

A Theoretical Study of the Inversion and Rotation Barriers in Methyl-Substituted Amines

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Barreiras de energia para os movimentos de inversão e rotação das moléculas metilamina, dimetilamina e trimetilamina foram calculadas usando a metodologia CCSD(T)//B3LYP com os conjuntos de funções de base de Dunning, cc-pVTZ, cc-pVQZ e cc-pCVTZ. O procedimento de extrapolação para o conjunto de base completa (*complete basis set*, CBS) e os efeitos da correlação dos elétrons do caroço também foram incluídos nos cálculos das barreiras de energia. Nossos melhores resultados estão em excelente concordância com os dados experimentais, indicando que a metodologia utilizada é recomendada para a predição exata de propriedades estruturais e de barreiras de energia de outros sistemas moleculares.

Barrier heights of the internal rotation and inversion motions of methylamine, dimethylamine and trimethylamine molecules were calculated with the CCSD(T)//B3LYP methodology in combination with the cc-pVTZ, cc-pVQZ, and cc-pCVTZ basis sets of Dunning. The complete basis set (CBS) extrapolation procedure and core-valence (CV) correlation effects are also examined to the barrier heights. Our best estimate results (CCSD(T)/CBS+CV//B3LYP/cc-pVQZ) are in very good agreement with the experimental data, indicating the use of this methodology to provide accurate predictions of structures and barrier heights for other systems.

Keywords: energy barriers, methylamine, dimethylamine, trimethylamine, CCSD//B3LYP

Introduction

The methyl-substituted amines, methylamine (CH_3NH_2), dimethylamine [$(\text{CH}_3)_2\text{NH}$], and trimethylamine [$(\text{CH}_3)_3\text{N}$] form an interesting group of molecules which are important in organic syntheses and biological processes, as well as they are efficient corrosion inhibitors of aluminum. Beyond their technological importance, these species are rich in structural features presenting large amplitude internal motions, rotation of the methyl groups and internal inversion of the amino group.

Methylamine has been extensively studied by experimentalists in which its internal rotation and inversion barrier heights were determined using microwave (MW), infrared (IR) and electron diffraction (ED) experiments.¹⁻⁷

Methylamine is considered a small molecule from the theoretical point of view, therefore it is appropriate to be studied using high level theoretical quantum chemical methodologies, having received many contributions.⁷⁻¹⁴ Lee *et al.*⁸ investigated the origin of the structural stability of methylamine concluding that the stereo electronic effect is the major interaction force affecting its stability. Csonka and Sztraka⁹ using density functional and post-Hartree-Fock methodologies showed that the density functional BP86/6-311G(d) method provides reliable results for geometry and vibrational frequencies, as compared with the experimental results. Smeyers and Villa¹⁰ discussed the influence of the zero-point energy correction to the rotation and inversion motions based on the MP2 results, and During and Zheng⁷ calculated these motions barriers using B3LYP and MP2 methods. Recently, we have examined the convergence of the geometries, harmonic vibrational

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frequencies, and the barrier heights of the internal rotation and inversion motions of methylamine using the CCSD(T) theory with a systematic improvement via cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pCVTZ basis sets and also including the contribution of the inner-shell and valence-shell electrons.¹¹ More recently, Levi *et al.*¹² carried out accurate calculations of the vibrational frequencies, Kim and Zeroka¹³ presented new and important results concerning the inversion and rotational barriers and Ducati *et al.*¹⁴ calculated the rotational barrier.

Geometries, vibrational frequencies and the inversion and rotation barriers of dimethylamine have been determined both experimentally and theoretically.¹⁵⁻²³ The experimental investigations were obtained using electron diffraction,¹⁵ microwave,^{16,17} and infrared and Raman^{18,19} spectra. Theoretically, the calculations have been carried out using *ab initio* methods up to MP4 level.²⁰⁻²³

The trimethylamine molecule has also received various experimental and theoretical studies.²⁴⁻³¹ The experimental data of the geometry, vibrational frequencies and internal-inversion and rotational barriers were obtained using microwave,^{24,26} infrared and Raman,^{25,27} techniques and employing analysis of the ultraviolet absorption and fluorescence spectra.²⁸ Theoretical results were also obtained using *ab initio* methods up to MP4 level.²⁹⁻³¹

It has been adequately demonstrated that a simultaneous consideration of basis set saturation and core correlation effects using coupled cluster method and extended basis set provide very accurate values of many molecular properties.^{32,33} Recently, using this methodology, we have investigated the geometries, harmonic vibrational frequencies, and the barrier heights of methylamine.¹¹ In this work, we are concerned with the calculations of the internal and rotational barrier heights of the methyl-substituted amines, methylamine (CH_3NH_2), dimethylamine $[(\text{CH}_3)_2\text{NH}]$, and trimethylamine $[(\text{CH}_3)_3\text{N}]$.

Methodology

For all conformers, geometry optimizations were performed using the B3LYP exchange-correlation functional at the density functional theory level^{34,35} and the cc-pVQZ basis set of Dunning.³⁶ Intrinsic reaction coordinate (IRC)³⁷ calculations were carried out in order to verify the connections of the transition states to the equilibrium geometries, as already done for methylamine by Kim and Zeroka¹³ and for trimethylamine by Tanaka and Aida.³¹ Next, using these optimized geometries, the barrier heights of the internal rotation and inversion motion of the methyl-substituted amines were calculated using coupled cluster theory, including a perturbative

treatment of the triple excitations (CCSD(T)).³⁸ The correlation-consistent polarized-valence triple and quadruple basis sets of Dunning,³⁶ named as cc-pVTZ, and cc-pVQZ, were employed. As it is well known, these basis set are built for frozen core electron calculations. The CCSD(T) total energies were extrapolated to the complete basis set (CBS) limit by using the extrapolation procedure of Halkier *et al.*³⁹

$$E_{\text{CBS}} = [E(n) \times n^3] - [E(n-1) \times (n-1)^3] / n^3 - (n-1)^3 \quad (1)$$

where n equals 4 for cc-pVQZ basis set. In order to provide the effect of core-valence correlation (CV) we have also used the correlation consistent core and valence polarization triple zeta basis set (cc-pCVTZ) of Woon and Dunning.⁴⁰ Thus, these calculations were carried out correlating both the valence electrons and all electrons. Therefore, the barrier heights (ΔE) were calculated using the expression,

$$\Delta E = (\Delta E_{\text{CBS, valence}}) + \Delta E (\text{cc-pCVTZ, all electrons}) - \Delta E (\text{cc-pCVTZ, valence}) \quad (2)$$

