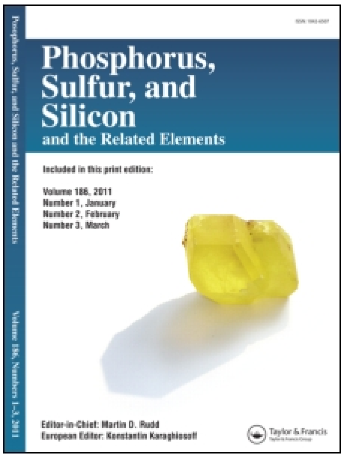

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AB INITIO STUDY OF RING FLIPPING OF THE OVERCROWDED *PERI*-SUBSTITUTED NAPHTHALENES

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*Ab inintio molecular orbital and density functional theory method were used to investigate the structural and dynamic behavior of 1,8-di-tert-butyl naphthalene (**1**), 1,8-bis(trimethylsilyl)naphthalene (**2**), 1,8-bis(trimethylgermyl)naphthalene (**3**), and 1,8-bis(trimethylstannyl)naphthalene (**4**). HF/3-21G//HF/3-21G results revealed that the ring flipping barrier height of compound **1–4** is 92.59, 32.13, 26.76, and 15.46 kJ mol*$^{-1}$ *respectively. The obtained results show that the transition state structure for ring flipping of the bulky-groups is in a planar form with naphthalene ring. Contrary to compound **1**, the ring flipping of compounds **2–4** occurred easily at room temperature. Also, MP2/3-21G//HF/3-21G energy calculation, show that the enantiomerization energy of compounds **1–4** are 97.99, 33.24, 26.80, and 15.38 kJ·mol*$^{-1}$ *respectively. The required energy for ring inversion of compounds **1–4** are 85.09, 27.26, 21.54, and 10.21 kJ mol*$^{-1}$ *respectively, as calculated by B3LYP/3-21G//HF/3-21G method. It can be concluded that the lower energy barrier of the ring flipping of compounds **2–4** is related to the increasing of the bond lengths of Si—C, Ge—C, and Sn—C, in contrast to C—C bond.*

Keywords: Ab initio calculations; molecular modeling; *peri*-substituted naphthalene; ring flipping

Steric strain associated with 1,8-disubstituted naphthalene is a case in point and much work has been done on the subject.[1] The subsituents in the 1 and 8 positions of naphthalene ring may be accommodate by distortion of the *peri* bonds in in-plane deflection or

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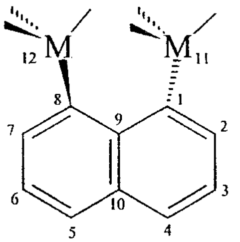
out-of-plane defection of the substituents. A notable example is the 1,8-di-*tert*-butylnaphtalene (**1**) compound, in which nonbonded repulsions results in a warped naphthalene ring.[2–7] Previously obtained results show that the skeletal distortion decreasing in the order 1,8-di-*tert*-butylnaphtalene (**1**) $\gg$ 1,8-bis(trimethylgermyl)naphthalene (**3**) $>$ 1, 8-bis(trimethylstannyl)naphthalene (**4**).[8] 1,8-di-tert-butylnaphtalene (**1**), 1,8-bis(trimethylsilyl)naphthalene (**2**), 1,8-bis(trimethylgermyl)-naphthalene (**3**), and 1,8-bis(trimethylstannyl)naphthalene (**4**) with C_2 symmetry are chairal and enantiomerization proceed via ring flipping in these molecules.

