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Benzene−Water (BZW$_n$ (n = 1 − 10)) Clusters

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The gas-phase geometries, binding energies (BEs), infrared spectra and electron density parameters of benzene (BZ)−water (W) clusters (BZW$_n$, where n = 1−10) have been calculated using Truhlar's meta hybrid functional, M05−2X, employing 6-31+G** basis set. Both basis set superposition error (BSSE) and zero point energy corrected BEs are in close agreement with the previously reported high level ab initio and experimental values. Among all of the BZW$_n$ clusters, the same with inverted book conformer of water hexamer has the highest BE when compared to all other water clusters. The Bader's theory of atoms in molecule (AIM) provides evidence for the presence of O−H···π interactions in all of these clusters. In addition, the roles of C−H···O and lone pair···π (lp···π) interactions in the stabilization of BZW$_n$ clusters are also evident from the AIM analysis. The trend in the electron density at the hydrogen bond critical points varies as O−H···π < lp···π < C−H···O. Spectral signatures of these clusters further reinforce the existence of weak H-bond between BZ and W$_n$ clusters. The red shift in all of these clusters ranges from 13 to 95 cm^{-1}. The results clearly show that the presence of π-cloud does not affect the H-bonded network of water clusters except in the case of W$_6$ ring.

1. Introduction

Noncovalent interactions such as hydrogen bonding (H-bonding) and van der Waals (vdW) interactions are ubiquitous in nature. The importance of these interactions in the stabilization of three-dimensional structure of biological macromolecules, molecular recognition phenomenon, biological activity, chemical reactivity, and supramolecular chemistry has been well documented.[1,2] In addition to the classical H-bonding, the significance of nonconventional H-bonding interactions, such as O−H···π, C−H···O, C−H···π, and N−H···π have been identified.[3] It is interesting to note from the history of structural biology, Ramachandran and co-workers have proposed the presence of C$_\alpha$-H···O H-bonding in the stabilization of proteins (for example collagen).[4]

With a view to understand the conventional and nonconventional H-bonding, numerous experimental and theoretical studies have been carried out.[5] In the nonconventional H-bonding type, O−H···π has received widespread attention.[6] In fact, in most of the previous studies, the interaction of water molecules with BZ have been considered as the prototype model system.[6] High resolution vibrational spectra of these clusters have been reported.[7] Geometries, BEs, and infrared (IR) spectra of BZW clusters have been obtained from different levels of theoretical calculations.[8]

Engdahl and Nelander have first observed the BZW cluster using IR spectroscopy combined with Argon matrix isolation technique.[9] Suzuki et al. have reported the first detailed structural analysis of BZW interaction.[10] Zwier and co-workers have experimentally determined the BEs of BZW complexes.[7] Zwier and Jordan and their co-workers have made seminal contribution to the understanding of BZW$_n$ clusters using both experimental and theoretical methods.[11] Resonant ion-dip infrared spectroscopy (RIDIR), resonant two photon ionization (R2PI) and UV−UV hole burning spectral studies of BZW$_8$, BZW$_9$, and BZ$_2$W$_8$ have been reported combined with density functional theory (DFT) calculation.[7,11]

From computational chemistry perspective, Augspurger et al. have used molecular mechanics for clusters (MMC) to investigate the structures and stabilities of BZW$_n$ (n = 2 to 12) clusters.[8b] Ma et al. have calculated the interaction energy of BZ with W using a variety of electronic structure methods including HF, MP2, CCSD, and DFT with exchange correlation functional with and without empirical vdW corrections as well as quantum Monte Carlo method.[12] Structure and stability of BZW has been calculated using LMP2/6-31+G* level of calculation with a view to quantify the O−H···π and lp···π interactions.[13] It is found from the calculations that the contribution from O−H···π and lp···π interactions are 2.7 and 0.6 kcal/mol, respectively. Information obtained from crystal structure database and CCSD(T) calculations show that both O−H···π and C−H···O interactions play important roles in the stabilization of BZW$_n$ clusters.[14] Results from previous studies further reveal that the interaction between W molecule and aromatic π system is not only stabilized O−H···π interaction, but also by the lp···π interaction.[15] Müller−Dethlefs and Hobza have reviewed the importance of lp···π interaction in these types of systems.[16]

Recently, Kim et al. have summarized results from quantum chemistry calculations on the structures and BEs for BZW$_n$ (n = 1−7) complexes.[6k] It is evident from all of these studies that water interacts with BZ via O−H···π H-bond.[6] In this arrangement, H atom of the W molecule points toward the π-cloud to form O−H···π H-bond. In addition to the BZW$_n$ clusters, studies have been carried out on other π-systems *viz* acetylene,[17a] naphthalene,[17b] styrene,[17c] anthracene,[17f] pentacene,[17f] triphenylene,[17g] coronene,[17f] circumcoronene,[17g] dicircumcoronene,[17g] dodecabenzocoronene,[17f] and graphite.[17d−f]

Jenness and Jordan have used Density Functional Theory-Symmetry-Adapted Perturbation Theory (DFT-SAPT)[17f] to

