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## A Density Functional and Molecular Orbital Study of the Methylamine Conformers<sup>#</sup>

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### Abstract

The physical process of the conformational isomerism of methylamine,  $\text{H}_3\text{C-NH}_2$ , molecule is studied by density functional theory, DFT and CNDO SCF MO theory. It is demonstrated that a number of molecular orbital and density functional parameters are quite efficient in depicting the rotation-induced fluctuation of molecular structure. The hardness profile demonstrates that the evolution of molecular conformations of methylamine under internal rotation about C–N bond is in accordance with the maximum hardness principle, MHP. An energy-partitioning quest of the origin of barrier to internal rotation is performed. A detailed study of the variation of the decomposed energy components as a function of torsional variables reveals that all the one- and two-center bonded and nonbonded interactions exhibit conformational dependence and have differential stabilizing effect on staggered and eclipsed conformations. The study of the nature of the profiles of the one and two center decomposed energy components as a function of torsional angle demonstrates that a number of such energetic effects follow the dynamics of internal rotation of the methylamine molecule so closely that a number of such energy components can be used as the descriptor potential functions of the process of rotational isomerization reaction of the molecule. The present study concludes unequivocally that barrier does not originate from some intramolecular nonbonded repulsion rather the process of the origin and development of barrier involves the whole skeleton of the molecule.

**Keywords.** DFT; hardness; chemical potential; barrier to internal rotation.

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## 1 INTRODUCTION

Methylamine,  $\text{H}_3\text{C-NH}_2$ , is an interesting chemical system for the study of conformational isomerism because, there is a lone pair on 'N' atom to influence its conformational preference. The molecule has one three-fold symmetry group ( $-\text{CH}_3$ ) at one end and the amino group,  $-\text{NH}_2$  at the other end of the skeleton (Figure 1). When the  $-\text{NH}_2$  group rotates around the 'C–N' bond keeping the  $\text{H}_3\text{C-}$  group fixed or vice-versa as a function of torsional variables, the staggered (S) and eclipsed (E) conformations arise periodically thrice during a full  $360^\circ$  rotation. A rough sketch of the two extreme conformations—staggered (S) and eclipsed (E) isomeric forms of the molecule is

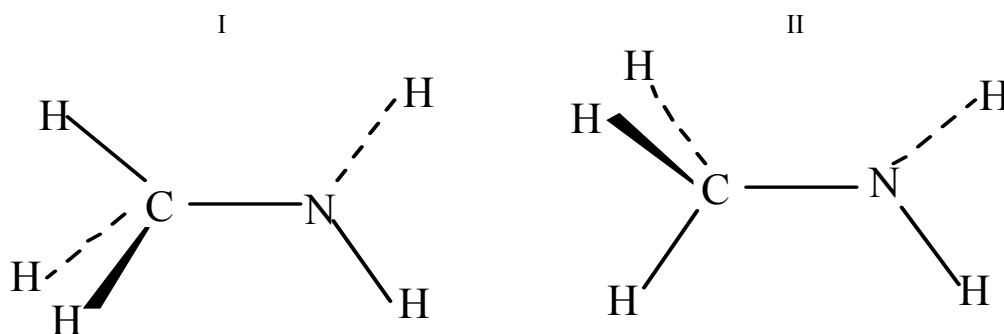
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presented in Figure 1.



**Figure 1.** The extreme conformations of methylamine,  $\text{H}_3\text{C-NH}_2$ , staggered (I) and eclipsed (II) forms.

The conformational isomerism of methylamine system has been studied extensively by experimental as well as theoretical methods [1–10]. The study of conformational isomerism is of prime importance in the present day scenario of chemical thinking and modeling in view of the fact that conformation has a critical effect on bioactivity and reactivity of molecules [11]. The stereochemical outcome of energies and conformation populations will enable more reasonable predictions concerning reactivity, stereochemistry, and product distribution in reactions [11]. Although the height of the barrier can be estimated very accurately by the experimental as well as theoretical methods, an understanding of the origin of barrier is still eluding. The staggered (S) and eclipsed (E) conformers are, in fact, structural isomers and the physical process of generation of  $\text{S} \rightleftharpoons \text{E}$  conformers is in fact a rotational isomerization reaction which can be viewed as a process of reorganization and redistribution of electron density among atoms in a molecule under internal rotation with the condition that the total number of electrons is conserved even though there may be an intramolecular charge transfer process. The physical process like rotational isomerization reaction can be theoretically followed by suitable potential functions of torsional variables. Theoretically various potential functions can be designed. 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 torsional angle dependant profiles of the eigenvalues of the canonical frontier SCF molecular orbitals, HOMO and LUMO, and the energy gap between such frontier orbitals, the HOMO–LUMO gap, can be good descriptors of the physical processes of internal rotation and inversion of molecules [12,13,14]. Since it is the electron density which changes continually under internal rotation of molecules satisfying the condition that the total number of electrons remaining constant, and since the density functional theory, DFT [15,16] is firmly based on electron density as variable, the event of rotational isomerization can be conveniently addressed by DFT. In fact the DFT has provided with certain fundamental theoretical parameters like global hardness ( $\eta$ ) and chemical potential ( $\mu$ ) as new cardinal indices of chemical reactivity and structural stability. Parr *et al.* [17] and Parr and Pearson [18], using the density functional theory, DFT as

basis, have rigorously defined the hardness,  $\eta$  and discovered this new fundamental quantity, the electronic chemical potential,  $\mu$ . The method became really challenging after the enunciation of the principle of maximum hardness, PMH [19] by Pearson, which states that “there seems to be a rule of nature that molecules arrange themselves as to be as hard as possible”. Parr and Chattaraj [20] provided a theoretical justification of PMH. Further studies and critical analysis of Pearson [21] and Parr *et al.* [22,23] have established the fundamental veracity and justification of PMH. However, theoretical considerations led to a refined statement of the principle. Under conditions of constant temperature and chemical potential, chemical systems tend to a state of maximum hardness. When the molecule evolves from an unstable form towards the stable equilibrium form, its global hardness increases and in the reverse process when the molecule evolves from equilibrium form to non-equilibrium form, its global hardness decreases. Chattaraj *et al.* [24] further held that chemical hardness has been out to be a cardinal index of molecular structure, reactivity, binding and dynamics. Although the PMH is strictly valid for constant chemical potential, its relaxation is also observed by Pearson and Palke [25], Ghosh [12] and Ghosh *et al.* [13,14], and Toro-Labbé *et al.* [26]. These workers have demonstrated that the operation of PMH is fulfilled by the structural situation associated with the formation of transition state (TS) in a chemical reaction, in inversion, asymmetric deformation, internal rotation, and many isomerization reactions when the chemical potential does not remain constant. The structural changes in molecules caused by the physical processes of inversion, deformation, internal rotation, and various types of simple reactions can be followed in terms of the computed profiles of hardness and softness. The hardness profiles of molecules have been computed by Chattaraj *et al.* [27], Sannigrahi *et al.* [28], Chattaraj *et al.* [29], and Ghosh [12] for the physical process of internal rotation, Datta [30], and Ghosh *et al.* [13,14] for the phenomenon of structural inversion. The new paradigm seems to usher a bright promise of better understanding of the physical process of evolution of conformations of molecules due to inversion and internal rotation around single bond. The prediction and understanding of changes in energy accompanying a change in state for the total system and for every atom in the system are among the most important challenge in chemistry. Fischer and Kollmar [31] decomposed the total energy of a molecular system into one- and two-center physical components. We [13,14] have noted that the energy-partitioning quest of the origin of barrier to inversion is a meaningful venture. In this study we propose to invoke some theoretical parameters provided by the molecular orbital and density functional theories to follow the dynamics of the internal rotation, and to perform an energy-partitioning search of the origin of barrier to the internal rotation of methylamine molecule.

## 2 METHOD OF COMPUTATION

The exact density functional definitions of the chemical potential,  $\mu$  and hardness,  $\eta$  are as follows [17,18]:

$$\mu = (\delta E / \delta N)_v \qquad \eta = 1/2(\delta \mu / \delta N)_v \qquad (1)$$

where  $N$  is the number of electrons and  $v$  is the potential due to the nuclei plus any external potential.

Although  $\eta$  and  $\mu$  are rigorously defined in terms of DFT, Pal *et al.* [32] have pointed out that these quantities can not be rigorously obtained using *ab initio* wave function formalism. The operational definitions are obtained by approximating the density functional equations in terms of ionization potential and electron affinity of the system as follows:

$$\mu = -(I + A)/2 \qquad \eta = (I - A)/2 \qquad (2)$$

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

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

$$-\epsilon_{\text{HOMO}} = I \qquad -\epsilon_{\text{LUMO}} = A \qquad (3)$$

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

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

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

The gap in energy,  $\Delta\epsilon$ , between the HOMO and LUMO is:

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

Each orbital energy or the eigenvalues of canonical SCF orbitals are in fact the eigenvalues of effective one–electron operator:

$$h \varphi_i = \epsilon_i \varphi_i \qquad (7)$$

where  $h$  is the effective one–electron Fock operator associated with the eigen function,  $\varphi_i$  and  $\epsilon_i$  is the eigenvalue.

