

***Ab initio* study of geminal steric hindrance effects on the stability of conformations of cyclohexane derivatives**

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Ab initio and density functional theory methods (HF/3-21G**/HF/3-21G*, MP2/3-21G**/HF/3-21G*, B3LYP/3-21G**/HF/3-21G*, B3LYP/LANL2DZ**/HF/LANL2DZ*, MP2/LANL2DZ**/HF/LANL2DZ* and HF/LANL2DZ**/HF/LANL2DZ*) used to investigate the conformational properties of cyclohexane, 1,1-dimethylcyclohexane, 1,1-di-*tert*-butylcyclohexane, 1,1-bis(trimethylsilyl)cyclohexane, 1,1-bis(trimethylgermyl)cyclohexane and 1,1-bis(trimethylstannyl)cyclohexane showed that the energy difference between the chair and twist-boat conformations and also the ring flipping energy barrier decreases from cyclohexane, 1,1-dimethylcyclohexane to 1,1-di-*tert*-butylcyclohexane, and increases from 1,1-bis(trimethylsilyl)cyclohexane, 1,1-bis(trimethylgermyl)cyclohexane to 1,1-bis(trimethylstannyl)cyclohexane.

Keywords: geminal substituted cyclohexane, steric hindrance, molecular modelling

The conformational features of six-membered rings are fundamental subjects in organic chemistry. Experimental evidence indicating that six-membered rings are non-planar began to accumulate in the 1920s. The most stable conformation of cyclohexane is the chair. Electron diffraction studies in the gas phase reveal a slight flattening of the chair compared with the geometry obtained when using tetrahedral molecular models.¹ Two other non-chair conformations of cyclohexane that have normal bond lengths are the twist and boat conformations.² Both twist and boat conformations are less stable than the chair. Molecular mechanics calculations indicated that the twist conformation is about 5 kcal mol⁻¹ and the boat about 6 kcal mol⁻¹ higher in energy than the chair conformation.³ A direct measurement of the chair-twist energy difference has been made using low-temperature IR spectroscopy.⁴ The enthalpy and Gibbs-free energy of activation of the interconversion of the chair form of cyclohexane derivatives is about 11.0 kcal mol⁻¹, as calculated by molecular mechanics⁵⁻⁷ and dynamic NMR methods.⁸

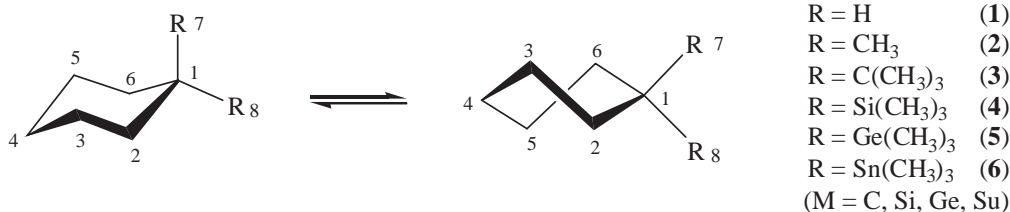
Substitution of a hydrogen atom on the cyclohexane ring with a bulkier group does not significantly affect the rate of conformational inversion (ring inversion), but influences the equilibrium between the alternative chair forms.⁹ All substituents that were axial in one chair conformation become equatorial on ring inversion, and vice versa and the conformations in which there is a 1,3-diaxial or gauche interaction between substituent groups larger than hydrogen are destabilised by van der Waals repulsion.

Weiser *et al.* have examined systems containing a cyclohexane ring with two substituted identical geminal substituents such as: Me, Et, Bu or *i*-Pro groups.¹⁰ However, they did not apply the MM3 method to calculate the barrier

height of the ring flipping of above mentioned compounds. Neither did they investigate the effect of the increase of the size of the bulky group on the energy gap between the chair and twist-boat conformations of the geminally disubstituted cyclohexane systems.

One may predict the change of the energy gaps between the chair and twist-boat forms of compounds **3–6** (see Scheme 1) by the increase of M–C_{cyclohexyl} bond lengths; however, the bond lengths of M–CH₃ increase simultaneously and also probably the 1,3-diaxial repulsions. Therefore, the influence of the M–CH₃ groups on the energy gaps and the barrier heights of the ring flipping of compounds **3–6** are not readily predictable. There is no reported quantitative experimental or theoretical data about the energy gap between chair and twist-boat forms or on barrier heights of ring flipping of compounds **3–6**. Therefore, one of the questions addressed in this work was how the effect of the increase of the atomic radius could affect the energy gap between chair and twist boat forms, and also the barrier heights of ring flipping of compounds **3–6**.

As we were especially interested to evaluate the impact of the 1,3-diaxial repulsions on the energy gap between chair and twist boat conformations in this family of compounds, we performed *ab initio* molecular orbital (MO)¹¹ and density functional theory (DFT) calculations (B3LYP)^{12,13} for structural optimisations and energy calculations of the chair, twist-boat and transition state structures of the ring flipping of the following compounds: cyclohexane (**1**), 1,1-dimethylcyclohexane (**2**), 1,1-di-butylcyclohexane (**3**), 1,1-bis(trimethylsilyl)cyclohexane (**4**), 1,1-bis(trimethylgermyl)cyclohexane (**5**) and 1,1-bis(trimethylstannyl)cyclohexane (**6**) (see Scheme 1).