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investigate the interaction of a water molecules with different acenes. DFT-SAPT calculation gives more accurate interaction energies than supermolecule MP2 calculation and provides the decomposition of the net interaction energy with physically well-defined components, such as electrostatic, exchange-repulsion, induction (polarization), exchange-induction, dispersion, and exchange-dispersion contributions. The results are extrapolated to obtain the interaction energies of a water molecule with infinite graphite sheet. It is found from the density fitting-DFT-SAPT analysis that the electrostatic contribution to the interaction energy significantly decreases in going from BZW to coronene−water. Furthermore, the comparison of coronene−water and dodecabenzocoronene−water reveals that there is no significant difference in their electrostatic contribution to the interaction energy. Only marginal increase in the dispersive interaction energy contribution can be observed from the results with increase in the size of the system. The exchange interaction component to the interaction energy decreases in going from benzene−water to coronene−water. The same contribution for coronene−water and dodecabenzocoronene−water are almost equal. The strength of the geometrical structure with one H atom pointing toward the ring system is 2.2 kcal/mol. The structure with two H atoms are pointed down has been found to be more stable with strength of 2.7 kcal/mol.[17f]

Lin et al. have been performed calculations on graphite−W_n (where $n = 1$ to 6) clusters.[6h] These studies have revealed that W_n cluster on a graphite surface retain the most of the structural motifs of W_n cluster except W_6 ring isomer. The presence of graphite sheet transforms the ring motif to a stable book like structure.

Even though a variety of computational methods have been applied to unravel the weak H-bonded systems in which the dispersive interaction is the predominant one, the MP2 and CCSD(T) methods consistently predict the structure and stabilities of weak complexes. However, due to computational demand, these calculations could not be carried out for larger clusters. While B3LYP method outperforms from the computational economy point of view, the inconsistency in the prediction of structure stability of weak H-bonded and vdW clusters has been reported.[18] With a view to improve the quality of prediction and expanding the applicability of DFT methods, two strategies have been employed: (i) Development of DFT-D methodology and (ii) development of new exchange and correlation functionals.[19,20] Recently, Truhlar and co-workers have made significant contributions to the development of density functionals which are suitable for the investigation of noncovalent interactions.[21]

Although, several studies have been carried out on BZW_n clusters, investigation on the characterization and quantification of O−H···π and lp···π interactions in BZW_n is limited. Hence, a detailed study has been carried out on BZW_n ($n = 1-10$) using hybrid meta DFT based M05−2X method. The structure, stability and IR spectra of various BZW_n (where $n = 1$ to10) clusters have also been calculated using M05−2X/6-31+G** method. In addition, both C−H···O and lp···π interactions in these clusters have been characterized using Bader's theory of Atoms in Molecule (AIM) approach.

2. Computational Details

Water clusters can interact with the BZ in different ways. In most of the case, one of the H atom of W molecule interacts with the π-cloud. Different BZW_n clusters considered in this study are classified based on (i) the donor−acceptor (*DA*) interactions present in the water clusters, (ii) the orientations of the O−H group with reference to the face of the BZ ring, and (iii) the stacking of water clusters with reference to the face of the π-ring.

The geometries of all the clusters were optimized using the DFT with M05−2X functional employing 6-31+G** basis set. M05−2X is a highly nonlocal functional with double the amount of nonlocal exchange (2X) and it is based on simultaneously optimized exchange and correlation functionals both including kinetic energy density.[22] Truhlar and co-workers have found that this functional yields very good performance for applications involving thermo chemistry and noncovalent interactions.[23] The BEs of various complexes were calculated using the following energy expression.

$$|BE| = (E_{\text{Cluster}} - (E_{\text{BZ}}) + (E_{Wn})) \tag{1}$$

Where E_{Cluster}, E_{BZ}, and E_{Wn} are the total energies of BZW_n, BZ, and W_n clusters, respectively. The BEs of all clusters were calculated using the supermolecule approach and corrected for basis set superposition error (BSSE) using the counterpoise (CP) procedure suggested by Boys and Bernardi.[24] Harmonic vibrational frequencies were computed at the same level and scaled by a factor of 0.9445.[25] BEs were also corrected for zero point energies (ZPEs). All calculations were performed using the Gaussian 03 (revision E 0.1) suite of programs.[26] The wave function was generated from M05−2X/6-31+G** calculation using the optimized geometries. The AIM analysis was carried out using the AIM2000 package.[27] The values of electron density ($\rho(r_c)$) and its Laplacian ($\nabla^2\rho(r_c)$) at the bond critical points (BCPs) of H-bonds were used to characterize the weak interactions in the BZW_n ($n = 1-10$) clusters.

3. Results and Discussions

3.1. Geometries of BZW_n Clusters. The optimized geometries of different types of BZW_n (where $n = 1$ to 10) clusters obtained from M05−2X/6-31+G** calculations are presented in Figure 1 along with the H-bonding distances. The O−H···π distance is measured with reference to the center of the BZ ring (x) to the H atom of the donor W molecule. The O−H and O−H···π distances are listed in Table 1. Three different modes of interaction of W with BZ can be seen from Figure 1. These geometrical arrangements are designated as BZW_{1a}, BZW_{1b}, and BZW_{1c}. In BZW_{1a} isomer, one of the O−H bonds directly interacts with the π-cloud of the BZ. The two H atoms form H-bonds with the π cloud in BZW_{1b}. BZW_{1c} is the typical model of the lp···π interaction in which the lone pair of water molecule exclusively interacts with BZ. However, the gradient optimization of the same geometry and frequency calculation reveals that it is a saddle point on the potential energy surface. This observation is in accordance with the recent findings from CCSD(T)/CBS calculation on the same geometry.[15d] O−H···π and O−H bond distances in BZW_{1a} are 2.428 and 0.963 Å, respectively. The O−H···π distance calculated from the earlier MP2/6-31+G(2d,p) and B3LYP/aug-cc-pVTZ calculations for BZW_{1a} are 2.302 and 2.800 Å, respectively. In $BZW_{1b,}$ the O···π distance is 3.284 Å which is in close agreement with the previously reported value of 3.257 Å obtained from MP2/6-31+G(2d,p) calculation. O−H···π distance (2.428 Å) obtained from the M05−2X/6-31+G** method for BZW_{1a} lies between MP2 and B3LYP values. It can be seen from the results that the M05−2X method performs well in the prediction of structure and stability of BZW clusters when compared to B3LYP method. Further, results are in close agreement with

