Theoretical study of molecular structure, IR and NMR spectra of pyrazolone and its derivatives

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ABSTRACT

Structure of pyrazol-5-one , 3-methyl pyrazol-5-one and 1-phenyl-3-methyl pyrazol-5-one and their IR spectra data have been determined by performing DFT molecular orbital calculations at B3LYP/6-31G(d) theory level . The geometry parameters, total energies, HOMO and LUMO orbitals energies, dipole moments and changes on the atoms as well as vibrational frequencies were calculated for the three molecules and the results were compared with the experimental measurements and discussed . The NMR chemical shifts were determined using TNDO/6-31G(d) method . The calculations showed that pyrazol-5-one is aplanar molecule and N-H vibrational frequency is lower than that in succimide . The methyl and phenyl substituents decrease N-H bond vibrational frequency whereas C=O frequency increase by phenyl substituent .

Keywords: Pyrazolones, structure, IR, NMR, theoretical calculation -DFT.

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INTRODUCTION

Pyrazolones are hetro aromatic five-membered ring compounds containing two bonded nitrogen atoms and carbonyl group in their structure . Pyrazolone is named pyrazol-5-one , its empirical formula $C_3H_4N_2O$ and represented by the structure (1) .

(1)
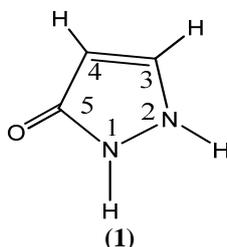
The pyrazolone and its derivatives have drawn especial wide interest by medical chemists for more than hundred years ago due to their intensting drug properties[1] . Pyrazolone was first prepared by Knorr in1883 when he was trying to synthesis quinoline derivatives, but he obtained pyrazolone derivative called antipyrin , and also called phenazone[2] . pyrazolone can be considered us intermediate compound for synthesis of various cyclic compounds of high biological activity [3-10] .

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These compounds have wide interesting medical and industrial applications such as anticancer[11], antiischenicefcets[12], antiflammatory[13], antifungal[14], antipyretic[15], antitubercular[16], antihypertensive[17], antiviral[18] and antimicrobial[19] . In industry they are used as colorizing agents[20,21] . In general pyrazolones are yellow solids with high melting points and moderate solubility in water , alkaline and acidic solutions[22,23] . The react with aldehydes in alcoholic basic medium and with the bromine to give high biologically active compounds[24,25]. It is reported that pyrazolones under go tautomerism to certain extent which effected by substituents and solvents[26-30] .

In the literature we have found neither quantitative IR and NMR data nor DFT/ molecular orbital calculations for title compounds, so the aim of the present study was to investigate the structure, IR and NMR of there compounds theoretically and experimentally .

EXPERIMENTAL SECTION

All used chemicals were supplied by Merck and Fluka companies: hydrazine, phenylhydrazine, metylacetoacetate and chloroform, with out further purification . CHN elemental analysis was carried out on Euro Vector 300 Altaly at Alalbait university/Jordan .

2.1 IR and UV-Visible spectra
IR spectra were recorded at FT-IR spectrometer model 8400 from Shimadzu company as KBr disc at room temperature in the Laboratory of petrochemical industries /Basrah .

The UV-Visible spectra were obtained using UV-Visible spectrophotometer model T80 in college of education /Basrah university .

2.2 NMR spectra
The spectra were recorded using Bruker instrument operating at 500.130 MHz for ^{1}H and ^{13}C and ^{14}N at 125.75MHz and 36.13MHz respectively. TMS was used as external standard for ^{1}H and ^{13}C whereas CH_3NO_2 was used for ^{14}N measurements. All the spectra was measured in CD_3OD at Tehran university. Relaxation times T_1 for ^{1}H were determined by Inversion Recovery method using the sequences $180^°$-τ-$90^°$ at various temperatures between – 20 and 40 ℃ .

3. Computations
DFT/B3LY computations have been performed at 6-31G(d) basis set . No scaling has been done for vibrational frequencies. The optimization was first performed at B3LYP/6-31G(d) theory level . The values of bond lengths, bond angles, total energy, electronic energy have been calculated as well as HOMO and LUMO orbitals energies with electric dipole moments and charges on the atoms . The chemical shifts were calculated by TNDO method for pyrazolone .