Scheme 1

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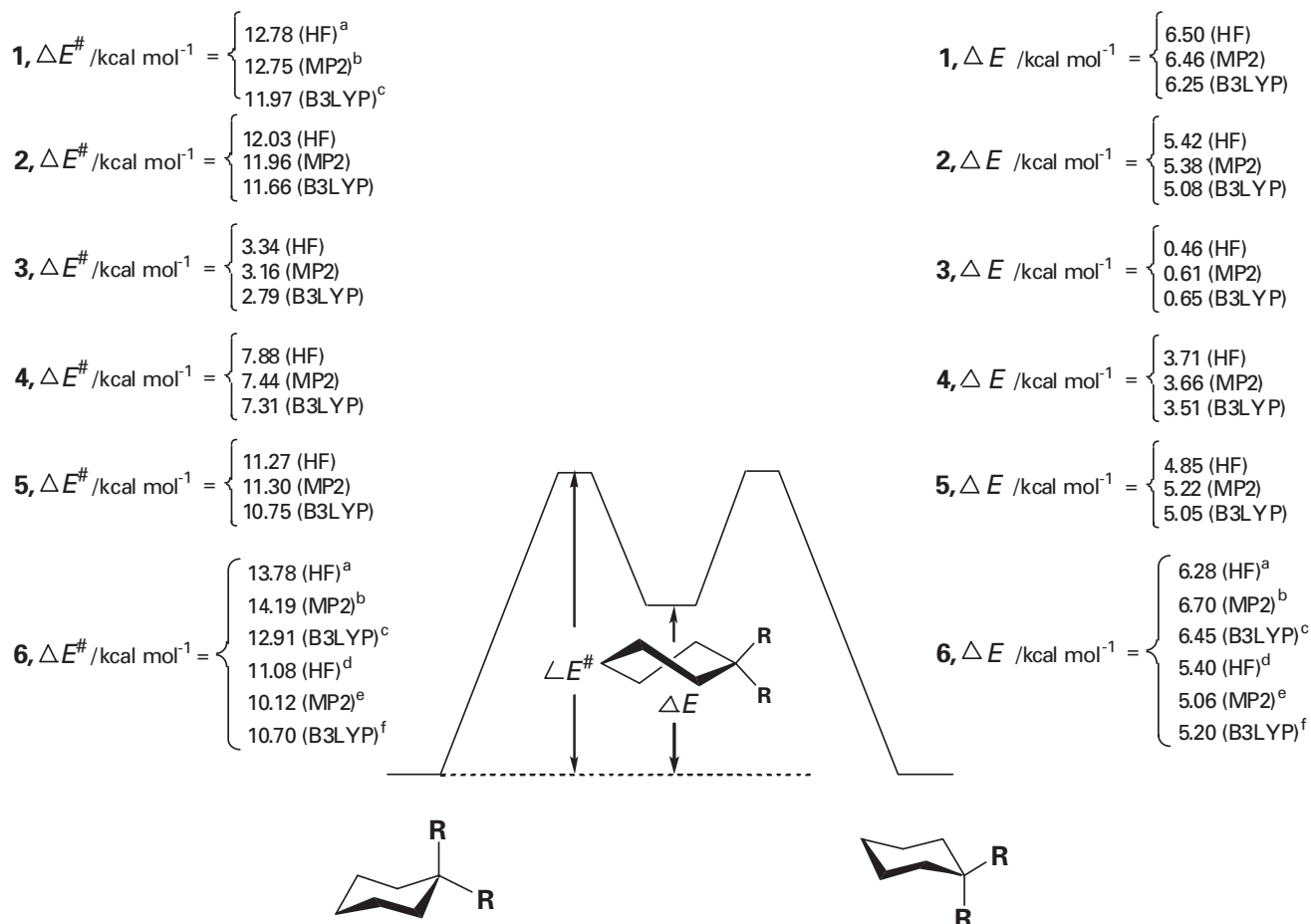


Fig. 1 Calculated energy diagram for ring inversion of compounds **1–6**. (a) HF/3-21G*//HF/3-21G*; (b) MP2/3-21G*//HF/3-21G*; (c) B3LYP/3-21G*//HF/3-21G*; (d) HF/LANL2DZ*//HF/LANL2DZ*; (e) MP2/LANL2DZ*//HF/LANL2DZ*; (f) B3LYP/LANL2DZ*//HF/LANL2DZ*

Recently, it has been argued that the B3LYP theoretical model often overestimates conformational energy differences, whereas MP2 appears to give values in better agreement with experiment.^{14,15} However, the results obtained in this work contradict the above argument. Compared to MP2, the calculated B3LYP results show smaller energy differences between the chair and twist-boat conformations for compounds **1–6**. In fact, the published literature B3LYP results showed the increasing applicability of density functional theory (DFT) as a successful computational method and now DFT methods are known as reliable approaches for determining activation barriers and molecular energies.^{12,13,16,17}

