Structure, Spectroscopic and Quantum Chemical Investigations of 4-Amino-2-Methyl-8-(Trifluoromethyl)Quinoline

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Abstract
This work deals with the spectroscopic properties (FT-IR, FT-Raman and NMR), structural and some electronic properties as well as theoretical calculations of 4-amino-2-methyl-8-(trifluoromethyl) quinoline (AMTQ) molecule. The vibrational, structural and some electronic properties observations of the AMTQ were reported, which is investigated using some spectral methods and DFT calculations. FT-IR and FT-Raman spectra were obtained for AMTQ at room temperature in the region 4000 cm⁻¹-400 cm⁻¹ and 3500-50 cm⁻¹, respectively. In the DFT calculations, the B3LYP functional with cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets was applied to carry out the quantum mechanical calculations of the spectroscopic, structural and some electronic properties of AMTQ. FT-IR and FT-Raman spectra were interpreted with the by using of normal coordinate analysis based on scaled quantum mechanical force field. The present work expands our understanding of the both the vibrational and structural properties as well as some electronic properties of the AMTQ by means of the theoretical and experimental methods.

Keywords: 4-amino-2-methyl-8-(trifluoromethyl)quinoine, FT-IR and FT-Raman spectra, NMR spectra, DFT, Electronic properties

1. Introduction
Quinoline and its derivatives possess an aromatic heterocyclic unit of benzene connected to a pyridine ring. It is a heterocyclic aromatic organic compound with the chemical formula C₉H₇N. It is a colorless hygroscopic liquid with a strong odor. Aged samples, especially if exposed to light, become yellow and later brown. Quinoline is only slightly soluble in cold water but dissolves readily in hot water and most organic solvents. Quinoline itself has few applications, but many of its derivatives are useful in diverse applications [1].

In addition to the medicinal and therapeutic applications of quinoline derivatives, these compounds have also shown technological properties. Because, it has the unique structural and electronic properties. Quinoline and its derivatives presents the electronic delocalization and material nonlinear optical properties in the manifestation of fluorescence effects [2]. They were given the important developments in the field of organic light emitting diodes [3–5].

Vibrational spectroscopy in combination with computational chemistry has been used systematically over the past decade to elucidate the spectroscopic, structures and some electronic properties of molecule. Various researchers [6-11] used simulation methods such as DFT, HF simulations to explained molecular structure and vibrational spectra. Such study supports the experimental data in interpreting the calculations results of the structural and spectroscopic properties of the isolated molecule. Erdogdu et al. [12-15] studied vibrational properties of the several molecules. Experimental results were favorable agreed with the results obtained by simulations.

Quinoline derivatives has been applied the characterize by Raman spectroscopy [16,17,20–22]. Especially, aminooquinolines have chromophoric groups and highly symmetric molecular structures. Therefore, they give rise to intense Raman signals [16,18,19,23,24]. The vibrational spectra of the some substituted quinolones have been experimentally recorded and theoretically analyzed [21,25–27]. It is reported that the solid state structure for 4,7- dichloroquinoline has been described [28]. In that work, Authors showed the two molecules with the quinolone asymmetric unit. That compounds have the crystallizes in a monoclinic system with P₂₁/n space group. Some quinolone derivative such as 4,7-dichloroquinoline and quinolin-8-ol, and 4-azido-7-
chboroquinoline molecules have been characterized by the Raman and infrared spectra. In that work, the 4-azido-7-chloroquinoline compound was synthesized from 4,7-dichloroquinoline according to the method described by Pereira et al. [29]. The molecular structure and vibrational spectra of these molecules have been calculated by DFT (B3LYP with 6-311+G(d,p)).

2. Theoretical and Experimental Details
Density functional theory (DFT) computations for the geometric optimization and frequency calculation were performed using Gaussian 09 program [30]. The calculations employed the B3LYP exchange-correlation functional, which combines the hybrid exchange functional of Becke with the gradient-correlation functional of Lee et al. and the cc-pVDZ, cc-pVTZ and cc-pVQZ basis set. Calculations were based on the isolated molecule model, so the environmental effects were not considered. The optimal geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. In the optimized structure, imaginary frequency modes were absent which provided a true minimum picture of the potential energy surface.

Following the geometry optimizations with B3LYP method, the optimized structural parameters used in the vibrational wavenumber calculation at DFT level to characterize all stationary points while minima. The potential energy distribution (PED) was calculated by using the scaled quantum mechanics (SQM) program [31] and the fundamental vibrational modes were characterized by their PED values. In addition, the frontier molecular orbital analysis and Molecular electrostatic potential (MEP) were performed.

AMTQ was purchased from Aldrich and used without further purification. Infrared spectra of the samples were recorded between for the 400-4000 cm\(^{-1}\) on a Mattson 1000 FTIR spectrometer which was calibrated using polystyrene bands. The samples were prepared as a KBr disc. FT-Raman spectrum of AMTQ has been recorded in the frequency range 50–3500 cm\(^{-1}\) on a Thermo Scientific DXR Raman Microscope with Nd: YVO\(_4\) DPSS laser operating with 532 nm excitation. The sample was prepared as a KBr disc. The \(^{13}\)C NMR spectra were recorded in chloroform solutions and all signals are referenced to TMS on a Bruker Ultrashield FT-NMR Spectrometer. All NMR spectra were measured at room temperature.

3. Molecular structure
The optimized structure of conformer of AMTQ was shown in Figure 1 which has the atom numbering scheme adopted in this study. The optimized structural parameters such as dihedral angles, bond angles and bond lengths of the AMTQ were given in Table 1.

![Figure 1. Molecular structure and atomic numbering of the 4-amino-2-methyl-8-(trifluoromethyl)quinoline molecule.](image)

4. Assignment of Vibrational Spectra
In order to assist in the assignment of the vibrational bands, predicted infrared and Raman spectra obtained by using DFT approximation. The AMTQ molecule consists of 25 atoms. So, it has 69 normal vibrational modes. Since it belongs to the Cs point group, these normal modes are distributed with 45 in-plane and 24 out-of-plane vibrations. The experimental and calculated infrared and Raman spectra for AMTQ are given in Figures 2 and 3. The corresponding data are gathered in Table 2.

