

Structure, Stability and Interaction Studies on Nucleotide Analogue Systems

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Abstract: Most of the biological molecules have a good interaction with water molecules. The hydrogen bonding interactions with the structural analogues of nucleic acid phosphate group namely dimethyl phosphate anion (DMP) and diethyl phosphate anion (DEP) are studied employing the ab initio and density functional theory methods. Inspections have been made to locate the reactive sites for the interactions of isomeric forms of mono, di and tri hydrates of alkyl phosphate anion using the above theories. It reveals, water molecules have a very strong interaction with the phosphate group in both the molecules and their interactions induce the changes in the structural parameters of the PO₄ group for both the DMP and DEP anions. The optimized structural parameters, total energy, dipole moment and rotational constants are calculated and are compared with the available experimental values. The chemical hardness and chemical potential for these complexes have been calculated at HF/6-31G* level of theory and discussed the conformational stability of these complexes.

Keywords: Ab initio; density functional theory; interaction energy; dimethyl phosphate anion; diethyl phosphate anion.

Introduction

The functional diversity of DNA or RNA involves specialized base sequences, but the flexibility of the sugar-phosphate backbone is expected to play a key role in nucleic acid polymorphism. Although x-ray crystallography and NMR spectroscopy can provide detailed information about the structural parameters of the nucleic acid phosphodiester backbone, the precise information on conformations of

phosphodiester linkages in many biologically important nucleic acids, remain beyond the scope of the above methods. On the basis of quantum chemical methods, extensive studies have been carried out on phosphodiester model compounds. The dimethyl phosphate anion $[(\text{CH}_3\text{O})_2\text{PO}_2^-]$, DMP] serves as the simplest structural analogue for the nucleic acid phosphate group. Raman and IR spectra of DMP were employed to develop a comprehensive molecular force field for the phosphate group [1] and to explore the conformational dependence of C-O-P-O-C skeletal vibrations. Changes in the phosphodiester torsions of DMP, which correspond to the nucleic acid backbone torsions α and ζ , generate the most significant frequency shifts in Raman bands and have thus provided an initial basis for correlating the empirical conformation marker bands of nucleic acids with specific internal coordinates of the phosphodiester moiety. The another molecule, diethylphosphate anion $[(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}_2^-]$, DEP] is also considered here as an improved structural analogue for the nucleic acid phosphate group. The back bone molecular skeleton, C-C-O-P(O₂⁻)-O-C-C, incorporates two C-C bonds capable of vibrational interaction with modes of the phosphodiester linkages and two C-C bonds with torsion angles analogous to the nucleic acid backbone torsions $\beta(\text{O}5'-\text{C}5')$ and $\varepsilon(\text{C}3'-\text{O}3')$ [2].

It is always interesting and important to study the water interactions with real building blocks of DNA. Since dimethylphosphate and diethylphosphate anions are the analogue systems of nucleotides, the water interaction with these systems will help to model the real building blocks of DNA molecules. To make the study more effective, we have considered the interaction of single, double, and triple water molecules with the DMP and DEP anions. We have not imposed any constraints for these complex molecules and optimized them using the supra molecular approach. The interaction of single water molecule can be possible either O4 or O5 atom of PO₄ group which is the most powerful proton acceptor, where the water molecules moves towards the PO₄ group and makes very strong interaction. Even di and tri hydrates are having strong interactions with PO₄ group. So, all water molecules have a very strong interaction with the PO₄ group of DMP and DEP anions. The present study helps to understand the most possible sites for the interaction of water molecules with the DMP and DEP anions. The interaction of mono-, di- and tri-hydrates with PO₄ group will elucidate the structural deformation of DMP and DEP anions. The HF, Post Hartree-Fock and density functional theory methods have been used for the above study. Even though the appreciable changes have been observed in the structural parameters of the PO₄ group, the water interactions occurred only with the PO₂⁻ anion.

2. Computational methods

The ab initio and density functional theory methods have been used to optimize the geometries of these complexes. The restricted Hartree-Fock (RHF), Møller-Plesset perturbation theory (MP2) [3] of ab initio method and Becke's three parameter exact exchange functional (B3) [4] combined with gradient corrected correlation functional of Lee- Yang- Parr (LYP) [5] and Perdew and Wang's 1991 (PW91) [6] functional of DFT have been employed to optimize the isolated and complex molecules by implementing 6-31G*

basis set. Boys and Bernardi's counter poise procedure [7] have been applied to correct the basis set superposition error for the interaction energy:

$$E_{\text{int(corr)}}=E(\text{AB})-[E_{\text{A}}(\text{AB})+E_{\text{B}}(\text{AB})]$$

where $E(\text{AB})$, $E_{\text{A}}(\text{AB})$, and $E_{\text{B}}(\text{AB})$ are the energies of complex and monomer structures in complex geometry. The chemical hardness (η) and chemical potential (μ) have been calculated using the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies determined by the HF/6-31G* method. The chemical hardness and chemical potential can be expressed within orbital basis as

$$\eta = \frac{I - A}{2} \qquad \mu = -\frac{I + A}{2}$$

where $I=-E_{\text{HOMO}}$ and $A=-E_{\text{LUMO}}$: I and A are the ionization potential and electron affinity of a molecule. All these calculations were performed using the Gaussian 98W program [8].

