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Neighboring group's effect in sigmatropic migration on indol rings. A theoretical study and NBO analysis

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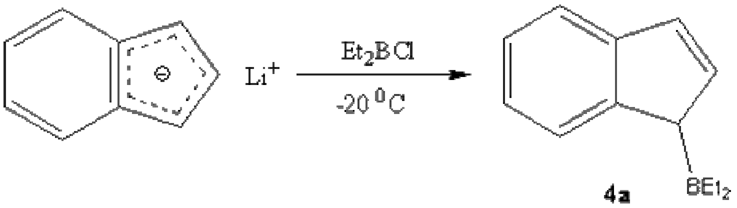
Structural properties, energies behavior and NBO analysis was performed for1-5 prototrophic shift endinel boran where substitutions like H, CH_3 and CF_3 that were placed on Benzene were investigated by using DFT-B3LYP/6-311+G** level of theory. The Results show that, -BH_2 shift doesn't take place and a kind of [1,3] shift for borotrophic occured. In prototrophic shift, however, [1,5] transition easily happened. The Results of calculations using B_3LYP, HF and MP2 [basic seyies 6-311+G**] show that Ea for CF_3 substitutionis is lower than H substitution; also, this amount of activation energy for CH_3 was lower than CF_3. But for prototrophic shift, activation energy changes, as will be shown in the following CF_3, H and CH_3 tables. Finally, prototrophic shift activation energy in proportion to that of borotrophic shift is higher. Lower amount of activation energy in bortorphic shift show that rotation of bore on the cycle can happen in the ambient temperature.

Keywords: DFT calculation; Borotropic shift; Prototropic shift; Indol

1. INTRODUCTION

Fluxional 1- Indenyl (dihydro) borane compounds were discovered by Gridnev and Meller.[1] The authors discussed in an undetailed but essentially correct manner why fast intramolecular sigmatropic migrations of the boron moiety around the 1-Indenyl ring occur. The order of relative thermodynamic stability of triorganoboranes nicely corresponds to the known order for the corresponding hydrocarbons [2].

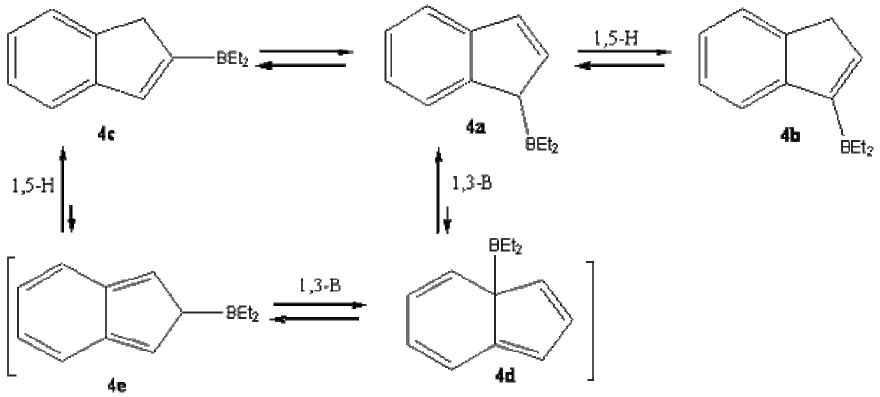
Fluxional 1-indenyl (diethyl) borane 19a was prepared from indenyllithium and diethylboron chloride in hexane (Scheme 1).



Scheme 1. Synthesis of 1-indenyl (diethyl) borane from indenyllithium and diethylboron chloride

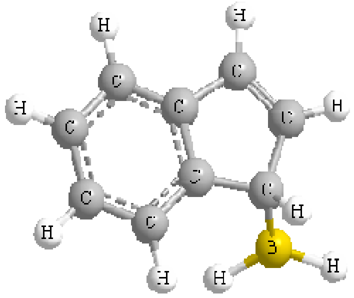
NMR spectra of borane **19a** taken in the temperature interval 25–80 °C, three cross-peaks corresponding to the migrations of the diethylboryl group from position 1 to position 3 have been found.

A sigmatropic migration of hydrogen takes place at elevated temperatures in **19a**. This leads to the establishment of a dynamic equilibrium between the three isomers **19a**, **19b**, and **19c** (Scheme 2). A small amount (about 6 %) of 2-indenyl (diethyl) borane **19c** apparently appears by a [1,5]-H shift in the *iso*-indenyl intermediate **19e**, which is formed from **19a** via two consequent [1,3]-B shifts.

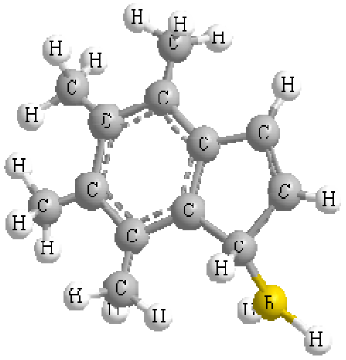


Scheme 2. Sigmatropic migration of hydrogen and boran groups on indol rings

Sigmatropic migration of many fragments on aromatic rings has been observed. These compounds are fluxional. Experimental [11] and theoretical [12] studies for barrier energies and rate of (σ)metallotropic and (σ)prototropic shift on Fluxional compounds were carried out. Those researches showed that (σ)prototropic shift has higher activation energy than (σ)metallotropic shift and therefore metal groups migration is very fast on room temperature[3-10]. In the chemical literature neighboring effect does not exist the in these migrations, therefore in this work, the results of a theoretical investigation of the structural and energetic properties of (1H-inden-1-yl)borane (**1**), (4,5,6,7-tetramethyl-1H-inden-1-yl)borane (**2**) and (4,5,6,7-tetratrifluorocarbone-1H-inden-1-yl)borane (**3**) will be reported. Effect of Methyl as electron donor and threeflouromethyl as electron acceptor groups in compounds **2** and **3** were investigated by ab initio molecular orbital (MO) and density functional methods (DFT), using the GAUSSIAN 2003 package programs and NBO 3.1[13-17].



