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Can Stereoelectronically Rich Heteocylclic Systems Used as Peroxosolvates?

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Abstract:- Hydrogen peroxide acts as a significant oxidant in atmospheric phases, as bleaching agents etc; and bonding and reactivity of such a species is always very important. To solvate and carry such an important species, peroxosolvates are important and forms through hydrogen bonding interactions of Hydrogen Peroxide (HP) with different organic compounds. Our DFT calculations showed that stereoelectronically rich heterocyclic compounds having one or more electronegative heteroatoms can have strong hydrogen bonding interactions with such species, which may lead to design of new peroxosolvates. Interactions of 1, 2 and 4 HP with the stable heterocyclic compounds have been calculated. Interactions through the Nitrogen site and with the 1,4- substrates are more favorable for 1 and 2 HP interactions. For 4 HP interactions all the systems showed very high HBE, with 1,3- interactions showing higher HBE.

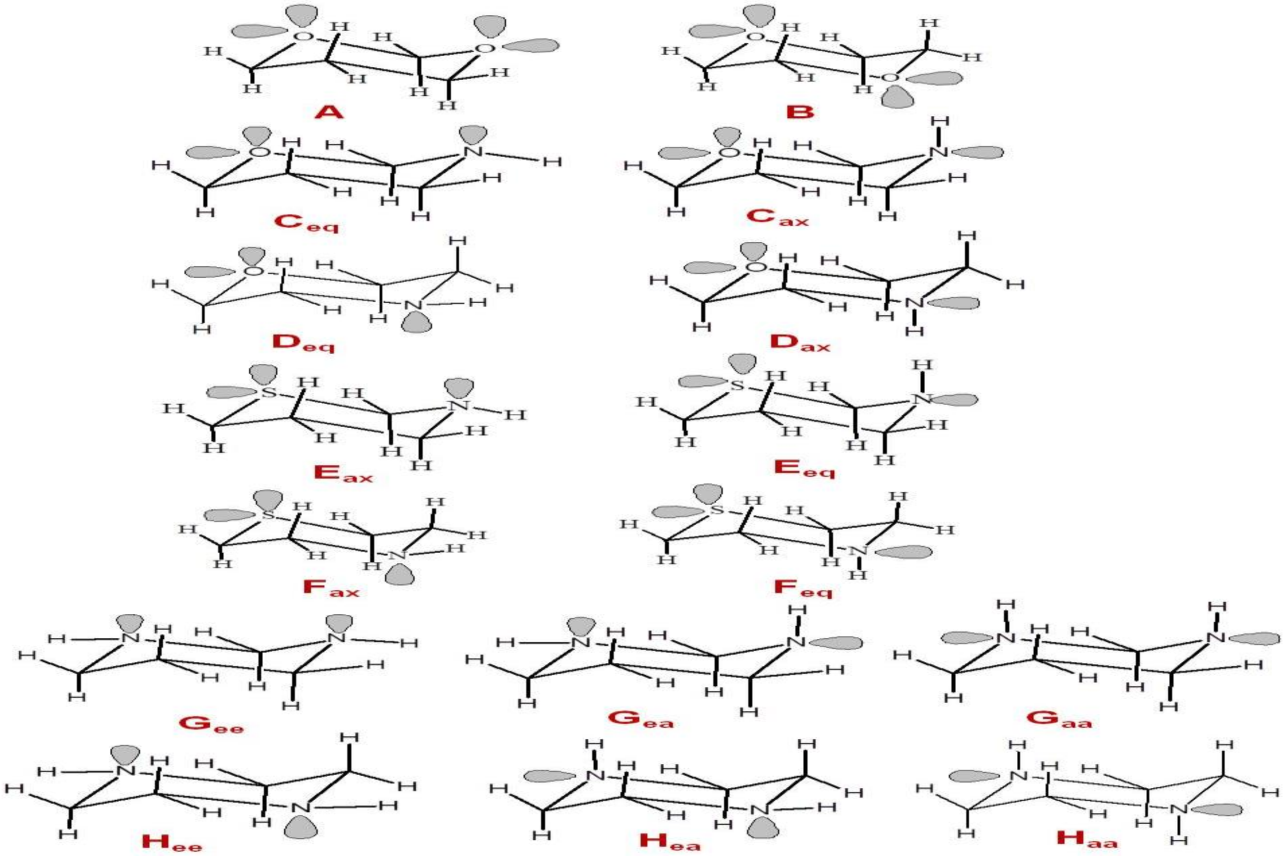
***Keywords**:- Density Functional Theory; Hydrogen Peroxide Solvates or Peroxosolvates; Heterocyclic Systems; Hydrogen Bonding Interactions.*

I. INTRODUCTION

Hydrogen peroxide (HP) formulated as H_2O_2 is the simplest peroxide and is a colorless liquid while slightly more viscous than water. HP acts as a strong oxidizing agent, thus important in many reactions. It is used as a bleaching agent and disinfectant. Concentrated hydrogen peroxide, is a reactive oxygen species and has been used as a propellant in rocketry.[1] It acts as a powerful oxidant in aqueous environment such as clouds, fog, and rain, effecting the aqueous oxidation of SO_2,[2] and also as catalysts for several inorganic and inorganic reactions.[3-9] It also plays an important role in diversified biological, chemical, environmental, and biochemical phenomena.[2,3,10-18] In particular, hydrogen bonded complexes of HP are a fascinating area that has been studied extensively employing experimental and theoretical techniques.[3-9,19-44] X-ray experiments[23,24] and theoretical studies[24-34] have been performed for the H_2O_2 reacting with DNA bases. Theoretical studies have also been performed on other HP complexes like HP dimer,[31-34] HP····water,[32,35-37] HP····hydrogen halides,[38] HP····urea,[39] HP····Nitrogen,[40] HP···· (F-, Cl-, Br-, Li+, Na+),[41] HP····(NO+, CN-, HCN, HNC and CO),[42] HP····amino acid,[43,44] etc.

