Structures, vibrational spectra and HOMO-LUMO analysis of 3-Mercapto-4-methyl-4H-1, 2, 4-triazole: an organic electroluminescent materials

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Abstract. 3-Mercapto-4-methyl-4H-1, 2, 4-triazole (MMTZ) is an Electron-transporting materials for organic electroluminescent devices. FT-Infrared and FT-Raman spectra of MMTZ were measured in the range 4000-400 cm⁻¹ and 3700-100 cm⁻¹, respectively. MMTZ exists in thiol and thione tautomeric forms. In order to make sure which one was the stable structure, the calculation of Gibbs free energy was calculated based on density functional theory (DFT) using B3LYP/6-311++G(d, p) basis set. The result showed that the thione form was the most stable tautomer. Vibrational assignments of MMTZ were made on the basis of potential energy distribution (PED). The calculated HOMO and LUMO energies showed that charge transfer occurred within the molecule.

1. Introduction
Organic electroluminescent materials (OLEDs) are double charge injection devices, which require to supply materials for electrons and holes between two electrodes simultaneously [1]. Most of these electron-transporting and hole-blocking molecules are electron-deficient aromatic nitrogen-containing heterocyclic compounds. 1, 2, 4-Triazole are the significant intermediates in the syntheses of nitrogen-contained heterocyclic compounds. Furthermore, highly electron-deficient triazole derivatives have been demonstrated to have a higher electron transporting capability than the oxadiazole derivatives in OLEDs [2]. 3-Mercapto-4-methyl-4H-1, 2, 4-triazole (MMTZ) is an important class of the derivatives of 1, 2, 4-triazole, and it is used as electron-transporting materials to increase the quantum efficiency in OLEDs. In addition, because of their special structures and biological activities of 1, 2, 4- triazoles derivatives, they have wide applications as intermediates for phytosanitary, pharma-ceutical, medicinal, pesticide, photoconductor, and copying systems [3].

Density functional theory has become very popular recently as a general approach to molecular properties. In this report, the molecular geometry and the normal vibrational frequencies of the title compound were calculated by Density functional theory, and the calculated frequencies are compared with the observed frequencies of Raman and infrared spectra. The potential energy distribution (PED) of the vibrational frequencies were obtained by normal vibrational analysis method, and thus all the fundamental vibrational frequencies of MMTZ have been assigned in detail.

2. Experimental details
MMTZ was purchased from commercial chemical company and used directly for the spectral measurements. The FT-IR spectrum was recorded with KBr pellet for data collection on a Nicolet
Nexus FT-IR spectrometer from 4000 to 400 cm$^{-1}$. The FT-Raman spectrum was collected using 1064 nm line of an Nd: YAG laser as an excitation wavelength on a Raman module of the Nexus spectrometer between 3700 and 100 cm$^{-1}$ at about 400 mw.

3. Theoretical calculations

Theoretical calculations were performed using the Gaussian 09 software package [4]. MMTZ molecule exists in two tautomeric forms, the thiol and the thione forms, as showed in Fig.1 by the Gauss View [5] molecular visualization program. The molecule was studied by conformational analysis to find the most stable structure by the density functional method. It was found that both forms can obtain an optimized configuration without a virtual frequency. We found the Gibbs free energy of thione form was 13.55 kcal/mol lower than the thiol tautomers. The results showed that thione tautomer b was the most stable form in the gas phase. Based on this configuration, the normal vibrational analysis were performed at the B3LYP level and using the 6-311++G (d, p) to get the optimized molecular geometry and the normal vibrational frequencies of MMTZ.

