DFT Study of the 1,3,4-Thiadiazole Ring molecules (Geometry, Thermodynamic functions, IR studies)

Kh. A. Khidhir[*] ,Rahman T.Haiwal[**]and Zaid H. Abood
*Dep. Of chemistry, college of Education, university of kerbala
**Dep. Of chemistry, college of Science, university of kerbala

الخلاصـــة

تضمنت هذه الدراسة اعتماد برنامج كاوس (Gaussian 03) لاستخدام طريقة الحساب التام على وفق نظرية دوال الكثافة (DFT) وبأسلوب (B3LYP) وباستعمال عناصر القاعدة (STO-3G) وذلك لغرض حساب الأبعاد الهندسية (أطوال وزوايا التآصر) عند الشكل الهندسي المتوازن ، الشحنات ، الدوال الثرموديناميكية وكذلك حساب وتصنيف الأنماط الاهتزازية العائدة لطيف الأشعة تحت الحمراء تكافؤياً وتماثلياً وبعدد (3N-6) لثلاثة جزيئات مشتقة من حلقة إلـــ(1,3,4-Thiadiazole) (والتي يرمز لها اختصاراً A, B، C) .
وقد وجد إن المركب (C) تكون لـه أعلى قيمة انتروبي (S^0) وسعة حرارية (C_v) ، كما تبين من خلال ملاحظة النتائج بان اغلب الذرات العائدة للمركب (C) تكون اقل كثافة الكترونية وقد يعود السبب في ذلك إلى مجموعة النايترو المعوضة ($-NO_2$) والتي تعمل على سحب الالكترونات بينما يكون المركب (B) على العكس من ذلك وهذا بدوره يبين مدلى تأثير مجموعة المثيل المعوضة ($-CH_3$) على الدفع الالكتروني مقارنة بالمركبين الأخريين . كما أظهرت النتاج بان التردد الأعلى للمركبات الثلاثة المدروسة (A, B, C) يكون للمط الاهتزازي الأساسي لمجموعة إلـ (N-H) وان اغلب الترددات ذات القيمة الأعلى تكون عائدة للمركب (C) مما يناظرها في المركبات الأخرى ، وربما تعود هذه النتيجة إلى نفس السبب أعلاه حيث تعمل مجموعة النايترو على سحب الالكترونات مما تؤدي إلى حصول قصر في أطوال الأواصر وأكد هذا التفسير النتائج المحسوبة للشكل الهندسي حيث لوحظ بان اغلب الأواصر ولاسيما القريبة منها للمجموعة المعوضة تكون اقصر من نظيراتها في المركبين الأخريين وبهذا سوف يحصل زيادة قي قيم الترددات وعلى العكس من ذلك في حالة المجموعة المعوضة ($-CH_3$) في المركب (B) . كما وتم اعتماد برنامج الموباك (MOPAC 2000) لاستخدام طريقة الحساب التقريبية شبه التجريبية ألـــ(MINDO/3) لحساب حرارة التكوين ، عزم ثنائي القطب ، طاقة المدارات (E_{HOMO}, E_{LUMO}) وطاقة التأين . وقد وجد إن المركب (C) يمتلك اقل حرارة تكوين وأيضا اقل طاقة تأين أي يكون أسهل تأيناً .

Abstract

This study involved the adoption of the program (Gaussian 03) to use the method of calculation the total according to the theory of functions density (DFT) and style (B3LYP) and the use of al-Qaeda (STO-3G) for the purpose of the expense of dimensional geometric (lengths and angles bond) when the geometry of a balanced, charges, functions thermodynamic as well as account and classification of vibrational patterns belonging to the infrared spectrum and the number of (3N-6) for the three molecules derived from the ring (1,3,4-Thiadiazole) (symbolized by the acronym A, B, C). It was found that the compound-C have the highest value Entropy (S^0) and heat capacity (C_v), as demonstrated by observing the results that most of the atoms belonging to the compound-C be less electron density was

largely due to a nitro group substitute effect (-NO_2), which is working to withdrawing the electrons while the compound-B on the contrary.

