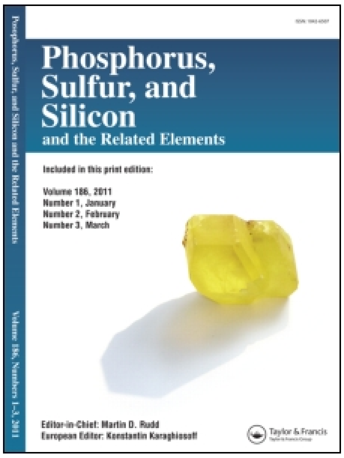

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An Ab Initio Study and NBO Analysis of the Stability and Conformational Properties of Hexakis(trimethylelementhyl)benzene (Element = C, Si, Ge, and Sn)

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An Ab Initio Study and NBO Analysis of the Stability and Conformational Properties of Hexakis(trimethylelementhyl)benzene (Element = C, Si, Ge, and Sn)

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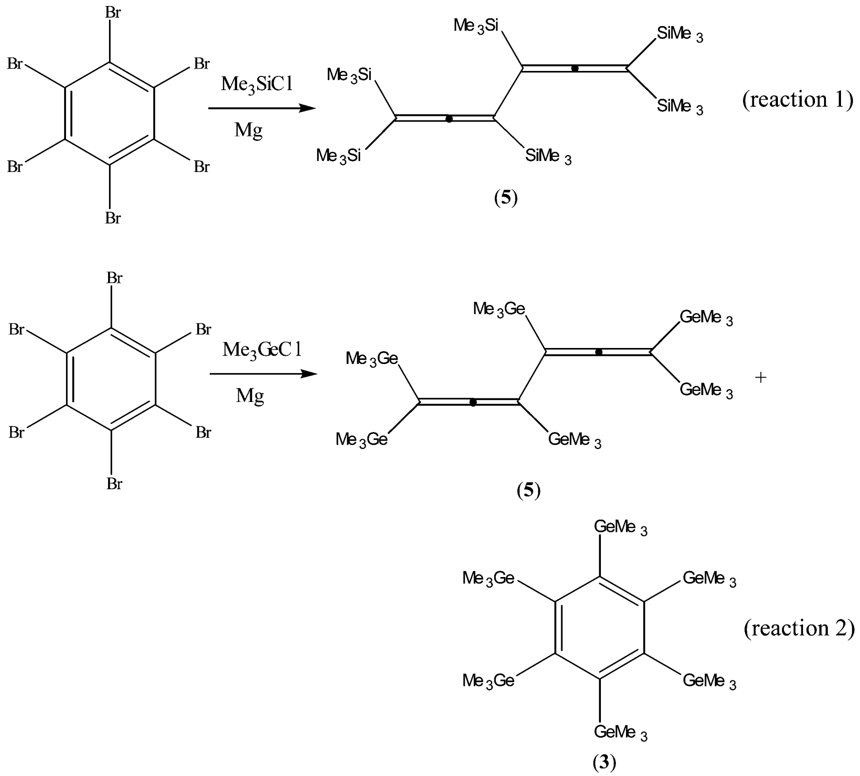
*Ab initio molecular orbital and density functional theory were used to investigate energetic and structural properties of the various conformations of hexa-*tert-*butylbenzene (**1**), hexakis(trimethylsilyl)benzene (**2**), hexakis (trimethylgermyl)-benzene (**3**), and hexakis(trimethylstannyl)benzene (**4**). HF/3-21G//HF/3-21G and B3LYP/3-21G//HF/3-21G results revealed that the Twist-Boat (**TB**) conformer of compound **1** is more stable than the **1**-Chair (**C**), **1**-Boat (**B**), and **1**-Planar (**P**) conformers. B3LYP/3-21G//HF/3-21G results show that the **1-TB** conformer is more stable than **1-C**, **1-B**, and **1-P** conformers of about 1.13, 4.34, and 99.94 kcal* mol^{-1}*, respectively. Contrary to the stability order of compound **1** conformers, the **C** conformer of compounds **2–4** is more stable than **TB**, **B**, and **P** conformations, as calculated by B3LYP/3-21G//HF/3-21G and HF/3-21G//HF/3-21G levels of theory. The energy gap between the **C** and **P** conformers in compounds **1–4** is decreased in the following order:* ΔE*(**4**: **C**, **P**) <* ΔE *(**3**: **C**, **P**) <* ΔE*(**2**: **C**, **P**) <* ΔE *(**1**: **C**, **P**). This fact can be explained in terms of the increase of* $C_{aromatic}$*-M (M=C, Si, Ge, and Sn) bond lengths and the decrease of steric (van der Waals) repulsions in the previously discussed compounds. **For compounds 1–3, the calculations were also performed at the B3LYP/6-31G*//HF/3-21G level of theory. However, the comparison showed that the results at B3LYP/3-21G//HF/3-21G methods correlated well with those obtained at the B3LYP/6-31G*// HF/6-31G method.** Further, NBO analysis revealed that in compounds **1–4**, the resonance energy associated with the* $\sigma_{M\text{-}C1}$ *to* $\sigma^*_{C2\text{-}C3}$ *delocalization is 5.20, 9.68, 11.15, and 12.27 kcal* mol^{-1}*, respectively. These resonance energy values could explain the easiness of the ring flipping processes of **C**, **B**, and **TB** conformers of compounds **4** to **1**. Also, the NBO results showed that by an increase of the* $\sigma_{M\text{-}C1} \rightarrow \sigma^*_{C2\text{-}C3}$ *resonance energies in compounds **1–4**, the* $\sigma_{M\text{-}C1}$ *bonding orbital occupancies decrease. This fact could fairly explain the increase of the* C_{aryl}*-M bond length from compound **1** to **4**. The NBO results are also in good agreement with the calculated energy barriers for the ring flipping of the chair conformations in compounds **1–4**, as calculated by B3LYP and HF methods.*

Keywords Ab initio; heteroatom; hexakis(trimethylelementyl) benzenes; molecular modeling