4. Preparations of phenyl pyrazolone and methyl pyrazolone[31]
They were prepared by reaction of hydrazine or phenyl hydrazine with methyl acetoacetate with continues stirring for 2hr at 100°C . The product was recrystallized from ethanol . The product was white crystals for Rh1 with m.p 223°C while Rh2 orange –yellow wish crystals with m.p 127°C . The preparation reactions are represented by the following equations:
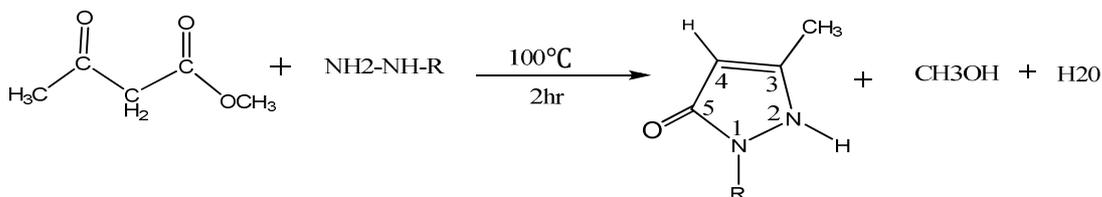
where R = H or Ph

The reactions were carried out at atmospheric pressure and followed by TLC . CHN analysis and physical properties are listed in Tables 1and 2 .

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RESULTS AND DISCUSSION

5.1 structure
  The studied compounds are represented by the following general structural formula:
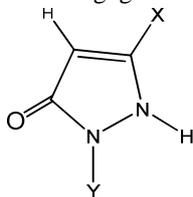
Where X= H, Y= H; X= CH₃, Y= H; X= CH₃, Y= Ph, and symbolized as Rh, Rh1 and Rh2 respectively.

The CHN elemental analysis and the calculated values are shown in Table1, they are in agreement which confirmed the proposal structures . However, the physical states, melting points and colours and listed in Table 2 .

Table 1. CHN elemental analysis

% N		% H		% C		*Empirical*	*symbol*
Exp.	Cal	Exp.	Cal	Exp.	Cal		
33.1	33.3	4.6	4.8	42.7	42.8*	C3H4N2O	Rh
14.0	14.2	6.0	6.1	24.0	24.4	C4H6N2O	Rh1
8.2	8.0	6.1	6.3	33.0	34.4	C10H10N2O	Rh2

*From ref. 32

Table 2. The physical properties and yield percentage of the studied compounds

Symbol	*Molecular mass*	*Physical state and coloere*	*Melting point/ ℃*	*Yield %*
Rh	84	Powder yellowish	270	98.0*
Rh1	98	White crystals	223	23.6
Rh2	174	Orange crystals	127	20.0

*From ref. 22

Table 3. Structure formula of the possible tautomers for compound(Rh)

Symbol	*Tuatomer Structure*
Rha	
Rhb	
Rhc	

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Pyrazolone (Rh), as shown in the Table 2, has the highest m.p compared with Rh1 and Rh2 which is attributed to the presence of strong hydrogen bonding, on the other hand the substituents, CH_3 and ph, lowered the m.p due steric effect Rh1 and steric effect and reduction in Number of N-H bonds in Rh2 .

5.2 Computational calculations

The total energy, electronic and nuclear energies were calculated for the three studied compounds, as well as HOMO, LUMO energies and the difference between then (ΔE) . Mullikan charges on the atoms and the dipole moments, and geometry parameters such as bond lengths and bond angles were also determined . However, since it is belived that these compounds under go tautomerisme to certain extent we first started to study the tautomers in the singlest studied compound (Rh) . This compound is expected to show three tautomeric isomers, as shown in Table 3. Theoretical calculations have been carried out on each tautomer of Rh and on Rh1 and Rh2, the results are listed in Table 4.