Calculations

Ab initio calculations were carried out using HF/3-21G*//HF/3-21G*, MP2/3-21G*//HF/3-21G* and B3LYP/3-21G*//HF/3-21G* levels of theory with the GAUSSIAN 98 package of programs¹¹ implemented on a Pentium-PC computer with 550 MHz processor. Since, according to the Gaussian 98 user's reference 2nd edition, the 6-31G* basis set cannot be applied to Sn compounds, for investigation of the stability of the various conformations of compounds **1–6** (which contain carbon, silicon, germanium and tin, respectively), we were limited to using the HF/3-21G*//HF/3-21G*, MP2/3-21G*//HF/3-21G* and B3LYP/3-21G*//HF/3-21G* methods. 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 basis set is known to be one of the best of these basis sets.¹¹ LANL2DZ is a double-zeta basis set containing effective core potential (ECP) representations of electrons near the nuclei for post-third row atoms. Therefore, in addition to the HF/3-21G* method and in order to compare the effect of all-electron with pseudo-potential basis sets, B3LYP/LANL2DZ*//HF/LANL2DZ*, MP2/LANL2DZ*//HF/LANL2DZ* and HF/LANL2DZ*//HF/LANL2DZ* methods were also used for the investigation of the conformational properties of compound **6** (containing Sn as a heavy atom). The MESSAGE keyword was also used in order to add additional uncontracted polarisation basis function to the LANL2DZ basis set. Further, for evaluating the relatively large basis set and post-HF method effects, we used MP2/6-311G** level of theory for geometry optimisation of compounds **1** and **2**.

Initial estimation of structural geometries of compounds **1–6** was obtained by a molecular mechanics program PCMODEL (88.0)¹⁸ and for further optimisation of geometries the PM3 method of MOPAC 7.0 computer program was used.^{19,20} 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 minimising energy with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for compounds **1–6** has been fixed by means of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition-state, only single imaginary frequency value was accepted.²¹ The structures of the molecular transition-state geometries

Table 1 Calculated total energies E , zero-point energies ZPE (from HF/3-21G*), and relative energies ΔE (E_h), (in hartree), for the energy-minimum and energy-maximum geometries of compounds **1-6**

System	Method	HF/3-21G*/HF3-21G*			MP2/3-21G*/HF3-21G*			B3LYP/3-21G*/HF3-21G*			
		ZPE	Eel	E0	ΔE_0^a	Eel	E0	ΔE_0^a	Eel	E0	ΔE_0^a
1-(Chair), (D_{3d})		0.182785	-232.916900	-232.734120	0.000000	-233.461190	-233.278405	0.000000	-234.606665	-234.423880	0.000000
1-(Twist-boat), (C_2)		0.182699	-232.906460	-232.723770	0.010352 (6.495983)	-233.450808	-233.268109 (6.460780)	0.0102959 (6.249999)	-234.596619	-234.413920	0.009960
1-[C→TB] [#] , C_1		0.182616	-232.896399	-232.713783	0.020337 (12.761671)	-233.440704	-233.258088 (12.749372)	0.023174 (11.969502)	-234.587422	-234.404806	0.019075
2-(Chair), (C_s)		0.242834	-310.557210	-310.314360	0.000000	-311.290567	-311.047733	0.000000	-312.810826	-312.567992	0.000000
2-(Twist-boat), (C_2)		0.242692	-310.548420	-310.305730	0.008632 (5.416666)	-311.281853	-311.039161 (5.379392)	0.008573 (5.081702)	-312.802586	-312.559894	0.008098
2-[C→TB] [#] , C_1		0.245710	-310.537765	-310.295194	0.019169 12.028739)	-311.271242	-311.028671 (11.961909)	0.019062 (11.657881)	-312.791985	-312.549414	0.018578
3-(Chair), (C_s)		0.427803	-543.412150	-542.984350	0.000000	-544.722415	-544.294612	0.000000	-547.368013	-546.940210	0.000000
3-(Twist-boat), (C_2)		0.427402	-543.411020	-542.983620	0.000731 (0.458709)	-544.721037	-544.293635 (0.613516)	0.000978 (0.654242)	-547.366570	-546.939168	0.001043
3-[C→TB] [#] , C_1		0.426746	-543.605761	-542.979015	0.005331 (3.345256)	-544.716318	-544.289572 (3.162588)	0.005040 (2.794177)	-547.362504	-546.935758	0.004453
4-(Chair), (C_s)		0.401052	-1043.220100	-1042.819100	0.000000	-1044.479690	-1044.078638	0.000000	-1047.801002	-1047.399949	0.000000
4-(Twist-boat), (C_2)		0.400697	-1043.213800	-1042.813100	0.005912 (3.709839)	-1044.473493	-1044.072796 (3.665913)	0.005842 (3.510291)	-1047.795052	-1047.394355	0.005594
4-[C→TB] [#] , C_1		0.400088	-1043.206546	-1042.806458	0.012561 (7.882153)	-1044.466870	-1044.066782 (7.439759)	0.011856 (7.313629)	-1047.788382	-1047.388294	0.011655
5-(Chair), (C_s)		0.397480	-4599.273572	-4598.876095	0.000000	-4600.590244	-4600.192753	0.000000	-4606.088245	-4605.690765	0.000000
5-(Twist-boat), (C_2)		0.396835	-4599.265201	-4598.868374	0.007721	-4600.5812806	-4600.184445	0.008318	-4606.079559	-4605.682723	0.008042
5-[C→TB] [#] , C_1		0.396818	-4599.254950	-4598.858131	0.017964 (11.272589)	-4600.571578	-4600.174759 (11.297690)	0.018004 (10.754894)	-4606.070444	-4605.673626	0.017139
6-(Chair), (C_s)		0.390675	-12461.700000	-12461.309620	0.000000	-12461.992091	-12461.601420	0.000000	-12470.315033	-12469.924360	0.000000
6-(Twist-boat), (C_2)		0.390473	-12461.690000	-12461.299610	0.010010 (6.281375)	-12461.981220	-12461.590740 (6.703689)	0.010683 (6.446411)	-12470.304562	-12469.914090	0.010273
6-[C→TB] [#] , C_1		0.389973	-12461.677633	-12461.287660	0.021960 (13.780120)	-12462.968784	-12462.578810 (14.188001)	0.022610 (12.914156)	-12470.293752	-12469.903780	0.020580