3. Results and discussion

3.1 DMP – Water

The optimized geometrical parameters, rotational constants and dipole moment of the DMP-anion are given in Table 1 and shown in Figure 1. The optimized structures are compared with the crystal structure of NH_4DMP molecule [9]. Though the optimized C-O bond length is shorter than the experimental value of NH_4DMP in all the four levels of theory, the value calculated at MP2/6-31G* level of theory is in good agreement with the crystal data. The calculated P-O2 and P-O6 bond lengths are longer by 0.1 Å in all the four levels of theory and the P-O4 and P-O5 bond lengths are in excellent agreement with the experimental values. Single water molecules can interact with PO_4 group in three different ways. The optimized structural parameters for the single water isomeric form with DMP anion are given in Table 2. The O4 or O5 atoms of the PO_4 group can interact with H atom of the water molecule and H atoms of water molecules simultaneously interact with O4 and O5 atoms. The interaction induces the change in the P-O2 and P-O4 bond distances. There is a decrease in the bond distance of P-O2 atoms and increase in the P-O6 bond distance, when the water molecule interacts with O4 atom. Suppose, if water molecule interacts with O5 atom, there is not much change in the P-O2 distance, where as P-O6 bond distance is decreasing. Another observation is that the bond distance P-O4 is increasing while the water interaction is with O4 atom and P-O5 bond distance is decreasing. The same trends have been found while the water interaction is with O5 atom. All the P-O bond distances are same when the water molecule interacts symmetrically with the O4 and O5 atoms of PO_4 . Recently many authors [10-12] have explained the charge transfer process during the hydrogen bond formation. PO_4 group is the proton acceptor and O-H bond of water molecule is proton donor group. So the charge is transferred from O4 atom to H atom of water molecule. This induces the electronic

Table 1. Optimized geometrical parameters (bond length in Å, bond angle in degrees), rotational constants R_A , R_B , R_C (in GHz), dipole moment μ_M (in Debye), chemical potential μ (in eV) and chemical hardness η (in eV) for DMP and DEP anions.

Parameters	DMP					DEP				
	HF	MP2	B3LYP	B3PW91	Crystal data (NH ₄ DMP)	HF	MP2	B3LYP	B3PW91	Crystal data (BaDEP)
R(P3-O4)	1.470	1.501	1.498	1.496	1.498	1.472	1.503	1.500	1.498	1.520
R(P3-O6)	1.642	1.684	1.684	1.680	1.582	1.642	1.684	1.684	1.679	1.620
R(C1-O2)	1.393	1.421	1.412	1.406	1.425	1.398	1.425	1.418	1.412	1.440
R(C1-C9)	1.521	1.522	1.530	1.525	1.510
θ (O4-P3-O5)	124.8	126.1	125.7	125.7	117.2	124.7	126.1	125.6	125.7	121.6
θ (O2-P3-O6)	99.3	98.4	98.6	98.6	104.8	108.3	99.5	99.7	108.8	103.5
θ (P3-O2-C1)	118.5	114.4	116.2	115.8	118.3	121.2	116.9	118.7	118.3	116.0
θ (P3-C1-C9)	112.6	110.7	111.5	112.2	114.0
μ_M	5.7602	5.7456	5.0369	5.0128	...	6.2006	6.1585	5.6216	5.5709	...
R_A	2.9685	2.8105	2.8279	2.8588	...	2.1345	2.0339	1.9972	2.0300	...
R_B	2.1982	2.2251	2.1738	2.1795	...	1.0695	1.1079	1.0831	1.0820	...
R_C	1.7632	1.7579	1.7329	1.7460	...	0.8705	0.8879	0.8585	0.8638	...
η	8.35	8.16
μ	2.28	1.97

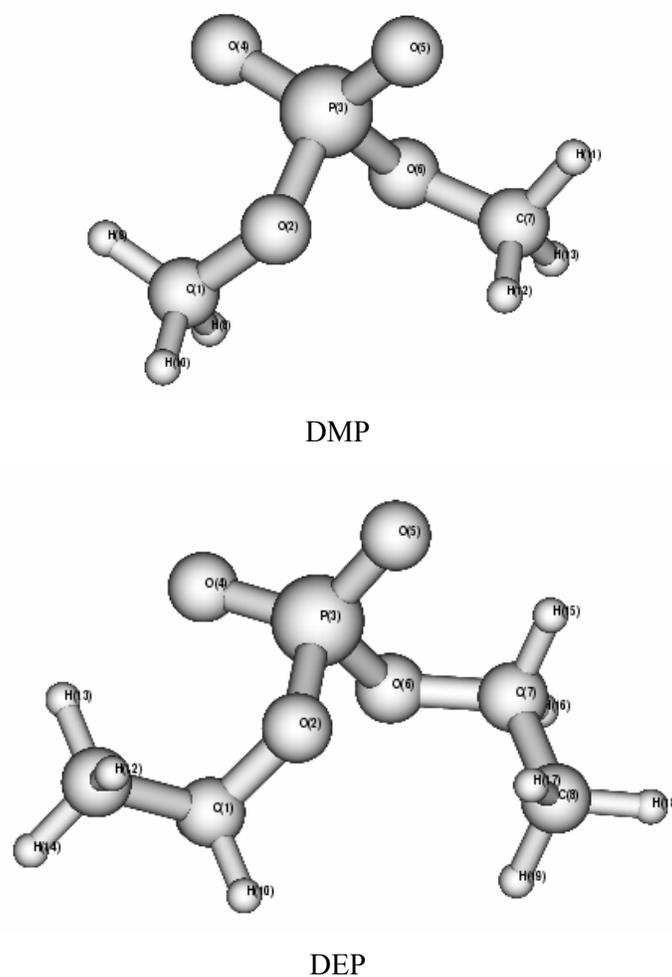


Figure 1. Structures of the DMP and DEP anions.

delocalization in the PO_2^- group, so to compensate this, the charge is transferred from O2 and O6 to PO_2^- group. Due to this process, the structural reorganization has occurred in the PO_4 and thus the P-O distances are found to be different where the water interaction takes place. The other bond length changes are found to be minimum. The various possible interactions of two water molecules with the DMP anion have been studied. The three isomeric forms of interaction have been identified for the two water molecule from the optimization of the complex using the supramolecular approach. The optimized structural parameters are tabulated in the Table 3 and the various interactions of water with DMP anion are shown in Fig. 2. The DMP-2W1 figure shows that both the water molecules point towards the same side. Here, the P-O4 bond distance is found to be more than the P-O5 bond distance by 0.001 Å and again P-O6 bond distance is more by 0.02 Å than the bond distance between P-O2 atoms. The reason for the above differences may be due to the possible dispersion force of second water molecule with O4 and O6 atoms. In the DMP-2W2, the interactions of water molecules are

Table 2. Optimized geometrical parameters (bond length in Å, bond angle in degrees), rotational constants R_A , R_B , R_C (in GHz), dipole moment μ_M (in Debye), chemical potential μ (in eV) and chemical hardness η (in eV) for DMP-1water complexes.

