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Solvation of H_3O^+ by Phenol: Hydrogen Bonding vs π Complexation

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Ab initio calculations at the second-order Møller-Plesset perturbation theoretic level have been carried out to study the solvation of protonated water by phenol molecules. The results show that in addition to classical O−H···O hydrogen bonds, C−H···O, π···H−O, and π···H−C bonds are also formed, thus stabilizing the $H_3O^+(C_6H_5OH)_3$ complex.

Introduction

Several experimental and theoretical studies have been carried out on protonated water clusters, $H^+(H_2O)_n$, over the years because of their fundamental importance and also because of their importance in ion chemistry in the earth's atmosphere.[1−13] However, detailed studies on the interaction of protonated water (H_3O^+) with other polar and nonpolar solvent molecules have been limited. It is evident from the recent X-ray crystallographic study on $[H_3O{\cdot}3C_6H_6][CHB_{11}Cl_{11}]{\cdot}C_6H_6$ that tribenzene solvates H_3O^+ by forming a π complex.[14] The importance of π complexation in biomolecules and supramolecular assembly of small molecules is well documented.[15] Ab initio calculations show that H_3O^+ interacts with phenol (P) through classical O···H−O hydrogen bonding.[16] It would be worth investigating the role of π···H−O type interaction in the solvation of H_3O^+ by phenol molecules. Therefore, further ab initio calculations were carried out. To compare the π complexation with the classical hydrogen bonding, solvation of H_3O^+ by benzene (BZ) has also been investigated. Stabilization energies and vibrational frequencies, along with an analysis of electron density topographs using atoms-in-molecules (AIM) approach are reported for $H_3O^+(C_6H_5OH)_3$ and $H_3O^+(C_6H_6)_3$ complexes.

Computational Details

Optimized geometries of $H_3O^+(C_6H_5OH)_3$ and $H_3O^+(C_6H_6)_3$ complexes were determined at Hartree−Fock (HF), density functional theory (DFT) with B3LYP parametrization and second-order Møller−Plesset perturbation (MP2) theory levels using computationally manageable 6-31G(d) basis set using the G98W suite of programs.[17] In each case, geometry optimization yielded a minimum energy structure, which was then used to calculate the harmonic vibrational frequencies. Frequency calculations were carried out at the HF level and scaled by 0.8929, as is the standard practice.[18] Stabilization energies (SE) of all the clusters have been calculated using the supermolecule approach and corrected for basis set superposition error (BSSE) using the counterpoise (CP) method suggested by Boys and Bernardi[19]

$$\mathrm{SE} = |E_{\mathrm{Complex}} - \{E_{\mathrm{A}} + E_{\mathrm{B}}\}| \tag{1}$$

where E_{Complex} is the total energy of the complex and E_{A} and E_{B} are the total energies of phenol or benzene clusters and H_3O^+, respectively. The theory of AIM has been used to quantify the strength of the interaction in hydrogen bonded and π complexes of H_3O^+ with P/BZ. The AIM calculations were carried out using the wave functions generated from the quantum chemistry calculations with the help of AIM2000 package.[20]

TABLE 1: Comparison of Stabilization Energies (SEs) for $H_3O^+-(P)_3$ and $H_3O^+-(BZ)_3$ Clusters

	SE (kcal/mol)					
	HF/6-31G(d)		B3LYP/6-31G(d)		MP2/6-31G(d)	
H_3O^+ clusters	BSSE uncorrected	BSSE corrected	BSSE uncorrected	BSSE corrected	BSSE uncorrected	BSSE corrected
C1	72.95	72.89	83.75	81.18	95.09	83.21
*C*2	55.35	51.99	68.73	65.65	76.47	63.06
C3	53.61	50.16	64.65	63.09	74.35	61.35
C4	49.74	46.10	58.06	54.73	66.62	55.65

Results and Discussion

The optimized geometries of $H_3O^+-(P)_3$ and $H_3O^+-(BZ)_3$ are shown in Figure 1. The calculated SE values at HF, DFT and MP2 levels of theory are listed in Table 1. Clearly, the most stable geometry is C1 in which H_3O^+ acts as the donor and the three phenol molecules act as the acceptors. Three classical O−H···O hydrogen bonds are formed. In the complexes C2 and C3, H_3O^+ forms weak hydrogen bonds with the π rings of the phenol molecules. In addition to the π···H−O interaction, O−H···O hydrogen bond also exists between two phenol molecules (C2). In C3, H_3O^+ interacts with the π clouds of all three phenol rings. This arrangement is comparable to that of π complexation (C4) in the solvation of H_3O^+ by benzene. However, the SE of C3 is larger than that of C4.

