Structure and Stability of Water Chains $(H_2O)_n$, $n = 5-20$[†]

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The structure and stability of linear (helical) water chains $(H_2O)_n$, $n = 5-20$ as obtained from ab initio/DFT calculations are reported along with an atoms-in-molecules (AIM) analysis of hydrogen bond critical points and their characteristics. The resulting helical chain arrangement is one of the predominant motifs in different host environments; although they may not be the most stable, it is shown that these linear water chain clusters could exist in their own right.

1. Introduction

The stability and structural features of water clusters continue to be the subject of active research due to their importance in various branches of science. The classic example of a hydrogen bond (H-bond) possibly arises between two water molecules in water dimer.[1−16] Vibration−rotation tunneling spectroscopic studies suggest that the water trimer is a chiral trigonal cyclic structure and the tetramer and the pentamer form square planar and slightly nonplanar pentagonal structures.[17,18] The real three-dimensional (3D) (cage/prism) structure seems to arise for the hexamer.[19] Hexameric water clusters adopt cyclic ring, bag, prism, cage and book structures. Theoretical calculations predict at least four nearly isoenergetic isomers for the hexamer.[19] The actual minimum energy structure obtained depends on the rigor of calculation and inclusion of zero point energy (ZPE) correction.[16] Recent studies suggest that the hexamer could form an open book structure too.[20] For $n = 7$, a cubelike structure with a corner missing is found to be the most stable. This structure has ten H-bonds and has a SE of 60.5 kcal/mol at the HF/6-31G(d,p) level, with a dipole moment (μ) of 1.35 D.[16] IR spectroscopic studies of water clusters under supersonic nozzle expansion conditions suggest a cubic structure for the octamer and a pentagonoid structure for the decamer. Good quality ab initio calculations predict the structure and stability of water clusters with near quantitative accuracy. They take us beyond what is easily obtained experimentally. The 12-mer, 16-mer and 20-mer of water molecules seem to prefer stacked cubes and stacked pentagons.[16] The much anticipated buckyball structure is not the most stable for the 20-mer!

Plummer has investigated the applicability of semiempirical potentials to study the small water clusters having cubic structures.[21] Wales employed empirical potentials to simulate water clusters with $n \leq 21$.[22] Extensive ab initio calculations have been performed using the HF/6-31G(d,p) and 6-311++G(2d,2p) methods for several possible and the most stable structures of water clusters $(H_2O)_n$, $n = 8-20$ in recent past.[16] It was found that the most stable geometries arise from a fusion of tetrameric and pentameric H-bonded rings.

Water clusters in various host environments have been studied with a view to understand the different structures exhibited by water clusters in a confined environment. Recently, ab initio calculations on clathrate-like water clusters with buckminsterfullerene as the guest species have been carried out by Ludwig and Appelhagen.[23] The effect of spatial confinement on the properties of water and other isoelectronic molecules has been studied by encapsulating them in a C_{60} fullerene cage.[24]

It is well-known from the crystal structure database that water molecules play different roles in the stabilization of these structures and exhibit a variety of geometries in the crystal structures and confined environments. An analysis of Cambridge crystal structure database reveals the role of water molecules in the stabilization of various organic and inorganic compounds. The presence of one to many water molecules in most of these structures has been reported.[25] The surge of recent activity in the supramolecular chemistry exemplifies the role played by H-bonding interaction and water clusters in different host environments. Overall, these studies indicate that water clusters could assume different arrangements under different crystal environments.[26−33]

