and free energy in the gas phase at 298 K are −28.4 and −21.8 kcal/mol, respectively.³¹ Comparing these results with a previous theoretical determination of the ammonium–benzene binding energy,¹⁸ we note that the monodentate H₃O⁺–benzene complex is about 9 kcal/mol more stable than the NH₄⁺–benzene system.

The binding energy of the most favorable **C1** complex can be broken down into two main contributions by recalculating at the MP2/6-31G(d) level the energy of the benzene and the H₃O⁺ cation, using the geometry each fragment has in the complex. These contributions are the distortion (ΔE_{dis}) and interaction energies (ΔE_{int}):

$$\Delta E_{\text{int}} = E(\text{C}_6\text{H}_6 - \text{H}_3\text{O}^+)_{\text{AB}} - E(\text{C}_6\text{H}_6)_{\text{AB}} - E(\text{H}_3\text{O}^+)_{\text{AB}}$$

$$\Delta E_{\text{dis}} = E(\text{C}_6\text{H}_6)_{\text{AB}} - E(\text{C}_6\text{H}_6)_{\text{A}} + E(\text{H}_3\text{O}^+)_{\text{AB}} - E(\text{H}_3\text{O}^+)_{\text{B}}$$

where the subscripts AB, A, and B refer to the geometry of the supermolecule and isolated fragments, respectively. Thus, the resultant binding energy for the **C1** complex (−27.4 kcal/mol) decomposes to −29.2 kcal/mol and only 1.8 kcal/mol corresponding to the interaction and distortion energies, respectively. In addition, the distortion energies of H₃O⁺ and benzene have values of 1.5 and 0.3 kcal/mol, indicating that the geometry of the aromatic system is almost unaltered as a consequence of the interaction (see Figure 1). On the other hand, the value of the BSSE-corrected interaction energy^{24,32} (−26.2 kcal/mol)

shows that BSSE has a small influence on the benzene–H₃O⁺ binding energy. Finally, to estimate the first-order electrostatic contribution to the interaction energy,^{19b} the electrostatic potential energy of a positive charge situated at the oxygen position and interacting with benzene was also calculated, rendering values of −12.0 and −13.6 kcal/mol using the MP2/6-31G(d) and HF/6-31G(d) electronic densities, respectively.

The bidentate complex between H₃O⁺ and benzene (**C2** in Figure 1) has a MP2/6-31G(d) binding energy of −27.2 kcal/mol, while the H₃O⁺ cation forms two unconventional hydrogen bonds directed toward opposite C–C bonds of the benzene ring (see Figure 1). As previously mentioned, this bidentate complex is a transition structure on the MP2/6-31G(d) potential energy surface (PES) which connects two equivalent monodentate complexes. The energy barrier of this transition structure has an almost negligible value of 0.2 kcal/mol. Single point MP4/6-31G(d) and MP2/6-311+G(3df,2p) calculations predict energy barriers of only 0.1 and 0.3 kcal/mol, respectively. Inclusion of the CP correction to the MP2/6-31G(d) binding energy predicts that **C1** and **C2** complexes have almost coincident binding energies (−24.4 kcal/mol). Therefore, fast equilibria between different monodentate H₃O⁺–benzene complexes passing through the corresponding bidentate transition structures can be expected. On the contrary, the tridentate H₃O⁺–benzene complex is clearly less stable than **C1** or **C2**. According to our results at different theory levels, the tridentate complex (**C3** Figure 2) is a second-order saddle point on the MP2/6-31G(d) PES which is about 2.5 kcal/mol higher in energy than the monodentate complex (see Table 1).

Figure 2 displays the optimized structure of pyrene at the MP2/6-31G(d) theory level, and the geometry of the pyrene–benzene–H₃O⁺ cluster studied in this work. The internal geometries of the pyrene and monodentate benzene–H₃O⁺ complexes are taken from their corresponding MP2/6-31G(d) optimized structures. Given that we intend to obtain some theoretical insight into the influence of π – π interactions on the intrinsic basicity of the basal plane, the selected arrangement of the pyrene–benzene represents a cluster model with the typical A–B packing of graphite layers. Although a quantitative description of π – π interactions requires correlated methods such as coupled cluster theory and extended basis sets,³³ the following BSSE-corrected MP2/6-31G(d) results may be an indication of the qualitative influence of the π – π contacts on the π –cation binding energies.