Parameters	DMP-1W1				DMP-1W2				DMP-1W3			
	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91
R(P-O2)	1.631	1.669	1.668	1.663	1.644	1.684	1.690	1.690	1.632	1.671	1.671	1.666
R(P-O4)	1.478	1.509	1.507	1.505	1.487	1.497	1.494	1.492	1.475	1.506	1.503	1.501
R(P-O5)	1.467	1.497	1.494	1.492	1.478	1.505	1.507	1.509	1.475	1.506	1.503	1.501
R(P-O6)	1.644	1.690	1.690	1.684	1.631	1.669	1.668	1.663	1.632	1.671	1.671	1.666
R(C1-O2)	1.399	1.429	1.422	1.416	1.397	1.410	1.416	1.424	1.396	1.424	1.416	1.410
R(C7-O6)	1.397	1.424	1.416	1.410	1.399	1.429	1.422	1.416	1.396	1.424	1.416	1.410
θ (O4-P3-O5)	108.5	125.7	125.2	125.2	124.6	125.2	125.2	125.7	106.7	106.0	106.0	105.9
θ (O2-P3-O6)	99.8	99.0	99.4	99.5	99.8	99.5	99.4	99.0	100.2	99.7	100.1	100.1
θ (P3-O6-H7)	118.6	114.6	116.5	116.2	118.7	114.9	117.0	116.4	118.8	114.7	116.6	116.2
θ (P3-O2-C1)	118.8	114.9	111.0	116.5	118.5	116.2	116.5	114.6	118.8	114.7	116.7	116.3
θ (O14-H15-O4)	154.9	153.4	155.5	155.7
θ (H16-O14-H15)	100.4	97.9	97.8	97.8
θ (H16-O14-H15)	100.4	97.8	97.8	97.9
θ (O5-H16-O14)	154.7	155.7	155.4	153.9
θ (O15-H14-O4)	145.1	147.6	147.8	147.5
θ (H16-O15-H14)	100.1	98.1	97.8	97.8
R(H15...O4)	1.950	1.930	1.876	1.863	1.953	1.862	1.877	1.926
R(H16...O5)
R(H14...O4)	2.157	2.081	2.060	2.052
$E_{int}(1W1)$	17.09	21.20	20.68	19.35
$E_{int}(1W2)$	17.09	21.20	20.68	19.35
$E_{int}(1W3)$	17.98	20.60	19.96	18.95
μ_M	5.3757	5.1110	4.4991	4.5156	5.3715	5.1209	4.4935	4.5130	7.1157	7.1973	6.6191	6.6145
R_A	1.8113	1.8325	1.8178	1.8318	1.8109	1.8326	1.8178	1.8315	2.1753	2.1752	2.1220	2.1308
R_B	1.3930	1.4048	1.4125	1.4214	1.3934	1.4042	1.4128	1.4218	1.2546	1.2461	1.2586	1.2716
R_C	1.2016	1.2352	1.2284	1.2359	1.2019	1.2352	1.2281	1.2357	0.9699	0.9764	0.9733	0.9822
η	8.39	8.39	8.50
μ	1.70	1.70	1.76

Table 3. Optimized geometrical parameters (bond length in Å, bond angle in degrees), rotational constants R_A , R_B , R_C (in GHz), dipole moment μ_M (in Debye), chemical potential μ (in eV) and chemical hardness η (in eV) for DMP-2 water complexes.

Parameters	DMP-2W1				DMP-2W2				DMP-2W3			
	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91
R(P-O4)	1.481	1.513	1.512	1.509	1.471	1.502	1.500	1.497	1.474	1.505	1.503	1.501
R(P-O5)	1.471	1.502	1.500	1.497	1.481	1.513	1.512	1.509	1.474	1.505	1.503	1.501
R(P-O6)	1.635	1.678	1.677	1.671	1.622	1.658	1.656	1.652	1.634	1.675	1.673	1.668
R(P-O2)	1.622	1.658	1.656	1.652	1.635	1.678	1.677	1.672	1.634	1.675	1.673	1.668
R(C1-O2)	1.402	1.433	1.427	1.420	1.428	1.428	1.420	1.414	1.403	1.433	1.426	1.420
R(C7-O6)	1.400	1.428	1.420	1.414	1.402	1.433	1.426	1.420	1.403	1.433	1.426	1.420
θ (O4-P3-O5)	122.6	123.8	123.2	123.3	122.6	123.8	123.2	123.3	124.4	125.5	124.9	124.9
θ (O2-P3-O6)	100.6	100.3	100.8	100.8	100.6	100.3	100.8	100.8	100.2	99.6	100.0	100.0
θ (P3-O2-C1)	119.1	115.2	117.4	116.9	118.8	114.8	116.9	116.5	118.8	115.0	117.1	116.6
θ (P3-O6-C7)	116.0	114.8	116.9	116.5	119.1	115.3	117.5	116.9	118.8	115.0	117.1	116.6
θ (O15-H14-O4)	143.0	145.9	145.3	145.2	146.3	148.0	149.0	149.1
θ (O17-H14-O4)	153.7	152.0	154.0	154.7
θ (H18-O17-H19)	100.8	98.4	98.3	98.4	100.8	98.4	98.3	98.3	100.8	98.4	98.3	98.2
θ (H14-O15-H16)	100.6	98.6	98.4	98.4	100.6	98.6	98.4	98.4	100.8	98.4	98.3	98.2
θ (O17-H19-O5)	153.6	152.0	153.9	154.2
θ (O4-H18-O17)	154.2	152.6	154.3	154.9
θ (O14-H16-O5)	154.2	152.5	154.3	154.9
R(O4...H18)	1.980	1.958	1.907	1.889	1.971	1.954	1.906	1.887
R(H16...O5)	2.141	2.084	2.048	2.034	2.216	2.118	2.115	2.105	1.971	1.954	1.906	1.887
R(O4...H14)	2.216	2.118	2.115	2.108	2.142	2.085	2.048	2.036
R(O5...H19)	1.982	1.958	1.907	1.894
E_{int} (H14O15H16)	16.47	18.92	18.12	17.09
E_{int} (O17 H18H19)	15.61	19.50	18.87	17.47
E_{int} (H14O15H16)	16.47	18.92	18.12	17.10
E_{int} (O17 H18H19)	15.61	19.50	18.16	17.48
E_{int} (O14H15H16)	15.94	19.81	19.29	18.00
E_{int} (O17 H18H19)	15.94	19.81	19.29	18.00
μ_M	6.7030	6.6456	6.0884	6.1401	6.7000	6.6447	6.0917	6.1175	4.5964	4.0106	3.4110	3.4750
R_A	1.2645	1.3211	1.3179	1.3193	1.2649	1.3225	1.3154	1.3220	1.7410	1.6946	1.6699	1.6933
R_B	0.9222	0.9252	0.9276	0.9353	0.9221	0.9253	0.9270	0.9352	0.8471	0.8849	0.8977	0.8998
R_C	0.8211	0.8260	0.8264	0.8345	0.8214	0.8249	0.8281	0.8348	0.7697	0.8160	0.8193	0.8228
η	8.53	8.53	8.47
μ	1.22	1.22	1.21

