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π−*π* Interaction in Pyridine

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π−*π* Interaction in pyridine dimer and trimer has been investigated in different geometries and orientations at the ab initio (HF, MP2) and DFT (B3LYP) levels of theory using various basis sets (6-31G*, 6-31G**, 6-311++G**) and corrected for basis set superposition error (BSSE). While the HF and DFT calculations show the pyridine dimer and the trimer to be unstable with respect to the monomer, the MP2 calculations show them to be clearly stable, thus emphasizing the need to include electron correlation while determining stacking interaction in such systems. The calculated MP2/6-311++G** binding energy (100% BSSE corrected) of the parallel-sandwich, antiparallel-sandwich, parallel-displaced, antiparallel-displaced, T-up and T-down geometries for pyridine dimer are 1.53, 3.05, 2.39, 3.97, 1.91, 1.47 kcal/mol, respectively. The results show the antiparallel-displaced geometry to be the most stable. The binding energies for the trimer in parallel-sandwich, antiparallel-sandwich, and antiparallel-displaced geometry are found to be 3.18, 6.14, and 8.04 kcal/mol, respectively.

1. Introduction

The *π*−*π* interaction in aromatic systems has been studied extensively in the past two decades by theoretical methods[1−9] as it plays an important role in the fields of chemistry and biology. It influences the crystal packing of organic molecules containing aromatic rings,[10] the three-dimensional structure of proteins[11] and DNA.[12] It is also important in molecular recognition.[13,14] In organic molecular crystals, it is found that many planar molecules tend to be stacked with an interplanar separation in the range 3.3−3.6 Å.[15] Recent ab initio calculations[16,17] have shown that benzene dimer has two isoenergetic structures (T-shaped and slipped-parallel) with a binding energy of 2.4−2.8 kcal/mol. These calculations emphasize the importance of dispersion interaction. The importance of electrostatic interaction in benzene dimer has also been suggested.[18,19]

Coupled cluster singles and doubles with noniterative perturbative triples (CCSD(T)) calculations using Dunning's augmented correlation consistent polarized valence triple-ζ basis set[20] have predicted the interaction energy of the sandwich configurations of benzene dimer, benzene−phenol, benzene−toluene, benzene−fluorobenzene, and benzene−benzonitrile to be in the range −1.5 to −2.8 kcal/mol. It became clear that the binding energy for all the substituted benzene dimers was greater than that of the benzene dimer. Recently, the binding energy for the mixed dimers of substituted benzene and pyridine in a parallel-slipped geometry has been estimated by Mignon et al.[21] to be in the range of 2.8−4.2 kcal/mol.

However, to the best of our knowledge, the binding energy for pyridine dimer has not been reported to date. Since pyridine and related systems play an important role in biological systems, we have undertaken a detailed electronic structure calculation for pyridine dimer and the trimer at the Hartree−Fock (HF), density functional theory (DFT) and Møller−Plesset perturbation theory of order two (MP2) levels of theory. Details of the method and the results are presented below.

2. Methodology

The Gaussian 03 suite of programs[22] was used for the electronic structure calculations. The geometry of a single pyridine molecule was optimized using MP2/6-311++G**, and then kept frozen in the subsequent single point energy calculations for the dimer and trimer. The basis set superposition error (BSSE) was computed in all cases using the counterpoise corrected method.[23]

3. Results and Discussion

The interaction energies for the pyridine dimer and the trimer in different geometries were calculated by the HF, DFT, and MP2 methods with different basis sets as listed in Table 1 and Table 2. The HF and DFT calculations predict the dimer and trimer to be unstable. However, the MP2 calculations show them to be clearly stable, thus emphasizing the need to include electron correlation while determining the stacking interaction in such systems. The dimer was considered in different geometries as illustrated in Figure 1. The interplanar separation (R) between the pyridine rings was varied, and a potential energy minimum was found in the MP2 calculations at $R = 3.6$ Å for both parallel-sandwich and antiparallel-sandwich geometries. The dimer was also considered in T-shaped geometries and the potential minima were found at $R = 3.4$ Å and at $R = 3.0$ Å, respectively, for the T-up and T-down geometries. Here it must be pointed out that the value of R for the T-up geometry includes the C−H bond distance (1.08 Å). Parallel-displaced geometries were also considered. The parallel-sandwich and antiparallel-sandwich geometries have a binding energy of 1.53 and 3.05 kcal/mol, respectively. The T-up and T-down geometries are relatively less stable with a binding energy of 1.91 and 1.47