INTRODUCTION

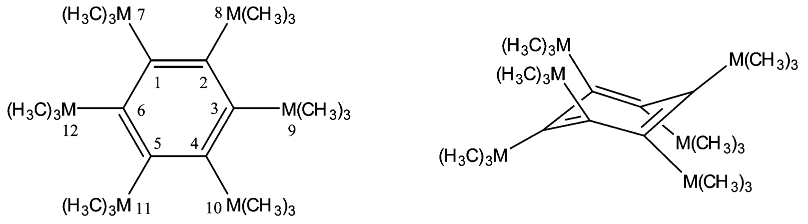
The effects of an unbonded interaction on molecule structure and internal mobility in hexaethylbenzene, hexa-isopropylbenzene, and several related hydrocarbons as strictly crowded molecules have already been investigated.$^{1-7}$ Attempt for the synthesis of hexakis(trimethylelementhyl)benzene [compound **1** (element = C), compound **2** (element = Si), compound **3** (element = Ge), and compound **4** (element = Sn)], was only successful for compound **3**, as reported by Weissensteiner et al.[8] They synthesized compound **3** from a reaction between hexaboromobenzene with magnesium and cholorotrimethylgermane. Their results showed also that in the reaction between hexabromobenzene, chlorotrimethylsilane, and Mg (reaction 1), only 1,2,4,5-tetrakis(trimethylgermyl)benzene (**5**) is formed, but when chlorotrimethylgermane is used (instead of chlorotrimethylsilane), the formation of compound **3** is accompanied as well with the formation of compound **5** (reaction 2) (see Scheme 1).



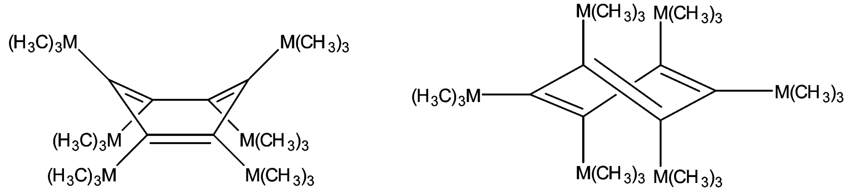
SCHEME 1

The quasi-D_3 symmetry structure has been reported for compound **3** by X-ray crystallographic study.[8] Furthermore, Weissensteiner et al. have employed empirical force field calculations for the structural optimization of D_3 and S_6 forms of compound **3**.[8] They have concluded that in the S_6 form, the benzene ring is planar, with higher energy compared to the D_3 form. However, they have not investigated other possible conformations of compound **3**, such as **B**, **C**, **TB**, and **P** structures (see Scheme 2).

The main goal of this work is to investigate from a the thermodynamic point of view the possible conformations and structural properties of compounds **1**, **2**, and **4**, and also to explore other possible



P, *quasi-D*$_{6h}$ symmetry **C**, *quasi-D*$_3$ symmetry



B, *quasi-C*$_{2v}$ symmetry **T-B**, *quasi-D*$_2$ symmetry

M = C (compound **1**), Si (compound **2**), Ge (compound **3**), Sn (compound **4**)

SCHEME 2

conformations of compound **3**. To this end, we have performed ab initio molecular orbital (MO) and Density Functional Theory (DFT) calculations using the Gaussian 98 package of programs.[9] Also, the stabilization energies (E_2) associated with $\sigma_{\mathrm{M-C1}} \rightarrow \sigma^*_{\mathrm{C2-C3}}$ delocalizations (see Figures 1 and 2) and their influences on the dynamic behavior of compounds **1–4** were quatitatively investigated by the NBO (Natural Bond Orbital) analysis.[10,11] The successful application of the DFT-based methods broadened the applicability of the computational methods and now represents an interesting approach for determining an activation barrier and molecular energies.[9,12–16] The B3LYP method combines Becke's three-parameter exchange (B3) function with the correlation function of Lee-Yang-Parr (LYP).[12,13]

The results obtained by the B3LYP/3-31G//HF/3-21G method concerning the energy differences and the ring-flipping energy barriers of compounds **1–3** were also compared to those obtained using the B3LYP/6-31G*//HF/3-21G level of theory.

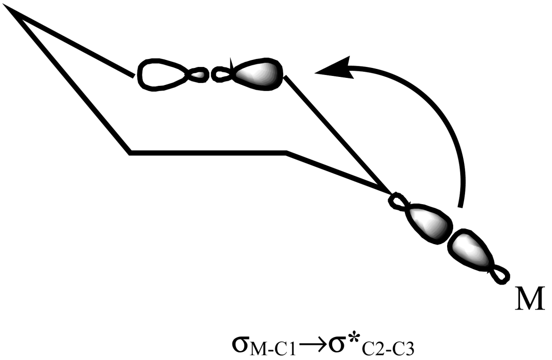


FIGURE 1 The delocalization from σ_{M-C1} bonding to σ^*_{C2-C3} antibonding orbitals.

COMPUTATIONAL DETAILS

Ab initio and DFT calculations were carried out using HF/3-21G//HF/3-21G and B3LYP/3-21G//HF/3-21G levels of theory with the GAUSSIAN 98 package of programs[9] implemented on a Pentium–PC computer with a 1.7 GHz processor. Since, according to the Gaussian 98 user's reference 2nd edition, the 6-31G* basis set cannot be applied to Sn compounds,

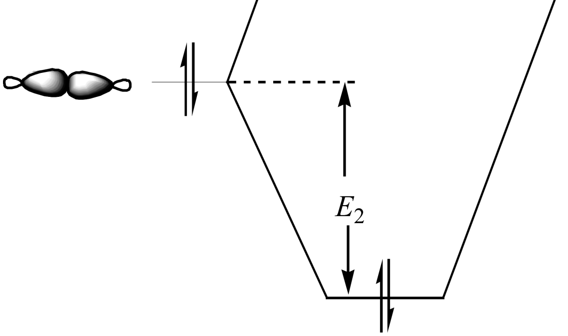


FIGURE 2 The resonance energy (E_2) from donor (σ_{M-C1}) to acceptor (σ_{C2-C3}) for bonding and antibonding orbitals.

for the investigation of stability of the various conformations of compounds **1–4** (which contain carbon, silicon, Germanium, and Tin, respectively), we were limited to use the HF/3-21G//HF/3-21G and B3LYP/3-21G//HF/3-21G methods.