(1)



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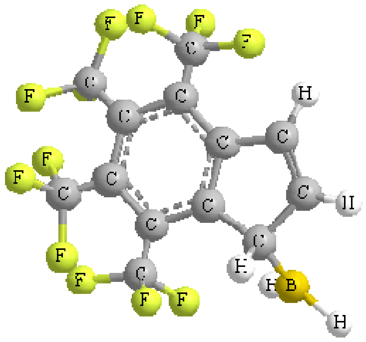


(3)

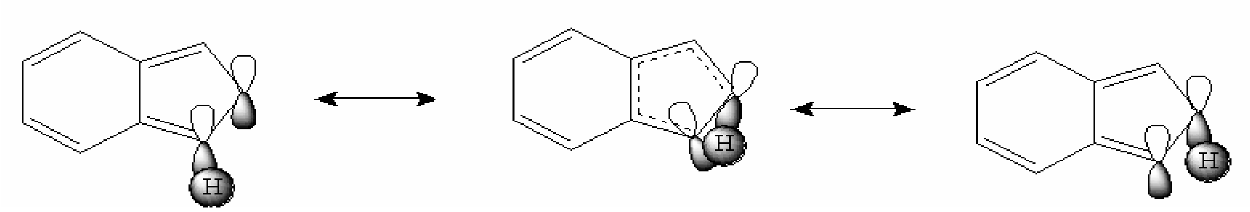
2. CALCULATION DETAIL

All structures were optimized at the B3LYP/6-311+G** level of density functional theory with the Gaussian 2003 program.[18] Vibrational frequency computations characterized all structures to be minimal, at B3LYP/6-311G** for the (1, 3) set. These computations were carried out at

B3LYP/3-21g levels of theory for the related (2) set due to their large sizes. The basis set and method dependencies were probed by computed at optimized B3LYP/6-311+G** , HF/6-311+G** and MP2/6-311+G** [3]. Single point energy for Threefluoro substitution on Benzene ring in MP2/6-311+G** for borotrpoic [1-3] shift did not seem to be applicable. Energy-minimum molecular geometries were located by minimizing energy with respect to all geometrical coordinates without imposing any symmetrical structure constraints and transition state structures obtained by QST2 subroutine. Natural Bond Orbital (NBO) analysis was then performed at the B3LYP/6-311+G** level by the NBO 3.1 program included in the GAUSSIAN 03 package of programs.

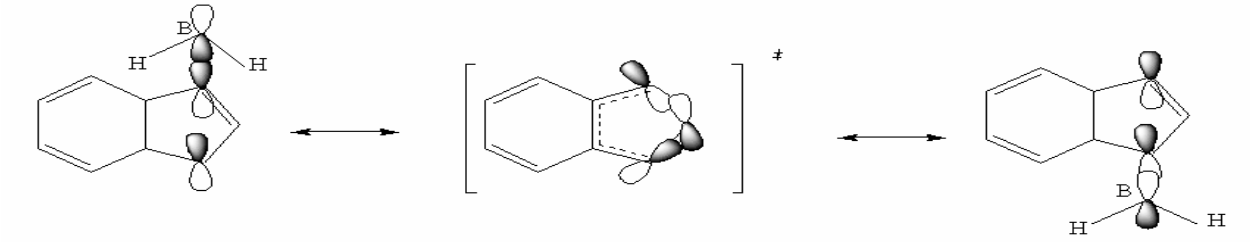
3. RESULTS AND DISCUSSION

Structural properties, energies behavior and NBO analysis was performed for 1,2-shift mechanisms for the BH_2 and hydrogen migrations were investigated by using B3LYP/6-311+G** , HF/6-311+G** and MP2/6-311+G** levels of theory for compounds **1**, **2** and **3**. In these three compounds [1,5] hydrogen shifts occur by a symmetry-allowed suprafacial rearrangement, as illustrated in scheme 3. In contrast with these thermal [1,5] sigmatropic hydrogen shift, however, thermal [1,3] hydrogen shifts are unknown**.**



Scheme 3. Symmetry-allowed suprafacial rearrangement of proton

BH_2 shifts cannot occur through [1,5] superafacial rearrangement. This migration is a [1,3] antrafacial rearrangement, as illustrate in scheme 4



Scheme 4. Symmetry-allowed antrafacial rearrangement of boran group

Reaction pathways are shown in Figures 1-3. The B3LYP/6-311G** calculated energies are given in Tables 1-13. The three compounds calculated results in these compounds showed that 1,2-borotropic shift is impossible. When BH_2 is in vinylic position these compounds are not in ground state. Vibrational frequencies illustrate one imaginary frequency and the other hand bond lengths of C-B that increased to 1.69 Angstrom at the compound 1, 1.98 for compound 2 and 2.00 for compound 3 showed that this structure is a transition state structure (Fig.1-3). Also IRC calculation confirmed that BH_2 in vinylic position, is a transition structure (Fig. 4).

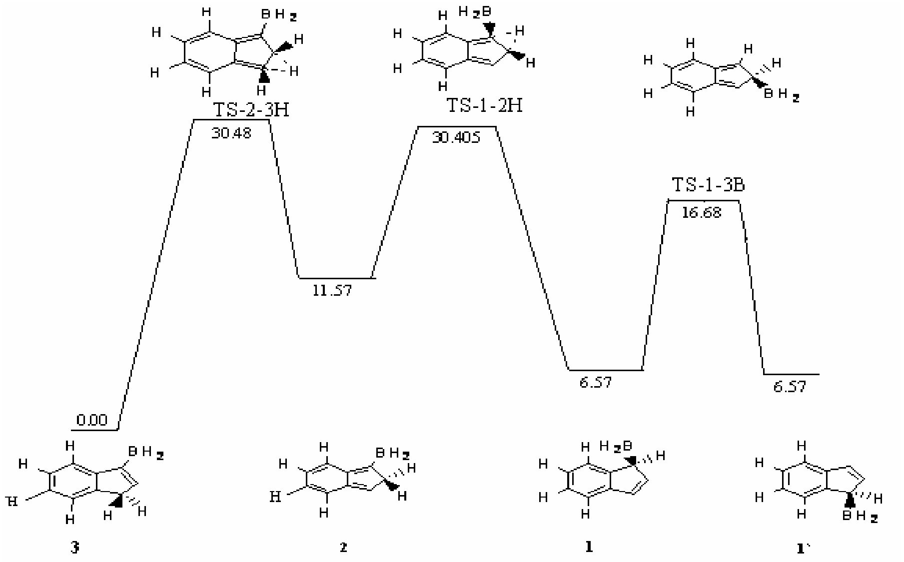


Fig. 1. B3LYP, HF and MP2 energy diagram for various sigmatropic shifts in compound 1.