This in turn shows the effect of a range Methyl group substitute (-CH3) on the electronic high pushing compared to the other two compounds. The higher frequencies values for the (N-H) stretch fundamental vibration mode, and most of the frequencies of higher value to be returned to the compound-C than their corresponding in other compounds, and may return this result to the same reason above where the group is working nitro to withdraw electrons, which lead to a palace in the lengths of bonds and affirmed this interpretation of calculated results on the geometry where it was noted that most of the bonds, especially nearby the group substitutes to be shorter than their counterparts in the two compounds the other two and this will get more valuable the values of frequencies and on the contrary in the case of substitutes for the group (-CH3) in the boat (B). Also, For (A, B and C) molecules the calculated some physical properties (ΔH_f (in kcal/mole), μ (in Debye) ,orbital energies (E_{HOMO}, E_{LUOMO}, in eV) and IP (in eV)) by using (semi-empirical method, MINDO/3 model) . The compound–C, it has less heats of formation, and easier ionization than compound-A and compound-B .

Keywords: *DFT study, 1,3,4-Thiadiazole ring, Thermodynamics functions, IR studies.*

Introduction

The resistance towards available drugs is rapidly becoming a major worldwide problem. The need to design new compounds to deal with this resistance has become one of the most important areas of research today. Thiadiazole is a versatile moiety that exhibits a wide variety of biological activities. Thiadiazole moiety acts as “hydrogen binding domain” and “two-electron donor system”[1].

It also acts as a constrained pharmacophore. Many drugs containing thiadiazole nucleus are available in the market such as acetazolamide, methazolamide, sulfamethazole, etc. Thiadiazole can act as the bio-isosteric replacement of the thiazole moiety. So it acts like third and fourth generation cephalosporins, hence can be used in antibiotic preparations [2-4]. Thiadiazole is a 5-membered ring system containing two nitrogen and one sulphur atom [5]. They occur in nature in four isomeric forms viz. 1,2,3-thiadiazole, 1,2,5-thiadiazole, 1,2,4-thiadiazole and 1,3,4-thiadiazole. The 1,3,4-thiadiazole isomer of thiadiazole series and its dihydro-derivatives provide a bulk of literature on thiadiazole [6]. A glance at the standard reference work shows that more work has been carried out on the 1,3,4-thiadiazole

than all other isomers combined. Members of this ring system have found their way into such diverse application as pharmaceuticals, oxidation inhibitors, cyanine dyes, & metal complexion agents [7-10].

Thiadiazoles are largely used as antibacterial [11], antifungal [12], antitumor [13,14], diuretic [15,16], antiepileptic [17], antiulcer [18] and antileukemia [19,20] agents. These compounds possess such interesting biological properties that may be conferred to them by their strong aromatic ring system [21].As ligands, they also provide many potential [22-25] binding sites for complexation and have obtained a diversified biological activity by the result of such chelation. It has been suggested [26] that the interaction of the metal ion with potentially biologically active compounds lead to destroy or greatly help to diminish [27-29] the role of bacteria-/virus-/cancer-associated organisms and therefore, represent a significant route for designing and establishing novel metal-based antibacterial, antiviral and anticancer therapies [30].

The aim of present work is to report the optimized geometries, charge, thermodynamic data and the fundamental vibration frequencies (3N-6) along with their assignments and the corresponding IR absorption intensities for each one of the three molecules (Fig. 1) by calculation based on the (DFT/B3LYP).

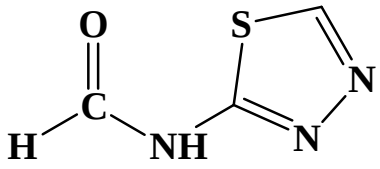
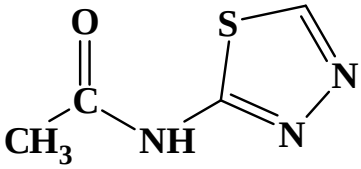
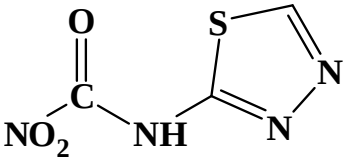
A	**B**	**C**
		
N-(1,3,4-thiadaizole-2-yl) formamide	N-(1,3,4-thiadaizole-2-yl)acetamide	1-nitro-N-(1,3,4-thiadaizole-2-yl)formamide

Fig 1: compounds A, B and C.