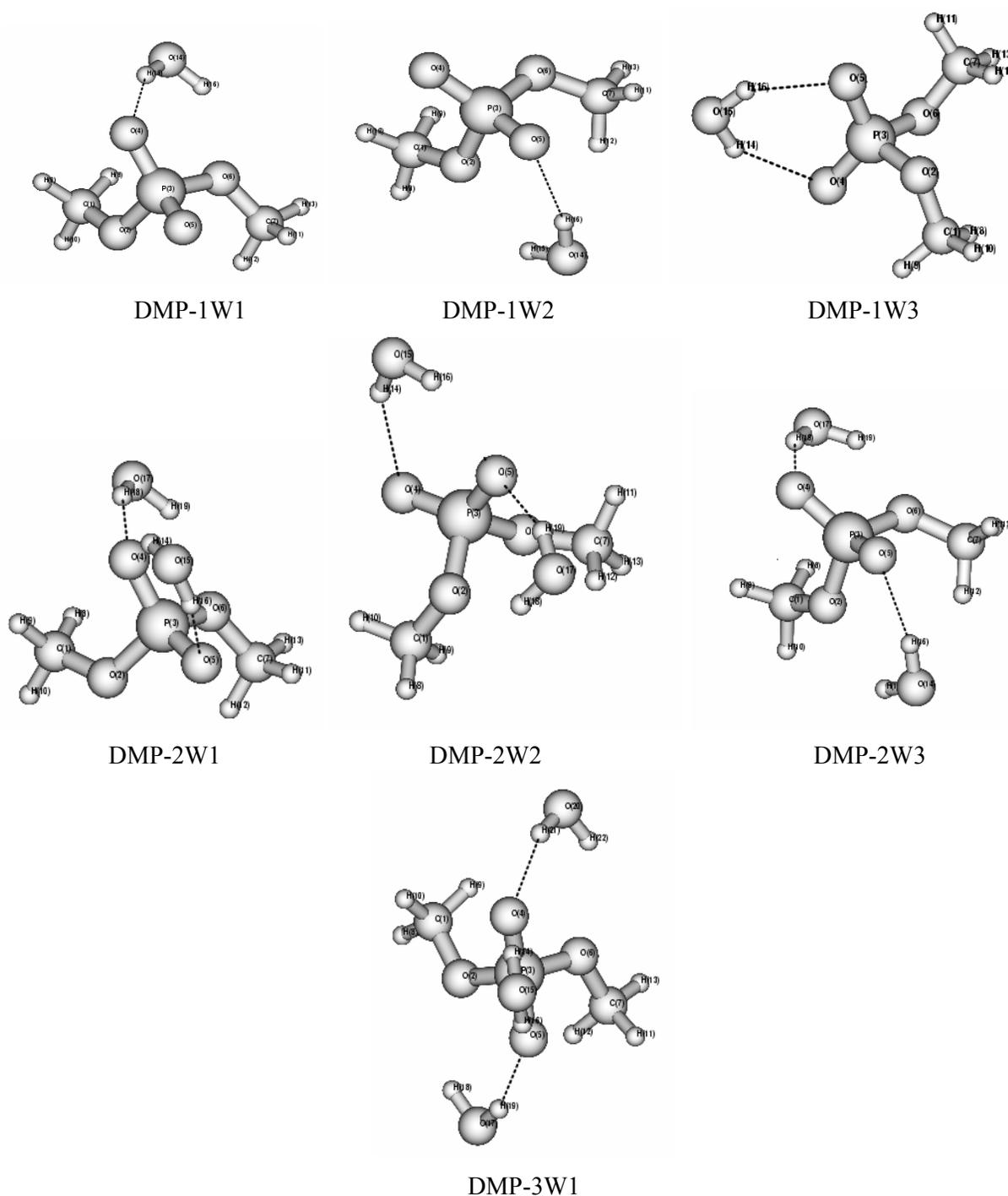


Figure 2. Structures of the DMP anions interacting with one, two, and three water molecules.

symmetrically opposite to each other. But one water molecule is near to the methyl group of DMP anion. This may be the reason that P-O5 bond distance is more by 0.01 Å than the P-O4 bond distance and P-O2 bond distance is more by 0.02 Å than the P-O6 bond distance. The one more isomeric form of DMP-2W3 is that two water molecules are symmetrically opposite to each other and interacts with O4 and O5 atoms of PO4 group. It is noted that P-O4 and P-O5 bond distances are found to be same

and other two bonds P-O2 and P-O6 are also found to be the same. It clearly shows that the two water molecules do not have any Van der Waals interactions with the nearby groups of the DMP anions.

