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Vibrational Normal Modes Investigation of 4-Methyl Triazole [4,5-c] Pyridine Using Density Function Theory (DFT)-Chemical Quantum Calculation: Computer Simulation Program

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Keywords:
4-methyl-1,2,3-triazole[4,5-c]pyridine tautomerization
DFT
IR

ABSTRACT

Fourier transform IR and Raman spectra, vibrational energy level, and potential energy distribution (PED) of 1H- and 3H-4-methyl-1,2,3-triazolo[4,5-c]pyridine tautomers, have been determined using density function theory (DFT) at the B3LYP/6-31G(d,p) level. The results of experimental values obtained an agreement with the theoretical model of geometry and vibration levels, the optimised bond lengths and bond angles are in good agreement with X-ray data of other triazole-pyridine compounds.

توصيف الأنماط الاهتزازية لمركبات 4-ميثيل تر ايزول [C-5,4] يبريدين باستخدام نظرية دالة الكثافة (DFT) والحساب الكمي الكيميائي: محاكاة باستخدام الحاسوب

اسلام عبدالعال ابوالوفا و عبدالرحمن فرج عبدالقادر

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الكلمات المفتاحية:
4-methyl-1,2,3-triazole [4,5-c]pyridine tautomerization
DFT
IR

الملخص

اطياف الاشعة تحت الحمراء ورامان والأنماط الاهتزازية ومستويات الطاقة الاهتزازية وطاقة الجهد التوزيعية PED ل(4-MTP-c) 1H- and 3H-4-methyl-1,2,3-triazolo[4,5-c] pyridine تم حسابها كميا وكيميائيا باستخدام دالة الكثافة النظرية DFT عند مستوى B3LYP/6-31G(d,p). قيم النتائج التجريبية المتحصل عليها تتفق مع النموذج النظري للمستويات الاهتزازية والهندسية، وأطوال الروابط والزوايا المضبوطة تتفق جيدا مع بيانات الأشعة السينية لمركبات الترايزول بيريدين الاخرى.

1. Introduction

In recent years, there has been a significant increase in the use of computational chemistry due to the development of efficient mathematical approximations, software advancements, and algorithms. These developments have enabled the utilization of computers to solve theoretical chemistry problems with lower costs and reduced time [1].

Computational chemistry allows researchers to explore a large and diverse chemical space because it is much easier to design a molecule on the computer than to synthesize, purify, and characterize it in the laboratory. Computational chemistry applications can bring molecules to life on a computer by accurately simulating and predicting relevant properties [2, 3].

Density Functional Theory (DFT) is a computational quantum mechanical modelling method extensively used in physics, chemistry, and materials science to investigate the electronic structure of atoms and molecules [4]. DFT is a versatile tool that allows researchers to understand the electronic and chemical properties of molecules across a wide range of systems, making it applicable to various molecular systems and their properties [5, 6].

The main goal of the density functional theory is to replace the wave function with the density function with only three variables and make it a base for calculation. Therefore, treating it as a mathematical or physical concept is much easier. The DFT principle is a reformulation of the quantum problem and its transformation from an issue of a multiparticle system to a single-particle matter [7]. The theoretical DFT results are quite satisfactorily close to experimental data and relatively cheap with traditional methods that consume both money and time [8]. As a result of the advantage of this method in performing calculations, it has been used to study many organic compounds, such as heterocyclic compounds.

Heterocyclic compounds are an integral part of organic chemistry, as they constitute more than 65% of organic chemistry [9]. They are cyclic organic compounds in which the ring contains at least one atom of an element other than carbon, and triazole-pyridine compounds constitute an essential part of these compounds used in various applications. Triazole compounds are characterized by their biological effects through their antibacterial, antifungal and antiparasitic effects [10-12]. Therefore, they have been used in the manufacture of some medical antifungal drugs, such as fluconazole and isavuconazole, and in the manufacture of insecticides to protect plants from fungi, such as paclobutrazol [13-15].

The triazole ring connected to the pyridine ring in the studied

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compound is one of the essential electron-giving compounds. It is also considered a material with a high nitrogen content due to its chemical composition and analysis of elements [16, 17]. They are used to prepare some drugs, such as tazobactam and mubritinib [14, 18].

In this paper, the Geometric optimization shape of the compound was calculated (Obtaining the best stable geometry for the compound) and the molecular spectra of the compound were studied theoretically by using density function theory (DFT).

The main method for studying the molecular spectra of any compound, no matter how complex the structure is infrared spectra IR, which depends on the interaction of electromagnetic radiation with the molecules of matter, where the molecule absorbs infrared radiation and converts its energy into vibrational energy for the atoms that construct the molecule [19]. Each molecule has different vibrational patterns that depend on the number of atoms that make it up.

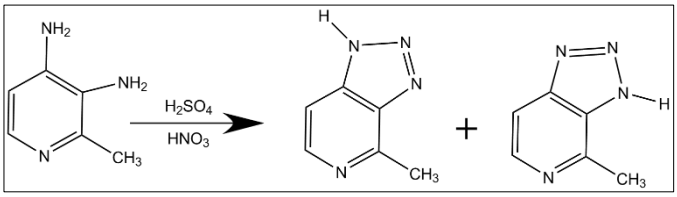
The results of chemical computing had an essential role in studying and solving complex and overlapping problems in the study of the system and seeing its results clearly, which simplified the determination of the structure of the studied system.

