

## Research Article



## Molecular Structures, Conformations, and Vibration Spectra of the 1,4-Diazabicyclo [2.2.0]Hexane

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## ABSTRACT

The equilibrium geometry structure for 1,4-Diazabicyclo[2.2.0]Hexane DABH, and Bicyclo[2.2.0]Hexane BH molecules were calculated using the Density Functional Theory (DFT) including the hybrid density function theory method {B3LYP/6-311G++(d,p)}. The results indicated that the total energy for cis-BH was lower than the trans-BH isomer, (-616099.4 and -615928.7 kJ mol<sup>-1</sup> respectively). So the cis-isomer was more stable by 170.7 kJ mol<sup>-1</sup>. The potential energy curve diagram for the dihedral angle between the two rings for both molecules demonstrated that the semi-sofa conformation was the more stable form. Furthermore, the vibrational spectrum was calculated for DABH molecule and the assignment was done for all its normal modes.

**Keywords:** DFT method; 1,4-diazabicyclo[2.2.0]Hexane; Bicyclo[2.2.0]Hexane; Molecular structure; conformations; Vibrational analysis.

## INTRODUCTION

The cyclobutane class of molecules is an interesting subject for both experimental and computational works, because these molecules have highly strained structures and highly reactive. Furthermore, they have bond lengths and bond angles that are different from those in ordinary saturated hydrocarbons<sup>1</sup>.

This work involve a theoretical study for 1,4-Diazabicyclo[2.2.0]Hexane DABH, and Bicyclo[2.2.0]Hexane BH molecules.

The BH molecule was synthesized by Cremer and Srinivasan<sup>2</sup> using mercury-sensitized photolysis for the bicyclo[3.2.0]hept-3-one, in the gas phase. This compound has two possible isomers cis- and trans-, but only the cis form was identified experimentally. The molecular structure for cis-BH in gas phase was determined by electron diffraction. While the molecular structure for both cis- and trans-BH were obtained theoretically<sup>1,3</sup>. The structure of monosubstituted bicyclo[2.2.0]hexane molecule was studied experimentally by X-ray, and theoretically by the ab initio method<sup>4</sup>.

Since, there are no available theoretical and experimental data presenting the 1,4-Diazabicyclo[2.2.0]Hexane DABH molecule, so the aim of the present theoretical study is to calculate the optimized molecular geometry, vibration spectra, and the conformational analysis for this molecule. Furthermore the study involved the BH molecule as a parent molecule.

## Computational Method

In this study, the quantum chemical density functional theory DFT was performed using Beck's three-parameter hybrid function<sup>5</sup> with the Lee-Yang-Parr correlation functional B3LYP method<sup>6,7</sup>. The DFT<sup>8</sup> level with standard 6-311G++(d,p) basis set were carried out using Gaussian

09<sup>9</sup>. The DFT method was employed to calculate the optimized geometrical parameter, total energy, and energy of the frontier molecular orbitals. The fundamental vibrational frequencies, IR intensity and Raman activity were computed only for DABH molecule. A conformational analysis treatment was done by plotting the potential energy curve. The minimum and maximum energies were determined from the curve, indicating the most stable and transition states. Then the conformational structures for the studied molecules (DABH and cis-BH) were evaluated.

## RESULTS AND DISCUSSION

Initially the total energy for both the cis and trans-isomers for BH were calculated. The results demonstrate that the total energy for cis- is lower than the trans-isomer, (-616099.4 and -615928.7 kJ mol<sup>-1</sup> respectively), which reveal that the cis-isomer is more stable, by 170.7 kJ mol<sup>-1</sup>. This result is compatible with Chen and Allinger<sup>1</sup>. So in this work the cis-isomer was adopted. The theoretical structure results, and the numbering of atoms for the, DABH and cis-BH molecules were presented in Figure 1. The theoretical geometry parameters results such as bond length, bond angle, and dihedral angle obtained by using the DFT and B3LYP method with basis set 6-311G++(d,p), were listed in Table 1.