As stated above, for methylamine, we have recently used CCSD(T) to optimize the geometries for all conformers and to calculate inversion and rotational barrier heights.¹¹ Kim and Zeroka have shown recently two transition state structures for the inversion mode, with one and two imaginary frequencies, respectively.¹³ In order to clarify the previous structures of the inversion motion,¹¹ we have also re-optimized the structures of all methylamine conformers using the CCSD(T) methodology.

All the calculations were carried out using the Gaussian 03 code⁴¹ and Molpro 2002.6.⁴²

Results and Discussion

The B3LYP/cc-pVQZ optimized geometries of all methylamine conformers are presented in Figure 1, and in Figure 2 are showed the dimethylamine and trimethylamine conformers.

Methylamine has its ground state equilibrium geometry represented by a staggered conformation, and the eclipsed conformation corresponds to the transition state of the internal rotation due to the torsional motion of a methyl moiety along the CN axis. The wagging motions of the amine hydrogen atoms present two planar conformations, which are first-order and second-order inversion transition states, as also determined by Kim and Zeroka.¹³ All of them belong to the C_s symmetry and are shown in Figure 1. Recently, we have optimized the geometry of methylamine

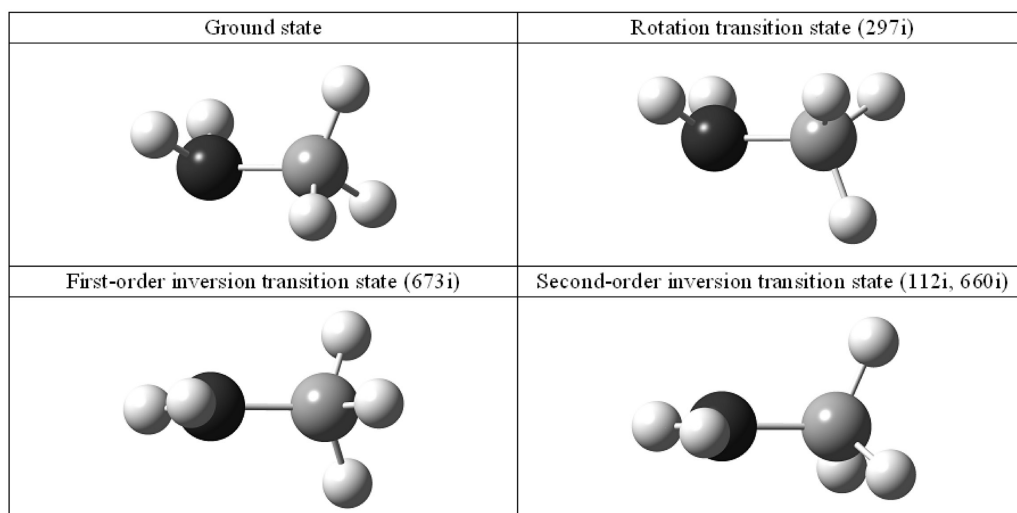


Figure 1. The conformation structures of methylamine. Values in brackets correspond to the imaginary frequencies (in cm^{-1}) calculated at B3LYP/cc-pVQZ level.

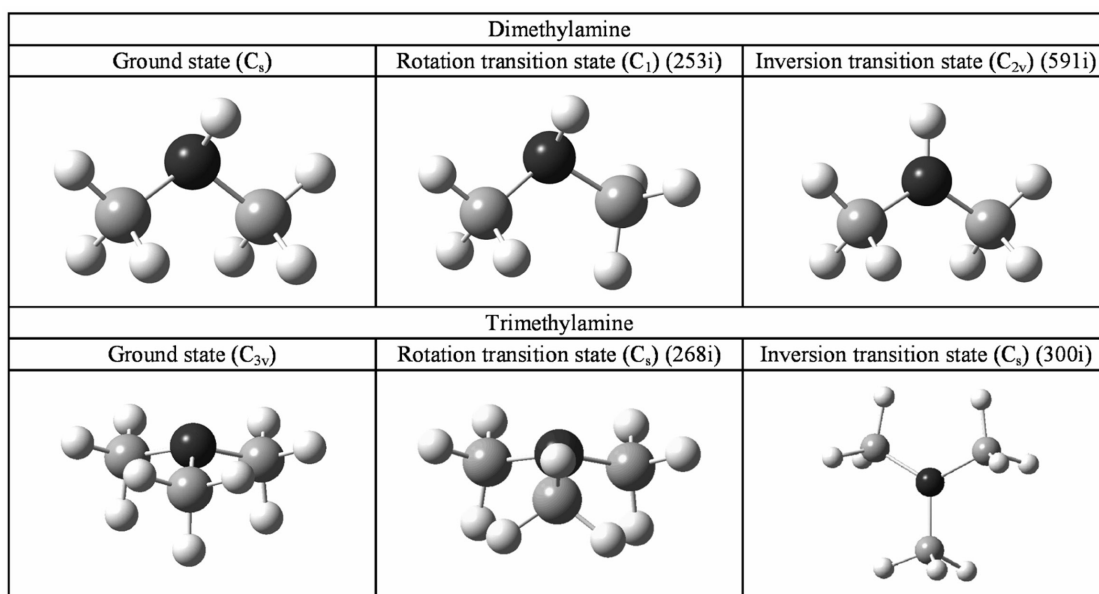


Figure 2. The conformation structures of dimethylamine and trimethylamine. Values in brackets correspond to the imaginary frequencies (in cm^{-1}) calculated at B3LYP/cc-pVQZ level.