2. Synthesis

4-methyl-[1,2,3]triazolo[4,5-c]pyridine (4-MTP) was prepared by dissolving 2.5 g of 3,4-diamino-2-methyl pyridine in 75 cm^3 of water and then 3 cm^3 of concentrated sulfuric acid was added.

This solution was cooled to 0ºC and then a solution made from 2.3 g $NaNO_2$ in 10 cm^3 water was added dropwise at 0ºC [20].

The mixture obtained was stored at room temperature for 1h giving a white precipitate. It was filtered off and washed with distilled water. The yield was 1.93g, (77.2%) (Scheme 1).



Scheme 1. Synthesis of 4-MTP

3. IR and Raman measurements

Room temperature Fourier transformed infrared spectra (IR) in the range 5000–30 cm^{-1} were measured on the BIORAD 575 spectrophotometer with a 2 cm^{-1} resolution.

Room temperature Fourier-transformed Raman spectra were measured in the range 4000–80 cm^{-1} using a BRUKER 110/S spectrometer with the Nd: YAG excitation and 2 cm^{-1} resolution.

4. Chemical quantum calculation

The molecular structure of the studied compound was studied at the theoretical density function (DFT) level using the Lee-Yang-Parr correlation functional (B3LYP), the 6-31G(d,p) basis has been used [21].

IR wavenumbers as well as the band intensities were also calculated at the same DFT level using Gaussian 03W software [22].

5. Results and discussion

The theoretical geometric parameters of the compound 1H&3H-4-MTP[4,5-c] (Figure 1) were calculated and compared with theoretical values of 1H&3H-5MTP[4-5-b] [20] and experimental values for 4,6M5HTPc(H2O)4 [23] (see Table 1).

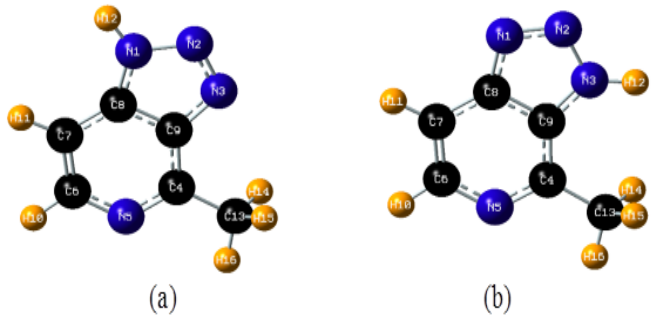


Fig.1: Theoretical optimized structure of 4-MTP[4,5-c] (a) 1H (b) 3H

Table 1: Selected experimental values for C7H16N4O4[a] and theoretical optimized structure parameters of 4-MTP(4,5-c) and 5-MTP(4,5-b)[b] using DFT at B3LYP/6-31G(d,p) level.

Bond length (Aº) and angles (º)	Optimized parameters from DFT data B3LYP/6-31G(d,p)				Experimental values[a]
	4-MTP(4,5-c)		5-MTP(4,5-b)[b]		
	1H	3H	1H	3H	
N_2/ (N_2-N_3)	1.372 Aº	Aº 1.360	1.369 Aº	1.365 Aº	1.351 Aº
=N_3/(N_1=N_2)	1.288 Aº	Aº1.293	1.290 Aº	1.296 Aº	1.317 Aº
C_8/ (N_3-C_9)	1.360 Aº	Aº 1.366	1.360 Aº	1.362 Aº	1.346 Aº
H_{12}/ (N_3-H_{12})	1.008 Aº	Aº1.008	1.008 Aº	1.009 Aº	--
C_9/ (N_1-C_8)	1.381 Aº	Aº1.381	1.382 Aº	1.378 Aº	1.365 Aº
N_5*(N_4-C_5)	1.331 Aº	Aº1.328	1.331 Aº	1.338 Aº	1.336 Aº
C_9	1.412 Aº	1.411 Aº	--	--	1.389 Aº
C_6	1.357 Aº	Aº1.358	--	--	1.381 Aº
C_7	1.385 Aº	Aº1.384	1.383 Aº	1.3384 Aº	1.359 Aº
H_{10}	1.087 Aº	Aº1.086	1.086 Aº	1.085 Aº	--
C_4-CH_3*(C_5-CH_3)	1.501 Aº	1.504 Aº	1.509 Aº	1.507 Aº	1.492 Aº
C_7-H_{11}	1.083 Aº	Aº1.084	1.085 Aº	1.085 Aº	--
C_8-C_9	1.406 Aº	Aº1.404	1.410 Aº	1.406 Aº	1.410 Aº
C_7-C_8	1.401 Aº	Aº1.402	1.400 Aº	1.402 Aº	1.409 Aº
C_{13}-H_{14}	1.095 Aº	Aº1.091	1.096 Aº	1.091 Aº	--
C_{13}-H_{15}	1.095 Aº	Aº1.096	1.096 Aº	1.096 Aº	--
C_{13}-H_{16}	1.090 Aº	Aº1.096	1.090 Aº	1.096 Aº	--
N_2=N_3-C_9/(N_2=N_1-C_8)	108.60º	108.34º	108.3º	108.2º	105.80º
N_1-N_2-N_3	108.56º	108.56º	109.0º	108.9º	113.08º
N_2-N_1-C_8/ (N_2-N_3-C_9)	110.85º	110.74º	110.5º	110.6º	106.09º
C_4-N_5-C_6*(C_9-N_4-C_5)	119.75º	120.32º	115.6º	113.9º	125.20º
N_5-C_4-C_9	119.24º	118.38º	--	--	115.96º
N_5-C_6-C_7	125.76º	125.03º	--	--	120.28º

[a] See reference [23], [b] See reference [20]

The geometric structure of 7MTP has been studied in several previous studies, and the double-ring system is the main component of this compound.

