Bull. Chem. Soc. Ethiop. **2009**, 23(2), 223-229.
Printed in Ethiopia

ISSN 1011-3924

THE SINGLET-TRIPLET ENERGY GAP IN DIVALENT THREE, FIVE AND SEVEN-MEMBERED CYCLIC C_2H_2M, C_4H_4M AND C_6H_6M (M = C, Si, Ge, Sn AND Pb)

E. Vessally*

Payame Noor University (PNU), Zanjan, Iran

(Received July 9, 2008; revised February 4, 2009)

ABSTRACT. Total energy gaps, $\Delta E_{t\text{–}s}$, enthalpy gaps, $\Delta H_{t\text{–}s}$, and Gibbs free energy gaps, $\Delta G_{t\text{–}s}$, between singlet (s) and triplet (t) states were calculated for three, five and seven-membered cyclic C_2H_2M, C_4H_4M and C_6H_6M (M = C, Si, Ge, Sn and Pb) at B3LYP/6-311++G**. The singlet-triplet free energy gaps, $\Delta G_{t\text{-}s}$, for C_2H_2M (M = C, Si, Ge, Sn and Pb) are found to be increased in the order: $C_2H_2Si > C_2H_2C > C_2H_2Ge > C_2H_2Sn > C_2H_2Pb$. The $\Delta G_{t\text{-}s}$ of C_4H_4M are found to be increased in the order: $C_4H_4Pb > C_4H_4Sn > C_4H_4Ge > C_4H_4Si > C_4H_4C$. Also, the $\Delta G_{t\text{-}s}$ of C_6H_6M are determined in the order: $C_6H_6Pb > C_6H_6Ge \geq C_6H_6Sn > C_6H_6Si > C_6H_6C$. The most stable conformers of C_2H_2M, C_4H_4M and C_6H_6M are proposed for both the singlet and triplet states. Nuclear independent chemical shifts (NICS) calculations were carried out for determination of aromatic character. The geometrical parameters are calculated and discussed.

KEY WORDS: C_2H_2M, C_4H_4M, C_6H_6M, Singlet-triplet gaps, Stability

INTRODUCTION

The chemistry of the divalent carbenes: silylenes, germylenes, stanylenes and plumbylenes has been studied [1-5]. The first silylene has been synthesized by Denk [6]. Isolation of the plumbylene has been reported by Lappert [7].

The cyclic conjugated species are important in the chemistry of divalent carbene intermediates [8]. The isolation of the stable five membered cyclic conjugated carbene has been reported by Arduengo [9]. Later, the stable five membered cyclic singlet silylenes and germylenes have been investigated [10, 11]. Also, considerable development has been made in the chemistry of divalent stanylenes [12]. Finally, the isolation of the plumbylenes and their derivatives has been reported [13-16].

The seven membered divalent rings have extensively been studied [17]. It has been proposed that allene isomer was the most stable of C_6H_6C.

As a continuation of our studies [8] we have carried out density functional theory (DFT) comparative studies on singlet-triplet gaps of conjugated C_2H_2M, C_4H_4M and C_6H_6M (M = C, Si, Ge, Sn and Pb) at B3LYP/6-311++G** level of theory. Also, nuclear independent chemical shifts (NICS) calculations were carried out for the determination of aromatic character. The concept of NICS was introduced by Schleyer *et al.* in 1996 as a measure of aromaticity and antiaromaticity (or non-aromaticity) [18]. It is based on a probe with no basis functions (bq) which is placed at or above the geometrical center of a conjugated ring. Its calculated isotropic NMR chemical shift indicates the aromatic properties of the ring, either as an individual moiety in a polycyclic compound or as a molecule. Initially the probe was placed at the geometrical center of the molecules, but after realizing that in some systems the chemical shifts are influenced by the σ system (e.g. cyclopropane) it was placed 0.5 Å above the center (denoted as NICS (0.5)). The method has been used for the assignment of aromatic character in many systems, generally very successfully.