Table 4. Theoretical calculated of some physical properties using DFT-B3LY/6-31G(d) of Rh tautomers, Rh1 and Rh2 compounds

ΔE The difference LUMO-HOMO	LUMO energy	HOMO energy	Dipole moment /Debye	Nuclear energy Kcal/mol	Electronic energy Kcal/mol	Total energy Kcal/mol	Symbol
9.800	1.410	-11.210	6.54	139998.2	-329027.1	-189041.8	Rha
11.090	2.010	-13.100	2.41	138933.4	-187270.3	-189038.6	Rhb
12.002	3.110	-15.112	2.30	140071.6	-187270.9	-189028.0	Rhc
8.787	1.312	-10.099	6.19	18222.9	-211666.7	-213699.3	Rh1
5.62	3.067	-8.729	5.76	462538.9	-355157.4	-358583.9	Rh2

It is clear from Table 4 that the tautomer Rha has a lowest total energy compound with the other tautomers, which indicates a relatively higher stability . On the other hand it has mallest energy difference between LUMO and HOMO (ΔE) which reflects a relatively low chemical stability of their tautomer of compound Rh . However, the energy gap in Rh2 compound is decreased to 5.662 due to phenyl group, and therefore expected to be more chemically active . The tautomer Rha shows high dipole moment value compared with the other tautomers and even higher than values of the compounds, Rh1and Rh2 . This fact explains its high melting point and it's predominance in very polar solvents[26]. However, this conclusion is in agreement with measured ^{1}H NMR and UV spectra .

5.3 Mullikan charges

Table 5 given Mullikan charges on the atoms in the studied molecules computed with B3LYP and 6-31G (d) basis set .

Table 5. Mullikan charges on the atoms in the studied molecules predicated by B3LYP and 6-31G (d)

Rh2	Rh1	Rha	Compounds Atomic No.
-0.336	-0.319	0.271	C1
0.441	0.416	0.108	C2
0.613	0.598	0.593	C3
-0.509	-0.483	-0.419	N4
-0.453	-0.470	-0.470	N5
-0.558	-0.565	-0.558	O6

It is clear from Table5 that C3 atom carries the largest positive charge among the other carbon atoms therefore expected to be the site for nucleophilic attach in Rha compound. The Table shows that the charges on nitrogen N4 and N5 are not identical in the three compounds. However , oxygen atom carries the highest negative charge in each compound and its value is nearly equal . The charge on C2 atom, in compounds Rh1 and Rh2 increased by methyl substituent . On the other hand the presence of the phenyl substituent reduced the negative charge on N5 atom due to delocalization of the nitrogen electron pair by resonance effect . This is confirmed by increased vibrational frequency of the C=O group in Rh2 compound (IR data) .

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5.4 Bond lengths and angles
Theoretical calculated geometry parameters using DFT B3LYP/6-31G(d) calculations for the studied compounds
and listed in Tables 6 and 7 with of the atoms as shown in the following structure:
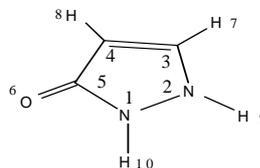
Table 6. Bond lengths calculated by using DFT B3LYP/6- 31G(d) theory level for Rha, Rh1 and Rh2 compounds

Compounds bond lengths/A$^{\cdot}$			
Rh2	*Rh1*	*Rha*	*Bond*
1.371	1.374	1.368	C1-C2
1.444	1.460	1.465	C1-C3
1.374	1.377	1.373	C2-N4
1.416	1.411	1.411	N4-N5
1.451	1.423	1.421	C3-N5
1.246	1.244	1.244	C3-O6

   Table 6 shows that the shortest bond in all studied compound is $C_3=O_6$, it is un affected by the substituent and has
value 1.244A$^{\circ}$ in Rha compound, whereas C1-C2 bond in Rha equals 1.368A$^{\circ}$ and its value increases by
substituents .

For comparison, we have recalculated the bond lengths C=O and C=C in formamide and ethylene compounds using
the same method and theory level, the results show that these bonds are shorter than that in studied compounds . CO
bond length in formaldehyde and formamide equal 1.202A$^{\circ}$ and   1.219 A$^{\circ}$ respectively whereas the C=C in
ethylene equals 1.321A$^{\circ}$.

The calculated bond angles are shown in Table7 indicate that the Rha molecule is planar while the C2-C1-C3 angle
is slightly affected by substituents on addition, the hydrogen atom (H9) is slightly deviated from the plane the
molecule .

Table 7. Bond angle calculated by DFT B3LYP/6-31G(d) (in deg.) for studied compounds

compounds			
Rh2	*Rh1*	*Rha*	*Bond angle*
123.3	123.9	125.6	H8-C1-C2
109.6	107.6	104.3	C3-C1-C2
127.0	126.5	130.0	H8-C1-C2
107.4	109.5	107.0	C2-N4-H9
109.3	108.3	105.1	C2-N4-N5
110.5	112.0	110.1	H9-N4-N5

5.5 NMR spectra
The theoretically calculated ^{1}HNMR data for pyrazol-5-one , 3-methyl pyrazol-5-one (Rh and Rh1) with the
experimental data for 3-methyl pyrazol-5-one are shown in Table 8 .

