Chapter IV

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CHAPTER - IV

4.1 Introduction

The infrared, microwave and NMR spectroscopic studies were reported for various allyl derivatives substituted in the 3-position (CH$_2$CHCH$_2$X (X=F, Cl, Br and I))$^{14}$, the alcohol$^{5}$, the thiol$^{6}$, the amine$^{7-10}$ and the nitrile$^{11,12}$, the conformational energies had also been calculated by MO calculations. These studies revealed that these compounds normally exist as a mixture of two conformers viz. cis and gauche in the liquid and vapour phase. The NMR spectroscopic measurements of 3-halopropenes by Bothner-By et al$^{13}$ have shown that the 3-halopropenes exist in cis and skew forms. Recently van der Vaken et al$^{13}$ have studied the structure and conformational energies of 3-fluoropropene molecule by FT-IR and ab initio calculation. The NCO moiety contained in the isocyanate have chemical properties similar to the halides, called pseudohalides along with cyanides and thiocyanates$^{15}$. It would be an interesting subject to investigate the conformational behaviour when a NCO group is substituted in the methyl carbon position. It is expected that more than one conformer would be arise as a result of the rotation around the C-C and C-N bonds. The Infrared spectra and microwave spectrum$^{15,16}$ of allyl isocyanate (CH$_2$=CHCH$_2$NCO) molecule have been reported and this molecule would be exist in number of conformations with the dihedral angles C=C-C-N (δ) and C-C-N=C (θ). Torgrimsen et al$^{15}$ have predicted the existence of a cis conformer in the solid state and gauche form in the liquid and vapour phases.

The measurement of microwave spectrum by Maiti et al$^{16}$ have shown the existence of the C-gauche (δ=120° and θ=0°) conformer in allyl isocyanate in the vapour phase. The microwave studies of methyl isocyanate revealed the low barrier to internal
rotation, equal to 0.36 ± 0.06 KJ/mol. The recent studies on structure and conformational
stability of CH₂CHCH₂X(X=F, Cl and Br) molecules reveal that the HF/6-31G* and
MP2/6-31G* levels of theory have predicted the cis conformer as the minimum energy
structure for 3-fluoropropene, which is in agreement with the experimental values where
as BLYP/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels of theory reverses the order of
conformation. The ΔE values calculated in the chapter 3 for 3-chloropropene and
3-bromopropene at MP2/6-31G*, BLYP/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels
of theory show that gauche form is more stable than the cis form which is in agreement
with the experimental value.

The structure and conformational stability of XC(O)OY (X, Y= F and Cl)
molecules have been studied using ab initio and DFT methods. The higher levels of electron-correla-
tion methods could predict the experimental conformational energy of FC(O)OF molecule. The DFT methods BLYP/6-311+G(2d,2p)
and BLYP/6-311++G(3pd,3df) levels of theory have reversed the conformational stability.
Even though the exchange correlation functionals are well defined in the DFT methods,
still the problem has occurred for many molecules. Though many experimental studies
have been reported for the halogen and pseudohalide substituted propenes, a limited
number of theoretical studies have been reported in the literature. So the aim of the
present investigation is (i) to study the possible conformations of allyl isocyanate arising
due to the internal rotation of C-C and N-C bonds (ii) to determine the structural and
physical parameters of the various conformers (iii) to study the role of chemical hardness
η and chemical potential μ in the conformational stability of the allylisocyanate
molecule.
4.2 Computational details

The calculations were performed with Gaussian 94W programme\textsuperscript{19}. The geometries were optimized using restricted Hartree-Fock (RHF), second order Møller Plesset perturbation theory (MP2)\textsuperscript{20} of ab initio method and BLYP, B3LYP, BPW91 and B3PW91 methods of DFT for C-gauche ($\delta=120^\circ, \theta=0^\circ$) and C-cis N-trans ($\delta=0^\circ, \theta=180^\circ$) forms of the allyl isocyanate molecule. The 6-31G* basis set was used in HF and MP2 methods. Becke’s exchange functional combined with gradient corrected functional of Lee, Yang and Parr (BLYP)\textsuperscript{21}, Becke’s exchange functional combined with Perdew and Wang’s 1991 gradient corrected correlation functional (BPW91)\textsuperscript{22}, Becke’s three parameter exact exchange-functional combined with gradient corrected functional of Lee, Yang and Parr (B3LYP)\textsuperscript{23} and Becke’s three parameter exact exchange-functional combined with Perdew and Wang’s 1991 gradient corrected correlation functional (B3PW91)\textsuperscript{22} were used implementing 6-311+G(d,p) basis set. The potential energy surface scan (PES) were performed at HF/6-31G* and MP2/6-31G* levels of theory. The dihedral angle C=C-C-N is varied in steps of 30° between ($|\phi|\geq 0$ and $\phi<180^\circ$, keeping $\theta=0^\circ$. The minimum energy C-gauche conformer was obtained at ($\delta=120^\circ, \theta=0^\circ$). The dihedral angle C=C-C-N is kept constant at $0^\circ$, the PES was performed by changing the $\theta$ values from $0^\circ$ to $180^\circ$ in steps of 30°. The minimum energy structure was obtained at $\delta=0^\circ, \theta=180^\circ$ which corresponds to C-cis N-trans conformer.