The NH stretching vibrations give rise to bands at 3500-3300 cm\(^{-1}\) [32]. According to Roeges, the N–H stretching vibration appears strongly and broadly in the region 3390 ± 60 cm\(^{-1}\) [33]. For the title compound N-H stretching modes are assigned at 3383 and 3494 cm\(^{-1}\) theoretically (cc-pVQZ) and a strong band is observed in the IR spectrum at 3383 cm\(^{-1}\) (FT-IR) 3388 cm\(^{-1}\) (FT-Raman). It is well-known that the amino group presents a characteristic band in the 1500-1600 cm\(^{-1}\) range of the IR spectrum, originated by the NH\(_2\) deformation mode (\(\delta_{\text{NH}}\)). The NH\(_2\) deformation band of the title compound detected at 1592 cm\(^{-1}\) (FT-IR) and 1594 cm\(^{-1}\) (FT-Raman). 1585 cm\(^{-1}\) peak predicted as the NH\(_2\) deformation band by means of B3LYP/cc-pVQZ level of theory.

The C-H stretching vibrations of the aromatic structure appear in the region 3200-3000 cm\(^{-1}\). It’s characteristic region for the identification of the C-H stretching vibrations [6-11]. The ring, which is coordinated trifluoromethyl group, has the three CH stretching vibrations. 3072 cm\(^{-1}\), 3091 cm\(^{-1}\) and 3114 cm\(^{-1}\) peaks were predicted the CH stretching vibrations by the B3LYP/cc-pVQZ calculation. According to the PED results, PED contributions were almost calculated as pure modes. In the FT-Raman spectra, CH stretching
vibrations of this ring were observed at 3072 cm$^{-1}$ and 3099 cm$^{-1}$.

Experimentally, the in-plane CH bending modes were measured at 1517/1525 cm$^{-1}$ (IR/Raman), 1442/1441 cm$^{-1}$ (IR/Raman) and -1309 (-/Raman) cm$^{-1}$, -1259 cm$^{-1}$ (-/Raman) 1228/1228 cm$^{-1}$ (IR/Raman), 1189/1182 cm$^{-1}$ (IR/Raman) and 1143/1144 cm$^{-1}$ (IR/Raman), whereas computed in-plane CH bending modes were found at 1501 cm$^{-1}$, 1441 cm$^{-1}$, 1320 cm$^{-1}$, 1252 cm$^{-1}$, 1209 cm$^{-1}$, 1170 cm$^{-1}$ and 1161 cm$^{-1}$ by DFT (B3LYP/cc-pVQZ) calculation. Additionally, the out of plane bending CH modes were observed at 842 (836) cm$^{-1}$, 852 cm$^{-1}$ and 771 (762) cm$^{-1}$ in the FT-IR (FT-Raman) spectra.

The identification of C-N vibration is a very difficult task, since the mixing of several bands is possible in this region. However, with the help of theoretical calculation (DFT), the C-N stretching vibrations are calculated. Several bands observed at 1375 1077 cm$^{-1}$ in the FT-Raman spectrum of the studied compound, with counterpart at 1076 cm$^{-1}$ in the infrared spectrum are assigned to the C-N stretching vibrations. The IR band observed at 1569 cm$^{-1}$, 1619 cm$^{-1}$ and 1638 cm$^{-1}$ assigned to the CC stretching vibrations. Their corresponding counterpart detected at 1572 cm$^{-1}$, 1621 cm$^{-1}$ and 1637 cm$^{-1}$ in the FT-Raman spectra. These vibrations calculated at 1557 cm$^{-1}$, 1615 cm$^{-1}$ and 1603 cm$^{-1}$ by means of B3LYP/cc-pVQZ level of theory. PED contribution of these vibrations predicted as mixed with CCC, CCH bending vibrations.

The C-H stretching frequencies of methyl group appear just below 3000 cm$^{-1}$ [34,35]. The title molecule possesses methyl (-CH$_3$) group. The strong and distinct C-H stretching band at 2924/2925 cm$^{-1}$ (FT-IR / FT-Raman) and 2956/2964 cm$^{-1}$ (FT-IR / FT-Raman) are in agreement with the theoretical values of 2933 cm$^{-1}$ (mode no: 61) and 2979 cm$^{-1}$ (mode no:62) by B3LYP/cc-pVQZ method and are well supported by the PED values. The asymmetric and symmetric bending vibrations of methyl groups normally appear in the around 1450 cm$^{-1}$ and around 1350 cm$^{-1}$ region, respectively [34,35]. In the present study, asymmetric CH$_3$ bending vibration (mode no 27) was observed at 1434 cm$^{-1}$ in the FT-Raman spectrum as very week band and its corresponding counterpart couldn’t be detected in the FT-IR spectrum. Asymmetric CH$_3$ bending mode of the methyl group was also predicted at 1423 cm$^{-1}$ at the B3LYP with cc-pVQZ level of theory. 1421 cm$^{-1}$ (FT-IR and FT-Raman) peak was assigned to the asymmetric bending vibration of the CH$_3$ group. Symmetric CH$_3$ peak was calculated at 1333 cm$^{-1}$ at the B3LYP/cc-pVQZ level of theory. This vibration was measured at 1332 cm$^{-1}$ in the FT-IR spectra.

The band at 1117 cm$^{-1}$ in the FT-IR spectrum was assigned as C-F stretching vibration. This mode was predicted 1112 cm$^{-1}$. According to the calculations 1140 cm$^{-1}$ and 717 cm$^{-1}$ are assigned to the symmetric C-F$_3$ stretching modes, while the 1132 cm$^{-1}$ vibration is the asymmetric C-F$_3$ stretching mode. In the predicted spectra, out-of plane F-C-F bending vibration is appointed at 656 cm$^{-1}$ with 31% contributions of PED.