Also, basis sets for atoms beyond the third row of the periodic table are, usually, handled somewhat differently. For these very large nuclei, electrons near the nucleus are treated in an approximate way via Effective Core Potentials (ECPs). This treatment includes some relativistic effects, which are important in these atoms. For this purpose, the LANL2DZ is known to be one of the best of these basis sets.[9] It should be noted that for all first row elements, the all-electron D95 double-zeta basis set (without an ECP) is used in LANL2DZ. Therefore, in addition to the HF/3-21G method and in order to compare the effect of all–electron with pseudopotential basis sets, B3LYP/LANL2DZ*//HF/3-21G methods were also used for the investigation of the conformational properties of compound **4**. The Massage keyword was further used in order to add an additional uncontracted polarization basis function to the LANL2DZ basis set for C and Sn atoms (note that no polarization functions were added to H atoms).

The results obtained by B3LYP/3-31G//HF/3-21G method concerning the energy differences and the ring-flipping energy barriers of compounds **1–3** were also compared to those obtained using the B3LYP/6-31G*//HF/3-21G level of theory.

An Initial estimation of the structural geometries of the compounds **1–4** was obtained by a molecular mechanic program PCMODEL (88.0),[17] and for further optimization of geometries, the PM3 method of MOPAC 7.0 computer program was used.[18,19] The GAUSSIAN 98 program was finally used to perform ab initio calculations at the HF/3-21G level. Energy minimum molecular geometries were located by minimizing energy with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for compounds **1–4** has been fixed by a means of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition-state, only a single imaginary frequency value, was accepted.[20,21]

In addition, it has to be pointed out that many attempt to calculate the Zero Point Energy (ZPE) and other thermodynamic parameters using the FREQ subroutine (by the available PC processors) were unsuccessful. However, because of the large electronic energies differences between the various conformers of compounds **1–4**, the ZPE calculations could not affect the order of the stability of the investigated conformers.

However, the choice of the less-consuming time 3-21G basis set for large systems (such as compounds **1–4**) could fairly be justified by the following arguments. From the energetic point of view, the use of the 3-21G basis set led to the satisfactory agreement between the corresponding calculated metallotropic shift energies and the experimental results in cyclopentadienyl(trimethyl)silane, -germane, and -stannane compounds.[22] Effectively, it is interesting to note that the calculated metallotropic shift energy barrier, using the 3-21G basis set for cyclopentadienyl(trimethyl)stannane, is closer to its reported experimental value, compared to the all electron 3-21G* and effective core potential (ECP) LANL2DZ* basis sets.[9] Besides, from the structural point of view, the use of this basis set showed also to be satisfactory for the calculation of structural parameters of the investigated compounds. For instance, it can be seen from the results reported in Table I, that the calculated HF/3-21G bond, length, bond and torsion angle values for compounds **3** agree well with the reported experimental values (by taking into account the resulting experimental standard deviations).[8]

RESULTS AND DISCUSSION

Total electronic (E_{el}) energies for various conformations of compounds **1–4**, as calculated by HF/3-21G//HF/3-21G and B3LYP/3-21//HF/3-21G levels of theory, are given in Table II. In addition, B3LYP/6-31G*//HF/3-21G and B3LYP/LANL2DZ*//HF/3-21G methods were used for the investigation of energetic and structural properties of compounds **1–3** and 4, respectively.

NBO analysis was performed to calculate the $\sigma_{M-C_{aryl}}$ bonding and antibonding orbital occupancies for compounds **1–4** (M=C (**1**), Si (**2**), Ge (**3**), Sn (**4**)), and the resonance energies (E_2) associated with $\sigma_{M-C1} \rightarrow \sigma^*_{C2-C3}$ delocalizations (see Table III).

HF/3-21G//HF/3-21G results showed that the Twist-Boat (**TB**) conformation of compound **1** is more stable than the **C**, **B**, and **P** forms of about 1.89, 8.91, and 112.07 kcal mol^{-1}, respectively. Also, the **TB** conformer of compound **1** is more stable than its **C**, **B**, and **P** conformations, about 1.13, 4.34 and 99.94 kcal mol^{-1}, respectively, as calculated by the B3LYP/3-21G//HF/3-21G level of theory. On the base of these results, it is clear that the **P** conformer of compound **1**, with its preserved aromaticity, is less stable than the **TB** conformer. This fact can be explained by the predomination of the steric repulsions of bulky groups over the resonance stabilization.

Apparently the **P** form of compound **1** is the saddle point structure for the ring flipping of **C**, **B**, and **TB** forms. The average of $C_{sp^2} - C_{sp^2}$ bond lengths in the benzene ring of the **C** conformer of compound **1** is about 1.422 Å, and the corresponding individual deviations

TABLE I HF/3-21G Calculated Structural Parameters for the Energy Minima and Transition Structure of Compounds 1–4. Bond Lengths Are in Angstrom (Å), Unit and Angles in Degrees (°)