using the CCSD(T)/CBS methodology¹¹ and, in this work, as discussed before, we have re-optimized the structures of all conformers using CCSD(T) methodology, in order to clarify the previous structures of the inversion motion. As one can see, the present results show that, in fact, the previous structures¹¹ refer to the first-order inversion motion with one imaginary frequency. The imaginary frequencies calculated at the CCSD(T)/cc-pVTZ level are 749i cm^{-1} for the first-order inversion structure, 166i and 740i cm^{-1} for the second-order, and 317i cm^{-1} for the rotation transition state. These imaginary frequencies calculated at B3LYP/cc-pVQZ level, are respectively 673i, 112i and 660i, and 297i cm^{-1} as reported in Figure 1. Note that the B3LYP

imaginary frequencies differ no more than 80 cm^{-1} from the CCSD(T)/cc-pVTZ results. All geometric parameters calculated using B3LYP/cc-pVQZ are, in general, in good agreement with the CCSD(T) results and also with previous theoretical calculations^{7-10,13,14} and experimental data.²⁻⁴ We have also carried out the IRC calculations using the B3LYP/cc-pVTZ method and the results confirm that the first-order inversion transition state and the rotation transition state connect to the ground state, as already shown by Kim and Zeroka¹³ using a more complete two-dimensional potential energy surface. In this work, the IRC paths for the rotation motion were calculated by changing the dihedral angle (ϕ) (H-C-N lone-pair). The changes in the energy relative

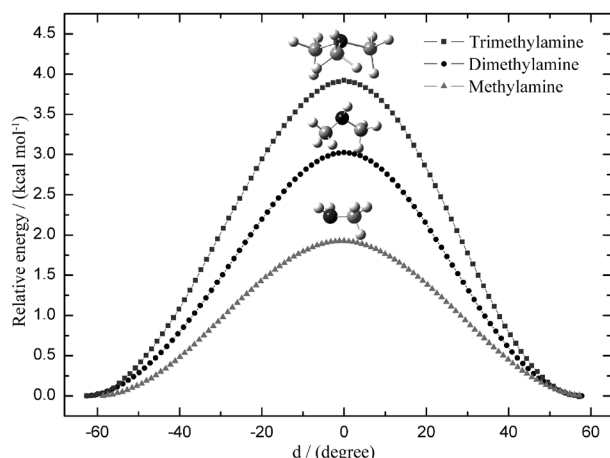


Figure 3. Potential energy curves (in kcal mol⁻¹) along the IRC path for the rotation motion at B3LYP/cc-pVTZ. The dihedral angle (d) = -60° and 60° corresponds to the ground state of each molecule and $d = 0^\circ$ corresponds to the rotation transition state structures (showed).

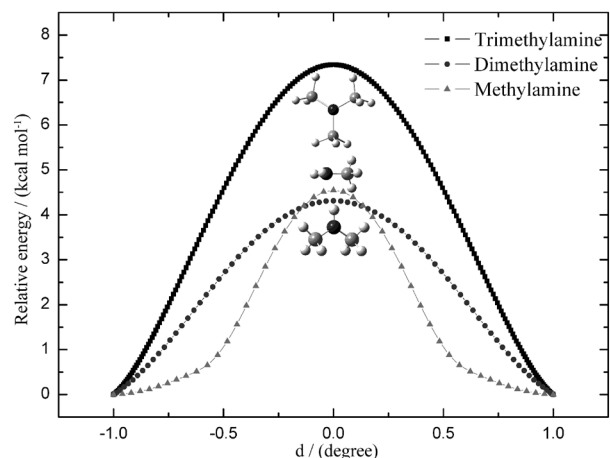


Figure 4. Potential energy curves (in kcal mol⁻¹) along the IRC path for the inversion motion at B3LYP/cc-pVTZ. The degree of inversion (d) for methylamine is defined in the text, for dimethylamine see Figure 5, and for trimethylamine see Figure 2 in reference 31. $d = -1.0$ or 1.0 correspond to the ground state of each molecule and $d = 0.0$ corresponds to the inversion transition state structures (showed).

to the ground state structure ($d = \pm 60^\circ$) are presented in Figure 3. The IRC calculations for the inversion motion are presented in Figure 4 that shows the potential energy as a function of the degree of inversion d , which is defined as:

$$|d| = \alpha / \alpha_{gs} \quad (3)$$

where, α is the H–N–C–H dihedral angle, which is $\pm 58.8^\circ$ at the ground state conformation (α_{gs}) and equal to zero at the first-order inversion transition state geometry.

The origin of the structural stability was confirmed to be essentially due to the stereo electronic effect. As obtained by Lee *et al.*,⁸ the change of rotational conformation energy (ΔE) and the change of the C–N distance (Δr_{CN}) varies

almost linearly with either the cosine of the dihedral angle d (H–C–N–lone-pair) or the cosine of $3d$.