![Figure 2. Experimental Infrared spectra of 4-amino-2-methyl-8-(trifluoromethyl)quinoline molecule](image)

![Figure 3. Experimental Raman spectra of 4-amino-2-methyl-8-(trifluoromethyl)quinoline molecule](image)
| Bond Lengths (Å) | cc-pVDZ   | cc-pVTZ   | cc-pVQZ   | Bond Angles (°) | cc-pVDZ   | cc-pVTZ   | cc-pVQZ   | Dihedral Angles (°) | cc-pVDZ | cc-pVTZ | cc-pVQZ |
|-----------------|-----------|-----------|-----------|----------------|-----------|-----------|-----------|-------------------|-----------|-----------|-----------|
| C1-C2           | 1.387     | 1.387     | 1.378     | C2-C1-C3       | 120.3     | 120.3     | 120.4     | C5-C1-C2-C3       | -0.999   | 1.013     | 0.674     |
| C1-C3           | 1.417     | 1.417     | 1.409     | C2-C1-H7       | 119.9     | 119.9     | 120.0     | C5-C1-C2-N14      | -178.2   | 178.3     | 178.2     |
| C1-H1           | 1.093     | 1.093     | 1.082     | C3-C1-H4       | 119.6     | 119.6     | 119.5     | H3-C2-C1-C3       | 179.8    | -179.8    | -179.8    |
| C2-C3           | 1.440     | 1.440     | 1.432     | C1-C2-C4       | 117.7     | 117.7     | 117.8     | H2-C3-C2-N14      | 2.531    | -2.525    | -2.262    |
| C1-N14          | 1.384     | 1.384     | 1.377     | C3-C1-N14      | 121.7     | 121.8     | 121.3     | C5-C1-C2-N13      | -0.727   | 0.736     | 0.611     |
| C5-C6           | 1.432     | 1.432     | 1.423     | C2-C5-N14      | 120.4     | 120.4     | 120.7     | C5-C1-C2-C17      | 179.9    | -179.9    | -179.5    |
| C3-C6           | 1.418     | 1.418     | 1.411     | C3-C3-C4       | 117.1     | 117.1     | 117.1     | H2-C1-C2-N13      | 178.4    | -178.4    | -178.8    |
| C5-C9           | 1.432     | 1.432     | 1.426     | C2-C3-C5       | 123.1     | 123.1     | 123.2     | H1-C1-C2-C17      | -0.887   | 0.897     | 0.957     |
| C7-C14          | 1.362     | 1.362     | 1.355     | C1-C7-C8       | 119.6     | 119.6     | 119.6     | C5-C2-C3-C4       | 2.055    | -2.081    | -1.530    |
| C3-N15          | 1.324     | 1.324     | 1.316     | C3-C3-C9       | 118.0     | 118.0     | 118.0     | C5-C2-C3-C8       | -177.2   | 177.2     | 178.1     |
| C4-C17          | 1.508     | 1.508     | 1.504     | C3-C4-N13      | 123.5     | 123.5     | 123.1     | N1-C2-C4-C8       | 179.3    | -179.4    | -179.1    |
| H1-C14          | 1.092     | 1.092     | 1.081     | C1-C14-N15     | 118.3     | 118.3     | 118.7     | N1-C2-C3-C8       | 0.093    | -0.121    | 0.600     |
| C10-C11         | 1.380     | 1.380     | 1.371     | C11-C10-N15    | 123.2     | 123.2     | 122.9     | C1-C2-N12-H15     | -149.4   | 149.4     | 155.1     |
| C11-C20         | 1.382     | 1.382     | 1.373     | C1-C11-C10     | 119.6     | 119.6     | 119.6     | C1-C2-N12-H16     | -15.91   | 15.89     | 15.32     |
| C9-C21          | 1.512     | 1.512     | 1.512     | C9-C11-N15     | 117.0     | 117.0     | 117.3     | C3-C2-N12-H15     | 33.31    | -33.28    | -27.30    |
| C10-H33         | 1.412     | 1.412     | 1.404     | C3-C10-C15     | 119.9     | 119.9     | 120.2     | C5-C2-C3-H6       | 166.8    | -166.8    | -167.1    |
| C11-H45         | 1.089     | 1.090     | 1.079     | C3-C15-C1     | 121.7     | 120.7     | 120.8     | C2-C1-C5-C9       | 178.7    | -178.6    | -178.9    |
| C11-H55         | 1.091     | 1.091     | 1.080     | H2-C1-H55      | 119.1     | 119.1     | 118.8     | C2-C1-C5-N13      | -1.629   | 1.647     | 1.283     |
| N14-H55         | 1.014     | 1.014     | 1.004     | C4-C4-C10      | 120.0     | 120.6     | 120.6     | C5-C1-C2-C9       | -1.982   | 1.995     | 1.333     |
| N14-H65         | 1.015     | 1.015     | 1.005     | C5-C4-C4       | 119.7     | 119.7     | 119.8     | C5-C1-C2-N13      | 177.6    | -177.6    | -178.4    |
| C17-H18         | 1.103     | 1.103     | 1.091     | C10-C10-C15    | 119.5     | 119.5     | 119.0     | C2-C2-C3-H6       | 2.444    | -2.459    | -2.132    |
| C17-H19         | 1.103     | 1.103     | 1.092     | C10-C10-C11    | 120.7     | 120.7     | 120.8     | C2-C3-C4-C11      | -179.0   | 179.0     | 179.2     |
| C17-H20         | 1.097     | 1.097     | 1.086     | C2-C10-H55     | 119.3     | 119.3     | 119.6     | C2-C3-C4-H6       | -176.8   | 176.8     | 177.5     |
| C21-F12         | 1.348     | 1.349     | 1.345     | C11-C10-H55    | 119.8     | 119.8     | 119.5     | C5-C4-C5-C11      | 1.647    | -1.656    | -1.078    |
| C21-F13         | 1.361     | 1.361     | 1.356     | C6-C11-C10     | 120.0     | 120.0     | 120.0     | C1-C5-C6-C10      | 0.987    | -0.994    | -0.675    |
| C21-F24         | 1.349     | 1.349     | 1.345     | C16-C15-H22    | 120.3     | 120.3     | 120.3     | C1-C15-C21-C21    | -179.2   | 179.2     | 179.5     |
Table 2. Vibrational assignment of 4-amino-2-methyl-8-(trifluoromethyl)quinoline by normal mode analysis based on SQM force field calculations.

