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# Theoretical study of structures, IR and NMR of some aliphatic hydrazones derived from aliphatic aldehydes and hydrazine by DFT method

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## ABSTRACT

*Aliphatic hydrazones are represented by a general formula $RCH=N-NH_2$ , Where R= H ; $-CH_3$ ; $-C_2H_5$ ,have been theoretically studied. The theoretical calculations were carried out using DFT method at B3LYP theory level and 6-31G(d,p) basis set.The bond lengths and bond angles ,charges on the atoms ,and dipole moments were determined as wellas HOMO and LUMO energies ,IR and NMR data were predicted, discussed and compared to the corresponding values for related compounds. The results showed that these compounds are mainly exist in trans form , and the bond lengths of C=N and N-N are 1.2809 and 1.3405 A° respectively for formaldehyde hydrazone. Nitrogen NMR chemical shifts are 105 and 340 ppm due to $NH_2$ and C=N respectively. The two $NH_2$ protons are maqnetically not equivalent.*

**Key words:** Aliphatic hydrazones, DFT calculations, structures, IR, NMR.

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## INTRODUCTION

Hydrazones are organic compounds containing hydrazone group $C=N-NH_2$ . They are important intermediates in hetero cyclic chemistry. Hydrazones are synthesized from aldehydes, ketones and hydrazine or substituted hydrazines. hydrazones have been found to possess many biological activities such as antibacterial[1,2], anticonvulsant[3], anti-inflamatory[4], anti-protozoal[5] and antitubercular[6,7], Recently some hydrazones were prepared from hydrazides and methyl acetoacetate or acetylacetone and found to have microbial activity[8] .

In addition, complexes of metals derived from hydrazones of isonicotinic acid hydrazide have biological properties[9]. Recently Takashi Mino et al have studied Palladium-catalyzed Mizovoki-Heck type reaction with aryl trialkoxysilanes using hydrazones ligands[10,11].

Zhang et al. have studied the crystal structure of 2,4-dinitro benzaldehyde hydrazone and showed that the molecule is essentially planar, with adihedral angle of 8.27° between the hydrazone group and the benzene ring. However ,because of the pi-pi conjugation and two nitryl groups electron withdrawing effect , the C=N bond (1.282 A°) is obviously shorter than that of the normal range[12,13]. Shih-I studied izomerization of acetaldehyde N,N-di methyl hydrazone in cyclohexane using DFT at B3LYP 6-31G(2dt,p)theory level and suggested that E-isomer is highly dominated because in this configuration the isomer would avoid the steric interaction between the methyl group in the amino group and the flanking methyl group anti to the lone-pair electron at the imine nitrogen.[14] The calculated bond lengths and bond angles ,C=N , N-N and C-N-N angle are 1.280 ,1.365 A° and 121.3 degree respectively. Theoretical study of the vibrational spectra and structural parameters of hydrazine and some methyl substituted hydrazines was carried out by James and chao using *ab inito* MP2(Full)/6-31G(d) calculations and found that bond length N-N and N-H are 1.428 and 1.015 A° respectively.

Shetgiri and Nayak have synthesized some hydrazones derived from aromatic ketones and measured their antimicrobial activity, and reported their IR and NMR data. In the literature we have found neither quantitative IR and NMR data nor DFT calculations for the hydrazones derived from aliphatic aldehydes. So the purpose of the present work is to study the spectral structural parameters and some physical properties for the title species formaldehyde hydrazone, acetaldehyde hydrazone and probanal hydrazone.

## EXPERIMENTAL SECTION

The DFT computations have been performed using Gaussian software G03, DFT method at B3LYP/ 6-31G (d,p) theory level. The geometry optimization was firstly performed at this theory level then the energies, charges on atoms, dipole moments, structural parameters and IR. Frequencies were calculated. NMR data were predicted using .SCF GIAO magnetics shielding implemented in Gaussian 03 program.

## RESULTS AND DISCUSSION

The geometry optimization calculations showed that the studied molecules exist in trans form, the vinyl proton and the amino group are on opposite side of the C=N bond.

### 3.1 energies and dipole moments

The total energy, dipole moments and HOMO and LUMO energies of the studied molecules ,calculated within buses set used are listed in Table 1. The molecules are represented H1=formaldehydehydrazone; H2=acetaldehyde hydrazone; H3=propanal hydrazone.