Compound	**1**				**2**				**3**					**4**			
conformer	**C**	**B**	**TB**	**P**	**C**	**B**	**TB**	**P**	**C**	Exp.	**B**	**TB**	**P**	**C**	**B**	**TB**	**P**
Bond Lengths (Å)																	
$\mathbf{r}_{1\text{-}2}$	1.420	1.425	1.398	1.441	1.430	1.411	1.420	1.420	1.393	—	1.403	1.413	1.411	1.402	1.409	1.418	1.415
$\mathbf{r}_{2\text{-}3}$	1.425	1.436	1.476	1.439	1.397	1.421	1.414	1.420	1.420	$(1.411)^a$ $(9)^b$	1.413	1.406	1.411	1.421	1.417	1.411	1.415
$r_{3\text{-}4}$	1.425	1.426	1.383	1.442	1.430	1.417	1.416	1.420	1.392	$(1.417)^a$ $(9)^b$	1.410	1.410	1.411	1.402	1.417	1.416	1.415
$\mathbf{r}_{4\text{-}5}$	1.420	1.427	1.465	1.439	1.397	1.411	1.420	1.420	1.420	$(1.439)^a$ $(14)^b$	1.403	1.413	1.411	1.421	1.408	1.419	1.415
$\mathbf{r}_{5\text{-}6}$	1.425	1.435	1.388	1.441	1.430	1.421	1.414	1.420	1.393	$(1.417)^a$ $(9)^b$	1.413	1.406	1.411	1.402	1.417	1.411	1.415
$\mathbf{r}_{6\text{-}1}$	1.425	1.427	1.485	1.439	1.397	1.416	1.416	1.420	1.420	$(1.412)^a$ $(13)^b$	1.409	1.410	1.411	1.421	1.416	2.196	2.220
$\mathbf{r}_{7\text{-}1}$	1.623	1.576	1.587	1.648	1.961	1.942	1.952	1.989	1.992	$(1.998)^a$ $(6)^b$	1.976	1.986	2.014	2.198	2.185	2.196	2.220
$\mathbf{r}_{8\text{-}2}$	1.623	1.612	1.610	1.649	1.961	1.961	1.959	1.989	1.992	$(1.976)^a$ $(7)^b$	1.994	1.988	2.014	2.198	2.196	2.195	2.220
$\mathbf{r}_{9\text{-}3}$	1.599	1.610	1.584	1.649	1.961	1.955	1.950	1.989	1.992	$(1.991)^a$ $(9)^b$	1.987	1.989	2.014	2.198	2.194	2.196	2.220
$\mathbf{r}_{10\text{-}4}$	1.623	1.576	1.591	1.648	1.961	1.942	1.9582	1.989	1.992	—	1.976	1.986	2.014	2.198	2.185	2.196	2.220
$\mathbf{r}_{11\text{-}5}$	1.599	1.612	1.612	1.649	1.961	1.961	1.959	1.989	1.992	—	1.994	1.988	2.014	2.198	2.196	2.195	2.220
$\mathbf{r}_{12\text{-}6}$	1.60	1.610	1.578	1.647	1.961	1.955	1.950	1.989	1.992	—	1.987	1.989	2.014	2.198	2.195	2.196	2.220
Bond Angles (°)																	
$\theta_{1\text{-}2\text{-}3}$	118.72	114.17	114.21	119.98	119.78	117.15	117.12	120.00	119.78	$(119.4)^a$ $(6)^b$	117.40	117.91	120.00	119.93	118.35	118.43	120.00
$\theta_{2\text{-}3\text{-}4}$	118.85	114.11	116.33	120.03	119.78	116.70	118.60	120.00	119.78	$(119.8)^a$ $(4)^b$	117.17	118.53	120.00	119.93	117.74	119.07	120.00
$\theta_{3\text{-}4\text{-}5}$	118.73	118.13	116.41	119.98	119.78	118.83	117.77	120.00	119.78	—	118.90	117.98	120.00	119.93	118.95	118.32	120.00
$\theta_{4\text{-}5\text{-}6}$	118.72	114.14	114.80	119.96	119.78	117.16	117.12	120.00	119.78	—	117.44	117.91	120.00	119.93	118.40	117.91	120.00
$\theta_{5\text{-}6\text{-}1}$	118.85	114.11	115.97	120.05	119.78	116.76	118.60	120.00	119.78	—	117.42	118.52	120.00	119.92	117.98	119.07	120.00
$\theta_{5\text{-}6\text{-}12}$	119.34	123.81	123.08	118.82	117.28	120.93	122.29	111.60	119.03	—	120.92	123.93	112.27	118.53	120.04	124.68	111.57
$\theta_{7\text{-}1\text{-}2}$	117.27	124.92	116.41	128.03	117.28	124.48	114.27	128.37	119.00	$(118.3)^a$ $(5)^b$	123.91	115.44	127.74	118.53	124.74	115.13	128.43
$\theta_{7\text{-}1\text{-}6}$	120.07	116.06	127.51	119.96	118.89	115.76	125.81	111.63	117.57	$(116.3)^a$ $(4)^b$	116.07	124.07	112.26	117.08	114.94	123.24	111.57
$\theta_{2\text{-}1\text{-}6}$	118.72	118.13	115.39	120.01	119.78	118.85	117.76	120.00	119.78	$(120.5)^a$ $(4)^b$	118.95	117.98	120.00	119.93	119.00	118.33	120.00
$\theta_{8\text{-}2\text{-}1}$	117.26	129.56	118.10	119.97	117.28	128.47	114.35	111.60	119.02	$(118.0)^a$ $(5)^b$	127.84	115.10	112.27	118.53	127.69	114.35	111.57
$\theta_{8\text{-}2\text{-}3}$	120.08	116.23	125.03	128.05	118.88	114.30	124.55	128.39	117.57	$(117.6)^a$ $(5)^b$	114.72	124.34	127.73	117.09	113.90	124.49	128.43
$\theta_{9\text{-}3\text{-}2}$	119.35	123.74	119.71	111.86	118.88	121.00	122.29	111.62	117.57	$(117.1)^a$ $(5)^b$	121.19	123.93	112.26	117.09	120.35	124.69	111.56
$\theta_{9\text{-}3\text{-}4}$	119.34	119.12	123.64	128.10	117.28	117.45	119.10	128.38	119.02	$(118.6)^a$ $(3)^b$	117.32	117.51	127.73	118.53	116.27	116.11	128.43
$\theta_{10\text{-}4\text{-}3}$	120.07	116.13	129.28	111.81	117.28	115.78	125.81	111.61	119.02	—	116.16	124.08	112.27	118.52	115.06	123.25	111.57
$\theta_{10\text{-}4\text{-}5}$	117.26	124.87	112.26	128.21	118.89	124.51	114.28	128.39	117.57	—	124.02	115.44	127.74	117.08	124.88	115.12	128.43
$\theta_{11\text{-}5\text{-}4}$	117.27	129.54	114.27	111.94	118.89	128.46	114.35	111.62	117.57	—	127.81	115.10	112.26	117.08	127.66	114.36	111.57
$\theta_{11\text{-}5\text{-}6}$	120.00	116.29	127.74	128.10	117.28	114.28	124.55	128.38	119.02	—	114.68	124.35	127.73	118.5311382		124.35	128.43
$\theta_{12\text{-}6\text{-}1}$	119.35	119.05	120.68	128.13	118.89	117.39	119.10	128.40	117.57	—	117.05	117.51	127.74	117.08	115.95	116.11	128.43