The pyrene–benzene–H₃O⁺ molecular model shown in Figure 2 has been analyzed using various MP2/6-31G(d) interaction energies at different interplanar distances d between benzene and pyrene (see Table 2). This cluster model enables us to use high-level levels of theory to evaluate the influence π – π contacts (simulating a typical A–B packing) on the π –cation interaction in the context of the carbon basicity problem.³⁴ Figure 3 shows that the energy profile corresponding to the π – π interaction between pyrene and benzene has a shallow minimum of −3.7 kcal/mol at a value of $d \approx 3.5$ Å. The interaction energy between the H₃O⁺ cation and pyrene,

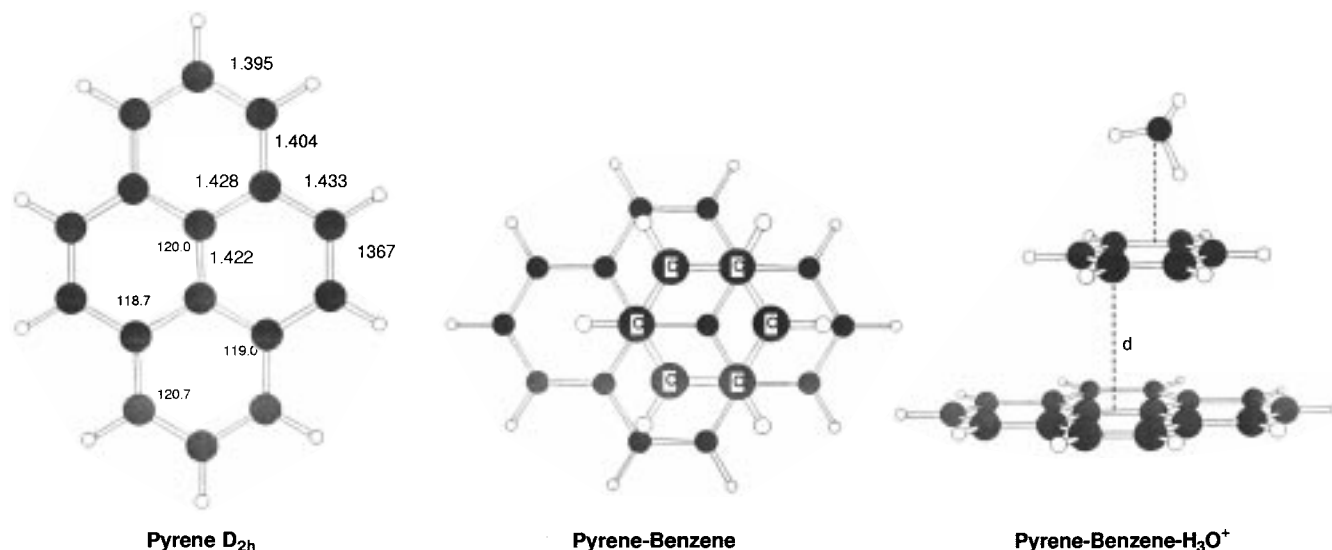


Figure 2. MP2/6-31G(d) optimized structure of pyrene (distances in angstroms and angles in degrees). The pyrene–benzene and the pyrene–benzene–H₃O⁺ cluster models are also shown.

TABLE 2: MP2/6-31G(d) BSSE-Corrected Interaction Energies (kcal/mol) for the Pyrene–Benzene–H₃O⁺, Pyrene–Benzene, and Pyrene–H₃O⁺ Model Complexes (See Figure 2) Computed at Different Values of the Pyrene–Benzene Interplanar Distance d (Å)^a