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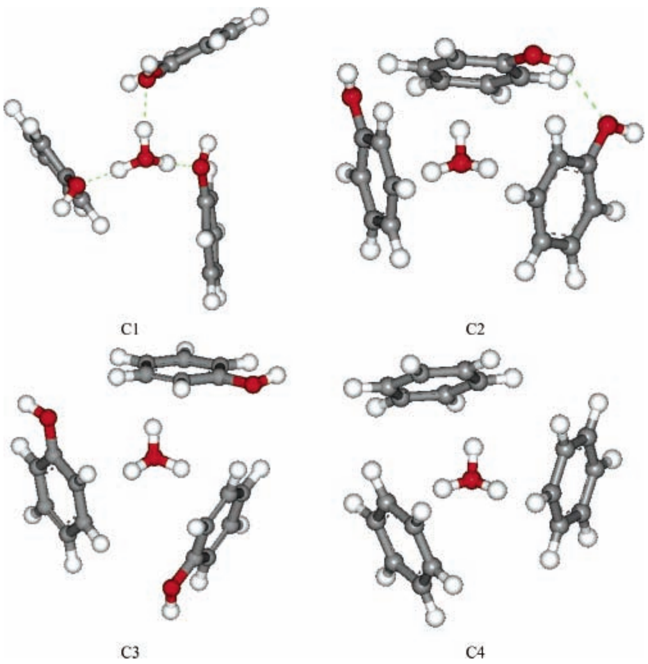

Figure 1. Optimized molecular structures of $H_3O^+-(P)_3$ and $H_3O^+-(BZ)_3$ complexes obtained at the MP2/6-31G(d) level of theory.

The percentage of electrostatic and dispersion interactions contributing to the stability of these complexes were obtained from HF and MP2 calculations. The electrostatic contribution to the stability for C1, C2, C3, and C4 were found to be 88, 82, 82, and 83%, respectively. Clearly, the electrostatic interaction contributes to a greater extent than the intermolecular dispersive interaction. The presence of the positively charged H_3O^+ ion increases the stability of the weakly bonded π systems.

TABLE 2: Comparison of Geometrical Parameters for $H_3O^+-(P)_3$ and $H_3O^+-(BZ)_3$ Clusters

H_3O^+ clusters	type of interaction	distances (Å)		
		HF/6-31G(d)	B3LYP/6-31G(d)	MP2/6-31G(d)
C1	H-bond	2.61−2.63	2.56−2.60	2.51−2.63
C2	OH...π	3.20−3.40	3.30−3.60	2.98−3.08
C3	OH...π	3.10−3.30	3.10−3.40	2.80−3.03
C4	OH...π	3.20	3.20	2.95

To compare the changes in the geometrical parameters revealed for the different complexes, the distance between the oxygen atom of the central H_3O^+ and the center of the π rings ($\pi\cdots H-O$) has been computed in addition to the classical $O-H\cdots O$ hydrogen bond distances in C1. The geometrical parameters are listed in Table 2. Clearly, the classical hydrogen bond distances in C1 are the shortest and are comparable to the distances reported in the literature.[21] The $O-H\cdots\pi$ distances are larger than the $O-H\cdots O$ distances as expected. The MP2 level of theory predicts shorter distances than HF and DFT.

The calculated vibrational frequencies for various complexes are listed in Table 3. It is found that the O−H stretching frequencies of the isolated molecules undergo substantial red shift upon hydrogen bonding. The shift observed in the classical hydrogen bonding is relatively larger than that of $\pi\cdots H-O$ interaction, reflecting their relative strengths.

It was shown in our earlier studies that electron density topographic analysis reveals the additional interactions, which stabilize the intermolecular complexes.[22] Recently, π proton-donor and π proton-acceptor systems were investigated using AIM theory.[23] With a view to characterize and probe the primary and secondary interactions in the solvation of H_3O^+ by P and BZ, a detailed AIM study has been carried out. The electron density topographical features of all the complexes were analyzed in terms of electron density ($\rho(r_c)$) and Laplacian of

