Conformational Studies on Divalent Seven-membered Ring C_6H_6M (M = C, Si, Ge, Sn and Pb): DFT Calculations

E. VESSALLY

Department of Chemistry, Payame Noor University, Zanjan, Iran
E-mail: e_vesali@yahoo.com

Conformational studies are carried out on divalent seven-membered C_6H_6M (M = Si, Ge, Sn and Pb) through DFT calculations. The most stable tautomers and conformers are suggested for singlet and triplet states of C_6H_6M. The Gibbs free energy differences between singlet and triplet states, ΔG_{s-t}, are calculated for C_6H_6C, C_6H_6Si, C_6H_6Ge, C_6H_6Sn and C_6H_6Pb, at B3LYP/6-311++G (3df,2p). The singlet-triplet gap, ΔG_{s-t}, of C_6H_6M (M = C, Si, Ge, Sn and Pb) are generally increased from M = C to M = Pb.

INTRODUCTION

The properties of divalent carbenes and their heavier analogues are studied through matrix isolation techniques[1]. Among the carbenes, cyclic planar conjugated carbenes and their non-planar allene isomers are intensively investigated[1-19]. Allene (C_6H_6C) is suggested to be a key intermediate in arylcarbene interconversions and related C_6H_6C rearrangements[17,18]. Interconversions of the isomeric tolylmethylenes, through substituted $\mathbf{1}_{TS}$, are also reported[19]. Early trapping studies suggested equilibration between C_6H_6C and $(C_6H_6C)(TS)$.

In this manuscript, DFT comparative studies on completely conjugated cyclohepta-2,4,6-trienylidenes (C_6H_6C, C_6H_6Si, C_6H_6Ge, C_6H_6Sn and C_6H_6Pb) are carried out. We comparatively studied the singlet-triplet splitting and stability for C_6H_6C, C_6H_6Si, C_6H_6Ge, C_6H_6Sn and C_6H_6Pb.

EXPERIMENTAL

Full geometry optimizations are carried out by B3LYP method[20,21]. This is using 6-311++G(3df,2p) basis set of the GAUSSIAN 98 system of program[22]. Global minima are specified on corresponding energy surfaces through relax scan at B3LYP/6-311++G (3df,2p) level of theory. Energy surfaces scanning is for obtaining more accurate values of change of electronic and thermal energies ΔE_{s-t}, enthalpies ΔH_{s-t} and Gibbs free energies ΔG_{s-t}. For

Sn and Pb atoms, the calculations are done *via* 'Extrabasis' keyword (hetero-atoms are optimized using LANL2DZ basis set)[23]. To confirm the nature of the stationary species, frequency calculations are carried out. For minimum state structures, only real frequency values are accepted.

RESULTS AND DISCUSSION

Sum of electronic and thermal energy differences, ΔE_{s-t}; enthalpy differences, ΔH_{s-t}; free energy differences between singlet and triplet states, ΔG_{s-t}, are calculated for C_6H_6C, C_6H_6Si, C_6H_6Ge, C_6H_6Sn and C_6H_6Pb, at B3LYP/6-311++G (3df,2p) (Table-1).

TABLE-1

THERMAL ENERGY DIFFERERNCES ΔE_{s-t}; ENTHALPY DIFFERERNCES ΔH_{s-t}; GIBBS FREE ENERGY DIFFERERNCES ΔG_{s-t}, BETWEEN SINGLET AND TRIPLET STATES FOR C_6H_6M (M = C, Si, Ge, Sn AND Pb) CALCULATED AT B3LYP/6 311++G (3df,2p)

Compound	ΔE_{s-t}	ΔH_{s-t}	ΔG_{s-t}
C_6H_6C	-18.097	-18.097	-16.662
C_6H_6Si	-29.695	-29.696	-30.010
C_6H_6Ge	-37.213	-37.213	-36.535
C_6H_6Sn	-36.767	-36.767	-36.331
C_6H_6Pb	-44.761	-44.761	-44.216