d	pyrene–benzene–H ₃ O ⁺ A	pyrene–benzene B	pyrene–H ₃ O ⁺ C	cooperative effect D	ΔE_{int} (A–B)	EP ^c
3.0	–34.4 (11.9, 11.8 ^b)	1.6 (8.8)	–5.5 (0.0)	–4.3	–36.0	–19.2
3.2	–36.7 (9.6 ^b)	–2.3 (6.6)	–5.0 (0.0)	–3.2	–34.4	–18.3
3.4	–36.8 (8.0 ^b)	–3.6 (5.0)	–4.6 (0.0)	–2.4	–33.2	–17.7
3.6	–36.0 (6.7 ^b)	–3.7 (3.7)	–4.2 (0.0)	–1.9	–32.3	–17.3
3.8	–34.7 (5.7 ^b)	–3.4 (2.7)	–3.9 (0.0)	–1.2	–31.3	–17.0
4.0	–33.9 (4.8 ^b)	–2.9 (1.8)	–3.6 (0.0)	–1.2	–31.0	–16.8
4.2	–33.0 (4.2 ^b)	–2.4 (1.2)	–3.3 (0.0)	–1.1	–30.6	–16.6

^a CP corrections are indicated in parentheses. The interaction ΔE_{int} (A–B) and electrostatic potential (EP) energies (kcal/mol) between the H₃O⁺ cation and the pyrene–benzene π – π complex are also included. ^b BSSE estimated in an additive fashion (see text for the details): BSSE(pyrene–benzene–H₃O⁺) \cong BSSE(pyrene–benzene) + BSSE(benzene–H₃O⁺) + BSSE(pyrene–H₃O⁺). ^c The HF/6-31G(d) electrostatic potential exerted by the pyrene–benzene complex is calculated at the oxygen position.

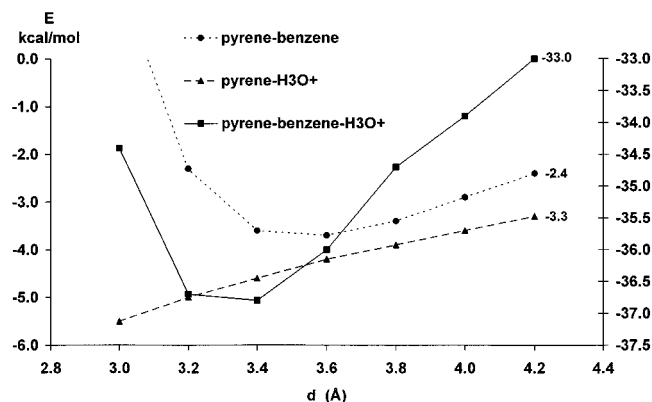


Figure 3. Plot of the MP2/6-31G(d) BSSE-corrected interaction energies (kcal/mol) for the pyrene–benzene–H₃O⁺, pyrene–benzene, and pyrene–H₃O⁺ complexes as a function of the pyrene–benzene interplanar distance d (Å).

which ranges from –3.3 kcal/mol at $d = 4.2$ Å to –5.5 kcal/mol at $d = 3.0$ Å, constitutes a clear stabilizing contribution favored by short interplanar distances. Table 2 also indicates that the H₃O⁺–pyrene interaction energies do not include any significant BSSE correction according to the corresponding CP calculations, given that distant *ghost* basis functions make only a tiny contribution to the fragment energies.

Concerning the interaction energy of the whole system (pyrene–benzene–H₃O⁺), we note that the CP correction to the interaction energy can be practically calculated as a sum of the CP corrections for the bimolecular interacting subsystems

(pyrene–benzene, pyrene–H₃O⁺, and benzene–H₃O⁺). At the shortest interplanar distance of 3.0 Å, a CP-correction value of 11.9 kcal/mol was obtained by calculating all fragment energies on the full cluster basis,²⁵ while an almost identical value of 11.8 kcal/mol results from the addition of the corresponding pyrene–benzene and H₃O⁺–benzene CP corrections. This simple additive scheme therefore was applied to the rest of the interplanar distances to obtain the BSSE-corrected interaction energies of the full cluster.

