Vibrational Analysis of “Dimethylbipyridinylzinc (0) [$C_{12}H_{14}N_2Zn$]”: A DFT Approach

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Abstract

Theoretical quantum chemical studies and spectroscopic investigations on “Dimethylbipyridinylzinc (0) $C_{12}H_{14}N_2Zn$*” have been carried out. The quantum chemical density functional theory (DFT) method at B3LYP/3-21G level is used to obtain the equilibrium geometries. We have also performed vibrational analysis of the title compound at their equilibrium geometries and established the complete assignments of the significant vibrational modes. The NLO behaviour of the title compound is described by electric parameters like dipole moment, polarizability and first hyperpolarizability. Besides it the thermodynamical and electronic parameters are also calculated to get a better insight of the molecule under study.*

1. INTRODUCTION

This study is in the continuation of our previous work [1] of novel compounds of Pyridine which presents a detailed investigation of the normal coordinate analysis of the title molecule”Di methyl bipyridinyl Zinc(0)($C_{12}H_{14}N_2Zn$)”, a derivative of pyridine due to itsbioactive properties. Pyridine is a heterocyclic aromatic tertiary amine and is also known as azobenzene and azine. It consists of a six member ring composed of five carbon atoms and a nitrogen atom which replaces one carbon hydrogen unit in the benzene ring (C_5H_5N). Pyridine is a base with chemical properties similar to tertiary amines. Pyridine and its derivatives are used as solvents and starting material for the synthesis of target compounds. It is used as insecticides, herbicides, medicines, vitamins, food flavorings, feed additives, dyes, rubber chemicals, explosives, disinfectants, and adhesives. It is also used as a denaturant for antifreeze mixtures, as a dyeing assistant in textiles and in fungicides [2, 3].

2. MATERIALS AND METHODS

The model molecular structure of the title compound is shown fig.1 and schematic diagram is shown in fig.2. The theoretical IR spectra plotted by Gausssum 3.0 program package is shown in fig.3.

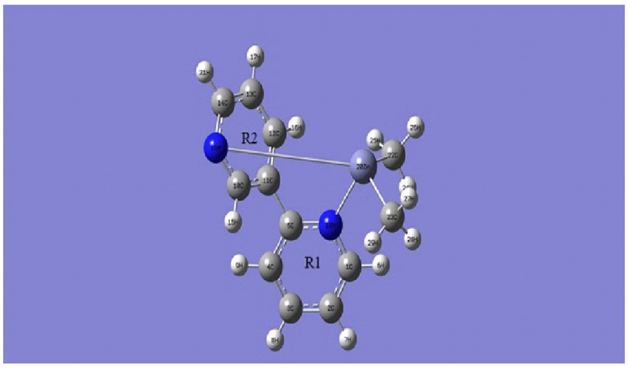

Fig.1: Model molecular structure of Dimethylbipyridinyl zinc (0) as seen by Gaussview 5.05 program

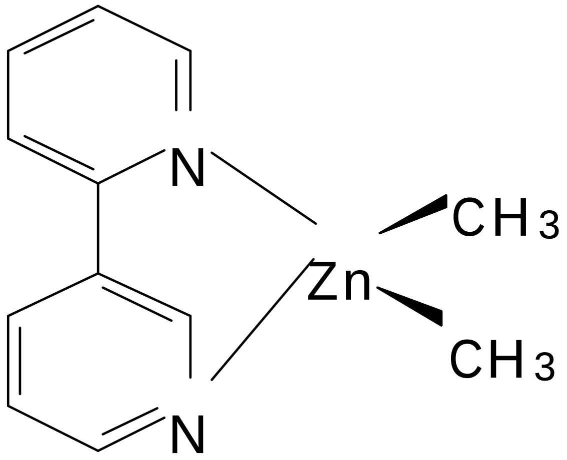

Fig.2: Schematic diagram of Dimethylbipyridinylzinc (0)