DFT calculations on singlet state of C_6H_6C show a ground state with non-planar, twist, conformer and allenic tautomer (1,2,4,6-cycloheptatetraene) (**Scheme-I**). This allenic tautomer with non-planar conformer is more stable than carbenic tautomer with planar conformer of 2,4,6-cycloheptatrienylidene (transition state). Racemization of allenic tautomer and non-planar 1,2,4,6-cycloheptatetraene are also shown (**Scheme-II**). The racemization of the allene is found to go through their corresponding planar singlet carbenic transition state of 2,4,6-cycloheptatrienylidene. In contrast, carbenic tautomer with planar conformer of singlet states for heavier analogues sila-, germa-, stana- and plumba-2,4,6-cycloheptatrienylidene is ground state and more stable than allenic tautomer (transition state) (**Schemes I** and **II**). Meanwhile, the quasi double bond is formed for singlet states of sila- and germa-2,4,6-cycloheptatrienylidene between C_3 and C_4 as well as C_5 and C_6 (**Scheme-I**).
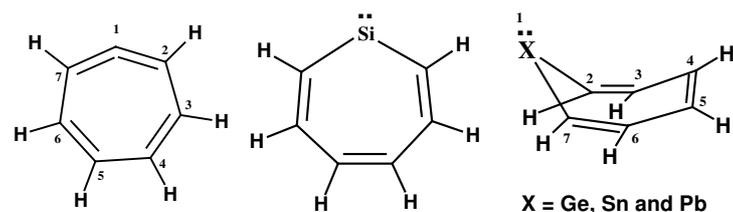
The planar conformer for triplet state of C_6H_6C with allenic tautomer is ground state (1,2,4,6-cycloheptatetraene) (**Scheme-III**). For triplet state of C_6H_6Si, the carbenic tautomer with planar conformer is ground state (sila-2,4,6-cycloheptatrienylidene). For triplet state of C_6H_6M (M = Ge, Sn and Pb), the carbenic tautomer with boat conformer is ground state.
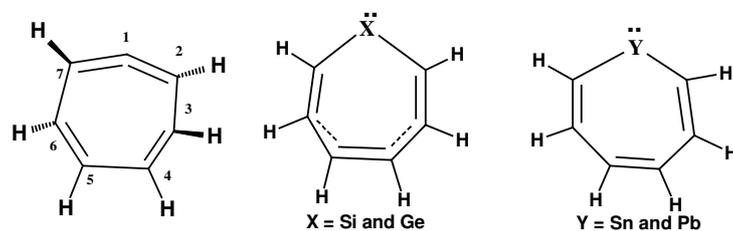
Scheme-I: Full optimized and ground state tautomers and conformers for singlet states: allenic tautomer of C_6H_6C with boat conformer and carbenic tautomer with planar conformer of C_6H_6M (M = Si, Ge, Sn and Pb)
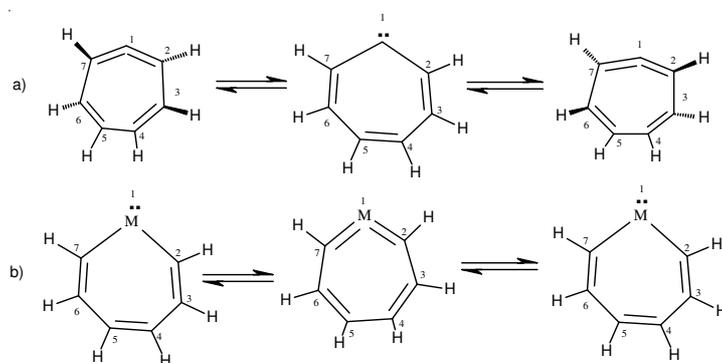
Scheme-II: a) Topologically singlet state racemization of allenic tatumer of C_6H_6C through their corresponding planar carbenic transition state. b) Interconversion of carbenic tautomer of C_6H_6M (M = Si, Ge, Sn and Pb) to their corresponding allenic transition state