**Table 1: The total energy, dipole moments and HOMO and LUMO energies of the studied molecules**

| **ΔE** | molecules | Total energy a.u | Dipole moment Debye | HOMO | LUMO |
|---|---|---|---|---|---|
| 0.2382 | H1 | -149.9652 | 1.9466 | -0.21448 | 0.02372 |
| 0.2367 | H2 | -189.2881 | 2.0690 | -0.20589 | 0.03082 |
| 0.2396 | H3 | -228.6064 | 2.0773 | -0.2225 | 0.0171 |

*a.u=27.2116 ev*

from Table 1 molecule H2 possesses the highest LUMO energy and smallest energy difference (ΔE=0.23671 a.u). Which reflects its chemical reactivity. On the other hand, H3 molecule shows the highest value of dipole moment ,as expected from its structure, due to inductive effect of ethyl group. The HOMO and LUMO orbitals for studied molecules are shown in Fig.1

The HOMO and LUMO orbitals for studied molecules are shown in Fig.1

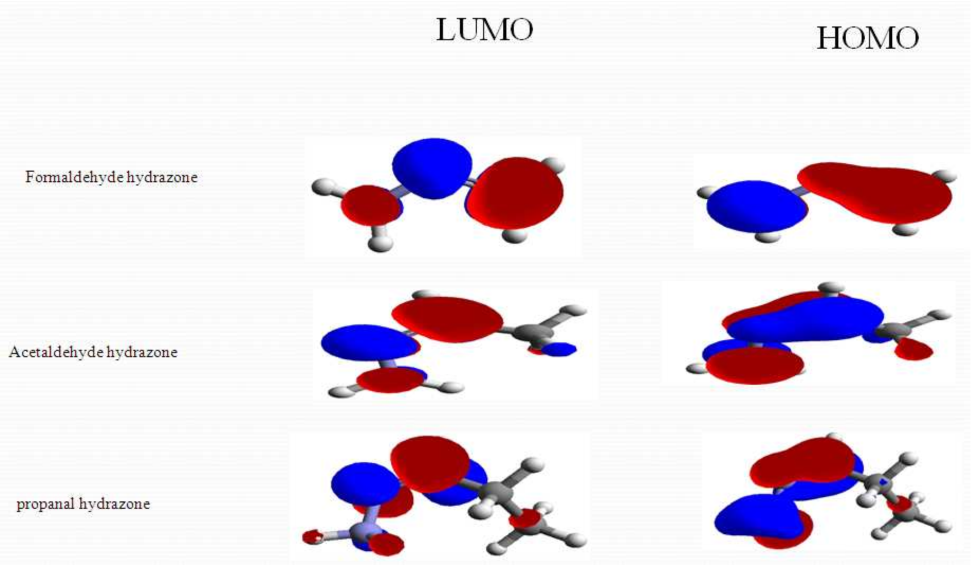


**Fig.1: The HOMO and LUMO orbitals for studied molecules**

### 3.2 Mulliken charges

The calculated Mulliken charges on the atoms for H1, H2 andH3 molecules are listed in Table 3,4,5 with their optimized structures and numbering atoms.

**Table 2: The calculated charges on atoms for H1**

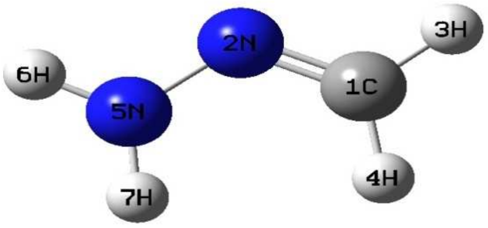


**Table 3: The calculated charges on atoms for H2**

| No. of Atom | charge | No.of Atome | charge |
|---|---|---|---|
| C1 | -0.088163 | N5 | -0.430653 |
| N2 | -0.184914 | H6 | 0.282388 |
| H3 | 0.105514 | H7 | 0.248166 |
| H4 | 0.067662 | | |