The distance between the atoms C_4–N_5 was calculated for 1H(3H)-4MTP as 1.331A°(1.328A°), using DFT/B3LYP/6-31G(d, p), and it is in good agreement with the experimental data 1.336A° [23]. The bond angle between the atoms N_2–N_3–C_9 was calculated for 1H(3H) as 108.6°(108.34°) using DFT/B3LYP/6-31G(d, p), and it is in good agreement with the experimental data 105.80° [23].

The comparison between the experimental and theoretical geometric parameters (bond lengths and angles) using DFT at the level B3LYP/6-31G(d, p) (**خطأ! لم يتم العثور على مصدر المرجع.** 1) shows that the experimental and theoretical data agree very well, indicating that the B3LYP function is suitable for predicting the geometry of the studied compound.

On the other hand, we can find some theoretical data vary slightly from the available experimental data because the experimental results were obtained from the solid phase, whereas the theoretical calculations were made from the gas phase of the molecule. Therefore, the differences between the experimental and theoretical values are normal [24].

The 4-MTP(4,5-c) has the formula C6H6N4, it has 48 movements, including three translational movements, three rotational movements, and 42 vibrational movements [25]. These vibrations include 27 in-plane movements, 12 out-of-plane movements, and 3 movements are a mixture of in-plane and out-of-plane for the 1H- isomer, and for the 3H- isomer, there are 26 in-plane movements, 14 out-of-plane movements, and 2 movements are a mixture of in-plane and out-of-plane.

•In-plane movements

There are three vibrational movements in the plane; ν-stretching, δ–bending, and δT–trigonal def (see Table 2).

There are two types of Stretching and bending: symmetric (s) and asymmetric (as).

Symmetric stretching appears in: (ν-NH) at ν1 by 100%, (ν-CH) at ν2, ν3 by 96%-97% for the 1H-3H-isomers, (ν-CH3) at ν6 by 100%, the pyridine ring (ν- ΦP) at ν8 by 67%, while the rest of the stretching appear as a mixture of vibrations for the 1H- isomer at ν7, ν9, ν13, ν16, ν17, ν19, ν21, ν25, ν31, ν33, and for 3H- isomer, it appears at ν7, ν8 by 74%, 52%, while the rest of the stretching appear as a mixture at ν9, ν12, ν15, ν16, ν19, ν21, ν26, ν31, ν33, and the trizole ring (ν-ΦT) at ν24 by 88% for the 1H-4MTP, and the rest of the stretching appear as mixtures at ν7, ν12, ν13, ν15, ν16, ν17, ν18, ν19, ν23, and

for 3H-4MTP, it appears at ν23 by 90%, while the rest of the stretching appear as mixtures at ν12, ν13, ν15, ν16, ν17, ν18, ν19, ν21, ν24 [26].
Asymmetric stretching appears in: (νas - CH3) at ν4, ν5.
Symmetric bending appears in: (δs-CH3) at ν14 by 82% for the 1H,3H isomers, the pyridine ring (δ-ΦP) at ν27, ν33, ν35, ν39 for the 1H-isomer and at ν27, ν31, ν37 for the 3H- isomer, and triazole ring (δ-ΦT) at ν14, ν23, ν33 for the 1H- and at ν24, ν31, ν33 for the 3H-isomer [27].
The trigonal def (δ_T) appears in: the pyridine ring (δ_T-Φ_P) at ν17, ν27 for the 1H-, and at ν18, ν27 for the 3H- isomer.

- **Out-of-plane movements**

There are three types of vibrational movements out-of-plane; γ-bending, τ-torsion, and τp-puckering.
The bending appears in: (γ-CH) at ν28 by 88% for the 1H- isomer, and appears as a mixture at ν26, ν31, while for the 3H-isomer, it appears at ν25, ν28 by 94%, 72%, (γ- NH) at ν30, ν34, ν36 for the 1H-, and at ν30, ν36 for 3H-isomer.
The twisting appears in; (τ-CH3) at ν42 by 95%, the pyridine ring (τ-ΦP) at ν32, ν34, ν36, ν38, ν40, ν41 for the 1H-isomer, and at ν32, ν33, ν34, ν35, ν38, ν39, ν40, ν41 for the 3H-isomer, the triazole ring (τ-ΦT) at ν29, ν30, ν32, ν36, ν38 for the 1H-isomer and at ν29, ν30, ν32, ν36, ν38 for the 3H-isomer [28].
Twisting of the pyridine ring and triazole ring together (τ-ΦP/ΦT) appears at ν40 for the 1H- isomer and at ν34, ν35, ν40 for the -3H-isomer [29].
The puckering appears in: the pyridine ring (τp- ΦP) at ν26, ν29, ν32 for the 1H-isomer, and at ν29, ν32 for the 3H-isomer.