The two CCSD(T) results of the methylamine barrier heights, the single point calculations with the geometries optimized at the B3LYP/cc-pVQZ level and those obtained with the geometries optimized with the CCSD(T), are presented in Table 1. The results obtained with B3LYP/cc-pVQZ and the experimental data^{1-3,5} are also presented. All the CCSD(T) results for barrier heights using the B3LYP/cc-pVQZ optimized geometries are similar to the results calculated with the CCSD(T) geometries, differing no more than 0.08 kcal mol⁻¹. It is important to mention that calculations of T_1 diagnostic were previously carried out¹¹ at the CCSD/cc-pVQZ level with values equal to 0.008 for all conformations, which are small enough to allow the use of the single reference CCSD(T) wave functions in the study of the present molecular conformations. As already noticed,¹¹ the increase of the basis set and the inclusion of core correlation reduce both barrier height values, as also observed if one compares the CCSD(T)/cc-pVTZ result for the first-order rotation barrier with the one calculated by Ducati *et al.*¹⁴ with CCSD(T)/aug-cc-pVTZ. The inclusion of ZPE correction decreases the values of barrier heights underestimating the CBS-DT (CBS extrapolation using double and triple basis set) results compared to the experimental data. The experimental rotation barriers range from 1.96^{2,3} to 2.05⁵ kcal mol⁻¹, and for inversion, from 4.83¹ to 5.56⁵ kcal mol⁻¹. The CCSD(T) results with the CBS extrapolation and core-valence correlation corrections (CV) (equation 2), but without ZPE correction, are 1.83 and 4.99 kcal mol⁻¹ for the rotation and inversion barriers. However, the CCSD(T)/cc-pVQZ (valence) results, without ZPE correction are 1.95 and 5.61 kcal mol⁻¹, respectively. As one can see, the inclusion of the ZPE correction from the B3LYP/cc-pVQZ or from the CCSD(T)/CBS-DT calculations provide barrier height values lower than the experimental data, which are accurate enough to encourage us in using this methodology in the calculation of larger systems as dimethyl and trimethyl amines. Also, as affirmed above, the CCSD(T) and CCSD(T)//B3LYP barrier height results differ no more than 0.08 kcal mol⁻¹ without ZPE. Including the B3LYP/cc-pVQZ ZPE correction in the single point CCSD(T) calculations, the difference from the optimized CCSD(T) result is not higher than 0.14 kcal mol⁻¹. Therefore, the CCSD(T) single point calculations are reliable enough to calculate barrier heights for similar structures, and in this work, were carried out for the larger systems.

The B3LYP/cc-pVQZ dimethylamine conformation structures are presented in Figure 2. The ground state equilibrium geometry has a pyramidal structure with C_s

Table 1. Ground state total energy (in a.u.), internal rotation and inversion barrier heights (in kcal mol⁻¹) of methylamine

Methods	Ground state total energy	First-order Rotation (ΔE)	First-order Inversion (ΔE)	Second-order Inversion (ΔE)
B3LYP/cc-pVQZ	-95.90917	1.86 (1.50) ^a	4.57 (3.41) ^a	4.62 (3.32) ^a
CCSD(T)/cc-pVDZ (valence)	-95.86989 ^c	2.75 ^c (2.19) ^{a,c}	8.16 ^c (6.95) ^{a,c}	8.24 ^c (6.87) ^{a,c}
CCSD(T)/cc-pVTZ (valence)	-95.96591 ^b	2.09 ^b	6.11 ^b	6.17 ^b
	-95.96673 ^c	2.10 ^c (1.72) ^{a,c}	6.19 ^c (5.09) ^{a,c}	6.25 ^c (4.99) ^{a,c}
CCSD(T)/cc-pVQZ (valence)	-95.72775 ^b	1.96 ^b	5.53 ^b	5.58 ^b
	-95.72781 ^c	1.95 ^c	5.56 ^c	5.61 ^c
CBS -DT (valence) (equation 1)	-95.74293 ^c	1.83 ^c (1.52) ^{a,c}	5.36 ^c (4.31) ^{a,c}	5.41 ^c (4.20) ^{a,c}
CBS -TQ (valence) (equation 1)	-95.75050 ^b	1.86 ^b	5.11 ^b	5.15 ^b
	-95.75049 ^c	1.85 ^c	5.10 ^c	5.14 ^c
CCSD(T)/cc-pCVTZ (valence)	-95.69970 ^b	2.07 ^b	6.13 ^b	6.18 ^b
	-95.69984 ^c	2.08 ^c	6.21 ^c	6.26 ^c
CCSD(T)/cc-pCVTZ (full)	-95.80144 ^b	2.06 ^b	5.99 ^b	6.04 ^b
	-95.80155 ^c	2.07 ^c	6.05 ^c	6.10 ^c
ΔE (CCSD(T)/equation 2)	-95.85224 ^b	1.85 ^b	4.97 ^b	5.02 ^b
	-95.85221 ^c	1.83 ^c	4.94 ^c	4.99 ^c
Experimental		1.96 ^d , 2.05 ^e		4.83 ^f , 5.56 ^e

^aValues in parentheses are with ZPE correction; ^busing geometries optimized at B3LYP/cc-pVQZ level; ^cusing the geometry optimized at the CCSD(T) level; ^dreferences 2 and 3; ^ereference 5; ^freference 1.

point group symmetry, and it will be denoted as the eclipsed conformation. The internal rotation of the methyl groups with C_1 point group symmetry has a staggered conformation, and the inversion motion of the amine hydrogen has a planar conformation within C_{2v} point group symmetry. As obtained to methylamine, all geometrical parameters are in good agreement with previous experimental^{15,16} and theoretical results.²¹⁻²³ In the planar structure, the H-C-N-C-H atoms are coplanar to the amine hydrogen atom, and in the ground state pyramidal structure, this amine hydrogen atom forms an angle of 53.4 degrees to the H-C-N-C-H plane. These results are in good agreement with the MP2/6-31G(d,p) value, equal to 55.2 degrees, and also with the experimental data of 54.6 degrees.¹⁶ The IRC paths using the B3LYP/cc-pVTZ method for the rotation motion were calculated by changing the dihedral angle (d) (H-C-N-H). As calculated for methylamine, the changes in energy relative to the ground state structure ($d = \pm 60^\circ$) are presented in Figure 3. For the inversion the degree of inversion d is defined as shown in Figure 5 and the IRC path is presented in Figure 4.

As analyzed for methylamine, the change of rotational conformation energy (ΔE) and the change of the C-N distance (Δr_{CN}) varies almost linearly with either the cosine of the dihedral angle d (H-C-N-lone-pair) or the cosine of $3d$. Thus, we also concluded that the origin of the structural stability is due to the stereoelectronic effect.