The magnitude of the cooperative effect present in the total energy interaction for the pyrene–benzene–H₃O⁺ cluster was obtained using the CP-corrected MP2/6-31G(d) interaction energy between benzene and H₃O⁺ (–26.2 kcal/mol, see above) and the previously mentioned pyrene–benzene and pyrene–H₃O⁺ interaction energies. These cooperative effects provide a moderate stabilization of the cluster model (to within a few kilocalories per mole; see Table 2), becoming more important as the interplanar distance decreases. For example, at $d = 3.0$ Å, the contribution of the cooperative effect to the total energy is –4.3 kcal/mol.

The various energy contributions and their dependency on the interplanar distance allow us to understand more clearly the energy profile of the total interaction energy for the pyrene–benzene–H₃O⁺ cluster model. When the interplanar distance decreases, we observe that the initial variation in all the energy components, namely, pyrene–benzene, pyrene–H₃O⁺, and the cooperative effect, tends to reinforce the total energy interaction of the full system. Comparing the energy profiles of the pyrene–benzene–H₃O⁺ and pyrene–benzene clusters, we see

that the π -cation interaction induces a greater slope in the global energy profile (Figure 3) and a corresponding shift of the equilibrium interplanar distance to a lower value (≈ 3.3 Å). Thus, the changes caused by the presence of the H_3O^+ cation above the pyrene-benzene cluster reveal a certain attenuation of the π - π repulsion. On the other hand, at the shortest interplanar distances the influence of the π - π interactions is clearly reflected in the energy profile given that the repulsion between the aromatic systems produces a notable diminution in the energy interaction, affecting the resultant slope of the energy profile (see Figure 3).

Considering the absolute magnitude of the interaction energies of the pyrene-benzene- H_3O^+ cluster (≈ -37 kcal/mol), the benzene-pyrene (≈ -3 kcal/mol), and the benzene- H_3O^+ complexes (-26.2 kcal/mol), it should be noted that π - π contacts may determine a significant rise in the intrinsic basicity of the aromatic clusters increasing the π -cation binding energies by 7 kcal/mol. Moreover, we see in Table 2 that the stabilization energy between the H_3O^+ cation and the pyrene-benzene complex is favored with shorter interplanar distances as expected from an electrostatic reasoning of π -cation interactions. The calculation of the electrostatic interaction energies between the pyrene-benzene complex and a positive charge situated in the oxygen position corroborates this interpretation. From data in Table 2, we see that the increments in stabilization energy between the H_3O^+ cation and the pyrene-benzene complex run parallel to the resultant changes in the computed electrostatic potential.³⁵

To obtain an initial estimation of the influence of more realistic models of the basal plane interacting with the H_3O^+ cation, the interaction energy of benzene- H_3O^+ , coronene- H_3O^+ , and $\text{C}_{54}\text{H}_{18}$ - H_3O^+ complexes were calculated, using the HF/6-31G(d) equilibrium geometry of the corresponding aromatics (see Figure 4), whereas the internal and relative coordinates of the H_3O^+ cation were taken from the MP2/6-31G(d) fully optimized monodentate benzene- H_3O^+ structure. We note that the MP2/6-31G(d) interaction energy of the C1 complex, using the internal HF/6-31G(d) equilibrium structure of benzene (-28.1 kcal/mol, excluding the CP correction), compares well with the fully optimized complex (-29.2 kcal/mol) given that the internal geometry of benzene is not affected so much by the π -cation interactions (see above).

At the MP2/6-31G(d) level the effect of increasing the area of the basal plane model is moderate. Thus, the substitution of benzene by coronene in the corresponding model complex reinforces the interaction energy with the H_3O^+ cation by 7.5 kcal/mol. This effect is most probably due to a greater contribution from the polarization term because, to first order, the electrostatic interaction at the HF/6-31G(d) level amounts only to -12.1 kcal/mol, very similar to the corresponding value of -12.9 kcal/mol for the benzene- H_3O^+ restricted complex.

