

A Density Functional and Molecular Orbital Study of the Physical Processes  
of the conformational Isomerism of Methylamine, H<sub>3</sub>C–NH<sub>2</sub> Molecule.

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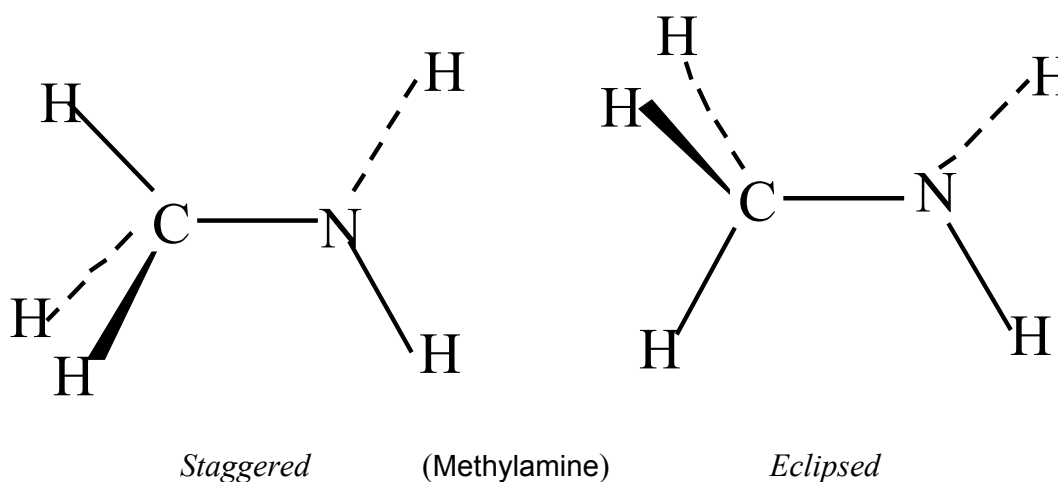
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ABSTRACT:

A density functional and molecular orbital study of the physical processes of the conformational isomerism of methylamine, H<sub>3</sub>C–NH<sub>2</sub> molecule is performed. We have seen that the profiles of the molecular orbital and density functional parameters are quite efficient in depicting the fluctuation of structural situation under torsional variables and following the dynamics of internal rotation of the methylamine molecule. In our quest of the origin of barrier to internal rotation, we have invoked the method of energy partitioning analysis and have made a detailed study of the variation of the decomposed energy components as a function of torsional variables and the analysis of results suggest that nonbonded repulsion is not the origin of barrier and the barrier involves the whole skeleton of the molecule.

## INTRODUCTION:

Methylamine,  $\text{H}_3\text{C}-\text{NH}_2$  is a well-known chemical system for conformational study. There is one three-fold symmetry group at one end of the skeleton of the molecule. When the  $-\text{NH}_2$  group rotates around the 'C-N' bond keeping the  $\text{H}_3\text{C}-$  group fixed, staggered and eclipsed conformations arise periodically as a function of torsional variables. A rough sketch of the staggered and eclipsed structural isomeric forms of the molecule is presented below:-



The conformational isomerism of the molecule is studied extensively by experimental as well as theoretical methods<sup>1-8</sup>. From the perspective of conformational study, the molecule is an interesting system because there is a lone pair on 'N' atom to influence the conformational preference in methylamine system.

In the present day scenario of chemical thinking the conformational study is of prime importance in view of the fact that conformation has a critical effect on bio-activity and reactivity on the stereochemical outcome of many reactions, and an understanding of relative energies and conformation populations will enable more reasonable predictions concerning reactivity, stereochemistry, and product distribution in reaction<sup>9</sup>. Although the barrier height can be estimated very accurately by the experimental as well as theoretical methods, the origin of barrier is still eluding. An understanding

of the origin and development of the barrier to internal rotation within a molecule is very crucial and is of interest to theoretical, experimental, and biological chemists.

In this study we have invoked some theoretical parameters provided by the molecular orbital and density functional theories in order to study the dynamics of the internal rotation of methylamine system. The rotational isomerization process can be conveniently addressed by density functional theory, DFT because DFT is firmly based on electron density which changes continually under internal rotation satisfying the condition that the total electron remaining constant. Parr<sup>10</sup> et al and Parr and Pearson<sup>11</sup>, using the density functional theory, DFT<sup>12, 13</sup> as basis have rigorously defined the hardness and discovered a new fundamental quantity,  $\mu$ , the electronic chemical potential, as a new index of chemical reactivity. The method became really challenging after the enunciation of the maximum hardness principle Pearson<sup>14</sup>. Pearson<sup>14</sup> stated, “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible”, and Parr and Chattaraj<sup>15</sup> provided a theoretical justification of PMH. A number of further studies<sup>16</sup> have critically analyzed the statement of PMH and have justified it. Chattaraj<sup>17</sup> et al hold that chemical hardness has been out to be a cardinal index of molecular structure, reactivity, binding and dynamics. The global hardness since then has been an index of stability of molecular structure. When the molecule evolves from an unstable form towards stable equilibrium form its global hardness increases and when the global hardness decreases the molecule evolves from equilibrium form to non-equilibrium form. Although the PMH is strictly valid for constant chemical potential, its relaxation is also observed. Pearson and Palke<sup>18</sup> have demonstrated that the operation of PMH is fulfilled by the structural situation associated with the formation of transition state, T.S, in a chemical reaction, in inversion, asymmetric deformation, internal rotation, and many isomerization reactions. The hardness profiles of molecules have been computed by Sannigrahi<sup>19</sup> et al and Ghosh<sup>20</sup> for the physical process of internal rotation, Datta<sup>21</sup>, and Ghosh<sup>22-23</sup> et al for the phenomenon of structural inversion. Thus one concludes that it is the prediction of the new paradigm of quantum chemistry, the density functional dressed HSAB principle, that when a molecule evolves from equilibrium to non-equilibrium structure its hardness,  $\eta$ , will decrease and in the reverse process of transition from

non-equilibrium towards equilibrium these quantities will increase and would be maximum at the equilibrium geometry. It is established<sup>19,24,20,22,23</sup> that the computed profiles of  $\eta$ ,  $S$  can follow the structural changes in molecules caused by the physical processes of (i) inversion, (ii) deformation, (iii) internal rotation, and (iv) various types of simple reactions. The new paradigm seems to usher a bright promise of better understanding of the physical process of evolution of conformations of molecules due to the internal rotation around single bond. The rotational isomerization process, in theoretical analysis of the physical process, can be followed by the profiles of hardness and softness which are found to be highly effective to describe the instant processes of the dynamics of internal rotation of molecules<sup>19,20,21</sup>.

It is well known that shapes adopted by a poly atomic molecule actually depends on many factors and there is no simple theory of molecular shape that can take all the relevant factors into account at once. We have already an encouraging result at our hand that the profiles of the eigen values of the canonical frontier orbitals, HOMO and LUMO and the energy gap between such frontier orbitals as a function of torsional variables can monitor the physical process of umbrella inversion and internal rotation of molecules<sup>20-23</sup>. We have also noted<sup>22, 23</sup> that energy partitioning quest of the origin of barrier to inversion is a meaningful venture and we have undertaken the present study of searching the origin of barrier of methyl amine in terms of the energy decomposed components suggested by Fischer and Kollmar<sup>24</sup>. thus our present venture is to compute (i) the molecular orbital parameters—the total energy, eigen values of canonical frontier orbitals, HOMO, LUMO and the HOMO-LUMO gap (ii) the density functional parameters, global hardness, global softness and chemical potential (ii) the decomposed total energy into one- and two-center components as a function of torsional angles.

Method of Computation:

We have invoked the CNDO SCF method of Pople<sup>25</sup> and co-workers in view of the fact Gordon<sup>26</sup> and we have calculated the overlap and electron repulsion integrals through the explicit formula laid down by Roothaan<sup>27</sup>. The necessary algorithm is presented below:-

Although the chemical potential,  $\mu$  and the global hardness,  $\eta$  are rigorously defined in terms of DFT, an exact calculation of such quantities through density functional equations

has not been possible. The operational definitions are obtained by approximating the density functional equations in terms of ionization potential and electron affinity of the system as follows:

$$\text{Global hardness:} \quad \eta = 1/2(I - A) \quad (1)$$

$$\text{Global softness:} \quad S = 1/\eta \quad (2)$$

$$\text{Chemical Potential:} \quad \mu = -1/2(I + A) \quad (3)$$

Where  $I$  is the ionization potential and  $A$  is the electron affinity of an atom, ion or a molecule

Koopmans' theorem can be used to further approximate and to write the working formula of  $\eta$  and  $\mu$  in terms of eigenvalues of HOMO and LUMO of a molecule. The working formulae of the density functional parameters on the orbital basis are

$$\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) / 2 \quad (4)$$

$$\mu = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}) / 2 \quad (5)$$

The gap in energy between the HOMO and LUMO is

$$\Delta\epsilon = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) \quad (6)$$

where,  $\epsilon_{\text{HOMO}}$  and  $\epsilon_{\text{LUMO}}$  are the eigenvalues of HOMO and LUMO, respectively.

The total CNDO energy of a system is

$$E = \sum E_A + \sum \sum E_{AB} \quad (7)$$

where  $E_A$  are monoatomic terms and  $E_{AB}$  are diatomic terms. The monoatomic terms  $E_A$  and the diatomic terms  $E_{AB}$  can be further broken down into physically meaningful components

as follows:

$$E_A = E_A^U + E_A^J + E_A^K \quad (8)$$

Where  $E_A^U$ ,  $E_A^J$  and  $E_A^K$  are total monoatomic orbital energy, electron- electron repulsion energy, and non -classical exchange energy, respectively.

$E_A^U$ ,  $E_A^J$  and  $E_A^K$  may be expressed as following way :

$$E_A^U = \sum_{\mu \in A} P_{\mu\mu} U_{\mu\mu} \quad (9)$$

Where  $P_{\mu\mu}$  are elements of bond order matrix and  $U_{\mu\mu}$  is the one electron energy of an AO  $\mu$  in the isolated atom.

$$E_A^J = \frac{1}{2} (P_A^2 \gamma_{AA}) \quad (10)$$

Where  $P_A = \sum_{\mu \in A} P_{\mu\mu}$  and  $\gamma_{AA}$  is electron-e repulsion between the two electron of atom A.

$$E_A^K = -1/4 \gamma_{AA} \sum \sum P_{\mu\nu}^2 \quad (11)$$

The physical components of the two-center terms are:-

$$E_{AB} = E_{AB}^R + E_{AB}^V + E_{AB}^J + E_{AB}^K + E_{AB}^N \quad (12)$$

$E_{AB}^R, E_{AB}^V, E_{AB}^J, E_{AB}^K, E_{AB}^N$  may be expressed in following manner :

$$E_{AB}^R = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} \beta_{\mu\nu} S_{\mu\nu} \quad (13)$$

Where  $S_{\mu\nu}$  is the overlap of the STO's  $\mu$  and  $\nu$ ,  $\beta_{\mu\nu}$  is a parameter which is dependent on the types of orbital  $\mu$  and  $\nu$ .

$$E_{AB}^V = -P_A \cdot V_{AB} - P_B V_{BA} \quad (14)$$

Where  $V_{AB}$  is the potential of an electron on atom A in the field of nucleus B and  $V_{BA}$  is the potential of an electron on atom B in the field of nucleus A.

$$E_{AB}^J = P_A P_B \gamma_{AB} \quad (15)$$

Where  $\gamma_{AB}$  is the electronic repulsion between an electron on atom A and an electron on atom B.

$$E_{AB}^K = -1/2 \gamma_{AB} \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^2 \quad (16)$$

$$E_{AB}^N = Z_A Z_B / R_{AB} \quad (17)$$

Where  $Z_A$  and  $Z_B$  are the nuclear charge and  $R_{AB}$  is the distance between two nuclei.

The physical significance of decomposed terms are discussed elsewhere<sup>22,23</sup>.

Coordinate system:

The Z-axis is made coincident with the 'C-N' bond and the H<sub>3</sub>C- end is kept fixed and the 'N-H<sub>2</sub>' group is rotated around the 'C-N' bond to generate conformations. We have started with the eclipsed conformation and its geometric parameters are optimized first then the computation cycle for all molecular orbital and density functional parameters is run. Thereafter, the 'N-H<sub>2</sub>' group is rotated through steps of 10<sup>0</sup> torsional angle to generate new conformations and the process is continued till the staggered conformation is reached. The geometry optimization and computation of molecular orbital and density functional parameters are cycled through each generated conformation and are presented in tables. We have drawn the computed results as a function of torsional variables to benefit the discussions and to elicit important conclusion. The optimized geometric parameters and the computed molecular and density functional quantities are presented in tables-1 and 2 respectively. The decomposed one-, two-center bonded and nonbonded interactions and their physical components are presented in tables 3-13.