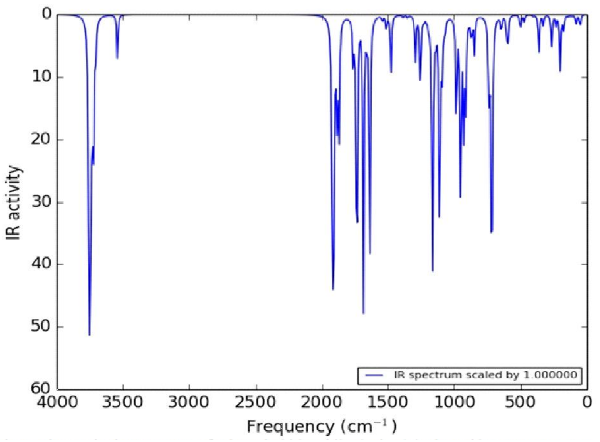

Fig.3: Theoretical IR spectra of Di methyl bipyridinyl Zinc(0) plotted by Gaussum 3.0

3. RESULT AND DISCUSSION

All the calculations were performed on an AMD dual core/2.71 GHz personal computer by the B3LYP [4, 5] method using the 6-31+g(d,p) level basis set of density functional theory. Allcomputations were carried out with the Gaussian 09 package [6] by combining the results of the Gaussview 5.0.8 program package [7] withsymmetry considerations and the VEDA 4 programto calculate the PED values [8].

3.1 Geometry Optimization

The optimized geometrical parameters of the title molecule Dimethylbipyridinylzinc(0)are listed in table 1, showing bond lengths and bond angles only. The out of plane and torsional vibrations are not shown for the sake of space and are with the corresponding author. The optimized geometry parameters of the title compound are calculated by the DFT-B3LYP method. The calculations converged to optimized geometries by allowing the relaxation of all the parameters, which also correspond to true energy minima. This is revealed by the absence of any imaginary frequencies in the vibrational spectra calculations. Subsequently the zero point vibrations energy obtained for structure optimization of the title molecule is calculated as 178.524 Kcal/mol.

3.2 Thermodynamic and Electronic Parameters

The thermodynamic functions like internal thermal energy (E), specific heat capacity at constant volume (Cv) and entropy (S) are shown in table 2. It is evident from the table 2 that of the total values of E and Cv, major contributions are due to the vibrational part. Whereas in the entropy calculated value the contributions of all three parts i.e. translational, rotational and vibrational motions of the atoms in the title molecule are comparable with again the vibrational part got the maximum contribution. This shows the importance of the study of vibrational nature of the molecule.

The HOMO -LUMO energy gap is an important measure of the stability of the compound. Molecule with small values of frontier orbital gap, are more polarizable, with high chemical reactivity and low kinetic stability and is called a soft molecule [9, 10] and vice versa. In our calculations the energy band gap of Dimethylbipyridinylzinc (0) is calculated as 8.5704 eV.

This shows that title molecule has a moderately high value of band gap and so is slightly less polarizable, slightly less chemically reactive and contains good kinetic stability. In the present DFT study the plots of LUMO and HUMO are shown in Fig 4 and Fig 5 respectively and their values are given Table 2.

From 2D plot of HOMO (-3.95 eV), it is clear that entire HOMO is distributed over Zinc atom Zn19 and carbon atom C22. From 2D plot of the LUMO (4.62 eV) it is evident that LUMO largely associated with Zn19, C22 atoms and also on rings R1 and R2 unlike HOMO. Fig 6 shows the molecular electrostatic potential plot of the title compound. The rotational constants are calculated as 0.6227175, 0.4162497, 0.2907811 GHz respectively.3.3 Electric Parameters (Dipole Moment, Polarizability & First Static Hyperpolarizability)

The calculated value of dipole moment μ for the title molecule Dimethylbipyridinylzinc (0), is found to be 6.2972 D.