Finally, we have considered the interaction of three water molecules with PO₄ group. Two hydrogen atoms of one water molecule symmetrically interact with the O4 and O5 atoms and other two water molecules, again interact with O4 and O5 atoms. It is interesting to note that P-O4, P-O5 distances are same and P-O2 and P-O6 bond distances are also found to be the same. Since all the water molecular interactions are symmetrical, the charge transfers from PO₄ group to water molecules are uniform, so there is no change in the structural parameters of the DMP anion. As the bonding in the hydrogen atoms could not be accurately located in the x-ray structure, their optimized parameters are compared with standard experimental values of similar model compounds. The bond angles O-P-O and P-O-C are smaller compared to the corresponding experimental values in all the levels of theory except for P-O-C bond angle at HF level, which is very close to the experimental value.

The interaction energies of water molecule with DMP anion are given in Table 2, 3, 4. The interaction energy is corrected for BSSE using full counterpoise method of Boys and Bernardi [7]. The interaction energies of single water molecule is same when the interaction is O4 or O5 atoms. The hydrogen bond lengths are also found to be the same. When the two water molecules interact with the O4 and O5 atoms, the interaction energies are found to be slightly smaller than the single water interaction. The hydrogen bond lengths are found to be slightly higher than the single water interaction. If the three water molecules are having interaction with PO₄ group, again the interaction energies are found to be slightly less and the hydrogen bond lengths are found to be slightly higher. The reason for the above variation may be due to the charge transfer from PO₂⁻ to OH of water molecule. If, more water molecules are interacting, then the charge transfer becomes less, due to the equal distribution of charge in the PO₂⁻ anion. The HF/6-31G* level of theory underestimated the interaction energy. But MP2/6-31G*, B3LYP/6-31G* and B3PW91/6-31G* levels of theory predicted the interaction energies and hydrogen bond lengths very reasonably.

3.2 DEP-Water Complex

In accordance with the x-ray crystal structure of BaDEP [13], the DEP anion and DEP-water have been fully optimized at HF, MP2, B3LYP, and B3PW91 levels of theory using 6-31G* basis set and are shown in Tables 1, 5, 6, 7. Figure 3 shows various interactions of water with DEP anion. The calculated structural parameters are compared with those obtained by x-ray crystallography of BaDEP. In the DEP anion, the optimized P-O bond lengths are slightly larger than the corresponding values in the x-ray structure of BaDEP. Conversely, the optimized P-O4 and C-O bonds are shorter than the values obtained from the x-ray methods. The C-C bond length is in good agreement with the experimental values. The optimized O2-P-O6 bond angle is smaller and P-O-C bond angles on the other hand, are generally close to the experimental values. Similar differences can be attributed to the effect of metal cation in the crystal structure [1,14,15]. In the present study the interaction of single,

Table 4. Optimized geometrical parameters (bond length in Å, bond angle in degrees), rotational constants R_A , R_B , R_C (in GHz), dipole moment μ_M (in Debye), chemical potential μ (in eV) and chemical hardness η (in eV) for DMP-3 water complex.

Parameters	HF	MP2	B3LYP	B3PW91
R(P-O4)	1.478	1.510	1.508	1.505
R(P-O5)	1.478	1.510	1.508	1.505
R(P-O2)	1.625	1.664	1.662	1.657
R(P-O6)	1.625	1.664	1.662	1.657
R(C1-O2)	1.406	1.437	1.430	1.423
R(C7-O6)	1.406	1.437	1.430	1.423
θ (O5-P3-O4)	122.5	123.6	123.0	123.1
θ (O4-P3-O2)	101.1	100.9	101.3	101.3
θ (P3-O2-C1)	119.1	115.4	117.5	117.0
θ (P3-O6-C7)	119.1	115.4	117.5	117.0
θ (O15-H14-O4)	144.3	146.6	146.7	146.8
θ (O20-H21-O4)	153.1	151.2	152.9	153.8
θ (H18-O17-H19)	101.2	98.8	98.8	98.8
θ (H14-O15-H16)	101.0	99.1	98.9	98.9
θ (O17-H19-O5)	153.1	151.2	152.9	153.8
θ (H22-O20-H21)	101.2	98.8	98.8	98.8
R(O4...H21)	1.999	1.981	1.935	1.915
R(O5...H16)	2.197	2.117	2.099	2.091
R(O4...H14)	2.197	2.117	2.099	2.091
R(O5...H19)	1.999	1.981	1.935	1.915
E_{int} (H14O15H16)	15.12	17.48	16.59	15.51
E_{int} (O17 H18H19)	14.61	18.34	17.68	16.27
E_{int} (O20 H21H22)	14.61	18.34	17.68	16.27
μ_M	5.9985	5.6388	5.1285	5.2152
R_A	0.9209	0.9092	0.9051	0.9170
R_B	0.7704	0.8128	0.8156	0.8165
R_C	0.5935	0.6127	0.6204	0.6218
η	8.60	--	--	--
μ	0.75	--	--	--

double and triple water molecules with the PO_4 group have been considered. The interaction of single water molecule either O4 or O5 atom induces the change in the structural parameters of PO_4 group. When the O4 atom of PO_4 group forms the hydrogen bond with H atom of water molecule, the P-O4 bond length is found to be increasing while P-O5 is decreasing. The bond distance P-O2 is decreasing while the other bond P-O6 is increasing. When the water molecule interacts with the O5 atom, the reverse trend has been observed. Two water molecules can interact with the PO_2^- in three different ways which have been shown in fig. In the first case, the P-O4 distance is larger than the P-O5 bond distance. The corresponding hydrogen bond lengths are 1.917 Å and 1.912 Å respectively at MP2/6-31G* level of theory. Both the water molecules pointed towards the P-O4 bond, so the latter bond distance is more. In the second case, both water molecules are in the opposite direction, so the P-O4

Table 5 Optimized geometrical parameters (bond length in Å, bond angle in degrees), rotational constants R_A , R_B , R_C (in GHz), dipole moment μ_M (in Debye), chemical potential μ (in eV) and chemical hardness η (in eV) for DEP-1water complexes.