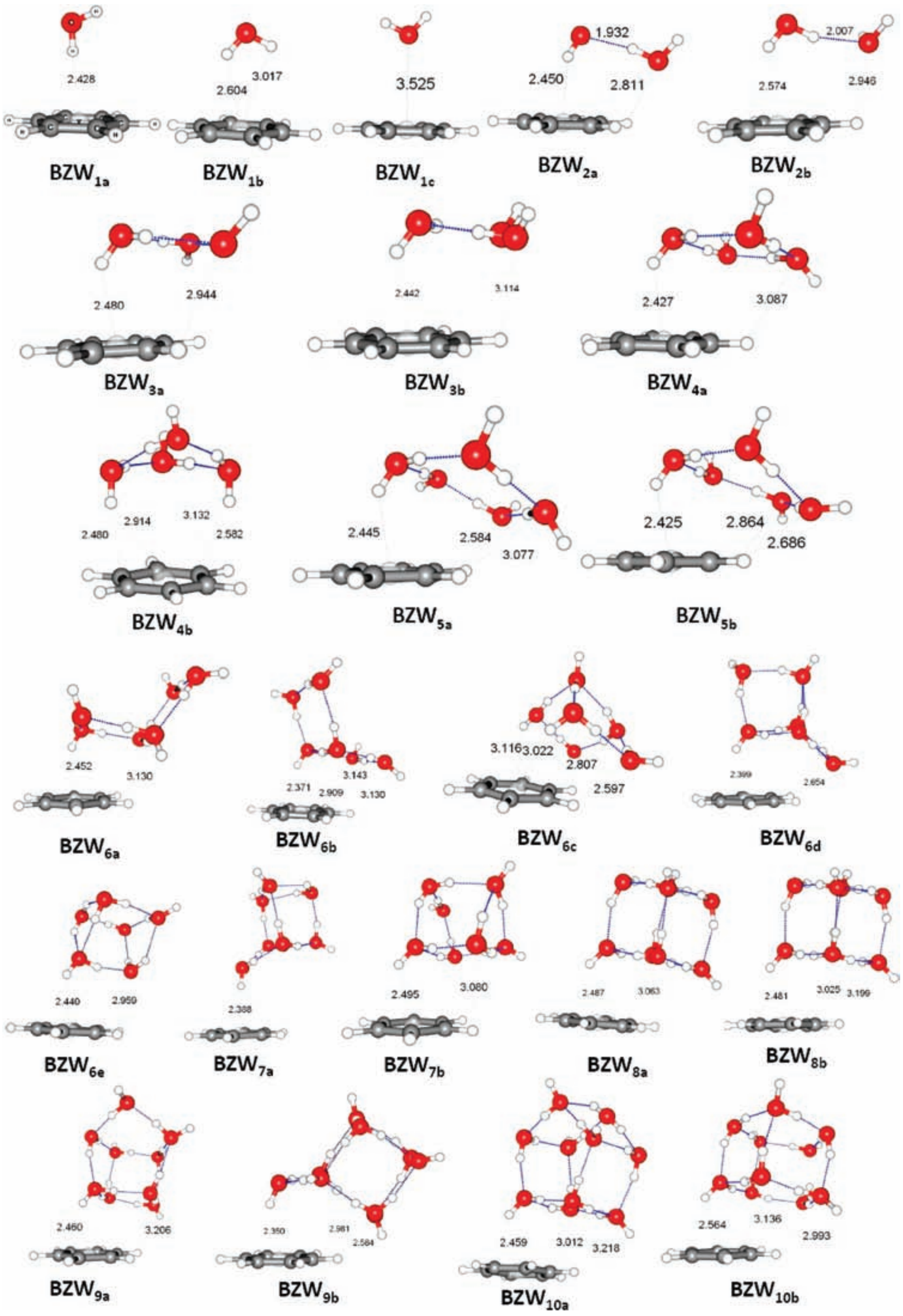

Figure 1. Optimized geometries of BZW$_n$ (where n = 1 to 10) Clusters at M05−2X/6-31+G** Method. Distances are in angstroms. (In BZW$_{1a}$, x is the indicates inversion center of the benzene molecule.)

MP2 geometries and BEs. The success of the M05−2X functional has been attributed to the exchange and correlation functional that include kinetic energy density and that were optimized together.[23]

BZW$_{2a}$ and BZW$_{2b}$ are the two clusters formed by W$_2$ with BZ. The two water molecules in W$_2$ can be differentiated as "donor (D)" and "acceptor (A)". In BZW$_{2a}$, free O−H of A monomer interacts with the face of the BZ ring and C−H forms a C−H···O type H-bond with the D monomer. In BZW$_{2b}$, W$_2$ is bound to BZ through one of the H atoms of D water molecule and via a weak C−H···O type H-bond with the A water molecule. In BZW$_{2a}$, O−H···π and C−H···O distances are 2.450 and 2.811 Å, respectively. When compared to BZW$_{2a}$ longer weak H-bond distances are observed in the case of BZW$_{2b}$. Table 1 shows that M05−2X/6-31+G** results are marginally longer than the MP2/6-31+G(2d,p) value and shorter than the B3LYP/aug-cc-pVTZ value for BZW$_{2a}$ due to the different levels of treatment of electron correlation effects.