However, such an important system is difficult to transfer or store and maximizing the number of hydrogen bonds with some organic compounds may be important to design stable hydrogen peroxide carriers[45] However due to low stability very few organic peroxosolvates have been structurally characterized. Churakov et. al in 2006, designed dicyclohexylamine crystals with 0.5 mole HP.[46] Recently Matzger et. al also discovered and characterized polymorphic energetic HP solvated systems.[47]

Stereoelectronically rich systems having X-C-Y or X-C-C-Y moeties, where X and Y are any electronegative atoms containing lone pairs or halogens have a strong ability to interact with one or more water molecules through hydrogen bonding as observed in the conformational studies of such systems in previous literatures.[48,49] However no theoretical reports were found for the hydrogen bonding interactions between hydrogen peroxide and such stereoelectronically rich systems. Here in this article we have discussed the interaction of stable cyclic X-C-Y and X-C-C-Y systems (X and Y are N/O/S) as shown in Scheme 1 with one or two Hydrogen peroxide (HP) and compared the interactions of the HP with the peroxosolvate dicyclohexylamine as observed in the crystal structure data.[46] Initially, the conformational analysis have been performed in solvent phase to obtain the most stable conformers for each of the stereo electronic compounds. The less stable conformers have been omitted for further calculations. The interactions of the HP have been performed only on the stable conformers. Further calculations on the interactions of 4 HP interactions with these stable stereo electronic compounds.



Scheme 1: Different Conformers of cyclic X-C-Y and X-C-C-Y systems (X,Y = O/N/S) performed. As observed from our calculations, stronger hydrogen bonding interactions are observed for all the systems with interaction with 4 HP (no 4 HP binding observed for dicyclohexylamine), and even for the compounds where X≠Y like C, D, F, G and H (scheme 1) the interactions of a single or two HP shows better interactions than dicyclohexylamine. The ability of such systems for such strong Hydrogen bonding interactions with one or more HP can be a step further towards developing better peroxosolvates.

II. COMPUTATIONAL METHODS

The structures are fully optimized at Becke's three parameter exchange functional with the correlation functional[50] of Lee et al. (B3LYP)[51] with 6-311+G(d,p) basis set. All the calculations are performed employing the polarizable continuum (PCM) solvation model.[52-54] The solvent dielectric constant is set to be the experimental value (ε = 78.4 for aqueous solution) Positive harmonic vibrational frequencies confirmed that the optimized structures are minima. The interactions of the HP with the different stable substrates have also been optimized at the same level of theory with PCM.

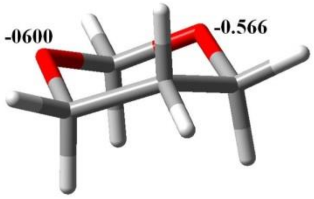
The HBE for the interactions are calculated with the equation:
$B.E = E_{complex} – (E_{substrate} + n*E_{H2O2})$

Single point calculations of the substrates for the conformational search as well as the interactions of HP have been performed at MP2/aug-cc-pVDZ[55-57] level of theory. The ChelpG charge[58-61] calculations are performed to calculate the electrostatic charge. All calculations are carried out using the Gaussian 03 suite of programs.[62]

III. RESULTS AND DISCUSSIONS

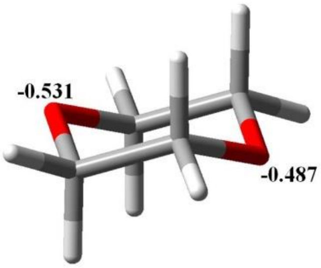
The optimized structure of HP molecule is given in the supporting information. MP2/aug-ccpvdz//B3LYP/6-311+G(d,p) calculated distances, angles and dihedral angles showed close resemblance to the experimental structure of HP in gas phase (Table S1, Supporting Information). The optimized structures at B3LYP/6-311+G(d,p) and energies at MP2/aug-ccpvdz of the different conformers of the stereoelectronic compounds as shown in scheme 1 are given in table 1. The relative energies of the respective conformers are also given in table 1. It was observed that the geometries with axial NH are more stable for the X-C-Y systems and the geometries with equatorial NH are stable for the X-C-C-Y systems. The crystal structure geometry of the Dicyclohexylamine[46] and the single point energy at MP2/aug-ccpvdz is also given in table 1.

1,3-dioxa-cyclohexane (**A**)



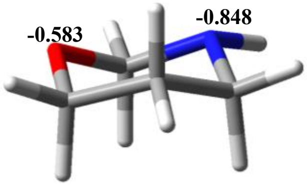
E = -306.85004380 a.u.

1,4-dioxa-cyclohexane (**B**)



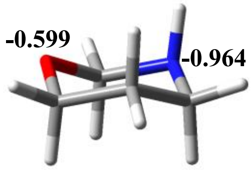
E = -306.84136065 a.u.

1-oxa-3-aza-cyclohexane (**C**$_{eq}$)



E = -287.00516093a.u.
R.E. = 2.48 kcal

1-oxa-3-aza-cyclohexane (**C**$_{ax}$)



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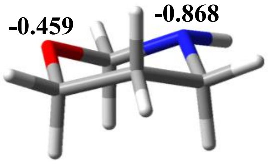
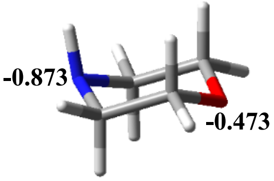
R.E. = 0.0 kcal

1-oxa-4-aza-cyclohexane (**D**$_{eq}$)



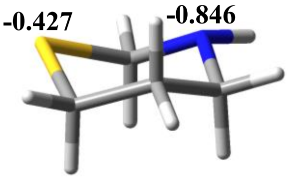
E = -287.00172612 a.u.
R.E. = 0.0 kcal

1-oxa-4-aza-cyclohexane (**D**$_{ax}$)



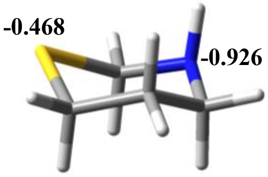
E = -287.00072215 a.u.
R.E. = 0.63 kcal

1-oxa-3-thio-cyclohexane (**E**$_{eq}$)