The larger contribution in the mean polarizability <α> is due to components αXX(-97.54), αYY (-87.52) and αZZ (-98.99), as compared to the other components. This suggests that the title molecule is elongated equally along X,Y and Z-axes. The total intrinsic hyperpolarizability β total and a component of the first static hyperpolarizability along the direction of the dipole moment are represented by β.

Table-1: Optimized ground state structural parameters of Dimethylbipyridinylzinc (0) at B3LYP method

S.No.	Modes	Bond Length	S.No.	Modes	Angle Bend (Deg)
1	R(1,2)	1.3817	43	A(5,4,9)	118.9328
2	R(1,6)	1.085	44	A(4,5,11)	118.7901
3	R(1,18)	1.3596	45	A(4,5,18)	121.4163
4	R(2,3)	1.3875	46	A(11,5,18)	119.7914
5	R(2,7)	1.0814	47	A(11,10,15)	119.6804
6	R(3,4)	1.3823	48	A(11,10,19)	124.5419
7	R(3,8)	1.0847	49	A(15,10,19)	115.7761
8	R(4,5)	1.3962	50	A(5,11,10)	119.7773
9	R(4,9)	1.0812	51	A(5,11,12)	121.9748
10	R(5,11)	1.5099	52	A(10,11,12)	118.1916
11	R(5,18)	1.3658	53	A(11,12,13)	118.6529
12	R(10,11)	1.3928	54	A(11,12,16)	120.6362
13	R(10,15)	1.0869	55	A(13,12,16)	120.7073
14	R(10,19)	1.3523	56	A(12,13,14)	119.0332
15	R(11,12)	1.3928	57	A(12,13,17)	120.8002
16	R(12,13)	1.3833	58	A(14,13,17)	120.1666
17	R(12,16)	1.0832	59	A(13,14,19)	124.079
18	R(13,14)	1.3891	60	A(13,14,21)	120.0363
19	R(13,17)	1.0816	61	A(19,14,21)	115.8838
20	R(14,19)	1.3527	62	A(1,18,5)	117.0707
21	R(14,21)	1.0871	63	A(1,18,20)	119.3633
22	R(18,20)	2.1758	64	A(5,18,20)	123.2133
23	R(19,20)	5.152	65	A(10,19,14)	115.4973
24	R(20,22)	1.974	66	A(10,19,20)	46.2267
25	R(20,23)	1.9756	67	A(14,19,20)	81.2969
26	R(22,24)	1.0832	68	A(18,20,19)	68.1203
27	R(22,25)	1.0824	69	A(18,20,22)	89.9321
28	R(22,26)	1.0826	70	A(18,20,23)	90.6511
29	R(23,27)	1.0822	71	A(19,20,22)	128.3791
30	R(23,28)	1.083	72	A(19,20,23)	118.949
31	R(23,29)	1.0827	73	A(22,20,23)	106.8326
	Angle Bend(Deg)		74	A(20,22,24)	114.5118
32	A(2,1,6)	120.3019	75	A(20,22,25)	112.1367
33	A(2,1,18)	123.9253	76	A(20,22,26)	109.9172
34	A(6,1,18)	115.7718	77	A(24,22,25)	106.9405
35	A(1,2,3)	118.5634	78	A(24,22,26)	106.553
36	A(1,2,7)	119.8511	79	A(25,22,26)	106.3113
37	A(3,2,7)	121.5851	80	A(20,23,27)	109.6002
38	A(2,3,4)	118.7265	81	A(20,23,28)	114.8054
39	A(2,3,8)	120.7552	82	A(20,23,29)	112.1127
40	A(4,3,8)	120.517	83	A(27,23,28)	106.4648
41	A(3,4,5)	120.2853	84	A(27,23,29)	106.2502
42	A(3,4,9)	120.7785	85	A(28,23,29)	107.1176

The largest βxxx component of hyperpolarizability β total indicates the charge delocalization occurs along X-axis and it suggests that the title molecule is relatively more optically active along X axis than other axes. All the values of μ, <α> and βtotal are listed in table 2. The calculated values of <α> is -94.6899 a.u. or (-0.792*10^-30 e.s.u) which is more than four times to that of urea (0.1947*10^-30 e.s.u) and the value of βtotal is calculated as

67.37453 a.u. or (0.563* 10^-30 e.s.u.) at B3LYP/ 6-311++ G(d,p) basis set. All these values are shown in table 3.