The six-term truncated Fourier expansion\textsuperscript{24,25} was used to derive the potential function for the internal rotation.

$$V(\phi) = \sum_{i=1}^{6} \frac{1}{2} V_i (1 - \cos(i\phi))$$

$V(\phi)$ is the relative energy at the rotational angle $\phi$ with the cis form defined as an origin ($\phi = 0$).
The chemical hardness ($\eta$) and chemical potential ($\mu$) were calculated and are defined as

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{\nu(r)} \quad \text{and} \quad \eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_{\nu(r)}$$

where $E$ is the total energy, $\nu(r)$ is the external potential, and $N$ is the number of electrons. In a finite difference approximation, with the assumption that the energy varies quadractically with the number of electrons, these two quantities can be expressed with an orbital basis set as

$$\eta = \frac{I - A}{2} \quad \text{and} \quad \mu = \frac{I + A}{2}$$

where $I$ is the ionization potential and $A$ is the electron affinity of a system.

4.3 Results and discussions

4.3.1 Geometry

The calculated geometrical parameters, rotational constants, dipole moment and total energy of the C-gauche ($\delta = 120^\circ, \theta = 0^\circ$) form of allyl isocyanate are listed in table 4.1. Since there was no experimental and theoretical structural data available for this molecule, the structural parameters of the related molecules methyl isocyanate and 3-fluoropropene were used for the comparison. The microwave adjusted C-N, N=C, C=O and C-H bond distances of the methylisocyanate molecule are 1.44Å, 1.207Å, 1.171Å and 1.091Å respectively. The calculated C-N bond distance of allylisocyanate is found to be in agreement with the C-N bond distance of methylisocyanate at HF and B3PW91 levels of theory and for the same bond, the difference is very high at BLYP/6-311+G(d,p) level of theory. For N=C and C=O bond distances B3LYP/6-311+G(d,p) and B3PW91/6-311+G(d,p) levels of theory reproduced the experimental values of methylisocyanate molecule. The microwave adjusted C=C, C-C...
Fig. 4.1. Schematic diagram of Allyl isocyanate.
Table 4.1. Geometrical parameters (bond distances in Å, bond angles in degree), rotational constants (in GHz), dipole moment (in Debye), and total energies (in Hartree) of C-gauche form of allylisocyanate molecule.