Discussion:

The molecular orbital parameters:

The total energy of methylamine molecule is plotted as a function of torsional angles in fig.1. The nature of the profile in fig.1 is reminiscent of the potential energy diagram of ethane molecule- (fig.

1 page 113, above). The extreme conformations are—staggered and eclipsed and they are nicely portrayed by the energy profile in fig.1. The difference of energy between the most stable isomer (staggered form) and most unstable isomer (eclipsed form) is 0.0024196 a.u; hence the barrier height is 1.52 kcal/mole. The experimental<sup>1</sup> value of the barrier height is 1.98 kcal/mole and the corresponding value in an *ab initio* calculation by Pedersen and Morokuma<sup>4</sup> is 2.02 kcal/mole. Thus the barrier height of the present work is in close agreement with the experimentally determined barrier of the methylamine molecule. Hence, the present calculation demonstrates once again that the CNDO is a sufficiently powerful quantum chemical paradigm to obtain the glimpses of the conformational behaviour of molecules under internal rotation. Now let us address the physical process of conformational isomerism by invoking the computed molecular orbital as well as density functional parameters; the quest of the origin and development of barrier will be addressed by the decomposed energy components.

#### The HOMO, LUMO and HOMO and LUMO gap:

The eigen values of the frontier canonical orbitals and the HOMO-LUMO gap ( $\Delta\varepsilon$ ) are plotted as a function of torsional angles in figs. 2 and 3 respectively. From analysis of results in table-2 and the nature of the profiles of the eigen values of the canonical frontier orbitals in fig.2 it can be argued that the profiles of eigen values of the frontier orbitals of the molecule express beautifully the process of staggering and eclipsing that are occurring periodically under internal rotation. A comparative analysis of in fig.2 vis-à-vis the potential energy diagram (fig.1) reveals that the theoretical parameters like the eigen values of the canonical frontier orbitals of methylamine molecule can be used to depict the rotational structural isomerization process of the molecule. From table-2 it is evident that the homo-lumo gap,  $\Delta\varepsilon$  is maximum for staggered conformation and minimum for the eclipsed conformation and the nature of variation of the energy gap is monotone continuous between the two extreme conformations as a function of torsional variables. Comparing the nature of profile in fig. 3 vis-à-vis the nature of profile of fig.1 we see that the profile of the homo-lumo gap is mirror the image of the potential energy diagram; thus, the molecular orbital parameter— homo-lumo gap can display the conformational behaviour of the molecule under internal



rotation. Hence the good correlation between the gap in energy of the frontier orbitals and the total energy under internal rotation suggest unequivocally that the eigen values of the two frontier orbitals can be used as a true descriptor of the physical process of the conformational isomerism of methylamine molecule.

Density functional parameters: – hardness, softness and chemical potential:

**The global hardness:** Table-2 shows that the global hardness of the staggered form is maximum and that of eclipsed form is minimum. The study of the hardness profile under internal rotation from fig.4 shows that when the molecule evolves from staggered conformation towards the eclipsed conformation the global hardness decreases and while the structure evolves in the reverse direction from eclipsed conformation towards the staggered conformation the global hardness increases. Thus, the pattern of the variation of global hardness as a function of structural evolution is in accordance with the principle of maximum hardness, PMH. A comparative study of the fig.1 vis-à-vis the fig.4 reveals that the profile of the global hardness is the mirror image of the total energy curve and this good correlation between the two curves suggest that the global hardness is a true descriptor of the physical process of conformational isomerism arising out of the dynamics of internal in the methylamine molecule.

**The global softness:** From table-2 we see that the global softness of the staggered form is minimum and that of eclipsed form is maximum and the change of the global softness between the extreme conformers is monotone continuous function of torsional variables. The softness is extrapolated as a function of torsional angle in fig.5. A close examination of the nature of the softness profile reveals that the fluctuation of the structural stability situation with internal rotation is nicely displayed by the curve. A comparison of the nature of softness profile with the potential energy diagram (fig.1) reveals that the softness curve mimics the pattern of total energy profile and this good correlation between the total energy parameter and softness parameter suggest that this density functional parameter is a true descriptor of the conformational isomerism of methylamine molecule.

**The chemical potential:**

Table-2 shows that, as the torsion starts from the eclipsed conformation, the chemical potential of methylamine system decreases monotonically and becomes minimum at the staggered conformation. The chemical potential is plotted as a function of torsional angle in fig.6. A closer look at the nature of chemical potential profile under internal rotation and its comparison with the potential energy diagram reveals that the chemical potential parameter of the methylamine system dances with tune of conformational isomerism of the molecule generated by the dynamics of internal rotation about 'C-N' bond. Hence it may be concluded that the chemical potential is a true descriptor of the physical process of conformational isomerism methylamine molecule. This pattern of variation of chemical potential is itself revealing and intriguing in view of the fact that we have already noted that the structural evolution under internal rotation of the molecule is in accordance with the principle of maximum hardness, PMH while Parr and co-workers put forward a mathematical proof of the theorem (PMH) under a constraint of constant chemical potential.

Thus in the above we have seen that the profiles of the molecular orbital and density functional parameters are quite efficient in depicting the fluctuation of structural situation under torsional variables and following the dynamics of internal rotation of the methylamine molecule.

#### Energy partitioning analysis: – one-center, two-center bonded, nonbonded interactions:

The methylamine ( $\text{H}_3\text{C-NH}_2$ ) molecule has the following type and number of one-center and two-center bonded and nonbonded interactions:-

1. four one-center interactions terms:-one on 'N' atom, one on 'C' atom, one on 'H' atom attached to 'C' in  $\text{H}_3\text{C}$ - fragment and one on 'H' attached to 'N' atom in  $-\text{NH}_2$  fragment. The computed one-center energy and their physical components of all the one-center energetic effects with torsional variables are presented in tables- 3 and 4. The one-center energies of 'N' and 'C' atoms are drawn as a function of torsional variables in fig. 7 and that on the 'H' atom centers are similarly drawn in fig. 8.
2. three two-center bonded interactions– (i) 'C-N' bonded interaction; the computed bonded interaction energy and its physical components with torsional variables are presented in table-5. The interaction energy is also plotted as a function of rotational variables in fig. 9.

(ii) 'C-H' bonded interaction; the computed interaction energy and its physical components with rotational variables are presented in table-6 and is plotted in fig. 10.

(iii) 'N-H' bonded interaction; the computed bonded interaction energy and its physical components with rotational variables are presented in table-7. The total energy is plotted with torsional variables in fig.11.

3. five different types of two-center nonbonded interactions—(i) two geminal 'H---H' nonbonded interactions—one between the 'H' atoms attached to 'N' atom i.e. on  $-NH_2$  fragment and the other between the 'H' atoms attached to 'C' atom i.e. on  $-CH_3$  fragment. The interaction energies and their physical components with rotational variables are presented in tables-8 and 9 respectively. The total energies are plotted as a function of torsional angles in the same diagram in fig. 12.

(ii) 'H---H' vicinal-cis interactions; this calculates the interactions between the 'H' atoms in cis position on 'C' and 'N' atoms. The interaction energy and its physical components are presented with the rotational variables in table-10. The energetic effect is also plotted against the rotational variables in fig.13.

(iii) 'H---H' vicinal-trans interactions; this calculates the energy of interactions between the 'H' atoms in trans position on 'C' and 'N' atoms. The interaction energy and its physical components are shown with the rotational variables in table-11 and plotted against the rotational variables in fig.14.

(iv) the "C-----H" nonbonded interactions; this term calculates the energy of interaction between the 'C' atom and the 'H' atoms attached to the 'N' atom. The interaction energy and its physical components with rotational variables are presented in table-12; the interaction energy is also plotted as a function of torsional variables in fig. 15.

(v) the "N-----H" nonbonded interactions; this calculates the energy of interaction between the 'N' atom and the 'H' atoms attached to the 'C' atom. The interaction energy and its physical components with rotational variables are presented in table-13; the energy is also plotted as a function of torsional variables in fig. 16.

One-center interactions:

On 'C' and 'N' atoms: - From tables-3 and 4 and also from fig. 7 it is evident that there is no definite pattern of variation of energy on 'C' atom center while that on 'N' atom center has a definite pattern. Table-3 shows that one-center energetic effect on 'C' atom, though not strictly constant of internal rotation, has no preference for either the eclipsed or the staggered conformation. But table-4 shows that as the torsion starts from the eclipsed conformation the one-center energetic effect on 'N' atom decreases monotonically and becomes minimum at the staggered conformation of the molecule. This shows that the one-center energetic effect on 'N' atom accelerates the process of staggering and hence tends to stabilize the staggered form in comparison with the eclipsed form; thus the one-center effect on 'N' tends to increase the barrier height. A close look at the nature of the energy profile of 'N' center reveals that it is a periodic function of the torsional variables and mimics the pattern of potential energy diagram in fig. 1. This beautiful correlation between two energy quantities as a function of torsional variables suggests that the one-center energy component on 'N' atom can be exploited as a depicter of the physical process of conformational isomerism of the methylamine molecule.

On 'H' atoms: - The table-3 shows that as the torsion starts from the eclipsed form the one-center energy on 'H' atom attached to 'C' atom decreases steadily and becomes minimum at the staggered form while table-4 shows that the one-center energy on 'H' atom attached to 'N' atom does not follow a definite trend of variation with torsional variables. The stated differential nature of variation of the one-center energetic effects on two different 'H' atoms attached to different centers is self evident from the nature of their energy profiles in fig. 8. The energy profile of the 'H' atom attached to 'C' is a periodic function of torsional variable and the curve mimics the potential energy curve in fig.1. This good correlation between the two energetic effects with torsional variables suggests that this energy component can be used as a descriptor of the physical process of conformational isomerism methylamine under internal rotation. The energy profile of 'H' atom attached to 'N' center though anomalous under torsional variable, distinctly shows that the staggered conformation is a bit more favoured than the eclipsed conformation by this energetic effect. Hence, the energetic effects on the both 'H' centers tend to stabilize the staggered form compared to the eclipsed form

and the effect under discussion goes to increase the magnitude of torsional barrier in the methylamine molecule.

The two-center bonded interactions: –

(i) 'C–N' bonded interaction: – Table-5 shows that as the torsion starts from the eclipsed conformation the two-center 'C–N' bonded interaction begins to decrease monotonically and becomes minimum at the staggered conformation. The nature of the profile of this bonded interaction in fig. 9 shows that this energetic effect is a periodic function of torsional variables and mimics the potential energy curve in fig.1. Thus the nature of evolution of this two-center energetic effect under torsional variables and its close correlation with the total energy of the molecule suggest that this energetic effect alone can be used as a descriptor of the physical process of conformational isomerism of methylamine molecule. Since the effect tends to stabilize the staggered form compared to the eclipsed form, it tends to increase the torsional barrier of the molecule.

(ii) 'C–H' bonded interaction: – The table-6 shows that as the torsion starts from the eclipsed form, the two-center 'C–H' bonded interaction energy begins to increase monotonically and becomes maximum at the staggered form. The computed numerical values of the 'C–H' bonded interaction with torsional variables suggests that this affect tends to stabilize the eclipsed form compared to the staggered form of the molecule and hence it tends to reduce the height of the torsional barrier. A look at the nature of profile of this energetic effect in fig. 10 reveals that it is a periodic function of the torsional coordinates and is the mirror image of the potential energy curve in fig.1. This good correlation between the two energetic effects with torsional variables suggests that this energy component can be used as a descriptor of the physical process of conformational isomerism methylamine under internal rotation.

(iii) 'N–H' bonded interaction: – The table-7 shows that as the torsion starts from the eclipsed form, the two-center 'N–H' bonded interaction energy begins to increase and becomes maximum at the staggered form. The computed numerical values of the 'N–H' bonded interaction with torsional variables suggests that this affect tends to stabilize the eclipsed form compared to the staggered form of the molecule and hence it tends to reduce the height of the torsional barrier. A look at the nature of profile of this energetic effect in fig. 11 reveals that it is a periodic function of the torsional

coordinates and is nearly the mirror image of the potential energy curve in fig.1. This good correlation between the two energetic effects with torsional variables suggests that this energy component can be a depicter of the physical process of conformational isomerism methylamine under rotation dynamics.

The two-center nonbonded interactions: –

(i) 'H---H' geminal interactions: On  $\text{NH}_2$ - fragment: From table-8 we see that the geminal interactions between the 'H' atoms attached to 'N' atom is repulsive in all conformations and its magnitude increases with staggering. Since the effect tends to stabilize the eclipsed form compared to the staggered form, this energetic effect tends to reduce the torsional barrier. A look at the nature of profile of this energetic effect in fig.12 reveals that it does not a follow any regular trend of variation with torsional coordinates and has no correlation with the total energy curve in fig.1.