**Table 8. Theoretically calculated ^{1}H chemical shifts using TNDO/6-31G(d) method for Rh and Rh1
compounds with experimental values for Rh$_1$**

Compound	Proton No.	Experimental δ/ppm	Theoretical δ/ppm
Rh	H$_7$ & H$_8$	-	6.257
	H$_9$ & H$_{10}$	-	10.434
Rh1	H$_7$	2.157	1.823
	H$_8$	5.275	6.650
	H$_9$ & H$_{10}$	-	10.875

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From Table 8, the singlet signal at 2.157ppm is assigned to CH$_3$ group while the single at 5.275ppm is attributed to the vinyl proton (H$_8$). The signals of H$_{10}$ and H$_8$ protons which are expected to appear in 10.2-11.0 ppm are outside the measured region. Although these protons are in unequivalent chemical environments, it is reported in literature that they show one signal[2]. The calculations showed that H$_7$ and H$_8$; H$_9$ and H$_{10}$ protons are equivalents. The theoretical and experimental values of the chemical shifts for Rh$_2$ compound are shown in Table 9.

Table 9. The proton theoretical chemical shifts (TNDO/6-31G(d)) and the experimental for Rh2 compound in ppm

Proton number	Experimental chemical shifts	Theoretical chemical sifts
H$_7$	2.201	1.958
H$_8$	4.983	6.950
H$_9$	-	11.401
H$_{11}$ & H$_{12}$	7.603	8.663
H$_{13}$ & H$_{14}$	7.440	7.712
H$_{15}$	7.278	6.842

In general the calculated values are lower than the experimental Table 9 probably due to solvent effect on one hand and the theory level on the other hand. However the H$_8$ signal in Rh2 is shifted the down field compared with Rh1 due phenyl ring effect. ^{13}C chemical shifts data using completely proton decoupled technique for the Rh,Rh1 and Rh2 compounds are shown in Table 10.

Table 10. ^{13}C chemical shifts data for Rh,Rh1and Rh2 compounds using completely proton decoupled technique

Compound	Carbon atom number	Chemical shifts /ppm
Rh	*C$_1$	89.3
	C$_2$	130.1
	C$_3$	161.0
Rh1	C$_1$	91.0
	C$_2$	144.7
	C$_3$	164.4
	C$_8$	11.4
Rh2	C$_1$	92.4
	C$_2$	150.3
	C$_3$	161.7
	C$_8$	16.6
	C$_{10}$	139.7
	C$_{11}$ & C$_{12}$	130.0
	C$_{13}$ & C$_{14}$	122.7

* From ref. 32

From Table 10, the two signals at 11.4 and 16.6ppm are attributed to carbon atom of CH$_3$ group in the Rh1 and Rh2 compounds respectively. The signal of CH$_3$ in Rh2 is shifted to down field due to phenyl group. The signal above 160ppm in the studied compounds is easily assigned to the CO groups. This signal has low intensity due to long spin relaxation time (T1). C$_2$ shows a signal at 130.1ppm in Rh compound shifted to 144.7 and 150.8ppm in Rh$_1$ and Rh$_2$ respectively due to CH$_3$ and phenyl substituent effects. In general, C1 shows a signal at up field compared with C2, which is expected, since C2 atom bonded to nitrogen atom. The aromatic carbon atoms in Rh2 compound show three signals at 122.7,130.0 and 139.7ppm.

The ^{14}N NMR spectra were measured in CD$_3$OD solvent using CH$_3$NO$_2$ as external reference for Rh1and Rh2 compounds. The spectra accidently showed one broad signal at 190.0ppm since the two nitrogen atoms are chemically unequivalent. The signal appeared very broad because of strong quadropole interaction.

