



## Theoretical study of molecular structure, conformations, and vibrational spectra for diazabicyclo[1.1.0]butane and diazabicyclo[2.1.0]pentane

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### ABSTRACT

The DFT[B3LYP/6-311G\*\*(d,p)] theoretical study have been performed to calculate the total energies, optimized geometry, molecular orbitals, and vibrational spectra of the following molecules diazabicyclo[1.1.0]butane (DABCB), bicyclo[1.1.0]butane (BCB), diazabicyclo[2.1.0]pentane (DABCP), and bicyclo[2.1.0]pentane (BCP). A complete vibrational assignment was proposed. The structural parameters and puckering potential profiles were analyzed. The DABCB molecule possess two conformations, the most stable form was the puckered which was 312.4 kJ mol<sup>-1</sup> lower than the planar form. While the DABCP molecule had three conformations, it can be arranged according to their stability in the following order; envelop, twist, and planar.

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### KEYWORDS

DFT method;  
Diazabicyclo[1.1.0]butane;  
Diazabicyclo[2.1.0]pentane;  
Molecular structure conformations;  
Vibrational analysis.

### INTRODUCTION

The establishments of the density function theory (DFT) method give the advantage to study the geometry, and the vibrational spectra accurately. In the DFT method the electronic energy (E) equal to  $E_T + E_V + E_J + E_{XC}$ . Where  $E_T$  is the electronic kinetic energy,  $E_V$  the electronic nuclear attraction,  $E_J$  the electron-electron repulsion energy, and  $E_{XC}$  is the electron correlation energy.  $E_{XC}$  represented the exchange energy from the antisymmetric wavefunction and the dynamic correlation in the motion for each electron, which makes the DFT plenary method<sup>[1]</sup>. Therefore, the DFT theoretical calculations encour-

age many workers to estimate the most stable conformers of cyclic and bicyclic compounds<sup>[2-4]</sup>.

Since small ring compounds consisting of three or four membered rings, play an important role in the modern organic chemistry<sup>[5]</sup>. The bicyclo[1.1.0]butane (BCB) is an interesting compound, because of its unusual bonding and high symmetry. It is formed from the combination of two highly strained rings (fused rings). This compound was found in 1960<sup>[6]</sup> and synthesized in 1963<sup>[7]</sup>. The structure of BCB molecule has been studied experimentally<sup>[8]</sup>, plus its photochemistry<sup>[9]</sup>. Jensen<sup>[10]</sup> examined the BCB molecular structure and the vibrational spectra theoretically using Hartree-Fock (HF),

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DFT(B3LYP), plus the MP<sub>2</sub> levels theory by employing the 6-311G\*\*basis set, while Berezin et al.<sup>[6]</sup> used the ab initio method. Jensen concluded that multiplying the calculated vibrational frequencies results by correction factors make them in agreement with the available experimental data. The bicyclo[2.1.0]pentane(BCP) was prepared using UV-irradiation on 2,3-diazabicyclo[2.2.1]hept-2-ene, which is a photochemical precursor of the (BCP) compound<sup>[11]</sup>. The BCP molecular structure was obtained experimentally by microwave. Gerent et al.<sup>[12]</sup> evaluated theoretically the optimized geometry, and the normal mode frequencies for BCP molecule [using semi-empirical PM<sub>3</sub> method] and comparing them with experimental data. They postulated that the differences between the theoretical and observed values related to the computational model approximation. Murray et al.<sup>[13]</sup> employed the HF/3-21G computational method to evaluate the strained of cyclic hydrocarbons with aza-substituted cyclic hydrocarbons. They pointed out that when two nitrogen atoms introduced in cyclopropyl ring, diaziridine molecule will be produced. The energy of diaziridine was 17 kJmol<sup>-1</sup> less than cyclopropane, which indicate a rise in ring stability.

Since, there are no available theoretical and experimental data presenting diazabicyclo [1.1.0]butane(DABCB), and diazabicyclo [2.1.0]pentane(DABCP) molecules, so the goal of the present theoretical study was to calculate the optimized molecular geometry, vibrational spectra, and conformational analysis for the following molecules DABCB, and DABCP. Furthermore the study involved the BCB, and BCP molecules in order to evaluate and standardize the work results.

### Computational method

In the present work, the quantum chemical density functional theory was employed using Beck's three-parameter hybrid function<sup>[14]</sup> with the Lee-Yang-Parr correlation functional B3LYP method<sup>[15,16]</sup>. The DFT<sup>[17]</sup> level with standard 6-311G\*\*(d,p) basis set were carried out using Gaussian 03<sup>[18]</sup>. The DFT method was used to compute the optimized geometrical parameter, energy of molecular orbitals (bonding, and frontier), total energy, and potential

energy curve for the following molecules DABCB, BCB, DABCP, and BCP. The fundamental vibrational frequencies, IR intensities and Raman activity were calculated only for DABCB, and DABCP molecules.

The conformational analysis treatment was done by plotting the potential energy curve: when the total energy of the molecular optimized geometry [equilibrium geometry ( $E_{eq}$ )] was obtained plus its dihedral angle  $\theta$  [represents the angle between the two ring plans] in molecule. The angle  $\theta$  was changed by 10 degree, and the total energy ( $E$ ) was calculated for each angle value. The potential energy curve was drawn between ( $\Delta E = E_{eq} - E$ ) as a function of the angle  $\theta$ . The minimum and maximum energies which were determined from the curve indicated the most stable and transition-state respectively. Then the conformational structures for the studied molecules were evaluated.

## RESULT AND DISCUSSION

### DABCB and BCB molecules

The structures and the numbering of atoms for the DABCB, and BCB molecules were depicted in Figure 1. The calculated optimized structural parameters for both molecules such as bond length, bond angles, and dihedral angles [using DFT and B3LYP method with basis set 6-311G\*\*(d,p)] were listed in TABLE 1. The table also revealed that the results of this work were in good agreement with other theoretical available data<sup>[10,19]</sup>. Furthermore the BCB molecules results were coincide with the obtainable experimental data<sup>[8]</sup>.

The theoretical optimized geometry results of this treatment demonstrated that DABCB and BCB molecules were puckered, Figure 1. The dihedral angle ( $\theta$ ) for the DABCB molecule ( $C_2-N_3-N_1-C_4$ ) equal 114.1°, and the angle ( $C_2-C_3-C_1-C_4$ ) for the BCB molecule was 122.0°, TABLE 1. The table also indicated that the values of the bond angle ( $C_2-N_1-C_4$ ) = 91.3° in DABCB was smaller than the similar bond angle ( $C_2-C_1-C_4$ ) = 98.7° for the BCB molecule. The deviation from planarity and also the smaller value of the angles ( $C_2-N_3-N_1-C_4$ ) and ( $C_2-C_3-C_1-C_4$ ) in DABCB molecule were presumably related to the

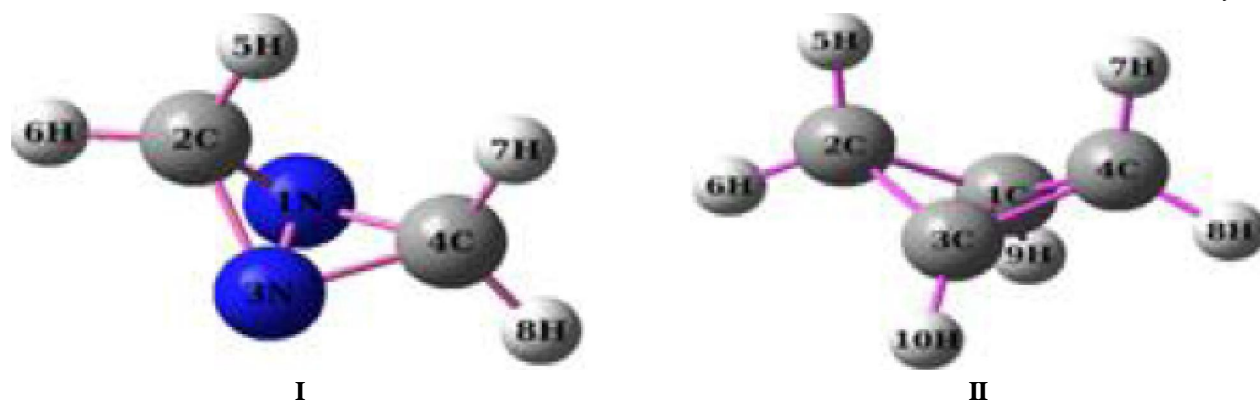


Figure 1 : The numbering scheme for the (I) DABCB, and (II) BCB molecules the N-atoms. But the deviation of the structure for the BCB molecule and its existence in puckered conformation may be related to the eclipsing in the planar form<sup>[20]</sup>.