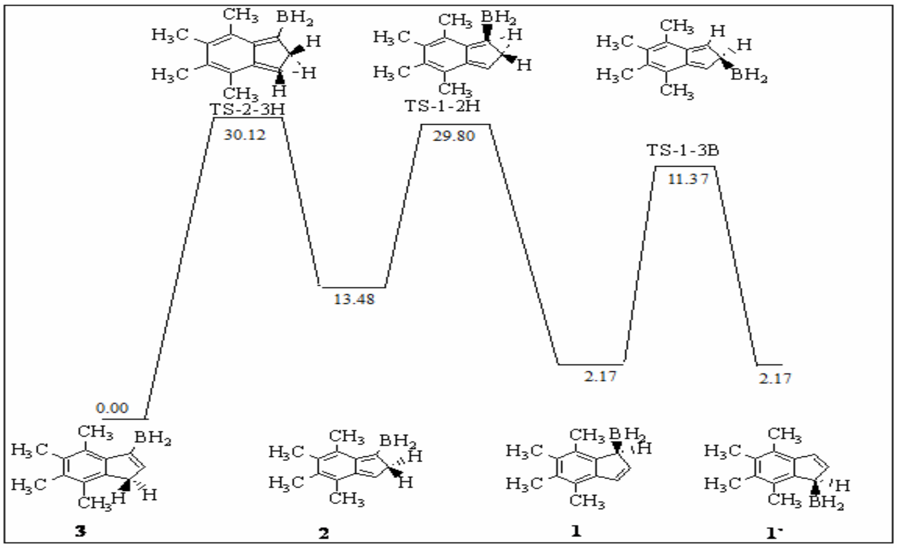


Fig. 2. B3LYP, HF and MP2 energy diagram for various sigmatropic shifts in compound 2**.**

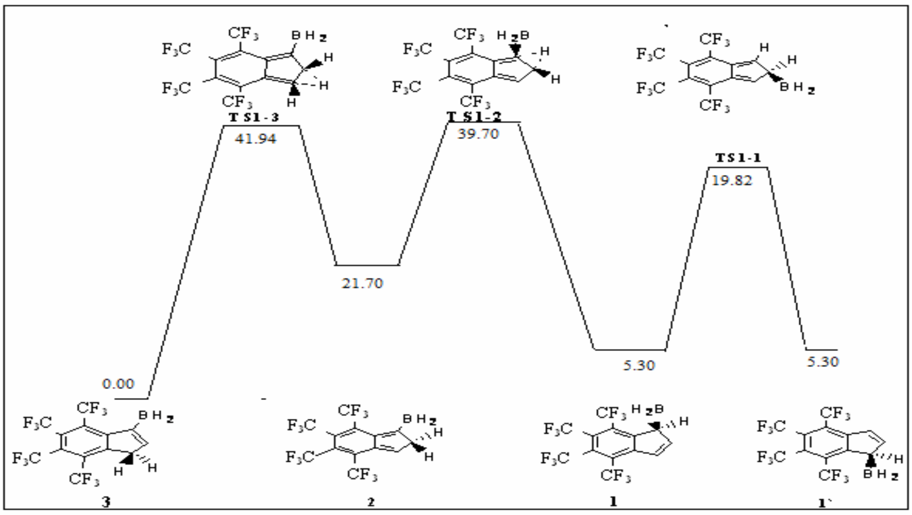


Fig. 3. B3LYP, HF and MP2 energy diagram for various sigmatropic shifts in compound 3.

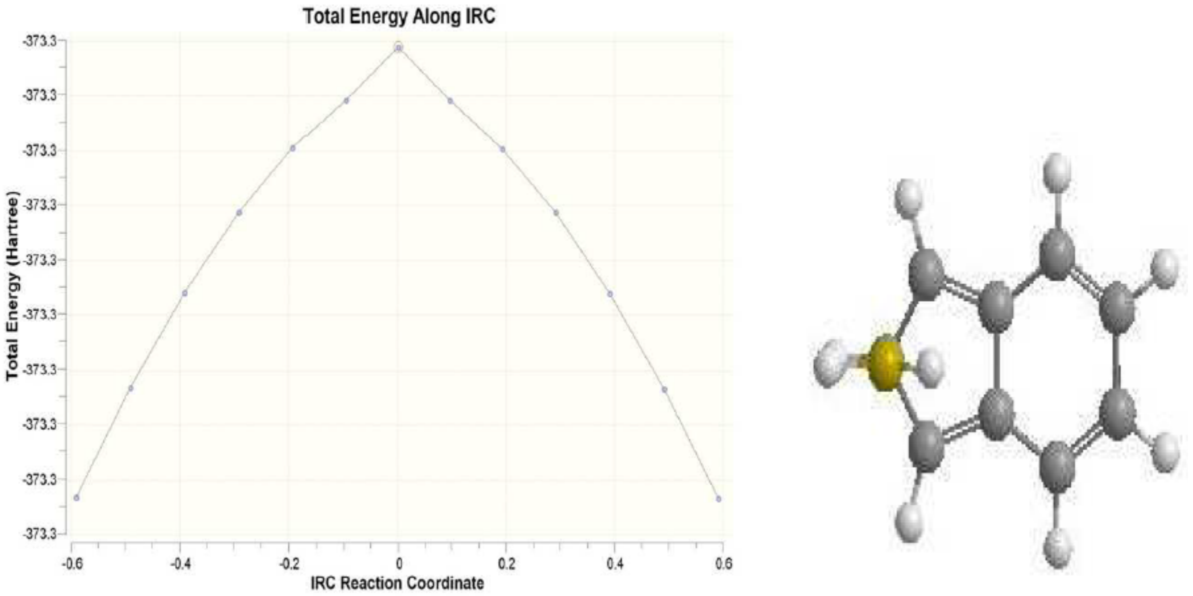


Fig. 4. IRC Plot of [1,3] shift for borotrophic compound 1.