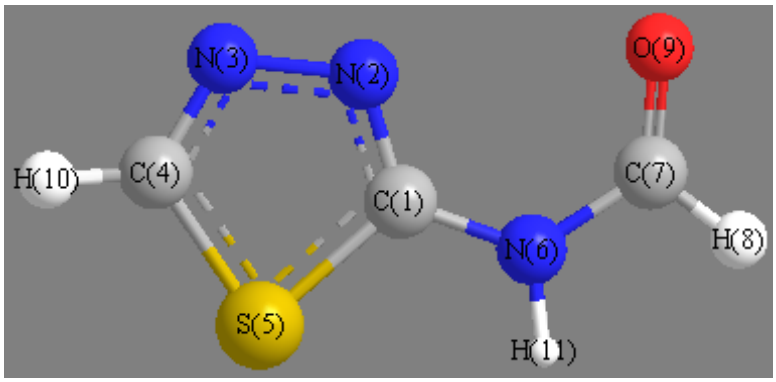
Results and Discussion

Geometrical parameter

Geometry was calculated for each molecule of a balanced three molecules studied (A, B, C), (bond lengths and bond angels), According to the results calculated and recorded in the (Table. 1), show that each one of a bond length (C_1–N_2, C_1–S_5, N_2–N_3, N_6–C_7) in compound-C smaller than their identical in compound-A and compound-B, and the bond angle value which is located the group substituted X, (X= H, CH_3, NO_2), ($<N_6C_7O_9$) and the bond angle value ($<N_2C_1S_5$) in compound-C bigger than its identical in compounds (A, B), whereas each one of the bond angles values ($<C_1N_6C_7$, $<C_1S_5C_4$, $<C_1N_2N_3$) in compound-C smaller than their identical in compounds (A, B), and all this might due to the group substituted effect (X) .

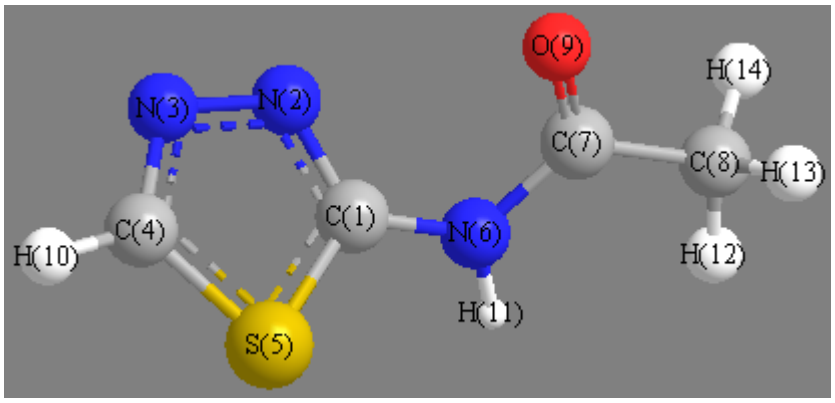
Table 1. Calculated geometric parameters (bond lengths in Angstrom and bond angles in degrees) of the Thiadiazole Ring compounds .

-A-



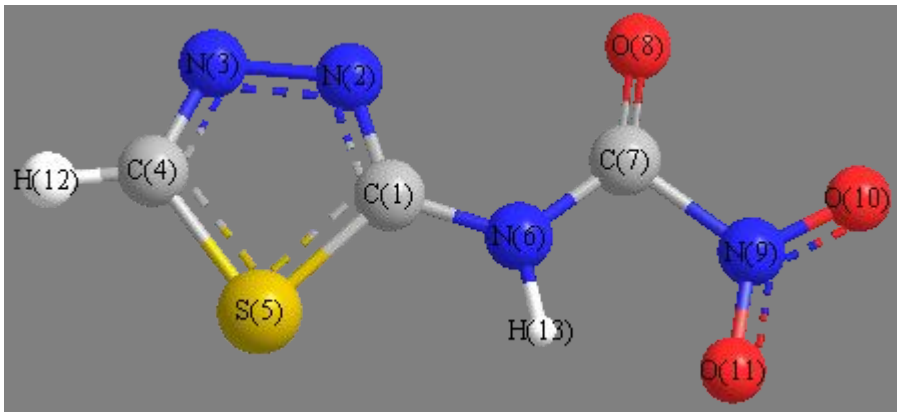
C_1N_2=1.306, C_1S_5=1.847, C_1N_6=1.381, N_2N_3=1.403, N_3C_4=1.299, C_4S_5=1.822, C_4H_{10}=1.077, N_6C_7=1.399, N_6H_{11}=1.010, C_7H_8=1. 100, C_7O_9=1.228, $<N_2C_1S_5$=114.3, $<N_2C_1N_6$=126.3, $<S_5C_1N_6$=119.2, $<C_1N_2N_3$=112.9, $<N_2N_3C_4$=114.2, $<N_3C_4S_5$=114.7, $<N_3C_4H_{10}$=124.5, $<S_5C_4H_{10}$=120.7, $<C_1S_5C_4$=83.6, $<C_1N_6C_7$=127.6, $<C_1N_6H_{11}$=116.7, $<C_7N_6H_{11}$=115.6, $<N_6C_7H_8$=110.2, $<N_6C_7O_9$=126.6, $<H_8C_7O_9$=123.0 .