Table-2: Thermodynamic and Electronic Parameters of Dimethylbipyridinylzinc (0)

Parameters	(Thermal)	CV	S
KCal/Mol	Cal/Mol-Kel	Cal/Mol-Kel	
Total	178.524	50.635	122.393
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	42.450
Rotational	0.889	2.981	32.722
Vibrational	176.746	44.673	47.221
Zero-point vibrational energy	178.524 (Kcal/Mol)		
Rotational constants (GHz):0.6227175, 0.4162497, 0.2907811			
HOMO = -0.31368*27.3 eV=-3.95904 eV **LUMO** = 0.10093* 27.3 eV=4.620798 eV **Energy Band Gap**= 8.5704 eV			

3.3 Vibrational Analysis

The maximum number of potentially active observable fundamentals of a nonlinear compound containing N-atoms is equal to (3N-6) [11]. The title compound "Dimethylbipyridinylzinc (0) ($C_{12}H_{14}N_2Zn$)" contains 29 atoms and hence exhibits 81 normal modes of vibrations.

The assignment of the calculated frequency, are supported by the animation of Gauss View 5.0.8, which gives a 3D-view of the vibrational modes. The potential energy distribution (PED) is calculated by VEDA 4 software program. To correct overestimations at the calculated harmonic frequencies an empirical uniform scaling factor of0.983 up to 1700 cm-1and 0.958 for above 1700 cm-1 were used [12]. All the vibrational assignments are presented in table 3.

3.3.1 (C-H) and Methyl (CH_3) stretch

The structure of the title compound show the presence of C-H stretching vibration including (C-H) and CH_3 in the region 3600- 3200 cm^{-1} which is the a bit higher than the characteristic region for the ready identification of C-H stretching vibration [13]. These vibrations are found to be affected due to the position of the substitution.

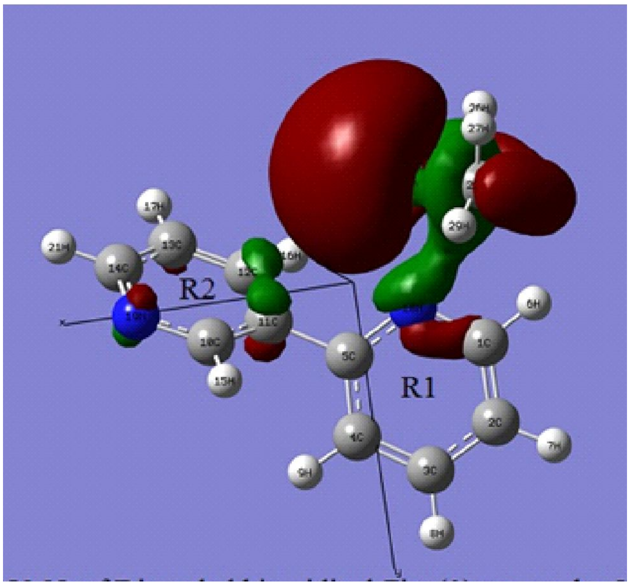

Fig.4: 2D Plot of HOMO of Dimethylbipyridinylzinc(0) as seen by Gaussview 5.05 program