Figure 1 reveals that in BZW$_n$ (where n = 3−5) clusters have similar type of DA interactions in the formation of W$_n$ (n = 3−5). Depending on the orientation of the O−H bonds with respect to the BZ ring, different modes of interactions can be observed. W$_3$ cluster consists of single donor (D) and single acceptor (A) H-bonding interactions. Two isomers are possible for BZW$_3$. These clusters are designated as BZW$_{3a}$ (1u) and BZW$_{3b}$ (2u), respectively. In BZW$_{3a}$ (1u), one of the three free

TABLE 1: Calculated Weak H-Bond Distances (in Å) for BZW_n (where n = 1−10) Clusters at M05-2X/6-31+G Level[a]**

BZW_n clusters	H-bonding distances (Å) in BZW_n clusters O−H···π	O···π	O−H	W_n clusters O−H	previous report O−H···π (Å)
BZW_{1a}	2.428	3.391	0.963	0.960	2.302[b], 2.800[c]
BZW_{1b}	2.604	3.284	0.963	0.960	3.257[b] (O···x)
BZW_{1c}		3.525	0.960	0.960	
BZW_{2a}	2.450	3.242	0.962	0.961	2.243[b], 2.937[c]
BZW_{2b}	2.574	3.326	0.966	0.959	
BZW_{3a}	2.480	3.234	0.964	0.959	2.360[b], 3.177[c]
BZW_{3b}	2.442	3.195	0.964	0.960	2.291[b]
BZW_{4a}	2.427	3.174	0.964	0.959	2.912[c]
BZW_{4b}	2.914	3.720	0.963	0.959	
BZW_{5a}	2.445	3.231	0.964	0.959	3.287[c]
BZW_{5b}	2.425	3.169	0.964	0.960	
BZW_{6a}	2.452	3.236	0.964	0.959	
BZW_{6b}	2.371	3.137	0.965	0.960	
BZW_{6c}	3.022	3.849	0.963	0.959	
BZW_{6d}	2.399	3.147	0.965	0.960	2.901[c]
BZW_{6e}	2.440	3.234	0.962	0.960	
BZW_{7a}	2.388	3.351	0.963	0.959	2.925[c]
BZW_{7b}	2.495	3.143	0.964	0.960	
BZW_{8a}	2.487	3.147	0.964	0.960	
BZW_{8b}	2.481	3.141	0.964	0.960	
BZW_{9a}	2.460	3.150	0.964	0.960	
BZW_{9b}	2.350	3.203	0.964	0.959	
BZW_{10a}	2.459	3.152	0.964	0.960	
BZW_{10b}	2.564	3.157	0.964	0.960	

[a] The x- is the inversion center of the benzene ring (see Figure 1); In BZW_{1b} corresponding calculated $W_{O..x}$ distance is 3.284 Å. [b] Taken from ref 6c. The method used was MP2 with 6-31+G[2d, p]. [c] Taken from ref 6k. The method used was MP2 with aug-aug-cc-pVTZ.

O−H bonds orients in the "up" direction with respect to the O···O···O plane. In the other cluster, two free O−H bonds project upward with reference to the same O···O···O plane. Evidences from the O−H···π distances show that W_3 strongly interacts with BZ in the BZW_3 (2u) isomer than the BZW_3 (1u).

Numerous studies have been devoted to understand the structure and stability of W_4.[28] The S_4 symmetric tetrameric cluster is the global minimum on the potential energy surface. In cyclic W_4, each water molecule acts as a single D and single A. The H-bonded ring contains nearly a planar O···O···O···O arrangement with free O−H bonds alternating "up" and "down" orientations with respect to this plane. It interacts with the π-cloud through two different modes leading to the formation of clusters, viz., BZW_{4a} and BZW_{4b}. In the former cluster, the plane formed by the cyclic water cluster is parallel to the π-cloud while in the later one the π-plane is slightly displaced with respect to the face of the BZ ring. Only one O−H···π (2.427 Å) interaction stabilizes the BZW_{4a} isomer where as in BZW_{4b}, the two alternating free O−H groups interact with the π-cloud. The corresponding O−H···π distances are 2.914 and 3.132 Å. The involvement of O−H···π and C−H···O interactions in the stabilization of BZW_5 clusters can be noted from the geometrical parameters. The O−H···π distance in BZW_{5a}(2u) and BZW_{5b}(3u) is 2.445 and 2.425 Å, respectively. In addition to the O−H···π and C−H···O interactions, three lp···π interactions add to the stability of the BZW_{5b}(3u) cluster.