The structures and $\mathrm{M{-}C_{naphthalene}}$ bond rotations in compounds **1–4** have been investigated experimentally (x-ray) and theoretically (empirical force filed, EFF).[9–11] There is no published data, experimentally or theoretically, for enantiomerization path of compounds **2–4**. In this work, the structures and the ring flipping of compounds **1–4** were investigated computationally using ab initio and DFT methods.[12–16] The successful application of density functional theory (DFT) based methods broadened the applicability of the computational methods and now represents an interesting approach for determining activation barrier and molecular energies.[12,13,15] The B3LYP method combines Becke's three-parameter exchange function with the correlation function of Lee et al.[13,14]



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

CALCULATIONS

Ab initio calculation were carried out using HF/3-21G level of theory with the Gaussian 98 package programs[12] implemented on a Pentium-PC computer with 550 MHz processor. Initial structure geometries of compounds **1–4** isomers were obtained by a molecular mechanic program PCMODEL (88.0),[17] and for future reoptimization of geometries PM3 method of MOPAC 6.0 computer program was used.[18,19] Gaussian 98 package programs (serial number: PC42919962W-0772N) finally was used to perform ab initio calculation at HF/3-21G level. Energy minimum molecular geometry was located by minimizing energy with respect to all geometrical coordinates without imposing any symmetrical constraints.

The nature of the stationary points for reactant compounds has been fixed by virtue of the number of imaginary frequencies. For minimum state structures, only real frequency values and in the transition state, only single imaginary frequency value (with negative sign) are accepted.[20]

The structure of the molecular transition state geometries was located by using the optimized geometries of the equilibrium molecular structure according to the procedure of Dewar et al. (keyword SADDEL).[21] These geometry structures were then reoptimized by QST3 option at the HF/3-21G level. The vibrational frequency of ground state and transition states was calculated by subroutine FREQ.

RESULTS AND DISCUSSION

Corrected zero point (ZPE^c) and total electronic (E_{el}) energies ($E_0 = ZPE^c + E_{el}$) for ground-state and transition-state structure of compounds **1–4**, as calculated on the ab initio HF/3-21G level of theory, are given in Table I. For single point energy calculations, the ab initio MP2/3-21G//HF/3-21G and DFT method (B3LYP/3-21G//HF/3-21G) were used.

Enantiomerization of the axial symmetrical (C_2, point group) structures of compounds **1–4** can take place via the plane-symmetrical (C_s) geometry (near C_{2v} or quasi C_{2v} symmetry).

The ring inversion (enantiomerization) energy barrier in compound **1**, as calculated by HF/3-21G//HF/3-21G, MP2/3-21G//HF/3-21G, and B3LYP/3-21G//HF/3-21G methods, are in good agreement with the reported empirical force filed (EFF)[10] and dynamic ^{1}H-NMR data.[5] However, there is no published data for rings flipping of compounds **2–4**. According to the HF/3-21G//HF/3-21G, MP2/3-21G//HF/3-21G, and B3LYP/3-21G//HF/3-21G calculation, the energy barrier for ring inversion of the axial symmetrical (C_2 point group) structure of **1** via the planar form is 92.59, 97.99, and 85.09 kJ mol^{-1} respectively. HF/3-21G//HF/3-21G and B3LYP/3-21G//HF/3-21G methods show lower energy barrier for enantiomerization of compounds **1–4** in comparison the obtained values by MP2/3-21G//HF/3-21G method (see Table I and Figure 1). Study on the B3LYP/3-21G//HF/3-21G method show that enantiomerization of compounds **2–4** is fast at room temperature. The energy barriers of the enantiomerization of compounds **2–4** are 27.26, 21.54 and 10.21 kJ mol^{-1}, respectively, as calculated by

TABLE I Calculated Total Energies (E) Zero-Point Energies (ZPE), and Relative Energies (ΔE (E_h)), (in Hartree) for the Energy-Minimum and Energy-Maximum Geometries Compounds **1–4**