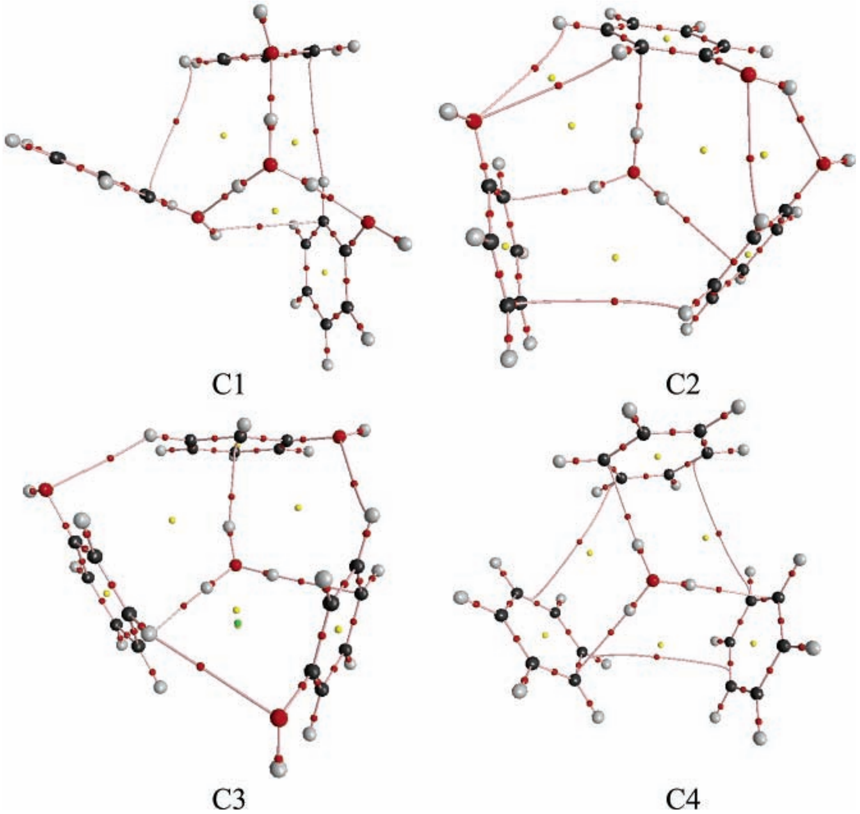

Figure 2. Molecular topography of $H_3O^+-(P)_3$ and $H_3O^+-(BZ)_3$ clusters as obtained from AIM analysis of electron density. Bond critical points are denoted by red dots and the ring critical points by yellow dots.

TABLE 3: Computed (Scaled) Vibrational Frequencies (cm^{-1}) for $-O-H$ in $H_3O^+-(P)_3$ and $H_3O^+-(BZ)_3$ Clusters

	symmetric stretch	asymmetric stretch	H_3O^+ $-O-H$ stretches in clusters	phenol $-O-H$ stretches in clusters
H_3O^+ [a]	3371	3469		
		3469		
phenol[a]	3681			
C1			2908	3630
			2971	3633
			3092	3641
C2			3048	3623
			3182	3653
			3254	3656
C3			3158	3656
			3172	3658
			3186	3659
C4	3221[b]	3230[b]		
		3230[b]		

[a] Isolated molecular vibrational frequency. [b] H_3O^+ vibrational frequency in the $H_3O^+-(BZ)_3$ cluster.

electron density ($\nabla^2\rho(r_c)$) at the bond critical points (BCP) and the results are shown in Figure 2. The magnitude of $\rho(r_c)$ at the hydrogen bond critical points (HBCPs) for the hydrogen-bonded complexes is of the order of 10^{-2} au and $\nabla^2\rho(r_c)$ values are positive (of the order of $\sim 10^{-2}$ au). Similarly, the respective parameters for the π complexes are also of the order of 10^{-2} au with positive $\nabla^2\rho(r)$ values (of the order of $\sim 10^{-2}$ au). It is interesting to note from the AIM molecular graphs that, in C1 complex, in addition to the primary OH$\cdots$O interaction, $\pi\cdots$H$-$C interactions stabilize the intermolecular complex formation. The formation of ring structure in this complex is also evident from the presence of ring critical points (RCPs) in the AIM features. The various secondary interactions present in C2 and C3 structures can be observed from the corresponding molecular topographs. In C2, O$-$H of one phenol molecule interacts with the C$-$H of another P. Three cyclic C$-$H$\cdots$O bonds are also present in the C3 complex in addition to the $\pi\cdots$H$-$O interaction. Although π complexation is similar in C3 and C4, the different secondary interactions play an important role in the stabilization of the $H_3O^+-(P)_3$ complex.

The molecular electrostatic potential maps[24] of different π complexes were obtained from the calculations and are depicted in Figure 3. They show clearly that H_3O^+ is captured by the π clouds of the ring structure in the phenol and benzene molecules.

In summary, classical hydrogen bonding as well as π complexation in the solvation of H_3O^+ by phenol and benzene have been characterized with the help of stabilization energy, AIM theory, red shifts in vibrational stretching frequencies and molecular electrostatic potential maps. Although the π complexation is similar in phenol and benzene, the presence of primary hydrogen bonding and other secondary interactions in the phenol complex results in increased stability. The complexes have the following stability order: C1 > C2 > C3 > C4.

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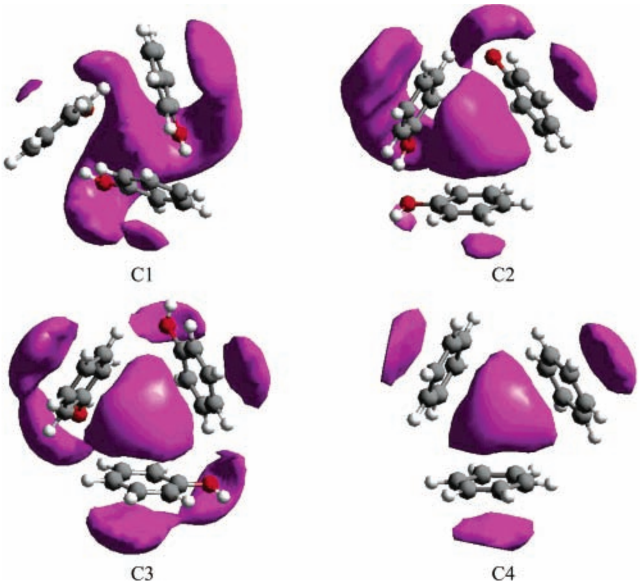

Figure 3. Molecular electrostatic potential isosurface (−0.02 au) of $H_3O^+-(P)_3$ and $H_3O^+-(BZ)_3$ clusters.

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