Several experimental and theoretical investigations have been carried out on the structures, BEs and vibrational spectra of isoenergetic W_6.[6b,29] Three dimensional structures in water clusters emerge from W_6 onward. The five lowest-lying isoenergetic conformers are referred to as ring, book, bag, cage, and prism. The number of H-bonds in the ring, book, bag, cage,

TABLE 2: Calculated BEs (in kcal/mol) of BZW_n (where n = 1−10) Clusters at M05-2X/6-31+G Level[a]**

BZW_n clusters (n = 1 to 10)	types of O−H···π interaction in BZW_n clusters	BE (kcal/mol) BSSE corrected	ZPE corrected	earlier studies on BZW_n clusters BEs (kcal/mol)
BZW_{1a}	one O−H bond interact with π cloud (O−H···π)	3.28	2.25	2.55[b], 2.83[c], 3.13[d,e], 3.36[f], 3.02[g]
BZW_{1b}	two OH interaction (OH···π)	3.56	2.83	3.55[h], 3.17[e,g] 3.46[f]
BZW_{1c}	lp···π interactions	0.93	0.69	
BZW_{2a}	$W_{OH\cdots\pi}$ acceptor H-bond (A)	6.28	5.15	4.63[c], 4.38[c], 5.67[h]
BZW_{2b}	$W_{OH\cdots\pi}$ donor H-bond (D)	3.00	2.03	
BZW_{3a}	1up free O−H (DA)	4.64	3.76	3.44[c], 4.66[h]
BZW_{3b}	2up free O−H (*DA*)	5.04	3.98	
BZW_{4a}	$W_{OH\cdots\pi}$ (DA)	4.81	4.58	4.24[h], 4.47[I]
BZW_{4b}	$W_{OH\cdots\pi}$ (DA)	5.00	4.63	
BZW_{5a}	2up free O−H (DA)	5.62	4.39	4.34[h]
BZW_{5b}	3up free O−H (*DA*)	5.99	4.90	
BZW_{6a}	book-edge O−H (DA)	4.55	3.92	
BZW_{6b}	book middle O−H (DAA)	5.99	5.37	
BZW_{6c}	inverted book two O−H (DA)	7.99	6.72	
BZW_{6d}	cage square face (DAA)	6.62	5.65	5.69[h], 4.94[l]
BZW_{6e}	prism square face (DAA)	5.00	4.63	
BZW_{7a}	edge O−H (DA)	3.29	3.05	
BZW_{7b}	square face (DAA)	5.12	4.74	5.49[j]
BZW_{8a}	cube S_4 (DAA)	5.20	4.19	2.41[k]
BZW_{8b}	cube D_{2d} (DAA)	5.24	4.45	2.21[k]
BZW_{9a}	square face (DAA)	5.39	5.01	
BZW_{9b}	pentamer face (DA)	5.58	5.24	
BZW_{10a}	square face (DAA)	5.62	5.11	
BZW_{10b}	pentamer face (DAA)	5.40	4.74	

[a] D and A are H-bond donor and acceptor in water clusters respectively. DA is single donor single acceptor and DAA is single donor double acceptor H-bond in water clusters. [b] Experimental BE of BZW_1 value taken from ref 6f. [c] Taken from ref 6c. The method used was MP2 with 6-31+G[2d,p] method. [d] Taken from ref 5g. The method used was MP2 with aVTZ; [e] Taken from ref 5h. The method used was MP2 with cc-pVQZ; [f] Taken from ref 5h. The method used was MP2(limit); [g] Taken from ref 5h. The method used was $CCSD(T)_{limit}$, [h] Taken from ref 6e. The method used was B3LYP/6-31+G ** and MP2 single point; [I] Taken from ref 6d. The method used was MP2 with aug-cc-pVDZ; [j] Taken from ref 6k. The method used was MP2 with aug-cc-pVTZ; [k] Taken from ref 7c. The method used was B3LYP with 6-31+G[d]; [l] Taken from ref 8d.

TABLE 3: Calculated Total Electron Density ($\rho(r_c)$) and Laplacian ($\nabla^2\rho(r_c)$) at HBCPs in BZW$_n$ Clusters at M05-2X/6-31+G Level (in au)**

BZWn clusters n = 1 to 10	various types of H-bonded bond critical point (HBCP) in between BZ and W$_n$ cluster					
	O−H···π		lp···π		C−H···O	
	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$\rho(r_c)$	$\nabla^2\rho(r_c)$
BZW$_{1a}$	0.0072	0.0063				
BZW$_{1b}$	0.0121	0.0103				
BZW$_{1c}$			0.0028	0.0026		
BZW$_{2a}$	0.0105	0.0083	0.0121	0.0114		
BZW$_{2b}$	0.0054	0.0048	0.0105	0.0092		
BZW$_{3a}$	0.0080	0.0068	0.0089	0.0075		
BZW$_{3b}$	0.0073	0.0061	0.0157	0.0133		
BZW$_{4a}$	0.0080	0.0065	0.0190	0.0160		
BZW$_{4b}$	0.0183	0.0144	0.0043	0.0038		
BZW$_{5a}$	0.0089	0.0073	0.0085	0.0072	0.0144	0.0135
BZW$_{5b}$	0.0090	0.0072	0.0136	0.0117	0.0118	0.0108
BZW$_{6a}$	0.0087	0.0071	0.0082	0.0069	0.0027	0.0023
BZW$_{6b}$	0.0096	0.0076	0.0099	0.0088	0.0034	0.0029
BZW$_{6c}$	0.0180	0.0151			0.0208	0.0199
BZW$_{6d}$	0.0094	0.0074	0.0065	0.0060	0.0130	0.0126
BZW$_{6e}$	0.0141	0.0130	0.0038	0.0035		
BZW$_{7a}$	0.0071	0.0064				
BZW$_{7b}$	0.0089	0.0072	0.0150	0.0125		
BZW$_{8a}$	0.0087	0.0071	0.0088	0.0074	0.0029	0.0025
BZW$_{8b}$	0.0089	0.0072	0.0092	0.0090	0.0029	0.0025
BZW$_{9a}$	0.0088	0.0071	0.0093	0.0061	0.0034	0.0030
BZW$_{9b}$	0.0095	0.0075	0.0055	0.0049	0.0115	0.0107
BZW$_{10a}$	0.0092	0.0073	0.0092	0.0078	0.0029	0.0025
BZW$_{10b}$	0.0089	0.0072	0.0151	0.0127	0.0065	0.0061

