研究简报

通过核独立化学位移(NICS)计算研究二价三、五、七元环 C_2H_2M, C_4H_4M and $C_6H_6M(M=C, Si, Ge, Sn and Pb)$的芳香族特性

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Aromatic Character Studies on Divalent 3, 5 and 7-membered Rings C_2H_2M, C_4H_4M and $C_6H_6M(M=C, Si, Ge, Sn and Pb)$ via Nucleus-independent Chemical Shifts (NICS) Calculation

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Abstract: The aromatic character of divalent three, five and seven-membered rings C_2H_2M, C_4H_4M and $C_6H_6M(M=C$, Si, Ge, Sn and Pb) is investigated through magnetic and geometric criteria by Density Functional Theory (DFT) method using 6-311 ++G (3df,2p) basis set of the GAUSSIAN 98 program. The result of Nucleus-independent Chemical Shifts (NICS) (0.5) calculations show an aromatic character for singlet state of $C_2H_2M(M=C$, Si, Ge, Sn and Sn) and nonaromatic character for triplet states of C_2H_2M (except M =Ge and Pb). NICS (0.5) calculations show nonaromatic character for the singlet state of C_4H_4C and antiaromatic character for C_4H_4M (M=Si, Ge, Sn and Pb). In contrast, NICS (0.5) calculations indicate antiaromatic character for the triplet state of C_4H_4C and nonaromatic character to C_4H_4M (M=Si, Ge, Sn and Pb). NICS (0.5) calculations show a slightly homoaromatic character for the singlet state of C_6H_6M and anti-aromatic character for triplet state of C_6H_6M.

Key words: carbene; silylene; germylene; stanylene; plumbylene; aromatic character; NICS calculation

　　The chemistry of the divalent carbenes: silylenes, germylenes, stanylenes and plumbylenes has been extensively discussed[1~8]. These compounds are unstable for experimental analysis. Therefore, the studies on

carbenes and their analogues have been carried out by theoretical calculations. In this work the aromatic character is discussed for divalent three, five and seven-membered rings C_2H_2M, C_4H_4M and $C_6H_6M(M=C$,

Si, Ge, Sn and Pb) (Scheme 1).

　　The aromatic character is not a directly measurable or computable quantity. Aromatic character is generally evaluated on the basis of magnetic, energetic and geometric criteria[9~15]. Magnetic criterion is the important way for determining of aromatic character. Magnetic criterion is measured through nuclear independent chemical shifts (NICS) calculations. The concept of NICS was introduced by Schleyer et. al. in 1996 as a measure of aromaticity and antiaromaticity (or non-aromaticity)[15a]. 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 (0.05 nm (i.e. 0.5Å)) 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. In this manuscript, NICS calculations are carried out on C_2H_2M, C_4H_4M and C_6H_6M(M=C, Si, Ge, Sn and Pb).

1　Computational method

　　Full geometry optimizations for singlet and triplet states of C_2H_2M, C_4H_4M and C_6H_6M(M=C, Si, Ge, Sn and Pb) are carried out by density functional theory DFT method using 6-311 ++G (3df, 2p) basis set of the GAUSSIAN 98 program[16~18] (Scheme **1**). To find a global minimum on a specific surface, all possible conformations of the given species are examined through scanning the specific dihedral angles at B3LYP/6-311 ++G (3df, 2p) level. This is for obtaining more accurate values of thermal energies (E), enthalpies (H) and Gibbs free energies (G). For stanylenes and plumbylenes, the calculations are done using LANL2DZ basis set[19].