-B-



C_1N_2=1.306, C_1S_5=1.852, C_1N_6=1.379, N_2N_3=1.403, N_3C_4=1.299, C_4S_5=1.822, C_4H_{10}=1.077, N_6C_7=1.411, N_6H_{11}=1.009, C_7C_8=1.517, C_7O_9=1.232, C_8H_{12}=1.096, C_8H_{13}=1.089, C_8H_{14}=1.096, <$N_2C_1S_5$=114.1, <$N_2C_1N_6$=127.0, <$S_5C_1N_6$=118.7, <$C_1N_2N_3$=113.0, <$N_2N_3C_4$=114.3, <$N_3C_4S_5$=114.7, <$N_3C_4H_{10}$=124.4, <$S_5C_4H_{10}$=120.7, <$C_1S_5C_4$=83.6, <$C_1N_6C_7$=127.6, <$C_1N_6H_{11}$=116.1, <$C_7N_6H_{11}$=116.2, <$N_6C_7C_8$=112.7, <$N_6C_7O_9$=123.5, <$C_8C_7O_9$=123.7, <$C_7C_8H_{12}$=110.9, <$C_7C_8H_{13}$=108.4, <$C_7C_8H_{14}$=111.5, <$H_{12}C_8H_{13}$=108.7, <$H_{12}C_8H_{14}$=108.1, <$H_{13}C_8H_{14}$=108.9 .

-C-



C_1N_2=1.305, C_1S_5=1.831, C_1N_6=1.385, N_2N_3=1.401, N_3C_4=1.300, C_4S_5=1.823, C_4H_{12}=1.077, N_6C_7=1.362, N_6H_{13}=1.017, C_7O_8=1.210, C_7N_9=1.595, N_9O_{10}=1.239, N_9O_{11}=1.267, <$N_2C_1S_5$=115.0, <$N_2C_1N_6$=125.2, <$S_5C_1N_6$=119.7, <$C_1N_2N_3$=112.7, <$N_2N_3C_4$=113.9, <$N_3C_4S_5$=114.7, <$N_3C_4H_{12}$=124.5, <$S_5C_4H_{12}$=120.7, <$C_1S_5C_4$=83.5, <$C_1N_6C_7$=126.0, <$C_1N_6H_{13}$=119.7, <$C_7N_6H_{13}$=114.2, <$N_6C_7O_8$=133.5, <$N_6C_7N_9$=107.2, <$O_8C_7N_9$=119.2, <$C_7N_9O_{10}$=116.3, <$C_7N_9O_{11}$=117.0, <$O_{10}N_9O_{11}$=126.6 .

Physical properties

The MOPAC computational packages (semi-empirical method , MINDO/3 model) employed to compute the some physical properties; heats of formation (ΔH_f, kcal.mol^{-1}), Dipole moments (μ in Debye), energies (eV) of the High Occupied Molecular Orbital (E_{HOMO}) and the Lower Unoccupied Molecular Orbital (E_{LUMO}) and according to Koopmans' theorem (the negative E_{HOMO} is equal to the ionization potential) the calculation has been ionization energies (eV) .

The shown this results (Table.2) that compound-C has lower heat of formation ΔH_f, (kcal/mol), due to the same previous reason, in addition to that compound-C has highest E_{HOMO} and lowest E_{LUMO} and ionization energy IP, (eV), which indicates that compound-C is easier ionization than compound-A and compound-B .

Table 2: Calculated ΔH_f (in kcal/mole), μ (in Debye) ,orbital energies (E_{HOMO}, E_{LUOM}, in eV) and IP (in eV) for the Thiodiazole Ring compounds .