- **mixture of in-plane and out-of-plane movements**

The rocking movement (ρ) is a mixture of vibrational motions between in-plane and out-of-plane; it appears in the (ρ-CH3) at ν20, ν22, ν25 for the 1H-isomer, and 3H-isomer, it appears at ν26, ν27 by 78%, 82% and as mixture at ν20, ν22, ν26 [29].
Theoretical and experimental IR and Raman spectra of 1H and 3H-isomers show in (Figures 2).

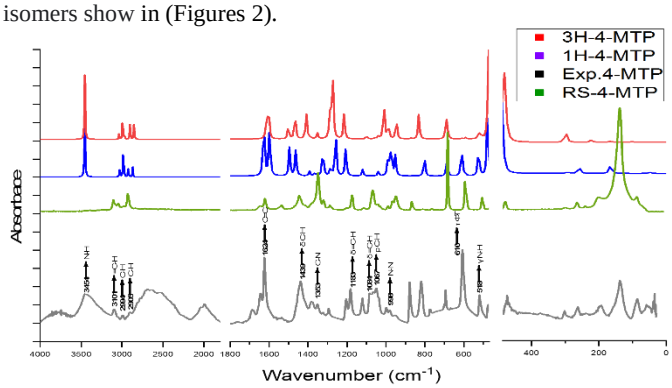
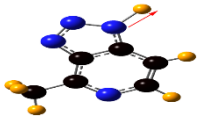
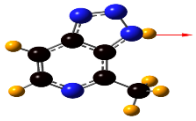
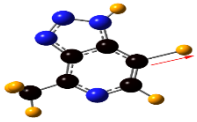
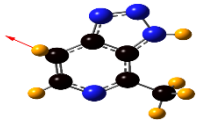
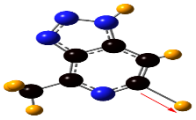
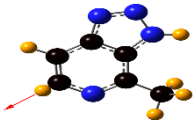
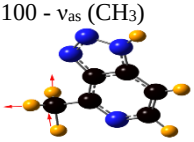
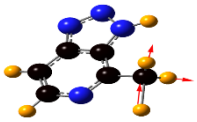
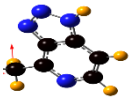
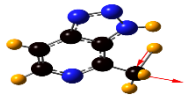
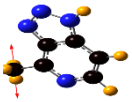
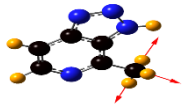
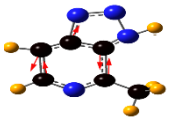
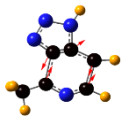
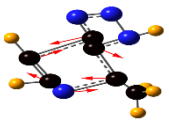
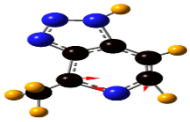
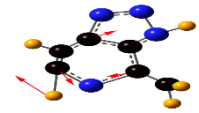
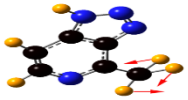
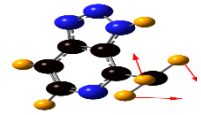
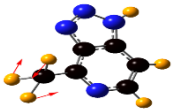
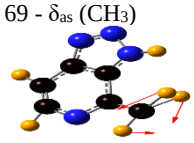
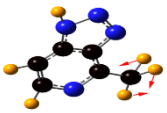
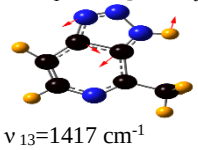
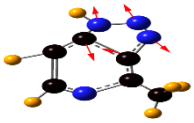
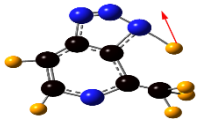
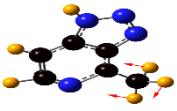
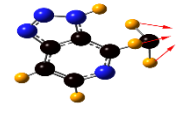
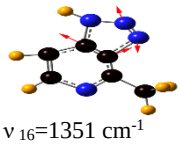


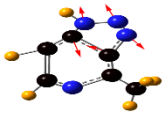
Fig.2: Infrared and Raman spectra of 4-MTP

Table(2): vibrational normal modes of the 1H-4MTP and 3H-4MTP using DFT at the B3LYP/6-31G(d,p) level.