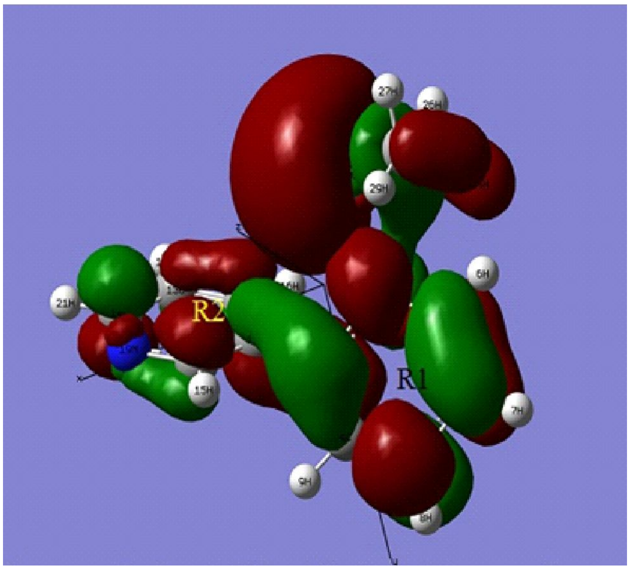

Fig.5: 2D Plot of LUMO of Dimethylbipyridinylzinc(0) as seen by Gaussview 5.05 program

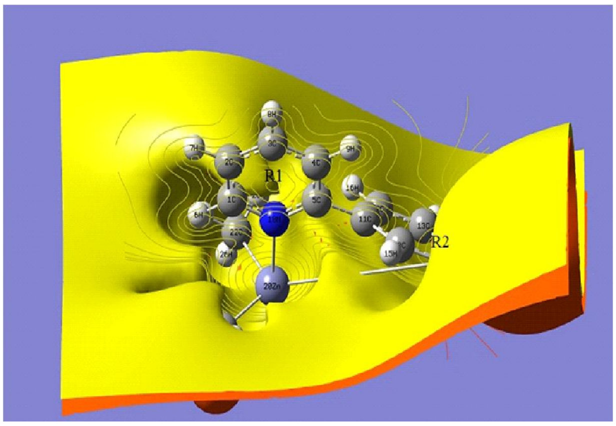

Fig.6: 2D Plot of MESP of Dimethylbipyridinylzinc(0) as seen by Gaussview 5.05 program

Table-3: Electric Parameters: (Polarizability, Hyperpolarizability, Dipole Moment)

(1 a.u.=8.3693*10^-33 e.s.u)

Polarizability	**Values (a.u)**	**Hyperpolarizability**	**Values (a.u)**	**Dipole Moment (Debye)**	**Values**
α_{XX}	-97.5485	β_{XXX}	-47.6066	μ_x	-0.3685
α_{XY}	-9.3040	β_{XXY}	-10.5328	μ_y	5.8304
α_{YY}	-87.5268	β_{XYY}	-9.8128	μ_z	-2.3505
α_{YZ}	-1.0896	β_{YYY}	12.7239	**μ_{total}**	**6.2972**
α_{ZZ}	-98.9944	β_{XXZ}	-27.4118		
α_{XZ}	-5.4943	β_{XYZ}	4.8489		
$\langle\alpha\rangle$	**-94.6899**	β_{YYZ}	-0.9136		
		β_{XZZ}	-4.1938		
		β_{YZZ}	-9.3673		
		β_{ZZZ}	2.0263		
		β_{total}	**67.37453**		

3.3.2 C=C stretch

The C=C aromatic stretchknown as semi-circle stretching, are calculated at 1839, 1829, 1807, 1789, 1688 and 1610 cm^{-1}. They are in good agreement with the reported frequencies with appropriate PED. The theoretically calculated C–C–C bending and C–C torsional modes have been found to be consistent with the reported values [13].

3.3.3 C=N and C-N stretch

The C=N stretching vibrations are calculated at frequencies 1807, 1789, 1688 and 1610 cm^{-1}, and are observed at 1878, 1750 and 1627 cm^{-1}. The C-N vibrational mode is not easily identified due to the mixing of vibrations of other modes in this region. In the title molecule, the C-N stretching vibrations are calculated at 1279, 1187, 1169, 1119, 1092 and 1071cm^{-1}. Various bending and torsional vibrations assigned to the ½(C-N) stretching mode are also supported by the literature [14].

