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FT-IR spectroscopic analyses of 3-Methyl-5-Pyrazolone (MP)

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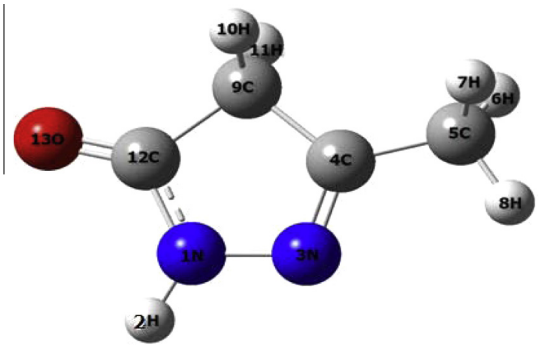
HIGHLIGHTS

- B3LYP as well as FTIR were utilized to analyze MP.
- Vibrational assignments for MP was aided at B3LYP/6-311G(d,p).
- MP has a dipole moment (2.83 Debye) and HOMO/LUMO band gap (5.8 eV).
- UV-Radiation changes the spin of MP from singlet to doublet state.
- MP undergoes anomalous Zeeman like effect.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work both experimental and computational FT-IR spectroscopic studies on 3-Methyl-5-Pyrazolone (MP) were reported. Experimental FT-IR spectrum for MP compound is recorded in powder form. Important physical parameters were reported such as structural parameters, vibrational frequencies, entropy, total energy, total dipole moment and HOMO–LUMO energy gap using DFT/B3LYP/6-311G(d,p) basis set. MP molecule has a total dipole moment of 2.83 Debye and HOMO–LUMO energy gap of 5.80 eV. Results indicate also that exposure to UV changes the spin from singlet to doublet state; one can conclude that MP compound may undergo anomalous Zeeman like effect.

Introduction

3-Methyl-5-Pyrazolone (MP) is a five-membered-ring lactam, derivative of pyrazole that has an additional keto (C=O) group. It has a molecular formula of $C_4H_6N_2O$. Pyrazolone derivatives are an important class of organic compounds which represent a big scientific and applied interest due to their high biological activity [1,2]. Pyrazolone derivatives such as antipyrine and amidopyrine are widely used in medicine as analgesics. Another application of pyrazolone derivatives is the chemistry of dyes; the insertion of conjugated systems to pyrazolone cycles leads to formation of compounds of intense and stable color [3,4]. Also, pyrazolone derivatives have a great ability for the complex formation with transition metals because of their electron-rich donor centers. Such reactions of pyrazolone derivatives are broadly used in analytical chemistry for determination and isolation of more than 50 elements [5] due to quite number of valuable properties of these complexes such as high stability, intense color of the complex extracts and low solubility in some solvents. FTIR is a powerful tool for studying molecular structure specially those of organic nature [6,7]. Triplet-state dynamics in Chl-a/Per mixtures in organic solvent and in native H-PCP were studied by means of step-scan spectroscopy [8]. A new three-dimensional structured was designed by anodizing of anisotropic KOH etched silicon wafer. The structure is applied for the detection of organic volatile by FTIR spectroscopy

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[9]. Photoacoustic spectroscopic experiments were carried out to investigate kerogen and minerals in oil shale [10]. The dissolved organic matter which extracted from fermentation effluent of swine manure slurry was characterized [11]. Other conformational spectroscopic tools could be helpful for better understanding of molecular structures. Many authors apply molecular modeling as promising conformational tool for confirming their FTIR experimental work [12–14]. Up to our knowledge no Density Functional Theory frequencies calculations of 3-Methyl-5-Pyrazolone (MP) have been reported so far. Therefore, the present investigation was undertaken to study the optimized molecular structural parameters, vibrational frequencies, thermo-dynamical parameters, total dipole moment and HOMO–LUMO energy gap for MP compound using DFT/B3LYP utilizing 6-311G(d,p) basis set.

Materials and method

1 mg of MP powder was mixed with 99 mg of vacuum dried IR-grad KBr then compressed to a circular disk for performing FT-IR analysis.

Thermo Scientific Nicollet 460_{plus} Fourier Transform Infrared FT-IR Spectrophotometer in the spectral range 500–4000 cm^{-1} was used for recording FT-IR spectrum at room temperature.

Computational details

Computational calculations were performed using Gaussian 03 W program package [15] at DFT/B3LYP on a Pentium IV/2.8 GHz personal computer. The ground state optimized geometry of MP molecule is shown in Fig. 1. First the input geometry of MP has optimized without imposing any external constraint in the potential energy surfaces at B3LYP/6-311G(d,p) basis set for C, O, N and H atoms Then resultant optimized geometry has been used as input for vibrational frequencies calculations. We add polarization functions for better treatment of polar bonds such as C=O, C=N, C—N, N—N, C—N, N—H and C—H groups.