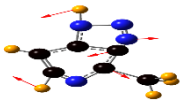
1H-4-methyl-1,2,3-triazole[4,5-c]pyridine	3H-4-methyl-1,2,3-triazole[4,5-c]pyridine
ν_1=3454cm^{-1} 100 -νNH 	ν_1=3455cm^{-1} 100 – νNH 
ν_2=3027 cm^{-1} 96 – νCH 	ν_2=3035 cm^{-1} 96 – νCH 
ν_3=2985cm^{-1} 96 – νCH 	ν_3=2993 cm^{-1} 97– νCH 
ν_4=2974cm^{-1} 100 - ν_{as} (CH_3) 	ν_4=2971 cm^{-1} 100 - ν_{as} (CH_3) 
ν_5=2923 cm^{-1} 100 - ν_{as} (CH_3) 	ν_5=2903 cm^{-1} 100 - ν_{as} (CH_3) 
ν_6=2870 cm^{-1} 100 - ν_s (CH_3) 	ν_6=2853 cm^{-1} 100 - ν_s (CH_3) 
ν_7=1661 cm^{-1} 54 - ν Φ_P + 14 - ν Φ_T 	ν_7=1650 cm^{-1} 52 - ν Φ_P 
ν_8=1631 cm^{-1} 67 - ν Φ_P 	ν_8=1637 cm^{-1} 74 - ν Φ_P 
ν_9=1526 cm^{-1} 35- ν Φ_P + 20- δ CH 	ν_9=1532 cm^{-1} 33- ν Φ_P + 28- δ CH 
ν_{10}=1494 cm^{-1} 48 - δ_{as} (CH_3) 	ν_{10}=1499 cm^{-1} 93 - δ_{as} (CH_3) 
ν_{11}=1492 cm^{-1} 93 - δ_{as} (CH_3) 	ν_{11}=1496 cm^{-1} 69 - δ_{as} (CH_3) 
ν_{12}=1471 cm^{-1} 27 - δ CH +29 - δ_{as} (CH_3) + 13 - ν Φ_T + 15 - δ NH 	ν_{12}=1447 cm^{-1} 19 - δ CH + 12 - ν Φ_P + 32 - ν Φ_T + 13 - δ_{as} (CH_3) 
ν_{13}=1422 cm^{-1} 36 - ν Φ_P + 16 - δ NH + 20 - ν Φ_T 	ν_{13}=1417 cm^{-1} 31 - δ NH + 20 - ν Φ_T 
ν_{14}=1400 cm^{-1} 82 - δ_s (CH_3) 	ν_{14}=1437 cm^{-1} 82 - δ_s (CH_3) 
ν_{15}=1393 cm^{-1} 31 - ν Φ_T + 14 - δ Φ_T + 11 - δ CH	ν_{15}=1380 cm^{-1} 59 - ν Φ_P + 16- ν Φ_T



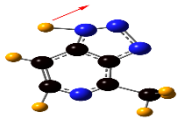
ν $_{16}$=1351 cm^{-1}
42 - ν Φ_P + 45 - ν Φ_T



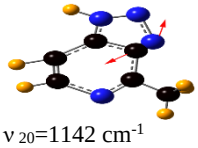
ν $_{17}$=1311 cm^{-1}
25 - ν Φ_T + 10 - ν Φ_P + 25– δ_T Φ_P



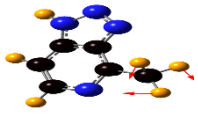
ν $_{18}$=1285 cm^{-1}
26 - δ NH +21 - δ CH + 22 - ν Φ_T



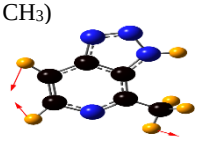
ν $_{19}$=1231 cm^{-1}
34 - ν Φ_T + 28 - ν Φ_P + 13 - δ CH



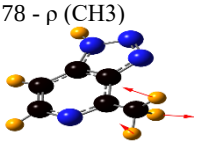
ν $_{20}$=1142 cm^{-1}
17- ρ (CH_3) + 13 - δ CH + 10 - ν (C-CH_3)



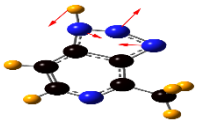
ν $_{21}$=1090 cm^{-1}
36 - ν Φ_P + 23 - δ CH + 12 - ν (C-CH_3)



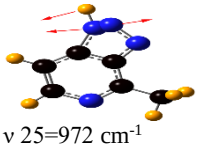
ν $_{22}$=060 cm^{-1}
78 - ρ (CH3)



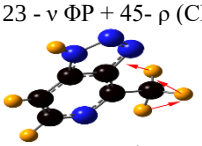
ν $_{23}$=1009 cm^{-1}
66 - δ ΦT + 16 - ν ΦT



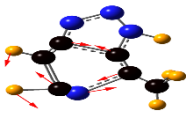
ν $_{24}$=994 cm^{-1}
88 - ν ΦT



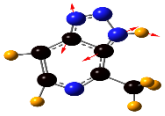
ν $_{25}$=972 cm^{-1}
23 - ν ΦP + 45- ρ (CH3)



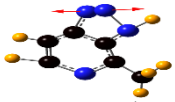
ν $_{26}$=971 cm^{-1}
79 - γ CH + 11 - τp ΦP



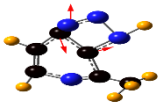
ν $_{16}$=1315 cm^{-1}
13 - ν Φ_P + 31 - ν Φ_T + 24 - δ CH



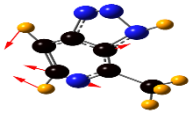
ν $_{17}$=1301 cm^{-1}
38 - ν Φ_T + 19 - δ CH + 12- δ NH



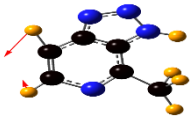
ν $_{18}$=1296 cm^{-1}
42 - ν Φ_T + 23 - δ_T Φ_P



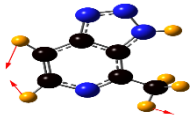
ν $_{19}$=1240 cm^{-1}
20 - ν Φ_T + 35 - ν Φ_P



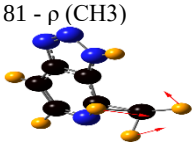
ν $_{20}$=1122 cm^{-1}
23 - δ CH +18 - ρ (CH_3)