Now, it has been amply demonstrated by Gordon [6], Brunck and Weinhold [9] and Ghosh [12] that the CNDO SCF method of Pople and co–workers [33] is sufficiently reliable for the study of molecular conformations. There is an added advantage of Pople's approximate SCF method that this is perhaps the only method in which the total energy of a molecule can be decomposed into one– and two–center physical components. The density functional quantities are inevitably approximate in nature and the approximate nature of Koopmans theorem is widely known [34]. It is also stated that the density functional quantities are independent of molecular orbital scheme [16] and it is amply demonstrated by Ghosh [12] and Ghosh *et al.* [13, 14, 35] that the density functional parameters can be efficiently evaluated by approximate SCF method of Pople. We have, therefore,

invoked the CNDO/2 version of Pople's method [33] in this study. The overlap and electron repulsion integrals are evaluated through the explicit formula laid down by Roothaan [36]. Accordingly, the STO basis set and standard parameters [33] are used in this calculation. The energy-partitioning algorithm due to Fischer and Kollmar [31] is laid down below.

The total CNDO energy  $E$  of a system is:

$$E = \sum E_A + \sum \sum E_{AB} \quad (8)$$

where  $E_A$  are monatomic terms and  $E_{AB}$  are diatomic terms.

The monatomic terms and the diatomic terms can be further broken down into the following components as follows:

$$E_A = E_A^U + E_A^J + E_A^K \quad (9)$$

where  $E_A^U$ ,  $E_A^J$  and  $E_A^K$  are total monatomic orbital energy, electron–electron repulsion energy, and non–classical exchange energy respectively.

The explicit formula for evaluation of these energy components are laid down below:

$$E_A^U = \sum_{\mu \in A} P_{\mu\mu} U_{\mu\mu} \quad (10)$$

where  $P_{\mu\mu}$  is an element of bond order matrix and  $U_{\mu\mu}$  is the one–electron energy of the  $\mu$ –th atomic orbital, AO in the isolated atom.

$$E_A^J = \frac{1}{2} (P_A^2 \gamma_{AA}) \quad (11)$$

where  $\gamma_{AA}$  is electron–electron repulsion between two electron of atom A and  $P_A$  is the charge density on atom A:

$$P_A = \sum_{\mu} P_{\mu\mu}, \quad (12)$$

where  $\mu$  runs through all the AO's of atom A.

$$E_A^K = -1/4 \gamma_{AA} \sum_{\mu} \sum_{\nu} P_{\mu\nu}^2 \quad (13)$$

where  $\gamma_{AA}$  is electron–electron repulsion between two electrons of atom A and  $P_{\mu\nu}$  are elements of charge density and bond order matrix.

The physical components of the two–center energy terms:

$$E_{AB} = E_{AB}^R + E_{AB}^V + E_{AB}^J + E_{AB}^K + E_{AB}^N \quad (14)$$

The physical meaning and explicit formulae of the components  $E_{AB}^R$ ,  $E_{AB}^V$ ,  $E_{AB}^J$ ,  $E_{AB}^K$ ,  $E_{AB}^N$  may be expressed in following manner:

The two center resonance integral,  $E_{AB}^R$  is:

$$E_{AB}^R = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} \beta_{\mu\nu} S_{\mu\nu} \quad (15)$$

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 orbitals  $\mu$  and  $\nu$  and  $P_{\mu\nu}$  are elements of density matrix.

$$E_{AB}^V = -P_A V_{AB} - P_B V_{BA} \quad (16)$$

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.

The two center coulomb repulsion,  $E_{AB}^J$  is:

$$E_{AB}^J = P_A P_B \gamma_{AB} \quad (17)$$

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

The two center exchange interaction term,  $E_{AB}^K$  is:

$$E_{AB}^K = -1/2 \gamma_{AB} \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^2 \quad (18)$$

The two center nuclear –nuclear repulsion,  $E_{AB}^N$  is:

$$E_{AB}^N = Z_A Z_B / R_{AB} \quad (19)$$

where  $Z_A$  and  $Z_B$  are the nuclear charges on atoms A and B respectively and  $R_{AB}$  is the distance between two nuclei of atoms A and B and all other terms in Eqs. (18) and (19) are already mentioned. The physical significance of decomposed energy components is discussed elsewhere [13,14,37] and is not repeated here.

**Table 1.** The optimized structural parameters of  $H_3C-NH_2$  as a function of torsional angles

Angle of torsion ( $\theta$ , degrees)	C–H ( $A^\circ$ )	$\angle$ HCH (degree)	C–N ( $A^\circ$ )	N–H ( $A^\circ$ )	$\angle$ 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), eigenvalues of the frontier orbitals ( $\epsilon_{HOMO}$ ,  $\epsilon_{LUMO}$ ), the HOMO–LUMO gap ( $\Delta\epsilon$ ), global hardness ( $\eta$ ) and chemical potential ( $\mu$ ) of  $H_3C-NH_2$  as a function of torsional angles.

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

## 2.1 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 adopted the method of geometry optimization technique, GOT, where the bond lengths and bond angles vary continuously under internal rotation of the molecule. 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° 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 conformations. The computed results 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.

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

Angles of rotation (θ, 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 and their physical components on ‘N’ atom and ‘H’ atom attached to ‘N’ as a function of torsional angles in H<sub>3</sub>C–NH<sub>2</sub>

The angles of rotation (θ, degrees)		E <sup>U</sup> (a.u)	E <sup>J</sup> (a.u)	E <sup>K</sup> (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



The decomposed one- and two-center bonded and nonbonded interactions and their physical components are presented in Tables 3–13.

**Table 5.** The C–N 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(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 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	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 geminal interaction (NH<sub>2</sub> fragment) and their physical components as a function of torsional angles in H<sub>3</sub>C–NH<sub>2</sub>

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 geminal interaction (CH<sub>3</sub>-fragment) and their components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub>

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 components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub>

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 components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub>

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 components as a function of torsional angles in H<sub>3</sub>C-NH<sub>2</sub>

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

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

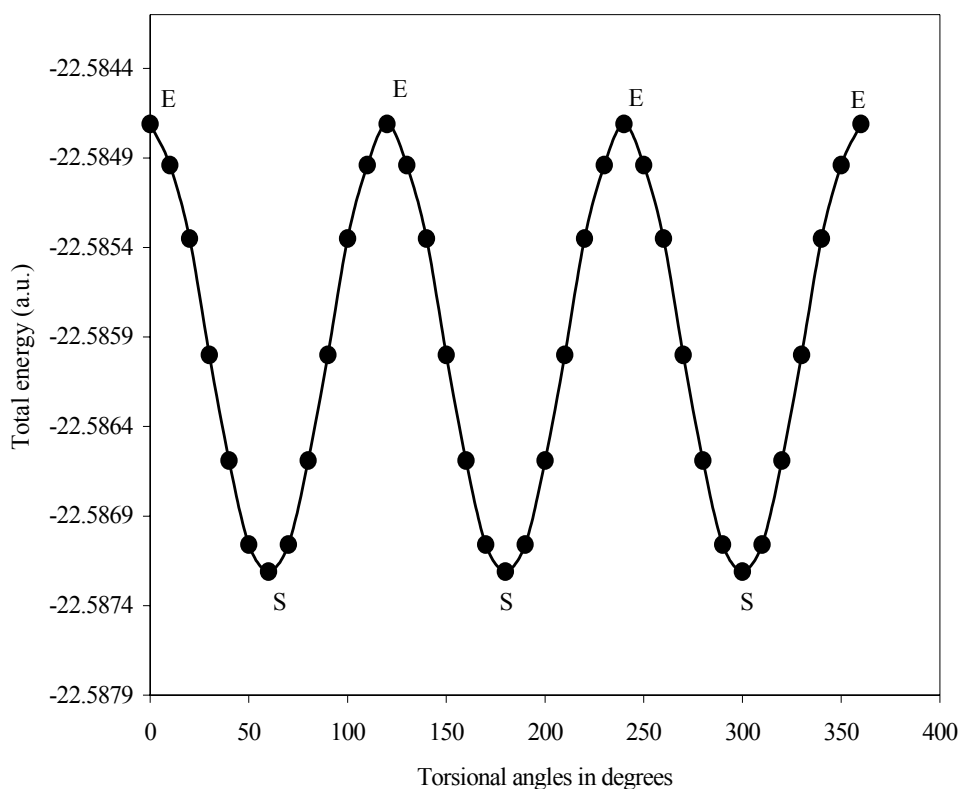
Angle of torsion ( $\theta$ , degrees)	E <sup>J</sup> (a.u)	E <sup>N</sup> (a.u)	E <sup>V</sup> (a.u)	E <sup>K</sup> (a.u)	E <sup>R</sup> (a.u)	E (N...H) (a.u)
0	1.32662	1.25753	-2.58064	-0.00082	0.00202	0.00471
10	1.33128	1.25753	-2.58513	-0.00123	0.00250	0.00495
20	1.33584	1.25753	-2.58953	-0.00164	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

## 2.1 Computer Software

We have developed the necessary computer program with the help of Pople's [33] book and standard diagonalization package. We have also developed the energy-partitioning program. The DFT parameters are coupled with the eigenvalues of the canonical SCF orbital energies through equations 3–5.