(The values in paranthesis is the Expt. values taken from ref. 17)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>MP2/6-31G*</th>
<th>BLYP/6-31G*</th>
<th>BPW91/6-311+G(d,p)</th>
<th>B3LYP/6-311+G(d,p)</th>
<th>B3PW91/6-311+G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Distances (Å)</td>
<td>MP2/6-31G*</td>
<td>BLYP/6-31G*</td>
<td>BPW91/6-311+G(d,p)</td>
<td>B3LYP/6-311+G(d,p)</td>
<td>B3PW91/6-311+G(d,p)</td>
</tr>
<tr>
<td>R(C-H)</td>
<td>1.077</td>
<td>1.092</td>
<td>1.086</td>
<td>1.077</td>
<td>1.085</td>
</tr>
<tr>
<td>R(C-C)</td>
<td>1.331</td>
<td>1.344</td>
<td>1.348</td>
<td>1.338</td>
<td>1.339</td>
</tr>
<tr>
<td>R(C-C)</td>
<td>1.500</td>
<td>1.504</td>
<td>1.504</td>
<td>1.504</td>
<td>1.489</td>
</tr>
<tr>
<td>θ(C-C-C)</td>
<td>116.9</td>
<td>116.7</td>
<td>116.8</td>
<td>116.8</td>
<td>117.0</td>
</tr>
<tr>
<td>θ(C-C-N)</td>
<td>124.1</td>
<td>124.0</td>
<td>124.1</td>
<td>124.0</td>
<td>124.0</td>
</tr>
<tr>
<td>θ(C-N-C)</td>
<td>113.5</td>
<td>113.4</td>
<td>113.5</td>
<td>113.5</td>
<td>113.5</td>
</tr>
<tr>
<td>θ(C-N-C)</td>
<td>136.6</td>
<td>136.6</td>
<td>136.6</td>
<td>136.6</td>
<td>136.6</td>
</tr>
<tr>
<td>Dipole moment (Debye)</td>
<td>MP2/6-31G*</td>
<td>BLYP/6-31G*</td>
<td>BPW91/6-311+G(d,p)</td>
<td>B3LYP/6-311+G(d,p)</td>
<td>B3PW91/6-311+G(d,p)</td>
</tr>
<tr>
<td>Total energy (-283+E) Hartree</td>
<td>0.609724</td>
<td>3.28</td>
<td>2.99</td>
<td>3.33</td>
<td>3.41</td>
</tr>
</tbody>
</table>

(283+E) Hartree
and C-H bond distances of cis-3-fluoropropene molecule are 1.333Å, 1.494Å and 1.100Å respectively. The MP2/6-31G*, BLYP/6-311+G(d,p) and BPW91/6-311+G(d,p) levels of theory have predicted the C=C bond distances, which are coincide with the C=C bond distance of 3-fluoropropene molecule. The calculated C=N-C bond angle of allylisocyanate at B3LYP/6-311+G(d,p) and B3PW91/6-311+G(d,p) levels of theory almost reproduced the experimental value of methylisocyanate. The microwave results of allylisocyanate molecule has shown that the NCO moiety is linear, but in the present study it has been found that N=C=O bond angle is 173° at all levels of theory. The H-C-H and C-C=C bond angles of 3-fluoropropene molecule are 108.0° and 123.6° respectively. The H-C-H bond angle of allyl isocyanate is found to be higher compared to that of 3-fluoropropene molecule.