Atwood and co-workers have reported the $(H_2O)_{10}$ water cluster in the supramolecular complex of Cu and Co.[27,28] Six water molecules, for example, form a planar hexagon in an organic supramolecular complex of bimesityl dicarboxylic acid.[34] Ghosh and Bharadwaj have shown that the hexamer could form a chair as well as a boat configuration in a metal−organic framework.[35] Larger clusters seem to assume different structures depending on the molecular environment.[36,37] There are only a few examples in the literature on the water helical assemblies. Helical water chain in aquapores of tribromophloroglucinal was observed in a recent study by Saha and Nangia.[38] In another study, the supramolecular self-assembly of a dicopper(II) complex acts as a helical template in the formation of an unprecedented type of helical one-dimensional (1D) chain of water molecules and the crystal structure of the complex illustrates a synthetic model for the water chains in helical membrane proteins.[38,39] Because different water clusters exhibit different structures under different conditions, it is worth comparing the H-bonding pattern in helices with the different

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cage and cyclic structures formed by the water molecules. Furthermore, 1D (linear or helical) water clusters are observed in the X-ray diffraction studies of crystals of organic and inorganic molecules. The prevalence and importance of linear water clusters in protein structures has been demonstrated in numerous studies. These conformations of water molecules are essential for biological activity. Hence, theoretical studies have been undertaken to explore the stability of these linear water clusters.

2. Computational Details

In the present study, the geometries of the $(H_2O)_n$, $n = 5-20$, clusters were optimized starting from linear chain-like structures without any constraint using the basis set 6-311++G** at Hartree−Fock (HF) and density functional theory (DFT) with B3LYP parametrization levels of theory using the G98W suite of programs.[40] In each case, the optimization yielded an energy minimum retaining the linear helical wire-like structure, which was then employed to calculate the harmonic vibrational frequencies. Stabilization energies (SE) of all the clusters were calculated using the supermolecule approach and corrected for basis set superposition error (BSSE) following the procedure adopted by Boys and Bernardi.[41]

$$\mathrm{SE} = -\left(E_{\mathrm{cluster}} - \sum_{i=1}^{n} E_i\right) \tag{1}$$

where E_{cluster} is the total energy of the cluster, E_i is energy of the monomer and n is the total number of monomers in the cluster. Specifically, BSSE was estimated for each monomer in its location by computing its energy with its own basis set and with basis set for $(n - 1)$-mer. The theory of AIM[42] was used to characterize the H-bonding interaction using topological properties of the electron density map at the H-bond critical points (HBCPs) using the AIM2000 package.[43] The sum of the electron density as well as the Laplacian of the electron density at the HBCPs of all the water helical chains was plotted against the stabilization energy to establish a relationship between topological parameters and the strength of H-bonding. A systematic comparison was also made with the most stable water clusters.

3. Results and Discussion

Stability of Water Chain. The optimized minimum energy molecular structures of linear $(H_2O)_n$ ($n = 5-20$) clusters are shown in Figure 1. Interestingly, these water clusters form a linear helical chain motif even in the absence of host molecules/scaffolds. All of them have $(n - 1)$ H-bonds. It is worth emphasizing here that the starting linear chain geometries were fully optimized without any structural constraints. Yet, cyclization or formation of cage/prism structures was not observed at the HF and B3LYP(DFT)/6-311++G** levels of theory. This suggests that some external influence or a driving force is needed to facilitate the self-assembly of one-dimensional water clusters to three-dimensional structures.

The SE values computed for various H-bonded water chains at different levels of theory using the 6-311++G** basis set are reported in Table 1. Geometry optimization using the HF and DFT/B3LYP levels of theory yielded similar stable linear conformations. However, MP2/6-311++G** calculations for $(H_2O)_{5-7}$ clusters led to the formation of open faced prism-like structures and a combination of trigonal cyclic and square planar arrangements and also spiro-cyclic assemblies.[44b] Linear clusters of $(H_2O)_8$ to $(H_2O)_{12}$ remained linear even after geometry optimization using MP2/6-311++G** calculations, thus suggesting the possibility of the existence of long linear water clusters without any scaffold. Due to computational limitations, only single-point calculations were carried out at the MP2 level of theory for clusters ranging from $(H_2O)_{13}$ to $(H_2O)_{20}$ using the geometrical parameters obtained from DFT(B3LYP)/6-311++G** calculations. In general, HF and DFT calculations predict slightly lower SE values than MP2 calculations without BSSE corrections, whereas BSSE corrected SE values predicted by the MP2 method lie in between the HF and DFT results.