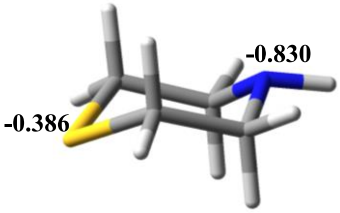
E = -609.62418906 a.u.
R.E. = 1.92 kcal

1-oxa-3-thio-cyclohexane (**E**$_{ax}$)



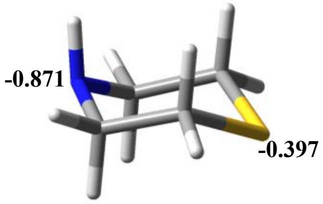
E = -609.62725151 a.u.
R.E. = 0.0 kcal

1-oxa-4-thio-cyclohexane (**F**$_{eq}$)



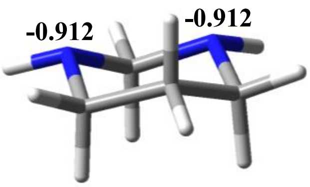
E = -609.62573282 a.u.
R.E. = 0.0 kcal

1-oxa-4-thio-cyclohexane (**F**$_{ax}$)

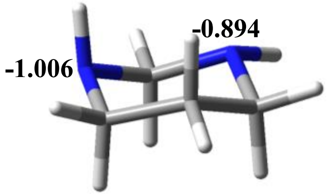


E = -609.62488053 a.u.
R.E. = 0.53 kcal

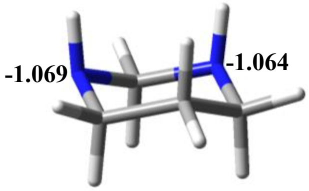
1,3-diaza-cyclohexane (**G**$_{eq-eq}$)



1,3-diaza-cyclohexane (**G**$_{ax-eq}$)



1,3-diaza-cyclohexane (**G**$_{ax-ax}$)



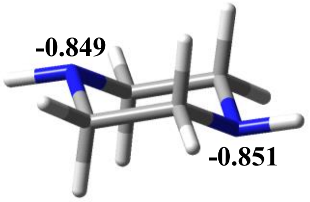
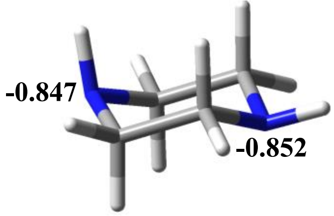
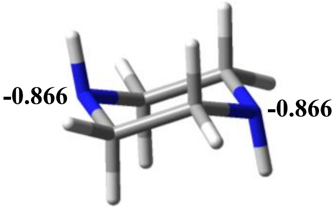
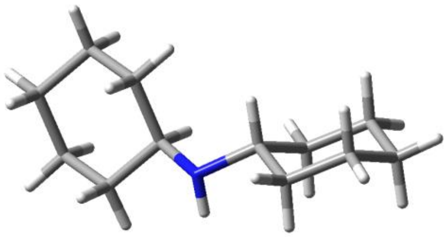
E = -267.15878250 a.u. **R.E. = 2.05 kcal**	E = -267.16118677 a.u. **R.E. = 0.54 kcal**	E = -267.16204567 a.u. **R.E. = 0.0 kcal**
1,4-diaza-cyclohexane (**H**$_{\text{eq-eq}}$)  E = -267.15827681 a.u. **R.E. = 0.0 kcal**	1,4-diaza-cyclohexane (**H**$_{\text{ax-eq}}$)  E = -267.15737770 a.u. **R.E. = 0.56 kcal**	1,4-diaza-cyclohexane (**H**$_{\text{ax-ax}}$)  E = -267.15597037 a.u. **R.E. = 1.45 kcal**
Dicyclohexylamine-crystal structure  E = -524.04334527 a.u.		

Table 1:- The eleoctronic energies at atomic units are given in MP2/aug-ccpvdz level of theory. The relative energies for the axial and equatorial positions of the respective systems at kcal/mol are also given here. The ChelpG charges for the different heteroatoms are also given.

As observed in earlier studies[63] our calculations on the conformations of the heterocycles, showed that 1-oxa-3-aza-cyclohexane with the axial conformation is more stable than the equatorial one while equatorial conformation of 1-oxa-4-aza-cyclohexane is more stable than the corresponding axial conformation. In case of 1,3-diaza-cyclohexane the one with both the N-H at the axial position is the most stable one,[48] while for 1,4-diaza-cyclohexane or piperazine, the one with both the N-H at the equatorial position is the most stable conformer.[49] For our further calculations, we have taken only the most stable conformers of the above heterocyclic systems.

The interactions of a single HP to the substrates have been shown in figure 1 and the corresponding binding energies are given in MP2/aug-cc-p-VDZ level of theory. It has been observed that the interaction of the one HP in the crystal structure geometry of dicyclohexylamine is -11.41 kcal/mol. The geometries in the crystal structure showed the O-O distance to be 1.475Å and a dihedral angle of 180 degree,[46] Interactions of water molecules with such hetero-cyclohexanes as discussed earlier,[48,49] shows strong hydrogen bonding interactions. The interactions of one HP to the different substrates showed that the interaction to N····H, yields stronger hydrogen bonding than the O····H and S···H. This phenomenon can be explained by the ChelpG charge of the systems (Table 1). The ChelpG charge[58-61] analysis for the systems showed that the charge of the Nitrogen atom was observed higher than the Oxygen which was again higher than the Sulphur atom and so interaction of the respective atoms shows such trends. The V_{min} values calculated for the substrates C, D, E and F also corroborates with the ChelpG charge (Figure S1, Supporting information). It is also observed that the interactions of the 1,4 systems are better than the 1,3 systems. The 1,3 analogues possesses anomeric effect which occurs between the lone pairs of Nitrogen/Oxygen/Sulphur and the perpendicular σ* of the nearby C-N, C-C, C-O or C-S bond. But the 1,4-analogues possesses the gauche effect which is the interaction between the lone pairs of Nitrogen/Oxygen/Sulphur and the perpendicular σ* of the nearby C-H bond. The increasing acceptor strength is σ*C-O > σ*C-N > σ*C-S > σ*C-C > σ*C-H.[43] Thus it is obvious that the anomeric effect will be much stronger than the gauche effect in these systems. Thus the availability of the lone pairs for hydrogen bonding will be relatively less for the 1,3-analogues and they form weaker H-bonds than the 1,4-analogues. The NBO analysis[61-64] of the respective systems (Table S3, supporting information) showed that the hyperconjugation energy 'E2' to be higher for the 1,3-analogues than the 1,4-analogues proving that Anomeric effects are stronger than the gauche effect. The HBE of the HP with the Nitrogen atom of the hetero-cyclohexanes are comparable with the interaction of 1-HP with the Nitrogen atom of the dicyclohexylamine.