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TABLE 1: Interaction Energies (in kcal/mol) for Different Geometries of Pyridine Dimer at Different Levels of ab Initio and DFT Calculations Using Different Basis Sets

basis set	R (Å)	E_{HF}	E_{DFT}	E_{MP2}	E_{MP2} (BSSE corrected)
Pyridine Dimer (Parallel-Sandwich)					
6-31G	3.6	6.19	3.03	−0.60	1.49
6-31G*	3.6	6.02	2.76	−2.14	0.31
6-31G**	3.6	6.00	2.71	−2.39	0.06
6-311++G**	3.6	5.86	3.89	−4.48	−1.53
Pyridine Dimer (Antiparallel-Sandwich)					
6-31G	3.6	4.05	1.23	−2.68	−0.25
6-31G*	3.6	4.28	1.31	−3.61	−1.09
6-31G**	3.6	4.26	1.26	−3.79	−1.3
6-311++G**	3.6	3.99	2.19	−6.10	−3.05
Pyridine Dimer (Parallel-Displaced)					
6-31G	3.6	3.75	1.38	−1.76	0.25
6-31G*	3.6	3.67	1.22	−2.70	−0.61
6-31G**	3.6	3.66	1.18	−2.89	−0.81
6-311++G**	3.6	3.45	2.15	−5.57	−2.39
Pyridine Dimer (Antiparallel-Displaced)					
6-31G	3.6	2.42	0.11	−3.37	−1.18
6-31G*	3.6	2.68	0.18	−4.24	−1.97
6-31G**	3.6	2.68	0.15	−4.37	−2.12
6-311++G**	3.6	2.38	1.01	−7.29	−3.97
Pyridine Dimer (T-Up)					
6-31G	3.4	2.47	0.63	−2.15	0.31
6-31G*	3.4	2.26	0.51	−3.21	−0.79
6-31G**	3.4	2.20	0.46	−3.34	−0.97
6-311++G**	3.4	2.36	1.10	−5.03	−1.91
Pyridine Dimer (T-Down)					
6-31G	3.0	4.17	1.05	−1.95	1.24
6-31G*	3.0	4.52	1.33	−2.52	0.8
6-31G**	3.0	4.49	1.26	−2.52	0.33
6-311++G**	3.0	3.86	2.16	−4.47	−1.47

TABLE 2: Interaction Energies (in kcal/mol) for Different Geometries of Pyridine Trimer at Different Levels of ab Initio and DFT Calculations Using Different Basis Sets[a]

basis set	E_{HF}	E_{DFT}	E_{MP2}	E_{MP2} (BSSE corrected)
Pyridine Trimer (Parallel-Sandwich)				
6-31G	12.48	1.06	−1.78	2.96
6-31G*	12.09	1.33	−4.33	0.6
6-31G**	12.06	1.26	−4.78	0.07
6-311++G**	11.89	2.16	−9.59	−3.18
Pyridine Trimer (Antiparallel-Sandwich)				
6-31G	8.32	2.58	−5.33	−0.46
6-31G*	8.57	2.73	−7.22	−2.17
6-31G**	8.72	2.63	−7.58	−2.60
6-311++G**	8.34	4.57	−12.63	−6.14
Pyridine Trimer (Antiparallel-Displaced)				
6-31G	5.04	0.26	−6.7	−2.31
6-31G*	5.53	0.40	−8.48	−8.77
6-31G**	5.53	0.33	−8.77	−4.26
6-311++G**	5.02	2.17	−14.89	−8.04

[a] The interplanar separation is taken to be 3.6 Å in all cases.