Scheme-III: Full optimized and ground state tautomers and conformers for triplet states: allenic tautomer of C_6H_6C with planar conformer, carbenic tautomer with planar conformer for C_6H_6Si and carbenic tautomer with boat conformer for C_6H_6M (M = Ge, Sn and Pb)

The singlet-triplet splitting, ΔG_{s-t} of C_6H_6C, C_6H_6Si, C_6H_6Ge, C_6H_6Sn and C_6H_6Pb are generally increased from C_6H_6C toward C_6H_6Pb. Heavier atoms prefer to have non-bonding electrons with a higher percentage of s-character. The higher s-character of heavier atoms in C_6H_6M leads to stabilize the singlet state state.

The bond lengths of singlet and triplet states indicate an allenic tautomer for C_6H_6C respect to a carbenic tautomer for heavier analogues of C_6H_6M (M = Si, Ge, Sn and Pb) (Table-2). So, the bond lengths R_{12} and R_{34} for singlet and triplet states of C_6H_6C are shorter than for C_6H_6M. The bond length R_{12} for singlet state is shorter than for triplet states of C_6H_6C while the bond length R_{12} for singlet state is larger than for triplet states of C_6H_6M.

TABLE-2
CALCULATED B3LYP/6-311++G (3df,2p) BOND LENGTHS (R), BOND
ANGLE (Å), FOR BOTH SINGLET (s) AND TRIPLET (t) STATES OF
C_6H_6M (M = C, Si, Ge, Sn AND Pb)
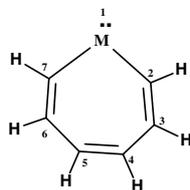
Compound	R_{12}	R_{34}	A_{712}
C_6H_6C (s)	1.33	1.37	146.2
C_6H_6Si (s)	1.88	1.43	102.5
C_6H_6Ge (s)	1.97	1.43	100.8
C_6H_6Sn (s)	2.15	1.44	96.98
C_6H_6Pb (s)	2.22	1.44	95.74
C_6H_6C (t)	1.36	1.36	139.8
C_6H_6Si (t)	1.84	1.46	116.8
C_6H_6Ge (t)	1.93	1.46	112.6
C_6H_6Sn (t)	2.13	1.46	106.4
C_6H_6Pb (t)	2.21	1.46	104.1

The bond angle A_{712} for singlet and triplet states is reasonably decreased for C_6H_6M from M = C to M = Pb. The bond angle A_{712} for singlet state is larger than for triplet states of C_6H_6C while the bond length R_{12} for singlet state is smaller than for triplet states of C_6H_6M[24,25].

Conclusion

The planar conformer for triplet state of C_6H_6C with allenic tautomer is ground state. For triplet state of C_6H_6Si, carbenic tautomer with planar conformer is ground state. For triplet state of C_6H_6M (M = Ge, Sn and Pb), the carbenic tautomer with boat conformer is ground state. The singlet-triplet splitting, ΔG_{s-t} of C_6H_6C, C_6H_6Si, C_6H_6Ge, C_6H_6Sn and C_6H_6Pb are generally increased from C_6H_6C toward C_6H_6Pb. For singlet state of C_6H_6C, the ground state is allenic tautomer and twist conformer. In contrast, the carbenic tautomer with planar conformer for C_6H_6M (M = Si, Ge, Sn and Pb) is ground state.