The table revealed that the structural data of cis-BH molecule coincidence with other existed theoretical and experimental data<sup>1,10</sup>. The bridge bond N<sub>1</sub>N<sub>4</sub> length was 1.537 Å for DABH, and C<sub>1</sub>C<sub>4</sub> was 1.576 Å for cis-BH molecule, while the dihedral angle C<sub>6</sub>-N<sub>1</sub>-N<sub>4</sub>-C<sub>3</sub> was larger than C<sub>6</sub>-C<sub>1</sub>-C<sub>4</sub>-C<sub>3</sub> (118.1° and 114.2° respectively).



**Table 1:** The Optimized Geometry Results of **DABH** and the **cis-BH** Using the DFT Method, plus the Available Theoretical and Experimental Data.

Structural Parameter DABH	DFT 6-311G++(d,p) In this work	Structural Parameter cis-BH	DFT 6-311G++(d,p) In this work	MP2/6-311++G (2d,2p) <sup>(1)</sup>	Experimental <sup>[10]</sup>
Bond Length in (Å)					
N <sub>1</sub> -N <sub>4</sub>	1.537	C <sub>1</sub> -C <sub>4</sub>	1.576	1.573	1.577
C <sub>2</sub> -C <sub>3</sub>	1.541	C <sub>2</sub> -C <sub>3</sub>	1.561	1.554	1.542
N <sub>1</sub> -C <sub>6</sub>	1.494	C <sub>1</sub> -C <sub>6</sub>	1.553	1.557	-
N <sub>1</sub> -C <sub>2</sub>	1.500	C <sub>1</sub> -C <sub>2</sub>	1.551	1.536	1.557
C <sub>6</sub> -H <sub>11</sub>	1.095	C <sub>6</sub> -H <sub>11</sub>	1.094	-	-
C <sub>6</sub> -H <sub>12</sub>	1.091	C <sub>6</sub> -H <sub>12</sub>	1.092	-	-
C <sub>2</sub> -H <sub>7</sub>	1.096	C <sub>2</sub> -H <sub>7</sub>	1.094	-	-
C <sub>2</sub> -H <sub>8</sub>	1.091	C <sub>2</sub> -H <sub>8</sub>	1.092	-	-
-	-	C <sub>1</sub> -H <sub>15</sub>	1.091	-	-
Bond Angle in Degree					
N <sub>4</sub> -N <sub>1</sub> -C <sub>6</sub>	89.9	C <sub>4</sub> -C <sub>1</sub> -C <sub>6</sub>	89.6	-	-
C <sub>2</sub> -N <sub>1</sub> -N <sub>4</sub>	90.0	C <sub>2</sub> -C <sub>1</sub> -C <sub>4</sub>	89.8	90.2	-
C <sub>2</sub> -N <sub>1</sub> -C <sub>6</sub>	112.7	C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub>	115.1	113.7	-
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	89.6	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	90.2	89.0	-
N <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	113.6	C <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	115.2	-	-
N <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	112.1	C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	113.4	-	-
C <sub>3</sub> -C <sub>2</sub> -H <sub>7</sub>	115.9	C <sub>3</sub> -C <sub>2</sub> -H <sub>7</sub>	116.3	115.8	-
C <sub>3</sub> -C <sub>2</sub> -H <sub>8</sub>	115.9	C <sub>3</sub> -C <sub>2</sub> -H <sub>8</sub>	113.0	-	-
H <sub>7</sub> -C <sub>2</sub> -H <sub>8</sub>	118.8	H <sub>7</sub> -C <sub>2</sub> -H <sub>8</sub>	108.1	109.2	105.3
-	-	C <sub>4</sub> -C <sub>1</sub> -H <sub>15</sub>	123.3	123.7	133.8
-	-	C <sub>2</sub> -C <sub>1</sub> -H <sub>15</sub>	116.9	119.5	114.0
Dihedral angle in Degree					
C <sub>6</sub> -N <sub>1</sub> -N <sub>4</sub> -C <sub>5</sub>	5.3	C <sub>6</sub> -C <sub>1</sub> -C <sub>4</sub> -C <sub>5</sub>	-0.9	-	-
C <sub>2</sub> -N <sub>1</sub> -N <sub>4</sub> -C <sub>3</sub>	5.3	C <sub>2</sub> -C <sub>1</sub> -C <sub>4</sub> -C <sub>3</sub>	-0.9	-	-
C <sub>6</sub> -N <sub>1</sub> -N <sub>4</sub> -C <sub>3</sub>	118.1	C <sub>6</sub> -C <sub>1</sub> -C <sub>4</sub> -C <sub>3</sub>	114.2	-	-
C <sub>2</sub> -N <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub>	84.7	C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub>	90.5	-	-
N <sub>4</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	113.1	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	120.3	-	-
N <sub>4</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	-123.1	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	-114.5	-	-
C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	23.2	C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	30.8	-	-
C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	147.0	C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	156.0	-	-
C <sub>2</sub> -N <sub>1</sub> -C <sub>6</sub> -H <sub>12</sub>	-159.0	C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub> -H <sub>12</sub>	-153.8	-	-
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	-107.6	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	-116.9	-	-
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub>	122.8	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub>	117.2	-	-
H <sub>7</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub>	6.6	H <sub>7</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub>	-1.2	-	-
H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	6.8	H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	-1.3	-	-
-	-	C <sub>5</sub> -C <sub>4</sub> -C <sub>1</sub> -H <sub>15</sub>	121.4	-	-
-	-	C <sub>2</sub> -C <sub>1</sub> -C <sub>4</sub> -H <sub>16</sub>	121.4	-	-
-	-	H <sub>15</sub> -C <sub>1</sub> -C <sub>4</sub> -H <sub>16</sub>	-1.3	-	-
-	-	H <sub>15</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	-111.8	-	-
-	-	H <sub>15</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	13.4	-	-