TABLE 1 : The optimized geometry results of DABCB and BCB molecules using the DFT (B3LYP) level with 6-311G\*\*(d,p) basis set, plus the available theoretical and experimental data

Structural parameter DABCB	DFT 6-311G**(d,p) In this work	DFT 6-31G*(d) [19]	Structural Parameter BCB	DFT 6-311G**(d,p) In this work	DFT 6-311G** [10]	Experimental [8]
<b>Bond Length in(Å)</b>						
N <sub>1</sub> -N <sub>3</sub>	1.529	1.535	C <sub>1</sub> -C <sub>3</sub>	1.493	1.491	1.497
N <sub>1</sub> -C <sub>2</sub>	1.460	1.462	C <sub>1</sub> -C <sub>2</sub>	1.499	1.499	1.498
C <sub>2</sub> -H <sub>5</sub>	1.091	-	C <sub>2</sub> -H <sub>5</sub>	1.091	1.091	1.096
C <sub>2</sub> -H <sub>6</sub>	1.085	-	C <sub>2</sub> -H <sub>6</sub>	1.086	1.087	1.088
-	-	-	C <sub>1</sub> -H <sub>9</sub>	1.078	1.078	1.076
<b>Bond Angle in degree</b>						
C <sub>2</sub> -N <sub>1</sub> -C <sub>4</sub>	91.3	-	C <sub>2</sub> -C <sub>1</sub> -C <sub>4</sub>	98.7	-	-
N <sub>1</sub> -C <sub>2</sub> -H <sub>5</sub>	118.0	-	C <sub>1</sub> -C <sub>2</sub> -H <sub>5</sub>	119.2	-	-
N <sub>1</sub> -C <sub>2</sub> -H <sub>6</sub>	115.4	-	C <sub>1</sub> -C <sub>2</sub> -H <sub>6</sub>	116.9	-	-
N <sub>1</sub> -N <sub>3</sub> -C <sub>2</sub>	58.4	-	C <sub>1</sub> -C <sub>3</sub> -C <sub>2</sub>	60.1	-	-
N <sub>1</sub> -C <sub>2</sub> -N <sub>3</sub>	63.2	-	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	59.7	59.6	60.0
H <sub>5</sub> -C <sub>2</sub> -H <sub>6</sub>	116.2	-	H <sub>5</sub> -C <sub>2</sub> -H <sub>6</sub>	114.2	114.8	115.8
-	-	-	C <sub>2</sub> -C <sub>1</sub> -H <sub>9</sub>	129.8	129.9	130.4
-	-	-	C <sub>3</sub> -C <sub>1</sub> -H <sub>9</sub>	129.8	129.4	128.4
<b>Dihedral angle in degree</b>						
C <sub>4</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>5</sub>	58.0	-	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>5</sub>	60.6	-	-
C <sub>4</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>6</sub>	-158.0	-	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>6</sub>	155.0-	-	-
C <sub>2</sub> -N <sub>3</sub> -N <sub>1</sub> -C <sub>4</sub>	114.1	114.1	C <sub>2</sub> -C <sub>3</sub> -C <sub>1</sub> -C <sub>4</sub>	122.0	-	-
-	-	-	H <sub>5</sub> -C <sub>2</sub> -C <sub>1</sub> -H <sub>9</sub>	-113.1	-	-
-	-	-	H <sub>5</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	113.1	-	-
-	-	-	C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub> -H <sub>6</sub>	155.0	-	-
-	-	-	H <sub>6</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	11.1-	-	-
-	-	-	H <sub>6</sub> -C <sub>2</sub> -C <sub>1</sub> -H <sub>9</sub>	11.1	-	-
-	-	-	H <sub>9</sub> -C <sub>1</sub> -C <sub>3</sub> -H <sub>10</sub>	0.0	-	-

two lone pairs electrons for

Since the DABCB molecule belongs to C<sub>2v</sub> point

group, therefore it has 18 normal modes distributed

as  $\Gamma_{\text{vib}} = 7A_1 + 3A_2 + 3B_1 + 5B_2$ . All the 18 fundamental

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TABLE 2 : The theoretical vibrational frequencies ( $\text{cm}^{-1}$ ), with its assignment for DABCB molecule

No.	Sym.	Freq. ( $\text{cm}^{-1}$ )	IR intensity ( $\text{km mol}^{-1}$ )	Raman activity ( $\text{A}^4 \text{amu}^{-1}$ )	Assignment
$\nu_1$	$A_1$	570	4.14	1.80	$\rho\text{CH}_2(+)$ + ring flap
$\nu_2$		786	0.13	7.31	NN + $\rho\text{CH}_2(+)$
$\nu_3$		1179	0.03	23.84	$\tau\text{CH}_2(+)$ + $\nu\text{NN}$
$\nu_4$		1261	14.40	16.87	$\tau\text{CH}_2(+)$ + $\nu\text{NN}$
$\nu_5$		1545	2.49	4.58	$\delta\text{CH}_2(+)$
$\nu_6$		3054	46.54	207.25	$\nu_s\text{CH}_2(+)$
$\nu_7$		3186	14.18	116.23	$\nu_{as}\text{CH}_2(+)$
$\nu_8$	$A_2$	829	0.00	4.03	Ring def. + $\tau\text{CH}_2(-)$
$\nu_9$		982	0.00	2.62	$\tau\text{CH}_2(-)$
$\nu_{10}$		1139	0.00	6.60	$\omega\text{CH}_2(-)$
$\nu_{11}$	$B_1$	763	37.80	0.99	$\gamma\text{CH}(+)$ + Ring def.
$\nu_{12}$		1129	3.08	8.17	$\tau\text{CH}_2(+)$
$\nu_{13}$		1204	13.05	0.94	$\omega\text{CH}_2(+)$
$\nu_{14}$	$B_2$	1112	4.82	0.09	$\rho\text{CH}_2(-)$
$\nu_{15}$		1173	18.57	10.22	$\omega\text{CH}_2(-)$ + $\nu_{as}\text{NCN}$
$\nu_{16}$		1507	0.10	5.20	$\delta\text{CH}_2(-)$
$\nu_{17}$		3054	19.39	2.53	$\nu_s\text{CH}_2(-)$
$\nu_{18}$		3185	15.50	45.71	$\nu_{as}\text{CH}_2(-)$

Abbreviations used;  $\nu_{as}$ -a symmetric stretching; def-deformation;  $\gamma$ -out-of-plane bending;  $\rho$ -rocking;  $\delta$ - scissoring;  $\nu$ - stretching;  $\nu_s$ - symmetric stretching;  $\nu$ - twisting;  $\omega$ - wagging.

vibrations are active in Raman scattering, and in Infrared except  $A_2$  species. The whole calculated results including the vibrational frequencies and intensities with the reliable assignment were presented in TABLE 2, and Figure 2, while the theoretical Infrared and Raman spectrums were presented in Figure 3. TABLE 2 and Figure 2 demonstrated four  $\text{CH}_2$  stretching vibrations ( $\nu_6, \nu_7, \nu_{17}, \nu_{18}$ ). Two of them ( $\nu_7, \nu_{18}$ ) were assigned as asymmetric stretch and the others identified as symmetric stretch. All of them were highly intensive modes in IR and Raman. This result was consistent with the assignments proposed for BCB molecule<sup>[10]</sup>. It is well known that the asymmetric stretch vibration of  $\text{CH}_2$  group always occurs at higher wavenumber compared with symmetric stretch vibration. In cycloalkane compounds, there is a linear relationship between the wavenumber of  $\text{CH}_2$  stretching and the angle of strain in the ring. The  $\text{CH}_2$  stretching vibration for cyclopropane occurs at a higher wavenumber as compared to that in cyclohexane.