Torsion Angels (°)																	
$\phi_{1\text{-}2\text{-}3\text{-}4}$	21.94	−40.97	30.00	0.00	9.33	−30.30	18.57	0.00	−9.37	—	−28.65	13.51	0.00	5.42	25.10	9.70	0.00
$\phi_{2\text{-}3\text{-}4\text{-}5}$	−21.94	40.47	15.75	0.00	−9.40	30.69	14.39	0.00	9.31	(6.81)[a]	29.50	17.16	0.00	−5.39	−25.94	16.71	0.00
$\phi_{3\text{-}4\text{-}5\text{-}6}$	21.92	1.19	−46.84	0.00	9.33	0.32	−33.20	0.00	9.38	—	−1.27	−30.93	0.00	5.41	1.94	−26.53	0.00
$\phi_{4\text{-}5\text{-}6\text{-}1}$	−21.95	−41.02	30.09	0.00	−9.40	−29.99	18.57	0.00	−9.32	—	−27.43	13.53	0.00	−5.38	23.65	9.70	0.00
$\phi_{5\text{-}6\text{-}1\text{-}2}$	21.95	40.53	15.49	0.00	9.32	30.38	14.39	0.00	9.38	—	28.26	17.14	0.00	5.41	−24.47	16.70	0.00
$\phi_{6\text{-}1\text{-}2\text{-}3}$	−21.92	1.14	−46.03	0.00	−9.39	0.00	−33.20	0.00	−9.31	—	0.00	−30.91	0.00	−5.39	0.00	−26.53	0.00
$\phi_{7\text{-}1\text{-}2\text{-}8}$	66.49	−7.76	−72.41	0.00	−55.16	−7.89	−70.24	0.00	−53.29	(−57.1)[a]	−9.81	−65.73	0.00	−54.15	10.83	−64.23	0.00
$\phi_{7\text{-}1\text{-}2\text{-}3}$	−140.13	−119.02	155.82	−180.00	147.72	124.53	162.48	180.00	148.70	—	127.81	−168.73	−180.00	150.23	127.94	−174.71	−180.00
$\phi_{7\text{-}1\text{-}6\text{-}5}$	140.13	120.53	158.75	180.00	−147.43	−125.07	164.59	−180.00	−148.95	—	−127.49	−160.75	180.00	−150.55	−128.26	−159.25	180.00
$\phi_{8\text{-}2\text{-}3\text{-}9}$	−62.78	−62.99	55.19	0.00	55.84	−58.60	41.30	0.00	52.72	—	−54.77	30.65	0.00	53.48	55.14	25.10	0.00
$\phi_{8\text{-}2\text{-}1\text{-}7}$	−62.79	−38.38	31.25	0.00	55.81	65.36	33.08	0.00	52.72	—	63.38	38.06	0.00	53.49	−64.24	42.31	0.00
$\phi_{8\text{-}2\text{-}3\text{-}4}$	−135.80	169.84	125.12	−180.00	147.73	168.59	−131.12	−180.00	148.70	—	167.73	131.89	−180.00	150.23	166.18	133.62	180.00
$\phi_{8\text{-}2\text{-}1\text{-}6}$	135.13	−129.17	−154.51	180.00	−147.43	−139.19	147.93	180.00	−148.95	—	−140.42	−144.05	180.00	−150.55	−143.02	−141.74	−180.00
$\phi_{9\text{-}3\text{-}2\text{-}1}$	−135.80	176.46	116.44	180.00	147.72	−176.49	125.42	180.00	148.70	—	−177.55	131.47	180.00	150.23	−177.01	135.61	180.00
$\phi_{9\text{-}3\text{-}4\text{-}5}$	135.13	−136.97	−131.06	−180.00	−147.42	146.68	137.66	−180.00	−148.95	—	149.22	−147.11	−180.00	−150.55	152.32	−150.49	−180.00
$\phi_{9\text{-}3\text{-}4\text{-}10}$	62.79	120.57	−26.19	0.00	−55.18	65.27	33.07	0.00	−53.28	—	63.02	38.05	0.00	−54.14	−63.77	42.32	0.00
$\phi_{10\text{-}4\text{-}5\text{-}11}$	−66.49	−7.80	−80.14	0.00	55.83	−7.71	−70.24	0.00	52.72	—	9.20	−65.73	0.00	53.49	10.06	−64.23	0.00
$\phi_{10\text{-}4\text{-}3\text{-}2}$	140.14	−119.07	−143.77	−180.00	−147.42	124.41	162.46	−180.00	−148.96	—	127.36	−168.74	180.00	−150.56	127.45	−174.71	180.00
$\phi_{10\text{-}4\text{-}5\text{-}6}$	−140.14	120.57	−170.78	180.00	147.71	−124.94	164.60	180.00	148.70	—	−127.45	−160.74	−180.00	150.24	−127.73	−159.25	−180.00
$\phi_{11\text{-}5\text{-}6\text{-}12}$	62.79	−62.85	45.72	0.00	−55.16	−58.71	41.28	0.00	−53.29	—	−55.17	30.65	0.00	−54.15	55.64	25.09	0.00
$\phi_{11\text{-}5\text{-}4\text{-}3}$	−135.13	129.34	−146.56	180.00	147.71	−139.10	147.93	−180.00	148.70	—	−140.02	−144.05	180.00	150.23	−142.57	−141.73	180.00
$\phi_{11\text{-}5\text{-}6\text{-}1}$	135.79	−170.03	118.43	−180.00	−147.42	168.51	−131.12	180.00	−148.95	—	167.38	131.88	−180.00	−150.55	165.80	133.62	−180.00
$\phi_{12\text{-}6\text{-}5\text{-}4}$	135.80	176.64	114.59	180.00	−147.42	−176.54	−125.43	180.00	−148.95	—	−177.84	131.46	180.00	−150.56	−177.35	135.62	180.00
$\phi_{12\text{-}6\text{-}1\text{-}2}$	−135.13	−137.11	−128.37	−180.00	147.72	146.76	137.67	−180.00	148.69	—	149.59	−147.09	−180.00	150.24	152.77	−150.50	−180.00

C: chair conformation; **B**: boat conformation; **TB**: twist boat conformation; **P**: planar conformation.