**Table 2:** The Theoretical Vibrational Frequencies, IR Intensities, Raman Activities with the all Normal Modes Assignment of the **DABH** Molecule.

No.	Sym.	Freq. (cm <sup>-1</sup> )	IR intensity km mole <sup>-1</sup>	Raman activity A <sup>°4</sup> amu <sup>-1</sup>	Assignment
$\nu_1$	A	3100	34.75	169.05	$\nu_{as}CH_2$
$\nu_2$		3080	1.60	97.97	$\nu_{as}CH_2$
$\nu_3$		3036	49.74	382.25	$\nu_sCH_2$
$\nu_4$		3014	20.81	85.32	$\nu_sCH_2$
$\nu_5$		1524	4.45	4.17	$\delta CH_2$
$\nu_6$		1492	0.001	20.52	$\delta CH_2$
$\nu_7$		1307	3.70	4.81	$\omega CH_2$
$\nu_8$		1288	0.001	0.42	$\omega CH_2$
$\nu_9$		1220	1.62	3.80	$\rho CH_2$
$\nu_{10}$		1208	2.35	6.77	$\tau CH_2$
$\nu_{11}$		1124	0.02	0.82	$\rho CH_2$ + Rings def.
$\nu_{12}$		1002	0.22	29.94	$\nu_s CC$ + $\omega CH_2$ + $\nu_s NN$
$\nu_{13}$		962	0.13	0.82	$\rho CH_2$ +Rings def.
$\nu_{14}$		918	10.98	15.34	$\nu_s CNC$ + $\tau CH_2$
$\nu_{15}$		807	8.31	4.46	$\nu_s NN$
$\nu_{16}$		779	0.36	2.02	$\rho CH_2$
$\nu_{17}$		702	0.37	2.31	Rings def. + $\tau CH_2$
$\nu_{18}$		411	2.47	3.17	$\rho CH_2$ + Butter fly
$\nu_{19}$		51	0.006	0.14	$\rho CH_2$
$\nu_{20}$	B	3096	74.15	68.47	$\nu_{as}CH_2$
$\nu_{21}$		3081	11.54	61.39	$\nu_{as}CH_2$
$\nu_{22}$		3031	83.62	32.11	$\nu_sCH_2$
$\nu_{23}$		3012	70.42	67.66	$\nu_sCH_2$
$\nu_{24}$		1505	0.73	6.71	$\delta CH_2$
$\nu_{25}$		1504	2.67	2.35	$\delta CH_2$
$\nu_{26}$		1311	0.28	0.98	$\omega CH_2$
$\nu_{27}$		1304	1.92	0.14	$\omega CH_2$
$\nu_{28}$		1213	0.51	6.59	$\tau CH_2$
$\nu_{29}$		1186	30.13	0.63	Rings def.+ $\rho CH_2$
$\nu_{30}$		1153	0.21	0.26	$\rho CH_2$ + Rings Puck.
$\nu_{31}$		1067	18.99	7.06	Rings def. + $\tau CH_2$
$\nu_{32}$		958	2.03	1.27	$\nu_{as} CC$ + $\omega CH_2$
$\nu_{33}$		911	14.82	0.50	$\nu_s CNC$ (Ring def.)
$\nu_{34}$		765	0.37	0.21	$\rho CH_2$
$\nu_{35}$		743	2.28	0.28	$\beta CNC$ + $\tau CH_2$
$\nu_{36}$		361	0.87	0.31	$\rho CH_2$