Molecules	ΔH_f *(Kcal/mol)*	Dipole moment ,μ	E_{HOMO} *(eV)*	E_{LUMO} *(eV)*	IP *(eV)*
A	-43.260	3.079	-8.727	0.069	8.726
B	-57.582	2.587	-8.517	0.171	8.516
C	-85.024	4.351	-7.971	-0.689	7.971

The Charges

In a comparison between every nitrogen atom (N_2, N_3, N_6), sulfur atom and in addition to that (C_1, C_7) atoms in compound-A with their identical in compounds (B, C) is found that most the atoms above in compound-B has lower charge values (highest electronic density) than the atoms in compounds (A, C) (Table.3), whereas the compound-C has highest charge values (lower electronic density) than the atoms in compounds (A, B), may be the reason in that is the high pushing of electrons effect of the Methyl group ($-CH_3$) in compound-B comparing with nitro group ($-NO_2$) and hydrogen atom (-H) of other compounds (A, C), in the other

hand, the high withdrawing of electrons effect of the Nitro group (-NO_2) in compound-C comparing with methyl group (-CH_3) and hydrogen atom (-H) of other compounds (A, B) .

Table 3: Calculated charge for the Thiodiazole Ring compounds, A, B and C (See Table 1 for numbering) .

Atom Symbol	A	Atom Symbol	B	Atom Symbol	C
C_1	0.8327	C_1	0.8784	C_1	0.8112
N_2	-0.3719	N_2	-0.3952	N_2	-0.3307
N_3	-0.2211	N_3	-0.2088	N_3	-0.2598
C_4	0.2433	C_4	0.2323	C_4	0.2518
S_5	-0.2703	S_5	-0.2892	S_5	-0.2078
N_6	-0.9850	N_6	-1.0456	N_6	-1.0047
C_7	1.0826	C_7	1.1548	C_7	1.1689
H_8	-0.0449	C_8	-0.1207	O_8	-0.5528
O_9	-0.5957	O_9	-0.6140	N_9	0.7687
H_{10}	0.1033	H_{10}	0.1004	O_{10}	-0.5022
H_{11}	0.2269	H_{11}	0.2231	O_{11}	-0.5961
		H_{12}	0.0223	H_{12}	0.1130
		H_{13}	0.0422	H_{13}	0.3404
		H_{14}	0.0200		

Thermodynamics functions

The fundamental vibration frequencies for the (A, B, C) molecule along with the rotational constants, obtained in this study, where used to calculate the vibration and rotation contributions to the thermodynamic functions according to the statistical thermodynamic equations.

$$U_{vib}^{0} = \sum_{i=1}^{3N-6} \frac{RTX_i}{e^{X_i}-1} \quad ,,, \quad X_i = \frac{hc\bar{\nu}}{kT} = \frac{1.44\bar{\nu}}{T} \quad ,,, \quad U^{0}_{rot}=1.5RT$$

$$S_{vib}^{0} = R\sum_{i=1}^{3N-6}\left[\frac{X_i}{e^{X_i}-1} - \ln\left(1-e^{-X_i}\right)\right] \quad ,,, \quad S_{rot}^{0} = R\left[\frac{3}{2} + \ln\frac{8\pi^2\left(8\pi^2 I_X I_Y I_Z\right)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma\hbar^3}\right]$$

These two contributions along with the others contributions, for the translation, electronic, and nuclear motions, where used to calculate U^o, H^o, S^o, A^o, and G^o

thermodynamic functions . Thermodynamics functions standard and heat capacity for the studied molecules (A, B, C) where listed in Table.4.

From this (Table.4), It was shown that the G^0, A^0, U^0, H^0, have it are highest value for (B) molecule, whereas S^0, C_v, have it are highest value for (C) molecule and (C) molecules has lowest one for G^0, A^0, values, the deferent Thermodynamics functions values due to deferent substituted groups (X), viz, the pair electrons in nitrogen atom for nitro group are less bounded consequently have the more freely motion . Therefore, the (C) molecules has the higher S^o, The reverse sequence is shown for G^o and the (C) molecules has the lowest value .

Table 4: The calculated standard thermodynamics functions at 298.15^{o}K of the Thiodiazole Ring compounds .