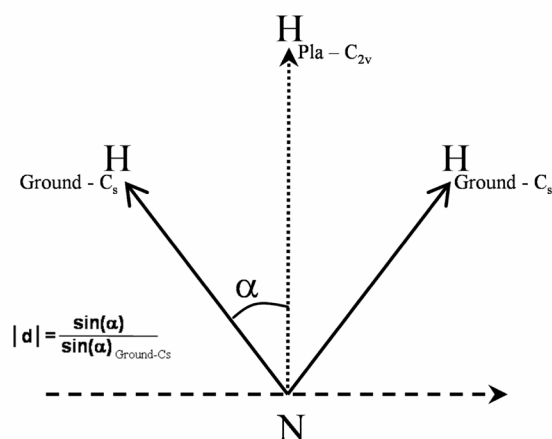


Figure 5. Definition of the degree of inversion (d) in dimethylamine molecule: The N-H vector is directed to N-H bond. In the planar (inversion transition state) structure the H-C-N-C-H atoms are coplanar to the hydrogen amine atom ($\alpha = 0$), and in the ground state pyramidal structure this hydrogen amine atom forms an angle of 53.4 degrees to the H-C-N-C-H plane ($\sin \alpha = \sin \alpha_{\text{ground-C}_s}$).

The dimethylamine barrier heights are calculated at the CCSD(T) level using the geometries optimized with B3LYP/cc-pVQZ and are presented in Table 2 together with the experimental data.¹⁶⁻¹⁹ As already discussed for the methylamine, the increase of the basis set and the inclusion of the core correlation reduce both barrier height values. The inclusion of core correlation is more important for the inversion barrier. For the internal rotation barrier, our

Table 2. Internal rotation and inversion barrier heights (in kcal mol⁻¹) of dimethylamine. The CCSD(T) results are calculated using the B3LYP/cc-pVQZ optimized geometries

Methods	Internal rotation (ΔE)	Inversion (ΔE)
B3LYP/cc-pVQZ	2.99 (2.67) ^a	4.23 (3.24) ^a
CCSD(T)/cc-pVTZ (valence)	3.20 (2.88)	6.13 (5.14)
CCSD(T)/cc-pVQZ (valence)	3.15 (2.83)	5.62 (4.63)
CBS (valence) (equation 1)	3.11 (2.79)	5.24 (4.25)
CCSD(T)/cc-pCVTZ (valence)	3.20 (2.88)	6.14 (5.15)
CCSD(T)/cc-pCVTZ (full)	3.20 (2.88)	6.01 (5.02)
ΔE (CCSD(T)/equation 2)	3.11 (2.79)	5.11 (4.12)
Theoretical	3.43 ^c	6.60 ^d ; 6.29 ^e
Experimental	3.013 ^f ; 3.029 ^g	4.4 ^h

^aValues in parentheses are with ZPE correction; ^bvalues in parentheses are with B3LYP ZPE correction; ^creference 15, MP2/6-31G (df,p); ^dreference 22, MP2/6-31G (d,p); ^ereference 23, MP4/6-31G (d,p)//MP2/6-31G (d,p); ^freference 18; ^greference 19; ^hreferences 16 and 17.

best result obtained at the CCSD(T)/CBS+CV//B3LYP/cc-pVQZ level (equation 2), is 3.11 kcal mol⁻¹, which include the CBS and core-valence correlation effects. The previous theoretical result¹⁵ at MP2/6-31G(df,p) level is 3.43 kcal mol⁻¹ and our B3LYP/cc-pVQZ result is 2.99 kcal mol⁻¹. The experimental infrared and Raman data are respectively 3.013¹⁸ and 3.029¹⁹ kcal mol⁻¹. Using ZPE correction, the B3LYP/cc-pVQZ result is 2.67, which is relatively small compared to the experimental data. Using B3LYP ZPE corrections in the CCSD(T)/equation 2 and CCSD(T)/cc-pVQZ results, the rotation barrier are 2.79 and 2.83 kcal mol⁻¹, respectively. For the inversion, our best results using equation 2 and cc-pVQZ basis set are 5.11 and 5.62 kcal mol⁻¹, respectively. The B3LYP/cc-pVQZ is 4.23 kcal mol⁻¹ and previous theoretical results using MP2/6-31G (d,p) and MP4/6-31G(d,p)//MP2/6-31G (d,p) are respectively 6.60 and 6.29 kcal mol⁻¹.^{22,23} The experimental result obtained from microwave spectra is 4.4 \pm 1 kcal mol⁻¹,^{16,17} which has an error limit somewhat large. A better comparison with the experimental data should include the ZPE correction obtained from the B3LYP/cc-pVQZ calculations, which are 3.24, 4.12 and 4.63 kcal mol⁻¹ calculated using B3LYP/cc-pVQZ, CCSD(T)/equation 2 and CCSD(T)/cc-pVQZ, respectively.

Trimethylamine has its ground state equilibrium geometry well determined^{24,26,29-31} as a pyramidal structure with C_{3v} point group symmetry with an eclipsed conformation. Figure 2 gives the C_{3v} equilibrium geometry and the two other conformations with C_s point group symmetry, the staggered and planar structures, which correspond respectively to the internal rotation of the methyl groups and to the skeletal inversion. All geometries were optimized using the B3LYP/cc-pVQZ method. The geometrical parameters, in general, are in

good agreement with previous experimental^{24,26,27} and theoretical results.^{29,30} The IRC paths using the B3LYP/cc-pVTZ method for the rotation motion were calculated by changing the dihedral angle ϕ (H–C–N–lone pair) and the relative energy from the ground state structure ($\phi = \pm 60^\circ$), which are presented in Figure 3. For the inversion, the IRC path is presented in Figure 4. The calculations were carried out using the degree of inversion d , as defined by Tanaka and Aida.³¹ As analyzed for methylamine and dimethylamine, the structural stability is essentially due to the stereo electronic effect.