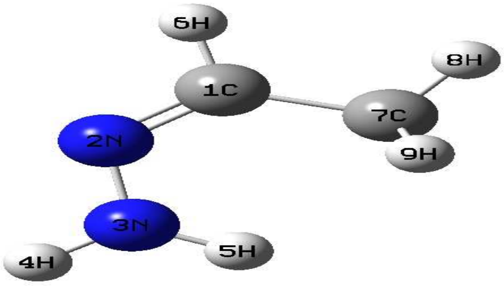
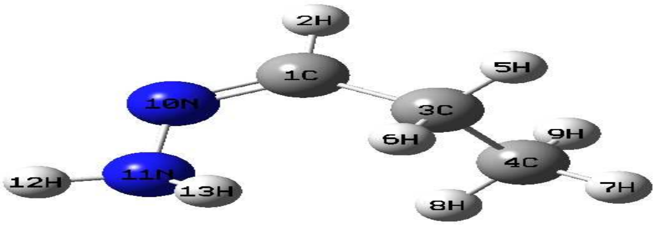


**Table 4: The calculated charges on atoms for H3**

| charge | No. of Atom | charge | No. of Atom |
|---|---|---|---|
| 0.094001 | H6 | 0.066489 | C1 |
| -0.379764 | C7 | -0.225904 | N2 |
| 0.117389 | H8 | -0.441928 | N3 |
| 0.118116 | H9 | 0.279978 | H4 |
| 0.118116 | H10 | 0.253507 | H5 |



| charge | No. of Atom | charge | No. of Atom |
|---|---|---|---|
| 0.128923 | H8 | 0.079829 | C1 |
| 0.112772 | H9 | 0.097252 | H2 |
| -0.251092 | N10 | -0.231222 | C3 |
| -0.435529 | N11 | -0.313501 | C4 |
| 0.270841 | H12 | 0.106166 | H5 |
| 0.239985 | H13 | 0.093141 | H6 |
| | | 0.102436 | H7 |

From Tables 2,3 and 4 , it is clear that the nitrogen atoms carry largest negative charges, although nitrogen atom of amine group carries negative charge twice the value of the nitrogen atoms of imine group. This means that the electrophilic reaction occur at $NH_2$ group, However hydrogens of $NH_2$ possess more positive charge than vinyl hydrogens in addition, the charges on nitrogens atoms are slightly vary with structure(Table5)

**Table 5: Mulliken charges on selected atoms in studied molecules**

| Molecule | *N=C | *$NH_2$ | *C=N |
|---|---|---|---|
| H1 | -0.184914 | -0.430653 | -0.088163 |
| H2 | -0.225904 | -0.441928 | 0.066489 |
| H3 | -0.251092 | -0.435529 | 0.079829 |

### 3.3 Geometrical parameters

The calculated bond lengths and bond angles for the studied molecules are listed in Tables 6,7 and 8.

**Table 6: Bond lengths and angles for H1 molecule**

| Bond | Length | angle | magnitude |
|---|---|---|---|
| C1-N2 | 1.2809 | H3-C1-H4 | 118.552 |
| C1-H4 | 1.0965 | H3-C1-N2 | 117.860 |
| C1-H3 | 1.0842 | N2-N5-H6 | 116.932 |
| N2-N5 | 1.3403 | H6-N5-H7 | 120.540 |
| N5-H7 | 1.0132 | H7-N5-N2 | 122.528 |
| N5-H6 | 1.0028 | N2-C1-H4 | 123.588 |
|  |  | H7-N5-N2-C1 | 0.0000 |
|  |  | H4-C1-N2-N5 | 0.0000 |

**Table 7: Bond lengths and angles for H2 molecule**

| Bond | Length | angle | magnitude |
|---|---|---|---|
| C1-N2 | 1.2858 | 120.122 | H4-N3-H5 |
| C1-H6 | 1.0868 | 123.576 | H5-N3-N2 |
| C1-C7 | 1.5057 | 118.975 | N3-N2-C1 |
| C7-H9 | 1.0998 | 125.859 | N2-C1-C7 |
| C7-H10 | 1.0998 | 111.712 | C1-C7-H9 |
| C7-H8 | 1.0919 | 107.009 | H9-C7-H10 |
| N2-N3 | 1.3474 | 107.576 | H10-C7-H8 |
| N3-H4 | 1.0026 | 111.026 | C1-C7-H8 |
| N3-H5 | 1.0100 | 114.999 | H6-C1-N2 |
|  |  | 116.303 | N2-N3-H4 |
|  |  | 0.0000 | H5-N3-N2-C1 |
|  |  | 0.0000 | N3-N2-C1-C7 |
|  |  | -59.916 | N2-C1-C7-H9 |