Thermodynamic data	**A**	**B**	C
U^0 , (kcal/mol)	47.934	66.556	50.412
H^0 , (kcal/mol)	48.527	67.149	51.005
S^0 , (kcal mol^{-1} deg^{-1})	0.086	0.097	0.099
G^0 , (kcal/mol)	22.886	38.230	21.490
A^0 , (kcal/mol)	22.293	37.636	20.896
C_V, (kcal mol^{-1} deg^{-1})	0.024	0.030	0.033

The Vibration Spectra

DFT theory calculations shows that all the three molecules (A, B, C) belongs to the C_s point group and it are have planar symmetry (σ_h) . According to the group theory (From the character table), the compound-A is has (3N-6=27) fundamental vibration modes, [$\Gamma_{vib.}$=19 A´+ 8A˝], where the 19 A´ modes are in plane, $\Gamma_{in\ plane}$= 19 A´ , and the others 8A˝ are out of plane, $\Gamma_{out\ of\ plane}$= 8A˝. The compound-B is has (3N-6=36) fundamental vibration modes, [$\Gamma_{vib.}$=25A´+ 11A˝], where the 25 A´ modes are in plane, $\Gamma_{in\ plane}$= 25A´ , and the others 11A˝ are out of plane, $\Gamma_{out\ of\ plane}$= 11A˝. Whereas the compound-C is has (3N-6=33) fundamental vibration modes,

[$\Gamma_{vib.}$=23A´+ 10A˝], where the 23A´ modes are in plane, $\Gamma_{in\ plane}$= 23A´ , and the others 10A˝ are out of plane, $\Gamma_{out\ of\ plane}$= 10A˝. In addition to that all these modes (for molecules A, B, and C) are active in IR region and Raman simultaneously.

The fundamental vibration frequencies values, cm^{-1}, for each one of the three studied molecules (A, B, C) along with their assignments and the corresponding IR intensities, $km.mol^{-1}$, where listed in (Table.5) . From Table.4 it was shown that the frequency with the higher value is that of ν_1, (N-H) st. . Most the fundamental vibration frequencies for compound-C has highest value, Whereas compound-B has the lower value with the other two compounds comparison . Where,

The vibration frequencies values in plane symmetry (Ring (CH st.), C=O st., δ N-H, δRing) and the vibration frequencies values out of plane symmetry (γN-H, γC-H), it have highest value for compound-C, Whereas The vibration frequencies values in plane symmetry (Ring (CH st.), δRing) and the vibration frequencies values out of plane symmetry (γN-H, γC-H), it have lower value for compound-B, may be due to the substituted group (X) viz, the nitro group (-NO2) in compound-C is withdrawing electrons group , and this results in shortage of bond length, so this results increase in vibration frequency , and this opposed for methyl group in compound-B which act as group pushing of electrons .

