Thermodynamic functions and IR modes Calculation for newly Azo compounds by Using DFT Model

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الخلاصـــــة :-

تضمن البحث 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) لاثنتين من جزيئات الآزو الغـــير محضرة سابـــقاً (التي يرمز لها اختصاراً A , B) ، كـما وتم اعتماد برنامج الموباك (MOPAC 2000) لاستخدام طريقة الحساب التقريبية شبه التجريبية (PM3) لحساب حرارة التكوين ، عزم ثنائي القطب ، طاقة المدارات (HOMO, LUMO) وطاقة التأين . وقد وجد إن المركب (B) أكثر استقراراً لكونه يمتلك اقل حرارة تكوين وأيضا اقل انتروبي ويكون أسهل تأيناً ، كما تبين من خلال ملاحظة النتائج بان ذرات النتروجين العائدة للمركب (B) تكون أعلى كثافة الكترونية أي أكثر منح للالكترونات لذا نستنتج عند سلوكه كليكاند يكون معقدات أكثر استقرارا .كما أظهرت النتاج بان التردد الأعلى لكلا المركبين (A, B) يكون للمط الاهتزازي الأساسي لمجموعة إلـ (O-H) .

Abstract

Depended on (Gaussian 03) program for using Density Function Theory calculations (DFT/B3LYP) have been done after complete optimization of geometry on the newly azo (A, B) molecules . The geometric parameter (bond lengths and bond angles) , 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 two molecules where , also, The MOPAC Computational Packages (semi-empirical method , PM3 model) employed through out this study to compute the heats of formations, dipole moments, orbital energies (HOMO, LUMO) and ionization energies . The compound –B is more stability because it has less heats of formation and entropy , and easier ionization than compound-A , the shown results that each one nitrogen atom of compound-B highest electron densities than compound-A . The higher frequencies values for the (O-H) stretch fundamental vibration mode.

Keyword: DFT study, thermodynamic functions, IR studies.

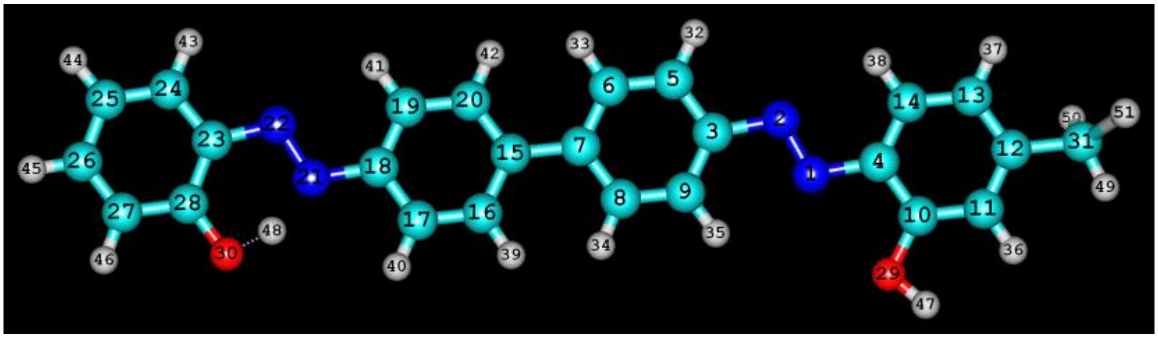
Introduction

Azo compounds, with tow phenyl rings separated by an azo (-N=N-) group, this molecules are a very important in research both fundamental and application.

Azo compounds have been used for a long time as dyes in industry [1]. In addition, azo compounds are used in analytical chemistry as indicators in pH, redox, or complexometric titration [2,3]. Some azo com- pounds have shown a good antibacterial activity [4,5]. The existence of an azo moiety in different types of compounds has caused them to show pesticidal activity [6]. Because of the good thermal stability of azo compound, one of the most important applications of azo compound is in the optical properties in applications such as optical recording medium [7-9], toner [10,11], ink-jet printing [12,13], and oil-soluble lightfast dyes [14]. Recently, azo metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements, and printing systems [8,10,15]. Metal azo complex dyes are used for DVD-R (digital versatile disc-recordable) as recording layer.

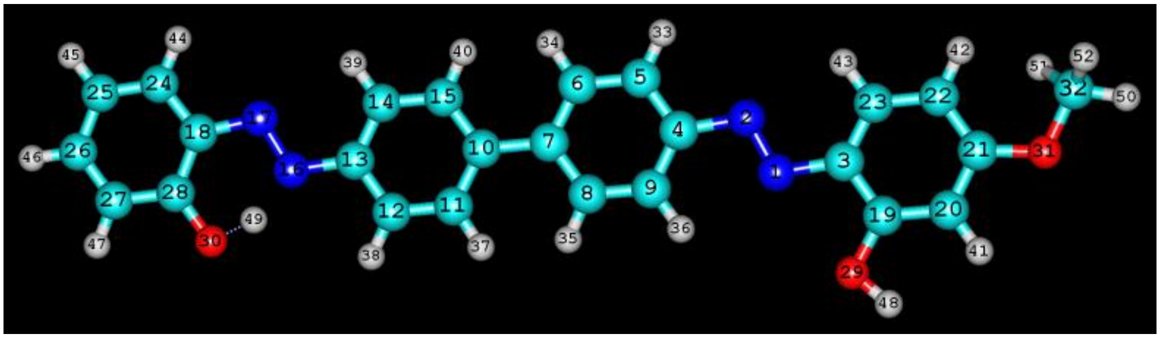
The aim of present work is to report the optimized geometries, heats of formations, dipole moments, orbital energies (HOMO, LUMO), ionization energies, charge, thermodynamic data and the fundamental vibration frequencies (3N-6) along with their assignments and the corresponding IR absorption intensities for each one of the tow molecules (Fig. 1) by calculation based on the (DFT/B3LYP) and (MINDO/3 model).

1-Compound –A



2-((*E*)-(4'-((*E*)-(2-hydroxyphenyl)diazenyl)biphenyl-4-yl)diazenyl)-5-methylphenol

2-Compound –B



2-((*E*)-(4'-((*E*)-(2-hydroxyphenyl)diazenyl)biphenyl-4-yl)diazenyl)-5-methoxyphenol

Fig 1: compounds A and B.

Results and Discussion

For the A and B molecules , the calculated geometric parameters (bond lengths and bond angels), According to the results of the calculated geometric parameters (table.1) , show that each one of a bond length (C_{11}–C_{12}, C_{12}–C_{13}) in compound-A smaller than their identical in compound-B (C_{20}–C_{21}, C_{21}–C_{22}), and the bond angle value which is located the group substituted in compound-A ($<C_{11}C_{12}C_{13}$) bigger than identical in compound-B ($<C_{20}C_{21}C_{22}$), whereas each one of the bond angles values ($<C_{13}C_{12}C_{31}$, $<N_2N_1C_4$) in compound-A smaller than their identical in compound-B ($<C_{22}C_{21}O_{31}$, $<N_2N_1C_3$), and all this might due to Resonance effect of Methoxy group which is stronger pushing of electrons than Methyl group. And the calculated some physical properties; heats of formation (ΔH_f, kcal.mol^{-1}), Dipole moments (μ in Debye), energies (eV) of the High Occupied Molecular Orbital (HOMO) and the Lower Unoccupied Molecular Orbital (LUMO), ionization energies (eV), the shown this results (table.2) that compound-B has lower heat of formation ΔH_f, (kcal/mol), that means it is more stability than compound-A, due to the same previous reason, in addition to that compound-B has highest E_{HOMO} and lowest E_{LUMO} and ionization energy IP, (eV), which indicates that compound-B is easier ionization than compound-A .
The results of the calculated thermodynamics data (Table.3), show the entropy value (S^0) less to compound-B , and it has highest heat capacity value, and which agree with the results of the calculated heat of formation, the reason as it is mentioned before.