These results revealed that barrier energy for migration of H is higher than BH_2. Calculation results showed that CF_3 (electronegative) and Me(electropositive) groups in compounds **2** and **3** increased the barrier heights during borotropic and prototropic shift.

Methyl group is electropositive and conducts electrons to indol rings and then electron density of B-C and H-C bonds as well as barrier height increased. Threefluoro is electronegative and does not conduct electrons to indol rings as a result electron density of B-C and H-C bonds decreased and finally barrier height decrease. These results have a good agreement with structural and NBO results.

In these compounds 1,2-borotropic shift is impossible. When BH_2 is in vinylic position these compounds are not in ground state. Infra Red (IR) vibrational frequencies (one imaginary frequency) and Aromatic Stabilization Energy (ASE = 3.62 Kcal.mol-1) results showed that this structure is a transition state one (fig.1). Therefore borotropic shift is a 1,3-sigmatropic shift.

Table 1. DFT/6-311+G**Calculated Structural Parameters and Energies of the Ground States and Transition States of 1H-inden-1-yl)borane.. Bond Lengths are in Angstrom Units (Å) and Angles in Degrees (º).

Compounds	1	2	3	1→2	2→3	1→1′′
Bond lengths						
B- C1	1.56273	1.51033	1.53260	1.51066	1.50681	----
B-C2	---	---	---	---	---	1.69025
C_1- C_2	1.51135	1.51257	1.36365	1.52426	1.43488	1.42411
C_2- C_3	1.34642	1.48755	1.50246	1.39680	1.46514	1.42408
C_3- C_9	1.46326	1.36747	1.51020	1.41786	1.42143	1.45149
C_1- C_8	1.51212	1.39362	1.48322	1.44162	1.43745	1.45151
C_3- H_2	1.08277	1.08283	1.09811	1.08114	1.08147	1.08004
C_1- H_1	1.11591	---	---	1.36322	---	1.08003
C_2- H_1	---	1.10046	---	1.25449	1.26195	---
C_3- H_1	---	---	1.09811	---	1.39146	---
Occupancy						
B- C_1	δ=1.94532	δ=1.97749	δ=1.97686	δ=1.97792	δ=1.97432	---
B-C2	---	---	---	---	---	---
C_1- C_2	δ=1.97204	δ=1.97433	δ=1.98051 π=1.79633	δ=1.90469	δ=1.97620	δ=1.95676

C_2- C_3	δ=1.98112 π=1.90399	δ=1.98029	δ=1.98053	δ=1.98158	δ=1.94330	δ=1.96830 π=1.52963
C_3- C_9	δ=1.97299	δ=1.97933 π=1.74179	δ=1.97656	δ=1.97492 π=1.58434	δ=1.97743 π=1.56231	δ=1.97352
C_1- C_8	δ=1.97093	δ=1.97523 π=1.69034	δ=1.96873	δ=1.97261 π=1.54679	δ=1.97013 π=1.58574	δ=1.97372
C_3- H_2	δ=1.98282	δ=1.98490	δ=1.95046	δ=1.98244	δ=1.98579	δ=1.98182
C_1- H_1	δ=1.88938	---	---	---	---	δ=1.98362
C_2- H_1	---	δ=1.93470	---	δ=1.54270	δ=1.53881	---
C_3- H_1	---	---	δ=1.95046	---	---	---
Bond angles(°)						
B-C_1-C_2	118.02271	125.90587	123.34432	124.92483	124.70329	56.90268
B-C_1-C_8	119.93351	128.04433	129.36956	131.34540	129.72983	---
B- C_2-C_3	---	---	---	---	---	78.20513
C_1-C_2-C_3	110.62816	105.72514	112.22000	108.75079	109.36508	107.58036
C_2-C_3-C_9	109.72225	109.17748	102.59078	108.94560	106.98556	107.32653
C_3-C_9-C_8	108.33501	108.52808	108.73209	108.80419	107.75667	107.50909
C_9-C_8-C_1	108.51049	110.51950	109.17101	109.74990	110.30320	107.50903
C_8-C_1-C_2	102.77879	106.04980	107.28612	103.70446	105.56395	107.32504
Torsion angles(°)						
B-C_1-C_2-C_3	132.84495	-179.99577	-179.99263	176.18452	178.54898	73.42660
B- C_2-C_3-C_9	---	---	---	---	---	89.77101
C_1-C_2-C_3-C_9	1.21045	-0.00397	0.00000	1.73259	1.55087	16.34794
C_2-C_3-C_9-C_8	-0.25985	0.00000	0.00000	-0.60049	-1.58258	-10.04310
C_8-C_1-C_2-C_3	-1.60868	0.00385	0.00000	-2.16235	-0.87733	-16.34587
ZPE[a]	0.1407435	0.13641949	0.1418039	0.1381100	0.138373	0.142049
Eel	-373.286206	-373.273922	-373.297751	-373.245477	-373.245865	-373.27141
Ea= Eel + ZPE	-373.145462	-373.137502	-373.155947	-373.107366	-373.1074915	-373.129360
ΔE[b]a(Hartree)	0.010485	0.018445	0.00	0.048581	0.048455	0.026587
ΔEa(kcal mol-1)	6.57	11.57	0.00	30.48	30.405	16.68
Eca(kcal mol-1)				23.91	18.83	10.11
ΔH				5.00	11.57	0.00

Table 2. HF/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and Transition States of 1H-inden-1-yl)borane.

Compounds	1	2	3	1→2	2→3	1→1′′
ZPE[a]	0.1407435	0.13641949	0.1418039	0.1381100	0.138373	0.142049
*E*el	-370.7891546	-370.7666385	-370.8010636	-370.7269038	-370.731217	-370.7508864
E_a= *E*el + *ZPE*	-370.648411	-370.6302190	-370.6592597	-370.5887938	-370.592844	-370.6088374
ΔE^b_a(Hartree)	0.0108487	0.0290407	0.00	0.0704659	0.0664157	0.0504223
ΔE_a(kcal mol^{-1})	6.80	18.22	0.00	44.21	41.67	31.63
E^c_a(kcal mol^{-1})				37.41	23.45	24.83
Δ*H*				11.42	-18.22	0.00

Table 3. MP2/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and Transition States of 1H-inden-1-yl) borane .