According to this work results the modes  $\nu_5$  and  $\nu_{16}$  were assigned as  $\text{CH}_2$  scissoring and possessed

symmetries  $A_1$  and  $B_2$ . The five following modes ( $\nu_3, \nu_4, \nu_8, \nu_9, \nu_{12}$ ) were specified as  $\text{CH}_2$  twisting vibrations. The  $\nu_9$  and  $\nu_{12}$  possessed the symmetries  $A_2$  and  $B_1$  respectively, and showing pure  $\text{CH}_2$  twisting motion. The modes  $\nu_3$  and  $\nu_4$  having coupled  $\text{CH}_2$  twisting, and N-N stretching vibrations. While  $\nu_8$  had mixed motions  $\text{CH}_2$  twisting and ring deformation. Modes  $\nu_{10}$  and  $\nu_{13}$  were assigned as  $\text{CH}_2$  wagging, while  $\nu_{15}$  showing  $\text{CH}_2$  wagging plus asymmetric NCN stretching.  $\nu_{14}$  indicated  $\text{CH}_2$  asymmetric rocking vibration to plan of symmetry.

The highly symmetric modes ( $\nu_1, \nu_2$ ) having two types of motions.  $\nu_1$  own the lowest wavenumber, so its vibrations can be describe as  $\text{CH}_2$  rocking plus ring flap, while  $\nu_2$  motions characterized as  $\text{CH}_2$  rocking mixed with N-N stretching, Figure 2. Generally all the  $\text{CH}_2$  deformation vibrations can be described in the following series according to its decreasing wavenumber as scissoring: twisting, and rocking. Finally  $\nu_{11}$  was assigned as CH out of plan bending, coupled with ring deformation.

Figure 4 described the energy values, shapes, and symmetry assignments for all bonding molecular



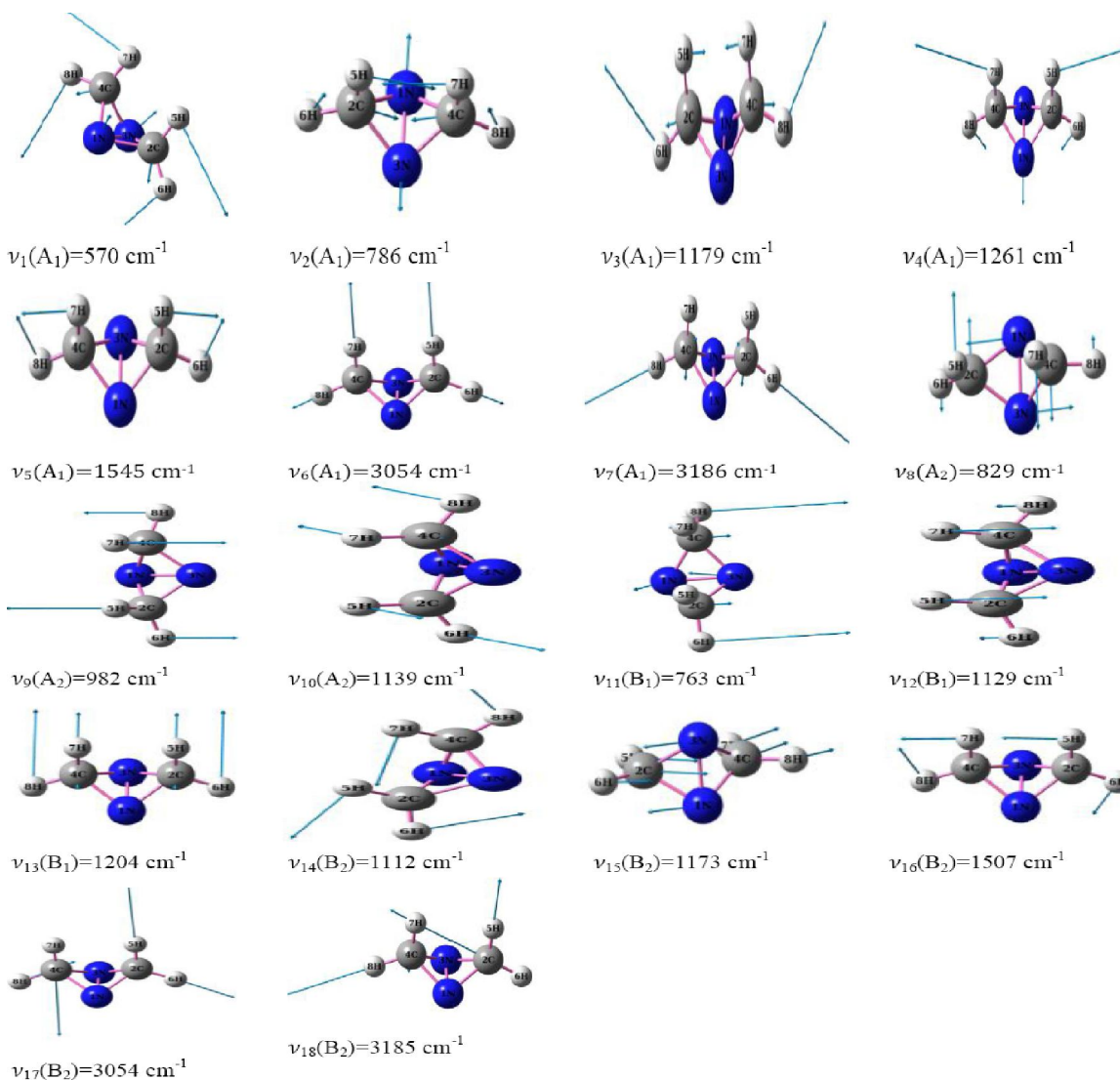


Figure 2 : The displacement vectors, wavenumber, and symmetries of eighteen normal mode of DABC molecule