Method		HF/3-21G//HF3-21G			MP2/3-21G//HF3-21G			B3LYP/3-21G//HF3-21G		
System	ZPE^c	E_{el}	E_0	ΔE_0^a	E_{el}	E_0	ΔE_0^a	E_{el}	E_0	ΔE_0^a
1 (MIN), (C_2)	0.376552	−691.697332	−691.320780	0.000000 $(0.000000)^b$	−693.331689	−692.955137	0.000000 $(0.000000)^b$	−696.521314	−696.144762	0.000000 $(0.000000)^b$
1 (TS), (C_s)	0.380185	−691.665699	−691.285514	0.035266 $(92.590949)^b$	−693.297997	−692.917812	0.037325 $(97.996857)^b$	−696.492537	−696.112352	0.032400 $(85.092515)^b$
2 (MIN), (C_2)	0.355079	−1191.320268	−1190.965189	0.000000 $(0.000000)^b$	−1192.855877	−1192.500790	0.000000 $(0.000000)^b$	−1196.781395	−1196.426316	0.000000 $(0.000000)^b$
2 (TS), (C_s)	0.357628	−1191.310578	−1190.952950	0.012239 $(32.133517)^b$	−1192.845757	−1192.488129	0.012661 $(33.241466)^b$	−1196.773562	−1196.415934	0.010382 $(27.257960)^b$
3 (MIN), (C_2)	0.352587	−4747.259163	−4746.906576	0.000000 $(0.000000)^b$	−4748.801317	−4748.448730	0.000000 $(0.000000)^b$	−4754.892460	−4754.539873	0.000000 $(0.000000)^b$
3 (TS), (C_s)	0.355032	−4747.251414	−4746.896382	0.010194 $(26.764366)^b$	−4748.793554	−4748.438522	0.010208 $(26.801123)^b$	−4754.886702	−4754.531670	0.008203 $(21.536992)^b$
4 (MIN), (C_2)	0.346964	−12609.849851	−12609.502887	0.000000 $(0.000000)^b$	−12611.389039	−12611.04243	0.000000 $(0.000000)^b$	−12619.322886	−12618.975920	0.000000 $(0.000000)^b$
4 (TS), (C_{2V})	0.348972	−12609.845972	−12609.497000	0.005887 $(15.456353)^b$	−12611.385354	−12611.03657	0.000562 $(15.380190)^b$	−12619.321005	−12618.972030	0.003890 $(10.213202)^b$

[a] Relative to the minimum.
[b] Numbers in parenthesis are the corresponding ΔE values in kJ mol^{-1}.
[c] Corrected by a scaling factor (0.9409).

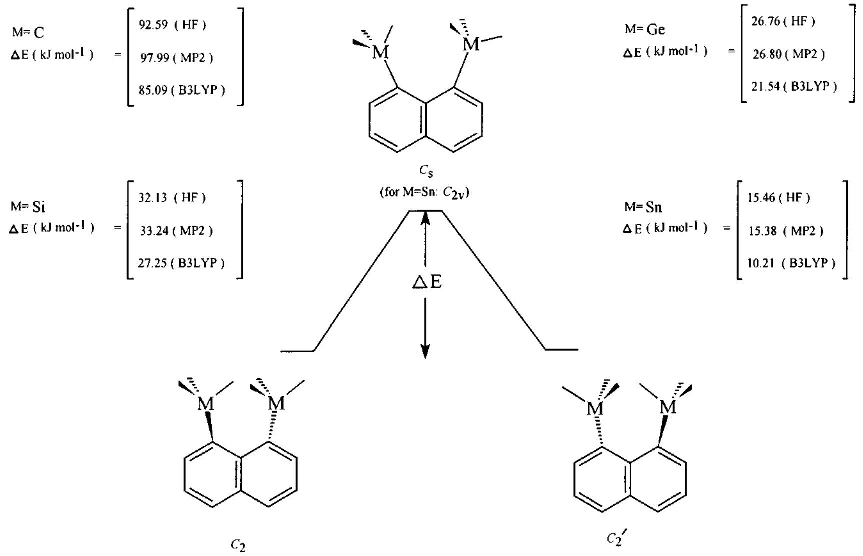


FIGURE 1 Calculated HF/3-21G//HF/3-21G, MP2/3-21G//HF/3-21G, and B3LYP/3-21G//HF/3-21G profile for rings flipping of compounds **1–4** with C_2 symmetry via C_s (for tin C_{2V}) transition-state structures.