![Fig.1 Tautomers of 3-Mercapto-4-methyl-4H-1, 2, 4-triazole](image)

There were 12 atoms and 30 normal vibration frequencies in MMTZ molecule. The full set of 46 internal coordinates (containing 16 redundancies) for MMTZ was defined. And then 30 self-contained local symmetry coordinates were made from these internal coordinates and the molecular symmetry. The local symmetry coordinates were defined using the method suggested by Pulay et al. [6] and can be found in Table 1. The potential energy distribution (PED) was calculated with the help of GAR2PED software [7], and each of the normal vibrational modes was decomposed into the contributions of these symmetric coordinates.

| symmetry Coordinate | Composition | Description |
|---------------------|-------------|-------------|
| 1                   | $R_1(1,2)$  | N$_1$N$_2$ stretch |
| 2                   | $R_2(1,5)$  | N$_1$C$_5$ stretch |
| 3                   | $R_3(2,3)$  | N$_2$C$_3$ stretch |
| 4                   | $R_4(2,8)$  | N$_2$H$_8$ stretch |
| 5                   | $R_5(3,4)$  | C$_3$N$_4$ stretch |
| 6                   | $R_6(3,7)$  | C$_3$S$_7$ stretch |
| 7                   | $R_7(4,5)$  | N$_4$C$_5$ stretch |
| 8                   | $R_8(4,9)$  | N$_4$C$_9$ stretch |
| 9                   | $R_9(5,6)$  | C$_5$H$_6$ stretch |
| 10                  | $R_{10}(9,10)$ + $R_{11}(9,11)$ + $R_{12}(9,12)$ | CH$_3$ symmetric stretch |
| 11                  | 2$R_{10}(9,10)$ - $R_{11}(9,11)$ - $R_{12}(9,12)$ | CH$_3$ antisymmetric stretch A |
| 12                  | $R_{10}(9,11)$ - $R_{12}(9,12)$ | CH$_3$ antisymmetric stretch B |
| 13                  | $\beta_{10}(10,9,4)$ - $\beta_{17}(11,9,4)$ - $\beta_{18}(12,9,4)$ + $\beta_{13}(10,9,11)$ | CH$_3$ symmetric |
+β_{14}(10,9,12) + β_{15}(12,9,11)

14  \beta_{14}(10,9,12) - β_{15}(12,9,11) - 2β_{13}(10,9,11)

15  β_{16}(10,9,12) - β_{17}(12,9,11)

16  2β_{16}(10,9,12) - β_{17}(11,9,4) - β_{18}(12,9,4)

17  -0.80902(a_{20} (1,2,3)+ a_{21} (4,5,1)) +0.30902(a_{22} (2,3,4) + a_{23} (3,4,5)) + a_{19} (5,1,2)

18  -1.11803(a_{20} (1,2,3) - a_{21} (4,5,1)) -1.80902 (a_{22} (2,3,4) - a_{23} (3,4,5))

19  0.30902 (D_{24}(5,1,2,3)+D_{25}(4,5,1,2)) -0.80902 (D_{26} (1,2,3,4)+D_{27}(3,4,5,1)+D_{28} (2,3,4,5)

20  -1.11803 (D_{27}(3,4,5,1)+ D_{28}(1,2,3,4)) -1.80902 (D_{25}(4,5,1,2)+

21  D_{30}(5,4,9,10) + D_{31}(3,4,9,11) + D_{32}(5,4,9,11)

22  + D_{33}(3,4,9,12) + D_{34}(5,4,9,12)

23  B_{35}(2,3,7) + β_{36}(4,3,7)

24  D_{37}(7,3,2,4)

25  B_{38}(1,2,8) - β_{39}(3,2,8)

26  D_{40}(8,2,1,3)

27  B_{41}(4,5,6) - β_{42}(1,5,6)

28  D_{43}(6,5,1,4)

29  B_{44}(3,4,9) - β_{45}(5,4,9)

30  D_{46}(9,4,5,3)

Note: R, refer to bond stretching, α, β, refer to bond angles, D, refer to dihedral angles.

4. Results and discussion

4.1 Molecular equilibrium geometry
The optimized geometric parameters of MMTZ were presented in Table 2. Our calculation results showed the title molecule almost lies in the same plane, except H11 and H12 atoms of CH3 groups. The five-membered ring structure of the title molecule was slightly irregular, the C-N bond lengths in five-member heterocyclic ring were not of equal values, the C1-N5 bond length was shorter than others C-N bond length, the bond lengths N1C5 was 1.298 Å, which showed the pure double bond property.

