Vibrational spectroscopic studies of 2-amino picoline

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ABSTRACT

The vibrational wavenumbers of 2-amino picoline were calculated using Gaussian03 software package at different levels and the fundamental modes are assigned. The predicted infrared and Raman activities are reported. The first hyperpolarizability is calculated and the 2-amino picoline is an attractive object for future studies of non-linear optics. The calculated wavenumbers are in agreement with the reported experimental values.

Key words: HF, DFT calculations, hyperpolarizability, amino.

INTRODUCTION

Pyridine has been extensively studied spectroscopically, due to its application in many chemical structures of high interest in a variety of biomedical and industrial fields.¹ Pyridine has the intrinsic interest of being the azine nearest to benzene. Amino pyridines attract the attention of many spectroscopists due to their wide application in pharmacology and agro chemistry. They serve as a good anesthetic agent and hence are used in the preparation of drugs for certain brain disease. The derivatives of picoline have potent hypolipidemic effects, antineoplastic and anti-inflammatory activities and show good activity against leukemia and human glioma cell growth.² Jose and Mohan³ reported the vibrational spectra and normal coordinate analysis of 2-amino picoline. Ab initio quantum mechanical method is at present widely used for simulating the IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis that modern vibrational spectroscopy is unimaginable without involving them. In the present study, we have calculated the vibrational wavenumbers of the title compound by using Hartree-Fock and DFT methods and compared with the IR and Raman bands observed by Jose and Mohan.³ Many organic molecules containing conjugated π electrons and characterized by large values of molecular first hyperpolarizabilities have been analyzed by means of vibrational spectroscopy.⁴ In this context, the hyperpolarizability of the title compound was calculated theoretically.

Computational details

Calculations of the title compound were carried out with Gaussian03 program⁵ using the Hartree-Fock and DFT (B3LYP) levels of theory using the standard 6-31G* set to predict the molecular structure and vibrational wavenumbers. Molecular geometry (Figure 1) was fully optimized by Beryn's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic
second derivatives to confirm the convergence to minima of the potential surface. The wavenumber values computed contain known systematic errors and hence we have used scaling factors 0.8929 and 0.9613 for HF and DFT methods. The absence of imaginary wavenumbers of the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The optimized geometrical parameters (DFT) are given in Table 1.

**RESULTS AND DISCUSSION**

The calculated scaled wavenumbers, experimental wavenumbers given by Jose and Mohan and the assignments are given in Table 2. The NH$_2$ stretching modes are expected in the region 3250-3480 cm$^{-1}$ and the DFT calculation give 3532 and 3425 cm$^{-1}$ as asymmetric and symmetric NH$_2$ stretching modes. Jose and Mohan reported bands at 3435, 3431 and 3407 cm$^{-1}$ as NH$_2$

| Bond lengths (Å) | Bond Angles (°) | Dihedral Angles (°) |
|------------------|-----------------|----------------------|
| C$_1$-C$_2$      | 1.4110          | A(2,1,6) 122.9       | D(6,1,2,3) 0.1 |
| C$_1$-N$_6$     | 1.3397          | A(2,1,10) 120.9     | D(6,1,2,7) 179.6 |
| C$_1$-N$_{10}$  | 1.3862          | A(6,1,10) 116.2     | D(10,1,2,3) -177.5 |
| C$_2$-C$_2$     | 1.3892          | A(1,2,3) 119.4      | D(10,1,2,7) 2.0 |
| C$_2$-H$_7$     | 1.0876          | A(1,2,7) 120.0      | D(2,1,6,5) -0.5 |
| C$_3$-C$_4$     | 1.4065          | A(3,2,7) 120.6      | D(10,1,6,5) 177.2 |
| C$_3$-C$_{13}$  | 1.5089          | A(2,3,4) 117.7      | D(2,1,10,11) -29.4 |
| C$_4$-C$_5$     | 1.3883          | A(2,3,13) 121.4     | D(2,1,10,12) -164.9 |
| C$_4$-H$_8$     | 1.0863          | A(4,3,13) 120.9     | D(6,1,10,11) 152.9 |
| C$_5$-C$_4$     | 1.3408          | A(3,4,5) 118.5      | D(6,1,10,12) 17.4 |
| C$_5$-H$_9$     | 1.0893          | A(3,4,8) 121.0      | D(1,2,3,4) 0.3 |
| N$_{10}$-H$_{11}$ | 1.0111         | A(5,4,8) 120.5      | D(1,2,3,13) -179.9 |
| N$_{10}$-H$_{12}$ | 1.0124         | A(5,4,8) 124.4      | D(7,2,3,4) -179.2 |
| C$_{13}$-H$_{14}$ | 1.0944         | A(4,5,9) 120.2      | D(7,2,3,13) 0.6 |
| C$_{13}$-H$_{15}$ | 1.0970         | A(6,5,9) 115.4      | D(2,3,4,5) -0.2 |
| C$_{13}$-H$_{16}$ | 1.0969         | A(1,6,5) 117.1      | D(2,3,4,8) 180.0 |
| A(1,10,11)       | 117.1           | D(13,3,4,5) 180.0 |
| A(1,10,12)       | 117.1           | D(13,3,4,8) 0.2 |
| A(11,10,12)      | 114.0           | D(2,3,13,14) 0.4 |
| A(3,13,14)       | 111.7           | D(2,3,13,15) 121.0 |
| A(3,13,15)       | 111.1           | D(2,3,13,16) -120.1 |
| A(3,13,16)       | 111.0           | D(4,3,13,14) -179.8 |
| A(14,13,15)      | 108.0           | D(4,3,13,15) -59.2 |
| A(14,13,16)      | 108.0           | D(4,3,13,16) 59.7 |
| A(15,13,16)      | 1070            | D(3,4,5,6) -0.3 |
| A(3,4,5,9)       | 179.8           |
| A(8,4,5,6)       | 179.6           |
| A(8,4,5,9)       | -0.0            |
| A(4,5,6,1)       | 0.06            |
| A(9,5,6,1)       | -179.8          |
Table 2: Calculated (scaled) wavenumbers and assignments