2　Results and discussion

　　The aim of this research is to determine the aromatic character for divalent three, five and seven-membered rings C_2H_2M, C_4H_4M and C_6H_6M (M=C, Si, Ge, Sn and Pb) through geometric, and magnetic criteria (Scheme 1). NICS calculation procedure is the most important magnetic criterion for the determination of the aromatic character. All structures are studied from both conformational view and NICS calculations.
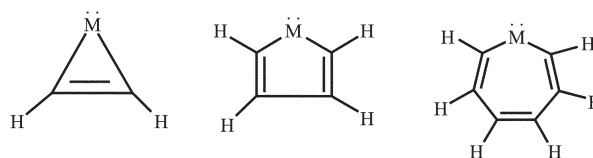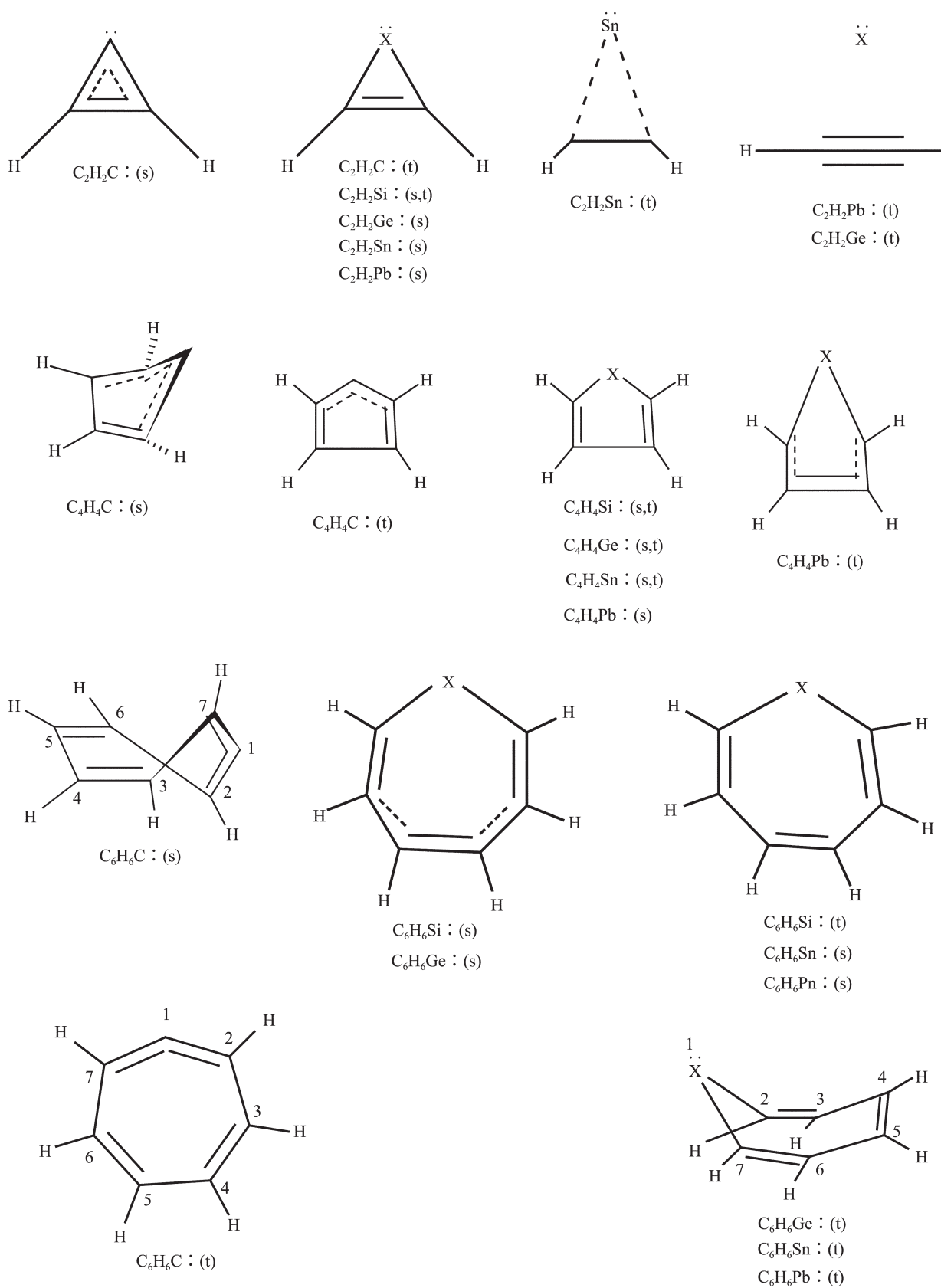

Scheme 1　Molecular structures of C_2H_2M, C_4H_4M and C_6H_6M(M=C, Si, Ge, Sn and Pb)

　　From conformational view, both singlet and triplet states of C_2H_2M have planar forms (Scheme 2). The bond lengths for singlet states of C_2H_2C indicate a prefect electron current in the ring. The $\angle C_2 - M_1 - C_3$ angles for singlet states of C_2H_2M(except M=C and Si) is larger with respect to their triplet states. For both singlet and triplet states of C_2H_2M, the $\angle C_2 - M_1 - C_3$ angle decrease from M=C toward M=Pb. Geometric results especially bond lengths data indicate high aromatic character for singlet state of C_2H_2M. All carbon-carbon bonds for singlet state of C_2H_2C have approximately the same distance. Therefore, the aromatic character is the highest for singlet state of C_2H_2C.