Parameters	DEP-1W1				DEP-1W2				DEP-1W3			
	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91
R(P-O2)	1.630	1.669	1.668	1.663	1.643	1.689	1.688	1.681	1.631	1.672	1.672	1.666
R(P-O4)	1.479	1.511	1.509	1.507	1.469	1.499	1.496	1.494	1.476	1.508	1.505	1.503
R(P-O5)	1.468	1.498	1.495	1.493	1.478	1.510	1.508	1.506	1.475	1.507	1.504	1.502
R(P-O6)	1.644	1.691	1.690	1.684	1.630	1.669	1.667	1.663	1.632	1.672	1.670	1.665
R(C1-O2)	1.405	1.436	1.431	1.424	1.404	1.431	1.425	1.419	1.403	1.432	1.425	1.419
R(C7-O6)	1.403	1.430	1.423	1.417	1.403	1.431	1.425	1.419	1.402	1.429	1.423	1.416
R(C1-C9)	1.520	1.518	1.525	1.521	1.520	1.518	1.526	1.521	1.520	1.518	1.526	1.521
R(C7-C8)	1.523	1.521	1.528	1.524	1.523	1.521	1.528	1.523	1.523	1.521	1.529	1.524
θ (O4-P3-O5)	124.4	125.6	125.0	125.0	124.3	125.5	124.9	124.9	106.7	105.7	105.8	105.8
θ (O6-P3-O2)	100.6	100.1	100.4	100.5	100.5	99.9	100.1	100.3	100.9	100.7	101.0	101.6
θ (P3-O6-C7)	121.1	117.0	118.8	118.4	121.9	117.7	119.7	119.2	121.5	117.1	119.0	118.6
θ (P3-O2-C1)	120.2	116.0	118.2	117.7	119.7	115.7	117.7	117.3	120.1	115.8	118.1	117.6
θ (O6-C7-C8)	112.4	111.8	112.2	112.1	113.0	112.9	113.4	113.4	112.4	112.1	112.1	112.2
θ (O2-C1-C9)	110.8	110.1	110.9	110.9	111.1	110.6	111.4	111.4	111.0	110.5	111.4	111.3
θ (O20-H22...O4)	155.4	153.7	155.8	156.4
θ (O20-H21...O5)	155.0	154.2	156.0	156.8
θ (O21-H20...O4)	145.2	147.9	147.6	147.7
θ (H21-O20-H22)	100.5	97.9	97.9	97.9
θ (H21-O20-H22)	100.4	97.9	97.8	97.8
θ (H22-O21-H20)	100.2	98.2	97.9	97.9
R(H20...O4)	2.154	2.078	2.062	2.050
R(H22...O4)	1.937	1.917	1.866	1.849
R(H21...O5)	1.945	1.912	1.869	1.850
E_{int} (DEP-1W1)	17.07	21.18	24.10	19.05
E_{int} (DEP-1W2)	17.23	21.27	20.72	19.27
E_{int} (DEP-1W3)	17.72	20.20	19.43	18.45
μ_M	5.9567	5.6933	5.1298	5.1449	5.8801	5.7067	4.9411	4.9602	7.8165	7.9597	7.4913	7.4760
R_A	1.1868	1.2138	1.2156	1.2238	1.2149	1.2287	1.2664	1.246	1.1190	1.1328	1.1393	1.1387
R_B	0.8566	0.8604	0.8366	0.8416	0.8644	0.8782	0.8507	0.8580	0.9503	0.9575	0.9290	0.9408
R_C	0.7503	0.7917	0.7802	0.7806	0.7467	0.7701	0.7469	0.7496	0.5945	0.6067	0.5929	0.5971
η	8.25	8.27	8.33
μ	1.48	1.50	1.50

Table 6 Optimized geometrical parameters (bond length in Å, bond angle in degrees), rotational constants R_A , R_B , R_C (in GHz), dipole moment μ_M (in Debye), chemical potential μ (in eV) and chemical hardness η (in eV) for DEP-2 water complexes.

Parameters	DEP-2W1				DEP-2W2				DEP-2W3			
	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91	HF	MP2	B3LYP	B3PW91
R(P-O2)	1.620	1.658	1.655	1.651	1.636	1.639	1.676	1.631	1.633	1.675	1.672	1.666
R(P-O4)	1.483	1.515	1.513	1.511	1.473	1.505	1.502	1.500	1.475	1.506	1.505	1.502
R(P-O5)	1.472	1.503	1.500	1.498	1.483	1.522	1.520	1.517	1.474	1.505	1.503	1.501
R(P-O6)	1.634	1.679	1.633	1.671	1.613	1.647	1.646	1.642	1.634	1.676	1.673	1.667
R(C1-O2)	1.409	1.440	1.435	1.428	1.409	1.439	1.433	1.426	1.409	1.440	1.434	1.427
R(C7-O6)	1.406	1.434	1.427	1.421	1.407	1.437	1.432	1.425	1.407	1.437	1.432	1.425
R(C1-C9)	1.519	1.517	1.524	1.520	1.523	1.521	1.529	1.523	1.519	1.517	1.524	1.520
R(C7-C8)	1.522	1.520	1.527	1.523	1.518	1.515	1.522	1.517	1.518	1.516	1.523	1.518
θ (O4-P3-O5)	122.3	123.6	123.0	123.0	120.9	121.3	121.0	121.1	124.2	125.2	124.5	124.5
θ (O4-H2O-O21)	143.2	146.2	145.7	145.9	145.8	147.0	147.3	147.6
θ (O5-H22-O21)	146.0	147.7	148.4	148.4	142.5	146.1	146.1	146.3
θ (O5-H24-O23)	154.6	152.8	154.2	154.4
θ (H2O-O21-H22)	100.6	98.7	98.4	98.4	100.5	98.3	98.1	98.0
θ (H25-O23-H24)	100.9	98.4	98.4	98.5	101.1	98.3	98.4	98.3	101.0	98.4	98.5	98.5
θ (O2-P3-O6)	101.4	101.3	101.5	101.6	99.3	97.7	97.7	97.8	100.3	99.5	100.0	100.1
θ (O23-H25-O4)	154.4	152.3	154.3	155.0
θ (O4-H25-O23)	155.4	153.2	155.6	156.5
θ (O5-H21-O20)	154.3	152.6	154.7	155.5
θ (H21-O20-H22)	100.8	98.4	98.3	98.3
R(O4...H25)	1.964	1.944	1.895	1.833
R(H22...O5)	2.146	2.091	2.058	2.043	2.190	2.065	2.042	2.029
R(H24...O5)	1.984	1.951	1.916	1.899
R(H20...O4)	2.214	2.116	2.110	2.099	2.114	2.062	2.048	2.028
R(H25...O4)	1.949	1.935	1.880	1.860
R(H21...O5)	1.970	1.952	1.900	1.881
E_{int} (H20O21H22)	17.66	20.45	19.01	18.04
E_{int} (O23H24H25)	15.84	19.86	18.05	18.04
E_{int} (H20O21H22)	15.94	19.30	19.81	17.60
E_{int} (O23H24H25)	15.29	20.24	19.87	18.08
E_{int} (O20H21H22)	15.86	19.81	19.21	17.85
E_{int} (O23H24H25)	15.94	19.91	19.10	17.74
μ_M	7.5567	7.4675	6.9837	6.9937	5.7230	5.0874	4.7555	4.7974	5.4329	5.0008	4.3157	4.3933
R_A	0.7720	0.7983	0.7961	0.7951	1.0243	1.0828	1.1000	1.1030	0.8120	0.8520	0.8573	0.8593
R_B	0.6982	0.7233	0.7181	0.7245	0.6044	0.6300	0.6146	0.6189	0.7531	0.7526	0.7429	0.7483
R_C	0.5785	0.5823	0.5709	0.5763	0.5348	0.5398	0.5362	0.5413	0.5284	0.5651	0.5543	0.5566
η	8.24	8.35	8.29
μ	1.03	1.13	1.07