Numbers in parenthesis are the corresponding ΔE values in kcal mol⁻¹.
^aRelative to the minimum.

Table 2 HF/3-21G* Calculated enthalpy, entropy and Gibbs-free energy in various conformations of compounds 1-6

Geometry	<i>H</i> /hartree	<i>S</i> /kcal mol ⁻¹ K ⁻¹	<i>G</i> /hartree	ΔH /hartree	ΔS /kcal mol ⁻¹ K ⁻¹	ΔG /hartree
1-(Chair), (<i>D</i> _{3d})	-232.277807	0.073456	-232.762708	0.000000	0.000000	0.000000
1-(Twist-boat), (<i>C</i> ₂)	-232.717166	0.075149	-232.752872	0.010641 (6.677334)	0.001693	0.009836 (6.172188)
1-[C→TB]#, <i>C</i> ₁	-232.707584	0.075069	-232.743252	0.020223 (12.690135)	0.001613	0.019456 (12.208835)
2-(Chair), (<i>C</i> _s)	-310.305612	0.084427	-310.345727	0.000000	0.000000	0.000000
2-(Twist-boat), (<i>C</i> ₂)	-310.296831	0.085503	-310.337456	0.008781 (5.510165)	0.001076	0.008271 (5.190135)
2-[C→TB]#, <i>C</i> ₁	-310.286520	0.086134	-310.327445	0.019092 (11.980421)	0.001707	0.018282 (11.472138)
3-(Chair), (<i>C</i> _s)	-542.969075	0.112411	-543.022485	0.000000	0.000000	0.000000
3-(Twist-boat), (<i>C</i> ₂)	-542.968902	0.109971	-543.021153	0.000173 (0.108559)	-0.002440	0.001332 (0.835843)
3-[C→TB]#, <i>C</i> ₁	-542.963863	0.112874	-543.017493	0.005212 (3.270582)	0.000463	0.004992 (3.132530)
4-(Chair), (<i>C</i> _s)	-1042.798792	0.136232	-1042.863520	0.000000	0.000000	0.000000
4-(Twist-boat), (<i>C</i> ₂)	-1042.792613	0.138319	-1042.858332	0.006179 (3.877384)	0.002087	0.005188 (3.255521)
4-[C→TB]#, <i>C</i> ₁	-1042.786320	0.137215	-1042.851515	0.012472 (7.826305)	0.000983	0.012005 (7.533258)
5-(Chair), (<i>C</i> _s)	-4598.854327	0.146245	-4598.923812	0.000000	0.000000	0.000000
5-(Twist-boat), (<i>C</i> ₂)	-4598.846167	0.150588	-4598.917716	0.008160 (5.120482)	0.004343	0.006096 (3.825301)
5-[C→TB]#, <i>C</i> ₁	-4598.836284	0.149099	-4598.907125	0.018043 (11.322163)	0.002854	0.016687 (10.471259)
6-(Chair), (<i>C</i> _s)	-12461.285463	0.164571	-12461.363656	0.000000	0.000000	0.000000
6-(Twist-boat), (<i>C</i> ₂)	-12461.275237	0.166759	-12461.354470	0.010230 (6.419427)	0.002188	0.009180 (5.760542)
6-[C→TB]#, <i>C</i> ₁	-12461.263516	0.168242	-12461.343454	0.021950 (13.773845)	0.003671	0.020200 (12.675702)

Numbers in parenthesis are the corresponding ΔE values in kcal mol⁻¹.

For transition state structures the ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger values are the corresponding ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger values.

were located using the optimised geometries of the equilibrium molecular structures according to the Dewar *et al.* procedure (keyword SADDLE).²² These geometry structures were reoptimized by the QST2 subroutine at the HF/3-21G* level. The vibrational frequencies of ground states and transition states were calculated by FREQ subroutine.