## 3 RESULTS AND DISCUSSION

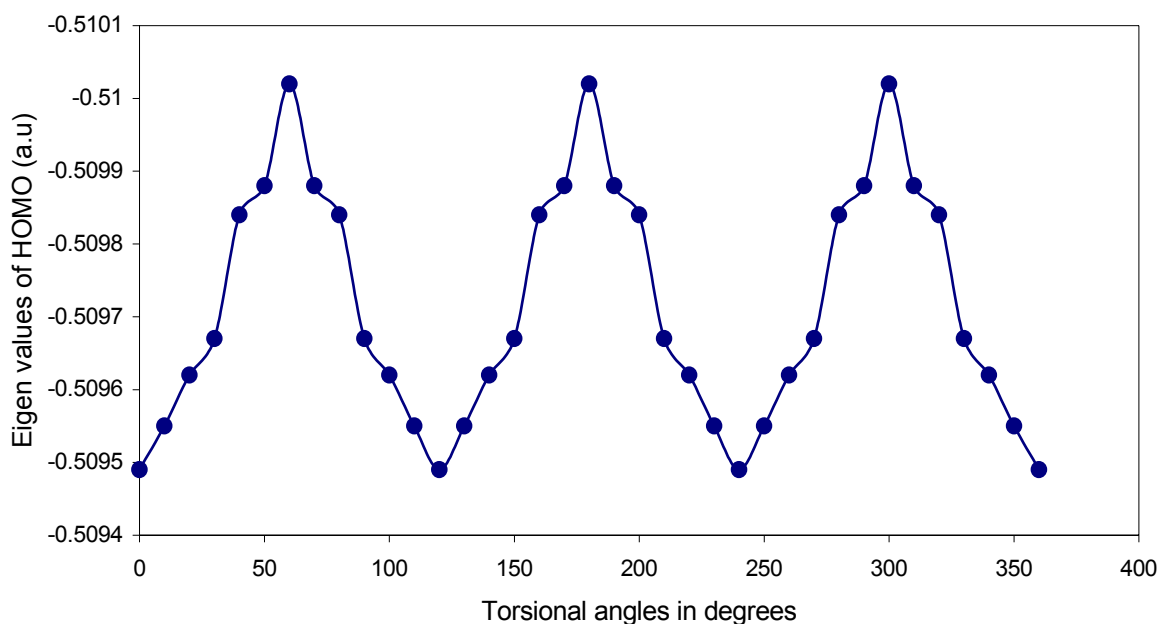
Looking at the optimized geometric parameters in the generated conformations of the molecule in Table 1 it is evident that all the bond lengths are invariant of internal rotation while clearly the bond angles relax and open with the gradual release of steric strain as the rotation starts from the eclipsed conformation. The total energy of methylamine molecule is plotted as a function of torsional angles in Figure 2 and the curve describes the change of the total energy induced by the reorganization of atoms in the molecule. The nature of the profile in Figure 2 is reminiscent of the corresponding potential energy diagram of ethane molecule.



**Figure 2.** Plot of total energy as a function of reaction coordinate in  $\text{H}_3\text{C-NH}_2$ .

The extreme conformations are staggered (S) and eclipsed (E). The difference of energy between the most stable isomer (S) and most unstable isomer (E) is 0.0024196 a.u; hence the barrier height is 1.52 kcal/mole. The experimental value of the barrier height is 1.98 kcal/mole [2,3] and the

corresponding value in an *ab initio* calculations by Pedersen and Morokuma [4] is 2.02 kcal/mole, Bader *et al.* [10] is 2.0 kcal/mole. Results demonstrate that the barrier height of methylamine molecule evaluated by the present work compares reasonably well with the corresponding experimental [2,3] and *ab initio* theoretical values [4,10]. Hence, the present calculation demonstrates once again that the approximate SCF MO method of Pople is a sufficiently powerful quantum chemical paradigm to obtain the correct glimpses of the conformational behavior of molecules under internal rotation.

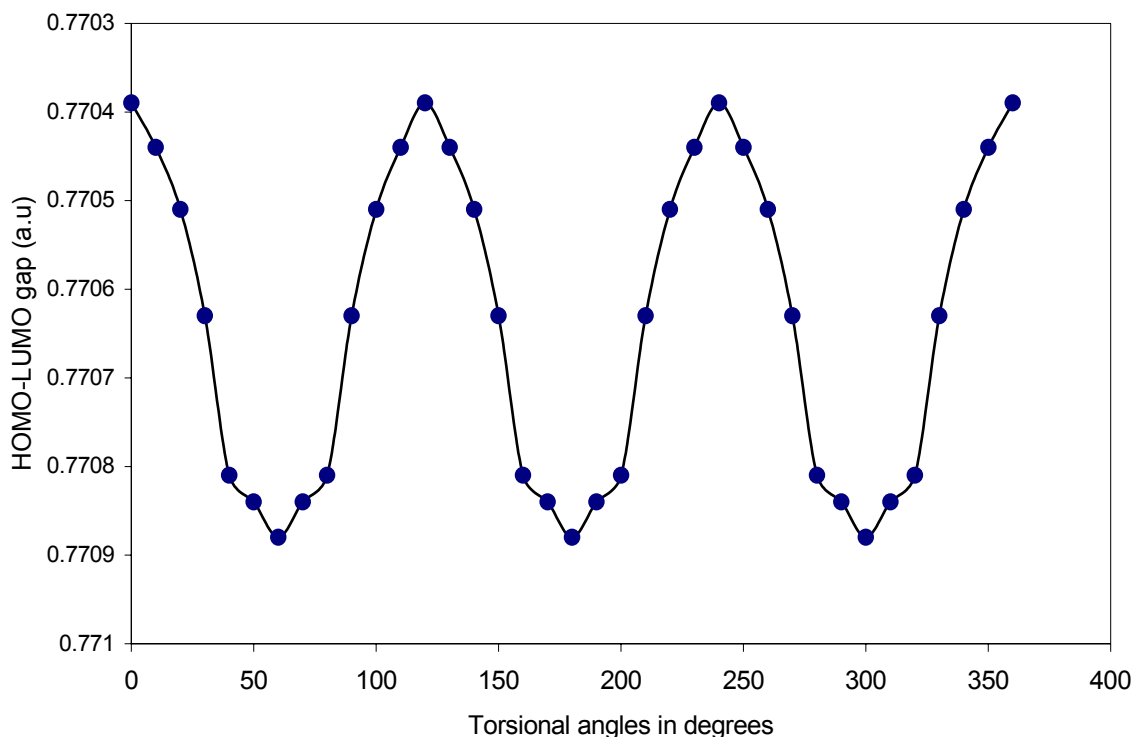


**Figure 3.** Plot of HOMO eigenvalues as a function of reaction coordinate in  $\text{H}_3\text{C-NH}_2$ .

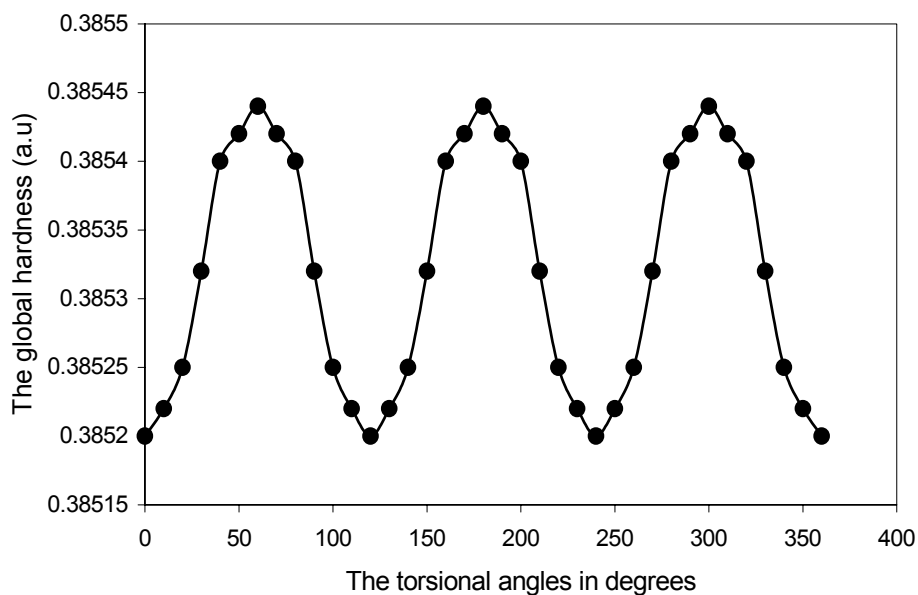
One can suggest, as a rationale of the success of approximate theory in computing correct barrier height, that the correlation effect is constant of molecular conformations and scientists believe that always there is some cancellation factor in both *ab initio* and approximate quantum chemical methods. Now let us address the physical process of conformational isomerism by invoking the computed molecular orbital as well as density functional parameters.