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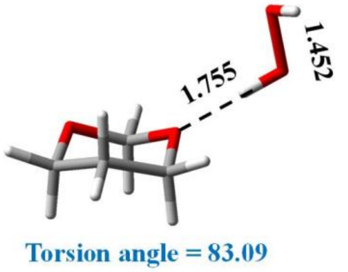
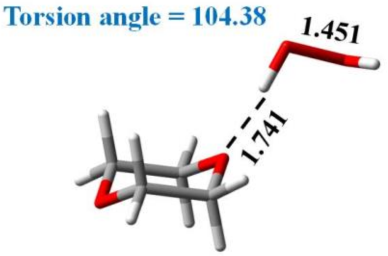
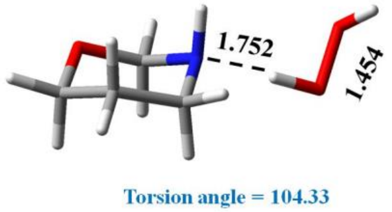
Dicyclohexylamine-1HP
HBE = -11.41



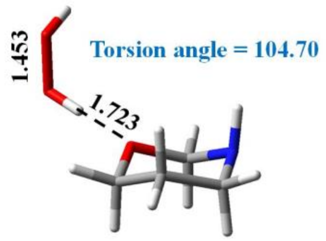
A-1HP
HBE = -9.17



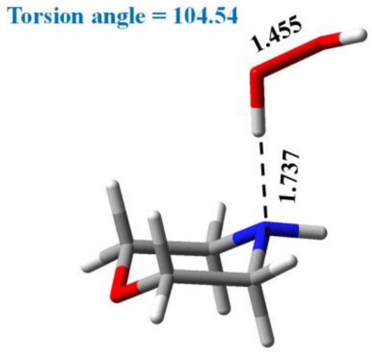
B-1HP
HBE = -9.33



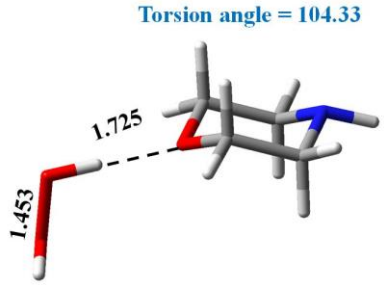
C_{ax}-1HP-N
HBE = -10.47



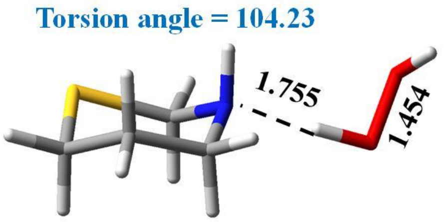
C_{ax}-1HP-O
HBE = -7.82



D_{eq}-1HP-N
HBE = -11.41



D_{eq}-1HP-O
HBE = -7.98

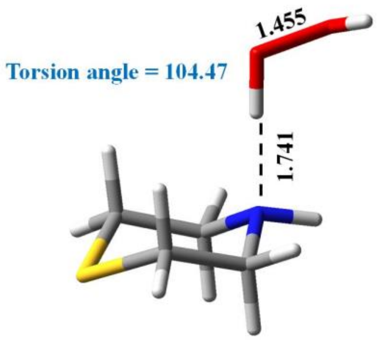


E_{ax}-1HP-N

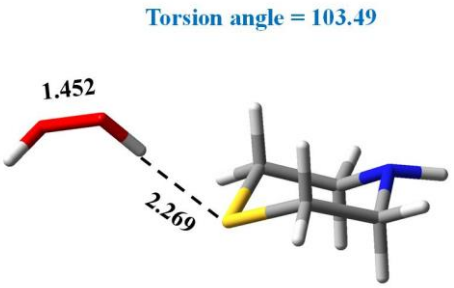
E_{ax}-1HP-S

HBE = -10.70

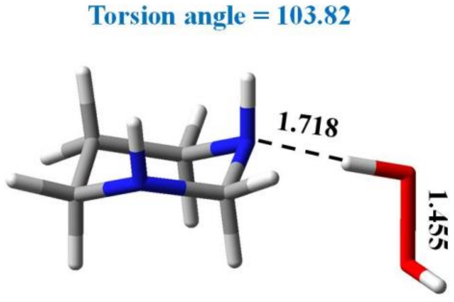
HBE = -5.95



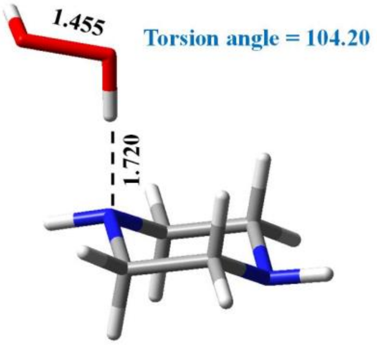
F$_{eq}$-1HP-N
HBE = -11.48



F$_{eq}$-1HP-S
HBE = -6.01



G$_{ax}$-1HP
HBE = -11.64

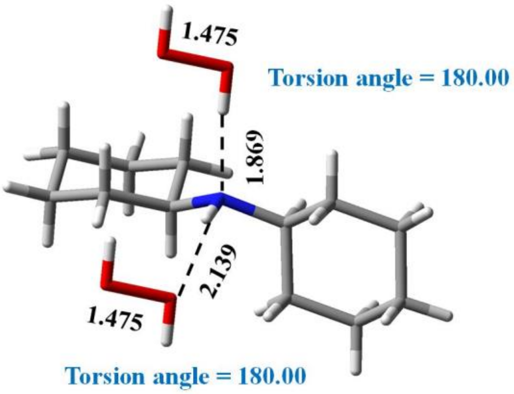


H$_{eq}$-1HP
HBE = -12.03

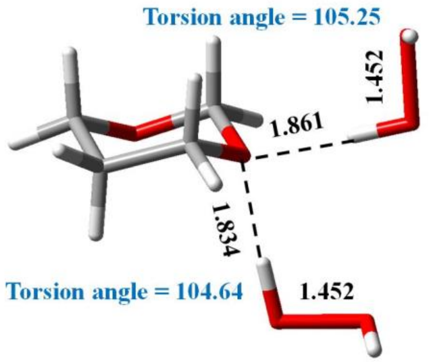
Fig 1:- Interactions of one HP with the substrates are given here. Hydrogen bonding energy in MP2/aug-cc-p-VDZ level of theory with PCM in kcal/mol are given here.