Calculated trimethylamine barrier heights are presented in Table 3 together with the experimental data.^{24,25,27,28} The inclusion of core correlation is more important for the inversion barrier, as already discussed for the methylamine and dimethylamine. The calculated barrier height results for the torsion of one methyl group are consistent with the experimental and previous theoretical results. The B3LYP/cc-pVQZ result without ZPE correction is 3.91 kcal mol⁻¹ and the result with ZPE is 3.54 kcal mol⁻¹, which seems underestimated compared to the experimental data, *i.e.*, 4.40,²⁴ 4.06²⁵ or 3.63²⁷ kcal mol⁻¹, as also observed to methylamine and dimethylamine. Our best result (equation 2) is 4.27 kcal mol⁻¹, but if one uses the ZPE correction from the B3LYP/cc-pVQZ calculations, this value becomes 3.90 kcal mol⁻¹. The previous MP4(SDQ)/aug-cc-pVTZ result without ZPE is 4.04 kcal mol⁻¹.³¹ For the inversion, the B3LYP/cc-pVQZ without and with ZPE are 7.45 and 6.29 kcal mol⁻¹, respectively. Our best result without ZPE is 9.51 kcal mol⁻¹, which is similar to the previous theoretical study at MP4(SDQ)/aug-cc-pVTZ level, equal to 9.42 kcal mol⁻¹.³¹ Using the ZPE correction from the B3LYP/cc-pVQZ calculations, our best result is 8.35 kcal mol⁻¹, which is in very close agreement with the experimental value of 8.29 kcal mol⁻¹.²⁸

Table 3. Internal rotation and inversion barrier heights (in kcal mol⁻¹) of trimethylamine. The CCSD(T) results are calculated using the B3LYP/cc-pVQZ optimized geometries

Methods	Internal rotation (ΔE)	Inversion (ΔE)
B3LYP /cc-pVQZ	3.91 (3.54) ^a	7.45 (6.29) ^a
CCSD(T)/cc-pVTZ (valence)	4.26 (3.89)	9.70 (8.54)
CCSD(T)/cc-pVQZ (valence)	4.27 (3.90)	9.65 (8.49)
CBS (valence) (equation 1)	4.27 (3.90)	9.61 (8.45)
CCSD(T)/cc-pCVTZ (valence)	4.28 (3.91)	9.73 (8.57)
CCSD(T)/cc-pCVTZ (full)	4.28 (3.91)	9.63 (8.47)
ΔE (equation 2)	4.27 (3.90)	9.51 (8.35)
Theoretical	4.04 ^e	9.42 ^c
Experimental	4.40 ^d ; 4.06 ^e ; 3.63 ^f	8.29 ^g

^aValues in parentheses are with ZPE correction; ^bvalues in parentheses are with B3LYP ZPE correction; ^creference 31, MP4(SDQ)/aug-cc-pVTZ; ^dreference 24; ^ereference 25; ^freference 27; ^greference 28.

Conclusions

In this work, we have used the cc-pVTZ, cc-pVQZ, and cc-pCVTZ basis sets of Dunning and the CCSD(T) theory in order to obtain accurate values of inversion and rotation barrier heights of the methylamine, dimethylamine and trimethylamine molecules using the optimized geometries and frequencies calculated at B3LYP/cc-pVQZ level. CBS extrapolation procedure and core-valence correlation effects are also employed in the calculations of the barrier heights using CCSD(T) single point calculations. Our best estimate results (equation 2) are in very good agreement with the experimental data. Therefore, the methodology, CCSD(T)/CBS+CV//B3LYP/cc-pVQZ, used in this study provides accurate and consistent predictions of structures and barrier height values of internal motions in methyl substituted amines, and it is also recommended to be applied to other systems.

Supplementary Information

Supplementary information is available free of charge at <http://jbcs.sbq.org.br> as a PDF file.

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Supplementary Information

A Theoretical Study of the Inversion and Rotation Barriers in Methyl-Substituted Amines

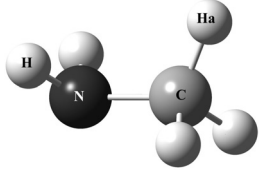
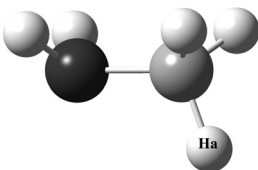
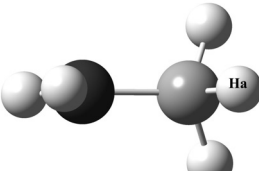
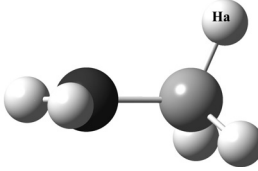
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Table S1. Optimized geometries of methylamine. Bond distances (in Å) and angle (in degrees)

Ground state	Rotation transition state
	
First order inversion transition state	Second order inversion transition state
	

Method/Basis	Ground State						
	CN	NH	CHa	CH	NCHa	NCH	CNH
B3LYP/cc-pVQZ	1.463	1.011	1.097	1.090	115.2	109.2	110.7
CCSD(T)/cc-pVTZ (valence)	1.469	1.014	1.097	1.091	115.1	109.1	109.2
CCSD(T)/cc-pVQZ (valence)	1.465	1.012	1.096	1.090	115.0	109.1	109.8
CCSD(T)-CBS (valence)	1.462	1.011	1.095	1.089	114.9	109.1	110.2
CCSD(T)/cc-pCVTZ (valence)	1.468	1.013	1.097	1.091	115.1	109.1	109.2
CCSD(T) /cc-pCVTZ (full)	1.466	1.012	1.096	1.090	115.1	109.1	109.4
CCSD(T)/(equation 2)	1.460	1.010	1.094	1.088	114.9	109.1	110.4
Method/Basis	Rotation transition state						
	CN	NH	CHa	CH	NCHa	NCH	CNH
B3LYP/cc-pVQZ	1.468	1.009	1.092	1.091	110.9	112.0	111.6
CCSD(T)/cc-pVTZ (valence)	1.473	1.010	1.092	1.093	110.9	111.7	110.6
CCSD(T)/cc-pVQZ (valence)	1.469	1.008	1.091	1.091	110.8	111.7	111.1
CCSD(T)-CBS (valence)	1.466	1.008	1.090	1.090	110.7	111.7	111.4
CCSD(T)/cc-pCVTZ (valence)	1.473	1.009	1.091	1.092	110.9	111.7	110.6
CCSD(T) /cc-pCVTZ (full)	1.470	1.008	1.090	1.091	111.0	111.7	110.7
CCSD(T)/(equation 2)	1.464	1.006	1.089	1.089	110.7	111.7	111.4