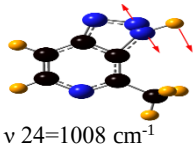
ν $_{21}$=1078 cm^{-1}
16 - ν (C-CH_3) + 15 - ν Φ_T +10 - ν Φ_P+ 16 - δ CH



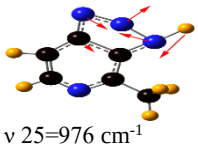
ν $_{22}$=1059 cm^{-1}
81 - ρ (CH3)



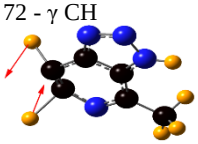
ν $_{23}$=1031 cm^{-1}
90 - ν ΦT



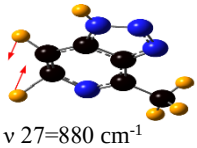
ν $_{24}$=1008 cm^{-1}
69 - δ ΦT + 17 - ν ΦT



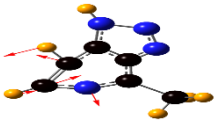
ν $_{25}$=976 cm^{-1}
72 - γ CH



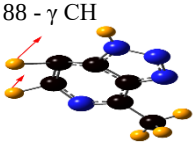
ν $_{26}$=966 cm^{-1}
45 - ρ (CH3) + 26- ν ΦP



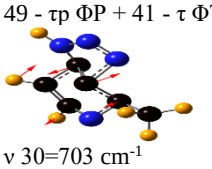
ν 27=880 cm^{-1}
44 -δT ΦP + 16 - δ ΦP



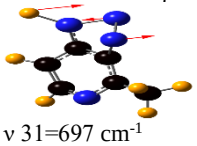
ν 28=820 cm^{-1}
88 - γ CH



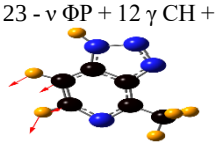
ν 29=798 cm^{-1}
49 - τp ΦP + 41 - τ ΦT



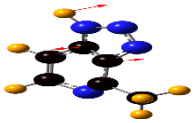
ν 30=703 cm^{-1}
71 -τ ΦT + 15 - γ NH



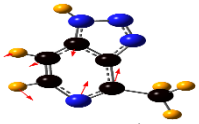
ν 31=697 cm^{-1}
23 - ν ΦP + 12 γ CH + 15 ν (C-CH3)



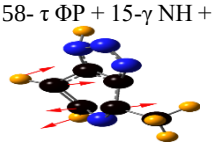
ν 32=624 cm^{-1}
28- τ ΦT + 21- τ ΦP + 23- τp ΦP



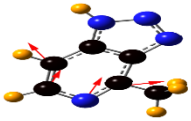
ν 33=607 cm^{-1}
25 - ν ΦP + 24 - δ ΦT + 18- δ ΦP



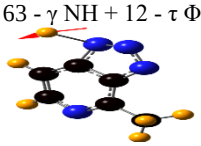
ν 34=536 cm^{-1}
58- τ ΦP + 15-γ NH + 12-τ (C-CH3)

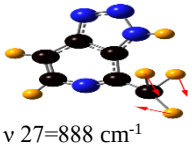


ν 35=521 cm^{-1}
69 - δ ΦP 77 + 10 - ν (C-CH3)

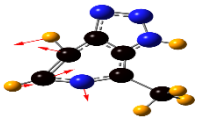


ν 36=490 cm^{-1}
63 - γ NH + 12 - τ ΦP + 11 - τ ΦT

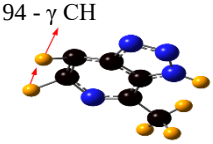




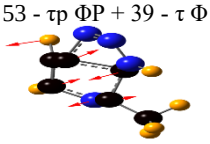
ν 27=888 cm^{-1}
44 - δT ΦP + 38 - δ ΦP



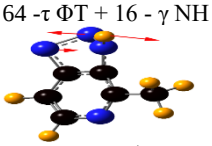
ν 28=848 cm^{-1}
94 - γ CH



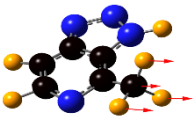
ν 29=792 cm^{-1}
53 - τp ΦP + 39 - τ Φ T



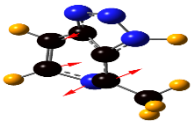
ν 30=705 cm-1
64 -τ ΦT + 16 - γ NH



ν 31=699 cm^{-1}
10 - ν ΦP+ 14 - ν (C-CH3) + 13 - δ ΦT + 13 - δ ΦP



ν 32=621 cm^{-1}
25 - τp ΦP + 24 - τ ΦT + 17 - τ ΦP



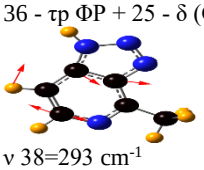
ν 33=602 cm^{-1}
26 - ν ΦP+ 23 - δ ΦT + 16 - τ ΦP

ν 34=534 cm^{-1}
50 - τ ΦP + 19 - τ ΦP/ ΦT + 13 - τ (C-CH3)

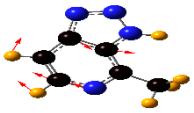
ν 35=519 cm^{-1}
71 - τ ΦP - + 21 - τ ΦP/ ΦT + 13 - τ (C-CH3)