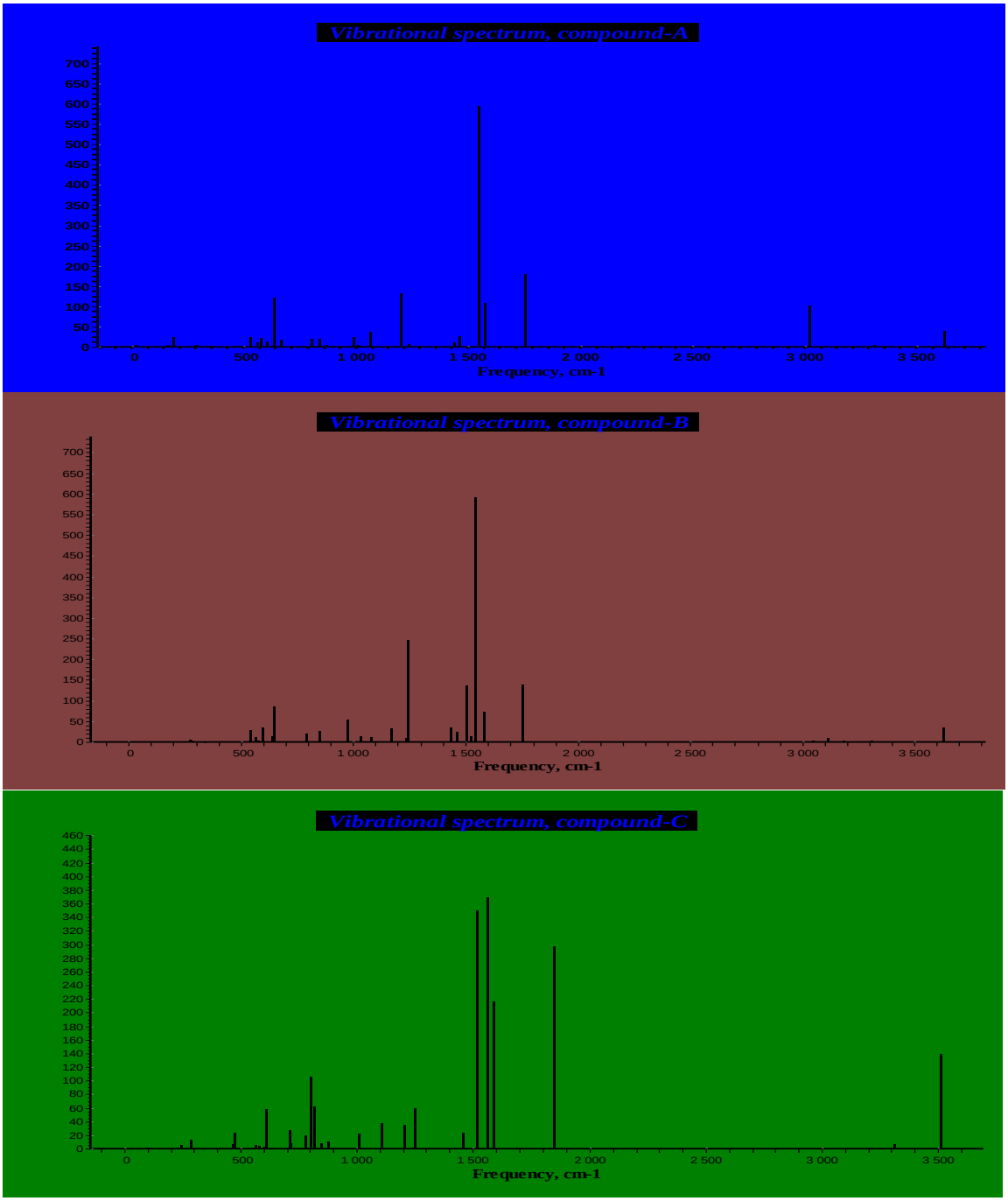
Table 5: The calculated fundamental vibration frequencies (ν in cm^{-1}) along with their assignments and the corresponding infrared absorption intensities (ir intensities in km. mol^{-1}) Thiodiazole Ring compounds, A, B and C .

No. of freq.	A		B		C	
	freq. cm^{-1}, (intensity, km mol^{-1})	Assignments	freq. cm^{-1}, (intensity, km mol^{-1})	Assignments	freq. cm^{-1}, (intensity, km mol^{-1})	Assignments
In plane, A´						
ν_1	3626 (40.35)	N-H st.	3636 (35.51)	N-H st	3523 (138.40)	N-H st.
ν_2	3316 (3.61)	Ring (CH st.)	3314 (3.14)	Ring (CH st.)	3318 (5.72)	Ring (C-H st.)
ν_3	3025 (102.41)	C-H st.	3189 (3.47)	CH_3 as. st.	1858 (296.50)	C=O st.
ν_4	1757 (178.60)	C=O st.	3119 (10.35)	CH_3 as. st.	1595 (216.89)	δ N-H