and prism are 6, 7, 7, 8, and 9, respectively. Among these, the cage-like structure is found to be the global minimum. In fact, it has been shown that the actual minimum energy structure depends on the level of calculation (with and without many body interaction) and inclusion of ZPE correction. Three kinds of water monomer are present in the W$_6$ single donor single acceptor (DA), single donor double acceptor (DAA), and double donor single acceptor (DDA). The ring structure comprises of six DA types of water molecules. Both book and bag conformers are composed of four DA, one DAA, and one DDA. Two DA, two DAA, and two DDA types of water molecules lead to the formation of cage conformer. The prism is made up of three DAA and three DDA types of water molecules. Previous experimental and theoretical studies on BZW$_6$ clusters show that BZ is H-bonded to three-dimensional surface of the water clusters.[7b]

Book motif interacts with BZ in two possible ways. The BZW$_{6a}$ is composed of two weak H-bonds; one of the edge O−H forms weak H-bond with the BZ ring and C−H of BZ interacts with the O atom of W. The O−H···π and C−H···O distances are 2.452 and 3.130 Å, respectively. The BZW$_{6b}$ contains four weak H-bonds. The middle O−H group of book motif directly forms H-bond with the π-cloud. Further, one C−H···O and two lp···π interactions (3.130, 2.909, and 3.143 Å) are observed. The ring structure stacked onto the benzene undergoes isomerization upon geometry optimization and it forms an inverted book motif. It is interesting to see that the inverted book motif strongly interacts with the π-cloud when compared to the other motifs. This structure is designated as BZW$_{6c}$. Close scrutiny of the geometrical parameters reveals that two O−H···π (3.022 and 3.116 Å) and three C−H···O (2.597−2.807 Å) H-bonding interactions are involved in the stabilization of this cluster. The complexes of BZ with water cage and prism are designated as BZW$_{6d}$ and BZW$_{6e}$, respectively. In BZW$_{6d}$, the O−H···π and C−H···O distances are 2.399 and 2.654 Å, respectively. The BZW$_{6e}$ contains only one O−H···π (2.440 Å) interaction.

The water fraction of BZW$_7$ clusters has more compact, cage-like structure with a DA and DAA water molecules. The O−H···π distances in BZW$_{7a}$ and BZW$_{7b}$ are 2.388 and 2.495 Å, respectively. In addition, C−H···O (3.080 Å) contributes to the stability of BZW$_{7b}$. The W$_8$ has an H-bonded cubic motif. It was first investigated by Stillinger and David.[30] Subsequently, several studies have been carried out on water cube.[7,11,31] There are 14 cubic isomers, each containing 12 H-bonds that differ primarily in the orientations of the H-bonds. Among them S_4 and D_{2d} structures can be considered as a fusion of two cyclic tetramers which are H-bonded by four of the eight dangling O−H groups on the cyclic tetramers. The S_4 and D_{2d} structures differ primarily in the direction of H-bond donation in the tetramer subunit, with donation occurring in the same direction in the S_4 and in the opposite direction in the D_{2d} species. Eight water molecules occupy the corners of cube. All of the water molecules are tricoordinated with four as DAA and four as DDA sites. Although, intrinsic pattern in the H-bonding interaction of S_4 and D_{2d} isomers are different, these clusters interact with BZ in a similar fashion. There is no significant change in the geometrical parameters of BZW$_{8a}$ and BZW$_{8b}$.

The interactions in BZW$_9$ clusters are similar to BZW$_7$. In this cluster, two different types of water molecules interact with π-cloud. The interacting water molecule in the clusters has DAA and DA types of interaction. These clusters referred to as BZW$_{9a}$ and BZW$_{9b}$, respectively. W$_{10}$ cluster consists of two stacked H-bonded pentagons. Two different facial interactions are responsible for the stabilization of the BZW$_{10}$ clusters. Faces of both four- and five-member rings of W$_n$ directly involve in the O−H···π (2.459 and 2.564 Å) interaction.

3.2. Energetics of BZW$_n$ Clusters. The calculated BEs of various BZW$_n$ clusters at M05−2X/6-31+G** level are listed in Table 2. The BEs are corrected for BSSE and ZPE. In