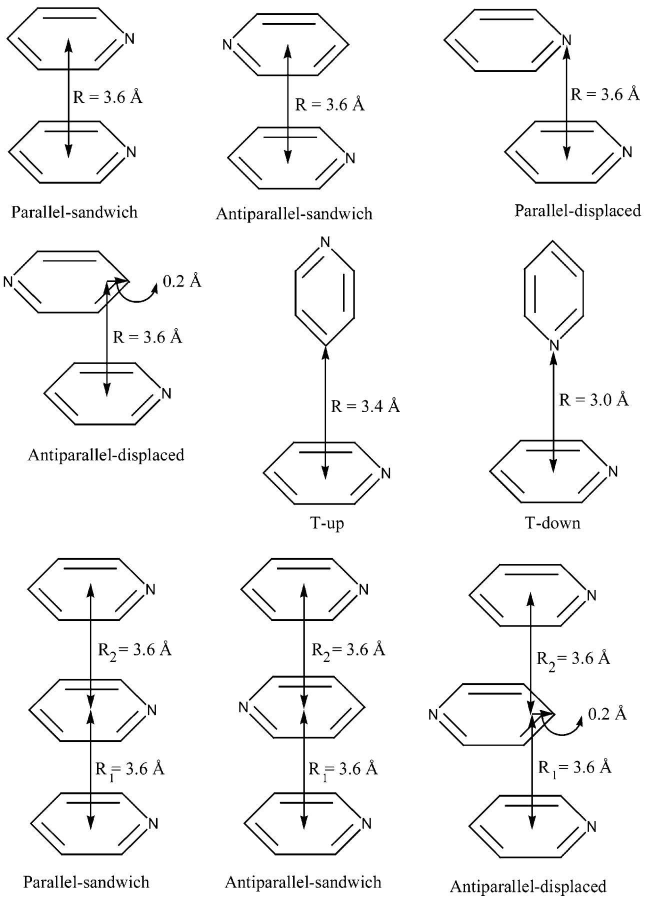

Figure 1. Different geometries of pyridine dimer and trimer.

kcal/mol, respectively. The parallel-displaced and antiparallel-displaced geometries have a binding energy of 2.39 and 3.97 kcal/mol, respectively. Clearly, the antiparallel displaced geometry is the most stable for pyridine dimer.

In the case of pyridine trimer parallel-sandwich, antiparallel-sandwich and antiparallel-displaced geometries were considered. In the antiparallel-displaced geometry, the middle pyridine was displaced with respect to the top as well as the bottom pyridine rings (which are stacked in a parallel configuration) to the same extent as was found in the minimum energy configuration for the dimer, such that it consists of two antiparallel-displaced pyridine geometries. The binding energies for the parallel-sandwich, antiparallel-sandwich, and antiparallel-displaced geometries were found to be 3.18, 6.14, and 8.04 kcal/mol, respectively. These BSSE-corrected values have been computed in the same way as for the dimer using the optimized monomer geometries and the effect of the basis set for the timer on the energy of the monomer. The binding energies of the trimer are seen to be approximately double that of the corresponding dimer configurations. Here it must be pointed out that the heat of vaporization of pyridine liquid is reported to be 8.48 kcal/mol.[24]

In contrast to the stacking interaction in benzene dimer, the stacking interaction in pyridine dimer (and the trimer) is likely to be influenced by the permanent dipole moment of pyridine. Our MP2/6-311++G** calculations predict the dipole moment of pyridine to be 2.44 D, in reasonable accord with the experimental value of 2.22 D.[25] The dipole−dipole interaction for the dimer was computed using the relation[19]

$$\Delta E = -\mu_A\mu_B(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\Phi)/4\pi\epsilon_0 R^3 \quad (1)$$

where θ_A and θ_B refer to the polar angles between the dipole vectors $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ on molecules A and B and the z-axis drawn through the line connecting their centers of mass. The azimuthal angle Φ refers to the difference between the azimuthal angles of $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ with respect to the z-axis. For the parallel-sandwich configuration, $\theta_A = \theta_B = 90°$ and $\Phi = 0°$ and $\Delta E_{\mu\mu} = \mu_A\mu_B/4\pi\epsilon_0 R^3 = 1.84$ kcal/mol. For the antiparallel-sandwich configuration, $\theta_A = \theta_B = 90°$ and $\Phi = 180°$, and hence $\Delta E_{\mu\mu} = -\mu_A\mu_B/4\pi\epsilon_0 R^3 = -1.84$ kcal/mol. For the T-up ($\theta_A = 90°$, $\theta_B = 0°$ and $\Phi = 0°$) and T-down ($\theta_A = 90°$, $\theta_B = 180°$ and $\Phi = 0°$) geometries, the dipole−dipole interaction energy is