[a] X-ray crystallographic data (see Ref. 8).

[b] Standard deviations.

TABLE II Calculated Total Electronic Energies E and Relative Energies $\Delta E(E_h)$ (in Hartree) for Various Conformations of Compounds 1–4

Method	HF/3-21G//HF/3-21G		B3LYP/3-21G//HF/3-21G		B3LYP/6-31G*//HF/3-21G	
Compound	E_{el}		ΔE[a]		E_{el}	ΔE[a]
1, **C**	−1160.755659	0.003017 (1.893198)[b]	−1169.144691	0.001804 (1.132154)[b]	−1175.481834	0.002404 (1.508534)
1, **B**	−1160.744476	0.014200 (8.910642)[b]	−1169.139575	0.006920 (4.342369)[b]	−1175.477261	0.006977 (4.378137)
1, **TB**	−1160.758676	0.000000 (0.000000)	−1169.146495	0.000000 (0.000000)[b]	−1175.484238	0.000000 (0.000000)
1, **P**	−1160.580085	0.178591 (112.067638)[b]	−1168.987228	0.159267 (99.941635)[b]	−1175.325177	0.159061 (99.812368)
2, **C**	−2659.720362	0.000000 (0.000000)[b]	−2670.008468	0.000000 (0.000000)[b]	−2684.157509	0.000000 (0.000000)
2, **B**	−2659.706276	0.014086 (8.838855)[b]	−2669.998439	0.100284 (6.292921)[b]	−2684.150156	0.007353 (4.614081)
2, **TB**	−2659.709284	0.011078 (6.951242)[b]	−2670.000386	0.008082 (5.071661)[b]	−2684.153312	0.004197 (2.633659)
2, **P**	−2659.643396	0.076965 (48.296558)	−2669.948562	0.059906 (37.591802)[b]	−2684.088490	0.069019 (43.310113)
3, **C**	−13327.598380	0.000000 (0.000000)[b]	−13344.345817	0.000000 (0.000000)[b]	−13397.247219	0.000000 (0.000000)
3, **B**	−13327.526423	0.013415 (8.417796)[b]	−13344.355462	0.010271 (6.445030)[b]	−13397.234388	0.012831 (8.051581)
3, **TB**	−13327.529438	0.104003 (6.526292)[b]	−13344.338035	0.007782 (4.883095)[b]	−13397.233901	0.013318 (8.357178)
3, **P**	−13327.483176	0.056662 (35.556226)[b]	−13344.307110	0.038707 (24.289155)[b]	−13397.196284	0.050935 (31.962222)
4, **C**	−3615.321031	0.000000 (0.000000)[b]	−36937.648325	0.000000 (0.000000)[b]	−967.197810[c]	0.000000 (0.000000)
4, **B**	−36915.310754	0.010277 (6.448983)[b]	−36937.640320	0.008005 (5.023344)[b]	−967.191779[c]	0.006031 (3.784513)
4, **TB**	−36915.312219	0.008123 (5.529806)[b]	−36937.641598	0.006728 (4.221699)[b]	−967.192897[c]	0.004913 (3.082957)
4, **P**	−36915.271535	0.049497 (31.059611)[b]	−36937.147448	0.033580 (21.072037)[b]	−967.151008[c]	0.046802 (29.368723)

[a] Relative to the most stable conformation.

[b] Numbers in the parenthesis are the corresponding ΔE values in kcal mol $^{-1}$.

[c] The B3LYP/LANL2DZ*//HF/3-21G method was used for compound **4**.

TABLE III NBO Calculated Stabilization Energies (E_2) (kcal mol^{-1}) for $\sigma_{\mathrm{M-C1}} \rightarrow \sigma^*_{\mathrm{C2-C3}}$ and Bonding Orbital Occupancies for the Chair Conformations of Compounds 1–4

Donor → acceptor delocalizations	**1**	**2**	**3**	**4**
$\sigma_{\mathrm{M-C1}} \rightarrow \sigma^*_{\mathrm{C2-C3}}$	5.20	9.68	11.15	12.27
occupancies				
$\sigma_{\mathrm{M-C1}}$	1.95984	1.95022	1.94271	1.93158

from this mean value are very small. These results show that in the **C** form of compound **1**, the aromatic character is somewhat reduced. Contrary to the **C** form of compound **1**, the benzene ring of compound **2**, the $C_{sp}{}^2 - C_{sp}{}^2$ bond lengths differ from each other and the exhibit partial π characters. Since the benzene ring in compounds **3** and **4** is less bent than in compounds **1** and **2**, consequently, the aromatic character of benzene rings in compounds **3** and **4** is increased, and as a result, the difference between $C_{sp^2} - C_{sp^2}$ bond lengths is decreased (see Table I).