Compounds	1	2	3	1→2	2→3	1→1′′
ZPE	0.1407435	0.13641949	0.1418039	0.1381100	0.138373	0.142049
*E*el	-372.1147183	-372.0951642	-372.1245096	-372.0754224	-372.0732901	-372.104577
E_a= *E*el + *ZPE*	-371.9739748	-371.9587447	-371.9827057	-371.9373124	-371.9349171	-371.962528
ΔE^b_a(Hartree)	0.0087309	0.023961	0.00	0.045393	0.047788	0.0201777
ΔE_a(kcal mol^{-1})	5.47	15.03	0.00	28.48	29.98	12.66
E^c_a(kcal mol^{-1})				17.43	14.95	7.19
Δ*H*				9.56	-15.03	0.00

Table 4. DFT/6-311+G** Calculated Aromatic Stabilization Energy of 1H-inden-1-yl)borane.

Compounds	1		2		3	
	Electron Transfer	Energy	Electron Transfer	Energy	Electron Transfer	Energy
	π c8-c7→π*c9-c4	19.03	π c8-c1→π*c8-c1	1.16	π c8-c9→π*c4-c5	21.55
	π c8-c7→π*c5-c6	20.52	π c8-c1→π*c9-c3	15.41	π c8-c9→π*c6-c7	20.18
	π c9-c4→π*c8-c7	19.59	π c8-c1→π*c6-c7	14.66	π c8-c9→π*c1-c2	12.40
	π c9-c4→π*c5-c6	21.33	π c9-c3→π*c8-c1	19.44	π c4-c5→π*c8-c9	20.89
	π c9-c4→π*c2-c3	11.67	π c9-c3→π*c9-c3	0.85	π c4-c5→π*c6-c7	20.17
	π c5-c6→π*c8-c7	18.95	π c9-c3→π*c4-c5	16.87	π c6-c7→π*c8-c9	20.60
	π c5-c6→π*c9-c4	18.72	π c4-c5→π*c9-c3	17.27	π c6-c7→π*c4-c5	20.25
	π c2-c3→π*c9-c4	15.17	π c4-c5→π*c6-c7	14.99	π c1-c2→π*c8-c9	14.23
			π c6-c7→π*c8-c1 π c6-c7→π*c4-c5	19.84 14.25	π c1-c2→π*c1-c2	1.95
Total Energy		144.98		134.74		152.22
Compounds	1→2		2→3		1→1′′	
	Electron Transfer	Energy	Electron Transfer	Energy	Electron Transfer	Energy
	π c8-c1→π*c9-c3	20.14	π c8-c1→π*c8-c1	1.38	π c_8-c_9→π*c_4-c_5	19.12
	π c8-c1→π*c6-c7	16.09	π c8-c1→π*c9-c3	20.55	π c_8-c_9→π*c_6-c_7	19.12
	π c9-c3→π*c8-c1	23.80	π c8-c1→π*c6-c7	15.28	π c_8-c_9→π*c_2-c_3	14.65
	π c9-c3→π*c4-c5	17.79	π c9-c3→π*c8-c1	24.30	π c_4-c_5→π*c_8-c_9	19.00
	π c4-c5→π*c9-c3	19.80	π c9-c3→π*c9-c3	5.21	π c_4-c_5→π*c_6-c_7	18.99
	π c4-c5→π*c6-c7	17.17	π c9-c3→π*c4-c5	18.73	π c_6-c_7→π*c_8-c_9	19.00
	π c6-c7→π*c8-c1	21.74	π c4-c5→π*c9-c3	19.62	π c_6-c_7→π*c_4-c_5	18.99
	π c6-c7→π*c4-c5	17.92	π c4-c5→π*c6-c7	17.72	π c_2-c_3→π*c_8-c_9	11.93
			π c6-c7→π*c8-c1	21.75	π c_2-c_3→π*c_2-c_3	0.56
			π c6-c7→π*c4-c5	17.21		
Total Energy		154.45		161.75		141.36

Table 5. B3LYP/3-21g Calculated Structural Parameters and Energies of the Ground States and Transition States of 4,5,6,7-tetrametyl-1H-inden-1-yl)borane.. Bond Lengths are in Angstrom Units (Å) and Angles in Degrees (º).

Compounds	1	2	3	1→2	2→3	1→1′′
Bond lengths						
B- C_1	1.57488	1.51404	1.53387	1.51172	1.50972	1.98676
B-C2	---	---	---	---	---	1.68487
C_1- C_2	1.51185	1.51520	1.36459	1.53095	1.43522	1.42301
C_2- C_3	1.36005	1.47899	1.49706	1.39004	1.45761	1.42295
C_3- C_9	1.45212	1.36676	1.51164	1.42060	1.42330	1.45257
C_1- C_8	1.49865	1.40276	1.49093	1.44899	1.44844	1.45271
C_3- H_2	1.08235	1.08187	1.09835	1.08000	1.08041	1.07916
C_1- H_1	1.09116	---	---	1.35351	---	1.07915
C_2- H_1	---	1.10080	---	1.25694	1.26648	---
C_3- H_1	---	---	1.09854	---	1.38464	---
Occupancy						
B- C_1	δ=1.89616	δ=1.97856	δ=1.97736	δ=1.97826	δ=1.97471	---
B-C2	---	---	---	---	---	---
C_1- C_2	δ=1.93481	δ=1.97459	δ=1.98109 π=1.79299	δ=1.89684	δ=1.97686	δ=1.96919 π=1.53052
C_2- C_3	δ=1.98205 π=1.82659	δ=1.98106	δ=1.98076	δ=1.98169	δ=1.94459	δ=1.95778
C_3- C_9	δ=1.97309	δ=1.97816 π=1.75434	δ=1.97610	δ=1.97399 π=1.58963	δ=1.97672 π=1.56773	δ=1.97272
C_1- C_8	δ=1.96750	δ=1.96784 π=1.68240	δ=1.96073	δ=1.96480 π=1.53927	δ=1.96312 π=1.57094	δ=1.97252