Abbreviations used;  $\nu_s$  - symmetric stretching;  $\nu_{as}$ - asymmetric stretching; def. – (deformation);  $\beta$ -in-plane bending;  $\rho$ -rocking;  $\delta$ -scissoring;  $\tau$ - twisting;  $\omega$ - wagging.



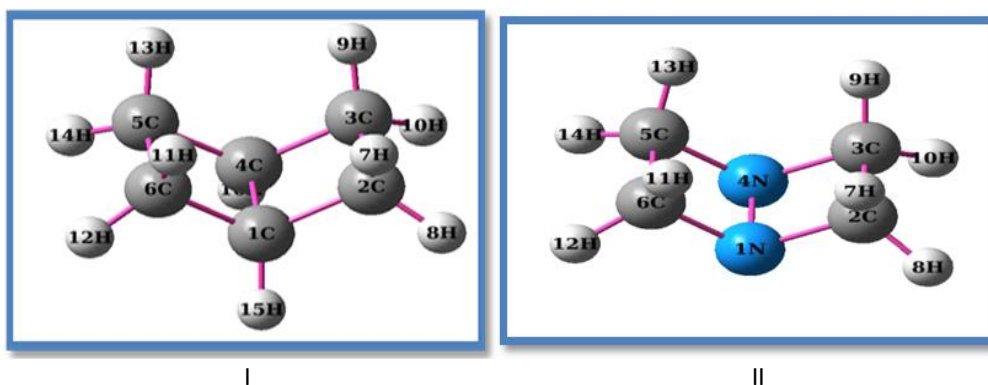


Figure 1: The Numbering Scheme for the **DABH** (I), and **cis-BH** (II) Molecules.