---

*Corresponding author. E-mail: e_vesali@yahoo.com

EXPERIMENTAL

Full geometry optimizations of C_2H_2M, C_4H_4M and C_6H_6M (M = C, Si, Ge, Sn and Pb) were carried out by DFT method using 6-311++G** basis set of the GAUSSIAN 98 program [19-21] (Scheme 1). To ensure that the minimum energy is a global minimum, all possible conformations of the given species were examined through scanning the specific dihedral angles. This is for obtaining more accurate values of total energies (E), enthalpies (H) and Gibbs free energies (G). For Sn and Pb atoms, the calculations were done using LANL2DZ basis set [22].

RESULTS AND DISCUSSION

Total energies (E), enthalpies (H) and Gibbs free energies (G) were calculated for the singlet (s) and triplet (t) states of C_2H_2M, C_4H_4M and C_6H_6M (M = C, Si, Ge, Sn and Pb) *via* B3LYP/6-311++G**. All singlet states (except for C_4H_4M) of C_2H_2M, C_4H_4M and C_6H_6M are more stable than their corresponding triplet states. Total energy gaps, ΔE_{t-s}; enthalpy gaps, ΔH_{t-s}; Gibbs free energy gaps between singlet and triplet states, ΔG_{t-s}, were calculated for C_2H_2M, C_4H_4M and C_6H_6M (Table 1). Geometrical parameters including bond lengths (R), bond angles (A), and dihedral angles (D) of C_2H_2M, C_4H_4M and C_6H_6M were calculated.

Table 1. Total energy gaps, ΔE(t–s); enthalpy gaps, ΔH(t–s); free energy gaps, ΔG(t–s), in kcal/mol, between singlet and triplet states for C_2H_2M, C_4H_4M and C_6H_6M (M = C, Si, Ge, Sn and Pb), calculated at B3LYP/6 311++G**.

Compound	$\Delta E_{(t-s)}$	$\Delta H_{(t-s)}$	$\Delta G_{(t-s)}$
C_2H_2C	48.376	48.376	46.558
C_2H_2Si	69.828	69.828	67.835
C_2H_2Ge	40.954	40.954	36.266
C_2H_2Sn	30.534	30.534	25.701
C_2H_2Pb	22.571	22.571	18.065
C_4H_4C	-9.249	-9.249	-9.598
C_4H_4Si	15.584	15.584	14.851
C_4H_4Ge	22.616	22.616	22.786
C_4H_4Sn	26.319	26.320	26.205
C_4H_4Pb	28.067	28.067	27.304
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

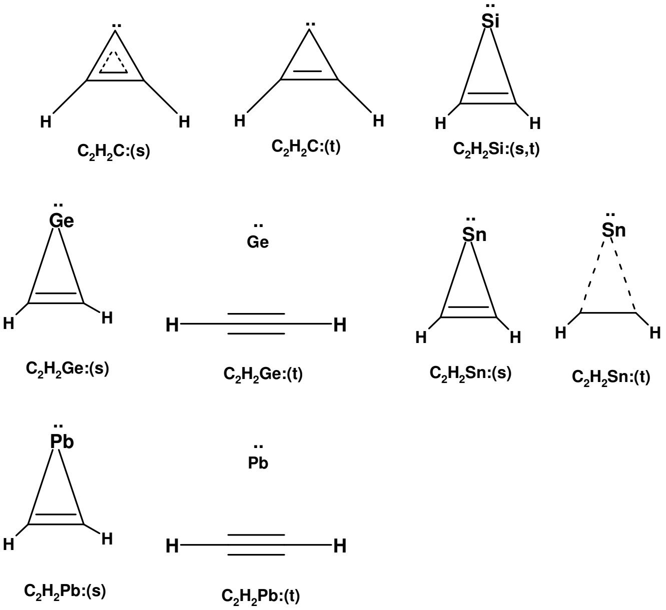
The singlet ground state is favored by a large σ-pπ gap. A large σ-pπ gap leads to a larger singlet-triplet energy gaps, ΔG_{t-s}. The singlet-triplet free energy gaps, ΔG_{t-s}, for C_2H_2M (M = C, Si, Ge, Sn and Pb) were increased in the order: $C_2H_2Si > C_2H_2C > C_2H_2Ge > C_2H_2Sn > C_2H_2Pb$. The ΔG_{t-s} of C_4H_4M were increased in the order: $C_4H_4Pb > C_4H_4Sn > C_4H_4Ge > C_4H_4Si > C_4H_4C$. Also, ΔG_{t-s} of C_6H_6M were determined in the order: $C_6H_6Pb > C_6H_6Ge \geq C_6H_6Sn > C_6H_6Si > C_6H_6C$ (Table 1).