From Table 2 it is apparent that the eigenvalues of the HOMO, the HOMO–LUMO gap, the global hardness and chemical potential vary in a regular pattern with torsional variable; but the eigenvalues of LUMO vary a bit anomalously under internal rotation.

The eigenvalues of the frontier canonical orbital, HOMO, the HOMO–LUMO gap ( $\Delta\epsilon$ ), the global hardness and the chemical potential are plotted as a function of torsional angles in Figures 3, 4, 5 and 6 respectively.



**Figure 4.** Plot of HOMO-LUMO gap as a function of torsional angles in methylamine.

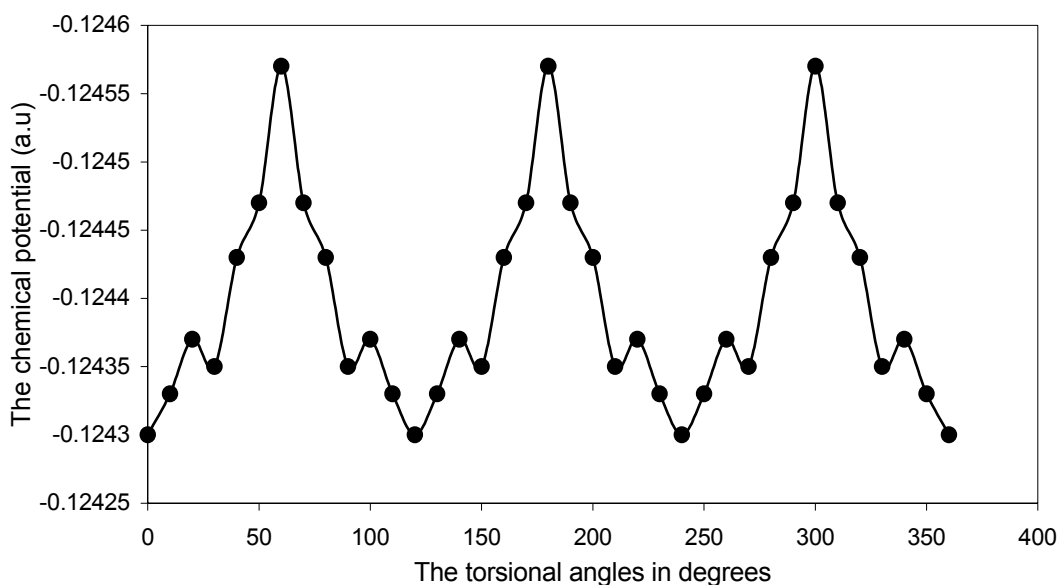


**Figure 5.** The plot of global hardness as a function of torsional angles in methylamine.

### 3.1 Molecular Orbital Parameters

From analysis of the nature of the profile of the eigenvalues of the canonical frontier orbital in fig.3 it can be argued that the profile can express beautifully the process of staggering and eclipsing that are occurring periodically under internal rotation of the molecule. A comparison of Figure 3

vis-à-vis Figure 2, the profile of the potential energy function, reveals that the profile of eigenvalues of the SCF canonical frontier orbitals of methylamine molecule under torsional variable can be used as potential function or descriptor of the rotational structural isomerization process of the molecule. The role of frontier [38,39,40] orbitals in deciding the equilibrium shapes of the molecules is well established. We [12] have already observed that the profiles of the eigenvalues of the canonical SCF frontier orbitals of ethane under internal rotation is good descriptors of the conformational isomerism of the molecule. The present investigation demonstrates once again the power of the torsional angle dependent eigenvalue profile of the canonical frontier orbitals to depict the conformational behavior of molecules under internal rotation.

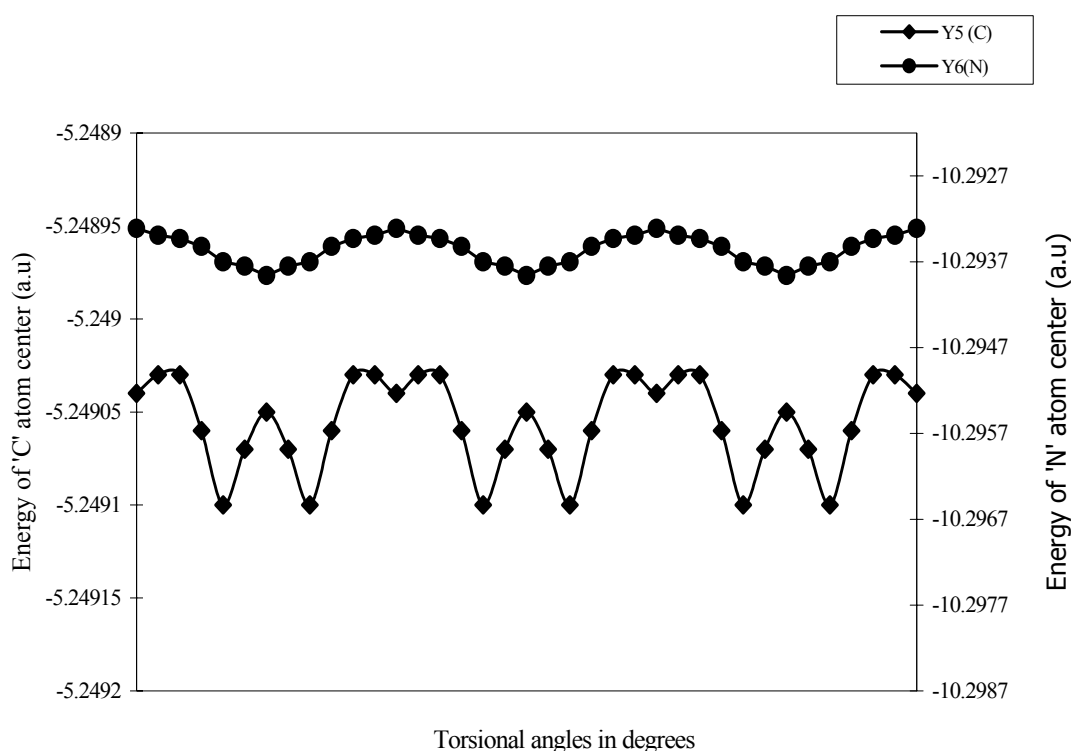


**Figure 6.** The plot of chemical potential as a function of torsional angles in methylamine.

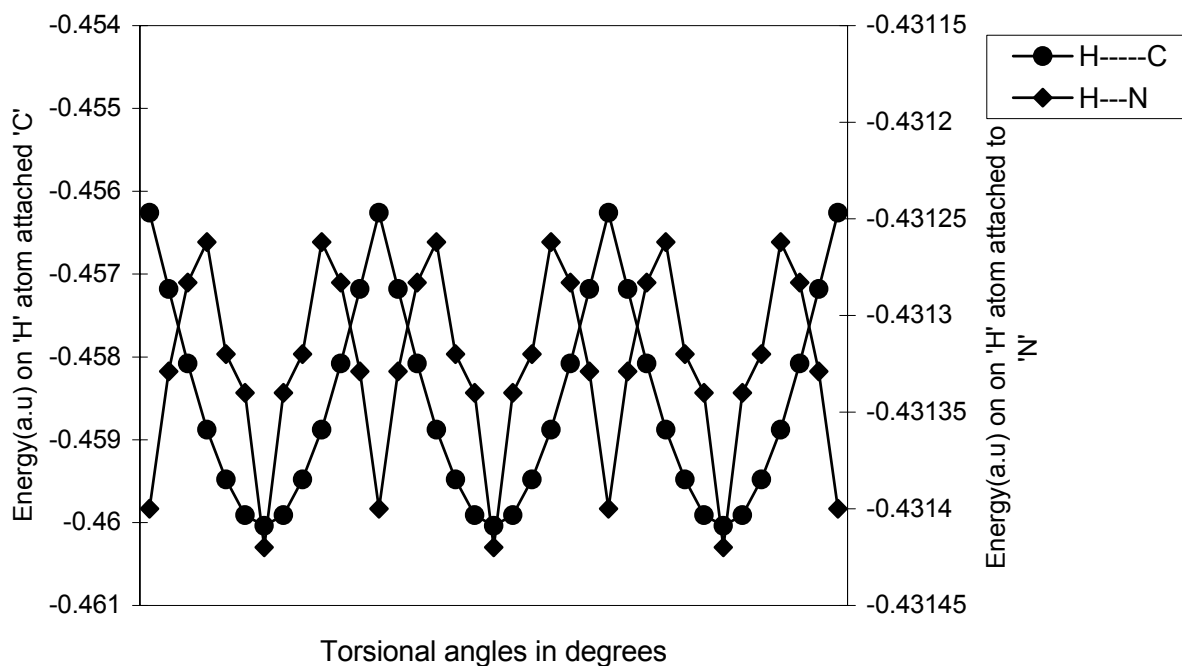
From Table 2 it is evident that the HOMO–LUMO gap,  $\Delta\epsilon$ , is maximum for staggered conformation and minimum for the eclipsed conformation. The role of the magnitude of  $\Delta\epsilon$  in predicting stability conditions in molecules is well known. Thus the nature of variation of  $\Delta\epsilon$  of the molecule under torsion is internally consistent. Comparing the nature of profile of  $\Delta\epsilon$  in Figure 4 vis-à-vis that of the potential energy profile in Figure 2 we see that the profile of the Homo–Lumo gap is the mirror image of the potential energy profile; thus, the HOMO–LUMO gap, a molecular orbital parameter—can be a descriptor of the dynamic isomerization process of the molecule under internal rotation. The above noted good correlation between the profiles of the eigenvalues of canonical frontier orbitals and the gap in energy of the frontier orbitals and the total energy as a function of torsional variables suggest unequivocally that the eigenvalues of the frontier orbitals and the HOMO–LUMO gap can be used as true descriptors of the rotational isomerization process of the methylamine molecule under the dynamics of torsion about single bond.