The geometrical parameters rotational constants, dipole moment and total energy of the C-cis N-trans (δ=0°,θ=180°) at various levels of theory are listed in table 4.2. The C-H and C=C bond distances of C-cis N-trans conformer are found to be decreased compared to C-gauche conformer of allylisocyanate molecule. The difference between the C-N bond distance of C-cis N-trans and C-gauche conformer is found to be minimum. This indicates the nonbonding interaction of N-atom with the H atom is increased due to the internal rotation of C-N bond. The N=C bond distance found to be higher than that of C-gauche conformer, but there is not much difference is observed between the C=O bond distances of the two conformers. The theories for the lone pair electrons are still not well resolved both at ab initio and DFT methods. So the bond angles and the bond distances near to the lone pair electrons could not be obtained very accurately.
Table 4.2. Geometrical parameters (bond distances in Å, bond angles in degree), rotational constants (in GHz), dipole moment (in Debye), total energies (in Hartree) and relative energies (in KJ/mol) of C-cis N-trans form of allylisocyanate molecule. (The values in paranthesis is the Expt. values taken from 17).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HF/6-31G*</th>
<th>MP2/6-31G*</th>
<th>BLYP/6-311+G(d,p)</th>
<th>B3LYP/6-311+G(d,p)</th>
<th>BPW91/6-311+G(d,p)</th>
<th>B3PW91/6-311+G(d,p)</th>
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<tbody>
<tr>
<td>r(C1-H)</td>
<td>1.074</td>
<td>1.083</td>
<td>1.090</td>
<td>1.084</td>
<td>1.090</td>
<td>1.084</td>
</tr>
<tr>
<td>r(C2-H)</td>
<td>1.075</td>
<td>1.085</td>
<td>1.091</td>
<td>1.083</td>
<td>1.091</td>
<td>1.084</td>
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<tr>
<td>r(C═C2)</td>
<td>1.316</td>
<td>1.319</td>
<td>1.328</td>
<td>1.328</td>
<td>1.335</td>
<td>1.329</td>
</tr>
<tr>
<td>r(C1-C2)</td>
<td>1.503</td>
<td>1.498</td>
<td>1.512</td>
<td>1.503</td>
<td>1.506</td>
<td>1.504</td>
</tr>
<tr>
<td>r(C2-H)</td>
<td>1.078</td>
<td>1.088</td>
<td>1.094</td>
<td>1.088</td>
<td>1.094</td>
<td>1.087</td>
</tr>
<tr>
<td>r(C3-H)</td>
<td>1.086</td>
<td>1.095</td>
<td>1.101</td>
<td>1.097</td>
<td>1.103</td>
<td>1.097</td>
</tr>
<tr>
<td>r(C3-H)</td>
<td>1.086</td>
<td>1.096</td>
<td>1.103</td>
<td>1.097</td>
<td>1.107</td>
<td>1.097</td>
</tr>
<tr>
<td>r(C3-N)</td>
<td>1.441</td>
<td>1.445</td>
<td>1.454</td>
<td>1.446</td>
<td>1.449</td>
<td>1.445</td>
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<tr>
<td>r(N=C)</td>
<td>1.182</td>
<td>1.216</td>
<td>1.202</td>
<td>1.200</td>
<td>1.203</td>
<td>1.199</td>
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<tr>
<td>r(C=O)</td>
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<td>1.190</td>
<td>1.185</td>
<td>1.173</td>
<td>1.175</td>
<td>1.173</td>
</tr>
<tr>
<td>(\angle CH_{1}H)</td>
<td>117.2</td>
<td>117.4</td>
<td>117.5</td>
<td>117.7</td>
<td>117.5</td>
<td>117.8</td>
</tr>
<tr>
<td>(\angle C_{2}C_{2}C_{3})</td>
<td>126.2</td>
<td>125.7</td>
<td>125.9</td>
<td>125.8</td>
<td>125.9</td>
<td>125.8</td>
</tr>
<tr>
<td>(\angle HC_{2}H)</td>
<td>120.3</td>
<td>120.1</td>
<td>120.3</td>
<td>120.3</td>
<td>120.4</td>
<td>120.3</td>
</tr>
<tr>
<td>(\angle C_{3}C_{2}N)</td>
<td>112.4</td>
<td>112.1</td>
<td>112.7</td>
<td>112.6</td>
<td>112.6</td>
<td>112.7</td>
</tr>
<tr>
<td>(\angle C_{3}C_{3}N)</td>
<td>141.0</td>
<td>136.2</td>
<td>137.9</td>
<td>139.0</td>
<td>137.8</td>
<td>139.1</td>
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<tr>
<td>(\angle NCO)</td>
<td>175.0</td>
<td>172.7</td>
<td>173.1</td>
<td>174.0</td>
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</tr>
<tr>
<td>Dihedral angles</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(\angle C_{1}C_{2}C_{3}N)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1.7365</td>
<td>1.6841</td>
<td>1.6987</td>
<td>1.7069</td>
<td>1.6897</td>
<td>1.7062(1.8636)</td>
</tr>
<tr>
<td>C</td>
<td>1.5545</td>
<td>1.5189</td>
<td>1.5208</td>
<td>1.5317</td>
<td>1.5198</td>
<td>1.5351(1.6003)</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>3.08</td>
<td>3.11</td>
<td>2.82</td>
<td>2.93</td>
<td>2.84</td>
<td>2.98</td>
</tr>
<tr>
<td>Total energy (-283+E)</td>
<td>0.669568</td>
<td>1.508035</td>
<td>2.383145</td>
<td>2.469270</td>
<td>2.436777</td>
<td>2.350198</td>
</tr>
<tr>
<td>Relative energy (\Delta E)</td>
<td>-0.410</td>
<td>0.559</td>
<td>0.761</td>
<td>1.160</td>
<td>1.026</td>
<td>1.095</td>
</tr>
</tbody>
</table>
4.3.2 Torsional Potential