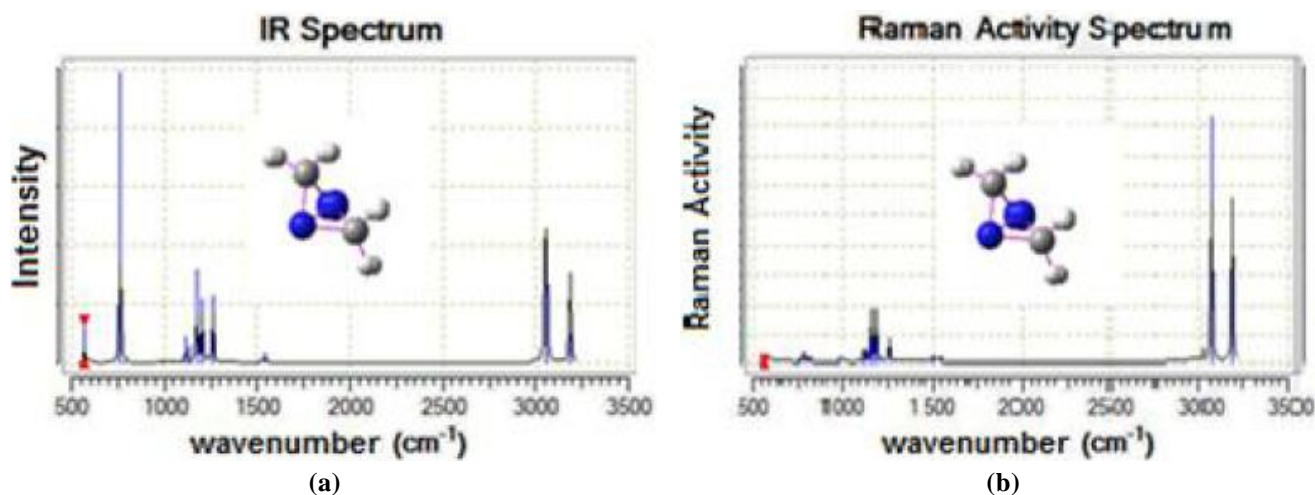
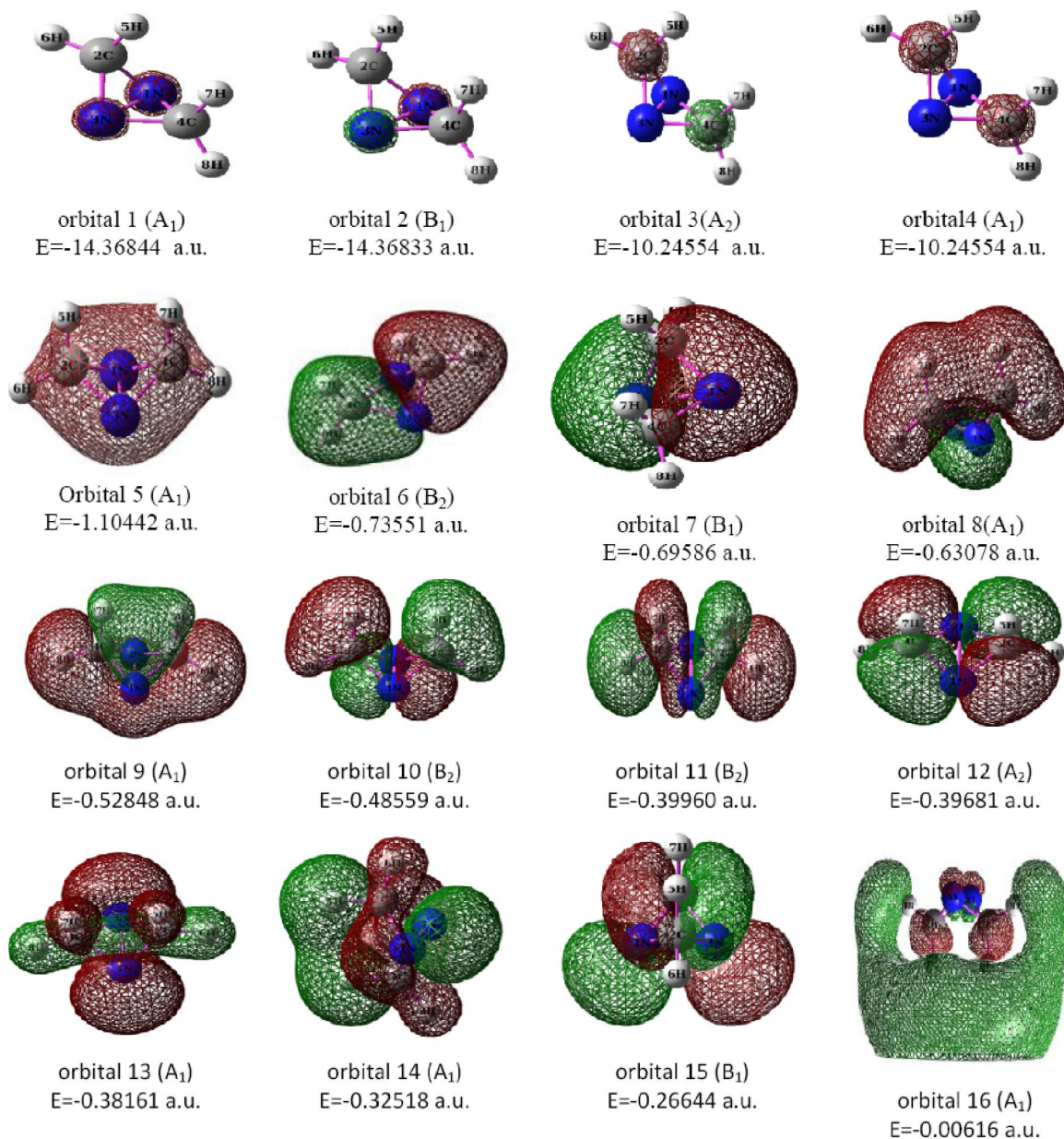


Figure 3 : The calculated (a) infrared, and (b) raman spectrum of DABC molecule

orbitals [including the highest occupied molecular orbital HOMO], plus the lowest unoccupied molecu-

lar orbital LUMO for DABC molecule. it also demonstrated the symmetry assignment for each molecu-

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**Figure 4 :** The calculated energy, shape, symmetry of (bonding and LUMO)molecular orbitals for DABCB molecule

lar orbitals. Both the HOMO and LUMO are the main orbitals in chemical stability. The high energy value of HOMO ( $E=-0.266$  a.u.) represented the ability to donate an electron, and the low energy value of LUMO ( $E=-0.006$  a.u.) indicated the ability to obtain electron. The energy gap between LUMO and HOMO orbitals was (0.260 a.u.)

The potential curve was plotted between  $\Delta E$  and the dihedral angle  $\theta$  ( $\angle C_2-N_3-N_1-C_4$ ) and ( $\angle C_2-C_3-C_1-C_4$ ) for DABCB and BCB molecules respectively, Figure 5. For the DABCB molecule, the dihedral angle  $\theta$  was changed from 70 to 290 degree with an

interval of  $10^\circ$ . The curve demonstrated symmetrical double minimum (a) with one maximum energy (b). The two minimum energy points found at  $(\theta) 114^\circ$ , and  $246^\circ$ , which revealed the most stable puckered conformer. The maximum energy (b) was located at  $(\theta) 180^\circ$ , which indicated planar conformer. Therefore, DABCB molecule had two conformations only (puckered and planar). The puckered was more stable than the planar form by  $312.4 \text{ kJ mol}^{-1}$ . The potential curve for BCB molecule, demonstrated asymmetrical form with two dissimilar minimum (Figure 5.a, and c.), and one maximum en-

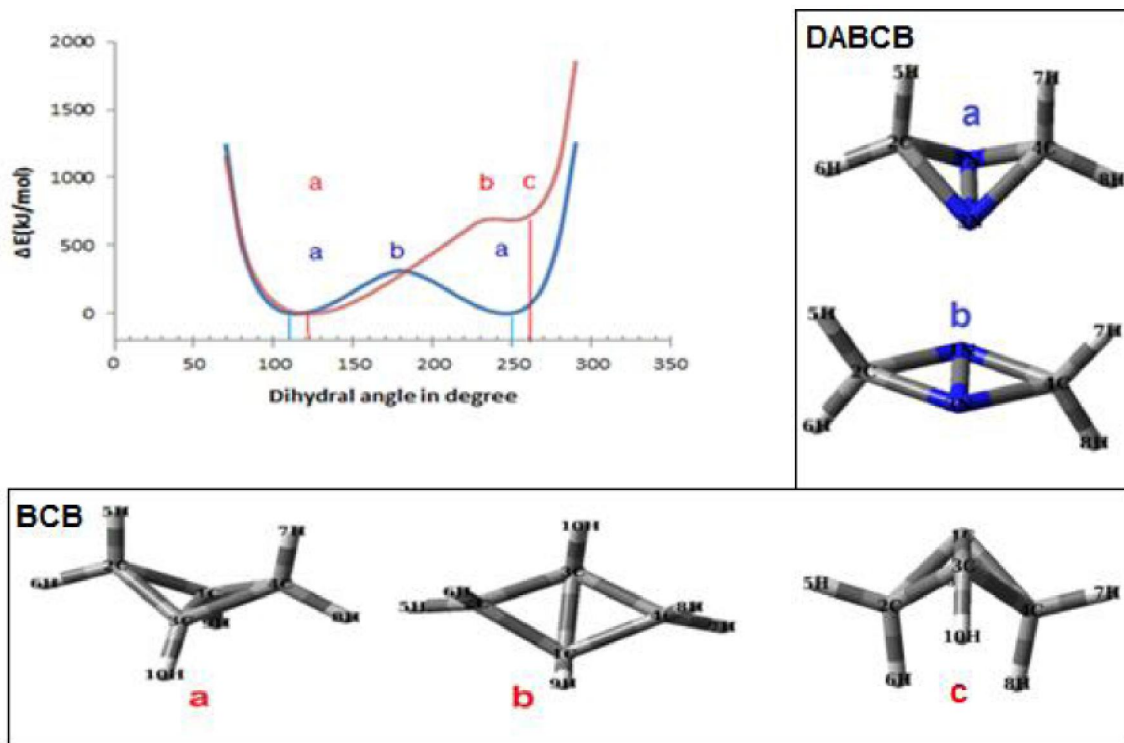


Figure 5 : Potentail energy curves for DABCB(blue), and BCB (red) molecules a, c presented thepuckerred and b planar conformation