The ΔG_{t-s} for C_2H_2M increases from M = C to M = Si while decreases from M = Si to M = Pb. Increase of the ΔG_{t-s} from M = C to M = Si will be reasonably described. The unpredicted decrease of ΔG_{t-s} for C_2H_2M from M = Si to M = Pb is related to triplet state structures obtained through full optimizations. Triplet state structure tends to break out from strained three membered ring during optimizations. Therefore, the triplet state of these structures is not actually a three membered rings. Thus, the triplet states of C_2H_2M (M = Si to M = Pb) achieve more stability and decrease of ΔG_{t-s}.

The singlet-triplet gaps, ΔG_{t-s}, of C_4H_4M and C_6H_6M are generally increased from M = C to M = Pb. These changes of singlet-triplet gaps ΔG_{t-s}, are consistent to those simple analogues CH_2, SiH_2, GeH_2 and PbH_2 [23].

The larger singlet-triplet gaps, ΔG_{t-s}, of C_2H_2M (from M = C to M = Si), C_4H_4M and C_6H_6M (from M = C to M = Pb) could be described by three factors [8c]. A lower electronegativity of M, polarity of the M-C bond and larger size of M stabilize the singlet state and rise the singlet-triplet energy gap.

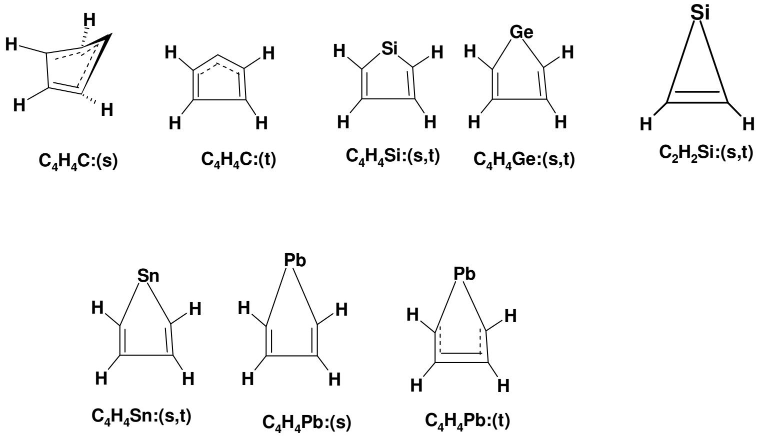
From a conformational point of view, the optimized singlet and triplet states of C_2H_2M have a planar form (Scheme 1). The bond lengths of singlet state C_2H_2C indicate an electronic current in the ring. Therefore, nuclear independent chemical shifts (NICS) calculations were carried out for determination of the aromatic character at B3LYP/6-311++G** level. A NICS (0.5) calculation generally gives reliable results. The order changes of NICS (0.5) calculations for the singlet state of C_2H_2M is: C_2H_2C 27.6 > C_2H_2Si 18.9 > C_2H_2Ge 13.9 > C_2H_2Pb 12.8 > C_2H_2Sn 10.3. The results show an aromatic character for the singlet state of C_2H_2M. Therefore, two nonbonding electrons are not contributed in the electron current ring. The highest aromatic character is belonging to C_2H_2C. The NICS results show nonaromatic character for triplet states of C_2H_2M.