The interactions of two HP with the different substrates are given in figure 2. The Interactions of two HP molecules to the cyclohexanes are possible both from one side or one from each side interacting to each heteroatom. The interaction of the diclohexylamine with the two HP as observed in the crystal structure was observed to have a HBE of -15.67 kcal/mol at MP2/cc-p-VDZ level of theory. The approach of 2 HP from one side or both sides for the heterocycles with X=Y, showed higher HBE interaction than the diclohexylamine (Figure 2).

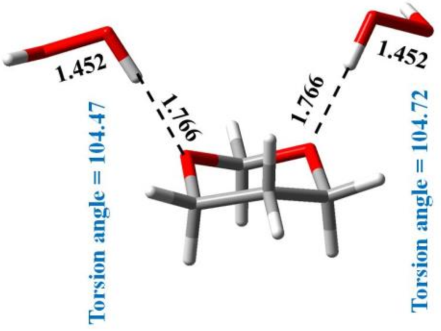
Approach of 2 HP from the Nitrogen site for the heterocylces with X=N; Y=O/S, showed lower interaction energy than the diclohexylamine, as one of the HP interacts to the hydrogen of the aza group, which gives lower interaction. Much lower interactions are observed with two HP interacting with the sulphur atom, which can be explained by its lower electronegativity than O/N and also its lower chelpg charge (Table 1). All other interactions showed higher HBE than the HBE for the diclohexylamine crystal structure. The two-side approach for 1,3- and 1,4-dioxa systems lower interactions than the one side approach, while for all other cases, the two side approach of the HP showed higher HBE. This is also due to the higher ChelpG charge of the Nitrogen atom on the oxa-aza; thio-aza or diaza systems.