ν 36=482 cm^{-1}
73 - γ NH + 20 - τ ΦT

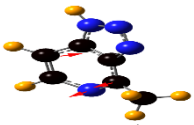
ν 37=477 cm^{-1}
36 - τp ΦP + 25 - δ (C-CH3)



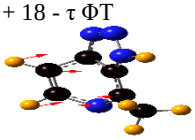
ν 37=472 cm^{-1}
31 - δ ΦP + 25 - δ (C-CH3)



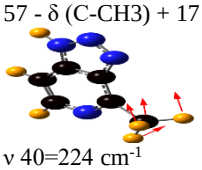
ν 38=293 cm^{-1}
46 - τ ΦP + 17 - τ (C-CH3) + 24 - τ ΦT



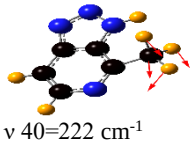
ν 38=298 cm^{-1}
47 - τ ΦP + 18 - τ (C-CH3) + 18 - τ ΦT



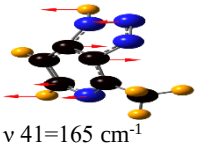
ν 39=259 cm^{-1}
57 - δ (C-CH3) + 17 - δ ΦP



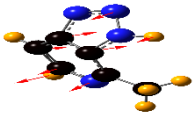
ν 39=256 cm^{-1}
57 - δ (C-CH3) + 14 - τ ΦP



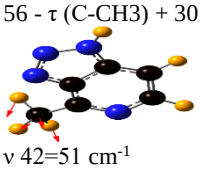
ν 40=224 cm^{-1}
69 - τ ΦP/ ΦT + 21 - τ ΦP



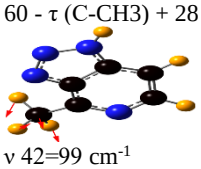
ν 40=222 cm^{-1}
20 - τ ΦP + 68 - τ ΦP /ΦT



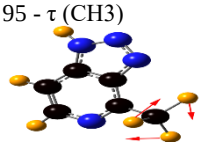
ν 41=165 cm^{-1}
56 - τ (C-CH3) + 30 - τ ΦP



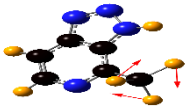
ν 41=166 cm^{-1}
60 - τ (C-CH3) + 28 - τ ΦP



ν 42=51 cm^{-1}
95 - τ (CH3)



ν 42=99 cm^{-1}
95 - τ (CH3)



[a].= nitrogen atom● = hydrogen atom, ● = carbon atom, ●
[b] uniform scaling factor f=0.96 for ν_1–ν_6; f=0.98 for ν_7–ν_{20}; f=1.00 for ν_{20}–ν_{42}.
[c] in-plane vibrations: ν-stretching, δ–bending, δ_T–trigonal def. out-of plane vibrations: γ–bending, τ–torsion, τ_P-puckering; ρ–rocking, Φ_P–pyridine ring, Φ_T–triazole ring.

6. Conclusion

- In this study 4-MTP compounds were synthesized.
- Molecular structure, FT-IR and FT-Raman spectra,and potential energy distribution(PED) of 4-MTP tautomers, have been determined using density function theory (DFT) at the B3LYP/6-31G(d,p) level.
- The experimental FT-IR and FT-Raman spectra 4-MTP are in a very good agreement with the calculated vibrational spectra.
- The optimized bond lengths and bond angles are in good agreement with the X-ray data of other triazole pyridine compounds in the literature.