The thermodynamic functions (all corrected for the zero-point energy), *i.e.* E_0 , enthalpy H (sum of the electronic and the thermal enthalpy), Gibbs free energy G (sum of the electronic and thermal free energy) and entropy S , were calculated according to the following relation: $E = E_0 + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$, $H = E + RT$, $G = H - TS$, as defined in the output of the frequency calculation in GAUSSIAN 98 manual. Finally, using the corresponding calculated thermodynamic data for ground and transition states, ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger were also determined.

Results and discussion

Zero point (ZPE) and total electronic (E_{el}) energies ($E_0 = E_{\text{el}} + \text{ZPE}$) for various conformations of compounds 1-6, as calculated by the *ab initio* HF/3-21G* level of theory are given in Table 1. For single-point energy calculations, both the *ab initio* MP2/3-21G*//HF/3-21G* and the DFT methods (B3LYP/3-21G*//HF/3-21G*) were used. Also Table 2 shows the values of the thermodynamic functions H , S , G and the activation parameters (ΔG^\ddagger , ΔS^\ddagger and ΔH^\ddagger). ΔS^\ddagger values are relatively small, so that the ΔH^\ddagger and ΔG^\ddagger values are close to the ΔE_0 values. Also, HF/LANL2DZ* was used to calculate the zero-point (ZPE) and total electronic energies of compound 6, and MP2/LANL2DZ*//HF/LANL2DZ* and B3LYP/LANL2DZ*//HF/LANL2DZ* levels of theory were, as well, used for single-point energy calculations. Both the structural and energetic parameters for compound 6 (containing Sn as a heavy atom) obtained by pseudo-potential B3LYP/LANL2DZ*//HF/LANL2DZ*, MP2/LANL2DZ*//

HF/LANL2DZ* and HF/LANL2DZ*//HF/LANL2DZ* methods were also used for comparison with those obtained by all-electron HF/3-21G*//HF/3-21G*, MP2/3-21G*//HF/3-21G* and B3LYP/3-21G*//HF/3-21G* methods.

The results obtained by the HF/3-21G*//HF/3-21G*, MP2/3-21G*//HF/3-21G* and B3LYP/3-21G*//HF/3-21G* levels of theory revealed that the most stable conformation of each of the compounds 1-6 is the chair form. In cyclohexane (1), the energy difference between the chair and the twist-boat conformation is 6.5, 6.45 and 6.25 kcal mol⁻¹, respectively, as calculated by HF/3-21G*//HF/3-21G*, MP2/3-21G*//HF/3-21G* and B3LYP/3-21G*//HF/3-21G* methods. Compared to the results obtained for compound 1, all three methods show that the energy difference between the chair and twist-boat conformation of compound 2 is reduced. In compound 2, the twist-boat conformation is less stable than the chair conformation by about 5.42, 5.40 and 5.08 kcal mol⁻¹, respectively, as calculated by mentioned above methods (see Table 1). In compound 3, the calculated energy difference between chair and twist-boat conformations by HF/3-21G*//HF/3-21G*, MP2/3-21G*//HF/3-21G* and B3LYP/3-21G*//HF/3-21G* methods is 0.46, 0.61 and 0.65 kcal mol⁻¹ respectively. The reason for the relative instability of the chair conformation of compound 3 (compared to compounds 1-2) could be explained by the stronger 1,3-diaxial and gauche repulsions between the large *t*-butyl groups and the axial hydrogens of the C3 and C5 carbon atoms of the cyclohexane ring. In the twist-boat conformation of compound 3, 1,3-diaxial and gauche repulsions are decreased and consequently both chair and twist-boat conformations are expected to be significantly populated at room temperature, while in compounds 1 and 2, only the chair conformation is expected to be populated. HF, MP2 and B3LYP results show that by increasing the C-M bond lengths (M=Si, Ge and Sn), the energy differences between the chair and twist-boat conformations increase (see Table 1). B3LYP/3-21G*//HF/3-21G* results show that the chair conformation of compounds 3-6 is about 3.51, 5.05 and 6.45 kcal mol⁻¹, respectively, more stable than the twist-boat conformation. These results are in good agreement with the results obtained by HF/3-21G*//HF/3-21G*

Table 3 Calculated total energies E , zero-point energies ZPE (from HF/LANL2DZ*), and relative energies ΔE (E_h), (in hartree) for the energy–minimum and energy–maximum geometries compounds **1–6**.

System	Method	HF/LANL2DZ**/HF/LANL2DZ*			MP2/LANL2DZ**/HF/LANL2DZ*			B3LYP/LANL2DZ**/LANL2DZ*		
		E_{el}	E_0	ΔE_0^a	E_{el}	E_0	ΔE_0^a	E_{el}	E_0	ΔE_0^a
6 -(Chair), (Cs)	0.391944	-477.076148	-476.684204	0.000000	-478.243535	-477.851591	0.000000	-480.848261	-480.456317	0.000000
6 -(Twist-boat), (C2)	0.391777	-477.067379	-476.675602	0.008602 (6.495983)	-478.835301	-477.843524	0.008067 (6.460780)	-480.839805	-480.448028	0.008289 5.201430
6 -[C→TB]#, C1	0.391155	-477.057695	-476.666540	0.017664 11.084336	-478.226613	-477.835458	0.016133 10.123619	-480.830414	-480.439259	0.017058 10.704066

^aRelative to the minimum.**Table 4** HF/3-21G* calculated structural parameters for the energy–minimum and energy–maximum geometries of compounds **1–6**. Bond lengths are in angstrom (Å) unit and angles in degrees (°).