| Normal Modes | cc-pVDZ | cc-pVTZ | cc-pVQZ | Experimental | PED(%)c |
|--------------|---------|---------|---------|--------------|---------|
|              | Freq.   | I<sub>IR</sub> | I<sub>Raman</sub> | Freq. | Freq. | FT-IR | FT-Raman |
| A" v₁        | 54      | 0.020   | 0.476   | 54    | 36     | τ<sub>CCCC(10)+t<sub>CCCC(17)+t<sub>CCCC(13)+t<sub>CCCC(10)+t<sub>CCCC(36)</sub></sub>
| A" v₂        | 59      | 0.100   | 1.105   | 58    | 57     | τ<sub>CCCC(20)+t<sub>CCCC(19)+t<sub>CCCC(18)+t<sub>CCCC(13)+t<sub>CCCC(20)</sub></sub>
| A" v₃        | 67      | 0.231   | 0.048   | 66    | 60     | τ<sub>CCCC(43)+t<sub>CCCC(44)</sub></sub>
| A" v₄        | 129     | 0.295   | 0.557   | 128   | 129    | τ<sub>CCCC(18)+t<sub>CCCC(22)+t<sub>CCCC(18)+t<sub>CCCC(12)+t<sub>CCCC(9)</sub></sub>
| A" v₅        | 132     | 0.257   | 0.429   | 131   | 132    | τ<sub>CCCC(18)+t<sub>CCCC(22)+t<sub>CCCC(19)+t<sub>CCCC(12)+t<sub>CCCC(10)</sub></sub>
| A" v₆        | 168     | 1.242   | 0.501   | 167   | 165    | 148 m  τ<sub>CCCC(29)+t<sub>CCCC(17)+t<sub>CCCC(23)+t<sub>CCCC(15)</sub></sub>
| A" v₇        | 184     | 0.318   | 0.279   | 183   | 183    | 199 m  τ<sub>CCCC(31)+t<sub>CCCC(12)+t<sub>CCCC(30)+t<sub>CCCC(10)</sub></sub> |
| $A^*$ | $v_8$ | 260  | 0.142 | 0.781 | 259 | 262 | 245 m | $\delta_{C=C}(19)+\delta_{C=C}(11)+\delta_{C=H}(10)+\tau_{C=H}(17)$ |
|--------|-------|------|-------|-------|-----|-----|-------|-------------------------------------------------|
| $A'$  | $v_9$ | 276  | 0.259 | 0.392 | 274 | 276 | 283 m | $\tau_{C=C}(24)+\tau_{C=C}(22)+\tau_{C=H}(23)$ |
| $A'$  | $v_{10}$ | 285  | 0.847 | 1.144 | 284 | 289 | 310 s | $\tau_{C=C}(10)+\tau_{C=C}(11)+\tau_{C=H}(14)+\tau_{C=H}(25)$ |
| $A'$  | $v_{11}$ | 309  | 1.552 | 0.394 | 307 | 314 | 334 m | $\tau_{C=C}(12)+\tau_{C=H}(41)$ |
| $A'$  | $v_{12}$ | 330  | 4.215 | 0.308 | 328 | 331 | 372 m | $\delta_{C=C}(13)+\delta_{C=C}(19)+\tau_{C=H}(13)+\tau_{C=H}(13)$ |
| $A'$  | $v_{13}$ | 357  | 0.314 | 0.792 | 355 | 358 | 465 s | $\tau_{C=C}(19)+\tau_{C=H}(14)+\tau_{C=H}(14)+\tau_{C=H}(33)$ |
| $A'$  | $v_{14}$ | 370  | 7.429 | 0.440 | 368 | 374 | 500 m | $\tau_{C=C}(17)+\tau_{C=H}(11)+\tau_{C=H}(10)+\tau_{C=H}(17)$ |
| $A'$  | $v_{15}$ | 453  | 0.413 | 3.426 | 451 | 454 | 527 | $\delta_{C=C}(14)+\delta_{C=C}(10)+\delta_{C=H}(13)+\delta_{C=H}(10)+\tau_{C=H}(16)$ |
| $A'$  | $v_{16}$ | 478  | 7.758 | 0.941 | 475 | 473 | 527 | $\delta_{C=C}(11)+\tau_{C=H}(10)+\tau_{C=H}(11)+\tau_{C=H}(17)$ |
| $A'$  | $v_{17}$ | 495  | 0.372 | 1.551 | 492 | 492 | 563 m | $\delta_{C=C}(11)+\tau_{C=H}(14)+\tau_{C=H}(12)$ |
| $A'$  | $v_{18}$ | 524  | 37.43 | 1.614 | 521 | 496 | 580 vw | $\tau_{C=C}(24)+\tau_{C=H}(17)+\tau_{C=H}(11)+\tau_{C=H}(17)$ |
| $A'$  | $v_{19}$ | 528  | 1.548 | 0.783 | 525 | 527 | 546 m | $\delta_{C=C}(15)+\tau_{C=H}(15)+\tau_{C=H}(10)$ |
| $A'$  | $v_{20}$ | 535  | 11.29 | 1.303 | 532 | 534 | 563 m | $\delta_{C=C}(12)+\tau_{C=H}(12)+\tau_{C=H}(11)+\tau_{C=H}(17)$ |
| $A'$  | $v_{21}$ | 546  | 16.48 | 3.182 | 543 | 545 | 605 s | $\tau_{C=C}(15)+\tau_{C=H}(20)+\tau_{C=H}(30)+\tau_{C=H}(12)$ |
| $A'$  | $v_{22}$ | 584  | 7.882 | 0.513 | 581 | 581 | 607 m | $\tau_{C=C}(15)+\tau_{C=H}(10)+\tau_{C=H}(10)+\tau_{C=H}(10)$ |
| $A'$  | $v_{23}$ | 590  | 5.028 | 1.585 | 587 | 590 | 625 | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(10)$ |
| $A'$  | $v_{24}$ | 625  | 5.617 | 0.533 | 622 | 625 | 716 | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{25}$ | 667  | 4.708 | 1.625 | 663 | 669 | 732 w | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{26}$ | 692  | 0.685 | 0.198 | 689 | 692 | 727 m | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{27}$ | 715  | 0.704 | 2.694 | 711 | 716 | 735 m | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{28}$ | 755  | 8.877 | 0.719 | 751 | 754 | 762 m | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{29}$ | 818  | 3.869 | 0.901 | 814 | 820 | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{30}$ | 821  | 4.431 | 1.664 | 816 | 825 | 1026 | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{31}$ | 829  | 3.605 | 0.861 | 825 | 839 | 836 vw | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{32}$ | 861  | 3.162 | 0.574 | 856 | 862 | 872 m | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{33}$ | 915  | 0.850 | 0.344 | 910 | 914 | 930 w | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{34}$ | 962  | 0.642 | 0.310 | 957 | 959 | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{35}$ | 967  | 3.711 | 0.394 | 962 | 971 | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{36}$ | 981  | 7.069 | 0.103 | 976 | 984 | 993 s | $\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)+\tau_{C=H}(15)$ |