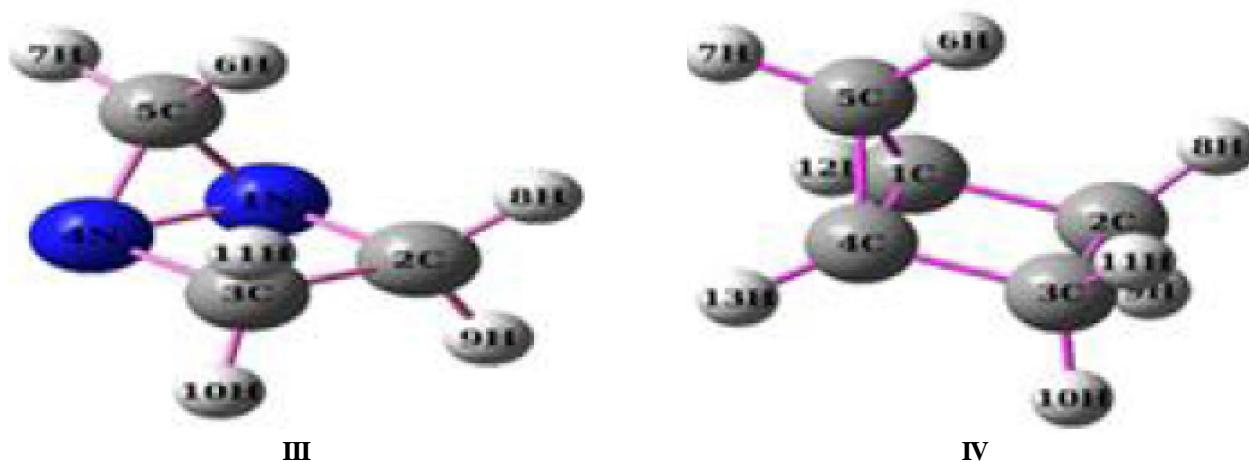


Figure 6 : The numbering scheme for the (III) DABCBP(III), and BCP(IV)

ergy (Figure 5.b).

The two minimum energies located at the following angles  $122^\circ$  and  $260^\circ$ , which illustrated two puckerred forms. The puckerred conformation (a) had lower energy than (c) by  $716.8 \text{ kJ mol}^{-1}$ . This may be related to the steric effect between the non-bonded hydrogen atoms. The unstable conformer (b) at the dihedral angle  $240^\circ$  may be due to the non-bonded interaction (steric effect or eclipsed arrangement) for the hydrogen. The energy difference between the

most stable conformer (a) and unstable conformer (b) was  $695.8 \text{ kJ mol}^{-1}$ .

### DABCP and BCP molecules

The optimized theoretical geometric parameters results for the DABCP and BCP molecules were presented in Figure 6, and TABLE 3, plus the available theoretical and experimental data<sup>[12, 21]</sup>.

From the table it can be concluded that this work results were in agreement with the observed<sup>[21]</sup> and other theoretical results<sup>[12]</sup>. The dihedral angle ( $\theta$ ) <



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TABLE 3:-The optimized geometry data of DABCP and BCP molecules using the DFT level with (B3LYP)6-311G\*\*(d,p) basis set, plus the available theoretical and experimental data

Structural parameter DABCP	DFT 6-311G**(d,p) In this work	Structural Parameter BCP	DFT 6-311G**(d,p) In this work	Ab initio <sup>[22]</sup>	Experimental [21]
<b>Bond Length in (Å)</b>					
N <sub>1</sub> -C <sub>2</sub>	1.503	C <sub>1</sub> -C <sub>2</sub>	1.534	1.531	1.528
C <sub>2</sub> -C <sub>3</sub>	1.534	C <sub>2</sub> -C <sub>3</sub>	1.566	1.559	1.565
N <sub>1</sub> -N <sub>4</sub>	1.579	C <sub>1</sub> -C <sub>4</sub>	1.535	1.518	1.536
N <sub>1</sub> -C <sub>5</sub>	1.443	C <sub>1</sub> -C <sub>5</sub>	1.504	1.498	1.507
C <sub>2</sub> -H <sub>9</sub>	1.089	C <sub>2</sub> -H <sub>9</sub>	1.091	1.084	1.085
C <sub>2</sub> -H <sub>8</sub>	1.094	C <sub>2</sub> -H <sub>8</sub>	1.095	1.086	1.097
C <sub>5</sub> -H <sub>6</sub>	1.091	C <sub>5</sub> -H <sub>7</sub>	1.085	1.077	1.088
C <sub>5</sub> -H <sub>7</sub>	1.085	C <sub>5</sub> -H <sub>6</sub>	1.088	1.088	1.090
-	-	C <sub>1</sub> -H <sub>12</sub>	1.083	1.076	1.082
<b>Bond Angle in degree</b>					
C <sub>2</sub> -N <sub>1</sub> -N <sub>4</sub>	89.1	C <sub>2</sub> -C <sub>1</sub> -C <sub>4</sub>	90.6	-	-
C <sub>2</sub> -N <sub>1</sub> -C <sub>5</sub>	105.1	C <sub>2</sub> -C <sub>1</sub> -C <sub>5</sub>	110.3	112.8	112.7
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	90.9	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	89.4	-	-
N <sub>1</sub> -C <sub>5</sub> -N <sub>4</sub>	66.3	C <sub>1</sub> -C <sub>5</sub> -C <sub>4</sub>	61.4	-	-
N <sub>1</sub> -N <sub>4</sub> -C <sub>5</sub>	56.8	C <sub>1</sub> -C <sub>4</sub> -C <sub>5</sub>	59.3	-	-
N <sub>1</sub> -C <sub>2</sub> -H <sub>9</sub>	109.8	C <sub>1</sub> -C <sub>2</sub> -H <sub>9</sub>	113.1	-	-
N <sub>1</sub> -C <sub>5</sub> -H <sub>7</sub>	113.9	C <sub>1</sub> -C <sub>5</sub> -H <sub>7</sub>	115.5	115.4	114.7
N <sub>1</sub> -C <sub>5</sub> -H <sub>6</sub>	119.4	C <sub>1</sub> -C <sub>5</sub> -H <sub>6</sub>	120.2	120.4	119.0
N <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	113.3	C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	115.8	115.8	115.2
C <sub>2</sub> -C <sub>3</sub> -H <sub>11</sub>	118.5	C <sub>2</sub> -C <sub>3</sub> -H <sub>11</sub>	117.0	-	-
C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	113.8	C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	112.0	-	-
H <sub>8</sub> -C <sub>2</sub> -H <sub>9</sub>	109.3	H <sub>8</sub> -C <sub>2</sub> -H <sub>9</sub>	108.6	112.0	111.9
H <sub>6</sub> -C <sub>5</sub> -H <sub>7</sub>	115.1	H <sub>6</sub> -C <sub>5</sub> -H <sub>7</sub>	114.2	114.3	116.7
-	-	C <sub>2</sub> -C <sub>1</sub> -H <sub>12</sub>	125.6	-	-
-	-	C <sub>1</sub> -C <sub>4</sub> -H <sub>13</sub>	128.7	-	-
-	-	C <sub>5</sub> -C <sub>1</sub> -H <sub>12</sub>	121.6	121.7	121.2
<b>Dihedral angle in degree</b>					
N <sub>4</sub> -N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	0.0	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	0.0	-	-
C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	55.2	C <sub>5</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	57.3	-	-
C <sub>5</sub> -N <sub>4</sub> -N <sub>1</sub> -C <sub>2</sub>	108.8	C <sub>5</sub> -C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub>	113.4	-	-
N <sub>1</sub> -N <sub>4</sub> -C <sub>3</sub> -H <sub>11</sub>	121.7	C <sub>1</sub> -C <sub>4</sub> -C <sub>3</sub> -H <sub>11</sub>	119.9	-	-
N <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub> -H <sub>9</sub>	-112.1	C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub> -H <sub>9</sub>	-114.8	-	-
N <sub>4</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>9</sub>	115.7	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>9</sub>	113.8	-	-
C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	-66.5	C <sub>5</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>8</sub>	-62.6	-	-
C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub> -H <sub>9</sub>	170.9	C <sub>5</sub> -C <sub>1</sub> -C <sub>2</sub> -H <sub>9</sub>	171.1	-	-
C <sub>2</sub> -N <sub>1</sub> -C <sub>5</sub> -H <sub>6</sub>	32.8	C <sub>2</sub> -C <sub>1</sub> -C <sub>5</sub> -H <sub>6</sub>	32.1	-	-
C <sub>2</sub> -N <sub>1</sub> -C <sub>5</sub> -H <sub>7</sub>	174.4	C <sub>2</sub> -C <sub>1</sub> -C <sub>5</sub> -H <sub>7</sub>	175.5	-	-
N <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub> -H <sub>8</sub>	117.3	C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub> -H <sub>8</sub>	118.9	-	-
H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	-130.6	H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	-126.3	-	-
H <sub>9</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	0.0	H <sub>9</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	0.0	-	-
H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>11</sub>	0.0	H <sub>8</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>11</sub>	0.0	-	-
-	-	H <sub>12</sub> -C <sub>1</sub> -C <sub>4</sub> -H <sub>13</sub>	0.0	-	-
-	-	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>13</sub>	140.9	-	-
-	-	H <sub>10</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>13</sub>	27.2	-	-
-	-	H <sub>11</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>13</sub>	-99.1	-	-
-	-	C <sub>3</sub> -C <sub>4</sub> -C <sub>1</sub> -H <sub>12</sub>	138.9	-	-
-	-	H <sub>7</sub> -C <sub>5</sub> -C <sub>1</sub> -H <sub>12</sub>	12.9	-	-
-	-	H <sub>6</sub> -C <sub>5</sub> -C <sub>1</sub> -H <sub>12</sub>	-130.5	-	-