### 3.2 Density Functional Parameters

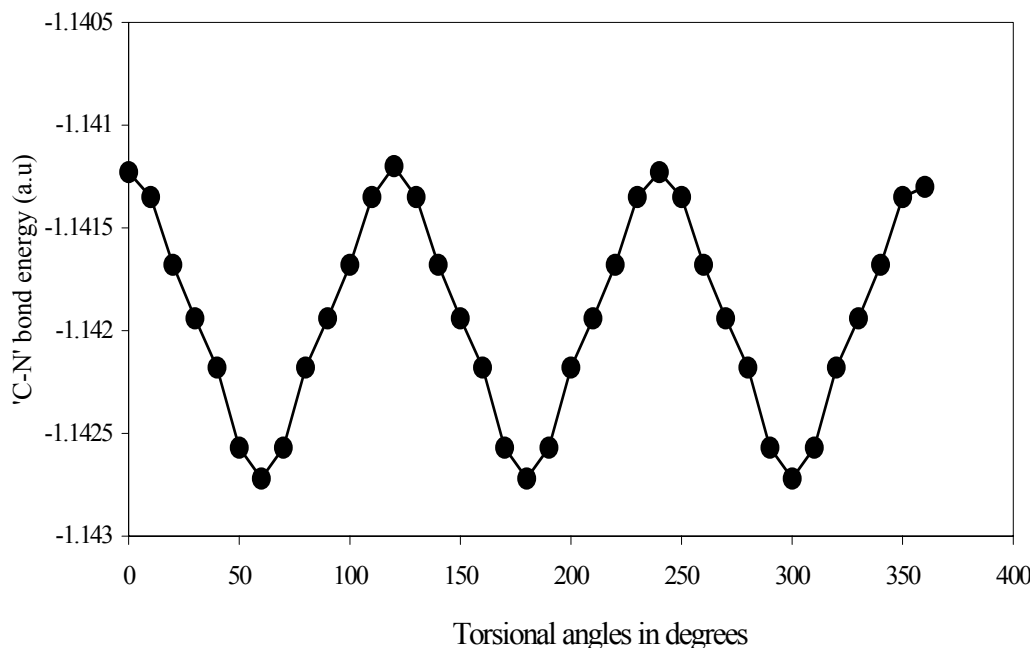
The global hardness ( $\eta$ ): It is the prediction of the density functionally dressed HSAB principle that when a molecule evolves from equilibrium to non-equilibrium structure its hardness,  $\eta$ , will decrease and in the reverse process of transition from non-equilibrium towards equilibrium form this parameter will increase and would be maximum at the equilibrium geometry. Table 2 shows that the global hardness of the staggered form is maximum and that of eclipsed form is minimum. Figure 5 shows that the hardness profile is a periodic function of torsional angle. It is distinctly evident from the nature of the profile that when the molecule evolves from the staggered conformation towards the eclipsed conformation the global hardness decreases and becomes minimum at the eclipsed conformation and while the structure evolves in the reverse direction from eclipsed conformation towards the staggered conformation the global hardness increases to become maximum at the staggered conformation. Thus, the pattern of the variation of global hardness with the structural evolution under internal rotation is in accordance with the principle of maximum hardness, PMH. A comparative study of the Figure 2 vis-à-vis the Figure 5 reveals that the profile of the global hardness is the mirror image of the potential energy curve. This good correlation between the profiles of hardness and potential energy under internal rotation suggest that the global hardness is a true descriptor of the physical process of conformational isomerism arising out of the dynamics of internal rotation in the methylamine molecule.



**Figure 7.** Plot of one-center energies on C and N centers as function of torsional angles in methylamine.



**Figure 8.** Plot one-center energies on 'H' atoms attached to 'C' and 'N' atoms in methylamine.



**Figure 9.** Plot of C–N bond energy as a function of torsional angles in methyl amine.

### 3.3 Energy Partitioning Analysis

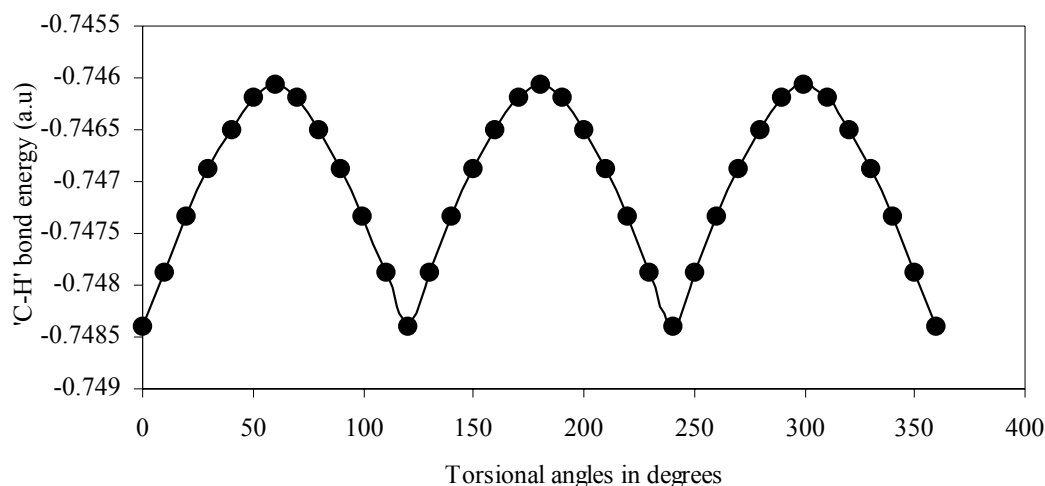
The type and number of one- and two-center bonded and nonbonded interactions in methylamine,  $\text{H}_3\text{C-NH}_2$ , molecule is straightforward from Figure 1 and can be easily tabulated and classified as follows:



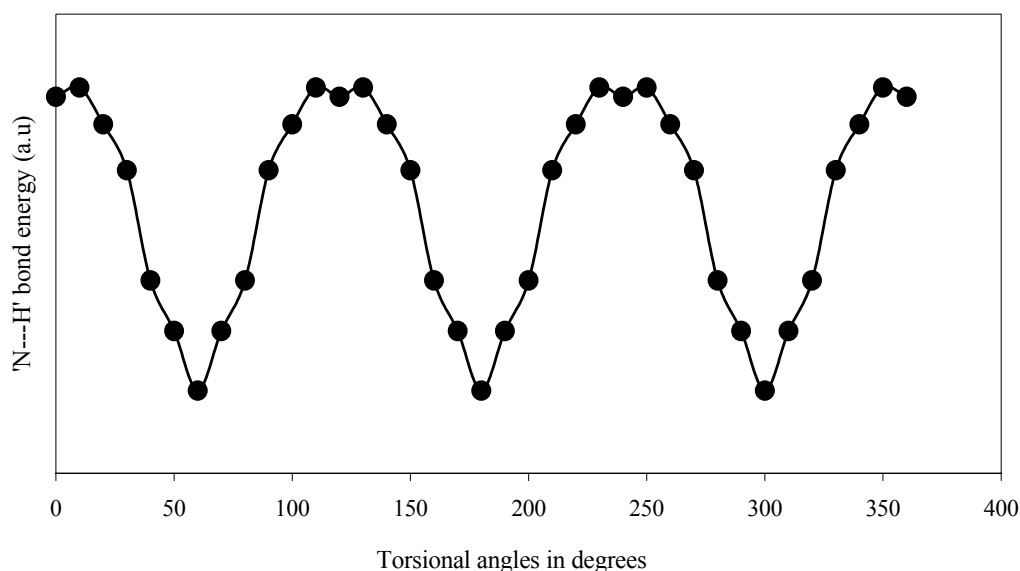
1. There are four different types of one-center interactions: one on each 'N' and 'C' atoms and two on 'H' atoms of the  $\text{H}_3\text{C}$ - and  $-\text{NH}_2$  fragments respectively.

The computed one-center energy and their physical components 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 Figure 7 and that on the 'H' atom centers are similarly drawn in Figure 8.