The SE values for the linear water chains along with the corresponding values for the most stable 2D and 3D structures are listed in Table 2. The number of H-bonds and the strength per H-bond for the various clusters are also listed in Table 2. It is clear that for any water cluster the (linear) helical structure is energetically less stable than the most stable 3D structure. However, the SE/n value is significantly larger (5.3−6.5 kcal/mol) for the linear water clusters than (3.8−5.6

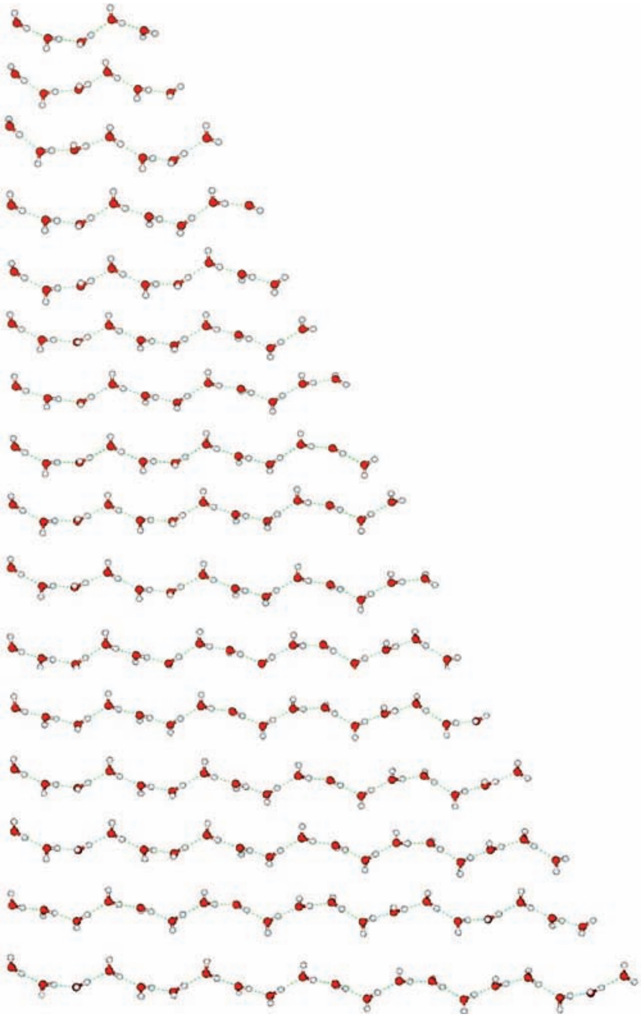


Figure 1. Optimized molecular structure of linear water clusters $(H_2O)_n$, $n = 5-20$.

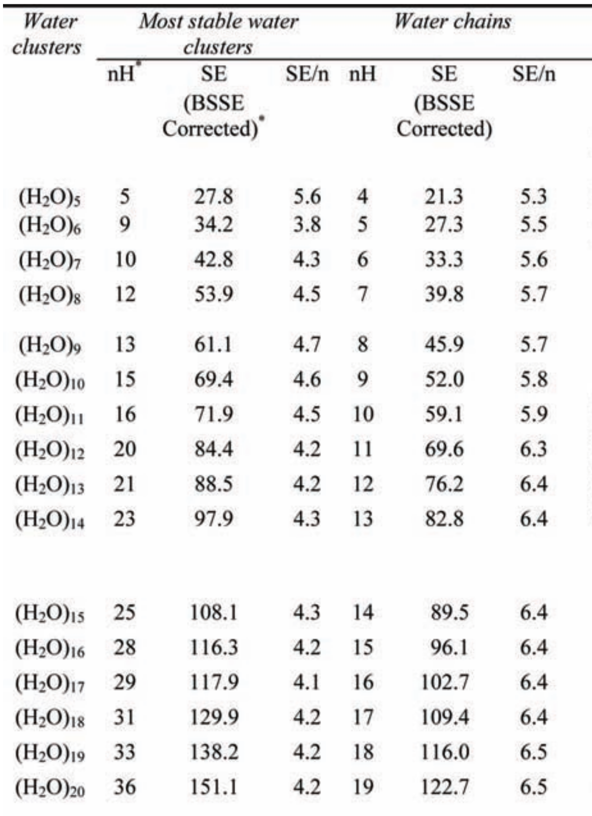
Figure 2. Molecular electrostatic potential maps generated for the HF/6-311++G** optimized structures of the $(H_2O)_{20}$ chain at the ±0.05 au isosurface. Red represents the negative potential, and blue, the positive potential.