**TABLE4:-** The theoretical vibrational frequencies, IR intensities and Raman activity with assignment for the 24 normal modes of the DABCP 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
v <sub>1</sub>	A'	488	3.40	2.60	Envelop Flap + $\rho$ CH <sub>2</sub> (1-br)
v <sub>2</sub>		658	0.38	7.30	v <sub>s</sub> NN
v <sub>3</sub>		792	0.96	1.46	$\rho$ CH <sub>2</sub> (+) (2-br)
v <sub>4</sub>		949	13.14	14.41	Ring elongation(dt)+ $\rho$ CH <sub>2</sub> (1-br)
v <sub>5</sub>		1005	2.27	21.42	v <sub>s</sub> C-C
v <sub>6</sub>		1104	2.96	5.62	$\rho$ CH <sub>2</sub> (+) (2-br)+ $\rho$ CH <sub>2</sub> (1-br)
v <sub>7</sub>		1204	4.66	7.34	$\rho$ CH <sub>2</sub> + Ring elongation (dt)
v <sub>8</sub>		1265	12.67	8.31	$\rho$ CH <sub>2</sub> (+) (2-br)+ v <sub>s</sub> NCN + Ring def.(dt)
v <sub>9</sub>		1321	2.16	3.22	$\omega$ CH <sub>2</sub> (+)(2-br) + v <sub>s</sub> C-C+Ring breath(dd)
v <sub>10</sub>		1508	0.60	8.40	$\delta$ CH <sub>2</sub> (+) (2-br)+ $\delta$ CH <sub>2</sub> (1-br)
v <sub>11</sub>		1528	3.08	2.82	$\delta$ CH <sub>2</sub> (+) (2-br)+ $\delta$ CH <sub>2</sub> (1-br)
v <sub>12</sub>		3042	45.68	127.88	v <sub>s</sub> CH <sub>2</sub> (+)(2-br)
v <sub>13</sub>		3063	32.44	133.57	v <sub>s</sub> CH <sub>2</sub> (1-br)
v <sub>14</sub>		3126	33.75	93.94	v <sub>as</sub> CH <sub>2</sub> (+)(2-br)
v <sub>15</sub>		3177	11.92	104.07	v <sub>as</sub> CH <sub>2</sub> (1-br)
v <sub>16</sub>	A''	297	4.18	0.23	Ring Pucker(dt)+ $\rho$ CH <sub>2</sub> (-)(2-br)
v <sub>17</sub>		765	3.01	1.60	Ring def.(dt)+ $\tau$ CH <sub>2</sub> (1-br)
v <sub>18</sub>		791	8.95	3.78	Ring def.(dd+dt)
v <sub>19</sub>		953	19.66	2.12	Ring def.(dt+dd)+ $\tau$ CH <sub>2</sub> (-)(2-br)
v <sub>20</sub>		1093	5.60	2.85	Ring puck.(dt)+ $\tau$ CH <sub>2</sub> (1-br)+ $\rho$ CH <sub>2</sub> (-)(2-br)
v <sub>21</sub>		1151	0.43	1.53	Ring puck.(dt)+ $\tau$ CH <sub>2</sub> (1-br) + $\rho$ CH <sub>2</sub> (-)(2-br)
v <sub>22</sub>		1189	2.34	1.00	$\omega$ CH <sub>2</sub> (1-br)
v <sub>23</sub>		1218	0.54	3.74	$\tau$ CH <sub>2</sub> (-) (2-br)
v <sub>24</sub>		1310	5.26	0.58	$\omega$ CH <sub>2</sub> (-) (2-br)
v <sub>25</sub>		1501	1.34	11.45	$\delta$ CH <sub>2</sub> (-) (2-br)
v <sub>26</sub>		3033	48.05	72.37	v <sub>s</sub> CH <sub>2</sub> (-)(2-br)
v <sub>27</sub>		3110	2.87	67.35	v <sub>as</sub> CH <sub>2</sub> (-)(2-br)

C<sub>5</sub>-N<sub>4</sub>-N<sub>1</sub>-C<sub>2</sub> in DABCP was smaller than the  $\theta < \theta < \theta$  in BCP molecules (108.8°, 113.4° respectively).

DABCP molecule consist of 11 atoms, therefore it contains 27 modes of fundamental vibrations. These modes are distributed into the irreducible representation under Cs symmetry as  $\Gamma_{\text{vib}} = 15A2 + 12A2$ . All the 27 fundamental vibrations are actively in both Raman scattering and Infrared absorption. The computed vibrational wavenumbers, IR intensities, Raman activity, with the complete assignment were summarized in TABLE 4. The DABCP molecule possesses three CH<sub>2</sub> groups, two of them existed in the diazetidine ring (2-bridge), and the remaining one belongs to the diaziridine ring (1-bridge). So it has

three CH<sub>2</sub> symmetric (v<sub>12</sub>, v<sub>13</sub>, v<sub>26</sub>) and three CH<sub>2</sub> asymmetric (v<sub>14</sub>, v<sub>15</sub>, v<sub>29</sub>) stretching vibrations. The normal modes v<sub>13</sub> (v<sub>s</sub> CH<sub>2</sub>) and v<sub>15</sub> (v<sub>as</sub> CH<sub>2</sub>) were related to the CH<sub>2</sub> vibration, which exist in diaziridine ring, Figure 7. While the other four modes belong to CH<sub>2</sub> group vibration in diazetidine ring, had the lowest wavenumber than the vibration of CH<sub>2</sub> in diaziridine ring. The same behavior was seen cycloalkane hydrocarbons<sup>[22, 23]</sup>.

Abbreviations used; v<sub>as</sub> -asymmetric stretching; (1-br)-1-bridge(N<sub>3</sub>); (2-br)-2-bridge(N<sub>2</sub>-N<sub>3</sub>) def-deformation; dd-diaziridine; dt-diazetidine; (+)-in-phase;  $\gamma$ -out-of-plane bending; (-)-out-phase;  $\rho$ -rocking;  $\delta$ -scissoring; v-stretching; v<sub>s</sub>-symmetric stretching; v-twisting;  $\tau$ -wagging.