| Bond length/ (Å) | Bond angle/(’)| Dihedral angle (”) |
|------------------|---------------|-------------------|
| Parameters       | calculated    | Parameters        | calculated    | Parameters              | calculated |
| R(1,2)           | 1.368         | A(2,1,5)          | 103.45        | D(5,1,2,3)             | 0.0        |
| R(1,5)           | 1.298         | A(1,2,3)          | 114.34        | D(5,1,2,8)             | 180.0      |
| R(2,3)           | 1.363         | A(1,2,8)          | 120.64        | D(2,1,5,4)             | 0.0        |
| R(2,8)           | 1.007         | A(3,2,8)          | 125.02        | D(2,1,5,6)             | 180.0      |
4.2 Vibrational frequency

The title compound was found to have Cs symmetry and consist of 12 atoms with 30 normal vibrations modes, which may be distributed as 21 in-plane and 9 out-of-plane vibrational species. Since the density functional method calculates the vibration frequency to be larger than the observed value, in order to make the calculated value more consistent with the experimental value, so we multiply the theoretical data of the MMTZ molecule by the correction factor of 0.9679[8] which Andersson M P calculated. After correction, the theoretical calculation frequencies were in good agreement with the experimental results. A few of differences may come from the actual measurement of the interaction between the sample molecules, and the theoretical simulation was a single molecule idealized model. At the same time, Table 3 showed the contribution percentage of the various vibrational modes obtained by the normal vibrational analysis software. We assigned this condition to those vibrations with a large proportion of energy. According to our calculations and experimental results, the vibrational frequencies of MMTZ molecule can be divided into several parts:

The peak at 3552 cm⁻¹ was attributed to the vibration associated with the expansion of the N-H bond in the molecule. Its vibration was relatively independent, and there was no coupling between other bond stretching and bending vibrations. The peak at 1436 cm⁻¹ was attributed to the vibration associated with the in-plane bending of the N-H bond, while being doped with a small amount of N₂N₃ stretching vibration and vibration related to the antisymmetric deformation of the CH₃ group. The peak at 497 cm⁻¹ was attributed to the vibration associated with the out-of-plane bending of the N-H bond, and it was accompanied by a component of the ring antisymmetric torsion vibration.

The stretching vibrations of the CH₃ group are expected in the range of 2900-3050 cm⁻¹[9]. The peak at 3155 cm⁻¹ was attributed to the vibration associated with the C-H bond expansion and contraction in the molecule; The peaks at 3041, 3020, 2954 cm⁻¹ were attributed to vibrations associated with C-H bond stretching in the CH₃ group; the peaks at 1475, 1424 cm⁻¹ were attributed to vibrations associated with antisymmetric deformation of the CH₃ group; The peak at 1418 cm⁻¹ was attributed to the vibration associated with the symmetrical deformation of the CH₃ group.

The peaks at 1135, 915, 635 and 214 cm⁻¹ were mainly attributed to the vibrations related to the five-membered ring in the molecule, from which 1135 cm⁻¹ belonged to the ring antisymmetric deformation vibration. The peak at 915 cm⁻¹ belonged to the ring symmetric deformation vibration. The peak at 635 cm⁻¹ belonged to the ring folding deformation vibration, and 214 cm⁻¹ belonged to the ring curl deformation vibration. In fact, it can be seen that the ring deformation vibrations mix much with many other vibrations.
Table 3 Experimental and Calculated frequencies (cm$^{-1}$), PED and assignments of MMTZ