On  $\text{CH}_3$ - fragment: – From table-9 we see that the geminal interactions between the 'H' atoms attached to 'C' atom is repulsive in all conformations. A look at the tabe-9 reveals that as the staggering starts from the eclipsed conformation the geminal interaction energy between the 'H' atoms begins to increase and the process continues monotonically until the staggered conformation is reached. Since the effect tends to stabilize the eclipsed form compared to the staggered form, it tends to reduce the height of the torsional barrier of the molecule. A look at the nature of the profile of this energy component in fig. 12 reveals that it is periodic function of the torsional variables and has a good correlation with the total energy profile in fig.1.

Thus we see that of the two geminal 'H---H' interactions in methylamine molecule, the effect on 'C' atom correlates with the conformational behaviuor of the molecule under internal rotation nicely while that on 'N' atom behaves anomalously with torsional coordinates.

(ii) 'H---H' vicinal-cis interactions: From table-10 we see that the nature of the vicinal–cis interactions between the 'H' atoms on 'C' atom and 'N' atom is repulsive in all conformations and the effect favours staggering. Since the effect tends to stabilize the staggered form compared to the eclipsed form, it tends to increases the barrier to torsion in the molecule. A look at the nature of the profile of this energetic effect in fig.13 reveals that the energetic effect is a periodic function of

torsional variables and bears mirror image relationship with the potential energy diagram in fig.1. The good correlation with the total energy with rotational coordinates indicates that the nonbonded vicinal–cis interaction between hydrogen atoms in methylamine molecule dances with the tune of conformational isomerism of the molecule under the dynamics of internal rotation.

(iii) 'H---H' vicinal-trans interactions: From table-11 we see that the nature of interaction between two non–bonded 'H' atoms in trans position is attractive at the eclipsed form. But as staggering starts from the eclipsed conformation, the interaction energy increases steadily and ultimately it becomes repulsive at the staggered form. A look at the nature of profile of this energetic effect in fig.14 reveals that the vicinal-trans nonbonded 'H---H' energetic effect is periodic under torsional variables. A comparative study of the profiles in figs. 1 and 14 reveals that the vicinal-trans nonbonded 'H---H' interaction energetic effect dances with the tune of conformational isomerism methylamine molecule due to the dynamics of internal rotation. Since this effect tends to stabilize the eclipsed form compared to the staggered form, the effect tends to reduce magnitude of torsional barrier. The rationale of the variation of the nature of this nonbonded interaction from attractive to repulsive is transparent from the analysis of the variation of the physical components of the interaction under internal rotation.

(iv) 'C---H' nonbonded interactions:- From table-12 we see that the nonbonded interactions between the 'C' atom and the 'H' atom attached to 'N' is repulsive in all conformations of the molecule. It is also transparent that the effect tends to stabilize the staggered form compared to the eclipsed form and hence the energetic effect tends to increase the barrier height of the methylamine molecule. A look at nature of the profile of this energy effect in fig. 15 reveals that the effect is periodic under torsional variable and the curve mimics the pattern of the potential energy diagram in fig.1. The good correlation between the two curves indicate that 'C---H' nonbonded interaction dances with tune of the physical process of conformational isomerism of the molecule under internal rotation.

(v) 'N---H' nonbonded interactions: - The nature and magnitude of the of the interaction between the 'H' atoms attached to 'C' atom and the 'N' atom is transparent from table-13. From

table-13 it transpires that the nature of the interaction is repulsive in all conformations and the energetic effect favours eclipsing and hinders staggering. Since the effect tends to stabilize the eclipsed form compared to staggered form, it tends to reduce the barrier height. Looking at the nature of profile of this energetic effect in fig. 16 we see that it is a periodic function of torsional variables and has a good correlation with the potential energy diagram in fig.1. Thus the nonbonded interaction between the 'H' atoms on 'C' atom and the 'N' atom of methylamine molecule dances with the tune of the physical process of conformational isomerism of the molecule due the dynamics of internal rotation.

From above analysis we see that all the energetic effects suffer change with torsion and the pattern of majority of effects correlate the pattern of the conformational behaviour of the molecule under the dynamics of internal rotation.



Table-1. The optimized structural parameters of H<sub>3</sub>C–NH<sub>2</sub> system as a function of torsional angles.

Angle of torsion ( $\theta$ , degrees)	C–H (A <sup>0</sup> )	$\angle$ HCH (degree)	C–N (A <sup>0</sup> )	N–H (A <sup>0</sup> )	$\angle$ HNH (degree)
0	1.12	106.8	1.41	1.07	103.9
10	1.12	106.8	1.41	1.07	104.0
20	1.12	106.8	1.41	1.07	104.0
30	1.12	106.9	1.41	1.07	104.1
40	1.12	106.9	1.41	1.07	104.1
50	1.12	106.9	1.41	1.07	104.2
60	1.12	107.0	1.41	1.07	104.2

Table-2. The total energy (E), eigen values of the frontier orbitals ( $\epsilon_{\text{HOMO}}$ ,  $\epsilon_{\text{LUMO}}$ ), the gap of HOMO-LUMO ( $\Delta\epsilon$ ), global hardness ( $\eta$ ), global softness (S) and chemical potential ( $\mu$ )

Angle of torsion (degrees)	E (a.u)	$\epsilon_{\text{LUMO}}$ (a.u)	$\epsilon_{\text{HOMO}}$ (a.u)	$\Delta\epsilon$ (a.u)	$\eta$ (a.u)	S (a.u <sup>-1</sup> )	$\mu$ (a.u)
0	-22.58471	-0.50949	0.2609	0.77039	0.3852	1.29804	-0.12430
10	-22.58494	-0.50955	0.26089	0.77044	0.38522	1.29790	-0.12433
20	-22.58535	-0.50962	0.26089	0.77051	0.38525	1.29784	-0.12437
30	-22.58600	-0.50967	0.26096	0.77063	0.38532	1.29764	-0.12435
40	-22.58659	-0.50984	0.26097	0.77081	0.3854	1.29734	-0.12443
50	-22.58706	-0.50988	0.26096	0.77084	0.38542	1.29729	-0.12447
60	-22.58721	-0.51002	0.26087	0.77088	0.38544	1.29721	-0.12457

Table-3. One– center energy on ‘C’ atom and the ‘H’ attached to it and their physical components as a function of torsional angles in H<sub>3</sub>C–NH<sub>2</sub> system.

Angles of rotation (degrees)		E <sup>U</sup> (a.u)	E <sup>J</sup> (a.u)	E <sup>K</sup> (a.u)	E (a.u)
0	C	-9.174512	4.48782	-0.56235	-5.24904
	H	-0.65110	0.38967	-0.19484	-0.45626
10	C	-9.17439	4.48769	-0.56234	-5.24903
	H	-0.65339	0.39241	-0.19621	-0.45718
20	C	-9.17444	4.48775	-0.56234	-5.24903
	H	-0.65563	0.39512	-0.19756	-0.45808
30	C	-9.17425	4.48752	-0.56233	-5.24906
	H	-0.65767	0.39757	-0.19878	-0.45888
40	C	-9.17486	4.48816	-0.56240	-5.24910
	H	-0.65917	0.39939	-0.19969	-0.45948
50	C	-9.17444	4.48773	-0.56235	-5.24907
	H	-0.66270	0.40072	-0.20036	-0.45991
60	C	-9.17478	4.48812	-0.56238	-5.24905
	H	-0.66060	0.40112	-0.20056	-0.46004

Table-4. One– center energy on ‘N’ atom and the ‘H’ attached to it and their physical components as a function of torsional angles in  $\text{H}_3\text{C-NH}_2$  system.

The angles of rotation (degrees)		$E^U$ (a.u)	$E^J$ (a.u)	$E^K$ (a.u)	$E$ (a.u)
0	N	-18.51799	9.52314	-1.29846	-10.29331
	H	-0.59303	0.32326	-0.16163	-0.43140
10	N	-18.51808	9.52315	-1.29846	-10.2933
	H	-0.59286	0.32307	-0.16154	-0.431329
20	N	-18.51791	9.52292	-1.29844	-10.2934
	H	-0.59277	0.32298	-0.16149	-0.431283
30	N	-18.51891	9.52312	-1.29845	-10.2935
	H	-0.59273	0.32294	-0.16147	-0.431262
40	N	-18.51743	9.52212	-1.29839	-10.29370
	H	-0.59286	0.32308	-0.16154	-0.43132
50	N	-18.51765	9.52228	-1.29838	-10.2937
	H	-0.59291	0.32313	-0.16156	-0.43134
60	N	-18.51693	9.52140	-1.29832	-10.29386
	H	-0.59306	0.32330	-0.16165	-0.43142

Table-5 The ‘C–N’ bonded interaction energy and its physical components as a function of torsional angles in  $\text{H}_3\text{C-NH}_2$  system.

Angle of torsion ( $\theta$ , degrees)	$E^J$ (a.u)	$E^N$ (a.u)	$E^V$ (a.u)	$E^K$ (a.u)	$E^R$ (a.u)	$E(\text{C-N})$ (a.u)
0	7.30808	7.50592	-14.54388	-0.19392	-1.21749	-1.14130
10	7.30797	7.50592	-14.54379	-0.19394	-1.21751	-1.14135
20	7.30793	7.50592	-14.54374	-0.19400	-1.21779	-1.14168
30	7.30782	7.50592	-14.54364	-0.19409	-1.21795	-1.14194
40	7.30796	7.50592	-14.54375	-0.19414	-1.21817	-1.14218
50	7.30767	7.50592	-14.54347	-0.19423	-1.21845	-1.14257
60	7.30764	7.50592	-14.54343	-0.19423	-1.21862	-1.14272

Table-6. The ‘C–H’ bonded interaction energy and its physical components as a function of torsional angles in  $\text{H}_3\text{C-NH}_2$  system.

Angle of torsion ( $\theta$ , degrees)	$E^J$ (a.u)	$E^N$ (a.u)	$E^V$ (a.u)	$E^K$ (a.u)	$E^R$ (a.u)	$E(\text{C-H})$ (a.u)
0	1.69599	1.88988	-3.40356	-0.20758	-0.72313	-0.74840
10	1.70193	1.88988	-3.40965	-0.20740	-0.72264	-0.74788
20	1.70779	1.88988	-3.41566	-0.20718	-0.72216	-0.74734
30	1.71304	1.88988	-3.42105	-0.20696	-0.72178	-0.74687
40	1.71708	1.88988	-3.42519	-0.20681	-0.72146	-0.74649
50	1.71986	1.88988	-3.42804	-0.20667	-0.72122	-0.74619
60	1.72078	1.88988	-3.42898	-0.20665	-0.72110	-0.74607

Table-7. The 'N-H' bonded interaction energy and its physical components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub> system.

Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (N-H) (a.u)
0	2.18578	2.47274	-4.46192	-0.22003	-0.71639	-0.73982
10	2.18514	2.47274	-4.46131	-0.22001	-0.71641	-0.73984
20	2.18482	2.47275	-4.46100	-0.21997	-0.71636	-0.73976
30	2.18469	2.47275	-4.46087	-0.21992	-0.71636	-0.73966
40	2.18506	2.47275	-4.46122	-0.21987	-0.71614	-0.73942
50	2.18525	2.47276	-4.46141	-0.21984	-0.71603	-0.73931
60	2.18572	2.47276	-4.46184	-0.21982	-0.71598	-0.73917

Table-8 The 'H...H' non-bonded interaction (geminal, NH<sub>2</sub>) and their physical components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub> system.

Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (H... H) (a.u)
0	0.26724	0.31400	-0.57566	-0.00005	0.00254	0.00807
10	0.26704	0.31379	-0.57526	-0.00005	0.00258	0.00808
20	0.26705	0.31379	-0.57528	-0.00005	0.00258	0.00808
30	0.26689	0.31357	-0.57492	-0.00005	0.00261	0.00810
40	0.26696	0.31357	-0.57500	-0.00005	0.00261	0.00809
50	0.26675	0.31336	-0.57460	-0.00005	0.00264	0.00810
60	0.26676	0.31336	-0.57461	-0.00005	0.00264	0.00810

Table-9 The 'H...H' non-bonded interaction (geminal, CH<sub>3</sub>) and their physical components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub> system.

Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (H...H) (a.u)
0	0.30310	0.29425	-0.59467	-0.00006	0.00248	0.00509
10	0.30323	0.29425	-0.59481	-0.00007	0.00256	0.00517
20	0.30351	0.29425	-0.59509	-0.00008	0.00280	0.00540
30	0.30376	0.29406	-0.59516	-0.00010	0.00320	0.00564
40	0.30420	0.29406	-0.59560	-0.00014	0.00364	0.00593
50	0.30477	0.29406	-0.59616	-0.00018	0.00413	0.00662
60	0.30538	0.29425	-0.59694	-0.00021	0.00456	0.00703

Table-10. The 'H...H' non-bonded interaction (vicinal-cis) and their physical components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub> system.

Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (H...H) (a.u)
0	0.21966	0.23248	-0.45208	-0.00149	0.00646	0.00504
10	0.21987	0.23195	-0.45182	-0.00146	0.00636	0.00495
20	0.21871	0.22994	-0.44874	-0.00134	0.00592	0.00449
30	0.21666	0.22707	-0.44390	-0.00113	0.00523	0.00392
40	0.21331	0.22295	-0.43651	-0.00087	0.00432	0.00320
50	0.20925	0.21828	-0.42785	-0.00060	0.00334	0.00242
60	0.20437	0.21298	-0.41770	-0.00035	0.00233	0.00163

Table-11. The 'H...H' non-bonded interaction (vicinal-trans) and their physical components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub> system.

Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (H...H) (a.u)
0	0.17474	0.18466	-0.35962	-0.00047	-0.00154	-0.00223
10	0.17894	0.18842	-0.36762	-0.00024	-0.00119	-0.00169
20	0.18359	0.19262	-0.37652	-0.00008	-0.00073	-0.00111
30	0.18875	0.19742	-0.38651	-0.00002	-0.00015	-0.00050
40	0.19398	0.20244	-0.39678	-0.00002	0.00056	0.00017
50	0.19935	0.20778	-0.40750	-0.00015	0.00140	0.00088
60	0.20437	0.21298	-0.41770	-0.00035	0.00233	0.00163

Table-12. The 'C...H' non-bonded interaction and their physical components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub> system.

Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (N...H) (a.u)
0	1.32662	1.25753	-2.58064	-0.00082	0.00202	0.00471
10	1.33128	1.25753	-2.58513	-0.00123	0.00250	0.00495
20	1.33584	1.25753	-2.58953	-0.00164	0.00309	0.00528
30	1.34070	1.25820	-2.59491	-0.00203	0.00368	0.00564
40	1.34370	1.25820	-2.59780	-0.00233	0.00415	0.00593
50	1.34595	1.25820	-2.59996	-0.00254	0.00450	0.00615
60	1.34584	1.25753	-2.59917	-0.00260	0.00462	0.00621

Table-13. The 'N...H' non-bonded interaction and their physical components as a function of torsional angles in H<sub>3</sub>C–NH<sub>2</sub> system.

Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (C...H) (a.u)
0	0.91077	1.01040	-1.91525	-0.00006	-0.00309	0.00277
10	0.91134	1.01088	-1.91628	-0.00006	-0.00316	0.00271
20	0.91153	1.01088	-1.91648	-0.00006	-0.00316	0.00270
30	0.91200	1.01135	-1.91741	-0.00006	-0.00323	0.00265
40	0.91212	1.01135	-1.91753	-0.00006	-0.00324	0.00264
50	0.91226	1.01182	-1.91812	-0.00006	-0.00331	0.00260
60	0.91210	1.01182	1.91796	-0.00006	-0.00331	0.00259

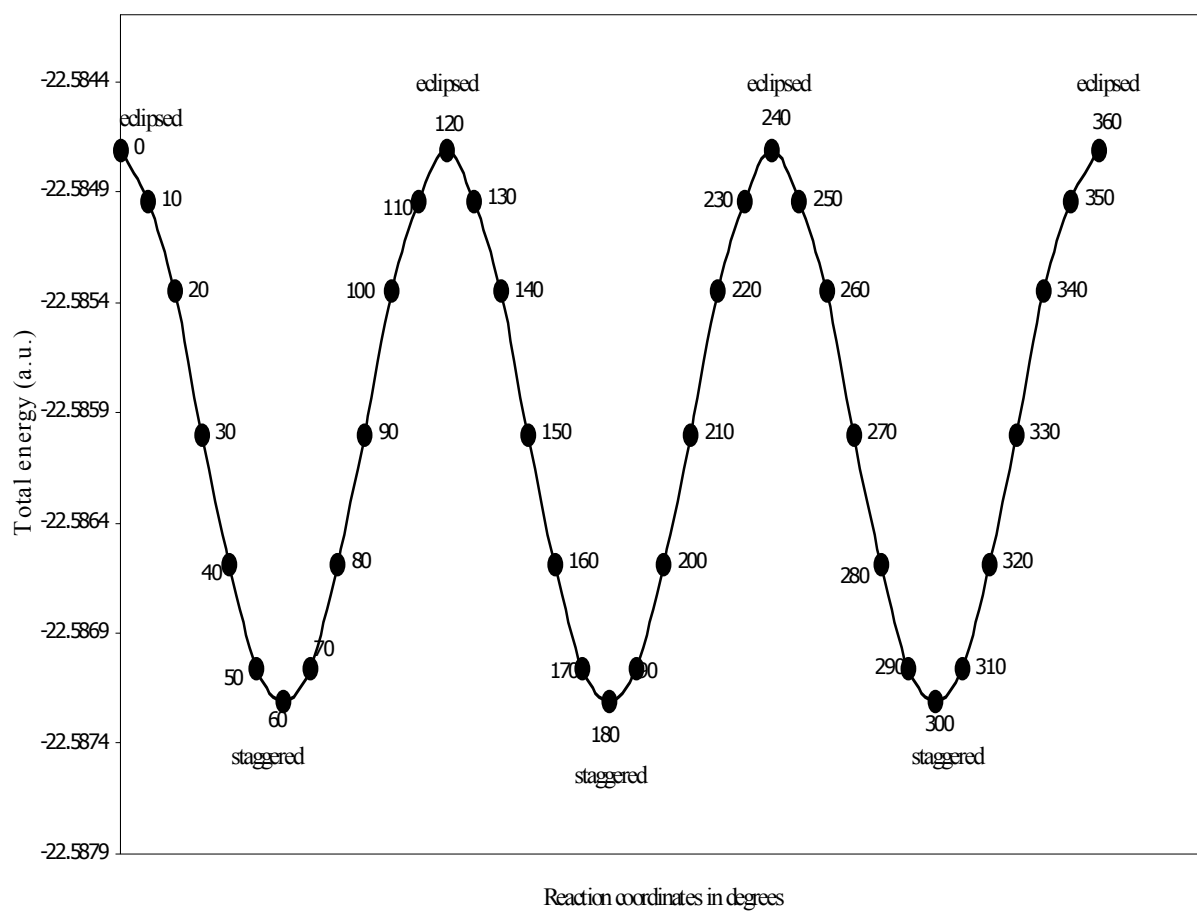


Fig 1 Plot of total energy as a function of reaction coordinate in H<sub>3</sub>C-NH<sub>2</sub> system

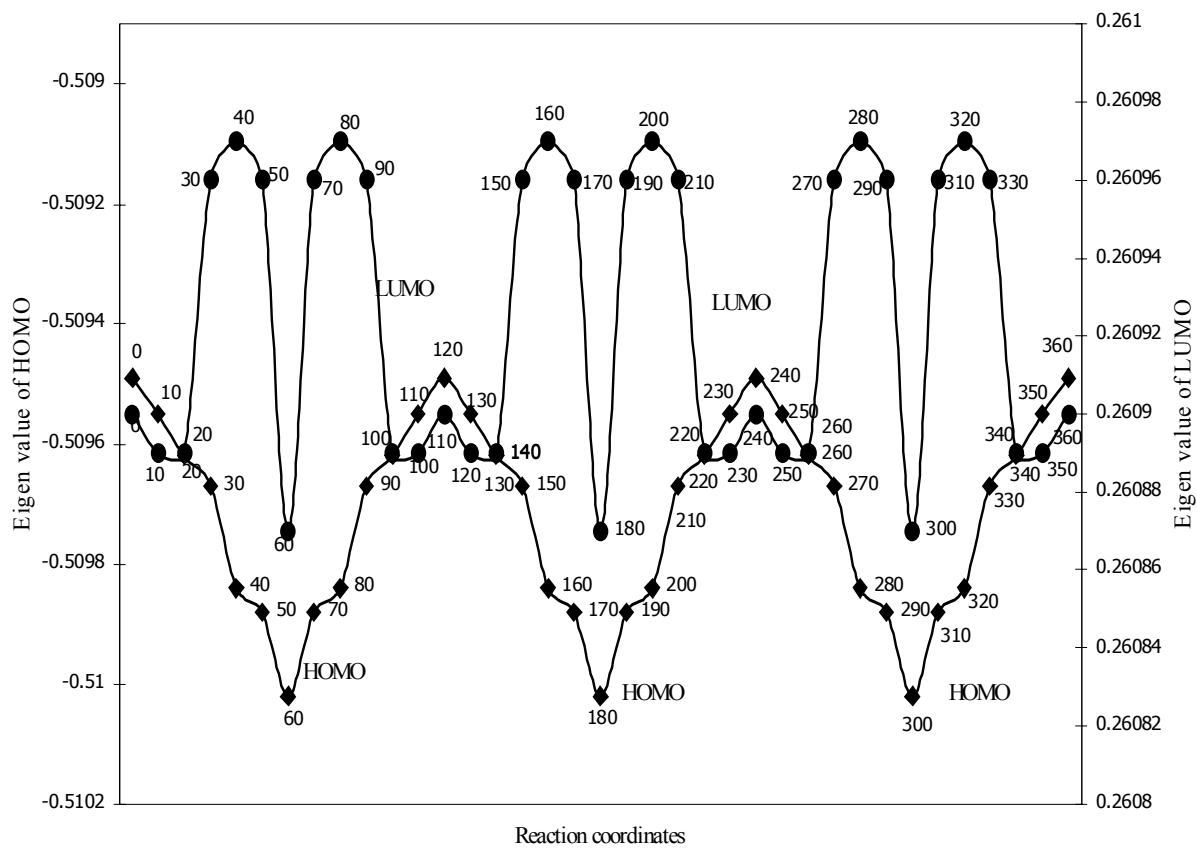


Fig. 2 Plot of eigen values of HOMO and LUMO as a function of reaction coordinates in  $\text{H}_3\text{C-NH}_2$  system

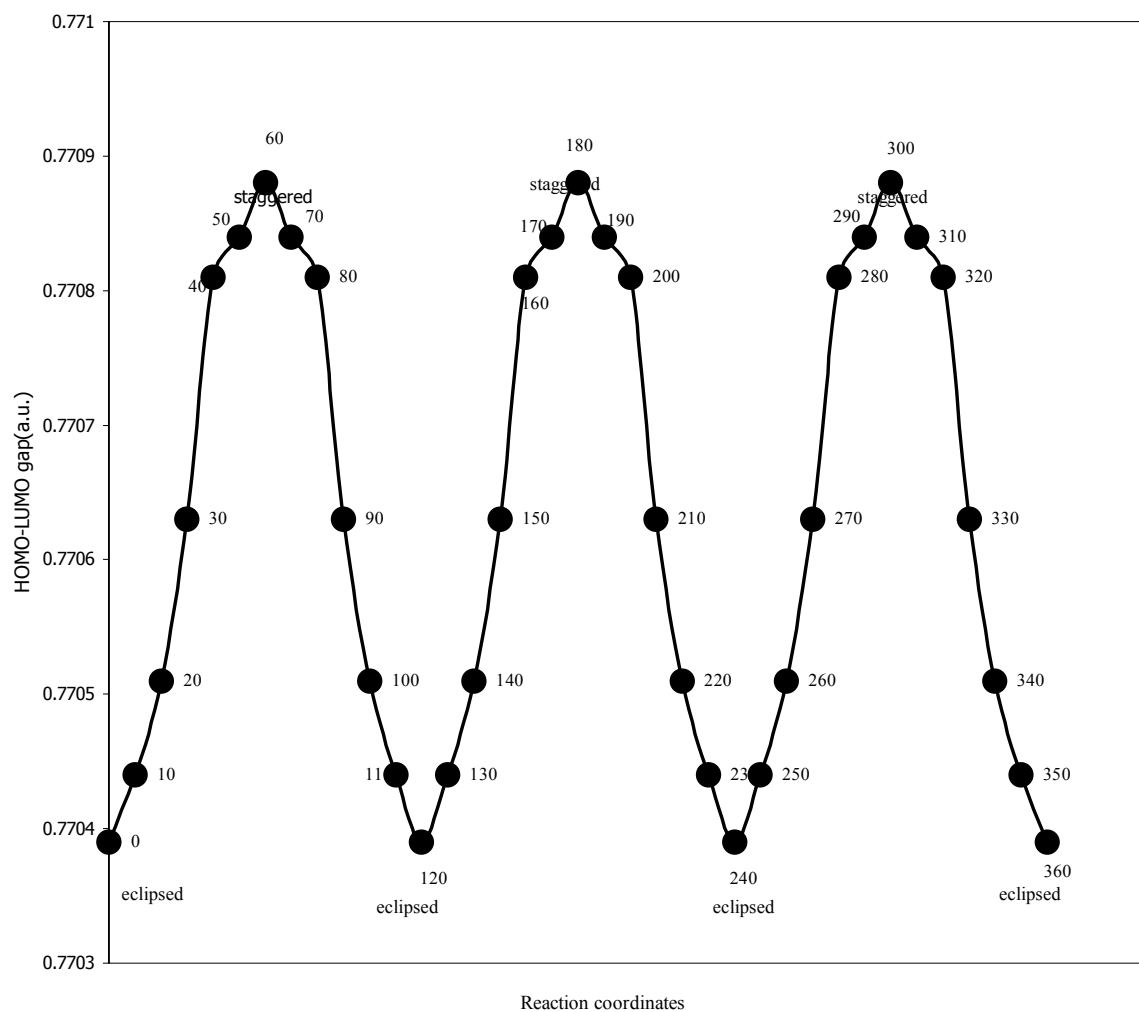


Fig.3 Plot of HOMO-LUMO gap as a function of reaction coordinates of H<sub>3</sub>C-NH<sub>2</sub> system