| $A'$  | $v_{37}$ | 1012 | 0.751 | 0.012 | 1007 | 1026 | $\delta_{C=C}(20)+\tau_{C=H}(27)+\tau_{C=H}(18)+\tau_{C=H}(10)$ |
| $A'$  | $v_{38}$ | 1057 | 6.566 | 2.253 | 1052 | 1051 | $\delta_{C=C}(20)+\delta_{C=C}(25)+\delta_{C=H}(11)$ |
| $A'$  | $v_{39}$ | 1065 | 12.98 | 1.076 | 1060 | 1062 | $\delta_{C=C}(18)+\delta_{C=H}(11)+\delta_{C=H}(24)$ |
| $A'$  | $v_{40}$ | 1097 | 18.23 | 1.021 | 1091 | 1085 | 1076 vs | $\delta_{C=C}(18)+\delta_{C=H}(11)+\delta_{C=H}(18)+\delta_{C=H}(14)$ |
| \(A'\) | v_41 | 1310 | 30.2 | 0.562 | 1124 | 1106 | \(v_{CC}(13)+\delta_{CC}(11)+\delta_{CC}(19)+\tau_{CCF}(14)\) |
| \(A'\) | v_42 | 1149 | 76.91 | 0.675 | 1143 | 1112 | 1117 vs \(v_{CF}(22)+\delta_{CF}(10)+\tau_{CCCF}(12)+\tau_{CCCF}(24)\) |
| \(A'\) | v_43 | 1155 | 3.657 | 1.666 | 1149 | 1161 | 1143 s | 1144 m | 1182 m | \(v_{CC}(11)+\delta_{CC}(10)+\delta_{CC}(45)\) |
| \(A'\) | v_44 | 1163 | 11.66 | 0.434 | 1157 | 1170 | 1189 m | 1182 m | \(v_{CC}(13)+\delta_{CC}(10)+\delta_{CH}(37)\) |
| \(A'\) | v_45 | 1202 | 4.782 | 0.757 | 1196 | 1209 | 1228 m.sh | 1228 m | \(v_{CC}(15)+\delta_{CC}(20)+\delta_{CH}(28)+\delta_{CH}(9)\) |
| \(A'\) | v_46 | 1256 | 0.527 | 0.734 | 1249 | 1252 | 1259 m | \(v_{CC}(23)+\delta_{CC}(12)+\delta_{CH}(26)\) |
| \(A'\) | v_47 | 1281 | 100 | 8.203 | 1274 | 1266 | 1308 vs \(v_{CC}(19)+\gamma_{CH}(19)+\delta_{CH}(14)+\delta_{CH}(26)\) |
| \(A'\) | v_48 | 1328 | 5.333 | 3.011 | 1321 | 1320 | \(1309 s v_{CC}(21)+\delta_{CC}(10)+\delta_{CH}(23)\) |
| \(A'\) | v_49 | 1338 | 0.613 | 7.879 | 1331 | 1333 | 1332 vw | \(v_{CC}(17)+\delta_{CH}(32)+\delta_{CH}(24)\) |
| \(A'\) | v_50 | 1360 | 6.484 | 54.59 | 1353 | 1357 | 1353 m.sh | 1352 vs \(v_{CC}(35)+\delta_{CC}(14)+\delta_{CH}(20)\) |
| \(A'\) | v_51 | 1383 | 6.340 | 2.339 | 1376 | 1377 | 1375w \(v_{CC}(14)+\delta_{CH}(14)+\delta_{CH}(16)+\delta_{CH}(19)+\tau_{CCCF}(10)+\tau_{CCCF}(10)\) |
| \(A'\) | v_52 | 1401 | 6.917 | 22.29 | 1394 | 1423 | 1421 vw | 1421 m | \(v_{CC}(11)+\delta_{CH}(14)+\delta_{CH}(23)+\tau_{CCCF}(13)+\tau_{CCCF}(13)\) |
| \(A'\) | v_53 | 1411 | 1.967 | 5.709 | 1404 | 1428 | \(v_{CC}(9)+\delta_{CH}(34)+\tau_{CCCF}(24)+\tau_{CCCF}(24)\) |
| \(A'\) | v_54 | 1421 | 2.239 | 17.66 | 1414 | 1441 | 1442 m | 1441 m | \(v_{CC}(22)+\delta_{CC}(19)+\delta_{CH}(27)\) |
| \(A'\) | v_55 | 1462 | 2.961 | 1.354 | 1454 | 1462 | \(v_{CC}(22)+\delta_{CC}(13)+\delta_{CC}(32)\) |
| \(A'\) | v_56 | 1510 | 17.10 | 0.910 | 1502 | 1501 | 1517 s | 1525 m | \(v_{CC}(26)+\delta_{CC}(12)+\delta_{CH}(30)\) |
| \(A'\) | v_57 | 1571 | 24.87 | 13.62 | 1563 | 1557 | 1569 vs | 1572 s | \(v_{CC}(34)+\delta_{CC}(18)+\delta_{CC}(19)+\delta_{CC}(11)\) |
| \(A'\) | v_58 | 1584 | 14.86 | 2.581 | 1576 | 1585 | 1592 vs | 1594 m | \(v_{CC}(16)+\delta_{CC}(10)+\delta_{CC}(13)+\delta_{CH}(12)+\delta_{CC}(19)+\tau_{CCF}(10)\) |
| \(A'\) | v_59 | 1609 | 36.23 | 4.025 | 1601 | 1603 | 1619 s | 1621 m | \(v_{CC}(21)+\delta_{CC}(13)+\delta_{CH}(22)+\tau_{CCF}(11)\) |
| \(A'\) | v_60 | 1619 | 46.79 | 12.29 | 1611 | 1615 | 1638 s | 1637 m | \(v_{CC}(27)+\delta_{CC}(17)+\delta_{CC}(16)\) |
| \(A'\) | v_61 | 2939 | 5.973 | 100 | 2924 | 2933 | 2924 m | 2925 m | \(v_{CC}(96)\) |
| \(A'\) | v_62 | 2996 | 4.207 | 43.04 | 2980 | 2979 | 2956 vw | 2964 m | \(v_{CC}(76)\) |
| \(A'\) | v_63 | 3057 | 1.382 | 22.50 | 3041 | 3039 | \(v_{CH}(77)\) |
| \(A'\) | v_64 | 3072 | 4.883 | 46.55 | 3056 | 3062 | \(v_{CH}(71)\) |
| \(A'\) | v_65 | 3084 | 1.362 | 17.98 | 3068 | 3072 | 3072 m | \(v_{CH}(78)+\delta_{CC}(10)\) |
| \(A'\) | v_66 | 3104 | 4.864 | 58.35 | 3088 | 3091 | 3099 vw | \(v_{CH}(81)\) |
| \(A'\) | v_67 | 3128 | 0.717 | 61.78 | 3112 | 3114 | 3252 m | \(v_{CH}(79)\) |
| \(A'\) | v_68 | 3443 | 6.661 | 71.51 | 3426 | 3472 | 3383 s | 3388 m | \(v_{NH}(87)\) |
| \(A'\) | v_69 | 3541 | 4.892 | 21.71 | 3524 | 3569 | 3494 s | \(v_{NH}(84)\) |