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Table S1. Optimized geometries of methylamine. Bond distances (in Å) and angle (degree) (cont.)

First order inversion transition state							
B3LYP/cc-pVQZ	1.437	0.997	1.089	1.096	109.1	113.2	121.2
CCSD(T)/cc-pVTZ (valence)	1.439	0.997	1.091	1.096	108.9	113.1	121.0
CCSD(T)/cc-pVQZ (valence)	1.438	0.996	1.089	1.095	109.0	112.9	121.1
CCSD(T)-CBS (valence)	1.437	0.995	1.088	1.094	109.1	112.8	121.2
CCSD(T)/cc-pCVTZ (valence)	1.438	0.997	1.091	1.096	108.9	113.1	121.0
CCSD(T) /cc-pCVTZ (full)	1.437	0.996	1.089	1.095	109.0	113.1	121.2
CCSD(T)/(Eq.2)	1.436	0.994	1.086	1.093	109.2	112.8	121.2
Second order inversion transition state							
B3LYP/cc-pVQZ	1.438	0.998	1.098	1.091	114.4	110.5	121.2
CCSD(T)/cc-pVTZ (valence)	1.439	0.997	1.098	1.093	114.0	110.6	121.0
CCSD(T)/cc-pVQZ (valence)	1.438	0.997	1.097	1.091	113.9	110.5	121.0
CCSD(T)-CBS (valence)	1.437	0.996	1.095	1.091	113.7	110.4	121.0
CCSD(T)/cc-pCVTZ (valence)	1.439	0.997	1.098	1.092	114.0	110.5	121.0
CCSD(T) /cc-pCVTZ (full)	1.437	0.996	1.097	1.091	114.0	110.5	121.0
CCSD(T)/(equation 2)	1.435	0.995	1.094	1.089	113.8	110.4	121.0

Table S2. Optimized geometries of dimethylamine. Bond distances (in Å) and angle (degree)

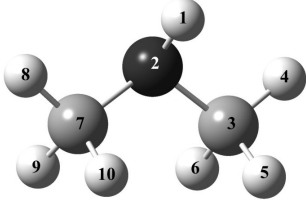
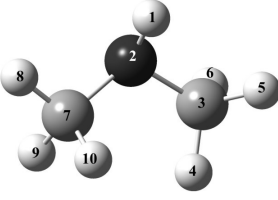
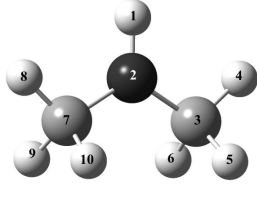
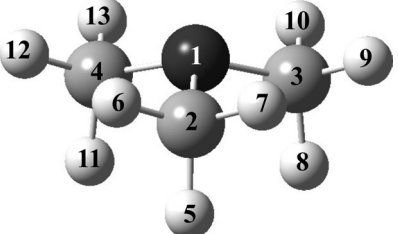
Ground State (C_s)		Rotation transition state (C_1)		Inversion transition state (C_{2v})	
					
Geometric parameters	Ground State (C_s)	Rotation transition state (C_1)		Inversion transition state (C_{2v})	
	B3LYP cc-pVQZ	B3LYP cc-pVQZ		B3LYP cc-pVQZ	
R (1-2)	1.011	1.008		0.997	
R (2-3)	1.454	1.464		1.432	
R (2-7)	1.454	1.454		1.432	
R (3-6)	1.091	1.092		1.099	
R (7-9)	1.091	1.091		1.099	
R (3-5)	1.101	1.093		1.099	
R (7-10)	1.101	1.101		1.099	
R (3-4)	1.089	1.092		1.089	
R (7-8)	1.089	1.090		1.089	
A(3,2,7)	113.3	115.1		120.6	
A(2,7,8)	109.8	109.5		109.9	
A(2,3,4)	109.8	110.9		109.9	
A(1,2,7)	109.9	110.1		119.7	
A(1,2,3)	109.9	110.5		119.7	
A(2,3,6)	109.5	111.4		112.5	
A(2,7,9)	109.5	109.8		112.5	
A(2,7,10)	114.0	114.4		112.5	
A(2,3,5)	114.0	112.3		112.5	
D(1,2,7,8)	53.2	51.1		0.0	
D(1,2,3,4)	53.2	129.7		0.0	
D(1,2,3,5)	68.5	10.1		119.5	
D(1,2,7,10)	68.5	70.4		119.5	
D(1,2,7,9)	171.1	168.6		119.5	
D(1,2,3,6)	171.1	110.7		119.5	
D(7,2,1,3)	125.4	128.2		180.0	

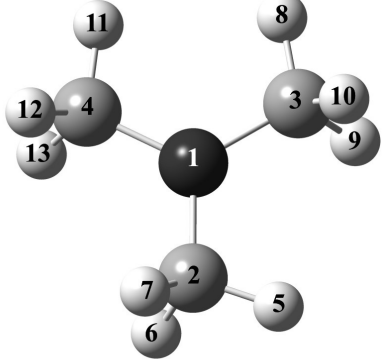
Table S3. Optimized geometries of trimethylamine. Bond distances (in Å) and angle (degree)