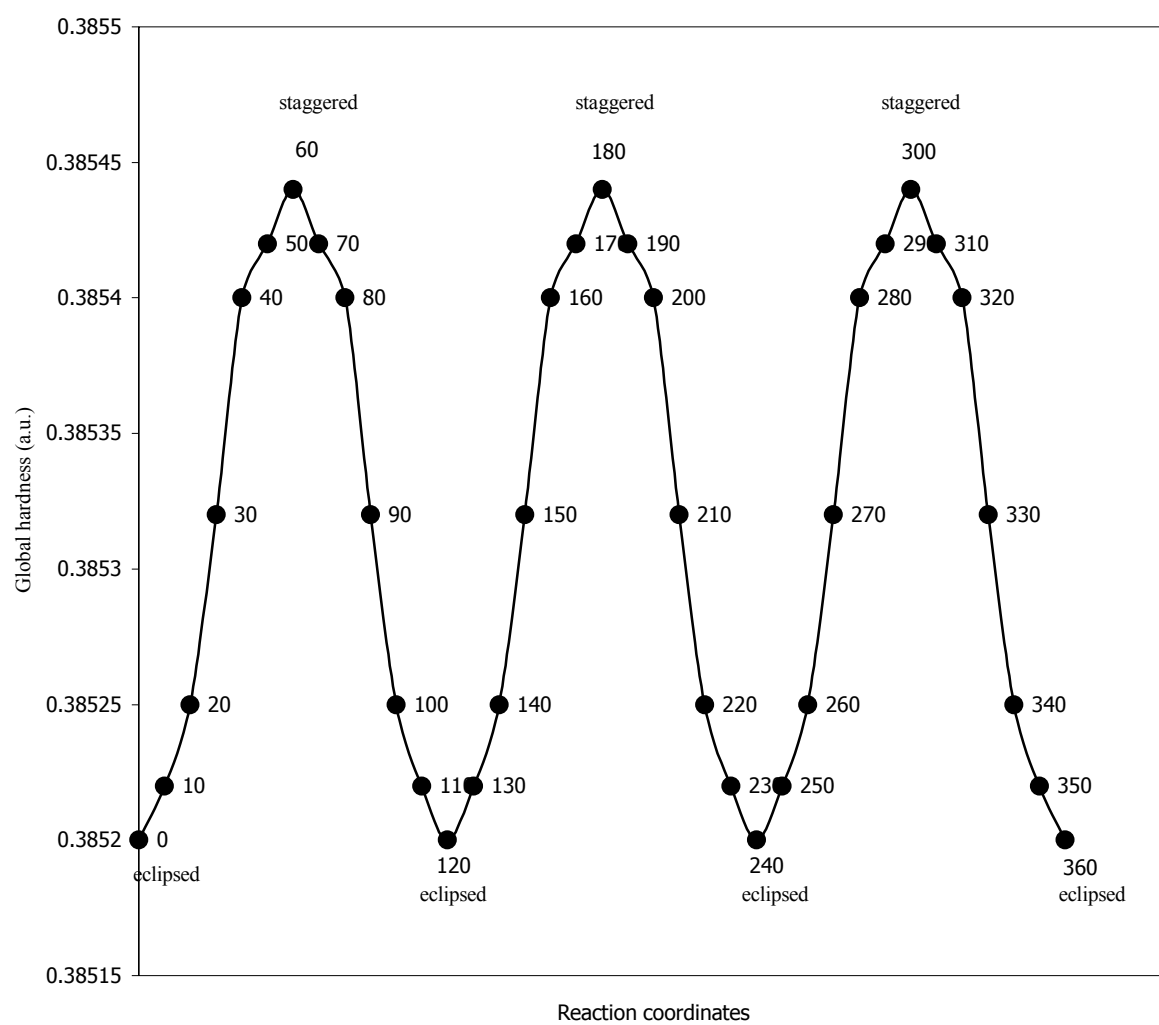


Fig. 4 Plot of global hardness as a function of reaction coordinates in  $\text{H}_3\text{C-NH}_2$  system

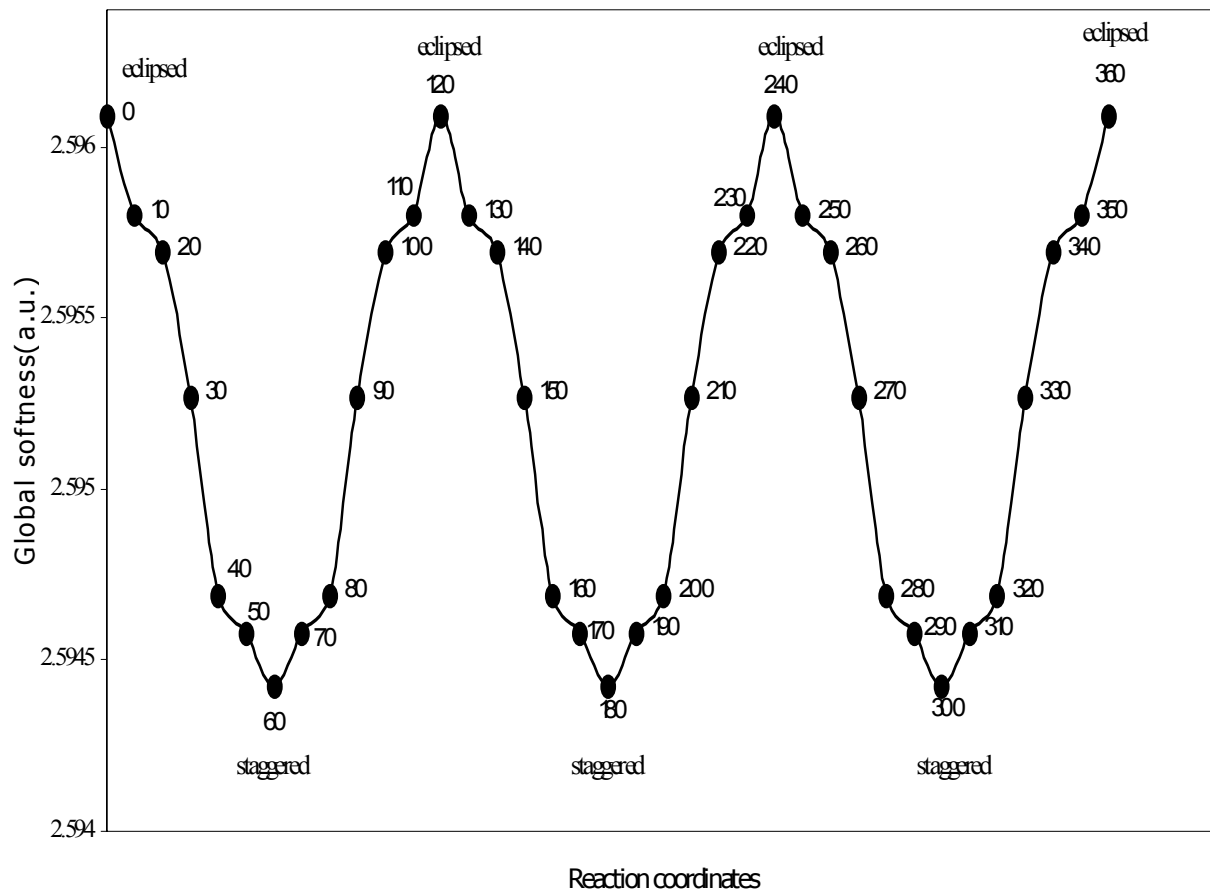


Fig.5 Plot of global softness as a function of reaction coordinates of  $\text{H}_3\text{C-NH}_2$  system

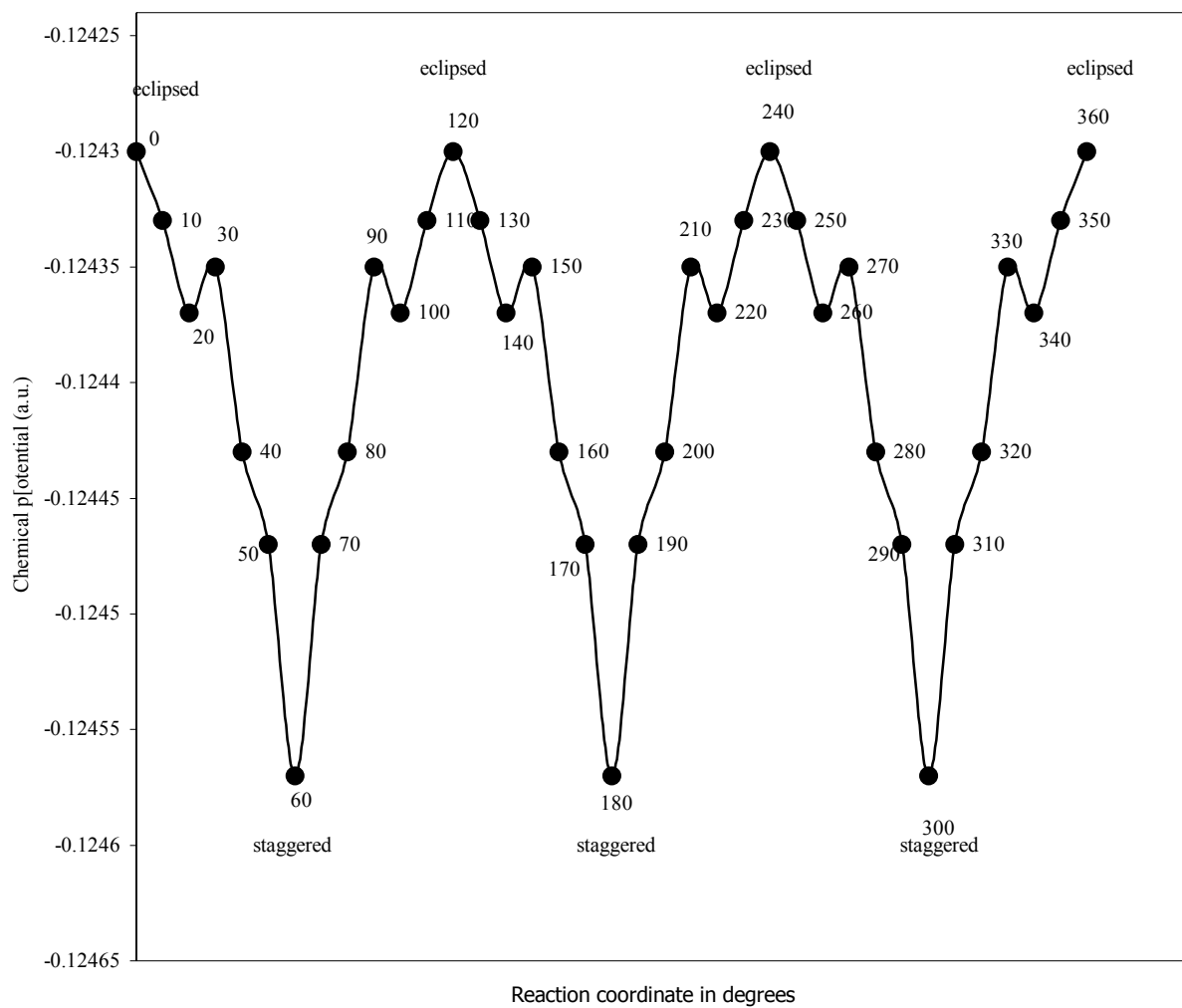


Fig.6 Plot of chemical potential as a function of reaction coordinates in H<sub>3</sub>C-NH<sub>2</sub> system