3.3.4 Zn-C modes

There are two calculated stretching modes for (Zn-C) stretch at frequencies 705 and 594 cm^{-1} and these modes are reported at 900 and 450 cm^{-1} respectively. These modes are seems to be a characteristic modes of the title molecule. Corresponding in plane bending modes is calculated at frequencies 198, 181, 171 and 52 cm^{-1} respectively. **(Annexure-1)**

3.3.5 Lower region vibrational modes

The study of low frequency vibrations is of great importance because it provides the in formation for weak intermolecular interactions, which occurs in enzyme reactions [15]. Study of low frequency modes is also useful for the interpretation of the effect of electromagnetic radiation on biological systems [16]. The torsional modes of Zn are found at frequencies 966, 935, 897 and 492 cm^{-1}. These modes are seems to be some of the characteristic modes of the title compound. Other lower order modes are calculated at frequencies 872, 855, 834, 722, 691, 635, 584, 484 and 397 cm^{-1}. In lower range discrepancies are observed in the experimental and theoretical intensity in lower range of frequencies which are due to the impurity of the sample used intermolecular interactions, anharmonicity and mixing of different modes of vibrations.

4. CONCLUSIONS

The optimized molecular geometry, vibrational wavenumbers, NLO behavior, thermodynamical and electronic parameters of the title "Dimethyl bipyridinylzinc(0)” molecule have been calculated using DFT B3LYP method adopting 6-311++G (d,p) basis set. The nonlinear optical (NLO) behavior of the title molecule has been observed by the dipole moment, the polarizability and the first hyperpolarizability measurements.

The frontier orbital energy gap is calculated as 8.57 eV. Dipole moment μ, molecular polarizability <α> and total first static hyperpolarizability βtotal are computed as 6.2972 D, 67.37453 a.u. and -67.37453 a.u. respectively. It is found that the heat capacities, entropies and enthalpies increase with the increasing temperature due to the intensities of the molecular vibrations increase with increasing temperature.

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Table-4 : Frequency assignments for Di methyl bipyridinyl Zinc(0) at B3LYP/6-311G(d,p) in cm-1, with PED % in Square Brackets