Compound	1			2			3			4			5			6				
	C	TB	[C→TB]#	C	TB	[C→TB]#	C	TB	[C→TB]#	C	TB	[C→TB]#	C	TB	[C→TB]#	C	TB	[C→TB]#		
Bond lengths (Å)		(C ₂)	(C ₁)	(C _s)	(C ₂)	(C ₁)	(C _s)	(C ₂)	(C ₁)	(C _s)	(C ₂)	(C ₁)	(C _s)	(C ₂)	(C ₁)	(C _s)	(C ₂)	(C ₁)	(C ₁)	
r_{1-2}	1.541	1.553	1.536	1.537	1.566	1.570	1.589	1.571	1.603	1.578	1.585	1.560	1.562	1.575	1.589	1.562	1.575	1.589	1.589	1.589
r_{2-3}	1.541	1.539	1.562	1.555	1.542	1.546	1.564	1.540	1.566	1.544	1.541	1.567	1.543	1.540	1.573	1.543	1.540	1.573	1.573	1.573
r_{3-4}	1.541	1.553	1.569	1.540	1.536	1.548	1.532	1.539	1.535	1.537	1.548	1.565	1.539	1.551	1.555	1.539	1.551	1.555	1.555	1.555
r_{4-5}	1.541	1.553	1.562	1.563	1.536	1.548	1.529	1.539	1.531	1.537	1.548	1.554	1.539	1.551	1.533	1.539	1.551	1.533	1.533	1.533
r_{5-6}	1.541	1.539	1.536	1.541	1.538	1.545	1.546	1.539	1.535	1.540	1.541	1.534	1.542	1.540	1.536	1.542	1.540	1.536	1.536	1.536
r_{6-1}	1.541	1.553	1.534	1.546	1.555	1.537	1.569	1.571	1.590	1.575	1.585	1.552	1.562	1.575	1.563	1.562	1.575	1.563	1.563	1.563
r_{1-7}	1.087	1.085	1.086	1.542	1.541	1.617	1.615	1.997	1.912	1.923	1.918	1.991	2.204	2.201	2.204	2.204	2.201	2.204	2.204	2.204
r_{1-8}	1.085	1.085	1.085	1.541	1.628	1.617	1.617	1.997	1.911	1.926	1.918	1.995	2.207	2.200	2.200	2.207	2.200	2.200	2.200	2.200
Bond angles (°)																				
θ_{1-2-3}	110.8	110.3	114.2	113.3	111.3	114.9	117.1	116.0	119.4	114.8	112.4	116.4	113.1	110.9	118.7	113.1	110.9	118.7	118.7	118.7
θ_{2-3-4}	110.8	110.3	118.0	110.6	110.1	117.0	109.2	112.5	115.7	111.8	111.4	119.3	111.1	110.3	118.2	111.1	110.3	118.2	118.2	118.2
θ_{3-4-5}	110.8	111.7	118.0	110.6	111.4	118.1	110.1	112.3	109.3	110.5	111.8	117.3	110.9	111.7	113.4	110.9	111.7	113.4	113.4	113.4
θ_{4-5-6}	110.8	110.3	114.2	110.6	110.1	115.8	112.6	109.2	108.8	109.8	111.4	113.3	110.3	110.3	108.0	110.3	110.3	108.0	108.0	108.0
θ_{5-6-1}	110.8	110.3	109.0	113.3	111.3	113.6	118.2	116.1	114.6	113.6	112.4	114.5	112.6	110.9	111.5	112.6	110.9	111.5	111.5	111.5
θ_{6-1-2}	110.8	111.7	109.0	109.3	109.8	106.7	108.2	107.4	114.5	108.2	108.7	108.6	108.7	109.6	113.1	108.7	109.6	113.1	113.1	113.1
θ_{6-1-7}	110.2	109.4	111.0	108.9	109.2	109.0	106.2	107.1	106.6	106.5	107.2	107.5	107.2	108.2	107.2	107.2	108.2	107.2	107.2	107.2
θ_{2-1-7}	109.1	109.4	110.7	110.8	109.2	111.6	110.5	107.1	106.3	112.9	107.2	110.9	113.6	108.2	109.3	113.6	108.2	109.3	109.3	109.3
θ_{2-1-8}	110.1	109.5	109.3	108.6	109.9	108.8	106.4	110.3	107.2	105.9	110.6	107.0	106.9	110.5	108.8	106.9	110.5	108.8	108.8	108.8
θ_{7-1-8}	107.5	107.3	107.6	108.1	108.7	108.6	114.5	114.4	115.3	112.1	112.1	110.5	109.5	109.8	110.4	109.5	109.8	110.4	110.4	110.4
Torsion angles (°)																				
$\phi_{1-2-3-4}$	-56.7	46.1	7.9	-56.0	66.8	19.5	-57.8	60.6	4.1	-52.0	64.884	-1.3	-55.0	66.8	-12.1	-55.0	66.8	-12.1	-12.1	-12.1
$\phi_{2-3-4-5}$	56.7	-31.8	13.4	56.7	-31.5	14.0	60.0	-28.3	-44.1	56.1	-30.8	13.7	56.1	-31.9	-16.2	-30.8	13.7	56.1	-16.2	-16.2
$\phi_{3-4-5-6}$	-56.7	-31.7	8.0	-56.7	-31.5	-7.5	-55.1	-27.5	71.2	-59.6	-30.8	14.3	-57.4	-31.9	56.5	-57.4	-31.9	56.5	56.5	56.5
$\phi_{4-5-6-1}$	56.7	66.1	-49.7	56.0	66.8	-32.4	46.1	60.4	-56.6	59.4	64.9	-55.4	57.8	66.8	-70.9	57.8	66.8	-70.9	-70.9	-70.9
$\phi_{5-6-1-2}$	-56.7	-31.8	71.9	-53.1	-32.0	64.5	-38.8	-29.1	15.9	-52.2	-30.9	66.8	-54.6	-31.9	41.4	-54.6	-31.9	41.4	41.4	41.4
$\phi_{6-1-2-3}$	56.7	-31.7	-49.7	53.1	-32.0	-57.4	45.2	-29.2	10.3	48.3	-30.9	-37.0	53.159	-31.9	-0.6	-37.0	-31.9	-0.6	-0.6	-0.6
$\phi_{8-1-2-3}$	178.7	89.6	-171.0	171.9	88.1	-175.0	159.0	87.3	-107.0	162.2	86.5	-152.0	168.6	87.3	-119.0	168.6	87.3	-119.0	-119.0	-119.0
$\phi_{8-1-6-5}$	-178.0	-153.0	-167.0	-171	-152.0	-178.0	-152	-147.0	134.2	-165.0	-150.0	-177.0	-169.0	-152.0	161.3	-169.0	-152.0	161.3	161.3	161.3