2. There are three two-center bonded interactions, namely C–N, C–H and N–H bonds.



**Figure 10.** Plot of C–H bond energy as a function of torsional angles in methylamine.

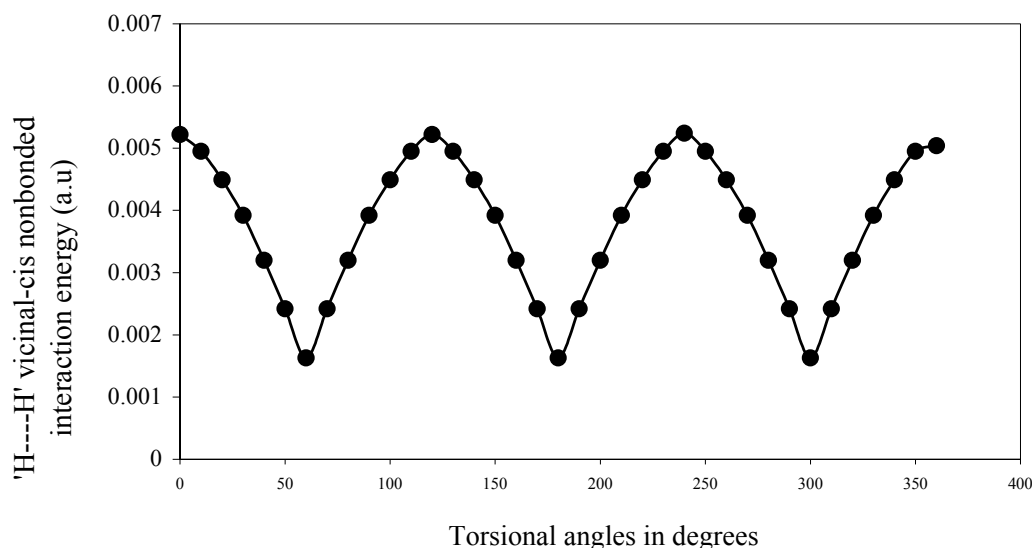


**Figure 11.** Plot of 'N–H' bond energy as a function of torsional angles in methylamine.

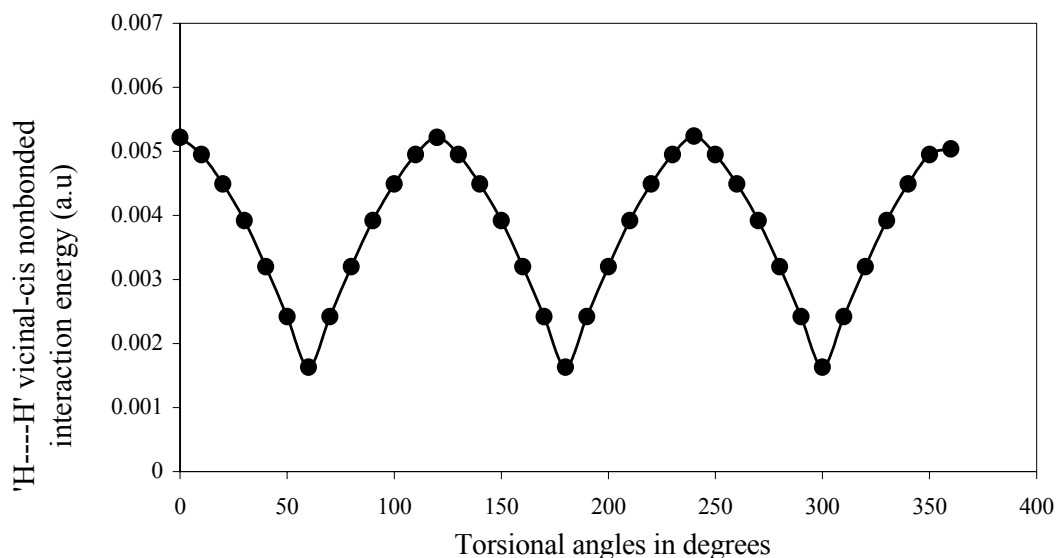
(i) The computed C–N bonded interaction energy and its physical components with torsional variables are presented in Table 5 and total bond energy is plotted in Figure 9.

(ii) The computed C–H bonded interaction energy and its physical components with rotational variables are presented in table–6 and the total bond energy is plotted in Figure 10.

(iii) The computed N–H bonded interaction energy and its physical components with corresponding rotational variables are presented in Table 7. The total N–H bond energy is also plotted as a function of torsional angles in Figure 11.



**Figure 12.** Plot of geminal H---H non-bonded interaction energy in CH<sub>3</sub> fragment of methylamine as a function of torsional angles.



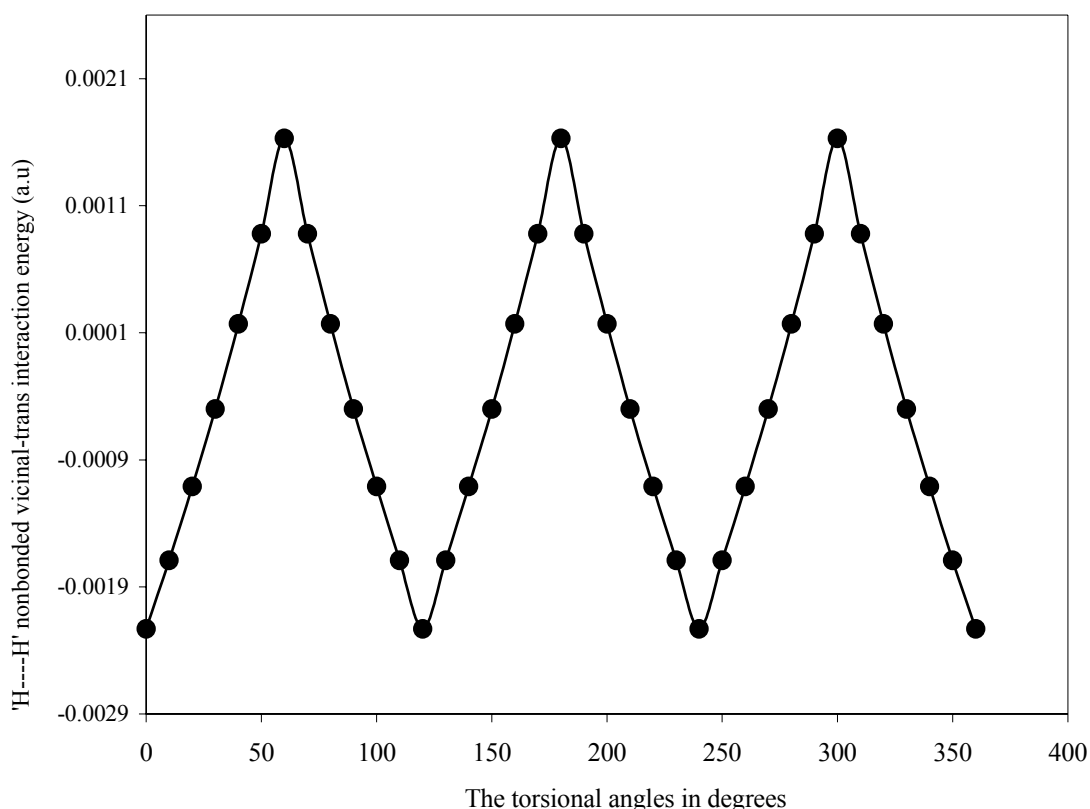
**Figure 13.** Plot of H---H non-bonded (vicinal-cis) interaction energy as a function of torsional angles in methylamine.

3. There are five types of two-center nonbonded interactions as follows:

(i) two geminal H---H nonbonded interactions between the H atoms of the  $-\text{NH}_2$  and the  $-\text{CH}_3$  fragments. The geminal H---H interaction energies and their physical components with rotational variables are shown in Tables 8 and 9 respectively. The total energy of H---H nonbonded interactions on  $-\text{CH}_3$  fragment is plotted as a function of torsional angles in Figure 12.

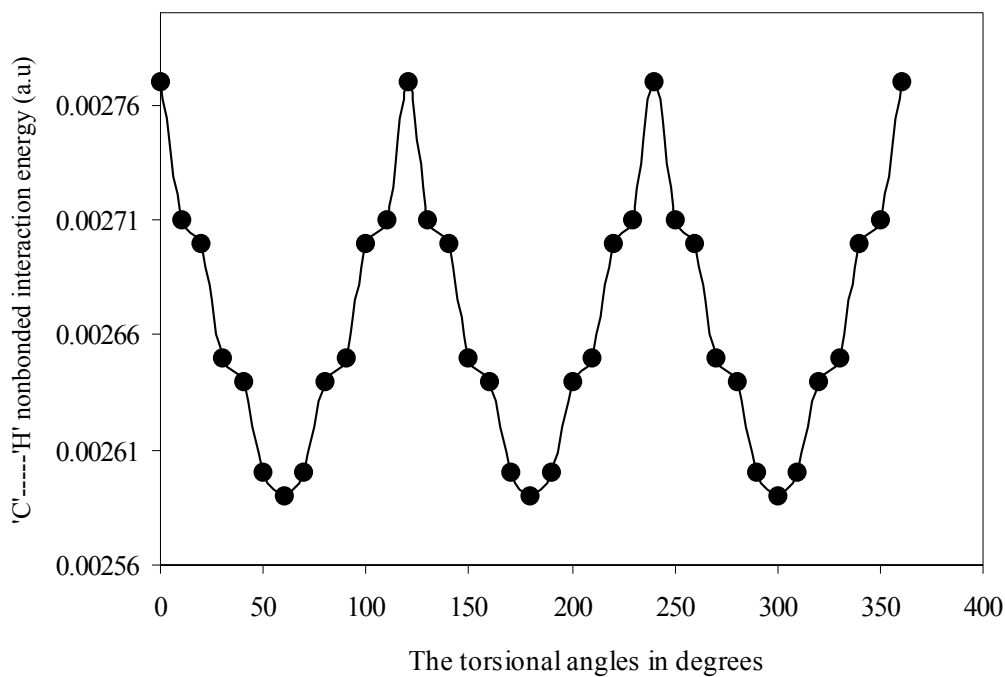
(ii) H---H vicinal-*cis* interactions; this calculates the interactions between the H atoms on C and N atoms situated at *cis* positions. The interaction energy and its physical components are presented with the rotational variables in Table 10. The energetic effect is also plotted against the torsional variable in Figure 13.