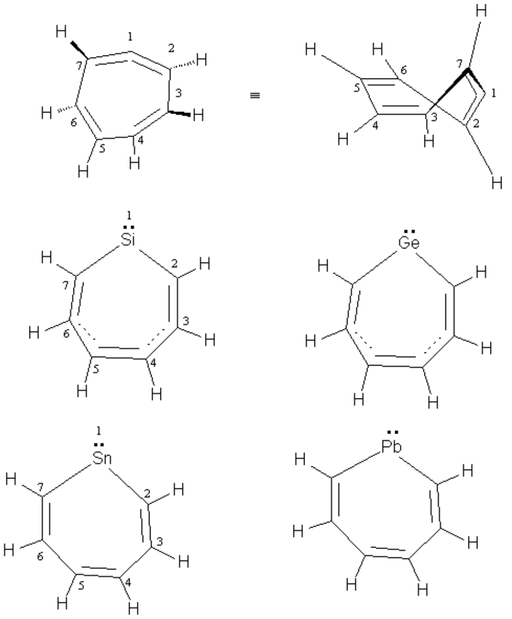
Scheme 1.Full optimized and ground state tautomers and conformers for singlet states (s) and triplet states (s) of C_2H_2M.

The ∠ C_2-M_1-C_3 angles of C_2H_2M (except M = C and Si) are larger for their singlet than their triplet states. For both singlet and triplet states of C_2H_2M, the ∠ C_2-M_1-C_3 angle decrease from M = C toward M = Pb.

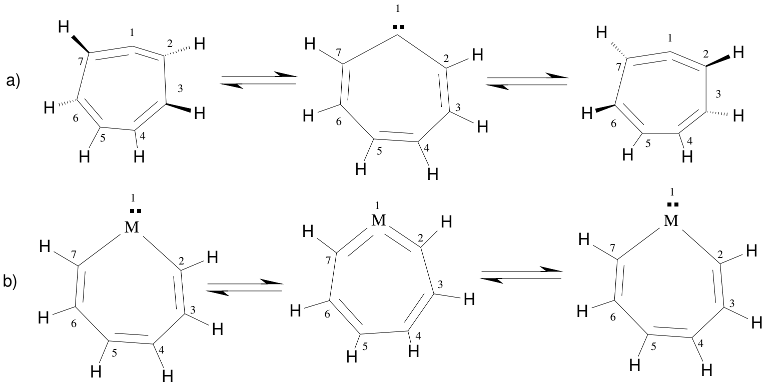
The B3LYP/6-311++G** calculations indicate that the planar triplet state of C_4H_4C is lower in energy than the corresponding non-planar singlet state (Scheme 2). For both singlet and triplet states of C_4H_4M (M = Si, Ge, Sn and Pb), the planar conformer is ground state.



Scheme 2. Full optimized and ground state tautomers and conformers for singlet states (s) and triplet states (s) of C_4H_4M.



Scheme 3. 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 4. 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.

NICS (0.5) calculations show non-aromatic character for the singlet state of C_4H_4C and slightly anti-aromatic character for C_4H_4M (M = Si, Ge, Sn and Pb). In contrast, NICS (0.5) calculations indicate slightly anti-aromatic character for the triplet state of C_4H_4C and non-aromatic character for C_4H_4M (M = Si, Ge, Sn and Pb).