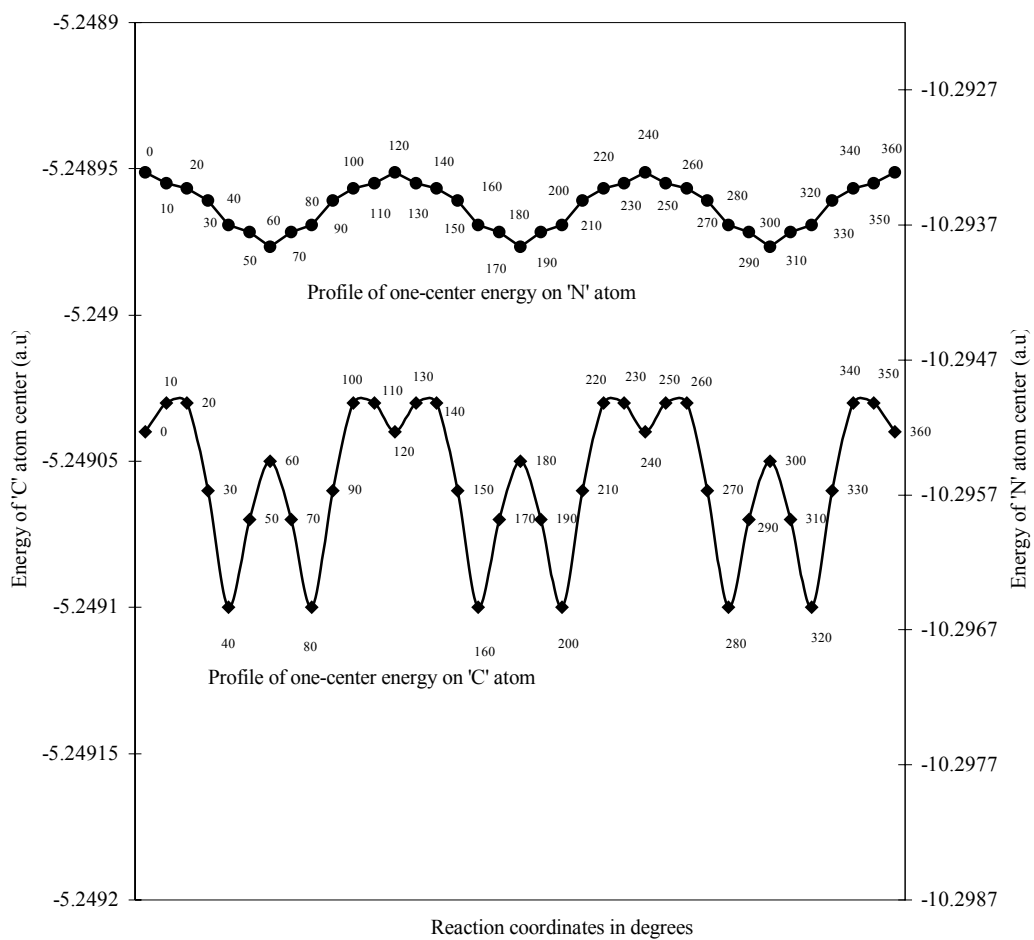


Fig.7 Plot of one -center energies on 'C' and 'N' centers as a function of reaction coordinates in H<sub>3</sub>C-NH<sub>2</sub> system

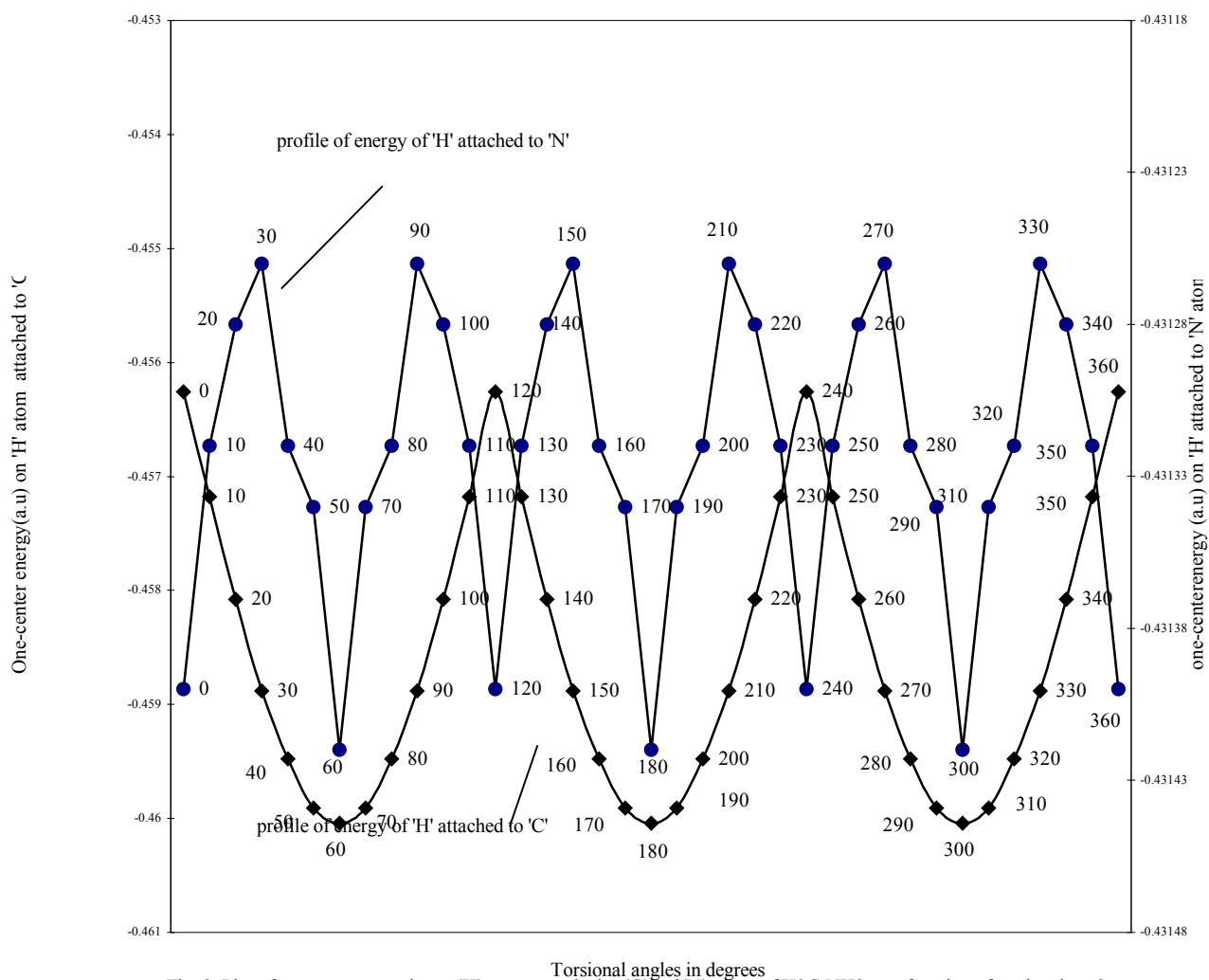


Fig. 8 Plot of one-center energies on 'H' atoms attached to 'C' and 'N' atoms of H<sub>3</sub>C-NH<sub>2</sub> as a function of torsional angles

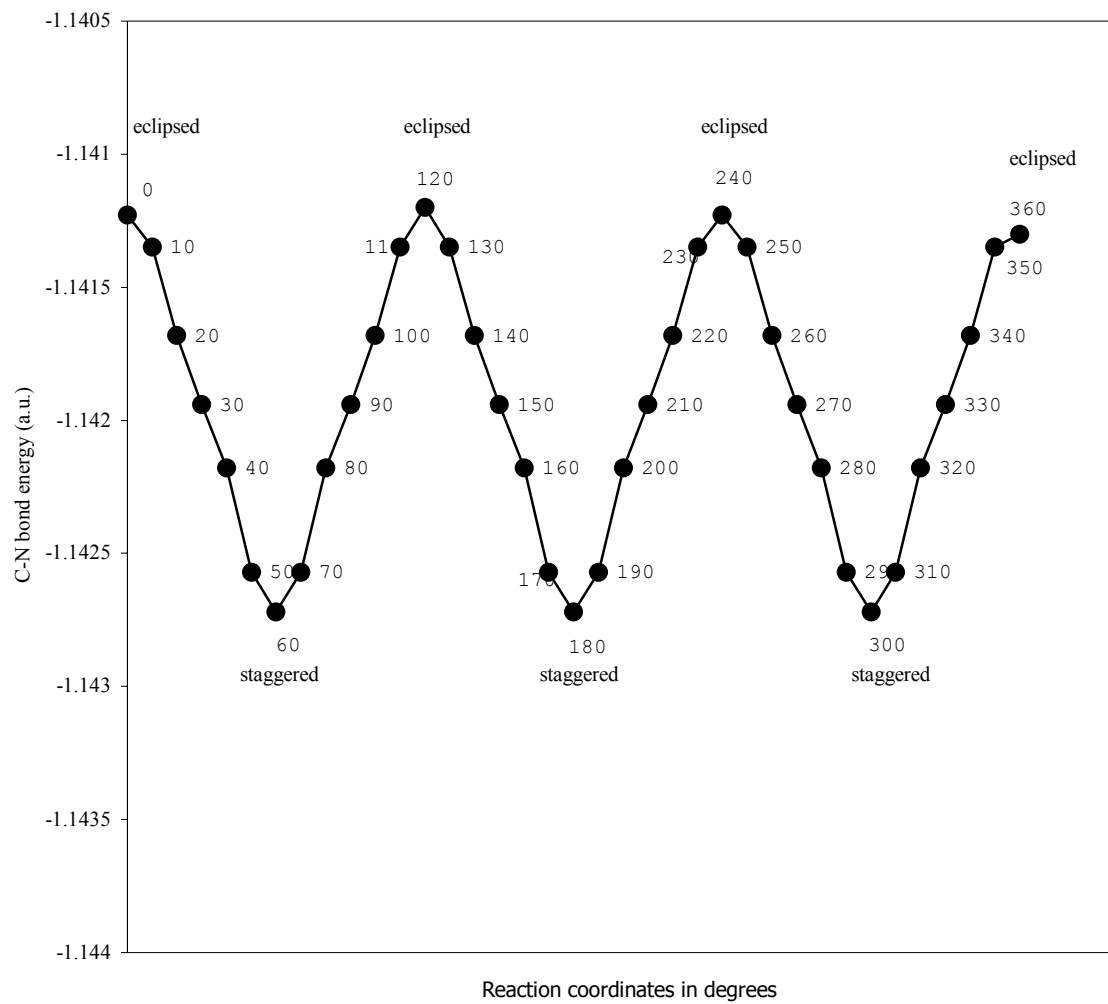
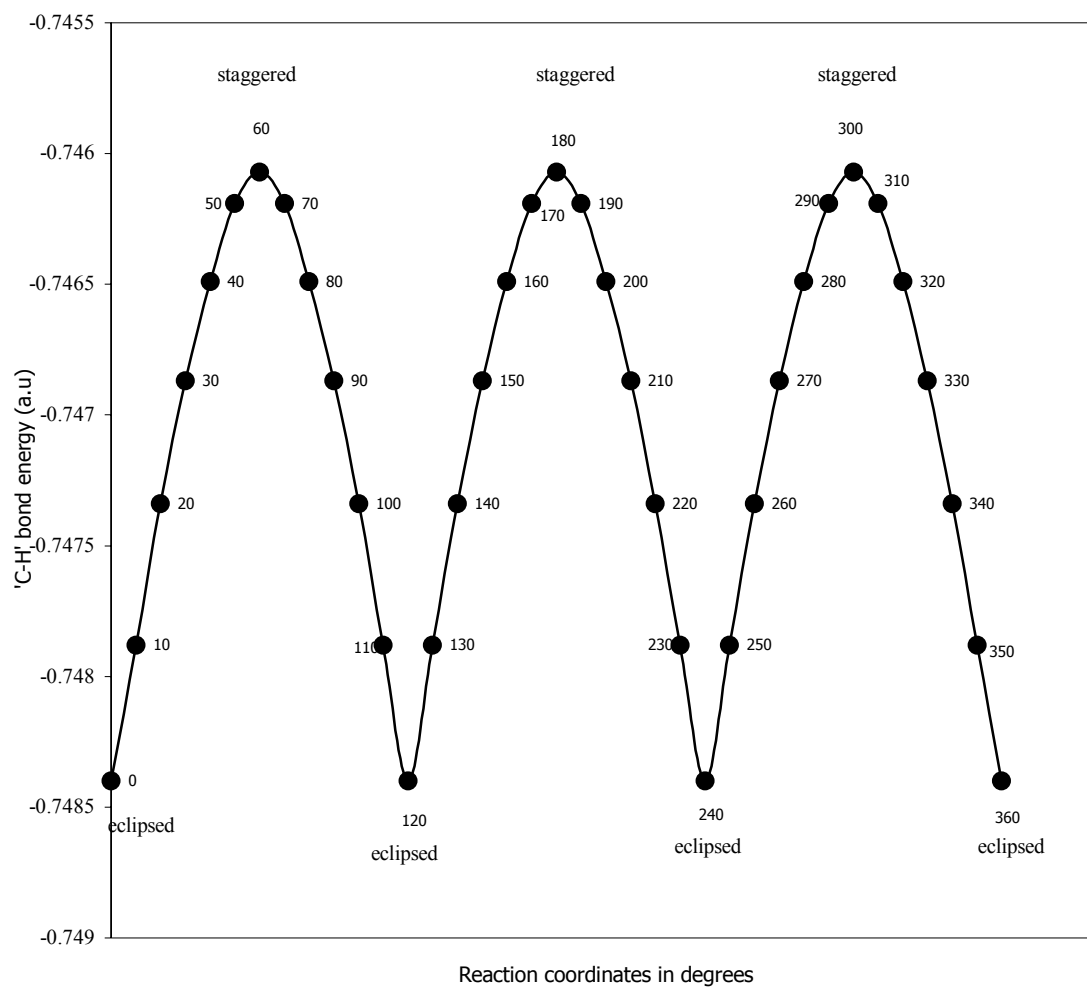