In a comparison between every nitrogen atom in compound-A with their identical in compound-B is found that all the nitrogen atoms in compound-B (N_1, N_2, N_{21}, N_{22}) has lower charge values (highest electronic density) than the nitrogen atoms in compound-A (N_1, N_2, N_{16}, N_{17}) (Table.4), the reason of this due to the high pushing of electrons effect of the Methoxy group comparing with Methyl group, so we can conclude compound-B form complexes more stability than compound-A because it has atoms give more electrons.

The compound-A belongs to the C_s symmetry point group and it is has (3N-6=147) fundamental vibration modes, whereas compound-B belong to the C_1 symmetry point group and it is has (3N-6=150) fundamental vibration modes . From the character table, it is shown that all the modes have the (A′, A″) symmetry for compound A and the (A) symmetry for compound B . The frequency values for all of these modes along with their assignments and the corresponding IR absorption intensities for the A and B compounds where listed in table 5 and 6 respectively.

From these two tables it was shown that the frequency with the higher value is that of ν_1, (O-H) st.; calculated with about the same value for the tow molecules . The next higher frequency values where these of the (C-H) stretch fundamental vibrations . The (CH_3 st., ν_3, ν_{19}) and (CH_3 sciss., ν_{29}) frequencies values in compound-A bigger than its identical in compound-B (ν_{15}, ν_{19}) and (ν_{29}) respectively .

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

Geometric parameter	Compound -A-	Geometric parameter	Compound -B-
N_1– N_2	1.350	N_1– N_2	1.352
N_1 – C_4	1.487	N_1 – C_3	1.481
N_2 – C_3	1.496	N_2 – C_4	1.495
C_3 – C_5	1.419	C_3 – C_{19}	1.441
C_3 – C_9	1.421	C_3 – C_{23}	1.418
C_4 – C_{10}	1.436	C_4 – C_5	1.419
C_4 – C_{14}	1.420	C_4 – C_9	1.421
C_5 – C_6	1.403	C_5 – C_6	1.402
C_5 – H_{32}	1.099	C_5 – H_{33}	1.099
C_6 – C_7	1.425	C_6 – C_7	1.425
C_6 – H_{33}	1.096	C_6 – H_{34}	1.096
C_7 – C_8	1.428	C_7 – C_8	1.428
C_7 – C_{15}	1.513	C_7 – C_{10}	1.512
C_8 – C_9	1.400	C_8 – C_9	1.400
C_8 – H_{34}	1.096	C_8 – H_{35}	1.096
C_9 – H_{35}	1.099	C_9 – H_{36}	1.099
C_{10} – C_{11}	1.423	C_{10} – C_{11}	1.426
C_{10} – O_{29}	1.408	C_{10} – C_{15}	1.428
C_{11}– C_{12}	1.408	C_{11}– C_{12}	1.401
C_{11} – H_{36}	1.099	C_{11} – H_{37}	1.096
C_{12} – C_{13}	1.423	C_{12} – C_{13}	1.420
C_{12} – C_{31}	1.539	C_{12} – H_{38}	1.098
C_{13} – C_{14}	1.400	C_{13} – C_{14}	1.421
C_{13} – H_{37}	1.097	C_{13} – N_{16}	1.465
C_{14} – H_{38}	1.099	C_{14} – C_{15}	1.400
C_{15} – C_{16}	1.426	C_{14} – H_{39}	1.098
C_{15} – C_{20}	1.428	C_{15} – H_{40}	1.096
C_{16} – C_{17}	1.401	N_{16} – N_{17}	1.364
C_{16} – H_{39}	1.096	N_{17} – C_{18}	1.452
C_{17} – C_{18}	1.420	C_{18} – C_{24}	1.431
C_{17} – C_{40}	1.098	C_{18} – C_{28}	1.460
C_{18} – C_{19}	1.421	C_{19} – C_{20}	1.413
C_{18} – N_{21}	1.465	C_{19} – O_{29}	1.408
C_{19} – C_{20}	1.400	C_{20} – C_{21}	1.422
C_{19} – H_{41}	1.098	C_{20} – H_{41}	1.098
C_{20} – H_{42}	1.096	C_{21} – C_{22}	1.428
N_{21} – N_{22}	1.364	C_{21} – C_{31}	1.416

$N_{21}-H_{48}$	1.451	$C_{22}-C_{23}$	1.400
$C_{22}-C_{23}$	1.431	$C_{22}-H_{42}$	1.094
$C_{23}-C_{24}$	1.460	$C_{23}-H_{43}$	1.099
$C_{23}-C_{28}$	1.392	$C_{24}-C_{25}$	1.392
$C_{24}-C_{25}$	1.099	$C_{24}-H_{44}$	1.099
$C_{24}-H_{43}$	1.429	$C_{25}-C_{26}$	1.429
$C_{25}-C_{26}$	1.097	$C_{25}-H_{45}$	1.097
$C_{25}-H_{44}$	1.392	$C_{26}-C_{27}$	1.392
$C_{26}-C_{27}$	1.099	$C_{26}-H_{46}$	1.099
$C_{26}-H_{45}$	1.442	$C_{27}-C_{28}$	1.442
$C_{27}-C_{28}$	1.097	$C_{27}-H_{47}$	1.097
$C_{27}-H_{46}$	1.364	$C_{28}-O_{30}$	1.364
$C_{28}-O_{30}$	1.027	$O_{29}-H_{48}$	1.027
$O_{29}-H_{47}$	1.100	$O_{31}-C_{32}$	1.476
$O_{30}-H_{48}$	1.103	$C_{32}-H_{50}$	1.106
$C_{31}-H_{49}$	1.103	$C_{32}-H_{51}$	1.110
$C_{31}-H_{50}$	1.095	$C_{32}-H_{52}$	1.110
$C_{31}-H_{51}$	1.092	$O_{30}-H_{49}$	1.095
$<N_2N_1C_4$	108.6	$<N_2N_1C_3$	109.3
$<N_1N_2C_3$	115.7	$<N_1N_2C_4$	108.5
$<N_2C_3C_5$	125.6	$<N_1C_3C_{19}$	115.8
$<N_2C_3C_9$	115.8	$<N_1C_3C_{23}$	125.6
$<C_5C_3C_9$	125.3	$<N_2C_4C_5$	115.8
$<N_1C_4C_{10}$	118.9	$<N_2C_4C_9$	125.4
$<N_1C_4C_{14}$	120.5	$<C_{19}C_3C_{23}$	118.6
$<C_{10}C_4C_{14}$	119.0	$<C_3C_{19}C_{20}$	119.8
$<C_3C_5C_6$	120.2	$<C_3C_{19}O_{29}$	117.2
$<C_3C_5H_{32}$	118.6	$<C_3C_{23}C_{22}$	122.0
$<C_6C_5H_{32}$	118.8	$<C_3C_{23}H_{43}$	117.4
$<C_5C_6C_7$	119.5	$<C_5C_4C_9$	118.8
$<C_5C_6H_{33}$	117.5	$<C_4C_5C_6$	120.5
$<C_7C_6H_{33}$	121.0	$<C_4C_5H_{33}$	118.9
$<C_6C_7C_8$	117.6	$<C_4C_9C_8$	120.3
$<C_6C_7C_{15}$	120.6	$<C_4C_9H_{36}$	118.6
$<C_8C_7C_{15}$	121.4	$<C_6C_5H_{33}$	120.5
$<C_7C_8C_9$	118.4	$<C_5C_6C_7$	121.5
$<C_7C_8H_{34}$	120.1	$<C_5C_6H_{34}$	118.4
$<C_9C_8H_{34}$	117.2	$<C_7C_6H_{34}$	120.1
$<C_3C_9C_8$	121.4	$<C_6C_7C_8$	117.2
$<C_3C_9C_{35}$	121.3	$<C_6C_7C_{10}$	121.4
$<C_8C_9H_{35}$	121.7	$<C_8C_7C_{10}$	121.4
$<C_4C_{10}C_{11}$	119.9	$<C_7C_8C_9$	121.7
$<C_4C_{10}O_{29}$	121.5	$<C_7C_8H_{35}$	119.9