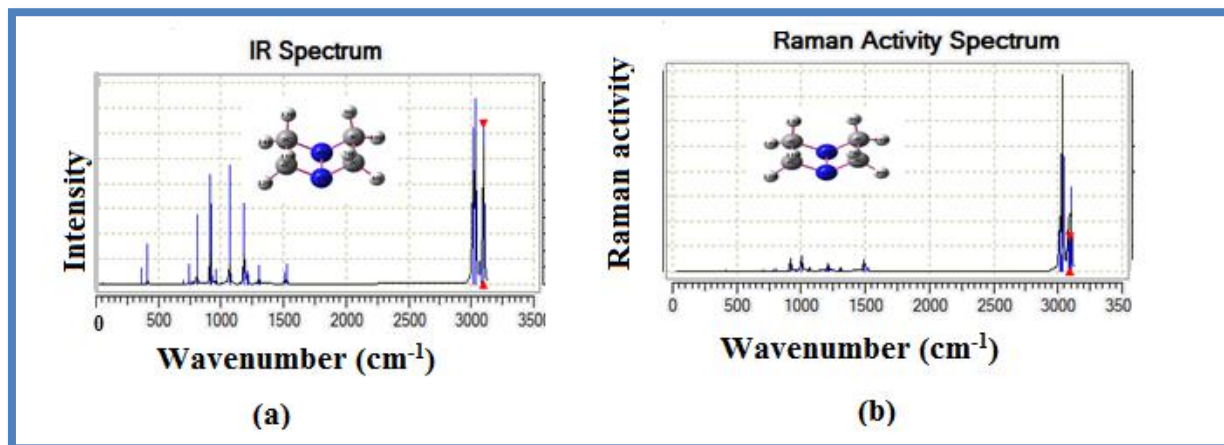


Figure 2: The Theoretical (a) IR Spectrum, and (b) Raman Activity Spectrum of **DABH** Molecule.

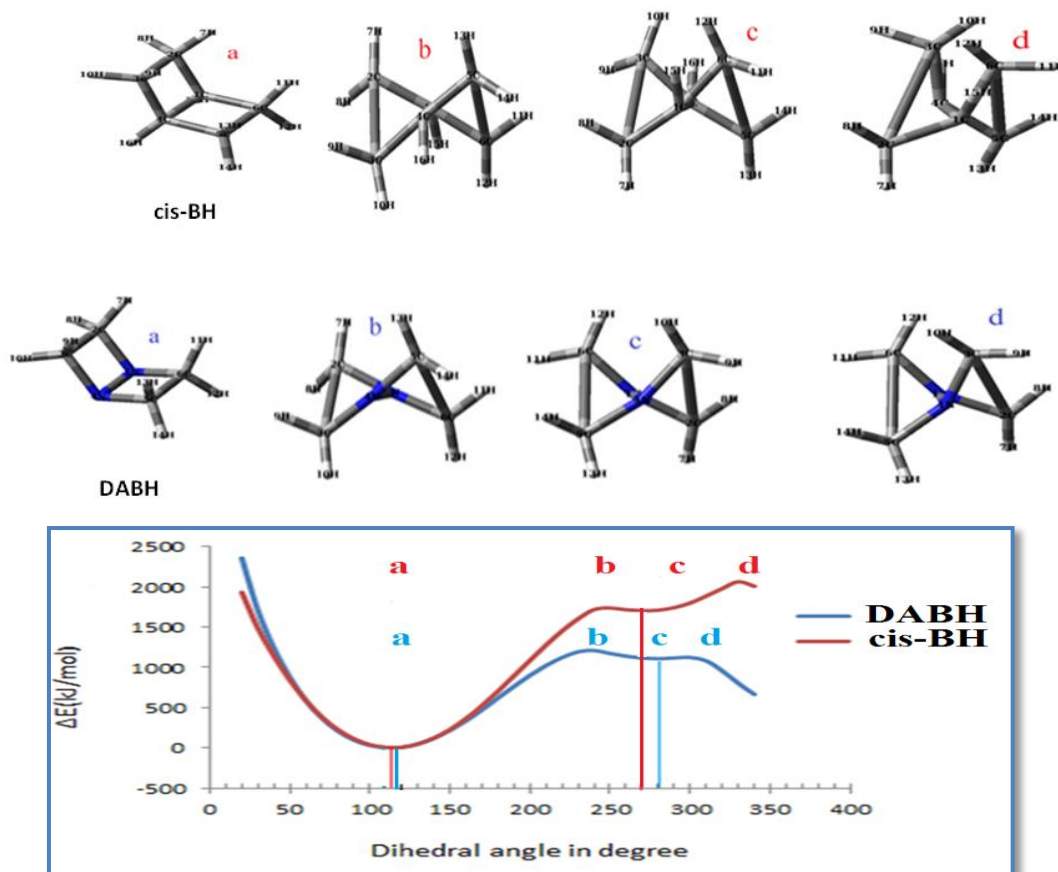
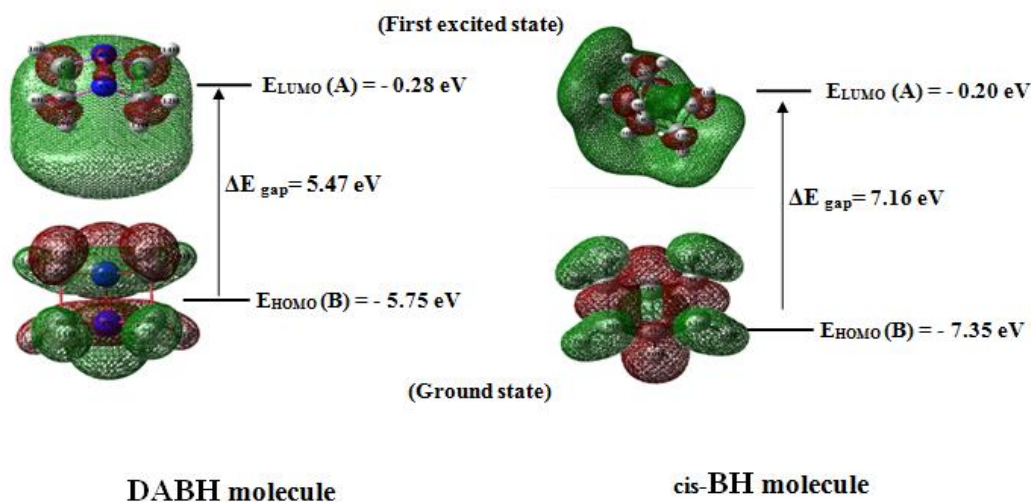