vs: very strong, ms: medium strong, s: strong, w: weak, vw: very weak, v: stretching, t: torsion, \(\gamma\): out of plane stretching, \(\delta\): in plane bending

* Obtained from the wavenumbers calculated at 0.970 for cc-pVDZ, 0.965 for cc-pVTZ, and 0.969 for cc-pVQZ basis sets [36].

* Relative absorption intensities and Relative Raman activities normalized with highest peak absorption equal to 100.

* Total energy distribution calculated B3LYP cc-pVDZ level of theory. Only contributions \(\geq 10\%\) are listed.
5. HOMO-LUMO analysis

HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are known as Molecular orbitals. They were very important electronic parameters for chemist and physicist. The LUMO are known as the inner-most orbital containing free places to accept electrons. It defines the ability of accepting electron. HOMO can be considered the outermost orbital containing electrons. It characterizes the ability of giving electron. HOMO and LUMO energies of chemical compounds are important quantum mechanical parameters. They are very useful to explain its reactivity. The plots of HOMO, HOMO-1, and LUMO, LUMO+1, molecular orbitals for the AMTQ were given in Figure 4.

![Figure 4. HOMO and LUMO plot of of 4-amino-2-methyl-8-(trifluoromethyl)quinolone molecule ( B3LYP / cc-pVDZ) ](image)

6. Nuclear Magnetic Resonance Spectra

Significant progress has been achieved in chemical shifts calculations which aids in spectral assignment and structural elucidation. Meanwhile, the Gauge Invariant Atomic Orbitals (GIAO) approach [37,38] that uses density functional theory, DFT-B3LYP and DFT-B3PW91 calculations have afforded excellent agreement with experimental NMR spectral analysis [39-41]. Therefore, we have used the optimized geometry of AMTQ structure from B3LYP using cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets in DMSO solution for further optimization, while employing Tomasi’s Polarized Continuum Model (PCM) [19]. The $^{13}$C NMR nuclear shielding constants were predicted using GIAO approximation with the above method. The calculated $^1$H and $^{13}$C absolute isotropic shielding (si, ppm) parameters were converted into $^1$H and $^{13}$C chemical shifts ($\delta_{\text{calc}}$, ppm) using ($\delta_{\text{calc}}=\delta_{\text{TMS}}-\delta_i$). The experimental peaks along with the simulated $^1$H (a) and $^{13}$C (b) nuclear magnetic resonance (NMR) spectra of 4-amino-2-methyl-8-(trifluoromethyl)quinoline molecule shown in Figure 5.

![Figure 5. $^1$H (a) and $^{13}$C (b) NMR spectra of 4-amino-2-methyl-8-(trifluoromethyl)quinoline](image)
8.406-2.441 ppm. In the proton NMR spectra, the signals are observed at 6.883 (H$_1$), 7.940 (H$_{12}$), 8.379 (H$_6$) and 8.406 (H$_{25}$) ppm. Hydrogen atoms attached to quinoline ring. The methyl hydrogen atoms are H$_{15}$, H$_9$ and H$_{20}$ and exhibit shift at 2.515, 2.509 and 2.441 ppm, respectively. The chemical shifts of the H$_{15}$ and H$_{16}$, which is attached to N$_{14}$, appeared at 3.400 ppm and 3.332 ppm by experimental data. We note that the experimental $^1$H NMR data agrees with them of the theoretical predicted.