$<C_{11}C_{10}O_{29}$	121.4	$<C_{7}C_{10}C_{11}$	121.5
$<C_{10}C_{11}C_{12}$	118.4	$<C_{7}C_{10}C_{15}$	121.4
$<C_{10}C_{11}H_{36}$	121.2	$<C_{9}C_{8}H_{35}$	118.4
$<C_{12}C_{11}H_{36}$	123.0	$<C_{8}C_{9}H_{36}$	121.2
$<C_{11}C_{12}C_{13}$	120.9	$<C_{11}C_{10}C_{15}$	117.1
$<C_{11}C_{12}C_{31}$	119.0	$<C_{10}C_{11}C_{12}$	121.7
$<C_{13}C_{12}C_{31}$	103.0	$<C_{10}C_{11}H_{37}$	120.0
$<C_{12}C_{13}C_{14}$	120.0	$<C_{10}C_{15}C_{14}$	121.8
$<C_{12}C_{13}C_{37}$	119.2	$<C_{10}C_{15}H_{40}$	119.9
$<C_{14}C_{13}C_{37}$	120.7	$<C_{12}C_{11}H_{37}$	118.3
$<C_{4}C_{14}C_{13}$	120.1	$<C_{11}C_{12}C_{13}$	120.2
$<C_{4}C_{14}H_{38}$	120.6	$<C_{11}C_{12}H_{38}$	120.4
$<C_{13}C_{14}H_{38}$	119.4	$<C_{13}C_{12}H_{38}$	119.4
$<C_{7}C_{15}C_{16}$	110.9	$<C_{12}C_{13}C_{14}$	119.2
$<C_{7}C_{15}C_{20}$	110.5	$<C_{12}C_{13}N_{16}$	117.2
$<C_{16}C_{15}C_{20}$	110.5	$<C_{14}C_{13}N_{16}$	123.6
$<C_{15}C_{16}C_{17}$	120.0	$<C_{13}C_{14}C_{15}$	120.0
$<C_{15}C_{16}H_{39}$	121.4	$<C_{13}C_{14}H_{39}$	118.7
$<C_{17}C_{16}H_{39}$	117.1	$<C_{13}N_{16}N_{17}$	113.6
$<C_{16}C_{17}C_{18}$	121.7	$<C_{15}C_{14}H_{39}$	121.3
$<C_{16}C_{17}H_{40}$	120.1	$<C_{14}C_{15}H_{40}$	118.3
$<C_{18}C_{17}H_{40}$	121.8	$<N_{16}N_{17}C_{18}$	109.4
$<C_{17}C_{18}C_{19}$	119.9	$<N_{17}C_{18}C_{24}$	116.4
$<C_{17}C_{18}N_{21}$	118.3	$<N_{17}C_{18}C_{28}$	123.8
$<C_{19}C_{18}N_{21}$	120.2	$<C_{24}C_{18}C_{28}$	119.8
$<C_{18}C_{19}N_{20}$	120.4	$<C_{18}C_{24}C_{25}$	120.7
$<C_{18}C_{19}H_{41}$	119.4	$<C_{18}C_{24}H_{44}$	117.9
$<N_{20}C_{19}H_{41}$	119.2	$<C_{18}C_{28}C_{27}$	117.9
$<C_{15}N_{20}C_{19}$	117.2	$<C_{18}C_{28}C_{30}$	121.9
$<C_{15}N_{20}H_{42}$	123.6	$<C_{20}C_{19}O_{29}$	123.0
$<C_{19}N_{20}H_{42}$	120.0	$<C_{19}C_{20}C_{21}$	120.4
$<C_{18}N_{21}N_{22}$	118.7	$<C_{18}C_{20}H_{41}$	120.6
$<N_{21}N_{22}C_{23}$	113.5	$<C_{19}O_{29}H_{48}$	103.0
$<N_{22}C_{23}C_{24}$	121.3	$<C_{21}C_{20}H_{41}$	119.0
$<N_{22}C_{23}C_{28}$	118.3	$<C_{20}C_{21}C_{22}$	119.9
$<C_{24}C_{23}C_{28}$	109.4	$<C_{20}C_{21}C_{31}$	113.9
$<C_{23}C_{24}C_{25}$	116.4	$<C_{22}C_{21}C_{31}$	126.2
$<C_{23}C_{24}H_{43}$	123.8	$<C_{21}C_{22}C_{23}$	119.3
$<C_{25}C_{24}H_{43}$	119.8	$<C_{21}C_{22}H_{42}$	120.9
$<C_{24}C_{25}C_{26}$	120.7	$<C_{21}O_{31}C_{32}$	113.1
$<C_{24}C_{25}H_{44}$	117.9	$<C_{23}C_{22}H_{42}$	119.8
$<C_{26}C_{25}H_{44}$	117.9	$<C_{22}C_{23}H_{43}$	120.6
$<C_{25}C_{26}C_{27}$	121.9	$<C_{25}C_{24}H_{44}$	121.4