　　The NICS calculations are carried out for both singlet and triplet states of C_2H_2M. NICS (0.5) calculation generally gives the reliable results (Table 1). The order of NICS (0.5) calculations for singlet state of C_2H_2M are:
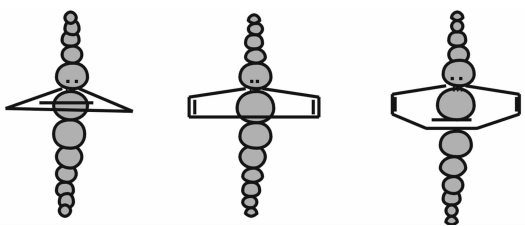
　　C_2H_2C 27.6 >C_2H_2Si 18.9 >C_2H_2Ge 13.9 >C_2H_2Pb 12.8>C_2H_2Sn 10.3. The results show aromatic character for singlet state of C_2H_2M. The highest aromatic character is belonging to C_2H_2C. The results of NICS (0.5) calculations show nonaromatic character for triplet states of C_2H_2M(except M=Ge and Pb).

　　The calculations indicate that the triplet state of C_4H_4C is ground state with planar conformer relative to its corresponding nonplanar singlet state. For C_4H_4M (M=Si, Ge, Sn and Pb), the stabilized structure of both singlet and triplet states have planar conformer. Singlet

C_2H_2C：(s)

C_2H_2C：(t)
C_2H_2Si：(s,t)
C_2H_2Ge：(s)
C_2H_2Sn：(s)
C_2H_2Pb：(s)

C_2H_2Sn：(t)

C_2H_2Pb：(t)
C_2H_2Ge：(t)

C_4H_4C：(s)

C_4H_4C：(t)

C_4H_4Si：(s,t)
C_4H_4Ge：(s,t)
C_4H_4Sn：(s,t)
C_4H_4Pb：(s)

C_4H_4Pb：(t)

C_6H_6C：(s)

C_6H_6Si：(s)
C_6H_6Ge：(s)

C_6H_6Si：(t)
C_6H_6Sn：(s)
C_6H_6Pn：(s)

C_6H_6C：(t)

C_6H_6Ge：(t)
C_6H_6Sn：(t)
C_6H_6Pb：(t)

Scheme 2   Full optimized and ground state tautomers and conformers for singlet and triplet states for C_2H_2M, C_4H_4M and $C_6H_6M(M=C, Si, Ge, Sn and Pb)$

Table 1　NICS calculations for aromatic determination for singlet (s) and triplet (t) states of C₂H₂M, C₄H₄M and C₆H₆M(in where M=C, Si, Ge, Sn and Pb) at B3LYP/6-311++G(3df, 2p) level