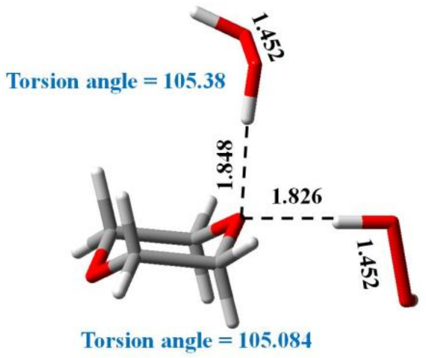
Dicyclohexylamine -2HP
HBE = -15.67



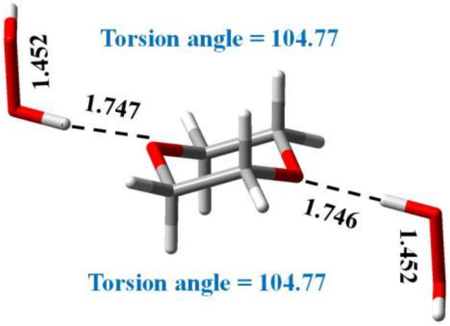
A-2HP-1side
HBE = -17.18



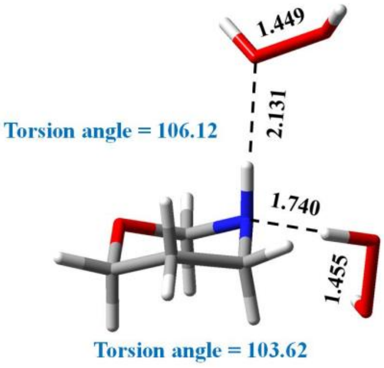
A-2HP-2side
HBE = -16.58

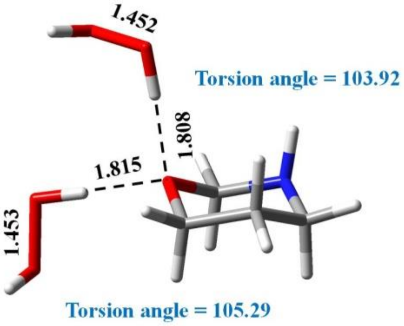


B-2HP-1side
HBE = -17.18

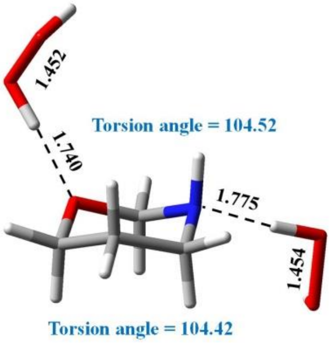


B-2HP-2side
HBE = -16.65





C$_{ax}$-2HP-O

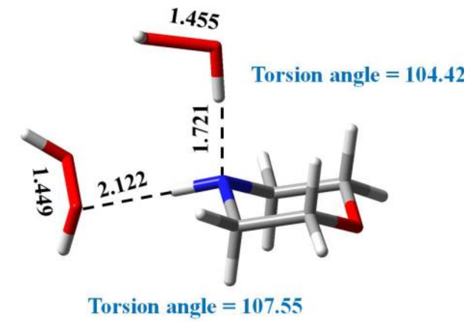


C$_{ax}$-2HP-2side

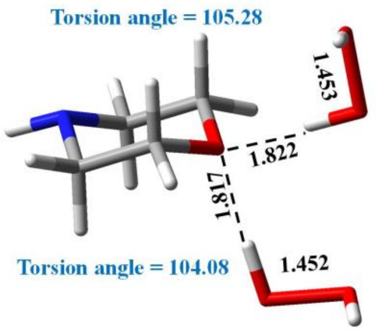
C$_{ax}$-2HP-N
HBE = -14.59

HBE = -16.45

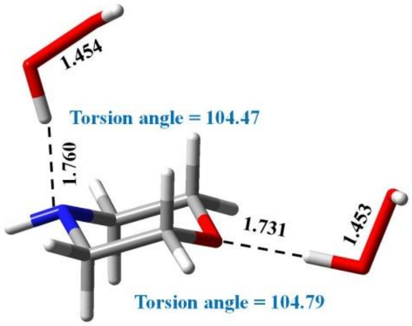
HBE = -16.44



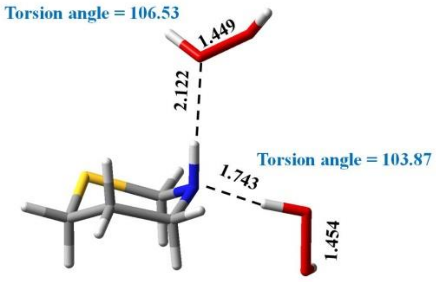
D$_{eq}$-2HP-N
HBE = -15.46



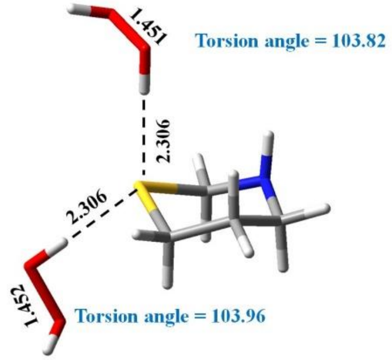
D$_{eq}$-2HP-O
HBE = -16.54



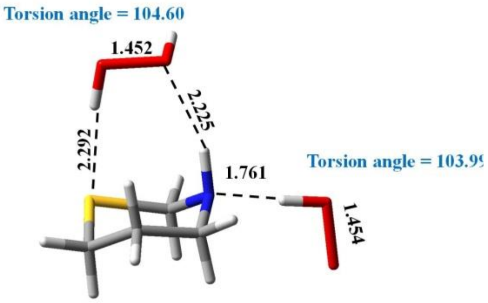
D$_{eq}$-2HP-2side
HBE = -19.45



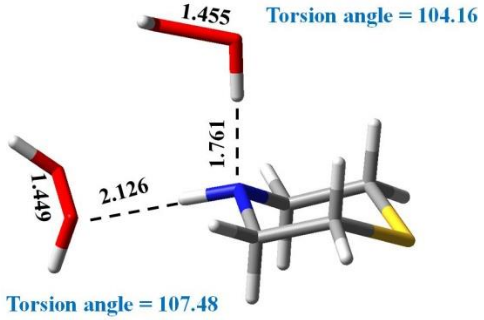
E$_{ax}$-2HP-N
HBE = -15.16



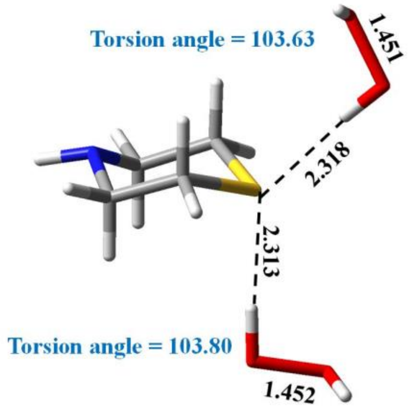
E$_{ax}$-2HP-S
HBE = -11.86



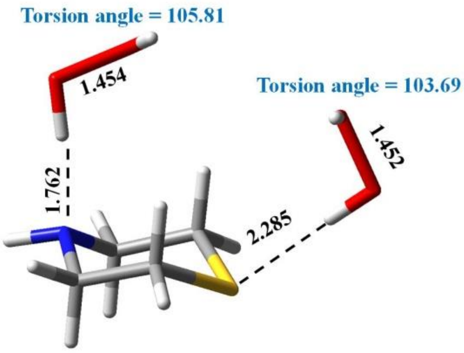
E$_{ax}$-2HP-2-side
HBE = -19.38



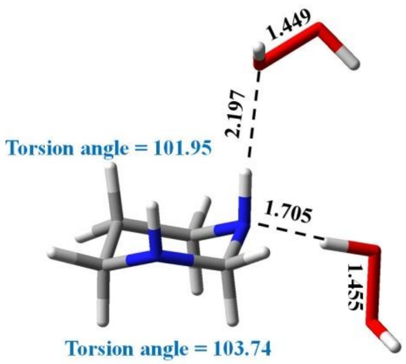
F$_{eq}$-2HP-N
HBE = -15.66



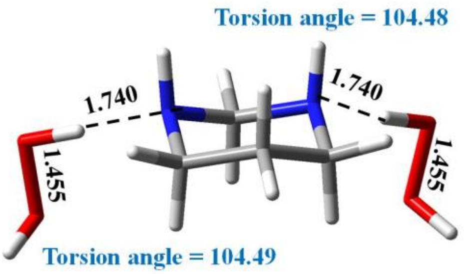
F$_{eq}$-2HP-S
HBE = -11.85



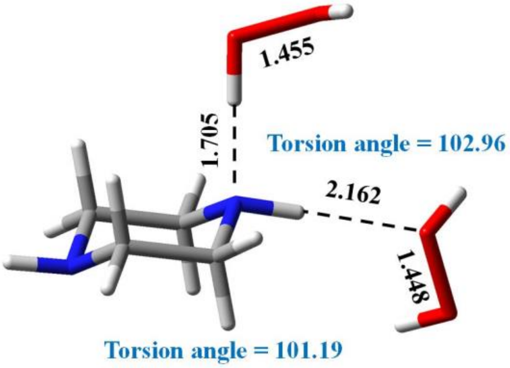
F$_{eq}$-2HP-2-side
HBE = -17.89



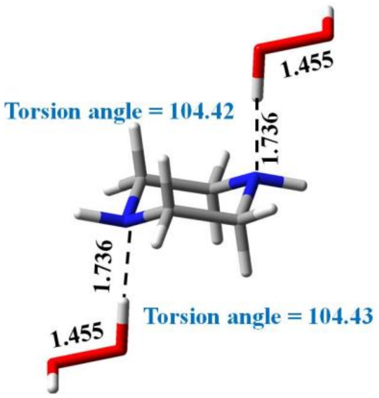
G_{ax}-2HP-1side
HBE = -15.22



G_{ax}-2HP-2side
HBE = -22.69



H_{eq}-2HP-1side
HBE = -15.69

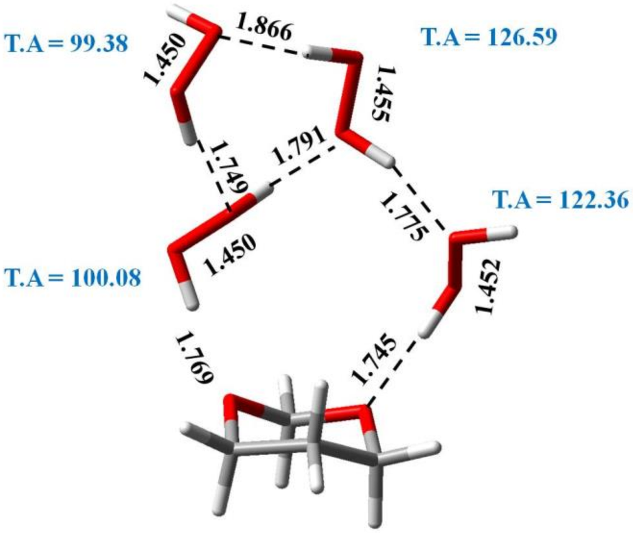


H_{eq}-2HP-2side
HBE = -23.56

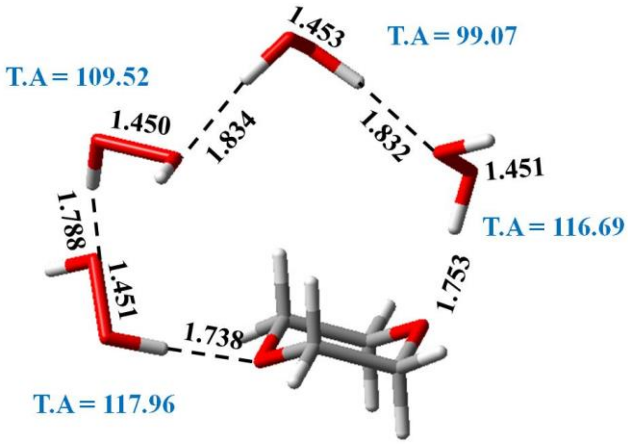
Fig 2:- Interactions of two HP with the stable conformations of the substrates from one side and both sides are given here. HBE at MP2/aug-cc-p-VDZ level of theory in kcal/mol are given.