| Table 3. Theoretical and experimental $^1$H and $^{13}$C spectra of the title molecule (with respect to TMS, all values in ppm) |
|---|---|---|---|---|---|---|---|
| Theoretical (B3LYP) | Exp. | Theoretical (B3LYP) | Exp. |
| cc-pVDZ | cc-pVTZ | cc-pVQZ | | cc-pVDZ | cc-pVTZ | cc-pVQZ | |
| H$_{25}$ | 8.028 | 8.410 | 8.492 | 8.406 | C$_3$ | 161.9 | 169.1 | 172.4 | 160.9 |
| H$_6$ | 7.849 | 8.206 | 8.263 | 8.379 | C$_2$ | 149.4 | 158.2 | 160.6 | 159.8 |
| H$_{12}$ | 7.430 | 7.723 | 7.770 | 7.940 | C$_4$ | 148.3 | 155.4 | 157.9 | 152.2 |
| H$_2$ | 6.474 | 6.831 | 6.883 | 6.883 | C$_3$ | 134.8 | 139.1 | 142.0 | 145.6 |
| H$_{15}$ | 3.954 | 4.429 | 4.563 | 3.400 | C$_{10}$ | 129.1 | 135.6 | 137.7 | 127.9 |
| H$_{16}$ | 3.385 | 3.896 | 4.064 | 3.332 | C$_{11}$ | 123.4 | 128.8 | 130.8 | 127.6 |
| H$_{18}$ | 2.825 | 2.940 | 2.949 | 2.515 | C$_4$ | 124.5 | 130.3 | 132.5 | 127.8 |
| H$_{19}$ | 2.817 | 2.946 | 2.957 | 2.509 | C$_1$ | 123.4 | 128.8 | 130.8 | 127.6 |
| H$_{20}$ | 2.651 | 2.925 | 2.980 | 2.441 | C$_3$ | 121.5 | 125.7 | 128.1 | 121.6 |
| H$_{21}$ | 2.651 | 2.925 | 2.980 | 2.441 | C$_{17}$ | 29.05 | 29.81 | 29.55 | 25.82 |

7. Molecular Electrostatic Potential Maps
The molecular electrostatic potential (MEP) maps of ground state of AMTQ are shown in Fig. 6. In the organic molecules, the MEP is generally used as a reactivity map displaying. These regions are the most probable regions for the electrophilic attack. The MEP contour map provides a simple way to predict how different geometries could interact. The calculated 3D MEP contour map (red is negative, blue is positive) shows the negative regions. In the AMTQ molecule is mainly over the Nitrogen atoms. The electrostatic potential maps have been used for predicting sites.

![Figure 6. Molecular ESP mapped on the isodensity surface for 4-amino-2-methyl-8-(trifluoromethyl)quinoline molecule](image)

8. Conclusion
This work deal with the vibrational, Nuclear Magnetic Resonance spectra, molecular structure and some electronic properties of AMTQ molecule by theoretical methods and experimental setup. The results of theoretical and experimental studies are combining with together. The most stable conformer of the AMTQ is predicted by DFT calculation. The ground state conformers of AMTQ are further studied using the Density Functional Theory at B3LYP with cc-pVQZ, cc-pVTZ and cc-pVDZ basis sets. The spectroscopic, structural and electronic properties of the ground state have been calculated by Gaussian09. The experimental work has focused on the assignment of the vibrational spectra from 400 to 4000 cm$^{-1}$. Computed results of the AMTQ are found to be in better agreement with the experimental findings.

References
1. Quinoline, Wikipedia, https://en.wikipedia.org/wiki/Quinoline, 2017, (accessed 20.05.2017).
2. Wang, L.Y., Chen, Q.W., Zhai, G.H., Wen, Z.Y., Zhang, Z.X., Theoretical study on the structures and absorption properties of styryl dyes with quinoline nucleus, Dyes and Pigments, 2007, 72, 357–362.
3. Dahule, H.K., Thejokalyani, N., Dhole, S.J., Novel Br-DPQ blue light-emitting phosphors for OLED, Luminescence, 2014, 4, 405–410.
4. Ciobotaru, I.C., Polosan, S., Ciobotaru, C.C., Dual emitter IrQ(ppy)$_2$ for OLED applications: Synthesis and spectroscopic analysis, Journal of Luminescence, 2014, 145, 259–262.
5. Camargo, H., Paolini, T.B., Niyama, E., Brito, H.F., Crémona, M., New rare-earth quinolinate complexes for organic light-emitting devices, Thin Solid Films, 2013, 528, 36–41.
6. Dereli, O., Erdogdu, Y., Gulhuoglu, M.T., Ozmen, A., Sundaraganesan, N., Vibration spectral and quantum chemical investigations of tert-butyl-hydroquinone, Journal of Molecular Spectroscopy, 2012, 1012, 168-176.

7. Dereli, O., Sudha, S., Sundaraganesan, N., Molecular structure and vibrational spectra of 4-phenylsemicarbazide by density functional method, Journal of Molecular Structure, 2011, 994, 379-386.

8. Yurdakul, Ş., Badoglu, S., An FT-IR and DFT study of the free and solvated 4-(imidazol-1-yl)phenol, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015, 150, 614-622.

9. Yurdakul, Ş., Badoglu, S., Ozkurt, L., An experimental and theoretical investigation of free Oxazole in conjunction with the DFT analysis of Oxazole (H₂O)₃ complexes, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2016, 162, 48-60.

10. Erdogdu, Y., Investigations of FT-IR, FT-Raman, FT-NMR spectra and quantum chemical computations of Escculetin molecule, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2013, 106, 25-33.

11. Erdogdu, Y., Unsalan, O., Gulhuoglu, M.T., FT-Raman and DFT spectra and DFT studies on 6, 8-dichloroflavone and 6, 8-dibromoflavone, Journal of Raman Spectroscopy, 2010, 40, 821-828.

12. Subashchandrabose, S., Saleem, H., Erdogdu, Y., Dereli, Ö., Thanikkachalam, V., Jayabharathi, J., Structural, vibrational and hyperpolarizability calculation of (E)-1-(2-hydroxybenzylideneamino)-3-methylbutan-2-one, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2012, 86, 231-241.

13. Sajan, D., Erdogdu, Y., Kuruvilla, T., Hubert Joe, I., Vibrational spectra and first-order molecular hyperpolarizabilities of p-hydroxybenzaldehyde dimer, Journal of Molecular Structure, 2010, 983, 12-21.

14. Erdogdu, Y., Unsalan, O., Sajan, D., Gulhuoglu, M.T., Structural conformations and vibrational spectral study of chloroflavone with density functional theoretical simulations, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2010, 76, 130-136.

15. Erdogdu, Y., Güllüoğlu, M.T., Yurdakul, Ş., Molecular structure and vibrational spectra of 1,3-bis(4-piperidyl)propane by quantum chemical calculations, Journal of Molecular Structure, 2008, 889, 361-370.

16. Frosch, T., Schmitt, M., Popp, J., Raman spectroscopic investigation of the antimalarial agent mefloquine, Analytical and Bioanalytical Chemistry, 2007, 387, 1749–1757.