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

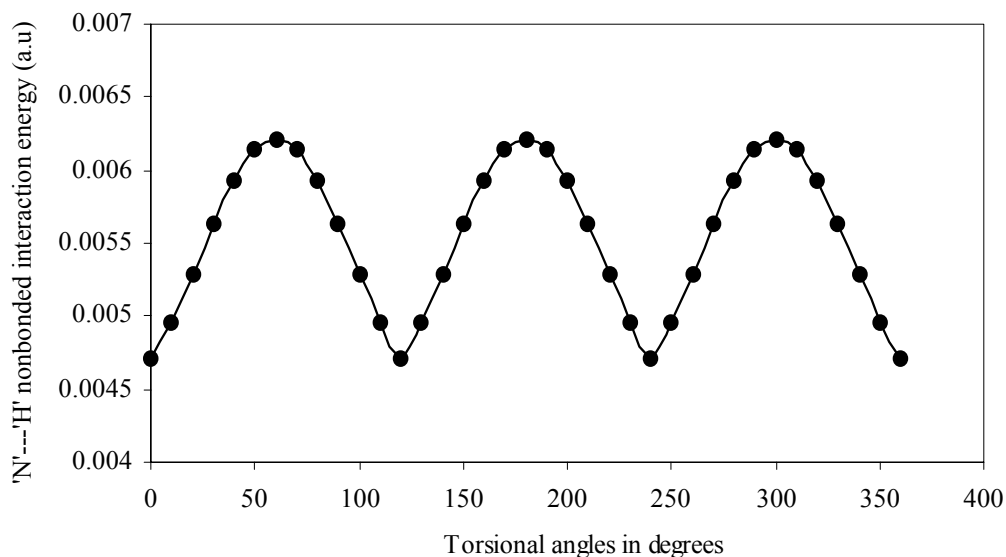


**Figure 14.** Plot of H---H non-bonded (vicinal-trans) interaction energy as a function of torsional angles in methylamine.

(iv) 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 plotted as a function of torsional variables in Figure 15.



**Figure 15.** Plot of C---H non-bonded interaction energy as a function of torsional angles in methylamine.



**Figure 16.** Plot of N---H non-bonded interaction energy as a function of torsional angles in methylamine.

(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 plotted as a function of torsional variables in Figure 16.

Having identified the types of one- and two-center bonded and non-bonded interaction terms, we now proceed to discuss how these energetic effects change during internal rotation and have their bearing on the origin and development of the torsional barrier. The computed data and nature of the profiles of such energetic effects are expected to be quite revealing.

**One-center interactions on C and N atoms.** From tables 3 and 4 and also from Figure 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 regular pattern under internal rotation. 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. Since the barrier height is the difference of energy between the energies of staggered and eclipsed conformers of the molecule, the one-center effect on N atom 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 profile of the potential energy in Figure 2. This beautiful correlation between the profiles of the two energy quantities as a function of torsional variables suggests that the one-center energy component on N atom can be exploited as a descriptor of the physical process of conformational isomerism of the methylamine molecule. A consideration of the physical components of the energetic effects from the tables reveals that the variation of total energy and their physical components under internal rotation are internally consistent.

**One-center interactions on H atoms.** 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 under torsion. 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 Figure 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 Figure 2. This good correlation between the nature of the profiles of the energetic effects on H atom of attached to C atom and the total energy with torsional variables suggests that this energy component can be used as a descriptor of the physical process of conformational isomerism methylamine can be used as a descriptor of the rotational isomerization reaction of

methylamine under internal rotation. The one center energetic effect on H atom attached to C atom stabilizes the staggered form compared to the eclipsed form. The profile of energy on H atom attached to N center, though anomalous under torsional variable, demonstrates distinctly that it stabilizes staggered conformation a bit more than the eclipsed conformation. Hence, the energetic effects on the both H centers tend to stabilize the staggered form compared to the eclipsed form and the net effect of variation of energies on H centers goes to increase the magnitude of torsional barrier in the methylamine molecule.

Summing up the nature variation of one-center energetic effects under internal rotation of methyl amine we see that, as expected, all the four one-center energy components change with torsion and three of these vary periodically with torsional angles and closely copy the nature of potential energy profile of the molecule closely and participate to build up the barrier height to internal rotation.

**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. A deeper analysis of the computed data in Table 5 shows the patterns of variation of the physical components are internally consistent. The nature of profile in Figure 9 shows that this energetic effect is a periodic function of torsional variable and mimics the potential energy curve in Figure 2 closely. Thus the nature of evolution of this two-center energetic effect under internal rotation and its close correlation with the potential energy profile 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 C–N bonded interaction accelerates the staggering and retards eclipsing, this energetic effect 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 Figure 10 reveals that it is a periodic function of the torsional coordinates and is the mirror image of the potential energy curve in Figure 2. This good correlation between the nature of profiles of potential energy and C–H bonded interaction energy suggests that this energy component can be used as a descriptor of the conformational isomerism of methylamine molecule.

(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 suggest that this effect 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 Figure 11 reveals that it is a periodic function of the torsional coordinates and is nearly the mirror image of the potential energy curve in Figure 2. This good correlation between the pattern of the profiles of N–H bonded interaction energy and total energy under internal rotation suggests that this bonded interaction energy component can be a descriptor of the physical process of conformational isomerism methylamine under the dynamics of internal rotation.

Now summing up the nature of changes of two–center bonded interactions with torsion and their effect on the height of barrier to internal rotation we see that all the bonded interactions follow closely the evolution of conformations under internal rotation and participate in building the barrier height. All the bonded interactions change periodically with torsion.

The two–center nonbonded interactions:

(i) H---H geminal interactions on –NH<sub>2</sub> and –CH<sub>3</sub> fragments:

From Table 8 we see that the interactions between the geminal H atoms on –NH<sub>2</sub> fragment 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 close look at the Table 8 reveals that energetic effect between these geminal H atoms does not follow any regular trend of variation with torsional coordinates and hence cannot be a descriptor of the rotational isomerization reaction of the molecule.

From Table 9 we see that the interactions between the geminal H atoms attached to C atom *i.e.* on the –CH<sub>3</sub> fragment is repulsive in all conformations. A closer look at the Table 9 further reveals that as the staggering starts from the eclipsed conformation, the interaction energy between the geminal H atoms begins to increase and the process continues monotonically until the staggered conformation is reached. Analysis of computed data reveals that this effect tends to stabilize the eclipsed form compared to the staggered form, and hence it tends to reduce the height of the torsional barrier of the molecule. Figure 12 shows that the nature of the profile of this energy component is periodic function of the torsional variables and has a good correlation with the profile of potential energy in Figure 2. Hence, this energy component can be used as the descriptor of the isomerization reaction of the molecule under the dynamics of internal rotational.

Thus we see that of the two geminal H---H interactions in methylamine molecule behave differentially under internal rotation but both effects tend to reduce the barrier height.

(ii) H---H vicinal–*cis* interactions. This is very important type of nonbonded interaction. According to Brunck and Weinhold [9], and Pophristic and Goodman [41] the vicinal–*cis*

interactions of nonbonded H atoms play a central role in deciding the equilibrium conformation of ethane and ethane like molecules under internal rotation. From Table 10 we see that the nature of the interaction between the vicinal-*cis* H atoms of  $-\text{CH}_3$  and  $-\text{NH}_2$  groups 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 increase the barrier to torsion in the molecule. A closer look at the Table 10 reveals that as torsion starts from the eclipsed form the  $E^J$ ,  $E^N$  terms decrease and  $E^V$  term increases steadily. This pattern of variation of  $E^J$ ,  $E^N$  and  $E^V$  terms can be easily rationalized from increase in H---H internuclear distance with increasing torsion starting from eclipsed form. The increase in H---H' internuclear distance with increasing torsion from eclipsed form also rationalizes the pattern of variation of  $E^K$ ,  $E^R$  terms of the two center nonbonded H---H vicinal *cis* interaction. Figure 13 demonstrates that the energetic effect is a periodic function of torsional variables and is isomorphic with the potential energy profile in Figure 2. The good correlation between the profiles of the total energy and the nonbonded vicinal-*cis* interaction between hydrogen atoms in methylamine with rotational coordinates suggests that the interaction between vicinal-*cis* between hydrogen atoms in methylamine may be used as a descriptor of the rotational isomerism of the molecule.