Further calculations have been performed with four HP interactions with the hetero-cyclohexanes, which was not possible for the dicyclohexylamine. There are many possibilities of four HP to interact with these hetero-cyclohexanes. Two HP from two sides and a four membered ring approach have been taken in account in this study as such approaches will have the maximum number of hydrogen bonding with the HP and the substrate. The most stable structures are given in figure 3. Other possibilities are given in the supporting information (Figure S2). The HBE for all the cases, were observed to be much higher than the dicyclohexylamine. Here the HBE for the 1,3- systems are always observed to be higher than the 1,4-systems. This can be explained for each systems.

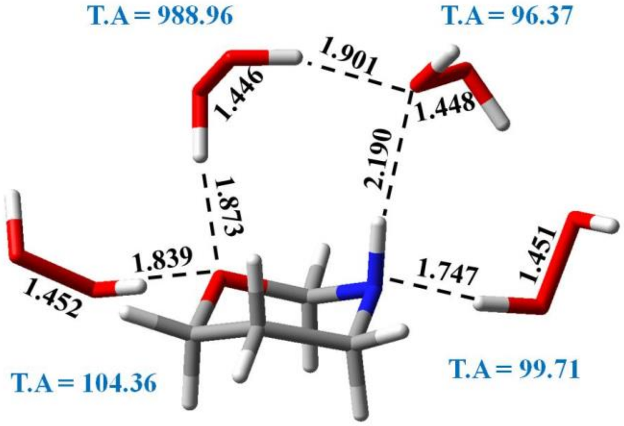
- A extra hydrogen bonding interaction between two HP is observed for 1,3-dioxa systems which resulted in a stronger HBE for these substrates than the 1,4-dioxa substrates.
- For 1,3 and 1,4 oxa-aza systems, it has been found that for the 1,3-systems two of the HP can interact with the substrate along with the hydrogen bonding among themselves, which was not possible for the 1,4-substrate due to longer distance between the heteroatoms. More symmetric hydrogen bonding for the 1,4-thio-aza systems results in stronger interactions for them thantheir 1,3-counterpart with similar number of hydrogen bondings.
- In case of 1,4-diaza, ring HP interactions one Nitrogen lone pair and one N-H is involved in the interaction with the HP, while for 1,3-diaza both the Nitrogen lone pairs are involved. Interactions to the lone pairs are far better than the N-H, so 1,3-diaza shows better interactions.