At this point, it seems useful to remember some useful aspects concerning the NBO analysis, which was effectively used in this work. In the NBO analysis,[10,11] the electronic wavefunctions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor–acceptor interaction, which is taken into consideration by examining all possible interactions between filled (donor) and empty (acceptor) orbitals and then evaluating their energies by second order perturbation theory. Accordingly, the delocalization effects (or donor–acceptor charge transfers) can be estimated from the presence of off-diagonal elements of the Fock matrix in the NBO basis. NBOs closely correspond to the picture of localized bonds and lone pairs as basic units of the molecular structure so that is possible to conveniently interpret ab initio wavefunctions in terms of the classical Lewis structure concepts by transforming these functions to NBO form. The interactions due to electron delocalization are generally analyzed by selecting a number of bonding and antibonding NBOs, namely, those relevant to the analysis of donor and acceptor properties. As a result, the NBO program searches for an optimal natural Lewis structure, which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula. However, these orbitals suffer from small departures from the idealized Lewis structure, caused by interactions among them, which are known as hyperconjugative or stereoelectronic interactions. Therefore, the new orbitals are more stable than pure Lewis orbitals, stabilizing the wave function and giving a set of molecular orbitals equivalent to canonical molecular orbitals. For each donor NBO (i) and acceptor NBO (j), the stabilization energy (E_2) associated with $i \rightarrow j$ delocalization is explicitly estimated by following Eq. (1).

$$E_2 = \Delta E_{ij} = q_i \frac{F^2(i, j)}{\varepsilon_j - \varepsilon_i}, \qquad (1)$$

where q_i is the ith donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies), and $F(\mathrm{i,j})$ are off-diagonal elements, respectively, associated with the NBO Fock matrix.

The NBO analysis of donor–acceptor interactions showed that the resonance energy for $\sigma_{\mathrm{M-C1}} \rightarrow \sigma^*_{\mathrm{C2-C3}}$ delocalizations in compounds **1–4** are 5.20, 9.68, 11.15, and 12.27 kcal mol^{-1}, respectively (see Table III). The results revealed that by an increase of $\sigma_{\mathrm{M-C1}} \rightarrow \sigma^*_{\mathrm{C2-C3}}$ delocalization, the ring-flipping barrier heights (ΔE_0) decrease from compound **1** to compound **4** (see Figure 3 and Table III). Also, the NBO results showed that by an increase of the $\sigma_{\mathrm{M-C1}}\sigma^*_{\mathrm{C2-C3}}$ resonance energies in compounds **1–4**, the $\sigma_{\mathrm{M-C1}}$ bonding orbital occupancies decrease (see Table III). The NBO results also showed that the $\sigma_{\mathrm{Caryl-M}}$ bonding orbital occupancies in the chair conformation of compounds **1–4** are 1.1.95984, 1.95022, 1.94271, and 1.93158, respectively (see Table III). The results revealed that by a decrease of $\sigma_{\mathrm{Caryl-M}}$ occupancies, the ring-flipping barrier heights (ΔE_0) decrease from compound **1** to **4** (see Figure 4).

It can be concluded that by the decrease of $\sigma_{\mathrm{Caryl-M}}$ bonding orbital occupancies in compounds **1–4**, the strength of the $\mathrm{C_{aryl}}$-M bonds decrease. This fact could fairly explain the increase of the $\mathrm{C_{aryl}}$-M bond length from compound **1** to **4**.

The results suggest also that in compounds **1–4**, the ring-flipping is controlled by $\sigma_{\mathrm{M-C1}} \rightarrow \sigma^*_{\mathrm{C2-C3}}$ resonance energies. It can be said

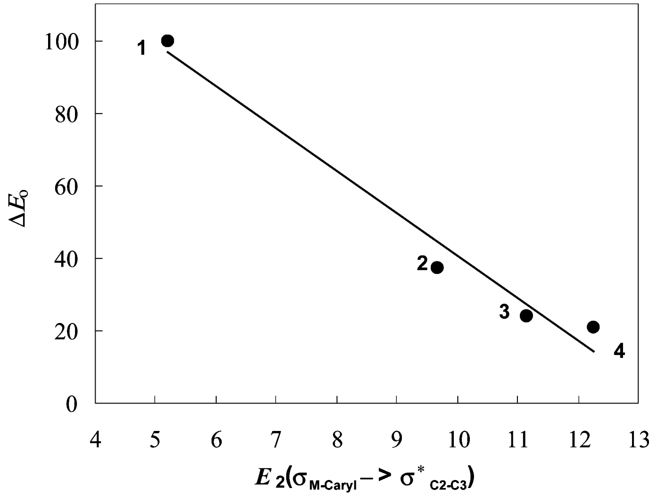


FIGURE 3 The calculated ring-flipping energy (ΔE_0 in kcal mol^{-1}) for the chair conformations of compounds **1–4**, plotted as a function of $E_2(\sigma_{\mathrm{M-Caryl}} \rightarrow \sigma^*_{C2-C3})$.

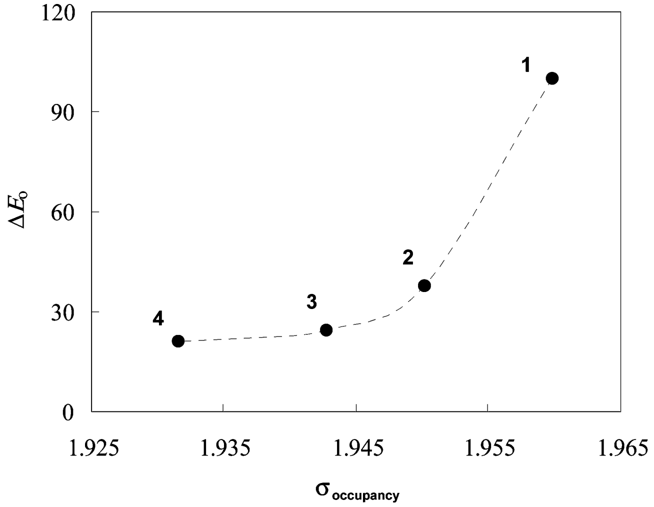


FIGURE 4 The calculated-ring-flipping energy (ΔE_0 kcal mol^{-1}) for the chair conformations of compounds **1–4**, plotted as a function of $\sigma_{\text{M-Caryl}}$ occupancies.

that by an increase of $\sigma_{\text{M-C1}} \rightarrow \sigma^*_{\text{C2-C3}}$ delocalizations, the planarity of the benzene moieties could easily take place from compound **4** to **1** (see Tables I and III). Therefore, the ring-flipping process in the chair conformation of compound **4** is faster than in **3**, in compound **3** it is faster than in compound **2**, and also in compound **2** it is faster than in compound **1**.