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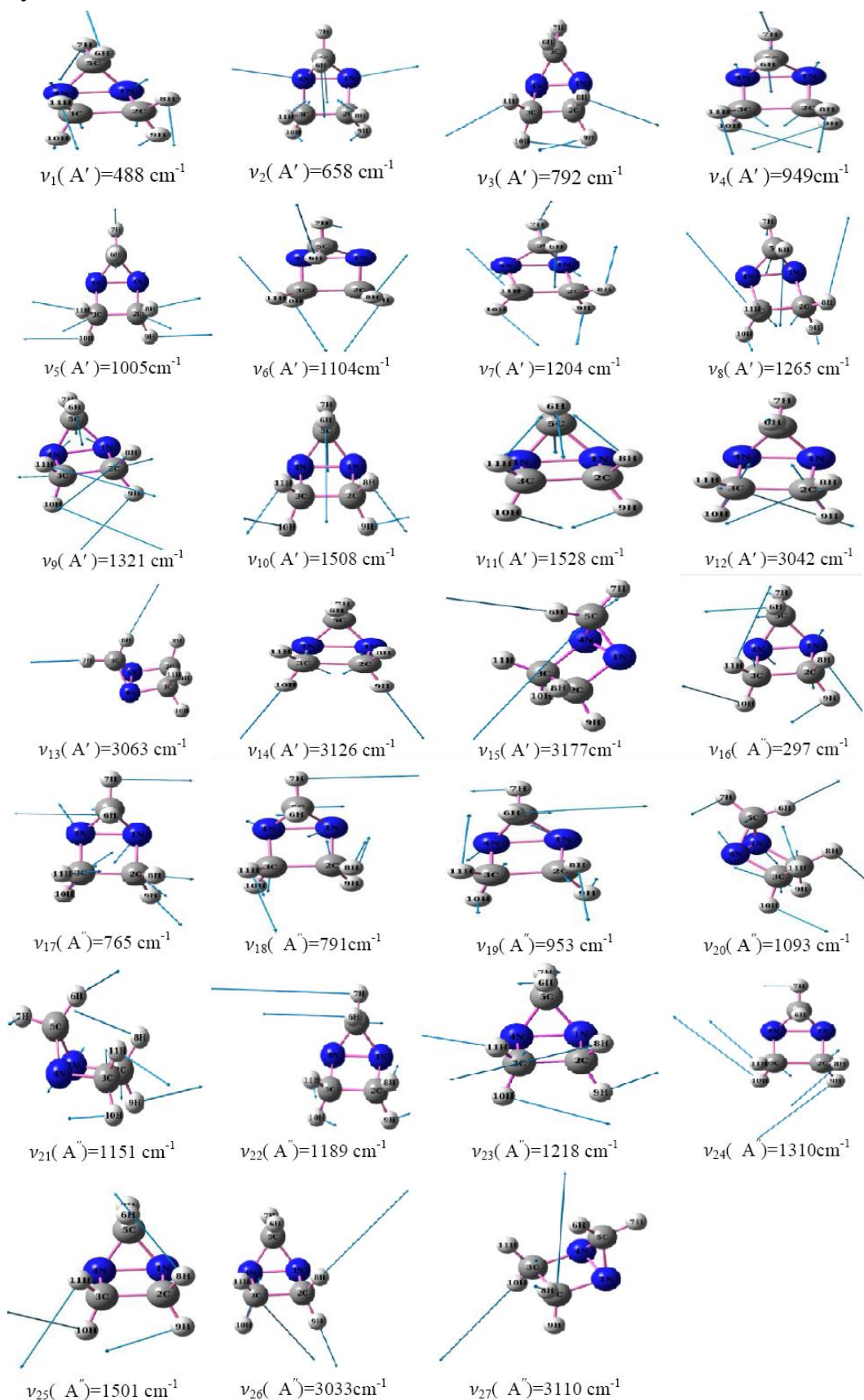


Figure 7 : The displacement vectors, wavenumber, and symmetries of the eighteen normal model of DABCP molecule