TABLE 1: Stabilization Energies (kcal/mol) of $(H_2O)_n$, $n = 5-20$, at Various Levels of Theory Using the 6-311++G Basis Set, for the Most Stable Water Chains**

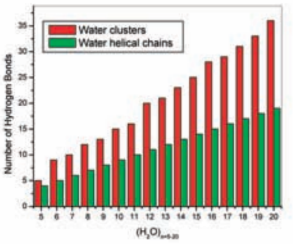
	stabilization energies					
	HF		DFT(B3LYP)		MP2[a]	
water chains	BSSE uncorrected	BSSE corrected	BSSE uncorrected	BSSE corrected	BSSE uncorrected	BSSE corrected
$(H_2O)_5$	23.5	21.3	29.2	26.2		
$(H_2O)_6$	30.1	27.3	37.4	33.8		
$(H_2O)_7$	36.6	33.3	45.6	41.4		
$(H_2O)_8$	43.2	39.8	53.9	49.0	55.2	42.2
$(H_2O)_9$	49.9	45.9	62.2	56.7	63.7	48.8
$(H_2O)_{10}$	56.5	52.0	70.6	64.5	72.2	55.4
$(H_2O)_{11}$	63.2	59.1	78.9	72.4	80.8	62.0
$(H_2O)_{12}$	69.9	69.6	87.3	81.0	89.3	68.7
$(H_2O)_{13}$	76.6	76.2	95.7	88.9	*97.1*	*77.2*
$(H_2O)_{14}$	83.3	82.8	104.2	96.9	*105.6*	*84.01*
$(H_2O)_{15}$	90.0	89.5	112.6	104.8	*114.1*	*90.9*
$(H_2O)_{16}$	96.7	96.1	121.0	110.9	*122.6*	*97.7*
$(H_2O)_{17}$	103.4	102.7	129.4	118.7	*131.1*	*104.6*
$(H_2O)_{18}$	110.1	109.4	137.9	126.6	*139.6*	*111.4*
$(H_2O)_{19}$	116.8	116.0	146.3	134.4	*148.1*	*118.3*
$(H_2O)_{20}$	123.5	122.7	154.7	142.1	*156.7*	*125.1*

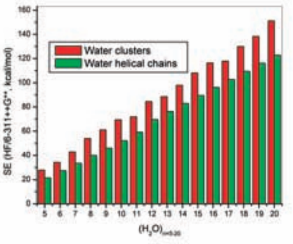
[a] For $(H_2O)_{13}$ to $(H_2O)_{20}$ *single-point energy calculations* carried out at the MP2/6-311++G** level using B3LYP/6-311++G** optimized geometries.