REFERENCES

1. P.P. Gaspar and R. West, in eds.: Z. Rappoport and Y. Apeloig, Chemistry of Organic Silicon Compounds, Wiley, Chichester, Vol. 2, p. 2436 (1997).
2. R.A. Seburg, B.T. Hill, R.A. Jesinger and R.R. Squires, *J. Am. Chem. Soc.*, **121**, 6310 (1999).
3. B.M. Armstrong, F. Zheng and P.B. Shevlin, *J. Am. Chem. Soc.*, **120**, 6007 (1998).
4. C.R. Kemnitz, W.L. Karney and W.T. Borden, *J. Am. Chem. Soc.*, **120**, 3499 (1998).
5. B.M. Armstrong, M.L. McKee and P.B. Shevlin, *J. Org. Chem.*, **63**, 7408 (1998).
6. W.L. Karney and W.T, Borden, *J. Am. Chem. Soc.*, **119**, 1378 (1997).
7. Y. Xie, P.R. Schreiner, P.V.R. Schleyer and H.F. Schaefer, *J. Am. Chem. Soc.*, **119**, 1370 (1997).
8. M.W. Wong and C. Wentrup, *J. Org. Chem.*, **61**, 7022 (1996).
9. S. Matzinger, T. Bally and E.Y. Patterson, McMahon, *J. Am. Chem. Soc.*, **118**, 1535 (1996).
10. R.J. McMahon and O.L. Chapman, *J. Am. Chem. Soc.*, **108**, 1713 (1986).
11. J.W. Harris and W.M. Jones, *J. Am. Chem. Soc.*, **104**, 7330 (1982).
12. B.L. Duell and W.M. Jones, *J. Org. Chem.*, **43**, 4901 (1978).
13. K. Saito, Y. Omura and T. Mukai, *Chem. Lett.*, 349 (1980).
14. E.E. Waali, J.M. Lewis, D.E. Lee, E.W. Allen III and A.K. Chappel, *J. Org. Chem.*, **42**, 3460 (1977).
15. (a) M.Z. Kassaee, S. Arshadi, M. Acedy and E. Vessally, *J. Organomet. Chem.*, **690**, 3427 (2005); (b) E. Vessally, N. Chalyavi, A. Rezaei and M. Nikoorazm, *Russ. J. Phys. Chem.*, **81**, 1821 (2007); (c) E. Vessally, A. Rezaei N., Chalyavi and M. Nikoorazm, *J. Chin. Chem. Soc.*, **54**, 1583 (2007); (d) E. Vessally, M. Nikoorazm, A. Rezaei and N. Chalyavi, *Asian J. Chem.*, **19**, 5000 (2007); (e) E. Vessally, *Heteroatom Chem.*, **19**, 245 (2008); (f) A.R. Rod and E. Vessally, *Asian J. Chem.*, **19**, 1709 (2007); (g) E. Vessally, M. Nikoorazm and A. Ramazani, *Chin. J. Inorg. Chem.*, **24**, 631 (2008); (h) E. Vessally, M. Nikoorazm, H.G. Afashar and T. Mohsenpour, *Asian J. Chem.*, **20**, 1121 (2008).
16. W. Kirmse and H.D. Sluma, *J. Org. Chem.*, **53**, 763 (1987).
17. R.J. McMahon and O.L. Chapman, *J. Am. Chem. Soc.*, **108**, 1713 (1986).
18. R.J. McMahon, C.J. Abelt, O.L. Chapman, J.W. Johnson, C.L. Kreil, J.P. Leroux, A.M. Mooring and P.R. West, *J. Am. Chem. Soc.*, **109**, 2456 (1987).
19. O.L. Chapman, J.W. Johnson, R.J. McMahon and P.R. West, *J. Am. Chem. Soc.*, **110**, 501 (1988).
20. C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
21. A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
22. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Znkrzewski, 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. Oritz, 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, J.A. Pople, GAUSSIAN 98, Revision A. 6, Gaussian Inc., Pittsburgh PA (1998).
23. H.B. Schlegel and M.J. Frisch, *Int. J. Quantum Chem.*, **54**, 83 (1995).
24. K. Balasubramanian, *J. Chem. Phys.*, **89**, 5731 (1988).
25. C. Gonzalez, A. Restrepo-Cossio, M. Márquez, K.B. Wiberg and M.D. Rosa, *J. Phys. Chem. A*, **102**, 2732 (1998).