5.6 ^{1}H-NMR relaxation times
^{1}H NMR relaxation times at various temperatures in the range -20 to 40°C for CH$_3$ and CH groups in Rh1 compound have been determined in diluted solution and listed in Table 11. The plot of T1 temperature dependence is shown in Fig.1, T1 decreases for both CH and CH$_3$ groups with decreasing temperature in the measured region, which indicates that measurements are in the narrowing region (Wτ_c << 1). However, T$_1$ for CH$_3$ group is shorter than that of CH group due to dipolar interaction of three protons and reorientational motion of CH$_3$. The same observation has been obtained for Rh2 compound (Table 12 and Figure 2). From Tables 11 and 12 it is clear that T$_1$ values in compound Rh2 become shorter which can be attributed to phenyl group effect.

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Table 11. ^{1}H spin – relaxation times (T_1) at different temperatures for CH and CH$_3$ groups in Rh1 compound

Temp/°C	Chemical shifts C-H /ppm	Relaxation time /s	Chemical shifts CH$_3$ /ppm	Relaxation time/s
40	5.300	6.365	2.181	2.937
25	-	-	2.182	2.389
10	5.295	6.079	2.189	1.757
-5	5.411	4.841	-	-
-20	5.510	3.795	2.192	1.388

(-) , not measured

Table 12. ^{1}H spin – relaxation times (T_1) at different temperatures for CH and CH$_3$ groups in Rh2 compound

Temp/°C	Chemical shifts C-H /ppm	Relaxation time /s	Chemical shifts CH$_3$ /ppm	Relaxation time /s
40	-	-	2.229	2.544
25	5.353	6.304	2.233	2.250
10	5.358	6.289	-	-
-5	5.366	4.983	2.239	1.790
-20	5.371	4.156	2.239	1.305

(-) , not measured
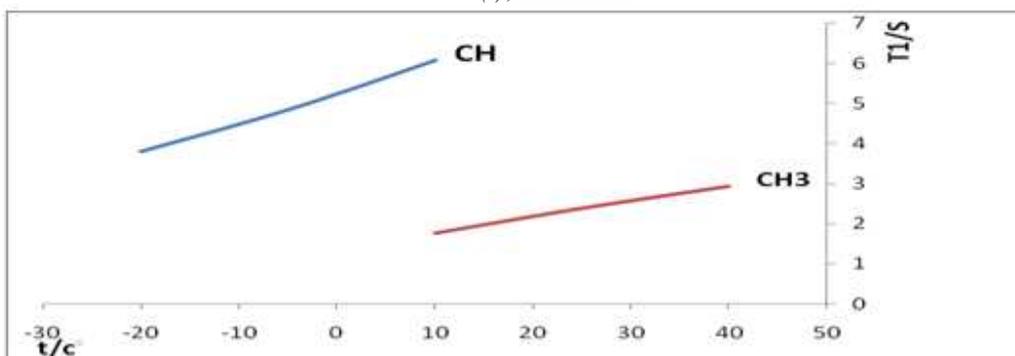
Fig. 1. Variation of T_1 with temperatures for Rh1 compound
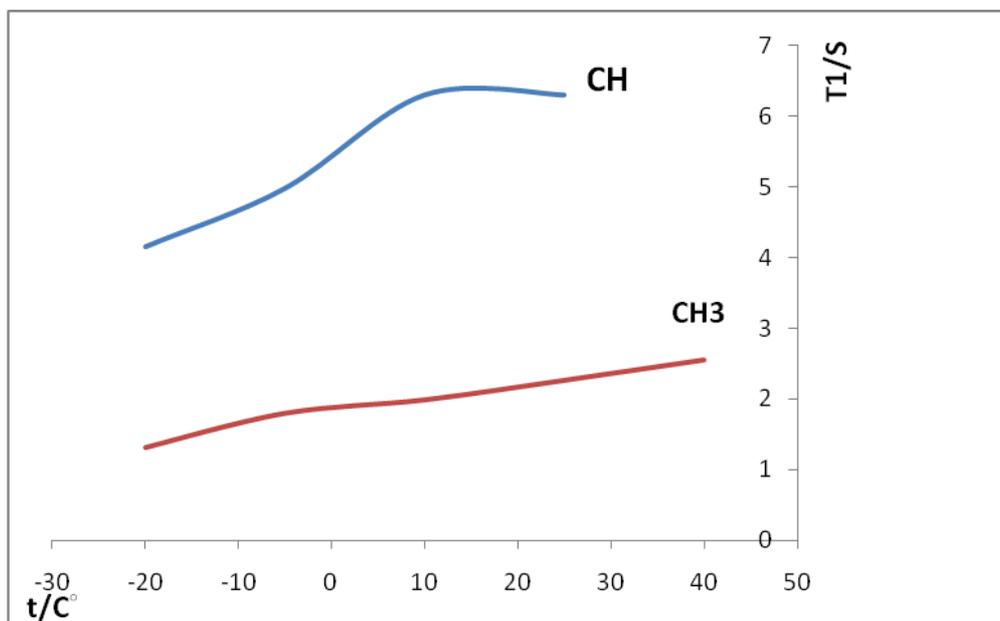
Fig.2. Variation of T_1 with temperatures for Rh2 compound