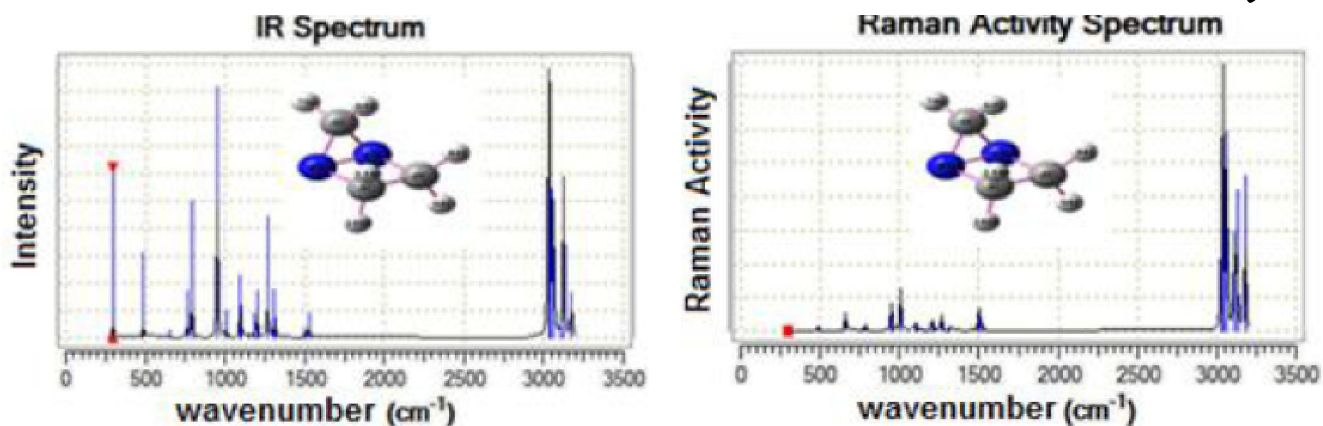


Figure 8 : The calculated (a) Infrared, and (b) Raman spectrum of DABCP molecule

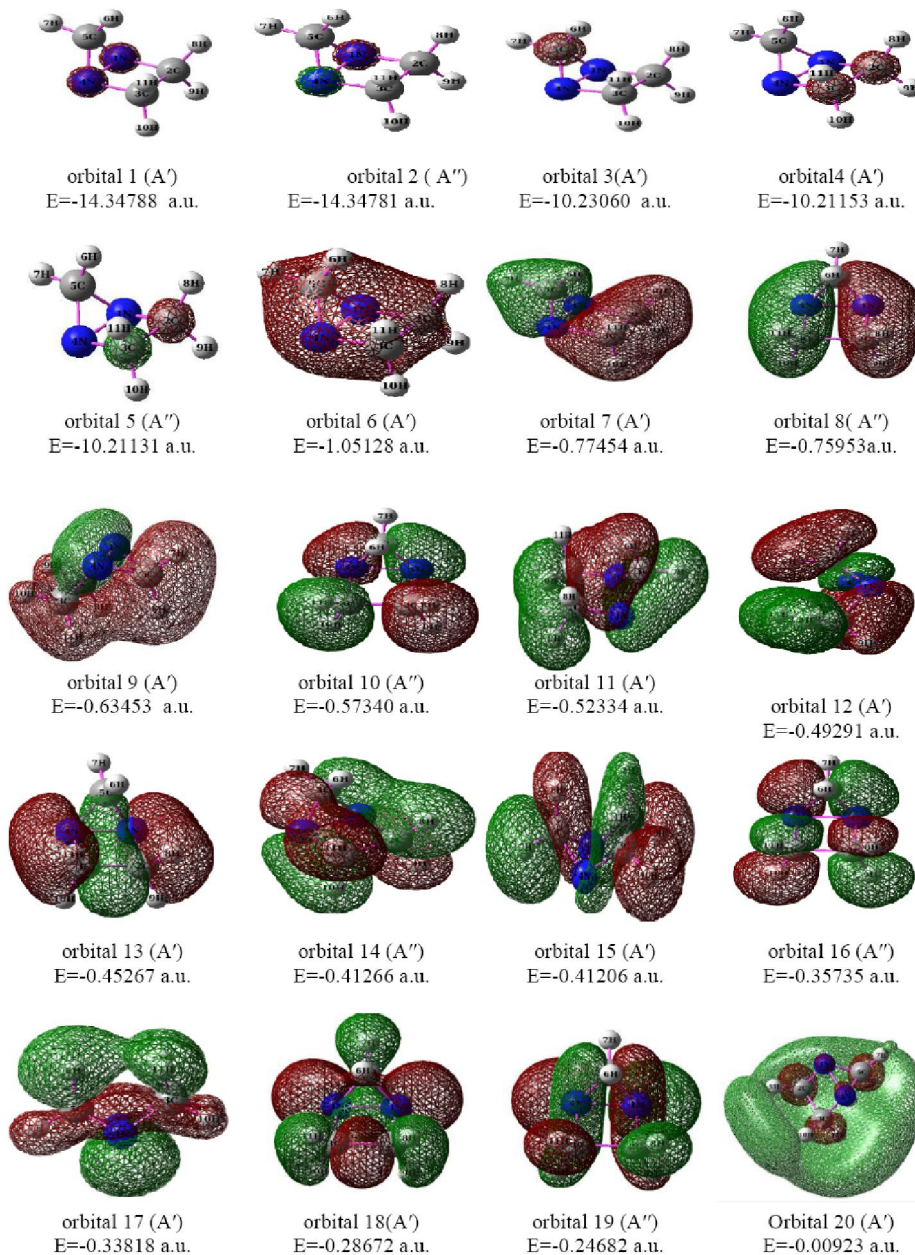


Figure 9 : The calculate energy, shape, symmetry of (bonding and LUMO)molecular orbitals for DABCP molecule



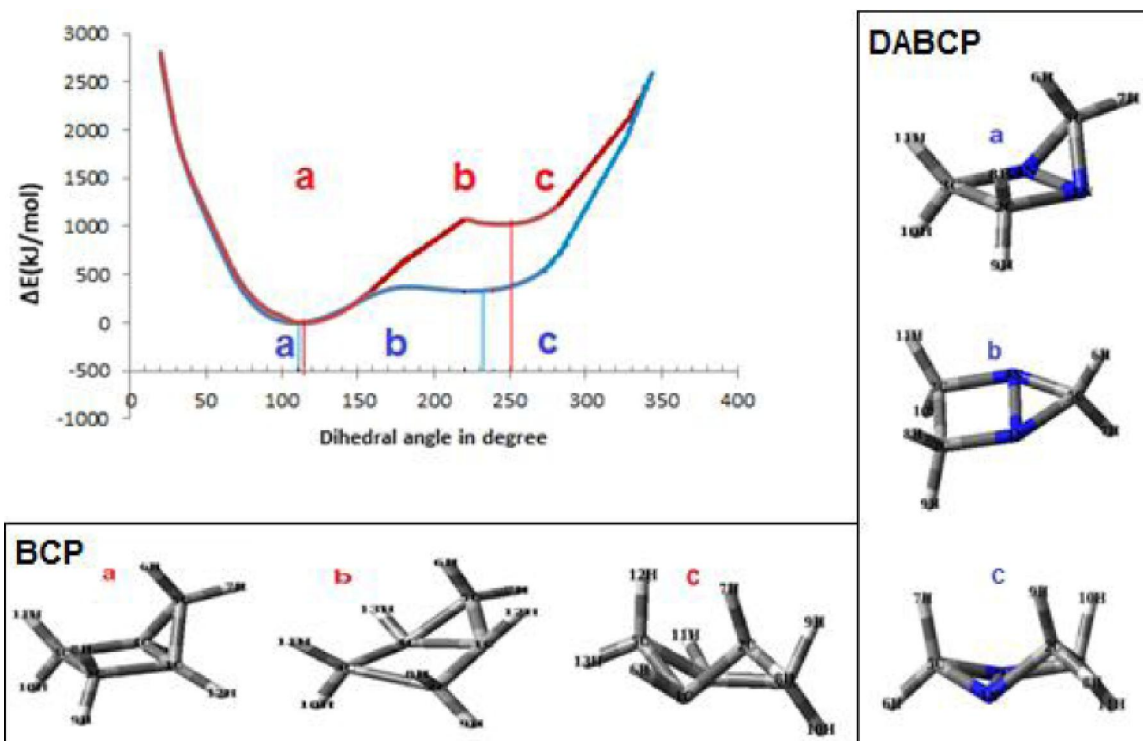


Figure 10 : Potentail energy curves for DABCP(blue), and BCP (red) molecules

TABLE 5 : The calculated energy of the four molecules under study

BCP	DABCP	BCB	DABCB	Molecule
-418328.53	-596975.32	409554.12-	493732.85-	Total energy kJ mol <sup>-1</sup>

Figure 9, depicted the shapes, and the values of the calculated energies for DABCP molecular orbitals. The energy for frontier molecular orbitals ( $E_{\text{HOMO}}$ , and  $E_{\text{LUMO}}$ ) were -0.247 and -0.009 a.u. consequently. The LUMO-HOMO energy gap was 0.238 a.u., which reflect the chemical activity of the molecule. The Figure elucidated that the HOMO localized at the nitrogen atoms, while the LUMO localized at all the rings atoms.

The potential energy curves (drawn as mentioned for DABCP and BCP molecules) which revealed by changing the dihedral angle ( $\theta$ ) ( $C_2-N_1-N_4-C_3$ ), and ( $C_2-C_1-C_4-C_5$ ) respectively, from 20° to 340°, Figure 10. The asymmetrical potential energy curve shows two minimum and one maximum.

In DABCP molecule the first minimum corresponded to the envelop conformation (a) at  $\theta$  equal 108.8°. The second minimum at 230° which matched the twist conformation (c), with energy of 333.4 kJ mol<sup>-1</sup> above the envelop form. The maximum energy appeared at 180°, which mean it form planar (b) with

372.8 kJ mol<sup>-1</sup> higher than the energy of envelops conformation. The stability of the three conformations for the DABCP molecule can be arranged in the following order envelop > twist > planar.

The potential energy curve of the BCP molecule, revealed three conformations, Figure 10. The most stable envelop form (a), and a shallow minimum conformation (c) occurred at the angles 113.4°, and 250° respectively, with the energy difference of 1023.9 kJ mol<sup>-1</sup>. The maximum semi-planar conformation (b) appeared at 220°, its energy 1068.6 kJ mol<sup>-1</sup> above the envelop conformation.

The computed total energies for the molecules under study were presented in TABLE 5. The total energy of BCB > DABCB, and BCP > DABCP. This can be attributed to the introduction of aza nitrogen in to the strained ring. Murray et al.<sup>[13]</sup> mentioned that increasing the number of nitrogen atoms in any cyclo strained series rising the molecular stability, due to lone pair  $\sigma$ -conjugation.



## CONCLUSION

Since the available data for the DABCB and DABCP molecules are rare this computational study is more proper for studying the structures, vibrational spectra and conformational analysis.

According to this theoretical calculation, the conclusion can be summarized in:

1- The calculated vibrational spectra for DABCB and DABCP molecules with reliable assignment revealed that the CH<sub>2</sub> stretching vibration (symmetric and asymmetric) for diaziridine ring occurs at a higher wavenumber than diazetidine ring.

2- The puckered conformations for (DABCB, BCB molecules) and the envelop for (DABCB, BCB molecules) were the most stable. The smallest value of the dihedral angles ( $\theta_{\text{DABCB}} = 114.1^\circ < \theta_{\text{BCB}} = 122.0^\circ$ ), and ( $\theta_{\text{DABCP}} = 108.8^\circ < \theta_{\text{BCP}} = 113.4^\circ$ ) caused by the lone pair of electrons for N-atoms.

3- The total energy of *BCB > DABCB and BCP > DABCP* molecules, this may be related to the introduce of aza nitrogen into the cyclic rings. This stability owing to lone pair  $\sigma$ -conjugation.

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