Table 7 Optimized geometrical parameters (bond length in Å, bond angle in degrees), rotational constants R_A , R_B , R_C (in GHz), dipole moment μ_M (in Debye), chemical potential μ (in eV) and chemical hardness η (in eV) for DEP-3 water complex.

Parameters	HF	MP2	B3LYP	B3PW91
R(P-O2)	1.624	1.664	1.660	1.655
R(P-O4)	1.479	1.511	1.509	1.507
R(P-O5)	1.478	1.509	1.508	1.505
R(P-O6)	1.625	1.665	1.661	1.656
R(C1-O2)	1.413	1.444	1.439	1.432
R(C7-O6)	1.411	1.441	1.436	1.430
R(C1-C9)	1.518	1.516	1.523	1.519
R(C7-C8)	1.517	1.515	1.521	1.517
θ (O4-H20-O21)	144.2	146.6	146.7	146.7
θ (H20-O21-H22)	101.0	99.0	98.9	98.9
θ (O4-H28-O26)	154.2	152.0	154.4	155.3
θ (H28-O26-H27)	101.3	98.9	98.9	99.0
θ (O5-H22-O21)	144.3	146.6	146.7	146.7
θ (H24-O23-H25)	101.2	98.7	98.7	98.8
θ (O5-H24-O23)	153.1	151.0	152.9	153.5
R(O4...H20)	2.202	2.118	2.100	2.091
R(O4...H28)	1.977	1.959	1.902	1.884
R(O5...H24)	1.997	1.980	1.930	1.913
R(O5...H22)	2.194	2.117	2.095	2.086
E_{int} (H20O21H22)	15.01	17.29	16.32	15.25
E_{int} (O23H24 H25)	14.58	18.40	17.56	16.17
E_{int} (O26H27 H28)	14.67	18.51	17.58	16.20
μ_M	7.7035	6.8302	6.2227	6.3122
R_A	0.5722	0.6053	0.6043	0.6061
R_B	0.5515	0.5626	0.5528	0.5573
R_C	0.4922	0.5005	0.5010	0.5043
η	8.44
μ	0.59

and P-O5 bond distances are found to be same. Moreover the hydrogen bond lengths are also almost the same. In the third isomeric form, one water molecule pointed towards the ethyl form. Here, again the P-O4 and P-O5 bond distance are the same, but the hydrogen bond lengths are different. In the last case, three water molecules are interacting with the PO_2^- , the bond lengths are almost same. Both the ab initio and DFT methods were produced the similar trends of result. The B3LYP/6-31G* and B3PW91/6-31G* levels of theory produced the structural parameters, which are very well coincide with the MP2/6-31G* level of theory. The bond angle O4-P3-O5 in DEP- water molecule is decreased by 2° compared to that of DEP anion due to the interaction of hydrogen atoms in the molecule and the oxygen atoms of phosphodioxy group. The same amount of decrease in the bond angle is also experienced in the DMP-water complex. Similarly all the P-O bond distances of DEP-water are slightly