| No. | Experimental frequencies (cm$^{-1}$) | Calculated frequencies (cm$^{-1}$) | IR, Raman activity | PED and assignments |
|-----|-----------------------------------|-----------------------------------|--------------------|---------------------|
|     | IR | Raman | IR | Raman unscaled | scaled |
| 1   | 74 | 72 | 0.11 | 0.60 | 22(70) 16(13) |
| 2   | 191 | 185 | 1.29 | 0.64 | 30(46) 20(25) 26(14) |
| 3   | 222 | 214 | 1.03 | 0.01 | 20(35) 30(34) 26(14) 24(12) |
| 4   | 253 | 232 | 225 | 4.53 | 3.13 | 23(54) 29(37) |
| 5   | 417 | 423 | 411 | 398 | 0.63 | 2.11 | 29(43) 23(33) |
| 6   | 536 | 535 | 513 | 497 | 54.50 | 0.82 | 26(68) 21(25) |
| 7   | 548 | 550 | 532 | 10.09 | 13.37 | 6(50) 19(26) 29(11) |
| 8   | 656 | 635 | 31.99 | 0.82 | 21(56) 20(25) |
| 9   | 672 | 671 | 677 | 656 | 8.06 | 2.03 | 24(38) 20(38) 21(19) |
| 10  | 698 | 699 | 700 | 677 | 6.41 | 14.18 | 8(49) 19(17) |
| 11  | 852 | 836 | 809 | 19.80 | 0.61 | 28(88) |
| 12  | 949 | 943 | 945 | 915 | 20.99 | 7.74 | 18(58) 5(20) |
| 13  | 1042 | 1045 | 1053 | 1019 | 52.70 | 4.44 | 1(23) 7(22) 17(22) |
| 14  | 1081 | 1082 | 1100 | 1065 | 5.17 | 1.69 | 1(59) 17(11) |
| 15  | 1156 | 1154 | 1150 | 1113 | 0.09 | 0.95 | 16(65) 17(22) 15(10) |
| 16  | 1173 | 1135 | 30.84 | 5.65 | 19(29) 6(19) |
| 17  | 1220 | 1217 | 1243 | 1203 | 48.77 | 3.12 | 3(42) 25(20) 6(10) |
| 18  | 1269 | 1276 | 1252 | 1212 | 38.46 | 5.99 | 27(56) 8(14) |
| 19  | 1326 | 1334 | 1328 | 1286 | 70.23 | 13.85 | 5(28) 18(13) 25(13) 7(12) |
| 20  | 1361 | 1365 | 1395 | 1350 | 45.47 | 21.00 | 8(25) 2(15) 7(14) 13(13) |
| 21  | 1393 | 1395 | 1465 | 1418 | 4.78 | 3.87 | 13(79) |
| 22  | 1471 | 1424 | 15.08 | 8.19 | 15(89) |
| 23  | 1428 | 1435 | 1483 | 1436 | 193.84 | 12.24 | 25(24) 14(19) 3(18) |
| 24  | 1489 | 1495 | 1524 | 1475 | 154.43 | 15.28 | 14(52) 17(11) |
| 25  | 1556 | 1551 | 1594 | 1543 | 41.42 | 32.95 | 2(59) 27(15) |
| 26  | 2641 | 2652 | 2954 | 23.77 | 152.22 | 11(37) 10(37) 12(26) |
| 27  | 3120 | 3020 | 3052 | 2954 | 6.73 | 45.01 | 10(50) 11(50) |
| 28  | 3120 | 3142 | 3041 | 6.02 | 49.89 | 12(74) 10(13) 11(13) |
| 29  | 3164 | 3131 | 3260 | 3155 | 0.50 | 112.28 | 9(99) |
| 30  | 3670 | 3552 | 107.79 | 87.29 | 4(99) |

4.3 HOMO-LUMO analysis
The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters in the electronic studies[10]. The HOMO energy characterizes the ability to donate an electron and the LUMO energy characterizes the ability to obtain an electron, and the gap between HOMO and LUMO characterizes chemical stability of the molecule. The HOMO and LUMO energies for MMTZ have been calculated by the B3LYP/6-311++G (d, p) method for the title compound and the calculation reveals that there were 30 occupied and 167 unoccupied molecular orbitals associated with MMTZ. The energy values were computed below
HOMO energy = -5.952766 eV
LUMO energy = -0.576882 eV
HOMO-LUMO energy gap = 5.375884 eV

5. Conclusion
The Raman and FT-IR spectra of MMTZ were measured. The optimized molecular geometry and
vibrational frequencies of MMTZ were calculated using B3LYP /6-311++G (d, p) basis sets. The scaled vibrational frequencies calculated of this molecule were agreed quite well with the experimental frequencies. Potential energy distribution of each frequency was obtained using the program GAR2PED, and the overall recognition of the vibrational frequencies assignment were made. The information from this report could be useful to analysis the molecular structure and vibrational spectra of the related compounds.

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