$<C_{25}C_{26}H_{45}$	121.4	$<C_{24}C_{25}C_{26}$	119.7
$<C_{27}C_{26}H_{45}$	119.7	$<C_{24}C_{25}H_{45}$	120.5
$<C_{26}C_{27}C_{28}$	120.5	$<C_{26}C_{25}H_{45}$	119.8
$<C_{26}C_{27}H_{46}$	119.8	$<C_{25}C_{26}C_{27}$	121.5
$<C_{28}C_{27}H_{46}$	121.5	$<C_{25}C_{26}H_{46}$	119.1
$<C_{23}C_{28}C_{27}$	119.1	$<C_{27}C_{26}H_{46}$	119.4
$<C_{23}C_{28}O_{30}$	119.4	$<C_{23}C_{27}C_{28}$	120.4
$<C_{27}C_{28}O_{30}$	120.4	$<C_{26}C_{27}H_{47}$	121.3
$<C_{10}C_{29}H_{47}$	121.3	$<C_{28}C_{27}H_{47}$	118.2
$<C_{28}O_{30}H_{48}$	118.2	$<C_{27}C_{28}O_{30}$	120.2
$<C_{12}C_{31}H_{49}$	120.2	$<C_{28}O_{30}H_{49}$	100.5
$<C_{12}C_{31}H_{50}$	100.5	$<O_{31}C_{32}H_{50}$	105.3
$<C_{12}C_{31}H_{51}$	108.5	$<O_{31}C_{32}H_{51}$	112.1
$<H_{49}C_{31}H_{50}$	108.5	$<O_{31}C_{32}H_{52}$	112.1
$<H_{49}C_{31}H_{51}$	107.7	$<H_{50}C_{32}H_{51}$	109.1
		$<H_{50}C_{32}H_{51}$	109.1
		$<H_{51}C_{32}H_{52}$	109.1

Table 2. Calculated heats of formation (in kcal/mole), dipole moments (in Debye), orbital energies (HOMO,LUOMO, in eV) and ionization energies (IP, in eV) for Azo compounds .

Parameter	**Compound -A**	**Compound -B**
ΔH_f (kcal/mol)	83.925	54.846
Dipole moment (μ in Debye)	3.524	4.501
HOMO energies (eV)	-8.688	-8.654
LUMO energies (eV)	1.211	1.196
Ionization potential IP, (eV)	8.688	8.653

Table 3. The calculated standard thermodynamics functions at 298.15^o K of the Azo compounds .

Thermodynamic Data	**Compound -A**	**Compound –B**
U^0 (kcal/mol)	277.223	280.237
H^0 (kcal/mol)	277.815	280.829
S^0 (kcal mol^{-1} deg^{-1})	182.051	181.938
G^0 (kcal/mol)	-54000	-53964
A^0 (kcal/mol)	-54001	-53965
C_V (kcal mol^{-1} deg^{-1})	97.107	100.473

Table 4. Calculated charge for the Azo compounds (See Table 1 for numbering) .

A- COMPOUND				**B-COMPOUND**			
Atom Symb.	Charge	Atom Symb.	Charge	Atom Symb.	Charge	Atom Symb.	Charge
N_1	-0.1191	C_{27}	-0.0986	N_1	-0.1212	C_{27}	-0.0987
N_2	-0.1282	C_{28}	0.0979	N_2	-0.1337	C_{28}	0.0977
C_3	0.0554	O_{29}	-0.1939	C_3	0.0300	O_{29}	-0.1939
C_4	0.0356	O_{30}	-0.2282	C_4	0.0554	O_{30}	-0.2285
C_5	-0.0735	C_{31}	-0.2230	C_5	-0.0746	O_{31}	-0.1570
C_6	-0.0761	H_{32}	0.0908	C_6	-0.0765	C_{32}	-0.1220
C_7	-0.0015	H_{33}	0.0805	C_7	-0.0027	H_{33}	0.0895
C_8	-0.0749	H_{34}	0.0807	C_8	-0.0753	H_{34}	0.0797
C_9	-0.0766	H_{35}	0.1037	C_9	-0.0774	H_{35}	0.0800
C_{10}	0.0898	H_{36}	0.0682	C_{10}	0.0009	H_{36}	0.1031
C_{11}	-0.1125	H_{37}	0.0781	C_{11}	-0.0740	H_{37}	0.0835
C_{12}	0.0147	H_{38}	0.1015	C_{12}	-0.0762	H_{38}	0.0889
C_{13}	-0.0921	H_{39}	0.0837	C_{13}	0.0669	H_{39}	0.1022
C_{14}	-0.0738	H_{40}	0.0892	C_{14}	-0.0765	H_{40}	0.0835
C_{15}	0.0007	H_{41}	0.1025	C_{15}	-0.0733	H_{41}	0.0767
C_{16}	-0.0737	H_{42}	0.0837	N_{16}	-0.1764	H_{42}	0.0785
C_{17}	-0.0761	H_{43}	0.0905	N_{17}	-0.1079	H_{43}	0.1026
C_{18}	0.0674	H_{44}	0.0792	C_{18}	0.0182	H_{44}	0.0903
C_{19}	-0.0763	H_{45}	0.0834	C_{19}	0.0922	H_{45}	0.0790
C_{20}	-0.0730	H_{46}	0.0860	C_{20}	-0.1262	H_{46}	0.0831
N_{21}	-0.1765	H_{47}	0.2047	C_{21}	0.0939	H_{47}	0.0858
N_{22}	-0.1076	H_{48}	0.2463	C_{22}	-0.1148	H_{48}	0.2052
C_{23}	0.0184	H_{49}	0.0802	C_{23}	-0.0700	H_{49}	0.2463
C_{24}	-0.0683	H_{50}	0.0860	C_{24}	-0.0684	H_{50}	0.0964
C_{25}	-0.0936	H_{51}	0.0860	C_{25}	-0.0938	H_{51}	0.0887
C_{26}	-0.0677			C_{26}	-0.0679	H_{52}	0.0887

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}) for the A molecule .

No. of Freq.	**Freq.** cm^{-1}	**Intensity** km mol^{-1}	**Assignments**
In plane, A′			
ν_1	3714	5.6618	(O-H) st.
ν_2	3485	0.2568	Ring (C-H) st.
ν_3	3484	1.4594	CH_3 st.
ν_4	3482	20.3900	Ring (C-H) st.
ν_5	3479	16.1540	Hydroxybenzene (C-H) st.
ν_6	3479	4.9932	Ring (C-H) st.
ν_7	3476	1.5379	Ring (C-H) st.
ν_8	3472	9.7005	Hydroxymethylbenzene (C-H) st.
ν_9	3469	10.1187	Hydroxybenzene (C-H) st.
ν_{10}	3466	5.5586	Ring (C-H) st.
ν_{11}	3463	4.1486	Ring (C-H) st.
ν_{12}	3459	0.2515	Ring (C-H) st.
ν_{13}	3458	2.6425	Ring (C-H) st.
ν_{14}	3456	2.1345	Hydroxymethylbenzene (C-H) st.
ν_{15}	3456	7.9894	Hydroxybenzene (C-H) st.
ν_{16}	3454	0.2343	Ring (C-H) st.
ν_{17}	3447	2.4926	Hydroxybenzene (C-H) st.
ν_{18}	3434	0.8622	Ring (C-H) st.
ν_{19}	3303	0.5035	CH_3 st.
ν_{20}	2619	81.1289	(O-H) st.
ν_{21}	1881	104.8377	δ(O-H) + Ring (δCCC)
ν_{22}	1738	100.3480	δ-Hydroxybenzene
ν_{23}	1732	65.2590	δ-Hydroxymethylbenzene + δ-Ring
ν_{24}	1731	5.0362	δ-Ring + δ-Hydroxymethylbenzene
ν_{25}	1722	33.1666	δ(O-H) + Ring (δCCC)
ν_{26}	1710	2.5669	Ring (δCH)
ν_{27}	1695	2.0157	Ring (δCH)
ν_{28}	1677	21.4059	δ-Ring
ν_{29}	1672	22.2003	CH_3scis.
ν_{30}	1637	37.2929	δ-Hydroxybenzene
ν_{31}	1634	3.4880	δ-Ring
ν_{32}	1625	3.7556	δ-Hydroxymethylbenzene
ν_{33}	1600	55.1361	δ-Ring
ν_{34}	1579	68.7489	δ-Hydroxybenzene
ν_{35}	1543	65.7152	δ-Hydroxymethylbenzene + δ-Ring
ν_{36}	1535	46.8499	δ-Hydroxybenzene + δ-Ring
ν_{37}	1532	16.9868	δ-Hydroxybenzene + δ-Ring
ν_{38}	1491	50.6271	δ-Ring
ν_{39}	1466	36.6582	δ(O-H) + δ-Ring
ν_{40}	1435	20.8787	δ-Hydroxybenzene + δ(N=N)
ν_{41}	1415	14.3420	δ-Ring + δ(N=N)

