

## Molecular Structure Studies on Seven-Membered Heterocyclic $C_6H_6M$ ( $M = O, S, Se, Te, NH, PH, AsH, SbH, CH_2, SiH_2, GeH_2, SnH_2$ and $PbH_2$ ): DFT Calculations

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Molecular structure optimization are carried out on seven-membered heterocyclic  $C_6H_6M$ , including: oxepine  $C_6H_6O$ , thiepine  $C_6H_6S$ , selenepine  $C_6H_6Se$ , tellurepine  $C_6H_6Te$ , azepine  $C_6H_6NH$ , phosphepine  $C_6H_6PH$ , arsepine  $C_6H_6AsH$ , stibepine  $C_6H_6SbH$ , cyclohepta-1,3,5-triene  $C_6H_6CH_2$ , silepine  $C_6H_6SiH_2$ , germepine  $C_6H_6GeH_2$ , stannepine  $C_6H_6SnH_2$  and plumbepine  $C_6H_6PbH_2$  at B3LYP/6-311++G\*\* level of theory.

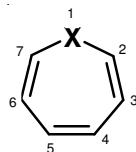
**Key Words:** Molecular structure, Seven-membered, Heterocyclic, DFT calculations.

### INTRODUCTION

Saturated and unsaturated seven-membered rings have been extensively studied<sup>1-8</sup>. The chair and twist-chair conformations of seven-membered rings have been classified as a function of the signs of their endocyclic torsion angles through MM3 analysis<sup>1</sup>. The conformational consequences of the anomeric effect have been determined for 3-methoxy-1,3,4,5-tetrahydro-2-benzoxepin by using  $^1H$  and  $^{13}C$  dynamic NMR techniques, two-dimensional COSY spectra at low temperatures<sup>3,4</sup>.

Geometrical and structural requirements for the ring planarization of cyclopolyolefins have been discussed<sup>5</sup>. The isomerizations of cycloheptatriene to norcaradiene, cyanocycloheptatrienes to cyanonorcaradienes, oxepin to benzene oxide and borepin to boranorcaradiene have been studied through *ab initio* molecular orbital theory<sup>6</sup>.

In this work, the molecular structure studies carried out on seven-membered heterocyclic  $C_6H_6M$  ( $M = O, S, Se, Te, NH, PH, AsH, SbH, CH_2, SiH_2, GeH_2, SnH_2$  and  $PbH_2$ ) through DFT calculations at B3LYP/6-311++G\*\* level of theory (**Scheme-I**).



**Scheme-I:** Seven-membered ring of  $C_6H_6M$  ( $M = O, S, Se, Te, NH, PH, AsH, SbH, CH_2, SiH_2, GeH_2, SnH_2$  and  $PbH_2$ )