Ground state (C_{3v})



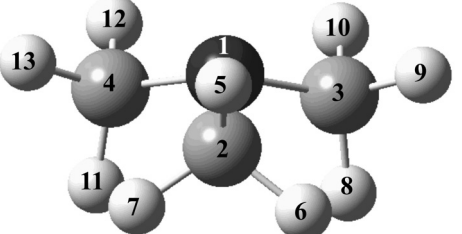
Geometric parameters	B3LYP/cc-pVQZ
R(1,2); R(1,3); R(1,4)	1.451
R(2,6); R(2,7); R(3,9); R(3,10); R(4,12); R(4,13)	1.090
R(2,5); R(3,8); R(4,11)	1.104
A(2,1,3); A(2,1,4); A(3,1,4)	111.8
A(1,2,5); A(1,3,8); A(1,4,11)	112.9
A(6,2,7); A(9,3,10); A(12,4,13)	108.1
A(1,2,6); A(1,2,7); A(1,3,9); A(1,3,10); A(1,4,12); A(1,4,13)	109.9
A(5,2,6); A(5,2,7); A(8,3,9); A(8,3,10); A(11,4,12); A(11,4,13)	108.0

Inversion transition state (C_s)



Geometric parameters	B3LYP/cc-pVQZ
R(1,2)	1.434
R(1,4)	1.434
R(1,3)	1.437
R(2,6); R(2,7); R(4,13); R(4,12)	1.100
R(3,9); R(3,10)	1.099
R(2,5); R(3,8); R(4,11)	1.089
A(2,1,4)	117.3
A(3,1,4)	122.8
A(2,1,3)	120.0
A(1,2,6); A(1,2,7)	112.4
A(1,4,11)	110.3
A(1,4,12); A(1,4,13)	112.4
A(1,2,5)	110.1
A(1,3,10); A(1,3,9)	112.8
A(1,3,8)	109.6
D(3,1,4,11); D(3,1,2,5)	0.0

Rotation transition state (C_s)



Geometric parameters	B3LYP/cc-pVQZ
R(1,2)	1.464
R(1,3) (1,4)	1.450
R(2,5)	1.093
R(2,6) (2,7)	1.092
R(3,8) (4,11)	1.104
R(3,10) (4,12)	1.090
R(3,9) (4,13)	1.090
A(2,1,3) (2,1,4)	113.3
A(3,1,4)	112.4
A(1,2,6) (1,2,7)	111.4
A(1,2,5)	111.5
A(5,2,6) (5,2,7)	107.7
A(6,2,7)	106.8
A(1,3,8) (1,4,11)	113.3
A(1,3,9) (1,4,13)	109.8
A(1,3,10) (1,4,12)	110.1
A(9,3,10) (12,4,13)	107.7
A(11,4,13) (8,3,9)	108.0
A(11,4,12) (8,3,10)	107.8

Table S4. Vibrational frequencies (cm⁻¹) of methylamine

Ground state			
B3LYP/cc-pVQZ	300	833	975
	1055	1173	1348
	1461	1499	1518
	1664	2965	3055
	3089	3496	3570
CCSD(T)/cc-pVTZ	302	877	976
	1066	1187	1359
	1458	1508	1528
	1666	2997	3080
	3116	3499	3580
Rotation transition state			
B3LYP/cc-pVQZ	297i	799	993
	1053	1158	1327
	1464	1495	1522
	1665	3009	3049
	3072	3532	3605
CCSD(T)/cc-pVTZ	350i	914	996
	1066	1166	1338
	1453	1485	1514
	1663	3025	3090
	3104	3496	3575
First order inversion transition state			
B3LYP/cc-pVQZ	672i	101	921
	1114	1169	1287
	1472	1482	1535
	1636	2967	2986
	3085	3659	3779
CCSD(T)/cc-pVTZ	749i	107	918
	1137	1174	1292
	1470	1493	1545
	1642	2993	3027
	3106	3700	3826
Second order inversion transition state			
B3LYP/cc-pVQZ	660i	112i	922
	1109	1170	1290
	1461	1502	1525
	1635	2948	3027
	3065	3660	3778
CCSD(T)/cc-pVTZ	740i	116i	916
	1129	1178	1295
	1462	1508	1537
	1641	2981	3053
	3093	3701	3826

Table S5. Vibrational frequencies (cm⁻¹) of dimethylamine

B3LYP/cc-pVQZ			
Groundstate	230	258	381
	761	938	1036
	1102	1168	1187
	1268	1443	1470
	1477	1488	1495
	1517	1518	2923
	2926	3041	3041
	3089	3089	3525
Rotation transition state	253i	236	391
	699	926	1057
	1106	1159	1187
	1260	1446	1473
	1481	1488	1497
	1515	1522	2925
	2998	3039	3042
	3061	3086	3556
Inversion transition state	591i	180	183
	381	944	1065
	1143	1189	1232
	1277	1453	1471
	1473	1474	1480
	1527	1540	2932
	2943	2943	2953
	3088	3089	3716

Table S6. Vibrational frequencies (cm^{-1}) of trimethylamine

B3LYP/cc-pVQZ

Groundstate	252	265	265
	357	422	422
	830	1057	1057
	1071	1121	1121
	1208	1306	1306
	1443	1443	1482
	1482	1483	1490
	1502	1511	1511
	2894	2894	2908
	3048	3048	3053
	3089	3093	3093
Rotation transition state	268i	242	246
	331	425	435
	820	1049	1055
	1081	1121	1131
	1183	1305	1306
	1445	1448	1484
	1486	1491	1497
	1501	1511	1513
	2889	2897	2997
	3041	3046	3051
	3058	3088	3091
Inversion transition state	300i	95	108
	134	384	433
	808	1074	1093
	1106	1122	1153
	1170	1331	1391
	1447	1458	1469
	1472	1484	1500
	1514	1528	1541
	2922	2927	2930
	2945	2947	2949
	3086	3090	3098