ν_{42}	1403	9.3215	δ-Ring
ν_{43}	1394	64.1438	δ-Hydroxymethylbenzene
ν_{44}	1385	24.3654	δ-Hydroxymethylbenzene
ν_{45}	1380	5.4003	δ-Ring + δ(N=N)
ν_{46}	1353	7.4277	δ-Ring
ν_{47}	1349	63.7841	δ-Ring
ν_{48}	1339	6.4088	δ-Ring + δ(N=N)
ν_{49}	1336	141.6631	Ring (δCCC) + δ(O-H) + δ(N=N)
ν_{50}	1329	35.1281	δ-Ring + δ(N=N) + δ(O-H)
ν_{51}	1316	55.2878	δ-Ring + δ(N=N) + δ(O-H)
ν_{52}	1300	63.5003	δ-Hydroxybenzene + δ-Ring
ν_{53}	1288	25.1431	Ring (δCH) + δ(O-H)
ν_{54}	1279	24.3582	δ-Ring + δ(O-H)
ν_{55}	1257	27.9144	δ-Ring + δ(O-H)
ν_{56}	1251	116.6396	δ-Ring + δ(O-H)
ν_{57}	1235	2.1758	δ-Ring
ν_{58}	1229	24.9266	δ-Hydroxymethylbenzene
ν_{59}	1207	189.7887	δ-Hydroxybenzene + δ(N=N)
ν_{60}	1202	50.8668	δ-Ring + δ(O-H)
ν_{61}	1190	3.6971	δ-Ring
ν_{62}	1183	265.7362	δ-Hydroxybenzene + δ(N=N)
ν_{63}	1176	8.2524	Ring (δCH)
ν_{64}	1151	53.0147	Ring (δCH) + δ(C-N) + δ(O-H)
ν_{65}	1100	20.1831	ρCH_3 + δ(O-H) + Ring (δCH)
ν_{66}	1084	13.5376	Ring (δCH)
ν_{67}	1081	11.2942	δ-Ring
ν_{68}	1064	2.0926	δ-Ring
ν_{69}	1052	17.0718	δ-Ring
ν_{70}	997	1.8548	δ-CH_3 + Ring (δCH)
ν_{71}	993	5.7769	δ(N=N) + Ring (δCH) + δ(O-H)
ν_{72}	936	3.3940	δ(N=N) + Ring (δCH)
ν_{73}	905	25.7455	Ring (δCCC) + Ring (δCH) + δ(N=N)
ν_{74}	838	35.7639	Ring (δCH) + δ(N=N)
ν_{75}	805	1.0317	Ring (δCH) + δ(O-H) + δ(N=N)
ν_{76}	757	3.3802	Ring (δCCC) + δ-CH_3
ν_{77}	747	12.8726	Ring (δCH) + δ-CH_3
ν_{78}	678	0.4546	Ring (δCH)
ν_{79}	677	0.6464	δ-Ring + δ(O-H)
ν_{80}	658	0.0053	δ-Ring
ν_{81}	608	13.1065	Ring (δCH)
ν_{82}	586	19.2956	δ-Ring + δ(N=N) + δ(O-H)
ν_{83}	577	19.0588	δ-Ring + δ(O-H) + δ(N=N)
ν_{84}	548	25.5553	δ(O-H) + δ(N=N) + δ-Ring
ν_{85}	529	5.1969	δ-CH_3 + δ-Ring + δ(O-H)
ν_{86}	515	5.4754	Ring (δCH) + δ(O-H)
ν_{87}	487	2.7418	δ(O-H) + Ring (δCH)
ν_{88}	454	12.3881	Ring (δCH) + δ(O-H) + δ-CH_3

ν_{89}	407	3.4041	δ-Ring + δ(O-H)
ν_{90}	384	1.3995	δ-Ring + δ-CH_3
ν_{91}	306	0.7707	δ-CH_3 + δ-Ring + δ(O-H)
ν_{92}	294	2.9114	δ-CH_3 + δ-Ring + δ(O-H)
ν_{93}	230	1.1195	δ(O-H) + δ-Ring
ν_{94}	212	2.2970	Ring (δCH) + δ(O-H)
ν_{95}	128	0.9081	δ(O-H) + δ-Ring
ν_{96}	117	0.3728	δ-Ring + δ-CH_3
ν_{97}	55	0.1792	δ-Ring + δ(O-H)
ν_{98}	26	0.2116	δ-CH_3 + δ(O-H) + δ-Ring
Out of plane, A″			
ν_{99}	1669	3.9395	ωCH_3
ν_{100}	1565	9.5390	ωCH_3
ν_{101}	1184	85.5990	γ(O-H)
ν_{102}	1142	6.5679	τCH_3
ν_{103}	1045	0.1767	Ring (γCH)
ν_{104}	1040	0.0104	Ring (γCH)
ν_{105}	1033	0.2637	Ring (γCH)
ν_{106}	1030	0.6673	Ring (γCH)
ν_{107}	1020	0.3843	Ring (γCH)
ν_{108}	1015	0.5004	γ-Ring
ν_{109}	1014	0.5891	Ring (γCH)
ν_{110}	904	2.5361	Ring (γCH)
ν_{111}	900	1.3292	Ring (γCH)
ν_{112}	896	0.1268	Ring (γCH)
ν_{113}	888	0.1573	Ring (γCH)
ν_{114}	878	3.8539	Ring (γCH)
ν_{115}	870	54.2377	Ring (γCH)
ν_{116}	864	13.2858	Ring (γCH)
ν_{117}	796	30.6621	Ring (γCH)
ν_{118}	774	0.0555	Ring (γCH)
ν_{119}	760	8.0183	γ-Ring
ν_{120}	751	0.2556	Ring (γCH) + γ-CH_3
ν_{121}	744	0.0159	γ-Ring
ν_{122}	600	0.0840	Ring (γCH) + τCH_3
ν_{123}	574	0.0073	Ring (γCH)
ν_{124}	559	0.0587	Ring (γCH)
ν_{125}	528	2.5374	γ-Ring
ν_{126}	498	46.2411	γ(O-H)
ν_{127}	477	18.3269	γ(O-H) + γ-Ring
ν_{128}	461	13.8353	γ-Ring
ν_{129}	424	0.4870	Ring (γCH)
ν_{130}	413	0.5130	Ring (γCH)
ν_{131}	410	0.9710	γ-Ring
ν_{132}	362	0.8974	γ-Ring + γ-CH_3 + γ(O-H)
ν_{133}	330	1.0525	γ(N=N) + Ring (γCH) + γ(O-H)
ν_{134}	302	0.3722	γ(N=N) + γ-Ring