**Table 8: Bond lengths and angles for H3 molecule**

| Bond | Length | angle | magnitude |
|---|---|---|---|
| C1-H2 | 1.0893 | N10-N11-H12 | 108.89 |
| C1-C3 | 1.5106 | H2-C1-N10 | 114.473 |
| C1-N10 | 1.2826 | C3-C1-H2 | 117.987 |
| C3-H6 | 1.1007 | H5-C3-C1 | 108.730 |
| C3-H5 | 1.0952 | H6-C3-H5 | 105.743 |
| C3-C4 | 1.5415 | C4-C3-H5 | 109.754 |
| C4-H9 | 1.0941 | H9-C4-C3 | 110.784 |
| C4-H7 | 1.0947 | H7-C4-H9 | 107.999 |
| C4-H8 | 1.0934 | H8-C4-H7 | 108.400 |
| N10-N11 | 1.3806 | H9-C4-H8 | 107.681 |
| N11-H13 | 1.0201 | C3-C4-H8 | 110.907 |
| N11-H12 | 1.0123 | H6-C3-C4 | 109.257 |
|  |  | C1-C3-H6 | 110.315 |
|  |  | C3-C1-N10 | 127.507 |
|  |  | N11-N10-C1 | 118.728 |
|  |  | N10-N11-H13 | 115.540 |
|  |  | H12-N11-H13 | 110.725 |
|  |  | N11-N10-C1-C3 | -1.497 |
|  |  | N10-C1-C3-C4 | 78.186 |

The bond length C=N and N-N are 1.2809 and 1.3403 $\overset{\circ}{A}$ respectively in good agreement with reported values for similar compounds. [12,14]. On the other hand the bond length of vinyl hydrogen bonds are noticeably longer than $NH_2$ hydrogen bond .The results show (Tables 6,7,8) That C=N bond in H2 and H3 molecules is longer than that in H1, probably due to inductive effect of CH3 and C2H5 groups. Similarly, N-N bond length increases with alky substituents on carbon atom of C=N bond .However , the value of hydrazone group angles are within the expected values.

### 3.4 IR vibrational frequencies

The theoretical vibrational frequencies calculated by DFT method B3LYP/6-31G(d,p) for studied molecules are listed in Tables 9,10 and 11.The molecules are characterized by vibrational frequencies arise from NH2 , C=N and N-N groups. The frequencies at 3544 and 3329 cm-1 are assigned to antisymmetrical stretching and symmetrical stretching of NH2 group ,while that at 1600 and 1552 cm-1 are due to C=N stretching and NH2 deformation[15,16] . for molecules H2 and H3 show the expected frequencies for CH3 and CH2 stretching and bending.

**Table 9: Theoretical vibrational frequencies for H1 molecules**

| Approximate description | Intensity A(Km/mol) | Frequencies $cm^{-1}$ |
|---|---|---|
| Torsion $NH_2$ | 253.9596 | 509.3990 |
| N-N-C bending | 8.7834 | 476.1807 |
| $CH_2$ s oop | 0.0037 | 518.235 |
| $CH_2$ s oop | 13.4183 | 736.3959 |
| $CH_2$ δ oop | 33.1566 | 835.9556 |
| N-N st. $CH_2$ δ | 51.1986 | 1042.9246 |
| $NH_2$ st. $CH_2$ rock | 26.8702 | 1103.7848 |
| $CH_2$ rock , $NH_2$ δ | 33.2519 | 1205.8076 |
| C=N st.$CH_2$ δ | 9.583 | 1407.7171 |
| $NH_2$ δ, N-N st | 66.8345 | 1552.3412 |
| C=N st.,$NH_2$ δ | 27.4561 | 1600.6307 |
| $CH_2$ s.st | 38.0444 | 2877.5946 |
| $CH_2$ as.st. | 14.9174 | 3043.1083 |
| $NH_2$ s.st | 6.8956 | 3329.3154 |
| $NH_2$ as.st | 46.2717 | 3544.0061 |

*Scaled by 0.9427*

*Abbreviations: δ : deformation ; τ: τorsion ; s: symmetrical, as: asymmetrical ; ip , in plane; oop: out of plan , st. : stretching .*