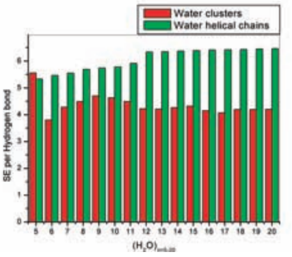
TABLE 2: Number of H-Bonds (nH), Stabilization Energies (SE, kcal/mol), and SE per H-Bond for the Most Stable Water Clusters and Water Chains As Obtained from HF/6-311++G Calculations**



Water clusters	*Most stable water clusters*			*Water chains*		
	nH*	SE (BSSE Corrected)*	SE/n	nH	SE (BSSE Corrected)	SE/n
$(H_2O)_5$	5	27.8	5.6	4	21.3	5.3
$(H_2O)_6$	9	34.2	3.8	5	27.3	5.5
$(H_2O)_7$	10	42.8	4.3	6	33.3	5.6
$(H_2O)_8$	12	53.9	4.5	7	39.8	5.7
$(H_2O)_9$	13	61.1	4.7	8	45.9	5.7
$(H_2O)_{10}$	15	69.4	4.6	9	52.0	5.8
$(H_2O)_{11}$	16	71.9	4.5	10	59.1	5.9
$(H_2O)_{12}$	20	84.4	4.2	11	69.6	6.3
$(H_2O)_{13}$	21	88.5	4.2	12	76.2	6.4
$(H_2O)_{14}$	23	97.9	4.3	13	82.8	6.4
$(H_2O)_{15}$	25	108.1	4.3	14	89.5	6.4
$(H_2O)_{16}$	28	116.3	4.2	15	96.1	6.4
$(H_2O)_{17}$	29	117.9	4.1	16	102.7	6.4
$(H_2O)_{18}$	31	129.9	4.2	17	109.4	6.4
$(H_2O)_{19}$	33	138.2	4.2	18	116.0	6.5
$(H_2O)_{20}$	36	151.1	4.2	19	122.7	6.5







* Reference 16.

kcal/mol) for the more stable nonlinear geometries. As the length of the helical chain increases, SE/*n* increases monotonically. Such a behavior is not seen in the case of more stable structures because different H-bonds have slightly different strengths.[44a,45a] Recently, the cooperativity effect that enhances halogen bonding has been analyzed in model systems.[46a] When compared to halogen bonding, the cooperativity effect in H-bond interaction is well-known and has been the subject of several studies.[47] It was found that when cooperativity effect enhances H-bond interaction, the covalent character increases and the electrostatic character becomes less important.[46]

TABLE 3: OH Stretching Frequencies, Dipole Moment, and Polarizability of Water Chains As Obtained from HF/6-311++G Calculations**

	frequency (cm^{-1})			
water chains	H-bonded O−H stretch	free O−H stretch	dipole moment (D)	polarizability (au)
$(H_2O)_5$	3566−3627	3692−3781	8.59	34.58
$(H_2O)_6$	3556−3624	3691−3780	10.3	41.70
$(H_2O)_7$	3547−3623	3692−3781	12.4	48.83
$(H_2O)_8$	3541−3623	3692−3781	15.0	55.96
$(H_2O)_9$	3537−3623	3692−3781	17.0	63.09
$(H_2O)_{10}$	3532−3623	3692−3781	19.1	70.22
$(H_2O)_{11}$	3531−3623	3692−3781	21.5	77.35
$(H_2O)_{12}$	3528−3623	3692−3781	23.6	84.49
$(H_2O)_{13}$	3526−3623	3692−3781	25.7	91.63
$(H_2O)_{14}$	3524−3623	3692−3781	28.1	98.76
$(H_2O)_{15}$	3523−3623	3692−3781	30.3	105.9
$(H_2O)_{16}$	3522−3623	3692−3781	32.3	113.0
$(H_2O)_{17}$	3522−3623	3692−3781	34.7	120.2
$(H_2O)_{18}$	3521−3623	3692−3781	36.9	127.3
$(H_2O)_{19}$			39.0	
$(H_2O)_{20}$			41.3	