ν_{135}	217	0.9940	γ(N=N) + γ-Ring
ν_{136}	215	0.0225	γ-Hydroxymethylbenzene
ν_{137}	207	0.0118	γ-Hydroxybenzene
ν_{138}	169	0.0015	γ(N=N) + γ-CH_3 + Ring (γCH) + γ(O-H)
ν_{139}	140	0.0175	γ(N=N) + Ring (γCH)
ν_{140}	91	0.1485	γ(N=N) + Ring (γCH)
ν_{141}	64	0.9724	γ-CH_3 + Ring (γCH)
ν_{142}	35	0.1163	Ring (γCH) + γ-CH_3
ν_{143}	29	0.0766	Ring (γCH)
ν_{144}	13	0.0776	τCH_3
ν_{145}	11	0.1011	γ(O-H) + Ring (γCH)
ν_{146}	10	0.1550	γ-CH_3
ν_{147}	6	0.0218	Ring (γCH)

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

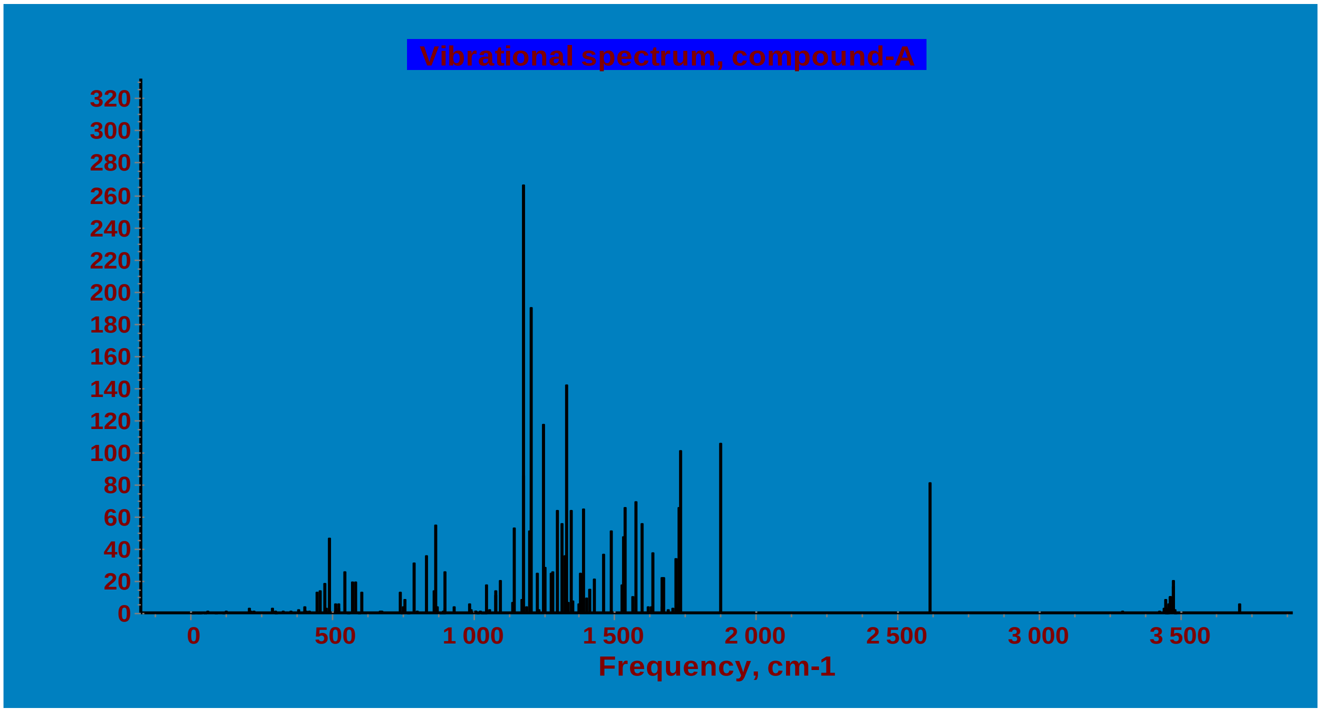


Fig.2: The vibration spectrum of the compound-A .

Table 6. 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}) for the B molecule .

No. of freq.	**Freq.** cm^{-1}	**Intensity** km mol^{-1}	**Assignments**
In plane, A			
ν_1	3715	6.8100	(O-H) st.
ν_2	3491	8.6613	Ring (C-H) st.
ν_3	3485	0.3448	Ring (C-H) st.
ν_4	3482	19.6165	Ring (C-H) st.
ν_5	3479	15.9420	Ring (C-H) st.
ν_6	3478	5.0684	Ring (C-H) st.
ν_7	3476	1.7122	Ring (C-H) st.
ν_8	3469	10.0212	Ring (C-H) st.
ν_9	3466	5.3720	Ring (C-H) st.
ν_{10}	3463	3.6000	Ring (C-H) st.
ν_{11}	3461	3.9941	Ring (C-H) st.
ν_{12}	3459	0.3190	Ring (C-H) st.
ν_{13}	3457	2.8060	Ring (C-H) st.
ν_{14}	3455	7.6612	Ring (C-H) st.
ν_{15}	3449	0.3516	CH_3 st.
ν_{16}	3447	2.5007	Ring (C-H) st.
ν_{17}	3446	4.7832	Ring (C-H) st.
ν_{18}	3409	3.7062	CH_3 st.
ν_{19}	3255	18.7841	CH_3 st.
ν_{20}	2617	83.3689	(O-H) st.
ν_{21}	1882	106.1954	δ(O-H)
ν_{22}	1738	99.4511	δ-Hydroxybenzene
ν_{23}	1732	17.0723	Ring (δCH)
ν_{24}	1720	350.9322	Ring (δCH) + Ring (CCC) st. + δ(O-H)
ν_{25}	1710	27.1434	Ring (δCH)
ν_{26}	1706	56.9708	δ(O-H) + Ring (CCC) st.
ν_{27}	1695	8.2097	Ring (δCH) + δ(O-H)
ν_{28}	1677	24.4626	δ-Ring
ν_{29}	1652	38.3161	CH_3scis.