|                  | HF/6-31G*   | B3LYP/6-31G* | v<sub>IR</sub> (cm<sup>-1</sup>) | v<sub>Raman</sub> (cm<sup>-1</sup>) | Assignments |
|------------------|-------------|--------------|----------------------------------|-------------------------------------|-------------|
| v(cm<sup>-1</sup>) | IR Intensity | Raman Activity | v<sub>IR</sub> (cm<sup>-1</sup>) | Raman Activity |                          |
| 3499             | 29.12       | 59.43        | 5352                             | 18.16                               | 69.78       | 3435  3431 v<sub>asNH<sub>2</sub></sub> |
| 3400             | 39.76       | 125.70       | 3425                             | 26.99                               | 179.72      | 3407  v<sub>sNH<sub>2</sub></sub>     |
| 3020             | 27.06       | 148.69       | 3077                             | 18.77                               | 137.09      | 3135  v<sub>CH</sub>                  |
| 3005             | 15.43       | 72.18        | 3057                             | 16.09                               | 85.78       | 3059  v<sub>CH</sub>                  |
| 2998             | 24.36       | 68.41        | 3043                             | 31.70                               | 97.98       | 3049  v<sub>CH</sub>                  |
| 2937             | 24.73       | 57.00        | 3007                             | 18.14                               | 54.08       | 3049  v<sub>sMe</sub>                |
| 2915             | 24.02       | 89.08        | 2980                             | 17.21                               | 93.09       | 2977  2970 v<sub>asMe</sub>          |
| 2866             | 25.03       | 140.20       | 2929                             | 22.22                               | 165.29      | 2914  2914 v<sub>sMe</sub>          |
| 1631             | 372.58      | 313.05       | 1631                             | 21.65                               | 1635  1642 δ<sub>NH<sub>2</sub></sub> |
| 1620             | 61.72       | 3.21         | 1596                             | 4.12                                | 1607  1603 v<sub>Py</sub>        |
| 1584             | 95.34       | 12.69        | 1558                             | 11.26                               | 1556  1549 v<sub>Py</sub>        |
| 1497             | 17.97       | 3.24         | 1482                             | 6.46                                | 1491  1484 δ<sub>Me</sub>        |
| 1463             | 56.35       | 6.91         | 1465                             | 8.50                                | 1470  v<sub>Py</sub>             |
| 1455             | 4.87        | 18.41        | 1454                             | 19.42                               | 1456  1456 δ<sub>Me</sub>        |
| 1416             | 104.07      | 8.52         | 1419                             | 6.37                                | 1470  δ<sub>Me</sub>             |
| 1397             | 2.21        | 8.74         | 1385                             | 20.24                               | 1379  1363 v<sub>Py</sub>        |
| 1309             | 0.09        | 3.99         | 1316                             | 6.51                                | 1335  1331 v<sub>Py</sub>        |
| 1296             | 40.15       | 5.84         | 1295                             | 21.63                               | 1307  1307 δ<sub>CH</sub>        |
| 1169             | 17.73       | 7.56         | 1273                             | 4.66                                | 1270  1266 v<sub>CN</sub>        |
| 1159             | 9.06        | 1.86         | 1163                             | 3.72                                | 1177  1173 δ<sub>CH</sub>        |
| 1123             | 6.18        | 6.57         | 1119                             | 7.88                                | 1128  1128 δ<sub>CH</sub>        |
| 1044             | 5.66        | 0.718        | 1047                             | 0.97                                | 1044  1044 p<sub>Me</sub>        |
| 1037             | 5.93        | 5.95         | 1031                             | 5.03                                | 1037  1037 p<sub>tNH<sub>2</sub></sub> |
| 994              | 3.73        | 5.95         | 997                              | 1.56                                | 984   994 v<sub>Py</sub>          |
| 991              | 0.13        | 1.32         | 965                              | 18.58                               | 977   977 p<sub>Me</sub>         |
| 959              | 12.10       | 13.37        | 936                              | 2.13                                | 935   γ<sub>CH</sub>             |
| 927              | 7.09        | 0.78         | 930                              | 4.33                                | 927   927 γ<sub>CC</sub>         |
| 850              | 25.54       | 1.38         | 830                              | 2.44                                | 842   842 γ<sub>CH</sub>         |
| 806              | 52.76       | 0.84         | 788                              | 1.76                                | 784   784 γ<sub>CH</sub>         |
| 754              | 22.27       | 1.39         | 751                              | 13.61                               | 756   756 δ<sub>Py</sub>(X)     |
| 742              | 0.56        | 12.40        | 733                              | 1.01                                | 742   742 δ<sub>Py</sub>         |
| 616              | 132.81      | 3.65         | 601                              | 3.73                                | 616   616 ω<sub>NH<sub>2</sub></sub> |
| 562              | 39.58       | 7.66         | 561                              | 7.47                                | 562   562 ω<sub>Py</sub>(X)     |
| 534              | 188.51      | 1.35         | 529                              | 2.01                                | 534   534 δ<sub>Py</sub>(X)     |
| 498              | 3.95        | 6.12         | 501                              | 4.98                                | 498   498 γ<sub>Py</sub>(X)     |
| 445              | 31.79       | 0.88         | 440                              | 0.62                                | 445   445 γ<sub>Py</sub>(X)     |
| 421              | 1.76        | 0.70         | 423                              | 1.18                                | 421   421 δ<sub>CC</sub>(X)    |
| 339              | 47.27       | 1.45         | 365                              | 1.53                                | 339   339 δ<sub>CN</sub>(X)    |
| 279              | 2.84        | 0.34         | 281                              | 0.81                                | 279   279 γ<sub>CC</sub>(X)    |
| 214              | 5.81        | 1.62         | 206                              | 1.39                                | 214   214 γ<sub>CN</sub>(X)    |
| 195              | 3.72        | 1.79         | 192                              | 1.57                                | 195   195 tMe                   |
| 51               | 0.28        | 0.12         | 48                               | 0.21                                | 51    51 tNH<sub>2</sub>         |