Table 6 Calculated HF/3-21G*, MP2/6-311+G** and experimental structural data for the chair conformation of compound **1** and calculated HF/3-21G*, MP2/6-311+G** and MP2/6-311G** data for the chair conformation of compound **2**. Bond lengths are in angstrom (Å) unit and angles in degrees (°).

	1-C, D_{3d}			2-C, C_s		
	HF/3-21G*	MP2/6-311+G** ^a	Exp. ^b	HF/3-21G*	MP2/6-311+G** ^a	MP2/6-311G** ^c
Bond lengths (Å)						
r_{1-2}	1.541	1.532	1.528	1.546	1.539	1.538
r_{2-3}	1.541	1.532	1.528	1.541	1.532	1.531
r_{3-4}	1.541	1.532	1.528	1.540	1.531	1.530
r_{4-5}	1.541	1.532	1.528	1.540	1.531	1.530
r_{5-6}	1.541	1.532	1.528	1.541	1.532	1.531
r_{6-1}	1.541	1.532	1.528	1.546	1.539	1.538
r_{1-7}	1.087	1.099	1.119	1.542	1.534	1.533
r_{1-8}	1.085	1.096	1.119	1.542	1.531	1.530
Bond angles (°)						
θ_{1-2-3}	110.8	111.1	111.1	113.3	113.5	113.6
θ_{2-3-4}	110.8	111.1	111.1	110.6	110.8	109.5
θ_{3-4-5}	110.8	111.1	111.1	110.6	110.9	111.2
θ_{4-5-6}	110.8	111.1	111.1	110.6	110.8	109.5
θ_{5-6-1}	110.8	111.1	111.1	113.3	113.5	113.6
θ_{6-1-2}	110.8	111.1	111.1	109.3	109.1	109.0
θ_{-1-7}	109.1	109.1	-	110.8	110.6	110.6
θ_{6-1-8}	110.2	110.3	-	108.9	109.1	109.1
θ_{7-1-8}	107.5	107.0	-	110.8	108.3	108.4
Torsion angles (°)						
$\phi_{1-2-3-4}$	-56.7	-55.9	-55.9	-56.0	-55.6	-
$\phi_{2-3-4-5}$	56.7	55.9	55.9	56.7	55.8	55.2
$\phi_{3-4-5-6}$	-56.7	-55.9	-55.9	-56.7	-55.8	-55.2
$\phi_{4-5-6-1}$	56.7	55.9	55.9	56.0	55.6	-
$\phi_{5-6-1-2}$	-56.7	-55.9	-55.9	-53.1	-53.1	-53.1
$\phi_{6-1-2-3}$	56.7	55.9	55.9	53.1	53.1	53.1
$\phi_{8-1-2-3}$	178.7	178.5	-	171.9	172.2	-
$\phi_{8-1-6-5}$	-178.0	-178.5	-	-171.9	-172.2	-
$\phi_{7-1-2-3}$	-63.5	-64.4	-	-69.4	-68.8	-
$\phi_{7-1-6-5}$	63.5	64.4	-	69.4	68.8	-

^aThis work.^bSee ref. 1.^cSee ref. 15.

and MP2/3-21G**/HF/3-21G* methods. Consequently, contrary to the compound **3**, but similar to cyclohexane (**1**) and 1,1-dimethylcyclohexane (**2**), only the chair conformations of compounds **4-6** are expected to be significantly populated at room temperature.