For $n = 5$, the most stable structure is puckered. The linear chain of $(H_2O)_5$ is an extended form of (water dimer)$_2$ = $(H_2O)_4$ by the addition of a water molecule, with a SE of 21.3 kcal/mol at the HF level of theory. It has four H-bonds of strength of 5.3 kcal/mol per bond as shown in Figure 1. Both experimental and theoretical results confirm that, for $n = 6$, the cage structure is the most stable structure. Our calculations show that the formation of a linear hexameric chain is possible with a higher SE/n. In the case of the chain structure, the SE/n is 5.5 kcal/mol, which is higher (by 1.7 kcal/mol) than that of the most stable 3D structure. For the longer chain structures (n = 7−20), the SE per H-bond is 1−2.3 kcal/mol higher than that for the most stable structure of the same n-mer. It is worth pointing out that, with an increase in the size of the water cluster, there is an increase in the number of H-bonds and hence, an increase in the SE. A careful analysis of SE/n values reveals that it increases slightly with an increase in n till $n = 11$; then there is a larger increase in going from $n = 11$ to $n = 12$. With further increase in n, the increase in SE/n is only 0.01−0.02 kcal/mol. The fact that there is a steady increase in SE/n in going from $n = 5$ to $n = 12$ is a clear indication of cooperativity effect in hydrogen bonding.[46,47]

Geometrical Analysis of Water Chain. Details of the calculated geometrical parameters such as covalent OH bond distances, H-bonded (OH···O) distances and end-to-end distances of water helical chains at both HF and DFT(B3LYP) levels of theory using the 6-311++G**basis set are provided in Table S1 in the Supporting Information. It is important to point out that the H-bond distances (O−H···O) in the middle of the water chain are shorter than those at the ends. As the length of the helical chain increases, the compression in the H-bond distances in the middle of the chain also increases. Overall, the trends in the geometrical parameters obtained from both levels of theory are similar. The OH bond that is not involved in a H-bond is referred to as "free" hydrogen, and it has a bond distance of 0.94 and 0.96 Å at the HF and DFT level of theory, respectively. The one that is involved in a H-bond is in the vicinity of 0.95 and 0.98 Å. Free O−H and H-bonded O−H distances are nearly equal in all the clusters; however, the HF values are consistently lower than the DFT values. DFT calculations tend to predict slightly stronger and shorter H-bonds than HF, as can be seen from the H-bonding distances and the calculated end-to-end distances $(H_2O\cdots OH_2)_{1-n}$.

Vibrational Spectral Analysis of Water Chain. With a view to characterize the H-bonding interaction in water chains, the OH vibrational frequencies have been calculated at the HF/6-311++G** level and scaled by a factor 0.8929[48] and are presented in Table 3. A strong H-bond normally results in a red shift of the O−H stretching frequency of the order of a few hundred cm^{-1} units. The red shift observed for the linear chains increases with increase in the chain length. Dipole moment and polarizability values for the various water chains are also listed in Table 3. Both of them increase with increase in the chain length.

Molecular Electrostatic Potential of Water Chain. The molecular electrostatic potential (MESP) map of the linear water 20-mer chain is shown in Figure 2. Clearly, the free oxygen atom at the left end of the chain and the free hydrogen atom at the right end of the chain exhibit strong negative and positive potentials, respectively. This means that they are available for further interaction, as are the noninteracting hydrogen atoms along the H-bonded water chain. The region around the interacting "lone pair" of each oxygen atom and the interacting hydrogen of each water molecules are