### COMPUTATIONAL METHODS

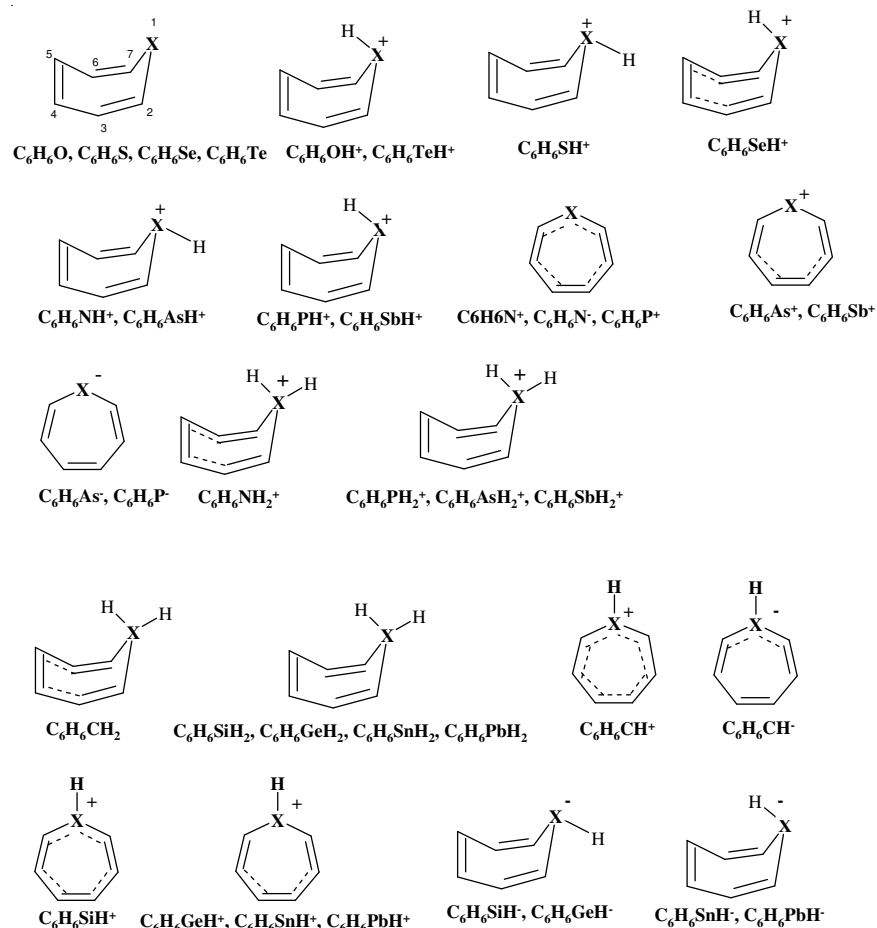
Full geometry optimizations are carried out for  $C_6H_6M$  ( $M = O, S, Se, Te, NH, PH, AsH, SbH, CH_2, SiH_2, GeH_2, SnH_2$  and  $PbH_2$ ) through DFT method using 6-311++G\*\* basis set (**Scheme-I**)<sup>9,10</sup>. The all of calculations are done with Gaussian 98 program<sup>11</sup>. For DFT calculations the Becke's hybrid three-parameters functional combined with the Lee-Yang-Parr non-local correlation functional (B3LYP) are used. The calculations are carried out by LANL2DZ basis set<sup>12</sup> for Te, Sb, Sn and Pb atoms, accompanying the 6-311++G\*\* basis set for other atoms *via* 'Extrabasis' keyword. To confirm the nature of the stationary species, frequency calculations are carried out. Thermodynamic functions obtained through frequency calculations, are multiplied by the suitable scaling factor and correction terms.

### RESULTS AND DISCUSSION

In this work, full molecular structure optimizations are carried out on seven-membered heterocyclic ( $C_6H_6M$ ) including: oxepine  $C_6H_6O$ , thiepine  $C_6H_6S$ , selenepine  $C_6H_6Se$ , tellurepine  $C_6H_6Te$ , azepine  $C_6H_6NH$ , phosphepine  $C_6H_6PH$ , arsepine  $C_6H_6AsH$ , stibepine  $C_6H_6SbH$ , cyclohepta-1,3,5-triene  $C_6H_6CH_2$ , silepine  $C_6H_6SiH_2$ , germepine  $C_6H_6GeH_2$ , stannepine  $C_6H_6SnH_2$  and plumbepine  $C_6H_6PbH_2$  at B3LYP/6-311++G\*\* level of theory (**Schemes-I and II**).

DFT calculations indicate that the compounds  $C_6H_6O$ ,  $C_6H_6S$ ,  $C_6H_6Se$  and  $C_6H_6Te$  have boat conformation (**Scheme-II**). The protonated  $C_6H_6O$  ( $C_6H_6OH^+$ ) and  $C_6H_6Te$  ( $C_6H_6TeH^+$ ) have a boat conformation with *endo* position of proton, while  $C_6H_6SH^+$  have boat conformation with *exo* position of proton. Protonated  $C_6H_6SeH^+$  has boat conformation with two quasi double bonds ( $C_3-C_4$  and  $C_5-C_6$ ). It is seemed that the protonated  $C_6H_6SeH^+$  construct a homoaromatic system.

$C_6H_6NH$  and  $C_6H_6AsH$  have boat conformation with *exo* position of proton (**Scheme-II**).  $C_6H_6PH$  and  $C_6H_6SbH$  have boat conformation with *endo* position of proton. The  $C_6H_6N^+$  and  $C_6H_6P^+$  construct a planar conformation with aromatic character.  $C_6H_6As^+$  and  $C_6H_6Sb^+$  have a planar conformation with homoaromatic character. Surprisingly, the  $C_6H_6N^-$  has a planar conformation but the DFT calculations indicated a negative imagine frequency.



**Scheme-II:** Full optimized conformations for seven-membered ring of  $C_6H_6M$  ( $M = O, S, Se, Te, NH, PH, AsH, SbH, CH_2, SiH_2, GeH_2, SnH_2$  and  $PbH_2$ )

$C_6H_6P^-$  and  $C_6H_6As^-$  have a planar conformation but don't show any aromatic character. Protonated  $C_6H_6NH_2^+$ ,  $C_6H_6PH_2^+$ ,  $C_6H_6AsH_2^+$  and  $C_6H_6SbH_2^+$  have boat conformations while  $C_6H_6NH_2^+$  construct quasi double bonds ( $C_3-C_4$  and  $C_5-C_6$ ) with homoaromatic character.