At the HF/6-31G(d) level the interaction energy between the H_3O^+ cation and the aromatic system passes from -22.5 to -27.3 kcal/mol when benzene is replaced by coronene, with the net stabilization energy being 4.8 kcal/mol, 2.7 kcal/mol lower than the MP2/6-31G(d) value. In the case of the $\text{C}_{54}\text{H}_{18}$ - H_3O^+ complex, the HF/6-31G(d) interaction energy and the electrostatic first-order contribution amount to -30.6 and -11.3 kcal/mol, respectively. As a consequence of its larger polarizability with respect to coronene, this model of the basal plane renders a moderate increment of only 3.3 kcal/mol to the π - H_3O^+ binding energy at the HF/6-31G(d) level. These calculations therefore might allow us to roughly estimate the

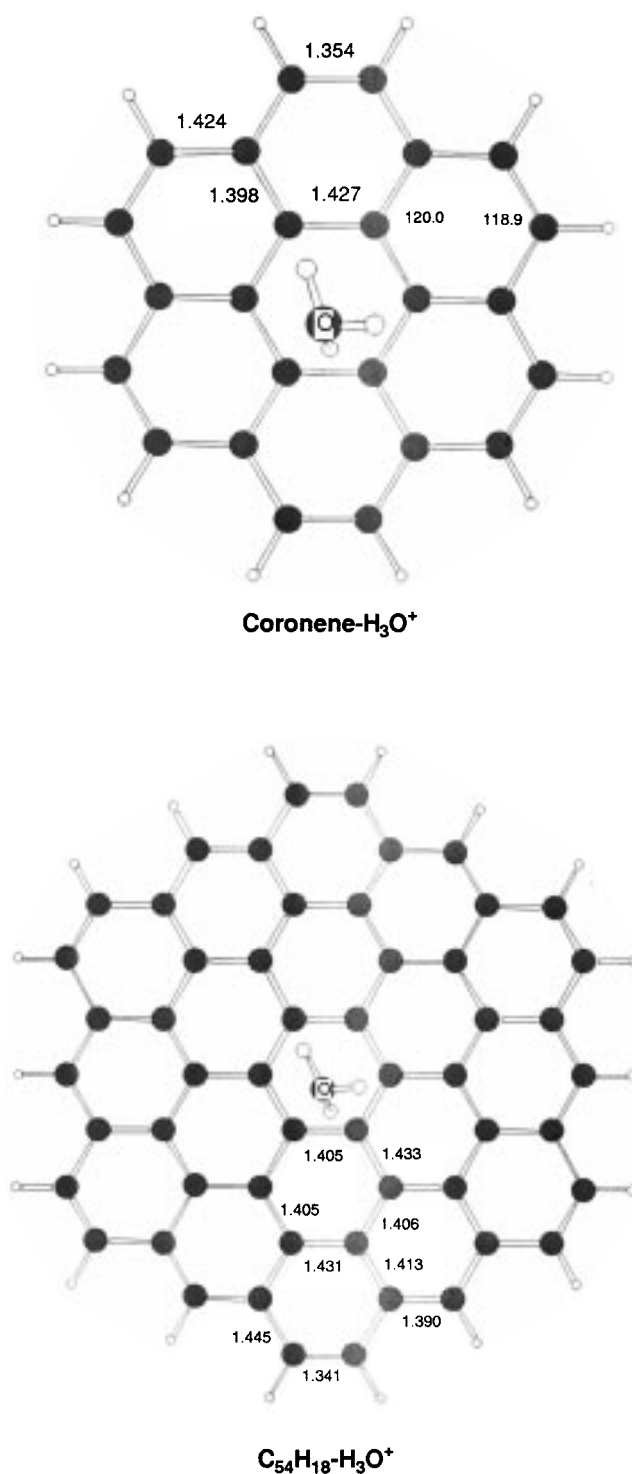


Figure 4. Coronene- H_3O^+ and $\text{C}_{54}\text{H}_{18}$ - H_3O^+ cluster models. HF/6-31G(d) bond distances and bond angles of coronene and $\text{C}_{54}\text{H}_{18}$ are also indicated (distances in angstroms and angles in degrees).

binding energy between the H_3O^+ cation and basal plane surface to be approximately 40 kcal/mol.