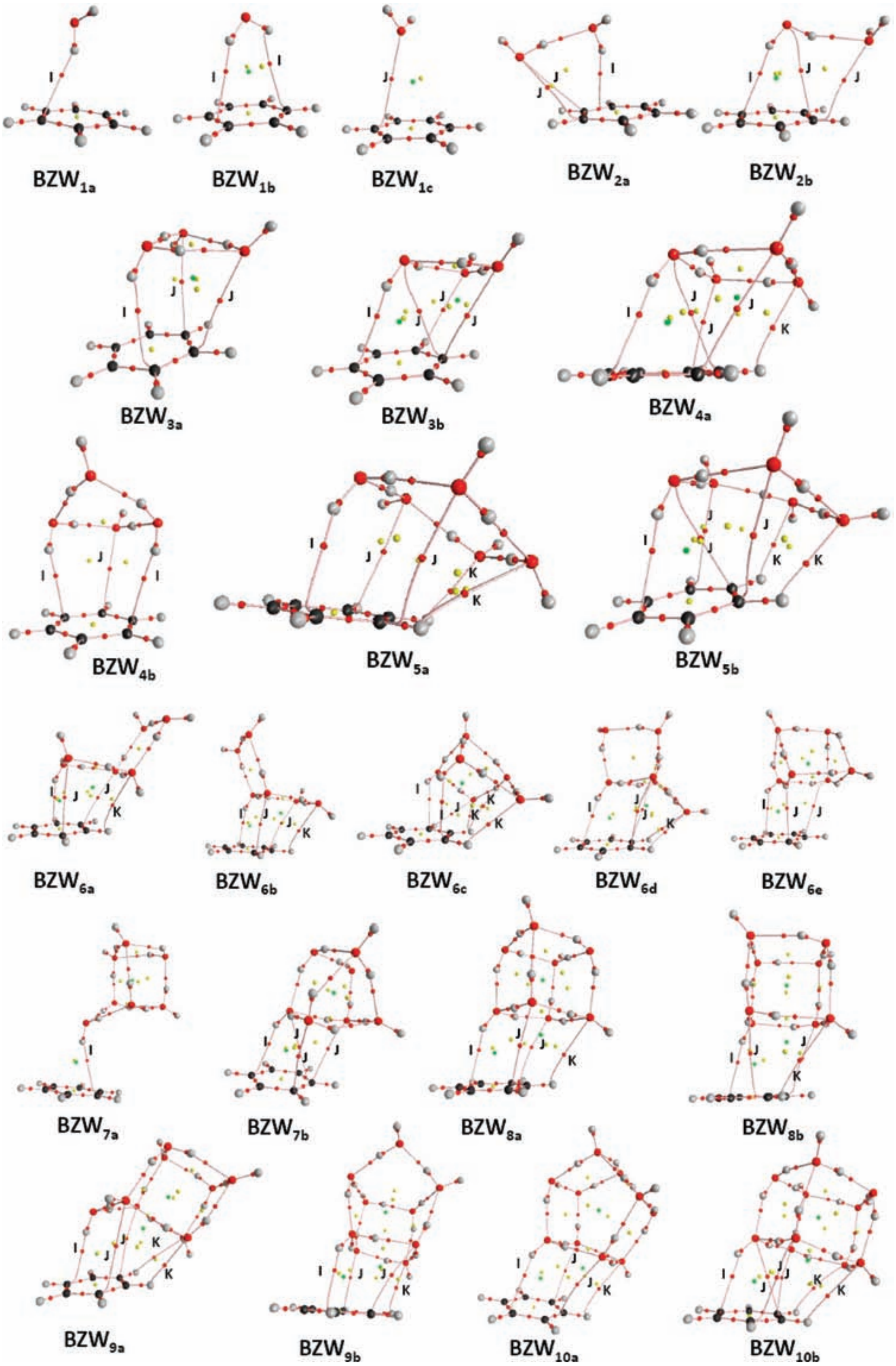

Figure 2. Molecular topography analysis of BZW_n clusters (where $n = 1$ to 10) as obtained from theoretical electron density. Bond critical points (BCP) are denoted by red dots, ring critical points (RCP) denoted by yellow dots and cage critical points (CCP) denoted by green dots. The bond paths corresponding to O−H···π, lp···π, and C−H···O interactions are denoted as I, J, and K, respectively.

addition, BEs obtained from previous theoretical and experimental values are also presented. The BSSE corrected BEs of BZW_{1a} and BZW_{1b} are 3.28 and 3.56 kcal/mol, respectively, which are in good agreement with the previous values obtained from B3LYP, MP2, and CCSD(T) calculations. Both BSSE and ZPE corrected BEs of the BZW_{1a} and BZW_{1b} clusters are 2.25 and 2.83 kcal/mol, respectively. The experimental BE of BZW cluster ranges from 1.63−2.70 kcal/mol. Both BSSE and ZPE corrected BEs of BZW clusters are in close agreement with the corresponding experimental values.

It can be found from the BEs of BZW_{2a} and BZW_{2b} clusters that BZW_{2a} is more stable than the other isomer. In BZW_n ($n = 3−5$) clusters have similar donor−acceptor interactions. The orientation of O−H group with respect to the BZ ring in BZW_3 and BZW_5 are similar and hence their BEs. Particularly, if all of the free O−H groups point "upward" in direction with respect to the face of the BZ, then BEs are larger than the other cluster with free O−H group pointing in the "downward" direction. This evidence clearly shows that the lone pairs of the oxygen atoms favorably interact with the π-cloud, which stabilizes the respective clusters. BEs of BZW_{4a} and BZW_{4b} isomers are 4.81 and 5.0 kcal/mol, respectively.