Fig. 9 Plot of 'C-N' bond energy as a function of reaction coordinates in H<sub>3</sub>C-NH<sub>2</sub> system



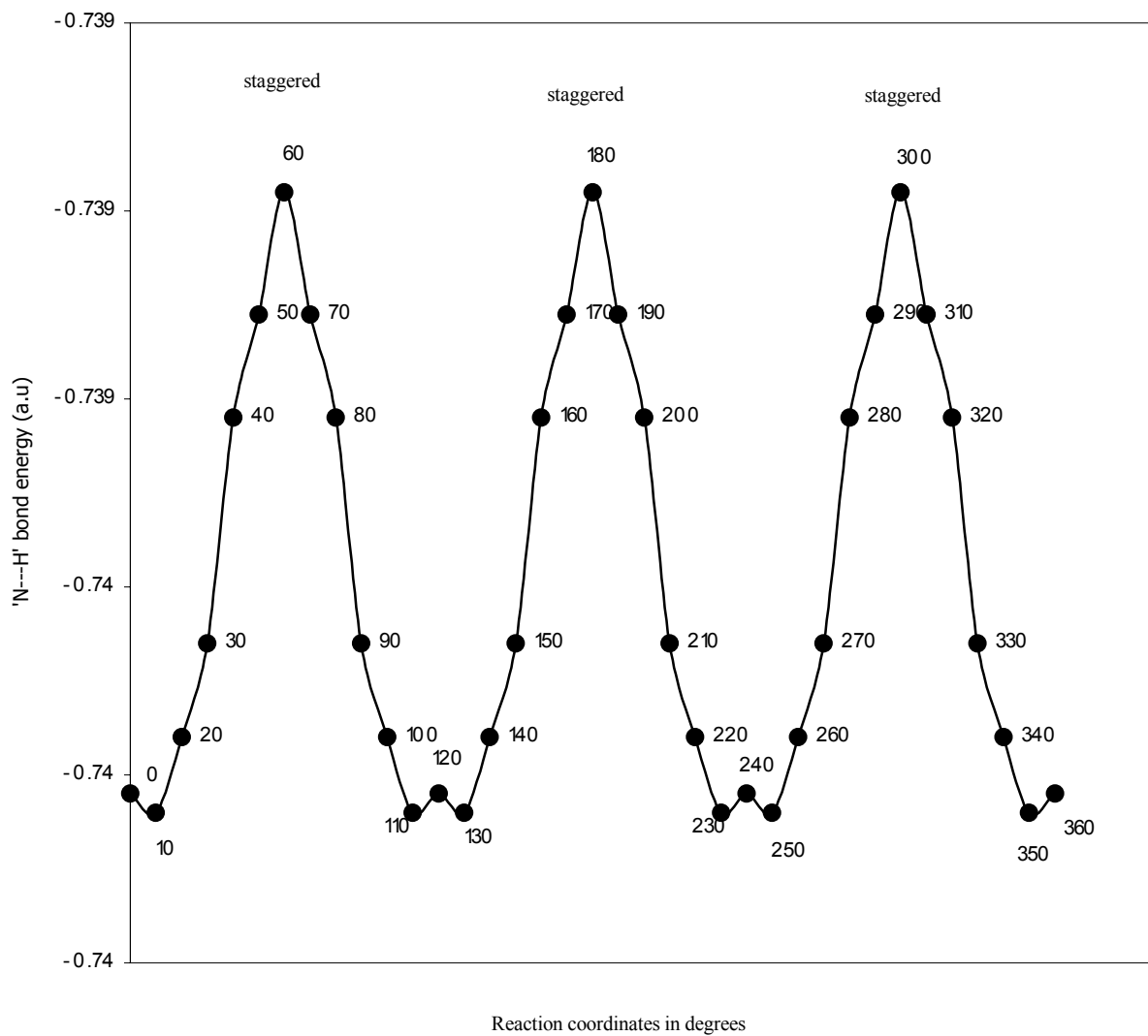


Fig. 11 Plot of 'N-H' bond energy as a function of reaction coordinates in  $\text{H}_3\text{C-NH}_2$  system



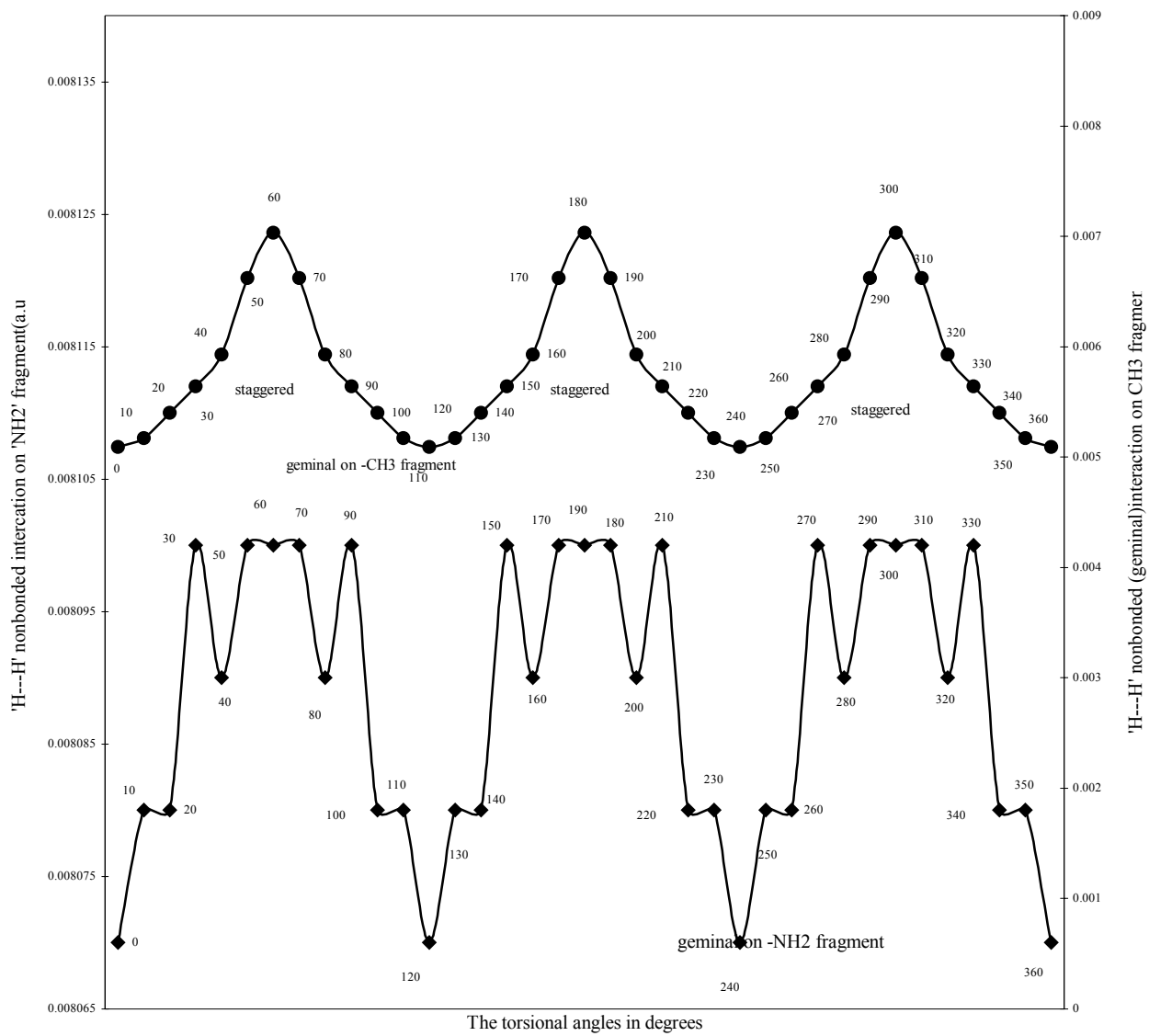


Fig.12 Plot of 'H---H' nonbonded (geminal-NH2 and geminal-CH3)repulsion as a function of torsional angles in H3C-NH2 system.1

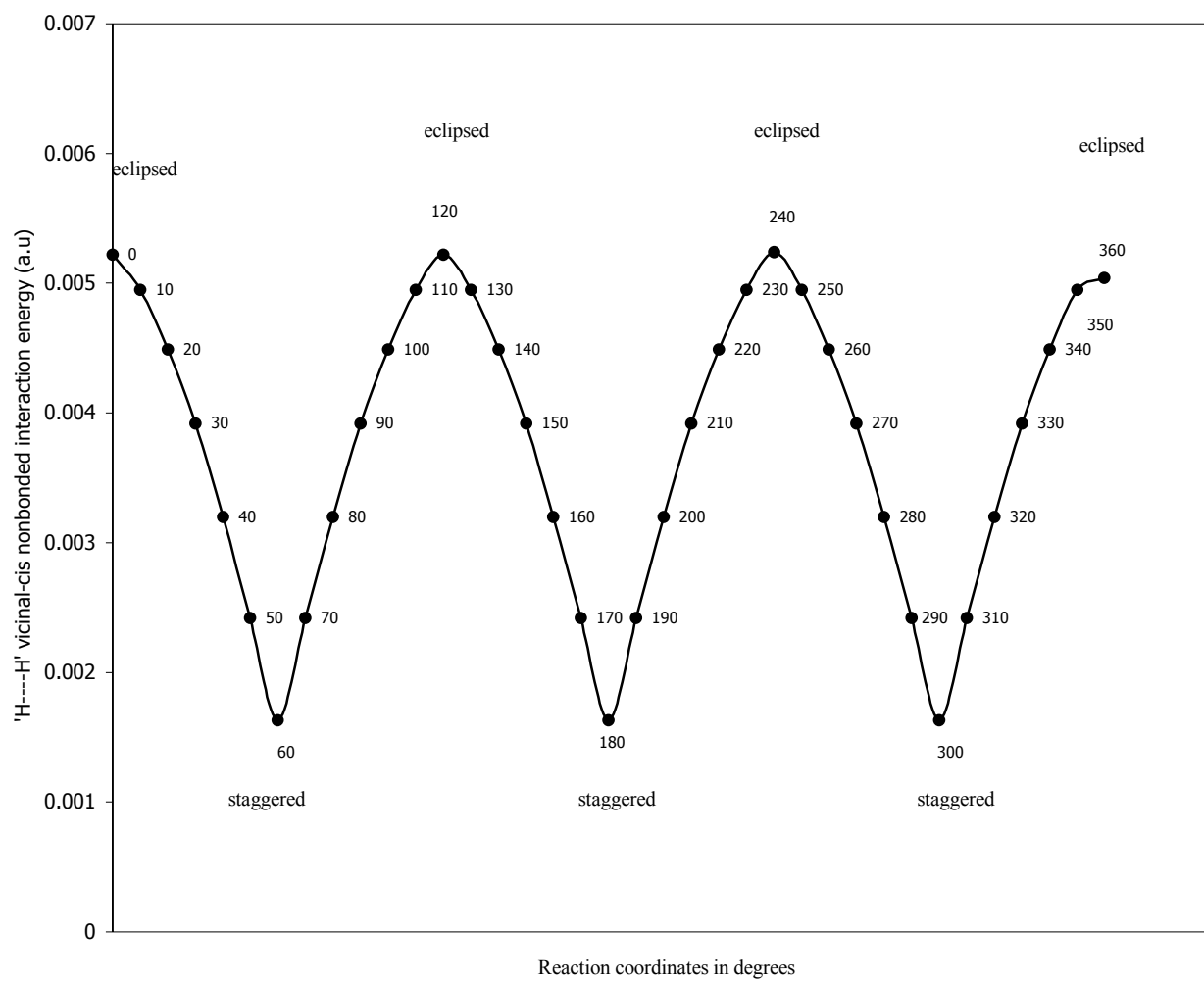


Fig. 13. Plot of 'H...H' (vic-cis) non-bonded interaction as a function of reaction coordinates in H<sub>3</sub>C-NH<sub>2</sub> system