ν_{30}	1642	5.0202	CH_3scis.
ν_{31}	1637	37.5624	δ-Hydroxybenzene
ν_{32}	1634	0.8109	Ring (δCH)
ν_{33}	1622	56.5582	δ-Hydroxymethylbenzene
ν_{34}	1600	57.5817	Ring (δCH)
ν_{35}	1579	68.3842	δ-Hydroxybenzene
ν_{36}	1569	72.3193	CH_3scis.
ν_{37}	1546	70.6883	δ-Hydroxymethylbenzene
ν_{38}	1536	46.2466	δ-Hydroxybenzene + δ-Ring
ν_{39}	1533	18.6818	δ-Hydroxybenzene + δ-Ring
ν_{40}	1492	46.2417	Ring (δCH)
ν_{41}	1458	55.7358	δ(O-H) + Ring (δCH) + δ-CH_3
ν_{42}	1434	20.4117	δ-Hydroxybenzene
ν_{43}	1415	0.6730	Ring (δCH) + δ(N=N)
ν_{44}	1404	144.4004	Ring (δCH) + δ(N=N) + δ(O-H)
ν_{45}	1398	178.3608	δ-Hydroxymethylbenzene
ν_{46}	1385	19.0405	δ-Hydroxybenzene + δ(N=N)
ν_{47}	1378	17.1190	Ring (δCH) + δ(N=N)
ν_{48}	1354	34.2971	Ring (δCH) + δ(N=N)
ν_{49}	1349	67.4009	Ring (δCH) + δ(N=N)
ν_{50}	1346	322.2940	δ-Hydroxymethylbenzene + δ(N=N)
ν_{51}	1339	14.5917	Ring (δCH) + δ(N=N)
ν_{52}	1329	21.9933	Ring (δCH) + δ(N=N)
ν_{53}	1316	59.0833	δ-Ring + δ(N=N)
ν_{54}	1300	82.3882	Ring (δCH)
ν_{55}	1287	125.6677	Ring (δCH) + δ-OCH_3 + δ(O-H)
ν_{56}	1279	20.0249	Ring (δCH) + δ-OCH_3 + δ(O-H)
ν_{57}	1260	54.5446	Ring (δCH) + δ(O-H) + δ-OCH_3
ν_{58}	1255	176.2497	Ring (δCH) + δ(O-H) + δ-CH_3
ν_{59}	1253	8.2539	Ring (δCH) + δ-CH_3 + δ(O-H)
ν_{60}	1235	1.4897	Ring (δCH)
ν_{61}	1229	7.7699	ρCH_3 + Ring (δCH)
ν_{62}	1208	215.1202	Ring (δCH)
ν_{63}	1202	23.0639	Ring (δCH) + δ(O-H)
ν_{64}	1190	4.7917	Ring (δCH)
ν_{65}	1183	263.0470	Ring (δCH) + δ(N=N)

ν_{66}	1176	11.9002	Ring (δCH)
ν_{67}	1169	0.5088	ρCH_3
ν_{68}	1152	182.5279	Ring (δCH) + δ-CH_3 + δ(N=N)
ν_{69}	1106	1.9090	Ring (δCH) + δ-OCH_3
ν_{70}	1085	13.8510	Ring (δCH)
ν_{71}	1082	11.0273	δ-Ring
ν_{72}	1064	2.1092	Ring (δCH)
ν_{73}	1052	17.2218	Ring (δCH)
ν_{74}	993	6.2278	δ(N=N) + δ-Ring
ν_{75}	983	1.4661	Ring (δCH) + δ-OCH_3
ν_{76}	938	1.3653	δ(N=N) + Ring (δCH)
ν_{77}	905	26.4107	Ring (δCH) + δ(N=N)
ν_{78}	837	28.6560	δ-Ring + δ(O-H) + δ(N=N)
ν_{79}	805	1.3245	δ-Hydroxybenzene + δ(N=N)
ν_{80}	755	1.4680	Ring (δCH) + δ-CH_3 + δ-Ring
ν_{81}	742	2.7973	Ring (δCH) + δ-CH_3 + δ-Ring
ν_{82}	678	0.3494	δ-Ring
ν_{83}	674	1.5239	δ-Ring + δ-OCH_3
ν_{84}	658	0.1021	δ-Ring
ν_{85}	606	3.4171	δ-Ring + δ-OCH_3 + δ(N=N)
ν_{86}	602	16.1252	δ-OCH_3 + δ(O-H) + δ(N=N)
ν_{87}	580	15.6587	δ-OCH_3 + Ring (δCH)
ν_{88}	576	39.4576	δ(N=N) + Ring (δCH)
ν_{89}	545	27.9798	δ(O-H) + δ(N=N)
ν_{90}	510	5.2071	δ(O-H) + Ring (δCH) + δ-Ring
ν_{91}	487	18.6077	δ(O-H) + δ(N=N)
ν_{92}	475	15.9346	δ(N=N) + δ-Hydroxybenzene + δ-Ring
ν_{93}	420	2.0345	δ-Ring + δ(N=N) + δ-OCH_3
ν_{94}	382	0.2506	δ-Hydroxymethylbenzene + δ-Hydroxybenzene
ν_{95}	372	1.0273	δ(O-H) + δ-OCH_3 + δ(N=N)
ν_{96}	300	2.3671	δ-Ring + δ(N=N) + δ(O-H)
ν_{97}	256	6.0527	δ-OCH_3+ δ(O-H) + δ(N=N)
ν_{98}	225	0.1372	δ(O-H) + δ(N=N) + δ-CH_3 + δ-Ring
ν_{99}	204	1.9504	δ-OCH_3 + δ-Ring
ν_{100}	127	1.1673	δ(O-H) + δ(N=N) + δ-Ring
ν_{101}	108	0.2443	δ(N=N) + δ-Ring

ν_{102}	53	0.1812	δ(N=N) + δ-Ring
ν_{103}	24	0.3455	δ-CH_3+ δ(N=N)
Out of plane, A			
ν_{104}	1184	85.5512	γ(O-H)
ν_{105}	1044	0.1772	Hydroxybenzene (γCH)
ν_{106}	1040	0.0114	Ring (γCH)
ν_{107}	1033	0.2541	Ring (γCH)
ν_{108}	1020	0.7150	Ring (γCH)
ν_{109}	1017	0.4961	Ring (γCH)
ν_{110}	1015	0.5149	Hydroxybenzene (γCH) + Ring (γCH)
ν_{111}	1014	0.6262	Hydroxybenzene (γCH) + Ring (γCH)
ν_{112}	900	1.3185	Hydroxybenzene (γCH)
ν_{113}	896	0.0322	Ring (γCH)
ν_{114}	888	0.0279	Ring (γCH)
ν_{115}	878	3.9176	Ring (γCH)
ν_{116}	875	19.2015	Ring (γCH)
ν_{117}	866	54.4395	Ring (γCH)
ν_{118}	836	15.1374	Ring (γCH)
ν_{119}	796	30.7789	Ring (γCH)
ν_{120}	773	0.0644	Ring (γCH)
ν_{121}	759	8.0894	Ring (γCH)
ν_{122}	749	0.8838	Ring (γCH)
ν_{123}	738	1.8192	Ring (γCH)
ν_{124}	625	0.0895	γ(O-H) + Ring (γCH)
ν_{125}	575	0.0006	Ring (γCH)
ν_{126}	559	0.0828	Ring (γCH)
ν_{127}	528	2.6384	Ring (γCH)
ν_{128}	497	54.6243	γ(O-H)
ν_{129}	477	11.4285	γ(O-H) + Ring (γCH)
ν_{130}	461	10.3663	γ(O-H) + Ring (γCH)
ν_{131}	426	0.0632	Ring (γCH)
ν_{132}	417	0.0038	Ring (γCH)
ν_{133}	412	0.0086	Ring (γCH)
ν_{134}	371	0.3130	γ-Ring
ν_{135}	331	2.1893	γ-Hydroxybenzene
ν_{136}	306	1.8112	γ(N=N) + γ-OCH_3 + γ-Ring