The BEs of BZW_6 clusters ranges from 4.55−7.99 kcal/mol. Among the six isoenergetic isomers of BZW_6, the inverted book motif (which arises due to the reorganization of the ring isomer) has the highest stability when compared to the other clusters. However, the BE per H-bond (BE/*n*) is the highest for BZW_{6d}. The BEs of BZW_n ($n = 7-10$) vary from 5.10−5.62 kcal/mol except $BZW_{7a.}$ Although, BZW_n ($n = 1-8$) have been investigated by several authors, BZW_9 and BZW_{10} have been investigated in this study for the first time. Basic interactions present in the BZW_7 and BZW_9 are similar and thus their BEs are comparable. The BEs of $BZW_{8a}(S_4)$ and $BZW_{8b}(D_{4d})$ are same due to similarity in the interaction of the tetrameric face with the BZ ring.

3.3. AIM Analysis. The AIM approach is a useful tool to quantify the H-bonding and vdW complexes.[32−36] The calculated values of the sum of electron densities ($\rho(r_c)$) and its Laplacian ($\nabla^2\rho(r_c)$) are presented in Table 3. The calculated values of $\rho(r_c)$ and $\nabla^2\rho(r_c)$ at the H-bonds (designated as HBCP) for all of the clusters range from 0.0054 to 0.0183 and 0.0048 to 0.0144 au, respectively. These values clearly indicate the involvement of weak H-bonding interactions in the stabilization of all the clusters. The molecular graphs of various clusters are shown in Figure 2. The red, yellow, and green dots indicate BCP, RCP, and CCP respectively.

Three bond paths have been observed from the AIM analysis: (a) the bond path connecting H atom of the water molecule and the C atom of the BZ-ring. It represents the O−H···π interaction, and it is denoted as I in the molecular graph. (b) The bond path connecting the O atom of the water clusters and any one of the ring C atom, referred to as lp···π interaction, represented as J in the molecular graph. (c) The bond path between oxygen atom of the water clusters and H atom of the BZ-ring, representing the C−H···O interaction, denoted as K in the molecular graphs. It is clear from Figure 2 that lp···π and C−H···O interactions are found in most of the clusters starting from BZW_{1c}−BZW_{10b}. The $\rho(r_c)$ values for O−H···π, lp···π, and C−H···O range from 0.0054−0.0183, 0.0038−0.0190, and 0.0027−0.0208 au, respectively. The AIM analysis shows that there is no major structural reorganization upon complexzation except in the case of ring isomer of W_6. The calculated electron density at the HBCPs roughly correlates with the strength of interaction.[36]

3.4. Vibrational Spectra of BZW_n (n = 1 to 10) Clusters. The calculated scaled O−H stretching frequencies at M05−2X/6-31+G** level for W_n and BZW_n ($n = 1-10$) clusters are presented in Table 4. It is interesting to note that the O−H group H-bonded to the BZ undergoes red shift. The calculated red shift in all clusters ranges from 13−95 cm^{-1}. Wherever the two O−H bonds participate in the O−H ... π interactions, two red shifts are also observed. The calculated O−H stretching frequencies of O−H···π interactions are in good agreement with the available experimental values of BZW_n clusters.

4. Conclusions

In this work, an attempt has been made to predict the structure and stability of BZW_n ($n = 1-10$) clusters using the M05−2X/6-31+G** level of calculations. Wherever possible, the results are compared with the B3LYP, MP2, and CCSD(T) methods. It is found that calculated geometrical parameters lie between the MP2 and B3LYP values. Further, calculated BEs are in close agreement with the MP2 and experimental values. The AIM analysis of all of the clusters clearly reveals the presence of O−H···π interaction in all the clusters. In addition, lp···π and C−H···O are evident from the presence of HBCPs. These interactions add to the stability of various clusters. It can be observed that the presence of π cloud does not affect the H-bonded network of water clusters except in the case of ring isomer of the W_6. A similar observation has also been found in the previous investigation on the W_6···graphite sheet interaction. The calculated red shifts in the O−H stretching frequencies further reinforce the presence of weak H-bonding interaction in all the clusters.

TABLE 4: Calculated π H-Bonded O−H Stretching Vibrational Frequencies of BZW_n and W_n (where $n = 1-10$) Clusters at M05-2X/6-31+G Level Along with Experimental and Corresponding Red Shifted Frequency (in cm^{-1})[a]**

BZW_n (n = 1 to 10)	vibrational frequencies (cm^{-1})			
	BZW_n	W_n	red shift	expt[b]
BZW_{1a}	3667	3680	13	3634
BZW_{1b}	3660	3680	20	
BZW_{2a}	3625	3678	53	3608
BZW_{2b}	3739	3772	33	
BZW_{3a}	3696	3751	55	3657
BZW_{3b}	3695	3751	56	
BZW_{4a}	3676	3764	88	3652
BZW_{4b}	3701	3764	63 & 79	
BZW_{5a}	3681	3764	83	3646
BZW_{5b}	3669	3764	**95**	
BZW_{6a}	3683	3765	82	3639
BZW_{6b}	3660	3747	87	
BZW_{6c}	3694	3765	71 & 75	
BZW_{6d}	3668	3758	**90**	
BZW_{6e}	3722	3762	40	
BZW_{7a}	3699	3764	65	3636
BZW_{7b}	3679	3751	72	
BZW_{8a}	3678	3755	77	3649
BZW_{8b}	3679	3760	81	3650
BZW_{9a}	3680	3752	72	3644
BZW_{9b}	3669	3763	**94**	
BZW_{10a}	3674	3754	80	
BZW_{10b}	3683	3754	71	

[a] Experimental O−H stretching frequencies of BZW_n clusters. [b] Taken from ref 6c for n = 1 to 3 and other cluster taken from ref 7 and ref 11.

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