CalcFreq		Theoretical	Assignment Modes
Unscaled	**Scaled**	**FTIR**	[%PED]
3759	3601	3752(vs)	ν(C12-H17)[96]
3742	3585		ν(C1-H6)[97]
3727	3570	3744(w)	ν(C23-H27)[92]
3724	3567		ν(C3-H8)[65] + ν(C4-H9)[12] + ν(C2-H7)[15]
3720	3564		ν(C22-H24)[61] + ν(C23-H28)[59]+ ν(C23-H29)[29]a
3706	3550		ν(C2-H2A)[15]a + ν(C3-H3A)[52]+ ν(C4-H4A)[30]a
3703	3547		ν(C10-H15)[88]
3542	3393		ν(C22-H26)[13] +ν(C22-H27)[18]
1919	1839	1920(s)	ν(C1=C5)[13]
1909	1829	1912(msh)	ν(C6=C10)[14]
1886	1807		ν(C10=C11)[13]+ν(C14=N19)[17]
1868	1789	1878(m)	ν(C18=N5)[17]+ν(C2=C3)[16]+ φ(H26-C22-H25)[17]
1762	1688	1750(vs)	ν(C18=N5)[12]+ν(C5=C11)[13]+ φ(H17-C13-H14)[17]
1684	1656	1655(s)	φ(H7-C2-C3)[29] + φ(H8-C3-C4)[20]
1637	1610	1627(s)	ν(C10=C11)[19]+ ν(C10=N19)[14]
1542	1516	1534(w)	φ(H15-C10-N19)[42] + φ(H16-C12-C13)[20]
1512	1487		ν(C5-C11)[29]+ φ(H9-C4-C3)[15]+φ(H15-C10-N19)[13]
1477	1452	1442(w)	φ(H6-C1-C2)[42]+φ(H9-C4-C3)[14]
1386	1363	1375(s)	φ(H15-C10-N19)[10]+φ(H17-C13-C14)[23]+φ(H21-C14-N19)[27]
1353	1330	1322(m)	φ(H7-C2-C3)[26]+φ(H8-C3-C4)[39]
1301	1279		ν(C14-N19)[13]+ φ(H16-C12-C23)[28]+φ(H17-C13-C14)[12]
1292	1270	1256(s)	ν(C3-C4)[13]+ φ(H7-C2-C3)[23]
1256	1234		ν(C2-C3)[14]+ φ(H9-C4-C3)[14]
1230	1209	1220(s)	τ(H7-C2-C3-C4)[14]+ τ(H8-C3-C4-C5)[42]
1208	1187	1193(w)	ν(C14-N19)[19]+τ(H11-C12-C13-C14)[18]+ τ(H17-C13-C14-N19)[38]
1194	1174		τ(H7-C2-C3-C4)[18]+ τ(H8-C3-C4-C5)[36]
1189	1169		ν(C9-N2)[10]+ν(C1-C2)[11]+ φ(C4-C3-2)[23]
1164	1145		τ(H7-C2-C3-C4)[13] + φ(C4-C5-C6)[17]
1157	1138	1123(m)	τ(H16-C12-C13-C14)[33]+ τ(H21-C14-N19-C10)[37]
1138	1119		ν(C2-C3)[12]+ ν(N18-C1)[25]+ν(N18-C5)[16]
1111	1092	993(s)	ν(C12-C13)[20]+ν(N19-C10)[27]
1089	1071		ν(C2-C3)[18]+ ν(N19-C10)[15]
983	966		τ(H26-C22-Zn20-C23)[27]+τ(H27-C23-Zn20-C22)[24]
951	935		τ(H28-C23-Zn20-C23)[27]+τ(H27-C23-Zn20-C22)[24]
928	912	919(m)	τ(H7-C2-C3-C4)[27]+ τ(H6-C1-C2-C3)[12]
912	897	668(wsh)	τ(H27-C23-Zn20-C22)[27]+τ(H26-C22-Zn20-C23)[19]+τ(H28-C23-Zn20-C22)[11]
888	872		τ(C2-C1-N18-C5)[31]+ τ(C4-C3-C2-C1)[13]
869	855		τ(H16-C12-C13-C14)[10]+ τ(H21-C14-N19-C10)[10]
848	834		τ(C11-C10-N19-C14)[17]+τ(C12-C13-C14-N19)[17]
735	722	522(wsh)	φ(C1-N18-C5)[15] + φ(C4-C3-C2)[26]+φ(C2-C1-18)[30]
717	705		ν(Zn20-C23)[50]+ ν(Zn20-C22)[48] {char mode}
703	691		φ(C12-C13-C14)[21] + φ(C10-N19-C14)[38]
646	635	505(s)	τ(C3-C2-C1-N18)[12]+τ(C1-N18-C5-C11)[14]+ω(C5-C10-C12-C11)[18]
604	594		ν(Zn20-C23)[46]+ ν(Zn20-C22)[45]{char mode}
594	584	449(s)	φ(C12-C11-C5)[10]+τ(C3-C2-C1-N18)[11]
500	492		τ(H8-C3-C4-C5)[10]+τ(C4-C3-C2-C1)[34]+τ(Zn20-C5-C1-N18)[21]
472	464	400(msh)	τ(H16-C12-C13-C14)[10]+τ(C12-C13-C14-N19)[31]+τ(C10-N19-C14-C13)[25]
404	397		τ(C3-C2-C1-N18)[10]+τ(C10-N19-C14-C13)[14]
266	261		φ(C23-Zn20-N18)[29] + φ(C22-Zn20-18)[19]
201	198		ν(Zn20-N18)[28]
184	181		φ(Zn20-N18-C1)[57]
174	171		ν(Zn20-N18)[42]