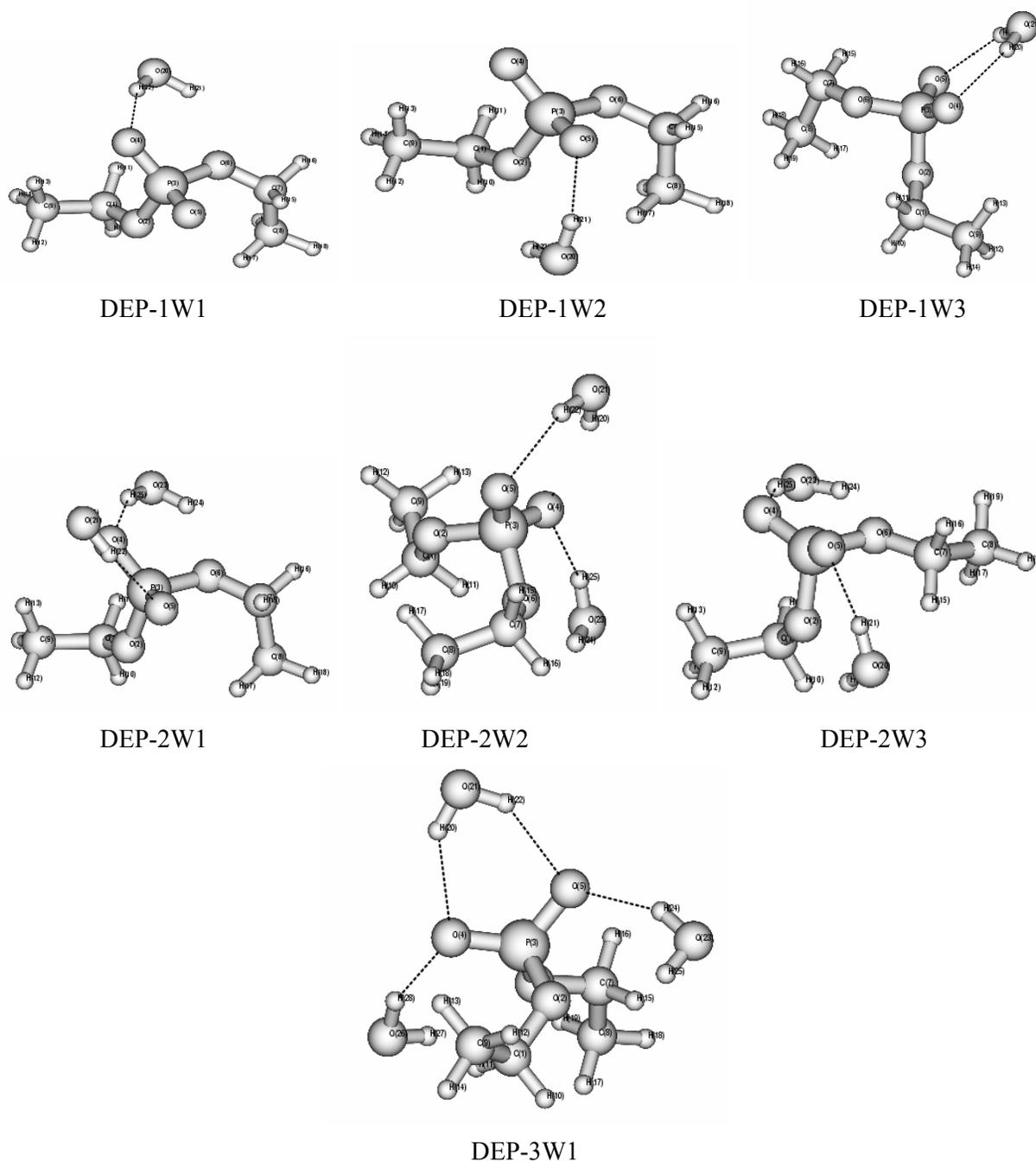


Figure 3. Structures of the DEP anions interacting with one, two, and three water molecules

shorter than those of DEP anion. The interaction energies and hydrogen bond lengths of DEP-water are given in tables 5, 6, 7. The interaction energies of mono-, di-, tri-hydrates with DEP anion is almost found to be the same. The hydrogen bond lengths are also approximately equal to 2 Å. For all the DEP-water interactions the HF/6-31G* level of theory underestimated the interaction energies, whereas B3LYP/6-31G*, B3PW91/6-31G* and MP2/6-31G* levels of theory predicted the interaction energies and hydrogen bond lengths reasonably.

The chemical hardness and chemical potential have been calculated for these complexes at HF/6-31G* level of theory and are tabulated in tables 1-7. In both the anions, the chemical hardness values are found to be increased after the formation of the complexes. This result indicates that the system tends to be stabilized after the formation of the complex. For the past few years, the chemical hardness is one of the important parameters to study the stability of the molecules. In the exothermic exchange reactions of the $AB+CD\rightarrow AC+BD$ type would produce the hardest possible species in one of the products [16]. Chattaraj and Schleyer [17] have concluded that in general this is not true for acid base reactions leading to binary complexes. Nath et al., [18] have shown the hardness profiles of hydrogen bond complexes, that the formation of $H_3N...HF$ complex is exothermic to the extent of 11.82 kcal/mol and is accompanied by an increase in η of 0.28 eV for proton-transfer reaction $(F-H...Cl)^- \rightarrow (F...H-Cl)^-$. Arulmozhiraja and Kolandaivel, who studied [19] hardness profiles for hydrogen-bonded system, indicate that hydrogen-bonding interactions do not create higher hardness complex species in the product side. But in the present case for both the complexes DMP-water and DEP-water, the chemical hardness values are found to be higher than the monomer DMP and DEP anions. The chemical hardness value is found to be more for tri hydrates interaction with DEP and DMP anions. While forming the hydrogen bond in complexes, the change of bond length and bond angles of PO_4 and the more charge transfer from O atoms induce the change in the electronic chemical potential, which in turn increases the chemical hardness value. So the proton transfer reactions, the minimum energy structure of the complex will have the maximum hardness, which is in agreement with the other studies also. In a similar way the dipole moment of the complexes is increased compared to that of the corresponding isolated anion. The earlier studies also show that dipole moment of the dimer is enhanced during the formation of hydrogen bonds in complexes [20]. Both the DMP and DEP water interactions, PO_2^- anion act as proton acceptor group. Moreover PO_2^- group is more polar. The charge from the σ orbital of the P-O bond is transferred to OH group of water molecule. Due to the charge transfer, the electron delocalization has been occurred in the PO_2^- anion, to compensate this, the other charges are reoriented and structural reorganization has been occurred in the PO_4 group of DMP and DEP anions. So the water interaction induces the reorientation in the PO_4 group rather than the other parts of the molecules.

4. Conclusion

The anionic forms of dimethyl phosphate and diethyl phosphate are optimized at HF, MP2, B3LYP and B3PW91 levels of theory using 6-31G* basis set. The interaction energies of isomeric forms of mono-, di-, and tri-hydrates with the above anions are further studied. The optimized structural parameters have been compared with the available experimental results and they are in good agreement with each other. The effect of charge transfer within these complexes makes the structural reorganization in the PO_4 group of DMP and DEP anions. The chemical hardness values have been

calculated for these complexes and it is found that interaction of more number of water molecules increase the stability of the complex.

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