Relevant structural parameters of compounds **1–4**, as calculated by the HF/3-21G level of theory, are given in Table I. There is a good agreement between the HF/3-21G calculated structural parameters of compound **3** and the previously reported experimental data (X-ray crystallographic data, see Table I). Theoretical calculations provide structural parameters for an isolated molecule at 0 K; therefore, theoretical calculations are not reported, in principal, to reproduce the experimental values quantitatively.[23] Nevertheless, it is possible to carry out ab initio calculations, for instance at the Hartree-Fock level, from which many properties and a structure can be obtained with an accuracy that is competitive with experiments.[24–27]

In the most stable conformer of compound **1**, the average of $C_{sp^2} - C_{sp^3}$ bond lengths (1.610 Å) is significantly longer than the usual C_{sp^2}-C_{sp^3} bond (1.500 Å). Furthermore, in the **TB** conformation of compound **1**, the maximum twisting of the benzene moiety from the **P** form is about 46° (see Table I). As a result, the bending of the benzene ring reduces the corresponding aromatic character.

Mislow et al. have employed MM2 calculations only for the **C** conformer of compound **1** and they have not studied other possible conformers. Contrary to the obtained results for compound **1**, the most stable conformer of compounds **2–4** is found to be the **C** form, as calculated by both B3LYP and HF methods. Also, HF/3-21G//HF/3-21G results show that in compound **2**, the **C** conformer is more stable than the **TB**, **B**, and **P** forms (about 6.95, 8.84, and 48.30 kcal mol^{-1}, respectively). Further, the **C** conformer of compound **2** is more stable than the **TB, B**, and **P** forms (about 5.07, 6.29, and 37.59 kcal mol^{-1}) as calculated by B3LYP/3-21G//HF/3-21G level of theory. A similar trend is also observed in compounds **3** and **4** (see Table II).

Parallel to the increase of C—M (M=Si, Ge, and Sn) bond lengths in compounds **2–4**, the corresponding energy gap between the **C** and **P** forms is decreased. Based on the HF/3-21G//HF/3-21G calculations, the energy gap between the **C** and **P** forms of compounds **2–4** is 48.30, 35.56, and 31.06 kcal mol^{-1}, respectively. Also, the B3LYP/3-21G//HF/3-21G method shows that the energy gap between the **C** and **P** forms of compounds **2–4** are 37.59, 24.29, and 21.07 kcal mol^{-1}, respectively.

Among compounds **1–4**, only compound **3** has been synthesized and until now attempts to synthesis compounds **1** and **2** were unsuccessful. This fact could be attributed to the more twisted benzene moiety in compounds **1** and **2**, compared to compound **3** (see Table III). The bending angle of the benzene moiety in the **TB** conformation of compound **1** is 46.84°, while in the most stable conformations of compounds **2–4** (C forms), the bending angle is 9.40, 9.38, and 5.42°, respectively.

From a thermodynamical point of view, the calculated structural data by the HF/3-21G//HF/3-21G level of theory suggests that the synthesis of compound **4** should be easier than compounds **1–3**.

On the base of HF and B3LYP results, the **C** and **TB** conformations of compound **1** are particularly important because they are expected to be significantly populated at r.t.

Contrary to compound **1**, the HF and B3LYP results showed that only the **C** conformations of compounds **2–4** are expected to be populated at r.t. Effectively, compared to the **C** form, due to the higher van der Waals repulsions between the bulky groups, other conformations of compounds **2–4** are instable.

B3LYP/6-31G*//HF/3-21G and B3LYP/LANL2DZ*//HF/3-21G levels of theory were also used to calculate the conformational properties of compounds **1–4** (see Table II). It has to be noted that the results obtained at HF/3-21G//HF/3-21G and B3LYP/3-21G//HF/3-21G levels correlate well with those obtained at B3LYP/6-31G*//HF/3-21G and B3LYP/LANL2DZ*//HF/3-21G levels of theory. In addition, HF/3-21G//HF/3-21G and B3LYP/3-21G//HF/3-21G levels have the advantage that it could directly be used (without Gen or Extrabasis keywords) for all compounds in these series (e.g., compound **1–4**, also including the Sn atom).

CONCLUSION

The investigated ab initio MO and DFT calculations performed in this work provided a clear picture from both structural and energetic points of view for compounds **1–4**. The B3LYP/3-21G//HF/3-21G level of theory calculations showed that the **TB** conformer of compound **1** is more stable than **C**, **B**, and **P** forms of about 1.13, 4.34, and 99.94, respectively. This fact was explained by the decrease of the involved van der Waals repulsions due to the occured longer alkyl groups distances from each other. HF and B3LYP results showed also that the **P** forms of compounds **1–4** are less stable than the twisted forms. This fact indicates also that the steric repulsions overcome the π-resonance stabilization.

C_{aryl}-M (M=C, Si, Ge, and Sn) bond lengths increase from compound **1** to compound **4**; therefore, the related steric hindrance should be reduced. This fact also cause a decrease in energy barriers for the ring flipping of the **C** conformers of compounds **3** and **4** (via **P** form) compared to compound **2**. All three methods revealed that the **P** conformer of compound **1** is significantly less stable than the twisted conformer of compound **1**. These results also explain the improbability of the ring flipping of the most stable conformations of compound **1** (**TB** and **C**) via the **P** form.

The NBO analysis revealed that the resonance energies from the σ_{M-C1} bonding orbital to σ^*_{C2-C3} antibonding orbital increase from compounds **1** to compound **4**. Also, the donor–acceptor interactions could fairly explain the decrease of occupancies of the σ_{M-C1} bonding orbital from compound **1** to **4**. Therefore, the results suggest that in compounds **1–4**, the ring flipping of the chair conformer are controlled by the $\sigma_{M-C1} \rightarrow \sigma^*_{C1-C2}$ resonance energies.

In conclusion, in order to perform a meaningful comparison in the studied parent compounds (C-family elements: C, Si, Ge, and Sn) and based on the mentioned limitations concerning the choice of a larger basis set, the calculated data could be considered as fairly acceptable and useful information from the QSAR point of view in the corresponding organometallic compounds, which are further confirmed by the corresponding energetic and structural results generated by the NBO analysis.

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