B3LYP/3-21G//HF/3-21G method. If the process is fast, the time-averaged symmetry of compounds **2–4** becomes C_{2v}, which is the maximum symmetry allowed by the chemical structure of these molecules (see Figure 1). It is interesting to note that all these three methods predict the higher energy barrier for ring flipping of compound **1** than **2–4**. The reason of this fact may be is the greater *peri*-repulsion in compound **1**.

As the C—M (M=C, Si, Ge, and Sn) bond lengths increase, the folding of the naphthalene rings also increase. This can be explain with increasing the crowding bulky effect in compound **1** to **4**, as a *peri*-substituted repulsion.

The relevant structural parameters for ground-state and transition-state geometries of compounds **1–4**, as calculated by HF/3-21G level of theory, are given in Table II.

The comparison of the calculated structural parameters by HF/3-21G level of theory with previously reported experimentally data shows fairly small difference.[6,7] Theoretical calculations provide structural parameters for isolated molecules at 0·K. Therefore, theoretical calculations are not reported in principle to reproduce the experimental values quantitatively.[22] Nevertheless, it is possible to carry out ab initio calculations at the Hartree-Fock level, from which many properties and

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

Compound	**1**		**2**		**3**		**4**	
State	MIN (C_2)	TIS (C_s)	MIN (C_2)	TS (C_s)	MIN (C_2)	TS (C_s)	MIN (C_2)	TS (C_{2v})
Bond lengths (Å)								
$r_{1\text{-M}}$	1.566 (1.558)^a	1.547	1.939	1.933	1.976 (1.975)^a	1.966	2.180 (2.160)^a	2.193
$r_{1\text{-}2}$	1.366 (1.376)	1.366	1.371	1.374	1.369 (1.375)	1.371	1.372 (1.383)	1.377
$r_{1\text{-}9}$	1.454 (1.443)	1.489	1.444	1.456	1.439 (1.448)	1.448	1.441 (1.426)	1.450
$r_{2\text{-}3}$	1.411 (1.420)	1.398	1.410	1.404	1.409 (1.405)	1.403	1.411 (1.405)	1.405
$r_{3\text{-}4}$	1.351 (1.361)	1.338	1.352	1.345	1.352 (1.332)	1.346	1.352 (1.349)	1.347
$r_{4\text{-}10}$	1.419 (1.417)	1.420	1.417	1.417	1.417 (1.425)	1.417	1.417 (1.408)	1.415
$r_{5\text{-}6}$	1.351 (1.362)	1.388	1.352	1.345	1.352 (1.370)	1.346	1.352 (1.363)	1.347
$r_{5\text{-}10}$	1.419 (1.415)	1.413	1.417	1.413	1.417 (1.400)	1.413	1.417 (1.410)	1.415
$r_{6\text{-}7}$	1.411 (1.417)	1.394	1.410	1.401	1.409 (1.407)	1.401	1.411 (1.401)	1.405
$r_{7\text{-}8}$	1.366 (1.377)	1.375	1.371	1.379	1.369 (1.381)	1.378	1.372 (1.381)	1.377
$r_{8\text{-M}}$	1.566 (1.558)	1.634	1.939	1.979	1.976 (1.973)	2.014	2.180 (2.163)	2.193
$r_{8\text{-}9}$	1.454 (1.454)	1.598	1.444	1.460	1.439 (1.435)	1.453	1.441 (1.433)	1.450
$r_{9\text{-}10}$	1.420 (1.433)	1.445	1.419	1.432	1.419 (1.439)	1.430	1.418 (1.444)	1.428
Bond angles (°)								
$\theta_{\text{M-}1\text{-}2}$	115.3 (114.5)	113.4	111.3	109.9	111.2 (113.0)	110.6	110.5 (112.2)	105.7
$\theta_{\text{M-}1\text{-}4}$	151.1 (150.7)	160.1	149.4	166.7	154.7 (154.8)	158.7	154.8 (155.8)	164.8
$\theta_{1\text{-}2\text{-}3}$	122.9 (124.6)	125.3	122.9	124.2	123.1 (123.1)	124.1	122.8 (122.4)	124.1
$\theta_{2\text{-}3\text{-}4}$	118.8 (115.8)	117.7	118.9	118.2	118.8 (119.3)	118.3	119.1 (119.3)	118.7
$\theta_{3\text{-}4\text{-}10}$	120.0 (121.7)	121.1	120.6	120.9	120.5 (121.5)	120.9	120.6 (121.3)	120.6
$\theta_{4\text{-}10\text{-}5}$	119.7 (118.9)	112.5	119.5	115.9	119.4 (119.8)	116.7	119.7 (119.8)	116.9
$\theta_{4\text{-}10\text{-}9}$	120.1 (120.6)	123.6	120.2	121.9	120.3 (119.6)	121.8	120.2 (119.7)	121.6