ν_{137}	248	0.7030	τCH_3
ν_{138}	227	0.8850	τCH_3 + γ-Hydroxymethoxybenzene
ν_{139}	216	1.3273	γ(N=N) + γ-Hydroxybenzene + γ-CH_3 + γ-Ring
ν_{140}	206	0.1348	γ-Hydroxybenzene + γ-Ring + γ(N=N) + γ-CH_3
ν_{141}	169	1.0167	γ(N=N) + τCH_3
ν_{142}	143	0.0216	γ(N=N) + γ-Ring
ν_{143}	100	1.9120	γ-OCH_3 + γ(N=N) + γ-Ring
ν_{144}	89	0.0167	γ-OCH_3 + γ-Ring
ν_{145}	60	0.7371	γ-OCH_3 + γ-Ring
ν_{146}	35	0.0549	γ-Ring
ν_{147}	29	0.1373	γ-Ring
ν_{148}	12	0.0000	γ(O-H) + γ-Ring
ν_{149}	10	0.1983	γ-OCH_3 + γ-Ring
ν_{150}	6	0.0220	γ-Ring

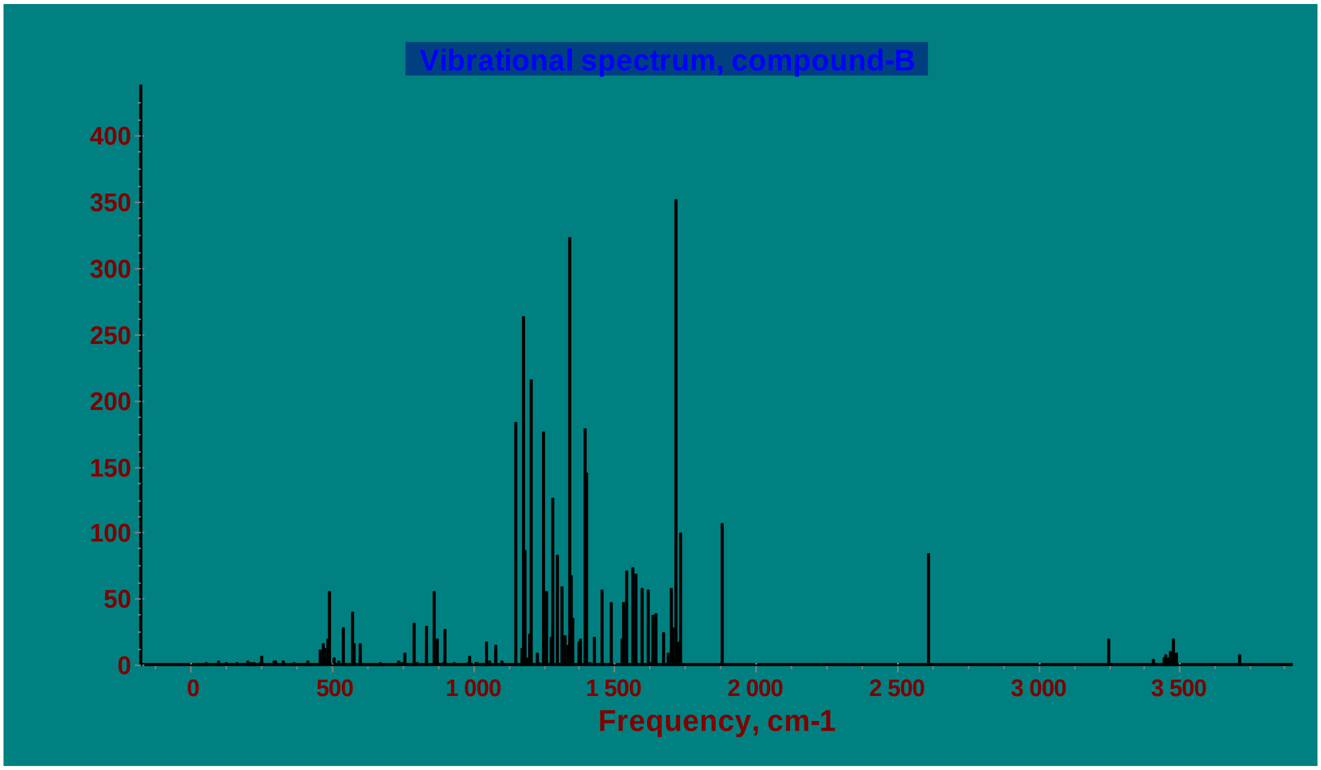


Fig.3: The vibration spectrum of the compound-B .

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References

[1] K. Hansongnern, S. Tempiam, J.C. Liou, F.L. Laio, T.H. Lu, **Anal. Sci.**; 19,x13 (2003) .
[2] P.L. Coort, M. Johansson, **Electroanalysis**; 12,565 (2000) .
[3] D. Choi, S.K. Lee, T.D. Chung, H. Kim, **Electroanalysis**; 12, 477 (2000) .
[4] P. Alka, P. Vinod, V.S. Jolly, Orient. **J. Chem.**; 10 (1),73 (1994) .
[5] A. Halve, A. Goyal, Orient. **J. Chem.**; 12 (1)87 (2001) .
[6] S. Samadhiya, A. Halve, Orient. **J. Chem.**; 17 (1)119 (2001) .
[7] H.E. Katz, K.D. Singer, J.E. Sohn, C.W. Dirk, L.A. King, and H.M. Gordon; **J. Am. Chem. Soc.;** 109 (21), 6561 (1987).
[8] T. Abe, S. Mano, Y. Yamada, and A. Tomotake; **J. Imag. Sci. Tech.**; 43, 339 (1999).
[9] S. Wang, S. Shen, and H. Xu; **Dyes Pigments**; 44**,** 195 (2000).
[10] K. Maho, T. Shintaro, K. Yutaka, W. Kazuo, N. Toshiyuki, and T. Mosahiko; **Jpn. J. Appl. Phys.;** 42, 1068 (2003).
[11] D.W. Rangnekar, V.R. Kanetkar, J.V. Malanker, and G.S. Shankarling; **Indian J. Fiber Text. Res.;** 24, 142 (1999).
[12] G. Hallas and J.H. Choi; **Dyes Pigments**; 40, 119 (1999).
[13] P. Gregory, D.R. Waring, and G. Hallos; **''The Chemistry and Application of Dyes''**; pp. 18-20, Plenum Press, London,(1990).
[14] S.S. Kandil; **Trans. Met. Chem.**; 23, 461 (1998).
[15] S. Wu, W. Qian , Z. Xia, Y. Zou, S. Wang, and S. Shen; **Chem. Phys. Lett.**; 330, 535 (2000).