The compounds,  $C_6H_6CH_2$ ,  $C_6H_6SiH_2$ ,  $C_6H_6GeH_2$ ,  $C_6H_6SnH_2$  and  $C_6H_6PbH_2$  form boat conformations (**Scheme-II**). However,  $C_6H_6CH_2$  construct quasi double bonds ( $C_3-C_4$  and  $C_5-C_6$ ) with homoaromatic character.  $C_6H_6CH^+$  and  $C_6H_6CH^-$  have planar structure while  $C_6H_6CH^+$  form an aromatic system.  $C_6H_6SiH^+$  have planar structure with aromatic character and  $C_6H_6GeH^+$ ,  $C_6H_6SnH^+$  and  $C_6H_6PbH^+$  have planar structure with homoaromatic character.  $C_6H_6SiH^-$  and  $C_6H_6GeH^-$  have boat conformation with *exo* position of proton

while  $C_6H_6SnH^-$  and  $C_6H_6PbH^-$  have boat conformation with *endo* position of proton. The DFT calculations indicated a negative imaginary frequency for  $C_6H_6CH^-$ ,  $C_6H_6N^-$ ,  $C_6H_6P^-$  and  $C_6H_6As^-$ .

### Conclusion

Molecular structure optimizations are carried out on seven-membered heterocyclic  $C_6H_6M$  through DFT calculations at B3LYP/6-311++G\*\* level of theory. DFT calculations indicate that the compounds  $C_6H_6O$ ,  $C_6H_6S$ ,  $C_6H_6Se$ ,  $C_6H_6Te$ ,  $C_6H_6NH$ ,  $C_6H_6AsH$ ,  $C_6H_6PH$ ,  $C_6H_6SbH$ ,  $C_6H_6CH_2$ ,  $C_6H_6SiH_2$ ,  $C_6H_6GeH_2$ ,  $C_6H_6SnH_2$  and  $C_6H_6PbH_2$  have boat conformations.  $C_6H_6CH_2$  show a homoaromatic character among of these compounds. Generally, the carbocationic state of these compounds show aromatic and/or homoaromatic character.

### REFERENCES

1. A. Entrena, J. Campos, J.A. Gómez, M.A. Gallo and A. Espinosa, *J. Org. Chem.*, **62**, 337 (1997).
2. K.R. Gibson, L. Hitzel, R.J. Mortishire-Smith, U. Gerhard, R.A. Jelley, A.J. Reeve, M. Rowley, A. Nadin and A.P. Owens, *J. Org. Chem.*, **67**, 9354 (2002).
3. S. Desilets and M. St-Jacques, *J. Am. Chem. Soc.*, **109**, 1641 (1987).
4. D. McCard and M. St-Jacques, *J. Am. Chem. Soc.*, **106**, 2055 (1984).
5. O. Ermer, F.G. Klärner and M. Wette, *J. Am. Chem. Soc.*, **108**, 4908 (1986).
6. J.M. Schulman, R.L. Disch and M.L. Sabio, *J. Am. Chem. Soc.*, **106**, 7696 (1984).
7. C.L. Anderson, W.J. Horton, F.E. Walker and M.R. Weiler, *J. Am. Chem. Soc.*, **77**, 598 (1955).
8. N.L. Allinger and N.A. Pamphilis, *J. Org. Chem.*, **58**, 316 (1973).
9. C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
10. A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
11. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Znkzrewski, G.A. Montgomery, R.E. Startmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pamelli, G. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokoma, D.K. Malick, A.D. Rubuck, K. Raghavachari, J.B. Foresman, J. Cioslawski, J.V. Ortiz, B.B. Stlefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Comperts, R.L. Martin, P.J. Fox, T. Keith, M.A. Al-laham, C.Y. Peng, A.N. Akkara, C.G. Gonzales, M.C. Combe, P.M.W. Gill, B. Johnson, W. Chem, M.W. Wong, J.L. Andres, C. Gonzales, M. Head-Gordon, E.S. Replogle and J.A. Pople, GAUSSIAN 98, Revision A. 6, Gaussian Inc., Pittsburgh PA (1998).
12. H.B. Schlegel and M.J. Frisch, *Int. J. Quantum Chem.*, **54**, 83 (1995).