$\theta_{5\text{-}6\text{-}7}$	118.8 (116.2)	118.1	118.6	118.6	118.8 (117.7)	118.5	119.1 (119.2)	118.7
$\theta_{5\text{-}10\text{-}9}$	120.7 (120.5)	123.9	120.2	122.1	120.3 (120.6)	122.0	120.2 (120.5)	121.6
$\theta_{6\text{-}7\text{-}8}$	122.9 (124.5)	127.4	122.9	125.0	123.1 (123.6)	125.0	122.8 (122.8)	124.1
$\theta_{7\text{-}8\text{-}9}$	117.3 (117.4)	115.9	118.1	117.3	118.2 (118.5)	117.3	118.2 (119.2)	118.1
$\theta_{7\text{-}8\text{-}M}$	115.3 (114.3)	105.9	111.3	103.0	125.5 (112.7)	102.6	110.5 (112.1)	105.7
$\theta_{7\text{-}8\text{-}M}$	115.3 (114.3)	105.9	111.3	103.0	125.5 (112.7)	102.6	110.5 (112.1)	105.7
$\theta_{8\text{-}9\text{-}1}$	128.2 (118.9)	133.0	125.4	127.8	125.5 (118.9)	127.1	124.4 (119.8)	126.5
$\theta_{8\text{-}9\text{-}10}$	115.9 (115.1)	114.3	117.3	116.5	117.3 (116.8)	116.7	117.8 (116.9)	116.8
$\theta_{9\text{-}1\text{-}M}$	124.7 (125.8)	127.1	127.5	131.3	128.0 (125.0)	130.4	128.2 (125.6)	136.2
$\theta_{9\text{-}8\text{-}M}$	124.7 (125.6)	137.9	127.5	139.6	128.0 (125.4)	140.0	128.2 (125.4)	136.2
Torsion angels (°)								
$\phi_{M\text{-}1\text{-}8\text{-}M}$	−72.3 (−68.6)	6.0	−59.1	1.1	−56.0 (−54.3)	0.6	−54.0 (−53.1)	−5.9
$\phi_{M\text{-}1\text{-}9\text{-}8}$	−44.0 (−41.8)	4.8	−37.0	0.3	−35.2 (−31.6)	0.0	−34.1 (−33.7)	−4.0
$\phi_{M\text{-}1\text{-}9\text{-}10}$	136.0 —	−176.5	143.0	179.7	144.8 —	179.6	145.9 —	176.0
$\phi_{M\text{-}8\text{-}9\text{-}1}$	−44.0 (−42.1)	2.8	−37.0	1.2	−35.2 (−34.7)	0.8	−34.1 (−33.7)	−4.0
$\phi_{M\text{-}8\text{-}9\text{-}10}$	136.0 —	175.9	143.0	−178.2	144.8 —	178.7	145.9 —	176.0
$\phi_{1\text{-}2\text{-}3\text{-}4}$	7.4 (6.5)	0.1	5.8	0.8	5.6 (5.6)	0.7	4.8 (5.7)	1.5
$\phi_{2\text{-}1\text{-}9\text{-}10}$	−24.4 (−23.6)	1.6	−101.8	−1.1	−14.7 (−9.3)	−1.0	−12.2 (−9.4)	−3.1
$\phi_{1\text{-}9\text{-}8\text{-}7}$	155.6 —	176.2	151.1	177.2	165.3 —	179.5	167.8 —	176.9
$\phi_{1\text{-}9\text{-}10\text{-}4}$	21.4 (19.2)	0.0	14.2	1.6	13.5 (11.0)	1.4	11.4 (10.8)	3.1
$\phi_{1\text{-}9\text{-}10\text{-}5}$	−158.6 —	−178.8	−165.8	−177.9	−166.5 —	−178.2	−168.6 —	−176.9
$\phi_{2\text{-}1\text{-}9\text{-}8}$	155.6 —	1.6	14.2	179.5	13.5 —	179.5	167.8 —	178.9
$\phi_{2\text{-}3\text{-}4\text{-}10}$	−11.0 (−11.6)	1.6	−7.2	−0.4	−7.0 (−4.0)	0.3	−5.8 (−4.3)	−1.5
$\phi_{3\text{-}2\text{-}1\text{-}9}$	10.7 —	−1.7	5.7	−0.1	5.5 —	0.0	4.3 —	0.9
$\phi_{3\text{-}4\text{-}10\text{-}5}$	176.2 —	177.2	177.1	178.6	177.3 —	178.8	177.6 —	179.2
$\phi_{3\text{-}4\text{-}10\text{-}9}$	−3.8 (−1.5)	−1.7	−2.9	−.09	−2.7 (−4.5)	0.8	−2.4 (−4.1)	0.8
$\phi_{6\text{-}7\text{-}8\text{-}9}$	10.7 (11.4)	3.2	11.8	1.3	5.5 (3.1)	0.0	4.3 (3.4)	0.6
$\phi_{7\text{-}8\text{-}9\text{-}10}$	−24.4 (−23.1)	−2.6	−29.5	−2.2	−14.7 (−12.0)	1.0	−12.2 (−8.8)	1.7