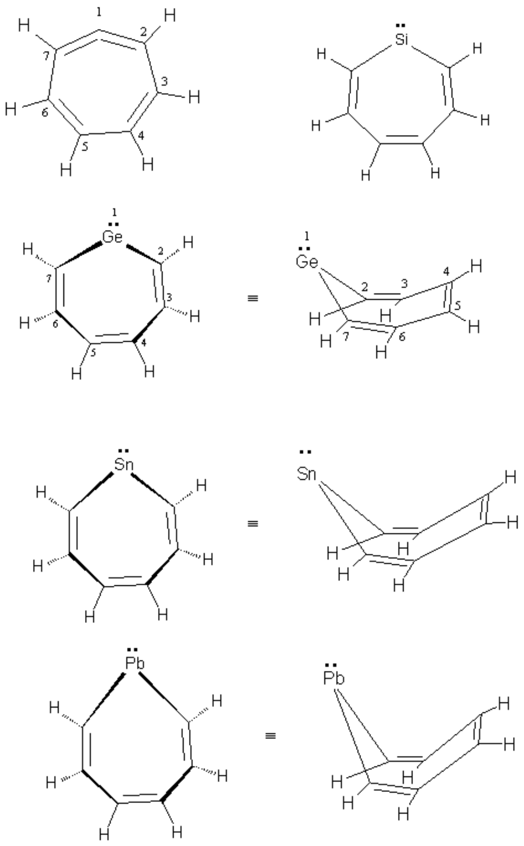
The B3LYP/6-311++G** calculations on the singlet state of C_6H_6C show a ground state with non-planar, twist, conformer and allenic tautomer (1,2,4,6-cycloheptatetraene) (Scheme 3). A quasi double bond is formed for the singlet states of C_6H_6M (M = Si and Ge) between C_3 and C_4 as well as C_5 and C_6 (Scheme 3). Racemization of allenic and carbenic tautomers has been reported (Scheme 4) [8c].

The planar allenic tautomer and planar carbenic tautomer for the triplet state of C_6H_6C and C_6H_6Si are the energy minimum, respectively (Scheme 5). The boat carbenic tautomer for the triplet state of C_6H_6M (M = Ge, Sn and Pb) is the energy minimum.

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). So, the bond lengths R_{12} and R_{34} for the singlet and triplet states of C_6H_6C are shorter than for C_6H_6M. The bond length R_{12} for the singlet state is shorter than for the triplet states of C_6H_6C while the bond length R_{12} for the singlet state is larger than for the triplet states of C_6H_6M.

The bond angle A_{712} for singlet and triplet states is reasonably decreased for C_6H_6M from M = C toward 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.

NICS (0.5) calculations show a slightly homoaromatic character for the singlet state of C_6H_6M (M = C, Si, Ge, Sn and Pb). The singlet-triplet gaps, $\Delta G_{t\text{-}s}$, is the most for C_2H_2M (M = C, Si and Ge) in compared with their corresponding C_4H_4M and C_6H_6M (Table 1). Change of order for $\Delta G_{t\text{-}s}$ is $C_2H_2M > C_6H_6M > C_4H_4M$. Aromatic character plays a significant role in the stabilizing of the singlet state for C_2H_2M (M = C, Si and Ge) with respect to the corresponding C_4H_4M and C_6H_6M.



Scheme 5. 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).

CONCLUSIONS

Gibbs free energy gaps between singlet and triplet states, ΔG_{t-s}, were calculated for three, five and seven-membered cyclic C_2H_2M, C_4H_4M and C_6H_6M (M = C, Si, Ge, Sn and Pb) at B3LYP/6-311++G**. The singlet-triplet free energy gaps, ΔG_{t-s}, for C_2H_2M (M = C, Si, Ge, Sn and Pb) are increased in the order $C_2H_2Si > C_2H_2C > C_2H_2Ge > C_2H_2Sn > C_2H_2Pb$. The ΔG_{t-s} of C_4H_4M are increased in the order: $C_4H_4Pb > C_4H_4Sn > C_4H_4Ge > C_4H_4Si > C_4H_4C$. Also, the ΔG_{t-s} of C_6H_6M are determined in the order: $C_6H_6Pb > C_6H_6Ge \geq C_6H_6Sn > C_6H_6Si > C_6H_6C$. The singlet-triplet gaps, ΔG_{t-s}, is the most for C_2H_2M (M = C, Si and Ge) in compared with their corresponding C_4H_4M and C_6H_6M.

AKNOWLEDGEMENTS

Payame Noor University (PNU) is gratefully acknowledged due to their financial support of this research.