Compared to the all-electron methods used in this work, the results obtained by pseudopotential B3LYP/LANL2DZ**/HF/LANL2DZ*, MP2/LANL2DZ**/HF/LANL2DZ* and HF/LANL2DZ**/HF/LANL2DZ* methods showed only a small underestimation for the gap and barrier energies between chair and twist-boat conformations (see Tables 1 and 3).

Representative structural parameters for various conformations of compounds **1-6**, as calculated by the HF/3-21G* level of theory, are given in Table 4. In comparison to compounds **1**, **2**, **4**, **5** and **6**, the chair conformation of compound **3**, is disfavoured by 1,3-diaxial and gauche repulsions, in which the destabilisation is associated with the interaction between the hydrogen atoms on C3 and C5 carbon atoms of the cyclohexane ring and the large *t*-butyl groups. It has to be noted that for compound **6**, apart from a lower C-Sn bond length, the structural parameters obtained by the HF/LANL2DZ* level of theory do not show any significant differences compared to those obtained by HF/3-21G* methods (see Table 5).

Comparison of the calculated structural parameters by the HF/3-21G* level of theory for compounds **1** and **2** with the only available reported data (experimental data for compound **1**¹ and theoretical data for compound **2**¹⁵) show only fairly small differences (see Table 6). Also, for compounds **1**, **2**, the results show that there are no major differences between the calculated geometric parameters using the MP2/6-311+G** or HF/3-21G* levels of theory (see Table 6). Theoretical calculations provide structural parameters for 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 structure can be obtained with an accuracy that is competitive with experiments.²⁴⁻²⁷

Studies on the HF/3-21G* method show that the cyclohexane rings in compounds **3-5** are not of plane symmetrical form, but are in twisted conformations. For example, the dihedral angles between planes C6-C1-C2 and C1-C2-C3 for compounds **3-5** are 45.2°, 54.3° and 48.3°, respectively (see Table 4).

The energy surface for interconversion of the minimum energy conformation of compounds **1-6** was investigated in detail by the change in ϕ_{1234} and ϕ_{1654} torsion angles, as illustrated in Fig. 1. The ring inversion of the chair conformation takes place *via* the twist-boat (C_2 symmetry) conformation (see Fig. 1). The boat form is not shown in the diagram because the chair forms can interconvert without passing through the boat conformation. In compound **3**, the ring flipping process is fast and, therefore, the time-averaged symmetry of **3** becomes C_{2v} , which is the maximum symmetry allowed by the chemical structure of this molecule.

The calculated energy barriers for ring flipping of compounds **1-6** are given in Tables 1 and 2. The results show that the energy barrier for compound **3** is significantly decreased in comparison to that of the cyclohexane (**1**). As previously reported,⁹ the rate of ring flipping of cyclohexane (**1**) and its mono-substituted derivatives is independent of the type and size of the substitution groups. However, in the present study, the HF/3-21G**/HF/3-21G*, HF/LANL2DZ**/HF/LANL2DZ*, MP2/3-21G**/HF/3-21G*, MP2/LANL2DZ**/HF/LANL2DZ*, B3LYP/3-21G**/HF/3-21G* and B3LYP/LANL2DZ**/HF/LANL2DZ* results revealed that the rate of ring flipping increases by increasing the steric hindrance of the geminal substituted groups (Fig.1), contrary to the well known mono-substituted derivatives of cyclohexane reported in the literature.⁹

Conclusion

The reported *ab initio* and density functional theory calculations provided a picture from both structural and energetic point of view for compounds 1–6. The calculated results by HF/3-21G*/HF/3-21G*, MP2/3-21G*/HF/3-21G* and B3LYP/3-21G*/HF/3-21G* levels of theory show that for compounds 1, 2, 4, 5 and 6, only the chair conformation is expected to be significantly populated at room temperature, whereas in compound 3, both the chair and twist-boat conformations are expected to be populated at this temperature. The conformational properties of compound 6 (containing Sn as a heavy atom) were also investigated using all-electron with pseudopotential basis sets B3LYP/LANL2DZ*/HF/LANL2DZ*, MP2/LANL2DZ*/HF/LANL2DZ* and HF/LANL2DZ*/HF/LANL2DZ* methods. The results obtained showed only a small underestimation for the gap and barrier energies between the chair the and twist-boat conformations, compared to the above all-electron basis-set (3-21G*). In compounds 1, 2, 4, 5 and 6, the twist-boat conformations are the relatively high-energy intermediates on the ring inversion energy profiles. Also, studies at the HF/3-21G*/HF/3-21G*, MP2/3-21G*/HF/3-21G* and B3LYP/3-21G*/HF/3-21G* levels of theory indicate that the ring flipping energy barrier of compound 3, in comparison to cyclohexane (1), is relatively reduced. Further, for compounds 1 and 2, the results show also that there is no major differences between the calculated geometric parameters using the MP2/6-311+G** or HF/3-21G* levels of theory. It would be valuable, of course, to have direct structural and dynamic experimental data on compounds 2–6 for comparison with the results of *ab initio* calculations.

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