**Table 10: Theoretical vibrational frequencies for H2 molecules**

| Approximate description | Intensity A(Km/mol) | Frequencies $cm^{-1}$ |
|---|---|---|
| $NH_2$ Torsion | 233.5874 | 540.3336 |
| $CH_3$rock | 0.003 | 134.3278 |
| N-N-C bending | 2.6222 | 274.8649 |
| $NH_2$ twist | 0.0431 | 382.1094 |
| $NH_2$ δ, $CH_3$ δ | 1.35 | 568.6986 |
| N-N-C bending | 9.6878 | 608.4999 |
| C-H δ oop | 21.0198 | 757.2313 |
| C-C st. | 1.9639 | 883.1766 |
| $CH_3$ rock | 0.0003 | 978.5424 |
| N-N st., C-C st. | 38.5446 | 1044.8238 |
| $CH_3$ δ , N-N st | 63.4285 | 1066.4177 |
| $NH_2$ rock | 3.2055 | 1171.2732 |
| N-N st.H-C=N bend | 14.9967 | 1305.8458 |
| $CH_3$ δ,C-H δ | 15.8256 | 1348.0551 |
| $CH_3$ δ,C-H δ | 7.0548 | 1411.2572 |
| $CH_3$ δ,C-H δ | 5.8318 | 1417.5377 |
| N-N st., $NH_2$ δ | 56.1345 | 1555.3475 |
| C=N st. , $NH_2$ δ | 11.1413 | 1601.9576 |
| $CH_3$ sy.st | 19.9904 | 2833.4844 |
| $CH_3$ as.st | 30.7808 | 2874.4408 |
| $CH_3$ as.st | 12.8159 | 2954.7277 |
| H-C= st. | 18.9992 | 2999.7161 |
| $NH_2$ s.st | 9.3619 | 3370.9259 |
| $NH_2$ as.st | 44.5334 | 3550.2382 |

*Scaled by 0.9427*

**Table 11: Theoretical vibrational frequencies for H3 molecules**

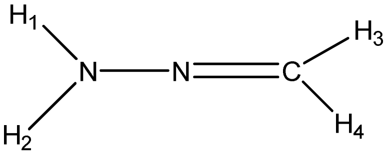
| Approximate description | Intensity A(Km/mol) | Frequencies $cm^{-1}$ |
|---|---|---|
| C-C,C=N-N bending | 0.2985 | 81.8583 |
| $CH_3$ twisting | 1.1639 | 199.2824 |
| $CH_3$ , $NH_2$ twisting | 8.0664 | 231.3291 |
| $NH_2$, $CH_2$ twisting | 6.8384 | 317.1745 |
| $NH_2$ Rock | 12.8088 | 389.5680 |
| C=N-N bending | 20.4715 | 546.6219 |
| $CH_2$ , C=N-N bending | 4.4424 | 624.1469 |
| N-N st , $NH_2$ oop | 238.6303 | 690.2557 |
| $NH_2$, $CH_2$ twisting | 13.2105 | 756.6684 |
| C-H oop, | 8.7483 | 809.3060 |
| C-C st. C-H bend | 3.772 | 837.9818 |
| C-H ip, C-C st | 2.2628 | 951.9169 |
| N-N st. | 25.5776 | 1016.9803 |
| C-H ip, N-N st | 7.7679 | 1035.7828 |
| . C-H ip, C-C st | 12.4452 | 1078.6298 |
| $NH_2$, $CH_2$ ip. | 0.7789 | 1210.8702 |
| $NH_2$ twisting | 7.9277 | 1238.5464 |
| $CH_2$ ip | 0.9107 | 1272.8531 |
| N=C-H, $CH_2$ bending | 8.1056 | 1323.0281 |
| N=C-H, $CH_3$ bending | 2.0143 | 1343.2101 |
| $CH_2$ scissorig | 1.1743 | 1416.9593 |
| $CH_3$ $\delta$ | 5.3478 | 1425.56 |
| $CH_3$ $\delta$ | 5.7413 | 1437.8592 |
| $NH_2$ $\delta$ | 30.6478 | 1573.6745 |
| $NH_2$ $\delta$, C=N st. | 4.138 | 1614.6365 |
| $CH_2$ sy.st | 32.5533 | 2830.2448 |
| $CH_3$ sy.st | 29.628 | 2875.18 |
| $CH_2$ as.st | 17.2975 | 2902.6129 |
| $CH_3$ sy.st | 30.6027 | 2941.2668 |
| $CH_3$ as.st | 22.1403 | 2953.4487 |
| N=C-H sy.st | 25.8285 | 2974.3532 |
| $NH_2$ sy.st | 5.4223 | 3250.0358 |
| $NH_2$ as.st | 8.9407 | 3408.5442 |