The HF/6-31G* and MP2/6-31G* levels of the theory have been employed for the potential energy surface scan and the conformational energy were obtained for allylisocyanate molecule. The HF/6-31G* level of the theory has predicted the C-gauche conformer is found to be the most stable than C-cis N-trans conformer of allyl isocynate by 409.5 J/mol. But the MP2/6-31G*, BLYP, B3LYP, BPW91 and B3PW91 levels of the theory have predicted that the C-cis N-trans conformer is found to be stable than C-gauche form by 0.559 kJ/mol, 0.761 kJ/mol, 1.16 kJ/mol, 1.026 kJ/mol and 1.10 kJ/mol respectively. The microwave studies of allyl derivatives (CH₂CHCH₂X)¹⁴ have established that the molecules exist in cis and gauche conformations. In the related molecules, N-methylene-methylamine²⁸ has the barrier 8.23 kJ/mol and methylketene²⁹ has the barrier 4.92 kJ/mol and all have a preferred cis conformation. The microwave studies²⁶ of methylisocyanate and methylisothiocyanate revealed barriers to internal rotation are 0.35±0.06 kJ/mol and 1.27±0.2 kJ/mol. This low barrier is because of the free rotation of the methyl group at room temperature. If the barrier to internal rotation of C-N bond was assumed to be very low for the allyl isocyanate molecule then the possible conformers will be reduced to cis and gauche for allyl halides. The earlier study on FC(O)OF molecule¹⁸ has shown that the higher basis sets 6-311++G(2d,2p) and 6-311++G(3df,3pd) in BLYP levels of theory could not able to predict the correct conformational energy. Torgrimsen et al¹⁶ have reported for the allylisocyanate molecule that cis conformer is found to exists in the solid with additional gauche forms in the liquid and vapour phases. The microwave spectrum for C-gauche conformer of allyl isocyanate in the vapour phase have been reported¹⁶ and the same spectrum could not obtained for the
C-cis conformer due to the lower abundance in the vapour phase. The HF/6-31G* and MP2/6-31G* levels of theory have predicted the cis conformer as the minimum energy structure for 3-fluoropropene, which is in good agreement with the experimental values. The MP2/6-31G*, BLYP/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels of theory have predicted that the gauche form is more stable than the cis form, which is in agreement with the experimental value for 3-chloropropene. The same levels of theory have also predicted the gauche form more stable than cis for 3-bromopropene molecule.

We would expect three fold barriers to internal rotation around the C-C as well as around the C-N bonds and the present compounds therefore represents complicated conformation problems. We might in principle consider five non-equivalent conformations in allylisocyanate and allyl isothiocyanate resulting form rotations around the C-C and C-N bonds. However if we assume a very low barrier to internal rotation the five conformers will be reduced to only two cis and gauche in complete correspondence.

The potential function governing the internal rotation of C-C bond of C-gauche conformer at HF/6-31G* and MP2/6-31G* levels of theory are given in figure 4.2. The Fourier fitted torsional potential of C-gauche allyl isocynate has been obtained at HF/6-31G* and MP2/6-31G* levels of theory and the potential coefficients were calculated. The $V_3$ parameter is found to be maximum value may be due to strong interaction of NCO with H atom. The calculated Fourier decomposition of the torsional potential at MP2/6-31G* levels of theory is plotted in figure 4.3. The potential function governing the internal rotation of N-C bond of C-cis N-trans conformer at HF/6-31G* and MP2/6-31G* levels of theory are given in figure 4.4. The Fourier torsional potential
Figure 4.2. Potential function governing the internal rotation of C-C bond of c-gauche allyl isocyanate.
Figure 4.3. Fourier decomposition potential of internal rotation of C-C bond of allyl isocyanate at MP2/6-31G* level of theory.
Figure 4.4. Potential function governing the internal rotation of the C-N bond of C-cis N-trans allylisocyanate.
parameters have been calculated and $V_2$ parameter is found to be high for this conformer. The calculated Fourier decomposition of torsional potential at MP2/6-31G* level of theory is plotted in figure 4.5.

4.3.3 Dipolemoment

The dipolemoment calculated for C-gauche form of allyl isocyante is given in table 4.1. The dipolemoment measured in the microwave spectrum by Curl30 for the methyl isocyanate is $2.81 \pm 0.6$ Debye. The microwave measurement of dipolemoment for the 3-fluoropropene molecule is only $1.91$ Debye. The calculated dipolement values for C-gauche allyl isocyanate at ab initio and DFT methods predicted higher than methyl isocyanate and 3-fluoropropene molecules. The dipolements values for the C-cis N-trans form of allyl isocyanate is also found to be greater than the value of methyl isocyanate and 3-fluoropropene. The dipolement value of C-gauche conformer is found to be higher than C-cis N-trans conformer. Griffith et al12 have found the gauche conformer to be more polar than the cis for the related cyanide molecules. In the present investigation also the dipolemoments of C-gauche conformer is found to be more than the C-cis N-trans conformer in all levels of theory. The lower value of dipolemoment of C-cis N-rans indicates that this conformer is less polar and therefore be relatively more stable in the vapour phase as well as in the polar solvents. The microwave studies also confirmed the C-cis is the more abundant conformer of the vapour.