ν_5	1582 (106.95)	δ C-H + Ring (C=N st.)	3053 (4.53)	CH_3 s. st.	1571 (368.26)	(N=C-N) st.
ν_6	1553 (593.46)	δ C-H	1761 (138.25)	C=O st.	1524 (349.89)	δ N-H + N=O st.
ν_7	1467 (26.03)	Ring (C=N st.) + Ring (δ C-H)	1591 (73.01)	δ N-H	1461 (24.00)	Ring [N=C st. + δ C-H]
ν_8	1446 (12.29)	δ C-H	1553 (590.87)	δ N-H	1255 (59.73)	δ_s NO_2 + Ring (δ C-H)
ν_9	1243 (6.09)	Ring (δ C-H)	1530 (14.26)	δ_s CH_3	1246 (1.56)	Ring (δ C-H)
ν_{10}	1204 (131.22)	δ N-H	1508 (136.03)	δ_s CH_3	1210 (34.25)	Ring (δ C-H) + δ N-H
ν_{11}	1068 (38.28)	δ (CNC)	1468 (23.52)	Ring (N=CH) st.	1112 (36.69)	(C=NH-C) st.
ν_{12}	995 (24.13)	Ring (N-N st.) + δ N-H	1443 (32.82)	δ_s CH_3	1012 (21.68)	Ring [N-N st. + δ C-H] + δ N-H
ν_{13}	876 (4.56)	Ring (δ NNC)	1249 (246.91)	Ring (δ C-H)	883 (10.27)	Ring [(δ N=CH) + (δ N-N)]
ν_{14}	844 (20.39)	Ring (δ N=CH) + δ N-H	1242 (10.73)	Ring (δ C-H)	851 (7.86)	Ring (δ N=CH) + δ N-H
ν_{15}	670 (18.73)	Ring (δ NCS)	1177 (31.59)	δ N-H + Ring (δ C-H)	787 (19.51)	δ_s NO_2
ν_{16}	583 (22.73)	δ Ring	1087 (11.73)	ρ CH_3	715 (26.67)	Ring (δ C-H) + δ N-H
ν_{17}	532 (23.66)	δ C-H + δ N-H	1042 (14.20)	ρ CH_3	616 (58.16)	δ Ring
ν_{18}	293 (2.11)	Ring (δ C-S) + δ C=O	981 (53.71)	δ N-H + CH_3 deform	587 (4.23)	δ Ring + δ N-H
ν_{19}	167 (2.92)	ρ CHO + δ Ring	902 (2.19)	δ N-H + δ C-H	478 (23.67)	δ C=O + δ N-H + δ N=O
ν_{20}	-------	----------	857 (25.94)	Ring (δ N=CH)	349 (0.58)	δ C=O + δ N=O
ν_{21}	-------	----------	650 (14.68)	Ring (δ C-H)	293 (3.84)	δ N-H + Ring (δ S-CH)
ν_{22}	-------	----------	575 (11.04)	δ Ring	251 (4.34)	Ring (δ C-H) + δ C=O
ν_{23}	-------	----------	547 (27.65)	CH_3 deform	109 (1.10)	δ Ring + ρ NO_2
ν_{24}	-------	----------	347 (0.88)	CH_3 deform	-------	----------

ν_{25}	-------	----------	147 (1.76)	Ring (δ C-H) + δ CH_3	-------	----------
Out of plane, A″						
ν_{20}	1015 (2.74)	γ C-H	-------	----------	-------	----------
ν_{21}	804 (19.14)	Ring (γ C-H)	-------	----------	-------	----------
ν_{22}	641 (121.46)	γ N-H	-------	----------	-------	----------
ν_{23}	607 (14.35)	γ N-H	-------	----------	-------	----------
ν_{24}	565 (10.20)	Ring (γ N=CH)	-------	----------	823 (61.65)	γ N-H + Ring (γ C-H)
ν_{25}	347 (0.24)	γ C-H + γ N-H	-------	----------	808 (105.16)	Ring (γ C-H)
ν_{26}	193 (23.21)	γ C-H	801 (18.98)	Ring (γ C-H)	720 (7.28)	γ N-H
ν_{27}	28 (3.36)	γ N-H	797 (1.45)	Ring (γ C-H)	612 (2.00)	Ring (γ C=N) + γ N-H
ν_{28}	-------	----------	657 (86.06)	γ N-H + τ CH_3	569 (5.04)	γ Ring
ν_{29}	-------	----------	603 (36.18)	γ N-H	475 (6.11)	γ C-N + γ N-H
ν_{30}	-------	----------	587 (3.68)	γ Ring + ω CH_3	293 (12.51)	Ring (γ C-H) + γ N-H
ν_{31}	-------	----------	546 (17.20)	Ring (γ C-H) + τ CH_3	102 (1.49)	γ N-H + Ring (γ C-H)
ν_{32}	-------	----------	287 (3.10)	Ring (γ C-H) + γ N-H	65 (0.07)	Ring (γ C-H) + γ N=O
ν_{33}	-------	----------	280 (5.66)	γ N-H + Ring (γ C-H)	28 (0.39)	γ Ring + γ C=O
ν_{34}	-------	----------	94 (1.17)	τ CH_3	-------	----------
ν_{35}	-------	----------	52 (0.04)	CH_3 torsion	-------	----------
ν_{36}	-------	----------	13 (2.03)	CH_3 torsion	-------	----------

Where, st. stretching; δ, in plane binding; γ, out of plane binding; δ_s, scissoring; ρ, rock; τ, twist; ω, wagging .



Bob.2: The vibration spectrum of the compounds (A, B and C)

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