*Scaled by 0.9427*

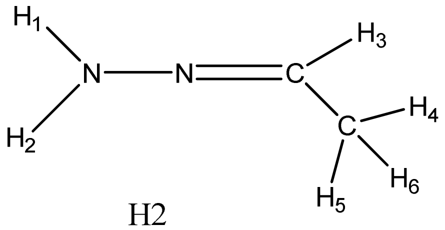
### 3.5 NMR data

The theoretical NMR chemical shifts for proton and nitrogen nuclei are listed in Table 12 and 13. The two protons of NH2 in all molecules give different chemical shifts and the difference increase in H2 and H3 molecules, which means that they are magnetically not equivalent. In general proton chemical shifts in aliphatic amines largely vary since H appear in the range (4-0.5 ppm) and may extend to 6.0 ppm, depends on temperature acidity of the solution, extent of hydrogen bonding, solvent effect and the nature of the substituent.

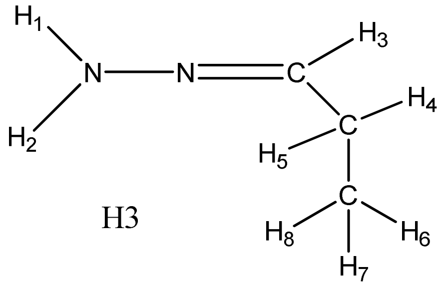
The nitrogen atom. On the other hand, practically the signal is very broad and may not be observed due to the effect quadrupole moment and rate of proton exchange. Indane-1,3-dione bis hydrazone gives NH2 singlet signal at 2.1 ppm in DMSO.[17] The molecule (H3) shows the signal at 4.9 ppm with that of H1 and H2 at 5.2 ppm, slightly downfield. 2,4-Dichloro phenyl methyl hydrazide shows NH2 signal in DMSO at 5.32 ppm[18]. Proton imine group N=C-H is expected to give Signal in the range between that of vinyl proton and aldehyde proton due to the difference in electronegativity and anisotropic effect of the double bond. Aldehydes and alkene show proton signal at 10-9 and 6.5-4.5 ppm respectively.2-methyl butyral aldehyde shows aldehyde proton at 9.6 ppm[19]. Banfi and patiny predicted the values of chemical shifts for vinyl protons in formaldehyde hydrazone 5.703 and 5.808 ppm which are in agreement with the present work (Table 12) ,5.54 and 5.98 ppm.



H1



H2



H3

**Table 12: Calculated $^1$H chemical shifts values by SCF GIAO using TMS as reference**

| Chemical shift/ppm | Proton no | molecule |
|---|---|---|
| 5.24 | 1 | H1 |
| 5.27 | 2 | |
| 5.54 | 3 | |
| 5.98 | 4 | |
| 5.11 | 1 | H2 |
| 5.22 | 2 | |
| 6.09 | 3 | |
| 1.40 | 4 | |
| 1.43 | 5 | |
| 1.40 | 6 | |
| 4.63 | 1 | H3 |
| 4.92 | 2 | |
| 6.73 | 3 | |
| 1.73 | 4 | |
| 2.21 | 5 | |
| 0.74 | 6 | |
| 0.74 | 7 | |
| 1.47 | 8 | |

**Table 13: Theoretical chemical shifts for nitrogen for studied molecules, $NH_3$ reference**

| $NH_2$ ppm nitrogen | C=N ppm nitrogen | molecule |
|---|---|---|
| 105.705 | 340.157 | Formaldehyde hydrazone |
| 98.5459 | 330.313 | Acetaldehyde hydrazone |
| 103.02 | 340.157 | Propanal hydrazone |

Theoretical Nitrogen NMR chemical shifts for studied compounds are listed in Table 13.The studied molecules contain two types of nitrogen. The chemical shift for the imine group expected to be at low field compare with amino group due to effect of the double bond.

Acetaldehyde hydrazone is expected to show two nitrogen signal at 330.313 and 98.5459 ppm attributed to C=N and $NH_2$ group respectively (Table13), which are lower values than that of formaldehyde hydrazone and propanal hydrazone.

## CONCLUSION

We can see in this work that aliphatic hydrazone exist in trans form. DFT can predict structures IR and NMR in good agreement with experimental results.

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