4.3.4 Rotational constants

The rotational constants calculated for the both conformers of allyl isocyanate is listed in the tables 4.1 and 4.2. The experimental values calculated by Maiti et al16 for the C-gauche conformer is $A= 8.0198$ GHz, $B= 2.0889$ GHz and $C= 1.7574$ GHz. The calculated
Fig. 4. Fourier decomposition of internal rotation of N-C bond of C-cis N-trans allylisocyanate at MP2/6-31G* level of theory.
Figure 4.6. Rotational constants as a function of dihedral angle of C-gauche form of allyl isocyanate at MP2/6-31G* level of theory.
Fig. 4.7. Rotational constants as a function of dihedral angle at MP2/6-31G* level of theory for C-cis N-trans allyl isocyanate.
rotational constants at ab initio and DFT methods agree well with experimental values for B and C rotational constants and the average error is found to be 0.7 GHz for rotational constant A. The same trend has been obtained for the C-cis N-trans conformer, where the A value has been overestimated by 3 GHz. The rotational constants calculated for different dihedral value of $\delta$ (C=C-C-N), varied from 0° to 180° at an interval of 30° is plotted in the figure 4.6 for the C-gauche conformer. The dihedral angle $\theta$ (C-C-N=C) has been varied form 0° to 180° at an interval 30° for the C-cis N-trans conformer and is plotted in figure 4.7.

4.3.5 Chemical hardness and chemical potential

The chemical hardness $\eta$ and chemical potentials of C-gauche and C-cis N-trans conformers of allyl isocynate molecule were calculated and are listed in table 4.3. The HF/6-31G* levels of theory predicts that C-cis N-trans ($\delta=0, \theta=180^\circ$) conformer is found to be more stable than C-gauche ($\delta=120, \theta=0^\circ$) conformer. But the chemical hardness value calculated at MP2/6-31G* levels of theory predicts that C-gauche conformer is more stable than the C-cis N-trans conformer. According to the maximum hardness principle (MHP), the most stable conformer (the minimum energy structure) should have maximum hardness value. This is failed at HF/6-31G* level of theory and reversed the conformational stability of the molecule. The maximum hardness principle at MP2/6-31G* level of theory predicted the minimum energy structure correctly. The same situation happened for 3-chloro propane and 3-bromo propane molecules where the hardness calculated at the HF/6-31G* level of theory fails to predict the minimum energy conformer, while MP2/6-31G* level of theory predicted the minimum energy conformer.
Table 4.3. Calculated chemical hardness $\eta$ and chemical potential $\mu$ of allylisocyanate molecule (both in eV).

<table>
<thead>
<tr>
<th></th>
<th>Chemical hardness $\eta$</th>
<th>Chemical potential $\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF/6-31G*</td>
<td>MP2/6-31G*</td>
</tr>
<tr>
<td>C-gauche</td>
<td>7.43</td>
<td>7.31</td>
</tr>
<tr>
<td>C-cis N-trans</td>
<td>7.49</td>
<td>7.27</td>
</tr>
</tbody>
</table>
4.4 Conclusions

The geometrical and physical parameters of C-gauche and C-cis N-trans conformers of allyl isocyanate molecule have been determined at HF/6-31G*, MP2/6-31G* of ab initio method and BLYP, B3LYP, BPW91 and B3PW91 methods of DFT employing the 6-311+G(d,p) basis set and were discussed with the experimental values of the related molecules methylisocyanate and 3-fluoropropene. In the present investigation the bond distance and the bond angles near the lone pair electrons could not be obtained very accurately. The N=C=O bond angle is found to be 173°, whereas the bond angle is established as linear in the experiment. The HF/6-31G* level of theory predicted the C-gauche conformer is more stable than the C-cis N-trans conformer by 0.41 KJ/mol, but the MP2 and DFT methods predicted the C-cis N-tans conformer is more stable.

The calculated chemical hardness η value at HF/6-31G* level of theory reverses the conformational order while MP2/6-31G* level of theory predicted correctly the minimum energy conformer.
References