Compound	NICS (0)	NICS (0.2)	NICS (0.4)	NICS (0.5)	NICS (0.6)	NICS (0.8)	NICS (1.0)	NICS (1.2)
				C_2H_2M				
M=C$_{(s)}$	1.7024	20.977	26.704	27.605	26.908	22.392	16.825	12.212
M=Si$_{(s)}$	13.834	15.514	18.246	18.856	18.715	16.621	13.450	10.399
M=Ge$_{(s)}$	13.095	13.283	13.694	13.864	13.900	13.346	11.954	10.071
M=Sn$_{(s)}$	9.170	9.324	9.906	10.351	10.801	11.257	10.696	9.344
M=Pb$_{(s)}$	11.888	12.448	13.151	13.109	12.711	11.091	9.059	7.202
M=C$_{(t)}$	10.902	6.671	2.359	−2.289	−6.513	−12.070	−13.534	−12.335
M=Si$_{(t)}$	1.486	0.267	−3.070	−5.198	−7.316	−10.639	−12.053	−11.777
M=Ge$_{(t)}$	20.957	19.658	16.337	14.311	12.258	8.539	5.693	3.732
M=Sn$_{(t)}$	17.589	14.046	6.524	2.483	−1.215	−6.789	−9.720	−10.584
M=Pb$_{(t)}$	25.314	24.191	21.204	19.288	17.258	13.277	9.846	7.167
				C_4H_4M				
M=C$_{(s)}$	2.043	2.568	2.345	2.075	1.805	1.429	1.308	1.290
M=Si$_{(s)}$	−15.685	−15.206	−13.849	−12.853	−11.856	−9.581	−7.377	−5.484
M=Ge$_{(s)}$	−15.563	−15.088	−13.748	12.772	−11.795	−9.580	−7.438	−5.590
M=Sn$_{(s)}$	−11.429	−11.096	−10.170	9.503	−8.835	−7.312	−5.798	−4.430
M=Pb$_{(s)}$	−10.080	−9.785	−8.980	8.410	−7.840	−6.557	−5.276	−4.095
M=C$_{(t)}$	−9.062	−9.520	−10.295	−10.318	−10.341	−9.295	−7.574	−5.773
M=Si$_{(t)}$	2.942	2.826	2.555	2.415	2.275	2.083	1.968	1.868
M=Ge$_{(t)}$	4.495	4.360	4.022	3.811	3.599	3.195	2.857	2.520
M=Sn$_{(t)}$	−1.214	−0.420	1.487	2.527	3.567	5.108	5.903	6.082
M=Pb$_{(t)}$	−1.427	−0.633	1.274	2.314	3.354	4.895	5.690	5.869
				C_6H_6M				
M=C$_{(s)}$	5.341	5.513	5.901	6.093	6.237	6.301	6.027	5.482
M=Si$_{(s)}$	2.457	2.773	3.568	4.044	4.513	5.286	5.706	5.751
M=Ge$_{(s)}$	2.093	2.395	3.158	3.615	4.065	4.811	5.229	5.298
M=Sn$_{(s)}$	1.346	1.573	2.139	2.478	2.815	3.398	3.780	3.945
M=Pb$_{(s)}$	1.141	1.343	1.847	2.149	2.451	2.984	3.360	3.560
M=C$_{(t)}$	−33.930	−33.643	−32.715	−31.972	−31.032	−28.614	−25.664	−22.479
M=Si$_{(t)}$	−39.792	−39.557	−38.758	−38.089	−37.218	−34.883	−31.897	−28.532
M=Ge$_{(t)}$	−13.306	−13.627	−13.431	−13.154	−12.777	−11.800	−10.651	−9.456
M=Sn$_{(t)}$	−3.947	−4.513	−4.580	−4.466	−4.283	−3.794	−3.253	−2.749
M=Pb$_{(t)}$	−2.563	−3.265	−3.396	−3.304	−3.144	−2.709	−2.244	−1.834

state of C_4H_4C may have a nonaromatic character due to its nonplanar conformation.

NICS (0.5) calculations show nonaromatic character for the singlet state of C_4H_4C and antiaromatic character to C_4H_4M(M=Si, Ge, Sn and Pb) (Table 1). In contrast, NICS (0.5) calculations indicate antiaromatic character for the triplet state of C_4H_4C and nonaromatic character to C_4H_4M(M=Si, Ge, Sn and Pb).

The calculations on singlet state of C_6H_6C show a ground state with non-planar, twist, conformer and allenic tautomer (Scheme 2). In contrast, for singlet state of C_6H_6M (M=Si, Ge, Sn and Pb), the carbenic tautomer with planar conformer is ground state (Scheme 2). Meanwhile, the quasi double bond is formed between C_3 and C_4 as well as C_5 and C_6 (Scheme 2). For triplet state of C_6H_6C, the planar conformer with allenic tautomer is ground state (Scheme 2). For triplet state of C_6H_6Si, the 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 bond lengths of singlet and triplet states indicate an allenic tautomer for C_6H_6C with 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 singlet and triplet states of C_6H_6C are shorter than that 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 that for triplet states of C_6H_6M. From geometric point view, it may be concluded that neither singlet states nor triplet states of C_6H_6M could have aromatic character.

NICS (0.5) calculations show a slightly homoaromatic character for the singlet state of C_6H_6M decreasing from M =C to M=Pb (Table 1). Also, NICS (0.5) calculations indicate anti-aromatic character for triplet state of C_6H_6M. The most anti-aromatic character is belonged to triplet state of C_6H_6Si.

3   Conclusion

The result of NICS (0.5) calculations show aromatic character for singlet state of C_2H_2M(M=C, Si, Ge, Sn and Sn) and nonaromatic character for triplet states of C_2H_2M (except M =Ge and Pb). NICS (0.5)

calculations show nonaromatic character for the singlet state of C_4H_4C and antiaromatic character for C_4H_4M(M= Si, Ge, Sn and Pb). In contrast, NICS (0.5) calculations indicate antiaromatic character for the triplet state of C_4H_4C and nonaromatic character to C_4H_4M (M=Si, Ge, Sn and Pb). NICS (0.5) calculations show a slightly homoaromatic character for the singlet state of C_6H_6M and anti-aromatic character for triplet state of C_6H_6M.

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