C_3- H_2	δ=1.98242	δ=1.98443	δ=1.95189	δ=1.98134	δ=1.98530	δ=1.98334
C_1- H_1	δ=1.95446	---	---	---	---	δ=1.98170
C_2- H_1	---	δ=1.93380	---	δ=1.54075	δ=1.53295	---
C_3- H_1	---	---	δ=1.95104	---	---	---
Bond angles(°)						
B-C_1-C_2	89.06508	119.44085	117.77038	119.49957	119.16705	56.34762
B-C_1-C_8	113.91680	134.45518	133.81754	136.36956	135.10459	---
B- C_2-C_3	---	---	---	---	---	79.02773
C_1-C_2-C_3	109.53576	105.84160	112.35012	108.65972	109.57147	107.50371
C_2-C_3-C_9	110.28396	109.24880	102.57490	109.21994	107.11610	107.52990
C_3-C_9-C_8	107.76968	109.00949	109.08368	108.94503	107.99095	107.50716
C_9-C_8-C_1	109.07674	109.81754	108.60217	109.43647	109.79842	---
C_8-C_1-C_2	102.99192	106.07304	107.34304	103.63931	105.49530	---
Torsion angles(°)						
B-C_1-C_2-C_3	108.54282	177.45242	167.62998	170.11284	173.73472	74.64887
B- C_2-C_3-C_9	---	---	---	---	---	90.02053
C_1-C_2-C_3-C_9	4.19029	0.31038	1.40739	2.13615	1.72695	15.40471
C_2-C_3-C_9-C_8	-0.65516	0.29391	-0.01899	-0.26758	-1.19536	-9.48124
C_8-C_1-C_2-C_3	-5.80974	-0.80904	-2.17260	-3.11973	-1.53568	-15.40477
ZPE^a	0.2451938	0.245060	0.245621	0.241938	0.242481	0.2452596
Eel	-530.589466	-530.571334	-530.593392	-530.542217	-530.54204	-530.571446
Ea= Eel + ZPE	-530.344272	-530.326274	-530.347771	-530.300279	-530.299559	-530.326186
ΔE^ba(Hartree)	0.003499	0.021497	0.00	0.04749	0.048212	0.021585
ΔEa(kcal mol-1)	2.17	13.48	0.00	29.80	30.125	13.54
E^ca(kcal mol-1)				25.31	16.64	11.37
ΔH				11.31	-13.48	0.00

Table 6. HF/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and TransitionStates of 4,5,6,7-tetramethyl-1H-inden-1-yl)borane.

Compounds	1	2	3	1→2	2→3	1→1′′
ZPE^a	0.2451938	0.245060	0.245621	0.241938	0.242481	0.2452596
Eel	-526.9570683	-526.9332015	-526.9661745	-526.8930162	-526.8966751	-526.9248458
E_a= Eel + ZPE	-526.7118892	-526.688141	-526.7205535	-526.6513636	-526.654194	-526.679586
$\Delta E^b{}_a$(Hartree)	0.0086643	0.0324125	0.00	0.0691899	0.0663595	0.0409675
ΔE_a(kcal mol^{-1})	5.43	20.33	0.00	43.41	41.64	25.70
$E^c{}_a$(kcal mol^{-1})				38.98	21.31	20.27
ΔH				14.9	-20.33	0.00

Table 7. MP2/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and TransitionStates of 4,5,6,7-tetramethyl-1H-inden-1-yl)borane.

Compounds	1	2	3	1→2	2→3	1→1′′
ZPE^a	0.2451938	0.245060	0.245621	0.241938	0.242481	0.2452596
Eel	-528.9188261	-528.8899541	-528.9184175	-528.8707101	-528.8675918	-528.9109544
E_a= Eel + ZPE	-528.673632	-528.6448941	-528.672796	-528.628772	-528.6251108	-528.665694
$\Delta E^b{}_a$(Hartree)	0.00	0.0287382	0.000836	0.0448603	0.0485215	0.0079383
ΔE_a(kcal mol^{-1})	0.00	18.03	0.524	28.14	30.44	4.98
$E^c{}_a$(kcal mol^{-1})				28.14	12.41	4.98
ΔH				18.03	-17.50	0.00

Table 8. DFT/6-311+G**Calculated Aromatic Stabilization Energy of 4,5,6,7-tetrametyl-1H-inden-1-yl)borane.

Compounds	1		2		3	
	Electron Transfer	Energy	Electron Transfer	Energy	Electron Transfer	Energy
	π c8-c9→π*c2-c3	18.28	π c8-c1→π*c8-c1	1.04	π c8-c7→π*c9-c4	21.39
	π c8-c9→π*c7-c6	19.80	π c8-c1→π*c9-c3	16.60	π c8-c7→π*c1-c2	10.87
	π c8-c9→π*c5-c4	19.70	π c8-c1→π*c6-c7	15.66	π c8-c7→π*c6-c5	20.61
	π c2-c3→π*c8-c9	12.16	π c9-c3→π*c8-c1	16.86	π c9-c4→π*c8-c7	16.09
	π c7-c6→π*c8-c9	23.07	π c9-c3→π*c9-c3	0.78	π c9-c4→π*c6-c5	19.94
	π c7-c6→π*c5-c4	17.00	π c9-c3→π*c4-c5	16.45	π c1-c2→π*c8-c7	13.03
	π c5-c4→π*c8-c9	19.24	π c4-c5→π*c9-c3	18.13	π c1-c2→π*c1-c2	1.56
	π c5-c4→π*c7-c6	21.58	π c4-c5→π*c6-c7	15.22	π c6-c5→π*c8-c7	18.96
			π c6-c7→π*c8-c1 π c6-c7→π*c4-c5	18.83 13.62	π c6-c5→π*c9-c4	20.16
Total Energy		150.83		133.19		142.61
Compounds	1→2		2→3		1→1″	
	Electron Transfer	Energy	Electron Transfer	Energy	Electron Transfer	Energy
	π c8-c1→π*c9-c3	21.08	π c8-c1→π*c8-c1	1.19	π c_8-c_9→π*c_4-c_5	18.24
	π c8-c1→π*c6-c7	16.89	π c8-c1→π*c9-c3	21.71	π c_8-c_9→π*c_6-c_7	19.39
	π c9-c3→π*c8-c1	21.00	π c8-c1→π*c6-c7	16.25	π c_8-c_9→π*c_1-c_2	15.57
	π c9-c3→π*c4-c5	17.65	π c9-c3→π*c8-c1	21.57	π c_4-c_5→π*c_8-c_9	20.01
	π c4-c5→π*c9-c3	21.35	π c9-c3→π*c9-c3	5.79	π c_4-c_5→π*c_6-c_7	20.20
	π c4-c5→π*c6-c7	17.71	π c9-c3→π*c5-c4	18.73	π c_6-c_7→π*c_8-c_9	19.64
	π c6-c7→π*c8-c1	20.50	π c6-c7→π*c8-c1	20.67	π c_6-c_7→π*c_4-c_5	16.98
	π c6-c7→π*c4-c5	18.13	π c6-c7→π*c5-c4	17.43	π c_1-c_2→π*c_8-c_9	11.78
			π c5-c4→π*c9-c3	21.17	π c_8-c_9→π*c_4-c_5	18.24
			π c5-c4→π*c6-c7	18.28		
Total Energy		154.31		162.79		141.86