7. References

[1]- L. He *et al.*, "Applications of computational chemistry, artificial intelligence, and machine learning in aquatic chemistry research," vol. 426, p. 131810, 2021.
[2]- Y. Yang *et al.*, "Efficient exploration of chemical space with docking and deep learning," vol. 17, no. 11, pp. 7106-7119, 2021.
[3]- A. V. Sadybekov and V. J. N. Katritch, "Computational approaches streamlining drug discovery," vol. 616, no. 7958, pp. 673-685, 2023.
[4]- P. Sharma, P. Ranjan, and T. J. M. P. Chakraborty, "Applications of conceptual density functional theory in reference to quantitative structure–activity/property relationship," p. e2331620, 2024.
[5]- J. Madsen, T. J. Pennycook, and T. J. U. Susi, "ab initio description of bonding for transmission electron microscopy," vol. 2 ,31p. 113253, 2021.
[6]- V. J. P. C. C. P. Butera, "Density Functional Theory Methods applied to Homogeneous and Heterogeneous Catalysis: a Short Review and a Practical User Guide," 2024.
[7]- S. Zavatski, E. Neilande, H. Bandarenka, A. I. Popov, S. Piskunov, and D. J. N. Bocharov, "Density functional theory for doped TiO2: current research strategies and advancements," 2024.
[8]- M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew, and K. A. J. S. Lyssenko, "Density functional theory is straying from the path toward the exact functional," vol. 355, no. 6320, pp. 49-52, 2017.
[9]- P. Chetti, V. Kumar, and V. J. Rao, "Photoirradiated synthesis of bioactive heterocycles".
[10]- N. Marepu, S. Yeturu, M. J. B. Pal, and m. c. letters, "1, 2, 3-Triazole fused with pyridine/pyrimidine as new template for antimicrobial agents: Regioselective synthesis and identification of potent N-heteroarenes," vol. 28, no. 20, pp. 3302-3306, 2018.
[11]- T. Soumya, C. M. Ajmal, D. J. B. Bahulayan, and M. C. Letters, "Synthesis of bioactive and fluorescent pyridine-triazole-coumarin peptidomimetics through sequential click-multicomponent reactions," vol. 27, no. 3, pp. 450-455, 2017.
[12]- M. Karnaš *et al.*, "Synthesis, antifungal, antibacterial activity, and computational evaluations of some novel coumarin-1, 2, 4-triazole hybrid compounds," vol. 18, no. 1, p. 2331456, 2024.
[13]- A. Nagaraj, M. Sunitha, R. L. Sanjeeva, D. M. Vani, and S. R. J. O. C. Ch, "Synthesis and biological evaluation of 3-benzyl/piperazino-methyl-1, 2, 3-triazol-4-yl)-2, 3-dihydro-1, 3, 4-thiadiazole-2-thione," vol. 8, no. 3, p. 70, 2015.
[14]- M. J. C. I. Asif, "Anti-neuropathic and anticonvulsant activities of various substituted triazoles analogues," vol. 1, no. 4, pp. 174-183, 2015.
[15]- Y. Tian *et al*" ,.Effects of Triazole Antifungal Agents on the Plasma Concentration and Dosage of Cyclosporin in Patients with Aplastic Anaemia," vol. 2024, 2024.
[16]- W. Zhao *et al.*, "Advances of antitumor drug discovery in traditional Chinese medicine and natural active products by using multi-active components combination," vol. 43, no. 5, pp. 1778-1808, 2023.
[17]- A. K. Bhatia and S. Dewangan, "N-Heterocyclics as Corrosion Inhibitors: Miscellaneous," in *Handbook of Heterocyclic Corrosion Inhibitors*: CRC Press, 2024, pp.270-249 .
[18]- L. da SM Forezi, M. F. Cardoso, D. T. Gonzaga, F. de C da Silva, and V. F. J. C. T. i. M. C. Ferreira, "Alternative routes to the click method for the synthesis of 1, 2, 3-triazoles, an important heterocycle in medicinal chemistry," vol. 1 ,8no. 17, pp. 1428-1453, 2018.
[19]- H. J. Byrne, P. Knief, M. E. Keating, and F. J. C. S. R. Bonnier, "Spectral pre and post processing for infrared and Raman spectroscopy of biological tissues and cells," vol. 45, no. 7, pp. 1865-1878, 2016.
[20]- J. Lorenc *et al.*, "Vibrational dynamics and molecular structure of 1H-and 3H-1, 2, 3-triazolo [4, 5-b] pyridine and its methyl-derivatives based on DFT chemical quantum calculations," vol. 334, no. 1-3, pp. 90-108, 2007.
[21]- B. Miehlich, A. Savin, H. Stoll, and H. J. C. P. L. Preuss, "Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr," vol. 157, no. 3, pp. 200-206, 1989.
[22]- M. J. Frisch *et al.*, "Gaussian 03, Revision C. 02. Wallingford, CT: Gaussian," 2004.
[23]- L. Dymińska, J. Janczak, K. S. M. Sheweshen, J. Lorenc, and J. J. J. o. M. S. Hanuza, "Crystal and molecular structures, temperature dependence of the IR and Raman spectra and vibrational dynamics of aquo 4, 6-dimethyl-5H-[1, 2, 3] triazolo [4, 5-c] pyridine in a new zwitterionic form," vol. 1144, pp. 482-495, 2017.
[24]- H. A. Dabbagh, M. Zamani, H. Farrokhpour, M. H. Habibi, and K. J. J. o. M. S. Barati, "Conformational analysis and intramolecular/intermolecular interactions of N, N′-dibenzylideneethylenediamine derivatives," vol. 983, no. 1-3, pp. 169-185, 2010.
[25]- C. J. Carmer, "Essential of Computational Chemistry," ed: Chichester: John Wiley and Sons, Ltd, 2002.

[26]- A. Duan, S. An, J. Xue, X. Zheng, and Y. J. R. a. Zhao, "Absorption, fluorescence ,Raman spectroscopic and density functional theoretical studies on the singlet and triplet excited state decay of 3-amino-5-mercapto-1, 2, 4-triazole," vol. 10, no. 23, pp. 13442-13450, 2020.

[27]- H. Gökce, N. Öztürk, M. Taşan, Y. B. Alpaslan, and G. J .S. l. Alpaslan, "Spectroscopic characterization and quantum chemical computations of the 5-(4-pyridyl)-1 H-1, 2, 4-triazole-3-thiol molecule," vol. 49, no. 3, pp. 167-179, 2016.

[28]- L. Dymińska, J. Hanuza, J. Janczak, M. Ptak, and R. J. M. Lisiecki, "The Structural and Optical Properties of 1, 2, 4-Triazolo [4, 3-a] pyridine-3-amine," vol. 27, no. 3, p. 721, 2022.

[29]- Ç. Y. Ataol and Ö. J. J. o. M. S. Ekici, "Experimental and theoretical studies of (FTIR, FT-NMR, UV–Visible, X-ray and DFT) 2-(4-Allyl-5-pyridin-4-yl-4H-[1, 2, 4] triazol-3-ylsulfanyl)-1-(3-methyl-3-phenyl-cyclobutyl)-ethanone," vol. 1065, pp. 1-9, 2014.