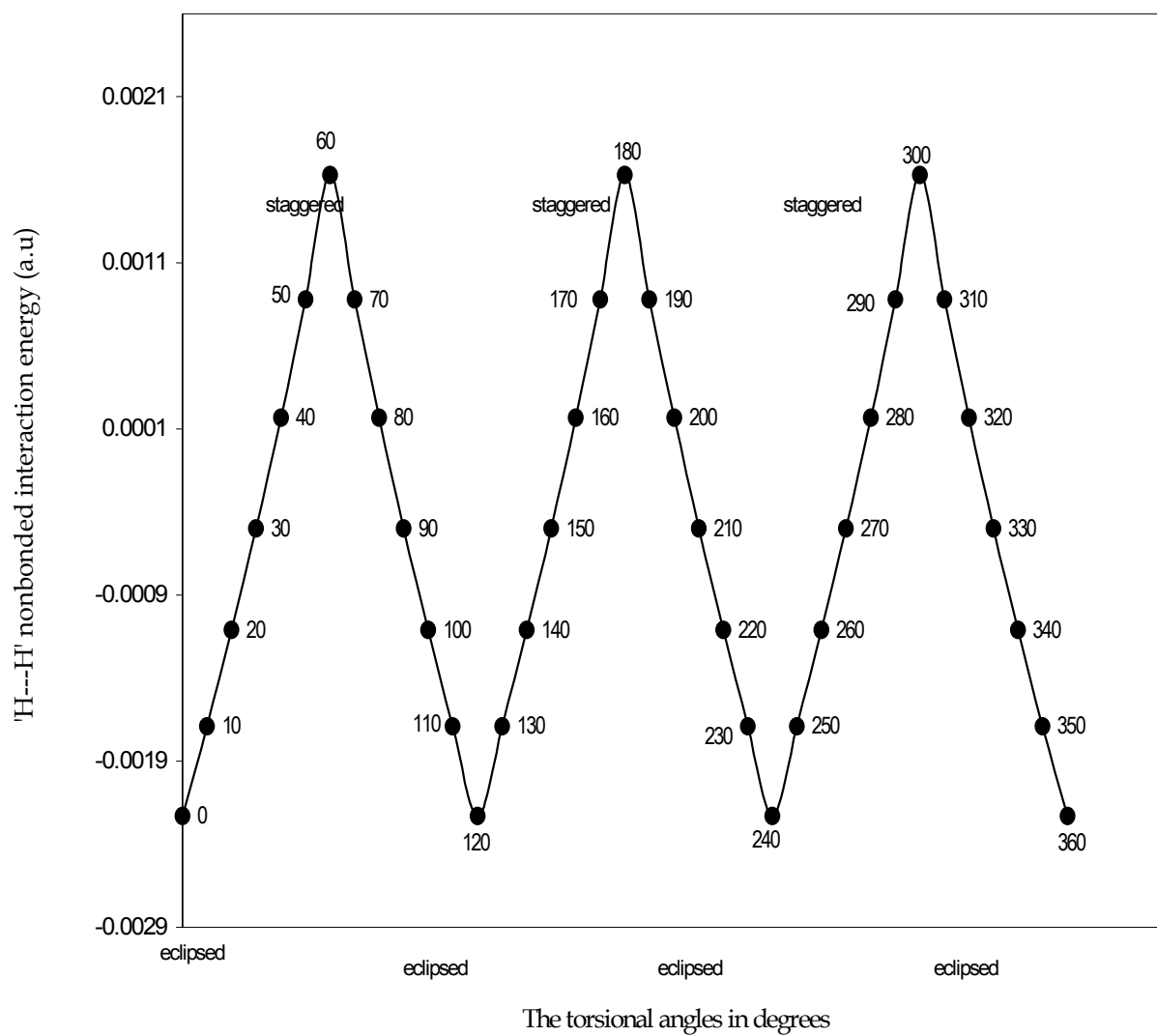
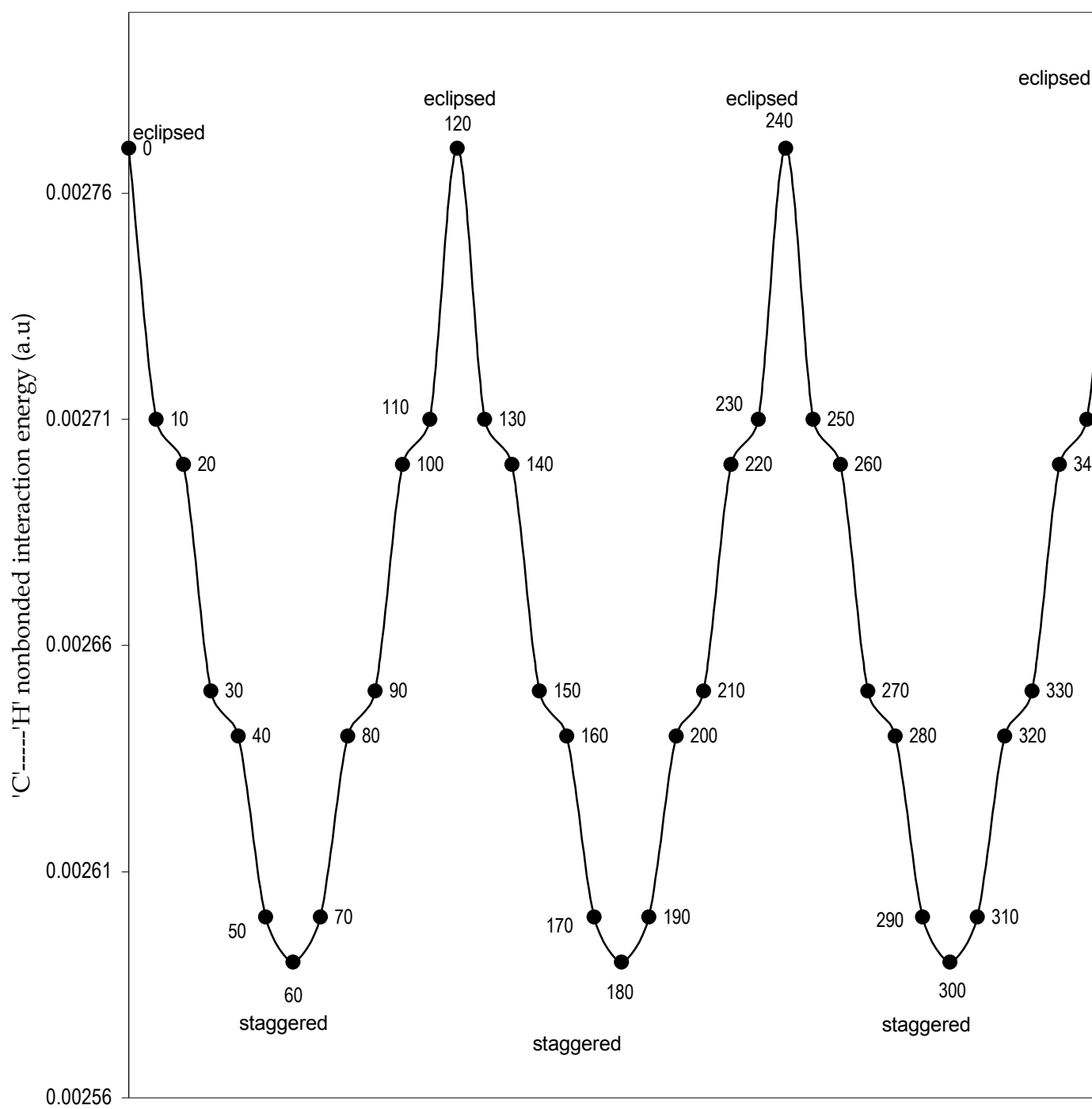


Fig.14 Plot of 'H---H' nonbonded (vicinal-trans) interaction energy as a function of torsional angles in  $\text{H}_3\text{C-NH}_2$  system.



The torsional angles in degrees

Fig. 15 Plot of 'C'----'H' nonbonded interaction energy in  $\text{H}_3\text{C-NH}_2$  system as a function of torsional

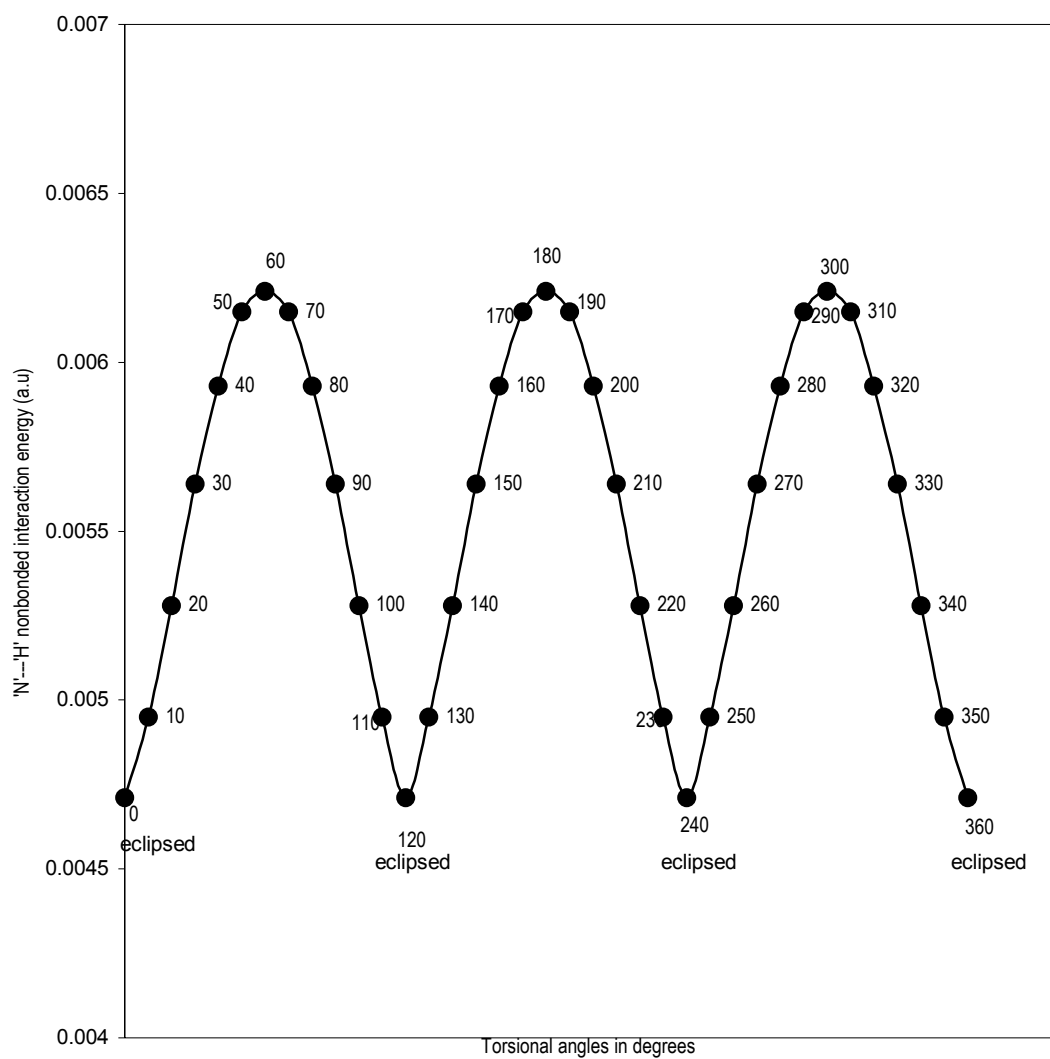


Fig.16 Plot of the 'N'-'H' nonbonded interaction energy as a function of torsional angles in  $\text{H}_3\text{C-NH}_2$  system.

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