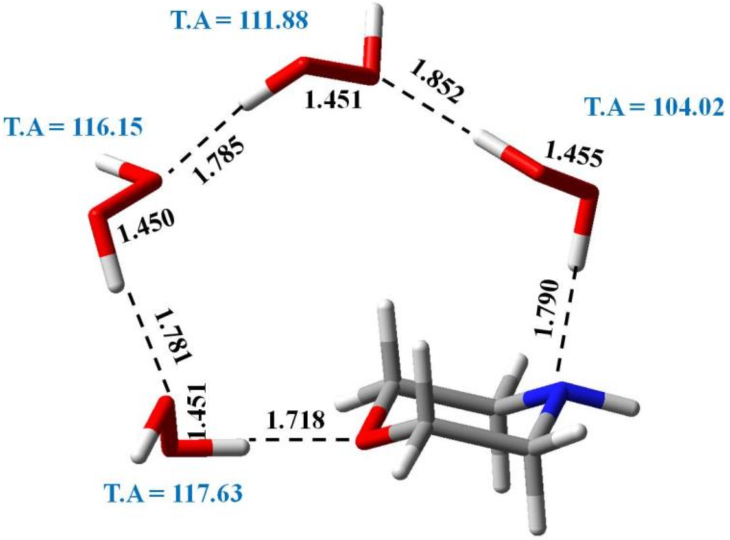
A-4HP
HBE = -37.92



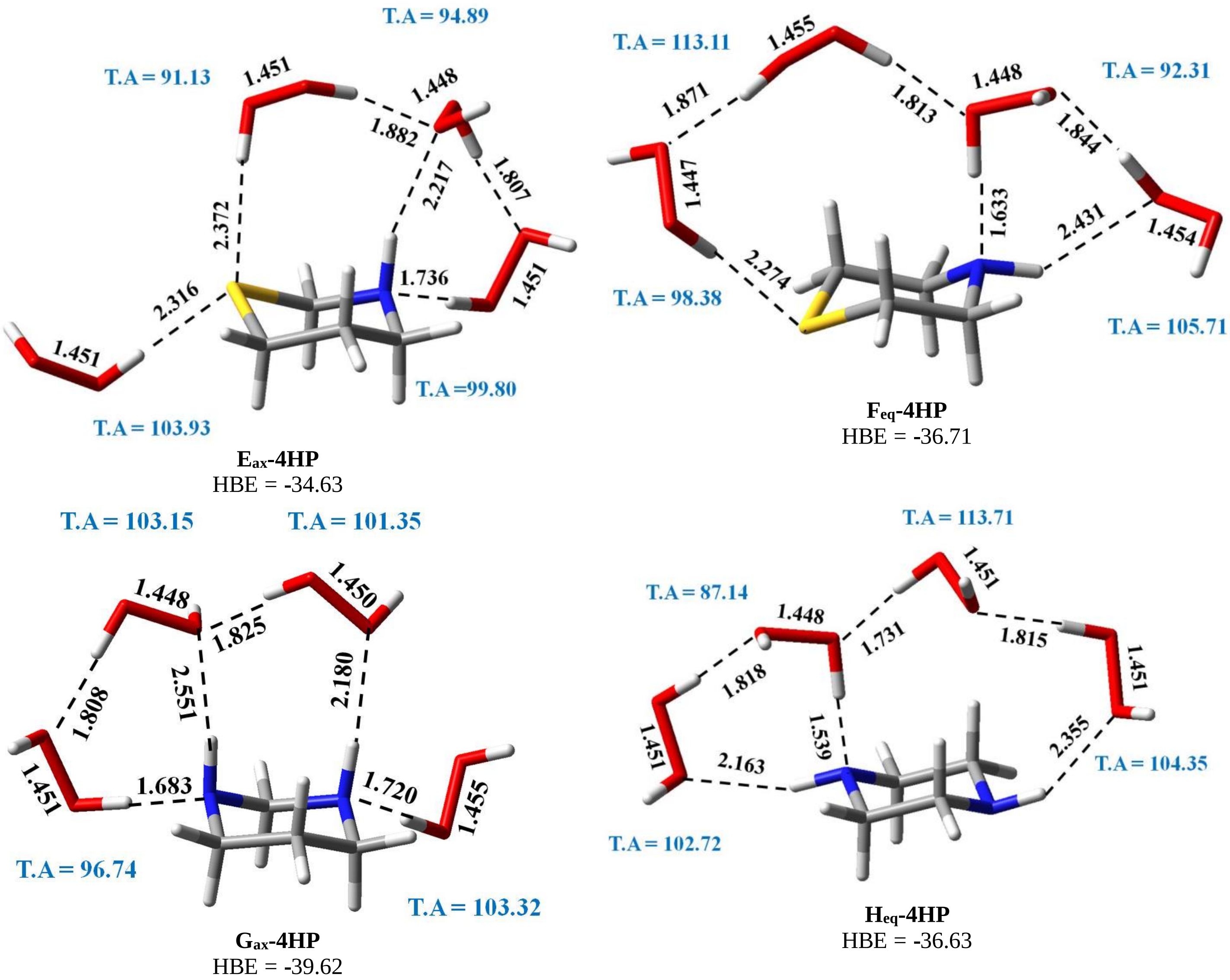
B-4HP
HBE = -35.08



C_{ax}-4HP
HBE = -38.43



D_{eq}-4HP
HBE = -36.49



E_{ax}-4HP
HBE = -34.63

F_{eq}-4HP
HBE = -36.71

G_{ax}-4HP
HBE = -39.62

H_{eq}-4HP
HBE = -36.63

Fig 3:- Interactions of four HP with the stable conformations of the substrates are given here. HBE at MP2/aug-cc-p-VDZ level of theory in kcal/mol are given. T.A. = Torsional Angle.

IV. CONCLUSION

In summary, we have calculated the interaction of one to four HP with the hetero-cylohexanes and calculated the HBE of the different interactions. Comparing with the known peroxosolvate, dicyclohexylamine, the heterocyclic systems 1,4-diaza, oxa-aza and thio-aza showed stronger hydrogen bonding for the one HP interaction. In case of two HP interactions, all the interactions with the different heterocycles showed stronger HBE than the dicyclohexylamine peroxosolvate. A two side approach is more efficient than a one side approach to the observed heterocycles. A possibility of four HP interactions is also possible for all the heterocyclic systems and the HBE for such interactions are much higher than the HBE in the known peroxosolvate. The reasons behind the difference in HBE within the different heterocycles have also been discussed through ChelpG charge and NBO analysis. This article will have an impact on the hydrogen bonding interactions of HP on such high stereoelectronic rich systems. This study also will lead us to design better HP-carrier or peroxosolvates.

ASSOCIATED CONTENT

- *Supporting Information*

The cartesian coordinates for all substrates and structures are available in the Supplementary material.

- *Acknowledgement*

Computer time on the JUSTUS cluster at Ulm University provided by the bwHPC initiative and the bwHPC-C5 project funded by the Baden-Württemberg government (MWK) and the German Research Foundation (DFG) is gratefully acknowledged. Dr. Biswajit Ganguly and

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