17. Frosch, T., Popp, J., Structural analysis of the antimalarial drug halofantrine by means of Raman spectroscopy and density functional theory calculations, Journal of Biomedical optics, 2010, 15 (4), 041516. doi:10.1117/1.3432656

18. Frosch, T., Schmitt, M., Schenzel, K., Faber, J.H., Bringmann, G., Kiefer, W., Popp, J., In vivo localization and identification of the antiprostaglandin D₂ cyclooxygenase in the tropical liana Triphyophyllum peltatum by a combination of fluorescence, near infrared Fourier transform Raman microscopy, and density functional theory calculations, Biopolymers, 2006, 82, 295–300.

19. Frosch, T., Küstner, B., Schlücker, S., Szigethalmi, A., Schmitt, M., Kiefer, W., Popp, J., In vitro polarization-resolved resonance Raman studies of the interaction of hematin with the antimalarial drug chloroquine, Journal of Raman Spectroscopy, 2004, 35, 819–821.

20. Ulahannan, R.T., Panicker, C.Y., Varghese, H.T., Van Alseneoy, C., Mussol, R., Jampilek, J., Anto, P.L., Spectroscopic (FT-IR, FT-Raman) investigations and quantum chemical calculations of 4-hydroxy-2-oxo-1,2-dihydroquinoline-7-carboxylic acid, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2014, 121, 404–414.

21. Frosch, T., Popp, J., Relationship between molecular structure and Raman spectra of quinolones, Journal of Molecular Structure, 2009, 924–926, 301–308.

22. Cinta-Pinzaru, S., Peica, N., Küstner, B., Schlücker, S., Schmitt, M., Frosch, T., Faber, J.H., Bringmann, G., Popp, J., FT-Raman and NIR-SERS characterization of the antimalarial drugs chloroquine and mefloquine and their interaction with hematin, Journal of Raman Spectroscopy, 2006, 37, 326–334.

23. Frosch, T., Schmitt, M., Bringmann, G., Kiefer, W., Popp, J., Structural Analysis of the Anti-Malaria Active Agent Chloroquine under Physiological Conditions, Journal of Physical Chemistry B, 2007, 111, 1815–1822.

24. Frosch, T., Schmitt, M., Popp, J., In situ UV Resonance Raman Micro-spectroscopic Localization of the Antimalarial Quinine in Cinchona Bark, Journal of Physical Chemistry B, 2007, 111, 4171–4177.

25. Fazal, E., Jasinski, J., Anderson, B., Kaur, M., Nagarajan, S., Sudha, B., Synthesis, Crystal and Molecular Structure Studies and DFT Calculations of Phenyl Quinoline-2-Carboxylate and 2-Methoxophenyl Quinoline-2-Carboxylate; Two New Quinoline-2-Carboxyl Derivatives, Crystals, 2015, 5, 100–115.

26. Diwaker, C.S., Chidan, Kumar, A., Chandraju, Kumar, S., Spectroscopic (FT-IR, 1H C NMR and UV–vis) characterization and DFT studies of novel 8-(4-(4-methylthio)-2-5-diphenylfuranyl, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015, 150, 602–613.

27. Ulahannan, R.T., Panicker, C.Y., Varghese, H.T., Musiol, R., Jampilek, J., Alseneoy, C.V., War, J.A., Manojkumar T.K., Vibrational spectroscopic studies and molecular docking study of 2-[(E)-2-phenylethyl]quinoline-5-carboxylic acid, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015, 150, 190–199.

28. Kulkarni, A., King, C., Butcher, R.J., Fortunak, M.D., 4,7-Dichloroquino-lone, Acta Crystallographica, 2012, E68, 1498.

29. Pereira, G.R., et al., 7-Chloroquinolinotriazoles: Synthesis by the azide–alkyne cycloaddition click chemistry, antimalarial activity, cytotoxicity and SAR studies, European Journal of Medicinal Chemistry, 2014, 73, 295–309.

30. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., et al., Gaussian 09, revision A2. Wallingford CT: Gaussian, Inc., 2009.

31. Pulay, P., Baker, J., Wolinski, K., Green Acres Road Suite A Fayetteville, Arkansas, 72703, USA, 2013.

32. Thanikkachalam, V., Periyayagasamy, V., Jayabharathi, J., Manikandan, G., Saleem, H., Subashchandrabose, S., Erdogdu, Y., FT-Raman, FT-IR spectral and DFT studies on (E)-1-4-nitrobenzylidenemethacryloylazide, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2012, 87, 86–95.

33. Roeges, N.P.G., A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures, Wiley, New York, 1994.

34. Güllüoğlu, M.T., Erdogdu, Y., Yurdakul, Ş., Molecular structure and vibrational spectra of piperidine and 4-methylpiperidine by
density functional theory and ab initio Hartree–Fock calculations, *Journal of Molecular Structure*, 2007, 834, 540-547.

35. Erdogdu, Y., Güllüoğlu, M.T., Analysis of vibrational spectra of 2 and 3-methylpiperidine based on density functional theory calculations, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2009, 74, 162-167.

36. CCCBDB listing of precalculated vibrational scaling factors NIST, http://srdata.nist.gov/cccbdb/vibscalejust.asp, 2017 (accessed 20.05.2017).

37. Ditchfield, J. R., Molecular Orbital Theory of Magnetic Shielding and Magnetic Susceptibility, *Journal of Chemical Physics*, 1972, 56, 5688

38. Wolinski, K., Hinton, J.F., Pulay, P., Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations, *Journal of American Chemical Society*, 1990, 112 (23), 8251-8260.

39. Azizi, N., Rostami, A.A., Godarzian, A., $^{29}$Si NMR Chemical Shift Calculation for Silicate Species by Gaussian Software, *Journal of Physical Society of Japan*, 2005, 74, 1609-1620.

40. Rohlfing, M., Leland, C., Allen, C., Ditchfield, R., Proton and carbon-13 chemical shifts: Comparison between theory and experiment, *Chemical Physics*, 1984, 87, 9-15.

41. Chesnut, D., Phung, C., Nuclear magnetic resonance chemical shifts using optimized geometries, *Journal of Chemical Physics* 1989; 91, 6238 – 6245