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5.7 UV- Visible spectra
The UV-Visible spectra of Rh1 and Rh2 compounds in method were measured and the data are listed in Table13. Compound Rh1 shows two strong absorption bands at 235 and 280 nm which can be attributed to $\pi \rightarrow \pi*$ transitions and therefore confirms the dominance of the Rh1a tautomer . The two bands are shifted to longer wavelength in Rh_2 compound probably due to phenyl ring effect .

Table 13. The UV- Visible spectra for Rh1 and Rh2 compounds in methanol solvent

Comp.	Band I		Band II	
	λ max(nm)	ɛmax(L.mol⁻¹.cm⁻¹)	λ max(nm)	ɛmax(L.mol⁻¹.cm⁻¹)
Rh1	235	1699	280	1855
Rh2	240	1370	340	2837

5.8 IR spectra
The theoretical vibrational frequencies have been determined using DFT B3LYP/6-31G(d) method for the studied compounds are listed in Tables 14,15 and 16 .

Table 14. Theoretical IR data for the Rh compound

Frequency/cm⁻¹	Intensity	Approximate description
3442.3	31.8	γ^{as}_{NH}
3425.9	10.6	$\gamma_{S\,NH}$
3158.9	29.1	$\gamma^{as}_{=CH}$
3089.3	18.3	$\gamma^{s}_{=CH}$
1964.3	294.6	γ_{CO} & δ^{ip}_{HCN}
1689.0	83.6	δ^{ip}_{NH}
1448.5	46.3	$\gamma_{C=C-C}$
1301.8	7.0	δ^{ip}_{CNN}
1289.7	1.0	δ^{ip}_{NH}
1162.8	17.1	$\delta^{ip}_{=CH}$
1132.3	16.2	γ_{CN}
1077.3	2.7	$\delta^{oop}_{=CH}$
970.0	9.6	δ^{oop}_{NH}
929.2	4.5	γ_{NN}
925.6	7.9	γ_{CNN}
802.9	49.4	δ^{oop}_{CH}
780.8	3.2	δ^{oop}_{CH}
643.5	2.7	$\delta_{C-C/ring}$
632.8	2.8	$\delta_{C-C/ring}$
423.8	3.3	δ^{ip}_{OCN} & δ_{HNC}
422.4	0.0	δ_{C-C} & δ_{HCN} weak
240.1	2.5	δ^{oop}_{C-C}
-575.3	197.7	δ skeletal
-823.5	15.0	δ skeletal

*Virational modes: γ, stretching; δ, deformation , superscripts; S, symmetrical; as, asymmetrical ; ip, in-plane ; oop, out-of-plane . * unscaled*

Rh molecule possess 24 mode of vibration, the frequencies of these mode are listed in Table 14 . we have not found theatrical calculation or experimental of vibrational frequencies for This molecule in the literature so for . The frequencies at about 3400 cm⁻¹ can easily assigned to N-H asymmetric and symmetric stretching vibrations .

These values are ingreement with that of the imides . The frequencies at 3158.9 and 3089.3 cm⁻¹ (Table 14) can be attributed to C-H asymmetric and symmetric stretching respectively for the vinyl group . The frequencies at 1900 is aised from CO stretching combined with C-N-H bending in plane, it is higher than the normal values . However, the frequencies at about 1000 and 802.9 cm⁻¹ are attributed to C-H bending vibration in plane and out of plane of the ring respectively .

Molecules, Rh1 and Rh2, have 33 and 63 modes of vibration the calculated and the measured frequencies are shown in Tables 15 and 16 . with approximate description . In both molecules, the vibrational frequency above 3400 cm⁻¹ is assigned to N-H stretching which is shifted to lower value in solid due to strong hydrogen

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bonding . The frequencies at about 3100 cm^{-1} are attributed to C-H stretching of the vinyl and aromatic hydrogens .