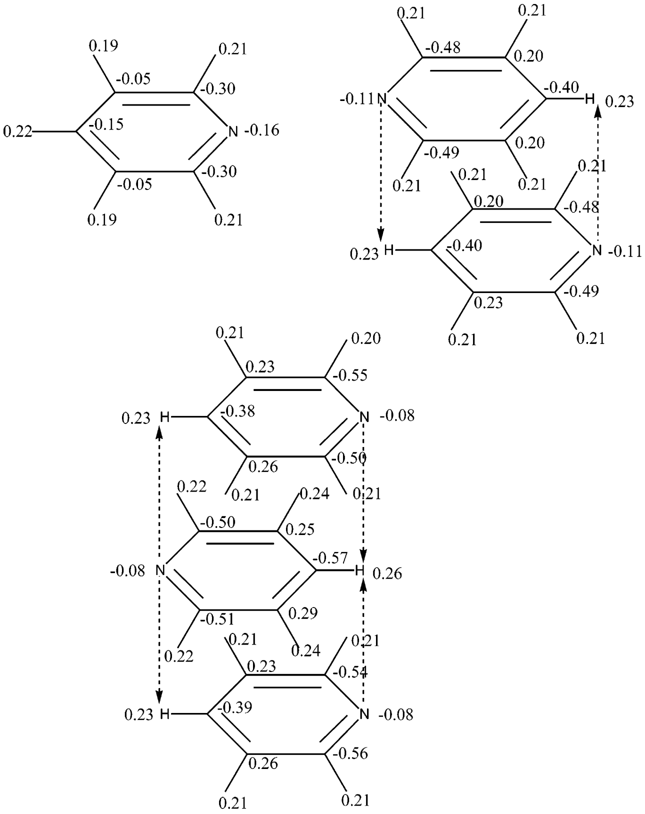

Figure 2. Mulliken charge distribution on atoms in pyridine monomer and the most stable dimer and trimer configurations.

clearly zero. The dipole−dipole interaction for the parallel-displaced and the antiparallel-displaced geometries are found to be 0.92 and −1.11 kcal/mol. Overall, therefore, the dipole−dipole interaction would suggest the antiparallel-sandwich geometry to be the most stable. However, the binding energy computed by MP2/6-311++G** calculations is the largest for the antiparallel-displaced geometry and it is much larger than what is obtained from dipole moment considerations only. For the parallel-sandwich geometry the MP2 calculations show the binding energy to be 1.53 kcal/mol, while $\Delta E_{\mu\mu}$ suggests it to be unstable by 1.84 kcal/mol. Similarly for the antiparallel-sandwich geometry the MP2 binding energy is 3.05 kcal/mol, while $\Delta \mathrm{E}_{\mu\mu}$ is only −1.84 kcal/mol. The binding energy for the mixed benzene−pyridine dimer is estimated to be 2.2 kcal/mol for the parallel-sandwich and 3.5 kcal/mol for the parallel-displaced geometries, even though there is no dipole−dipole interaction in the system. Clearly, dispersion forces arising from electron correlation are much more important than dipole moment considerations. Therefore, it is not surprising that the HF and DFT calculations fail to predict the stability of the pyridine dimer and trimer.

The charge distributions on atoms in the monomer, dimer (antiparallel-displaced), and trimer (antiparallel-displaced) as obtained from Mulliken population analysis are listed in Figure 2. It can be seen that for the antiparallel-displaced geometry of the dimer the positively charged H atom of one ring lies on top of the negatively charged nitrogen atom of the other ring, thus explaining the origin of the most stable geometry of the dimer and also the trimer.

4. Conclusion

MP2 calculations using the 6-311++G** basis set show the antiparallel-displaced geometry to be the most stable for the pyridine dimer with a binding energy of 3.97 kcal/mol (100% BSSE corrected). The binding energy in the antiparallel-displaced geometry for the trimer is found to be 8.04 kcal/mol, in reasonable agreement with the heat of vaporization of 8.48 kcal/mol for pyridine liquid.

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