DFT method, including local or non-local functionals, yields molecular force fields and vibrational wavenumbers in excellent agreement with experimental results. Among the numerous available DFT methods, we have selected the B3-LYP [16–18] method, which combines the Becke's three-parameter exchange functional (B3) with the Lee, Yang and Parr correlation functional (LYP). All the calculations are visualized by using GaussView 4.1 molecular visualization program Package [19].

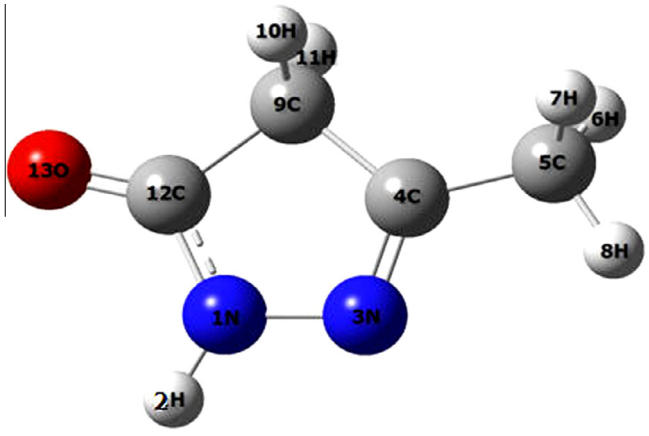

Fig. 1. Molecular structure of MP which optimized at B3LYP/6-311G(d,p).

Results and discussion

Geometry optimization

The first task for the present computational work is to determine optimized geometry for MP molecule. The atomic numbering for the MP molecule is shown in Fig. 1. The calculated optimized geometrical parameters at B3LYP/6-311G (d,p) basis set are listed in Table 1. Since the exact crystal structure of the MP compound is not available till now, the optimized structure can be only compared with other similar systems for which the crystal structures have been solved.

Vibrational assignments

MP molecule has 13 atoms and 33 normal vibrations are distributed as 23A′ + 10A″ considering C_1 symmetry. All calculated modes are gradually numbered from the lowest to the highest frequency within each fundamental wavenumber. The calculated vibrational wavenumbers for MP at B3LYP/6-311G(d,p) has been scaled with scaling factor 0.96 [18] according to level of theory used in our calculations. Both calculated and experimental FT-IR wavenumbers and the corresponding assignments are collected in Table 2. Both experimental and calculated FT-IR spectrum for MP at B3LYP/6-311G(d,p) are shown in Fig. 2.

Comparison of the vibrational frequencies calculated at B3LYP/6-311G(d,p) with experimental values (see Table 2) revealed that 6-311G(d,p) basis set gives reasonable deviations from the experimental values. Any discrepancy noted between calculated and experimental vibrational frequencies may be due to the fact that the calculations have been actually performed on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. The assignment could be achieved extensively as in the following:

The N—H stretching vibrations are observed in the region 3440–3420 cm^{-1} [20]. The computed vibration (mode 33) is assigned to N—H stretching vibrations at 3515 cm^{-1} which is comparable with experimental result at 3400 cm^{-1}.

The aromatic C—H stretching vibrations are observed in the region 3000–3100 cm^{-1} [20]. The computed vibration (mode 32) is assigned to C—H aromatic stretching vibration at 3000 cm^{-1} which is comparable with experimental result at 3000 cm^{-1}. The com-

Table 1
Computational optimized structural parameters at B3LYP/6-311G(d,p) for MP molecule.

Structural parameters			
Bond length (Å)			
N1—H2	1.0	C5—H7	1.1
N1—N3	1.5	C5—H8	1.1
N1—C12	1.5	C9—H10	1.1
N3—C4	1.5	C9—H11	1.1
C4—C5	1.5	C9—C12	1.5
C4—C9	1.5	C12—O13	1.3
C5—H6	1.1		
Bond angle (°)			
H2—N1—N3	113.7	H6—C5—H8	109.5
H2—N1—C12	106.1	H7—C5—H8	109.5
N3—N1—C12	108.0	C4—C9—H10	73.9
N1—N3—C4	108.0	C4—C9—H11	162.9
N3—C4—C5	129.1	C4—C9—C12	108.0
N3—C4—C9	108.0	H10—C9—H11	109.5
C5—C4—C9	123.0	H10—C9—C12	163.0
C4—C5—H6	109.5	H11—C9—C12	74.0
C4—C5—H7	109.5	N1—C12—C9	108.0
C4—C5—H8	109.5	N1—C12—O13	125.9
H6—C5—H7	109.5	C9—C12—O13	126.2