Table 9. B3LYP/3-21g Calculated Structural Parameters and Energies of the Ground States and TransitionStates of 4,5,6,7-tetratrifluoro-1H-inden-1-yl)borane.. Bond Lengths are in Angstrom Units (Å) and Angles in Degrees (º).

Compounds	1	2	3	1→2	2→3	1→1″
Bond lengths						
B- C_1	1.60306	1.56120	1.57181	1.57007	1.56860	2.00767
B-C2	---	---	---	---	---	1.73327
C_1- C_2	1.51235	1.52080	1.35608	1.50245	1.42368	1.43169
C_2- C_3	1.35103	1.51180	1.51588	1.41951	1.50323	1.42919
C_3- C_9	1.46877	1.36323	1.52196	1.40855	1.41543	1.45504
C_1- C_8	1.51379	1.37242	1.47664	1.42466	1.41457	1.45553
C_3- H_2	1.07438	1.07443	1.09554	1.07260	1.07279	1.07273
C_1- H_1	1.10249	---	---	1.40474	---	1.07215
C_2- H_1	---	1.10055	---	1.28628	1.28125	---
C_3- H_1	---	---	1.09594	---	1.40933	---
Occupancy						
B- C_1	δ=1.93579	δ=1.97518	δ=1.97214	δ=1.97357	δ=1.97008	---
B-C2	---	---	--- ----	---	---	---
C_1- C_2	δ=1.96897	δ=1.97041	δ=1.97683 π =1.84103	δ=1.95257	δ=1.97325	δ=1.96275
C_2- C_3	δ=1.98284 π=1.86486	δ=1.98060	- δ=1.98251	δ=1.98141	δ=1.94671	δ=1.96845 π=1.54268
C_3- C_9	δ=1.97193	δ=1.97636 π=1.81933	δ=1.97585-	δ=1.97342 π=1.68494	δ=1.97561 π=1.62988	δ=1.97158
C_1- C_8	δ=1.96826	δ=1.96906 π=1.74606	δ=1.96437-	δ=1.96815	δ=1.96546 π=1.63487	δ=1.97210

C_3- H_2	δ=1.98417	δ=1.98546	δ=1.95305	δ=1.98335	δ=1.98530	δ=1.97969
C_1- H_1	δ=1.93091	---	---	---	---	δ=1.98358
C_2- H_1	---	δ=1.94198	---	---	δ=1.55916	---
C_3- H_1	---	---	δ=1.96027	---	---	---
Bond angles(°)						
B-C_1-C_2	116.97526	127.48463	130.55780	131.10692	129.24435	57.64810
B-C_1-C_8	111.45466	126.13660	122.45093	124.80360	124.78024	---
B- C_2-C_3	---	---	---	---	---	78.85524
C_1-C_2-C_3	111.62402	105.27132	112.65567	109.34997	109.27576	108.31748
C_2-C_3-C_9	109.18996	108.54197	102.19073	108.00098	105.88791	106.89811
C_3-C_9-C_8	107.84685	108.67013	107.72629	108.42693	107.59144	107.82904
C_9-C_8-C_1	109.33992	111.13589	110.33606	110.33111	111.23026	107.82904
C_8-C_1-C_2	101.83501	106.36355	1106.97658	108.83505	105.95143	106.89811
Torsion angles(°)						
B-C_1-C_2-C_3	123.70161	-178.84015	177.43777	171.46279	-179.48927	73.86935
B- C_2-C_3-C_9	---	---	---	---	---	88.60210
C_1-C_2-C_3-C_9	0.44809	0.97389	2.80511	2.96112	2.36338	15.25476
C_2-C_3-C_9-C_8	-2.90666	-1.33253	-3.35019	-1.90379	-2.48880	-10.01100
C_8-C_1-C_2-C_3	1.96685			-2.81896	-1.23015	-14.59584
ZPE^{a}	0.1607085	0.15969425	0.1609315	0.1569364	0.1566504	0.16045167
Eel	-1711.96742	-1711.940243	-1711.976092	-1711.908828	-1711.90497	-1711.944017
Ea= Eel + ZPE	-1711.806711	-1711.780548	-1711.8151605	-1711.751891	-1711.748319	-1711.783565
ΔEba(Hartree)	0.0084495	0.0346125	0.00	0.0632695	0.0668415	0.0315955
ΔEa(kcal mol-1)	5.30	21.71	0.00	39.70	41.94	19.82
Eca(kcal mol-1)				34.4	20.23	14.52
ΔH				16.41	-21.71	0.00

Table 10. B3LYP/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and TransitionStates of 4,5,6,7-tetratrifluoro-1H-inden-1-yl)borane.