Figure 3: The Potential Energy Curves for **DABH** (blue), and **cis-BH** (red) Molecules.



**Figure 4:** The Atomic Orbital Compositions of the Frontier Molecular Orbital for **DABH**, and **cis-BH** Molecules.

The calculated results of the vibrational frequency, IR intensity and Raman activity for **DABH** molecule with its assignment were presented in **Table 2**, while the calculated spectrum for the infrared and Raman are demonstrated in **Figure 2**.

Since the **DABH** molecule belongs to  $C_2$  point group, so its 36 normal modes were distributed as  $\Gamma_{\text{vib}} = 19A + 17B$ . All these fundamental vibrations are active in both Infrared and Raman.

According to this work data, eight of the normal modes were assigned as pure  $CH_2$  stretching vibrations. Four of them ( $\nu_3$ ,  $\nu_4$ ,  $\nu_{22}$ , and  $\nu_{23}$ ) were assigned as symmetric stretch and the others identified as asymmetric stretch, **Table 2**.

The six following modes ( $\nu_{10}$ ,  $\nu_{14}$ ,  $\nu_{17}$ ,  $\nu_{28}$ ,  $\nu_{31}$ , and  $\nu_{35}$ ) were specified as  $CH_2$  twisting vibrations. The  $\nu_{17}$ , and  $\nu_{31}$  possessed **A** and **B** symmetry species respectively, having  $CH_2$  twisting gather with rings deformation.  $\nu_{10}$ , and  $\nu_{28}$  were showing pure  $CH_2$  twisting motion.  $\nu_{14}$  belong to the symmetry species **A**, possessing mixed of  $CH_2$  twisting and CNC symmetric stretching motions.  $\nu_{35}$  is related to the **B** symmetry species, assigned as  $CH_2$  twisting with CNC - in plane bending.

Modes  $\nu_7$ ,  $\nu_8$ ,  $\nu_{26}$ , and  $\nu_{27}$  had pure  $CH_2$  wagging vibration motion (the first two were symmetric and the others asymmetric).  $\nu_{12}$  was showing of  $CH_2$  wagging, CC, and NN symmetric stretch. The modes  $\nu_5$ ,  $\nu_6$ ,  $\nu_{24}$ , and  $\nu_{25}$  were assigned as pure  $CH_2$  scissoring.