(iii) H---H vicinal-*trans* interactions: From Table 11 we see that the nature of interaction between the 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 Figure 14 reveals that the vicinal-*trans* nonbonded H---H energetic effect is periodic under torsional variables. A comparative study of the profiles in Figures 2 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 vicinal-*trans* nonbonded H---H interaction tends to reduce magnitude of torsional barrier. The rationale of the change of the nature of this nonbonded interaction from attractive to repulsive is transparent from the analysis of the variation of the sign and magnitude of the physical components of the interaction. Table 13 shows the physical components of the interaction with internal rotation. As the torsion begins from the eclipsed form, the  $E^J$ ,  $E^N$  components increase steadily and  $E^V$  component decreases steadily but the sum of  $E^J$  and  $E^N$  is nearly offset by  $E^V$  components at all the conformations. The binding or antibinding effects of the vicinal-*trans* nonbonded 'H---H' interaction at any torsional angle is decided by the sum of exchange ( $E^K$ ) and resonance ( $E^R$ ) terms. A deeper analysis of the data for  $E^K$  and  $E^R$  as a function of torsion shows that these effects evolve from attractive to repulsive when the conformation swings from eclipsed to staggered form.

(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 but it stabilizes



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 Figure 15 reveals that the effect is periodic under torsional variable and the curve mimics the pattern of the potential energy profile in Figure 2. 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 interaction between the H atoms attached to C atom and the N atom is transparent from Table 13. It transpires from the table that the nature of the interaction is repulsive in all conformations and the energetic effect favors eclipsing and hinders staggering. The nature of this nonbonded interaction deserves special mention. Since N atom is strongly electronegative and H atom electropositive, the nature of the intramolecular nonbonded interaction between such atoms is expected to be attractive from ordinary chemical consideration. But the present quantum chemical calculation shows that the interaction between these two atoms is repulsive and not attractive. The rationale of the repulsive nature of interaction is evident from the Table 13 that shows that resonance term,  $E^R$ , the most important factor of binding, is repulsive in all conformations. Thus the myth regarding the nature of the intramolecular nonbonding interactions ordinarily in vogue in chemical thinking is contradicted by the present quantum chemical calculation. 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 Figure 16 we see that it is a periodic function of torsional variables and has a good correlation with the potential energy curve in Figure 2. 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 to the dynamics of internal rotation and this effect can be used as a descriptor of the conformational isomerism of the molecule.

Looking at the physical components of C---H and N---H nonbonded interactions in Tables 12 and 13 we see that  $E^J$ ,  $E^N$  components are nearly constant and other terms are either constant or vary extremely slowly under internal rotation around C–N bond. The near constancy of the  $E^J$ ,  $E^N$  physical components and small or negligible variation of  $E^V$ ,  $E^K$  and  $E^R$  components of C---H and N---H nonbonded interactions can be easily rationalized from the constancy of C---H and N---H inter-nuclear distance under internal rotation about C–N bond.

We have noted above that all the two-center nonbonded interactions in the molecule change periodically with torsion and participate to build up the barrier height of the molecule. The detailed analysis of the nonbonded effects has revealed that some nonbonded effects tend to increase barrier height while other nonbonded effects tend to reduce the height.

### 3.4 Origin of Barrier

The structure of methylamine,  $\text{H}_3\text{C}-\text{NH}_2$  has some close resemblance to the structure of the most widely studied chemical system ethane,  $\text{H}_3\text{C}-\text{CH}_3$ . Chemists usually attribute the structural preference to some steric effects. It is deeply implanted in the mind of chemists that the steric effect develops from some intramolecular nonbonded interaction in the molecule. According to this view, the increased repulsion between C–H and N–H bonds drawn closer in the eclipsed conformation should destabilize the structure. However, we must point out one recent interpretation of the origin barrier in ethane molecule and discuss its possible extrapolation to the present case. Brunck and Weinhold [9] pointed out that the preference for staggered conformations in ethane molecules is due to the differential stabilization effects of *cis* and *trans* bonding–antibonding interactions. Brunck and Weinhold [9] further pointed out on the basis of a localized model that the bond–antibond interaction operates through charge delocalization from an occupied orbital to an unoccupied orbital. Pophristic and Goodman [41] have made a detailed NBO analysis of the hyperconjugatively induced preferential stabilization of staggered conformer of ethane and concluded that the bond–antibond interaction hypothesis of the origin of barrier is basically a quantum mechanical hyperconjugative effect and the vicinal charge transfer interactions are the ones that keep the molecule in the staggered conformation. It, therefore, transpires that charge delocalization through hyperconjugation between two *cis*  $-\text{CH}_3$  groups preferentially stabilize the staggered form of ethane. Pophristic and Goodman [41] have also ascertained that the stabilization in hyperconjugative interaction is due to the change in the attractive nuclear–electron potential. But it appears that no valid reason is adduced to justify as to why the eclipsed form is not stabilized by hyperconjugative interaction. More over, it seems difficult to fit the above model of stabilization through charge delocalization based on localized orbitals into canonical SCF MO Theory. In chemical perturbation theory, the efficiency of charge delocalization from occupied molecular orbital (HOMO) to the unoccupied molecular orbital (LUMO) is inversely proportional to the HOMO–LUMO gap [14]. It is widely accepted that the global hardness and the HOMO–LUMO gap of the staggered form are greater than that of the eclipsed form. Hence, the efficiency of charge delocalization from occupied to unoccupied orbitals in the eclipsed form is expected to be greater than the staggered form. We [14] have pointed out the inconsistency in the theory of stabilization of molecular structure through a similar process of charge delocalization from HOMO to LUMO. The hyperjugative *cis* stabilization model of the origin of rotation barrier of Brunck and Weinhold [9], and Pophristic and Goodman [41] appears to be a regional effect and entire skeleton of the molecule and other energetic effects, except the nuclear–electron attraction, have no role whatsoever in building the barrier. We may refer to Table 10 once again to ascertain the role of H---H vicinal–*cis* interaction on the conformational preference. It is transparent that though this interaction decides in favor of the staggered form as the preferred conformation, this is certainly not the only energetic effect that controls the phenomenon of rotational isomerization reaction of methylamine molecule.

We may say that the present study of rotation dynamics in terms of decomposed energy components demonstrate unequivocally that all the one and two center energetic interactions in the molecule evolve continuously with torsion and the nature of variation of the majority of the energy components under internal rotation is periodic and sinusoidal. It is also transparent that all the energetic effects participate conjointly to determine the conformational behavior under internal rotation. The noted pattern of change in the total energy and its components is consistent with the continuous change of the electron density distribution in the molecule under internal rotation with the condition that the total number of electrons remaining constant. It is also observed that a number of such energetic effects mimic the pattern of the potential energy profile under internal rotation so closely that all such effects can be used, like the total energy parameter, as the descriptors of the conformational isomerism of the molecule. We have noted above that some of the energetic effects go to stabilize the staggered form and some other energetic effects go to stabilize the eclipsed conformer. Thus, the energy partitioning analysis seems to prove unequivocally that the entire one and two center bonded and nonbonded interactions change as a function of the dynamics of internal rotation. It is demonstrated unequivocally that the entire one and two center bonded and nonbonded energetic effects participate to build up the barrier height. It is also demonstrated unequivocally that the barrier does not originate singularly from some intramolecular nonbonded repulsion involving particular region of the molecular structure.

#### 4 CONCLUSIONS

Using the potential energy diagram of the molecule (Figure 2) as the benchmark, it has been demonstrated above that the conformation dependent canonical SCF orbital energies, HOMO–LUMO gap, hardness and chemical potential and a number of one and two center decomposed energy components closely follow the potential energy profile of the isomerization process of methylamine molecule under internal rotation. Thus in theoretical analysis of rotational isomerization process and in our quest of the origin of barrier to internal rotation of methylamine system we have seen that the profiles of eigenvalue of frontier SCF orbitals, DFT parameters like hardness and chemical potential and a number of one and two center energy components can be used as potential function descriptors of the physical process of conformational isomerism of the molecule. Complete energy decomposition reveals that all the one and two center energetic effects change accompanying the rotation dynamics arising out of rotation of one end group around the C–N bond. It is demonstrated that, although the nature of interaction is repulsive in the entire domain of internal rotation and more repulsive in the eclipsed form and less repulsive in the staggered form, the H---H nonbonded *cis* interaction alone can neither account for the barrier height nor can it compute the mechanism of development of barrier in the molecule. The details of the pattern of changes in decomposed energy components with internal rotation have supplied important

information in elucidating the origin and development of barrier to internal rotation. The present analysis seems to conclude unequivocally that barrier does not originate from a particular region of the molecule rather whole skeleton of the molecule is involved in its development. The energy–partitioning quest of the origin and development of barrier to internal rotation seems to be a meaningful venture in this direction.

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