Compounds	1	2	3	1→2	2→3	1→1′′
ZPE^{a}	0.1607085	0.15969425	0.1609315	0.1569364	0.1566504	0.16045167
*E*el	-1721.8102146	-1721.7409319	-1721.77596	-1721.7166925	-1721.7127253	-1721.7608513
E_a= *E*el + *ZPE*	-1721.649506	-1721.58123765	-1721.6150285	-1721.5597561	-1721.5560749	-1721.6003996
ΔE^{b}_{a}(Hartree)	0.00	0.06826835	0.0344775	0.0897499	0.0934311	0.0491064
ΔE_a(kcal mol^{-1})	0.00	42.83	21.63	56.31	58.62	30.81
E^{c}_{a}(kcal mol^{-1})				56.31	15.79	30.81
Δ*H*				42.83	-21.63	0.00

Table 11. HF/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and TransitionStates of 4,5,6,7-tetratrifluoro-1H-inden-1-yl)borane.

Compounds	1	2	3	1→2	2→3	1→1′′
ZPE^{a}	0.1607085	0.15969425	0.1609315	0.1569364	0.1566504	0.16045167
*E*el	-1713.5389508	-1713.4711949	-1713.513974	-1713.4354715	-1713.430785	-1713.4883668
E_a= *E*el + *ZPE*	-1713.3782423	-1713.3102634	-1713.3530425	-1713.2785351	-1713.2741346	-1713.32791513
ΔE^{b}_{a}(Hartree)	0.00	0.0679789	0.0251998	0.0997072	0.1041077	0.05032717
ΔE_a(kcal mol^{-1})	0.00	42.65	15.81	62.56	65.32	31.58
E^{c}_{a}(kcal mol^{-1})				62.56	22.67	31.58
Δ*H*				42.65	-26.84	0.00

Table 12. MP2/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and TransitionStates of 4,5,6,7-tetratrifluoro-1H-inden-1-yl)borane.

Compounds	1	2	3	1→2	2→3	1→1´´
ZPE[a]	0.1607085	0.15969425	0.1609315	0.1569364	0.1566504	0.16045167
*E*el	-1717.8214802	-1717.7841212	-1717.8244783	-1717.768184	-1717.7647575	-1717.8233779
E_a= *E*el + *ZPE*	-1717.6607717	-1717.6244269	-1717.6635468	-1717.6112476	-1717.6081071	-1717.66292623
ΔE^b_a(Hartree)	0.0027751	0.0391199	0.00	0.0522992	0.0554397	0.0006
ΔE_a(kcal mol^{-1})	1.74	24.54	0.00	32.81	34.78	0.38
E^c_a(kcal mol^{-1})				31.07	10.24	
Δ*H*				22.8	-24.54	0.00

Table 13. DFT/3-21g Calculatd Aromatic Stabilization Energy of 4,5,6,7-tetratrifluoro-1H-inden-1-yl)borane.

Compounds	1		2		3	
	Electron Transfer	Energy	Electron Transfer	Energy	Electron Transfer	Energy
	π c_2-c_3→π*c_9-c_4	19.63	π c_1-c_8→π*c_3-c_9	16.69	π c8-c7→π*c9-c4	16.50
	π c_9-c_4→π*c_2-c_3	8.53	π c_1-c_8→π*c_7-c_6	25.12	π c8-c7→π*c1-c2	7.85
	π c_9-c_{10}→π*c_8-c_7	18.50	π c_3-c_9→π*c_1-c_8	14.27	π c8-c7→π*c6-c5	23.83
	π c_9-c_{10}→π*c_6-c_5	23.07	π c_3-c_9→π*c_5-c_4	19.73	π c9-c4→π*c8-c7	18.51
	π c_8-c_7→π*c_9-c_4	16.74	π c_7-c_6→π*c_1-c_8	13.50	π c9-c4→π*c6-c5	21.00
	π c_8-c_7→π*c_6-c_5	21.72	π c_7-c_6→π*c_5-c_4	12.48	π c1-c2→π*c8-c7	21.59
	π c_6-c_5→π*c_9-c_4	16.97	π c_5-c_4→π*c_3-c_9	14.84	π c6-c5→π*c8-c7	16.22
	π c_6-c_5→π*c_8-c_7	17.08	π c_5-c_4→π*c_7-c_6	12.91	π c6-c5→π*c9-c4	17.49
Total Energy		142.24		129.54		142.99
Compounds	1→2		2→3		1→1´´	
	Electron Transfer	Energy	Electron Transfer	Energy	Electron Transfer	Energy
	π c_3-c_9→π*c_5-c_4	20.43	π c_1-c_8→π*c_3-c_9	23.01	π c_2-c_3→π*c_2-c_3	1.01
	π c_7-c_6→π*c_5-c_4	16.01	π c_1-c_8→π*c_7-c_6	23.97	π c_2-c_3→π*c_9-c_4	14.23
	π c_5-c_4→π*c_3-c_9	17.97	π c_3-c_9→π*c_1-c_8	18.34	π c_9-c_4→π*c_2-c_3	11.80
	π c_5-c_4→π*c_7-c_6	15.96	π c_3-c_9→π*c_3-c_9	0.86	π c_9-c_4→π*c_8-c_7	17.16
			π c_3-c_9→π*c_5-c_4	21.54	π c_9-c_4→π*c_6-c_5	22.41
			π c_7-c_6→π*c_1-c_8	16.39	π c_8-c_7→π*c_9-c_4	17.16
			π c_7-c_6→π*c_5-c_4	14.82	π c_8-c_7→π*c_6-c_5	23.01
			π c_5-c_4→π*c_3-c_9	18.35	π c_6-c_5→π*c_9-c_4	19.74
			π c_5-c_4→π*c_7-c_6	17.02	π c_6-c_5→π*c_8-c_7	19.52
Total Energy		70.34		154.3		146.04

4. CONCLUSION

The calculated results for compounds **1**, **2** and **3** show that the most stable isomers of these compounds are the allylic isomers and prototropic shift has higher barrier energy than borotropic shift. IR and ASE calculation results and NBO analysis showed that prototropic shift is a 1,2-sigmatropic migration while borotropic shift is a 1,3-sigmatropic shift.

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