Discussion

The theoretical results reported in this work are useful for establishing some interesting conclusions regarding the contribution of the basal plane to carbon basicity throughout π -cation interactions. First, it is reasonable to expect that the nature of the π -cation complexes between the H_3O^+ cation and the π faces of the aromatic systems is well-represented by the prototypical benzene- H_3O^+ complexes. As previously men-

tioned, our calculations predict a considerable binding enthalpy of -28.4 kcal/mol for a stable monodentate structure, representing a close intermolecular contact through an unconventional hydrogen bonding between H_3O^+ and the π cloud of benzene. Our results note the role played by electrostatics as the major aspect of these π -cation interaction as also reported in previous literature with related systems.^{19,20}

The calculations carried out at the MP2/6-31G(d) level on the pyrene-benzene- H_3O^+ , coronene- H_3O^+ , and $\text{C}_{54}\text{H}_{18}$ - H_3O^+ complexes indicate that the π -cation binding energy is enlarged due to the effects produced by π - π contacts and the condensed aromatic rings. Although these factors were studied separately and consequently the possible cooperative effects are still unknown, it may be expected from our theoretical results that the H_3O^+ interaction with a multilayer cluster model of graphite would result in binding enthalpies greater than 40 kcal/mol. Interestingly, the MP2/6-31G(d,p) binding energy in the gas phase for the H_3O^+ - H_2O complex amounts to -39.3 kcal/mol (-38.4 kcal/mol at the MP4/6-31G(d,p)/MP2/6-31G(d,p) level) while the $\text{O}\cdots\text{O}$ equilibrium distance is 2.388 Å. Consequently, it may be inferred that the water-oxonium and basal plane-oxonium interactions are of comparable magnitude. In addition, very recently, Chipot et al.²⁰ examined the π -cation interactions in water for a related system (toluene-ammonium) by means of a detailed molecular dynamic (MD) simulation. These authors showed that the inclusion of water molecules demonstrates that these π -cation associations at contact distances are favorable in a polar aqueous solution and preferentially maintain the perpendicular orientation of the aromatic ring with respect to ammonium. From these theoretical results, it is clear that the π -cation interaction of H_3O^+ with the basal plane of a carbon surface could energetically compete with full aqueous solvation in binding the H_3O^+ cations. Further understanding of this point could be gained by means of a MD study using multilayer carbon clusters, a large number of solvent molecules, and a potential function fitted to reproduce the magnitude of the attractions between H_3O^+ and the aromatic clusters as estimated from our ab initio calculations.

Recently, Menéndez et al.¹⁷ carried out an extensive characterization of the chemical surface properties of activated carbons subjected to several treatments. In particular, they determined the point of zero charge (PZC) of these materials by mass titration, obtaining a significant decrease (from 8.5 to 7.2) in carbons with negligible oxygen content but different structural order (less graphitic to more graphitic, respectively). According to our results, the relative increase (from 48.6 to 72.8 Å) observed by the authors mentioned in the L_a parameter (i.e., the number of condensed rings of the aromatic layers) would have no special relevance for the contribution of the basal plane to carbon basicity. The impact of the enlargement of the π system on the π -cation interaction seems to be minimized when the models (from benzene to coronene and from coronene to the $\text{C}_{54}\text{H}_{18}$ cluster used in the present study) become large enough to attenuate the border effects in the benzene- H_3O^+ cluster. On the other hand, from our theoretical results concerning the role of the π - π contacts in the basal plane- H_3O^+ interactions, the reported lower values of the interplanar distance d_{002} as the level of graphitization increase,¹⁷ would be expected to reinforce the basicity of the same activated carbons. However, an opposite trend has been obtained by Menéndez et al.,¹⁷ indicating that other factors must be taken into account to explain this behavior. Nevertheless, the PZC values of the more

graphitized materials reflect the intrinsic basicity of the π system and can be clearly understood on the basis of the π -cation interactions.

In conclusion, all the theoretical evidence leads us to conclude that the H_3O^+ cations and the basal plane on carbon surfaces may establish *close-contact* structures throughout π -cation interactions in which the aromatic rings effectively behave as hydrogen bond acceptors^{29b} while counterions would be held at *solvent-separated* distances to satisfy electroneutrality. These theoretical results therefore support experimental data^{12,13,15-17} concerning the ability of the basal planes to contribute to carbon basicity and suggest that π -cation interactions may play an important role in the surface chemistry of carbon materials.

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