ω-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ω-wagging; t-torsion; τ-twisting; ρ-rocking; Py-pyridine ring; X-Substituent sensitive; subscripts: as-asymmetric, s-symmetric. IR and Raman spectral data are taken from reference 3.
stretching modes. The NH$_2$ scissoring vibrations, expected around 1650 cm$^{-1}$ appear at 1642 cm$^{-1}$ Raman spectrum and at 1635 cm$^{-1}$ in the IR spectrum. The DFT calculations give this mode at 1613 cm$^{-1}$. The $\delta$NH$_2$ scissoring vibrations are reported at 1629 cm$^{-1}$ for sulfanilamide and at 1637 cm$^{-1}$ in IR, 1634 cm$^{-1}$ in Raman and 1642 cm$^{-1}$ in HF for orthanilic acid. According to Roeges $\rho$NHNH$_2$ vibration is expected in the region 1070 ± 50 cm$^{-1}$ and in the present case the DFT calculation give this mode at 1031 cm$^{-1}$. Kurt et al. observed the $\omega$NH$_2$ vibration at 667 cm$^{-1}$ in the IR spectrum and at 695 cm$^{-1}$ theoretically. Tzeng et al. calculated the wavenumber of the wagging vibration of amino group at 649 cm$^{-1}$ and experimentally at 665 cm$^{-1}$.

The pyridine CH stretching vibrations are observed in the range 3000-3100 cm$^{-1}$. Jose and Mohan reported CH stretching vibrations at 3135, 3059 cm$^{-1}$ in the IR spectrum and at 3049 cm$^{-1}$ in the Raman spectrum. The DFT calculations give these modes at 3077, 3057 and 3043 cm$^{-1}$. The pyridine ring stretching vibrations occur in the general region 1600-1300 cm$^{-1}$. These vibrations involve stretching and contraction of all the bonds in the ring and interaction between the stretching modes. In the present case the DFT calculations give $\nu$Py modes at 1596, 1558, 1465, 1385, 1316 cm$^{-1}$. The pyridine ring breathing mode is assigned at 997 cm$^{-1}$ (DFT). The in-plane and out-of-plane CH deformations are expected above 1000 and below 1000 cm$^{-1}$ and all these bands (Table 2) are assigned.

Analysis of organic molecules having conjugated $\pi$-electron systems and large hyperpolarizability using infrared and Raman spectroscopy has been evolved as a subject of research. The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectrum. The calculated first hyperpolarizability of the title compound is 2.47 $\times$ 10$^{-30}$ esu, which is comparable with the reported values of similar derivatives. We conclude that the title compound is an attractive object for future studies of non linear optics.
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