REFERENCES

1. Bourissou, D.; Guerret, O.; Gabbaï, F.P.; Bertrand, G. *Chem. Rev.* **2000**, 100, 39.
2. Jiang, P.; Trieber, D.; Gaspar, P.P. *Organometall.* **2003**, 22, 2233.
3. Crev, R.S.; Schaefer, H.F.; Gaspar, P.P. *J. Am. Chem. Soc.* **1991**, 113, 5638.
4. Kira, M.; Ishida, S.; Iwamoto, T.; Yauchibara, R.; Sakurai, H. *J. Organomet. Chem.* **2001**, 636, 144.
5. Kühl, O. *Coord. Chem. Rev.* **2004**, 248, 411.
6. Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A.V.; Verne, H.P.; Haaland, A. *J. Am. Chem. Soc.* **1994**, 116, 2691.
7. Davidson, P.J.; Harris, D.H.; Lappert, M.F. *J. Chem. Soc. Dalton Trans*. **1976**, 2268.
8. (a) Vessally, E. *Heteroatom Chem.* **2008**, 19, 245; (b) Vessally, E.; Nikoorazm, M.; Ramazani, A.; *Chin. J. Inorg. Chem.* **2008**, 24, 631; (c) Vessally, E.; Rezaei, A.; Chaliyavi, N.; Nikoorazm, M. *Russian J. Phys. Chem.* **2007**, 81, 1821; (d) Vessally, E.; Rezaei, A.; Chaliyavi, N.; Nikoorazm, M. *J. Chin. Chem. Soc.* **2007**, 54, 1583; (e) Vessally, E.; Nikoorazm, M.; Rezaei, A.; Chaliyavi, N. *Asian J. Chem.* **2007**, 19, 5000.
9. Arduengo, A.J.; Harlow, R.L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361.
10. Herrmann, W.A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, 11, 1485.
11. Haaf, M.; Schmedake, T.A.; West, R. *Acc. Chem. Res.* **2000**, 33, 704.
12. Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, 180, 593.
13. Davidson, P.J.; Harris, D.H.; Lappert, M.F. *J. Chem. Soc. Dalton Trans.* **1976**, 2268.
14. Kano, N.; Shibata, K.; Tokitoh, N.; Okazaki, R. *Organometallics* **1999**, 18, 2999.
15. Harrison, P.G. *Comprehensive Organometallic Chemistry II* , Vol. 2, Pergamon: New York; **1995**.
16. Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, 115, 10428.
17. McMahon, R.J.; Abelt, C.J.; Chapman, O.L.; Johnson, J.W.; Kreil, C.L.; Leroux, J.P.; Mooring, A.M.; West, P.R. *J. Am. Chem. Soc.* **1987**, 109, 2456.
18. (a) Schleyer, P.V.R.; Maerker, C.; Dransfield, A. *J. Am. Chem. Soc.* **1996**, 118, 6317; (b) Cyranski, M.K.; Schleyer, P.V.R.; Krygowski, T.M.; Jiao, H.; Hohlneicher, G. *Tetrahedron* **2003**, 59, 1657.
19. Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev.* B **1988**, 37, 785.
20. Becke, A.D. *J. Chem. Phys.* **1993**, 98, 5648.
21. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Znkrzewski, V.G.; Montgomery, G.A.; Startmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pamelli, C.; Adamo, G.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokoma, K.; Malick, D.K.; Rubuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslawski, J.; Oritz, J.V.; Stlefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Comperts, R.; Martin, R.L.; Fox, P.J.; Keith, T.; Al-laham, M.A.; Peng, C.Y.; Akkara, A.N.; Gonzales, C.G.; Combe, M.C.; Gill, P.M.W.; Johnson, B.; Chem, W.; Wong, M.W.; Andres, J.L.; Gonzales, C.; Head-Gordon, M.; Replogle E.S.; Pople, J.A.; Gaussian 98, Revision A. 6, Gaussian Inc.: Pittsburgh PA; **1998**.
22. Curtiss, L.A.; McGrath, M.P.; Blaudeau, J.P.; Davis, N.E.; Binning Jr. R.C.; Radom, L. *J. Chem. Phys.* **1995**, 103, 6104.
23. Balasubramanian, K.J. *Chem. Phys*. **1988**, 89, 5731.