[a] Experimental data, Ref.[11].

structures can be obtained with an accuracy that is competitive with experiment.[23–26]

Study on the HF/3-21G method show that the naphthalene rings in compounds **1–4** are fairly twisted from coplanar form (see Table II); for example, the dihedral angle between planes C1-C9-C10 and C9-C10-C5 for compounds **1–4** is 158°, 165.8°, 166.5°, and 168.6° respectively.

Since in compounds **2–4** the $C_{(aryl)}$—M bond lengths increase, consequently, the bond angle M-C1-C9 and M-C8-C9 were expanded in ground-state and transition-state structures (see Table II). The average of bond angles M-C1-C9 and M-C8-C9 in the transition structures of compounds **1–4**, are 132.5, 135.45, 135.2, and 136.2 respectively, This fact causes that the flipping of the crowded groups in compounds **2–4** occur easily at room temperature (see Table I).

CONCLUSION

Ab initio HF, MP2, and B3LYP density functional theory calculations provide a picture from both structural and dynamic point of view for compounds **1–4**. The results calculated by HF/3-21G//HF/3-21G, MP2/3-21G//HF/3-21G, and B3LYP/3-21G//HF/3-21G methods show that the energy barrier of ring flipping in compounds **2–4** is higher than compounds.

The reason of this may be the increase of the M—$C_{(Aryl)}$ bond lengths in carbon family atoms and the expansion of the M-C1-C9 and M-C8-C9 bond angles. Further, a part of two bulky groups is due to the increase in bond lengths of M—C_{aryl} and further expansion of M-C1-C9 and M-C8-C9 bond angles. Consequently, in compounds **2–4**, the flipping of crowded bulky groups occur easily at room temperature, as calculated by all these three methods.

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