The potential energy curve for the **DABH**, and **cis-BH** molecules were plotted between  $\Delta E$  and the dihedral angle  $\theta$  ( $C_2-N_1-N_4-C_5$ ), and ( $C_2-C_1-C_4-C_5$ ) respectively, **Figure 3**.

The figure demonstrated asymmetrical potential energy curves with two minimum and two maximum.

The first minimum for **DABH** molecule corresponded to the **semi-sofa** (belong to the  $C_2$  point group) conformation (**a**) at  $\theta$  equal to  $118^\circ$ .

The second shallow minimum (**c**) at  $280^\circ$  match twist conformation, with energy of  $1107.9 \text{ kJ mol}^{-1}$  above the **semi-sofa** form. The first maximum energy (**b**) appeared at  $240^\circ$ , and the second maximum (**d**) at  $300^\circ$  with energy  $1210.4$  and  $1123.7 \text{ kJ mol}^{-1}$  greater than the **sofa** conformer. The potential energy curve of **cis-BH** molecule showed two minimum; one of them (**a**) at the angle  $114^\circ$  related also to **semi-sofa** form, and the next one (**c**) at angle equal  $270^\circ$  with energy higher than **semi-sofa** by  $1714.5 \text{ kJ mol}^{-1}$ . The two maximum (**b**) and (**d**) appeared at  $250^\circ$  and  $330^\circ$  with energies above than the **semi-sofa** conformation by  $1738.0$  and  $2008.5 \text{ kJ mol}^{-1}$  respectively. Therefore the **semi-sofa** conformation (**a**) is the most stable form for both **DABH** and **cis-BH** molecules.

The results including energies of the highest occupied molecular orbital **HOMO**, plus the lowest unoccupied molecular orbital **LUMO** for both molecules under study demonstrated in **Figure 4**. From this figure, the **HOMO** was assigned as **B** symmetry species (asymmetric to  $C_2$  rotational axis). But the **LUMO** is symmetric for all the symmetry elements (belongs to **A** symmetry species) and diffused over all atoms for both molecules. The energy of the frontier molecular orbital's ( $E_{\text{HOMO}}$ , and  $E_{\text{LUMO}}$ ) for **cis-BH** molecule were  $-7.35$  and  $-0.20 \text{ eV}$  respectively, and for **DABH** molecule were  $-5.75$  and  $-0.28 \text{ eV}$  consequently; which reflect of the chemical activity of the molecule. A molecule with a small value of  $E_{\text{LUMO}} - E_{\text{HOMO}}$  energy gap is more polarisable, generally associated with a low kinetic stability, high chemical reactivity, and is characterized as soft molecule. The frontier orbital gap for **DABH** and **cis-BH** was  $5.47$  and  $7.16 \text{ eV}$  respectively. This smaller value of **DABH** makes it more reactive than **cis-BH** molecule.

The total dipole moment results of **DABH** and **cis-BH** molecules were  $2.887$  and  $0.177$  Debye respectively.



The total dipole moment of **DABH** molecule was higher than **BH** molecule, this can be attributed to the existence of the **N**-atoms.

Since the **N**-atoms have high electronegativity and lone pair of non-bonding electrons.

### CONCLUSION

The following points summaries the important conclusion that can be drawn from this work:-

- The dihedral angle  $\theta$  (between the two fused rings) which belong to the **cis-BH** molecule is smaller than the corresponding angles for molecule contain aza nitrogen **DABH**. This may be related to the steric effect for **H** atoms in **cis-BH** molecule.
- The **semi-sofa** form (has point group  $C_2$ ) is the most stable form for both **DABH**, and **BH** molecules.
- **DABH** has the smaller value of frontier orbital gap than **cis-BH** molecule. This meaning that the **DABH** molecule is more chemical reactive and more softer than **cis-BH** molecule.

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