Table 15. Some of theoretically calculated frequencies using DFT B3LYP/6-31G(d) method and the experimental as KBr disc for Rh1 compound

Theoretical /cm^{-1}	Intensity	Experimental /cm^{-1}	Approximate description
3435.8	33.5	3300.0 broad	γ^{as}_{NH}
3424.1	7.7		γ^{s}_{NH}
3169.2	2.3	3088.5	$\gamma^{as}_{=CH}$
3157.7	27.9		$\gamma^{s}_{=CH}$
3075.1	2.4	2940.5	$\gamma^{as}_{CH\ aliphatic}$
3072.0	1.6	2922.7	$\gamma^{s}_{CH\ aliphatic}$
1964.5	305.4	1670.5*	γ_{CO} & δ^{ip}_{CNH}
1773.7	58.0	1560.0	γ_{CN} & γ^{oop}_{NH}
1513.6	78.3	1496.0	$\gamma_{C=C\ ring}$
1400.4	4.4	1322.1	$\delta^{ip}_{CH\ aliphatic}$
1385.3	2.5		$\delta^{ip}_{CH\ ring}$
1370.7	1.5		$\delta^{ip}_{CH\ aliphatic}$
1303.1	7.3	1200.0	γ_{CNN} & δ_{NH}
1288.0	7.5		γ_{CNN}
1160.6	5.3		$\delta^{ip}_{=CH}$
1045.6	4.9		$\delta^{ip}_{=CH}$
998.4	3.7	1010.0	δ^{oop}_{NH}
992.5	5.8	995.7	δ_{NN}
855.8	37.0	870.5	$\delta^{oop}_{=CH}$
666.4	3.0	610.5	$\delta^{oop}_{CH\ aliphatic}$
628.4	5.5		$\delta_{C-C\ ring}$
529.0	4.9		$\delta_{C-C\ ring}$
459.4	2.5		δ_{OCN}

* From ref. 33

Table 16. Some theoretically calculated frequencies by DFT B3LYP/6-31G(d) method and the experimental values for RH$_2$ compound

Theoretical /cm^{-1}	Intensity	Experimental /cm^{-1}	Approximate description
3391.7	3.6	3420.2	γ_{NH}
3166.4	3.0	3090.5	$\gamma^{as}_{=CH}$
3142.9	30.0		$\gamma^{s}_{=CH}$
3079.3	7.7	2990.7	$\gamma^{as}_{CH\ aliphatic}$
3077.6	1.1	2900.2	$\gamma^{s}_{CH\ aliphatic}$
3068.9	28.8		$\gamma_{CH\ aromatic}$
3053.5	2.1		$\gamma_{CH\ aromatic}$
1986.4	207.5	1610.0	γ_{CO} & δ^{ip}_{CNH}
1787.8	1.2	1522.5	γ_{CN} & γ_{NH}
1588.2	15.9	1495.0	$\gamma_{C=C\ ring}$
1457.7	27.4	1354.0	$\delta^{ip}_{CH\ aliphatic}$
1391.4	7.5		$\delta^{ip}_{CH\ aliphatic}$
1384.6	2.5		$\delta^{ip}_{CH\ aliphatic}$
1301.2	7.3		γ_{CNN} & δ^{ip}_{NH}
1261.0	25.9		γ_{CNN}
1190.0	18.0	1100.0	$\delta^{ip}_{CH\ aromatic}$
1129.7	9.4	1000.0	$\delta^{ip}_{CH\ aromatic}$
847.2	2.5	750.5	δ^{oop}_{NH}
893.8	34.7	688.0	$\delta^{oop}_{=CH}$
795.1	4.5		$\delta^{oop}_{CH\ aromatic}$
777.4	15.8		$\delta^{oop}_{=CH}$
687.9	2.1		$\delta^{oop}_{CH\ aliphatic}$

The frequency of CO group in molecule Rh2 is sifted to higher value compound with that in Rh1 and Rh . Theis fact can be explained in them of resonance effect of the phenyl ring . However , the frequencies at 1400 and 700 cm^{-1} can the assigned to aliphatic C-H bending and to the aromatic C-H bending out of plane as expected .

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CONCLUSION

DFT B3LYP / 6-31G (d) calculation showed that Pyrazol-5-one is the predominant tautomer and it has aplanar structure . Theoretically predicted IR and NMR were in agreement with the experimental data .

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