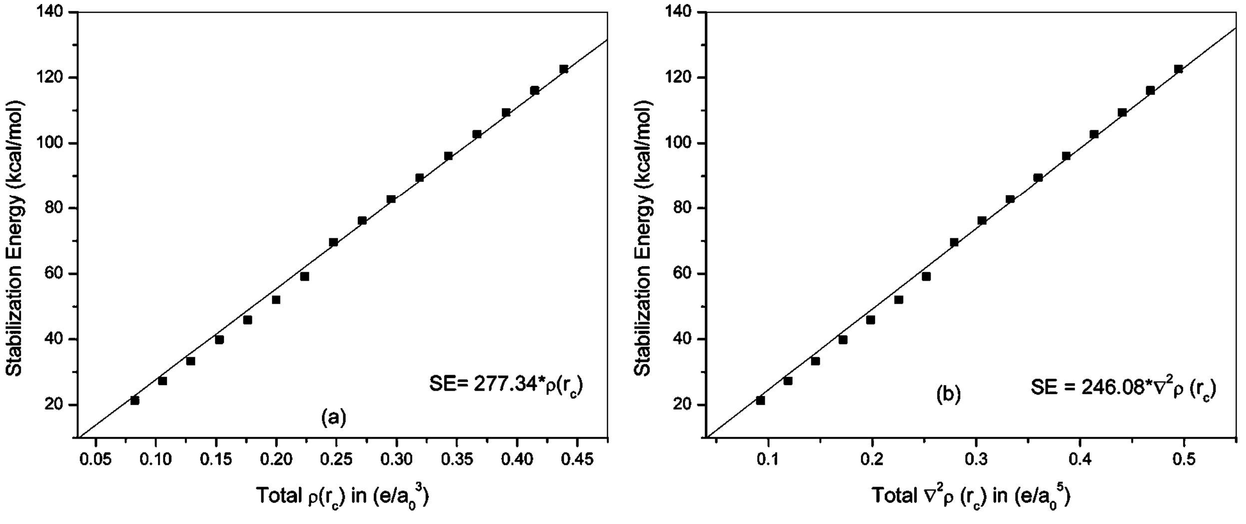


Figure 3. Relationship between SE (HF/6-311++G**) and (a) the sum of the $\rho(r_c)$ values and (b) the sum of the $\nabla^2\rho(r_c)$ values for water chains $(H_2O)_{n=5-20}$.

"neutralized" by the interaction and are no longer available for further interaction. A cavity/scaffold with a complementary electrostatic potential would significantly stabilize the 1D structure.

AIM Analysis of Water Chain. The theory of atoms-in-molecules has been applied to a study of H-bonds in a variety of systems.[42,44a,45,49] The calculated electron density and its Laplacian at the H-bond critical points (HBCPs) are listed in Table S2 of Supporting Information. The calculated electron density values for the middle region ($\sim$0.023 e/a_0^3) are marginally higher than that for the terminal ones ($\sim$0.019e/a_0^3). The positive values of the Laplacian of the electron density also follow a similar trend. These values are in accordance with the standard values reported for hydrogen bond interactions.[42] They also show that the H-bonds in the middle of the chain are slightly stronger than the peripheral ones.

There are several reports on the use of electron density and its Laplacian as a descriptor to quantify the strength of H-bonds.[44a,45,49,50] It was reported earlier that the sum of the $\rho(r_c)$ values at the HBCPs in the water clusters is a measure of the strength of the H-bonds and that it increases linearly with SE.[49] The sum of the $\rho(r_c)$ values and the sum of the $\nabla^2\rho(r_c)$ values for linear $(H_2O)_n$ clusters are listed in Table S2 (Supporting Information) and also plotted in Figure 3. These values are significantly less than that of the most stable water clusters and hence suggest a lesser stability for the 1D water helices. It may be noted that not all H-bonds in the nonhelical clusters are equivalent and that they exhibit slightly different properties as reflected in the AIM, NMR, and NBO analysis.[44a,45a]

4. Conclusion

In summary, the stability of a linear chain of water molecules $(H_2O)_n$, $n = 5-20$ has been investigated using HF, DFT and MP2 levels of theory and compared with the stability of the corresponding most stable 2D and 3D water clusters. An analysis of the stabilization energy, the red shift in O−H stretching frequencies, electron density properties and the MESP map reveals that these H-bonded water chains are stable by themselves, even though there exist more stable 2D and 3D water clusters. Appropriately designed cavity/scaffold/host systems based on MESP complementarity could, of course, add to the stability of these linear clusters.

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Supporting Information Available: Geometrical parameters of water chains as obtained from HF and DFT(B3LYP)6-311++G** calculations (Table S1) and the range of electron density ($\rho(r_c)$) and the Laplacian of electron density ($\nabla^2\rho(r_c)$) values for water chains of varying length and also for the most stable water clusters (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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