Spectroscopic investigations of (*E*)-5-(2-phenyldiazenyl)-2-hydroxybenzaldehyde using DFT method

S. Bharanidharan^a, H. Saleem^a, A. Nathiya^a, A. Arokiasamy^b,
V. Thanikachalam^b

^aDepartment of Physics, Annamalai University, Annamalaiagar-608 002, Tamil Nadu, India

^bDepartment of Chemistry, Annamalai University, Annamalaiagar-608 002, Tamil Nadu, India

*Corresponding author

E-mail: saleem_h2001@yahoo.com (Dr. H. Saleem).

Mobile: +91 9443879295

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ABSTRACT. The Spectral Characterization of (*E*)-5-(2-phenyldiazenyl)-2-hydroxy benzaldehyde (PDHB) were carried out by using FT-IR, FT-Raman and UV-Vis spectroscopic techniques. All the recorded spectral results were compared with calculated results. The optimization has been performed on the title compound using B3LYP/6-311++G(d,p) level of theory. The optimized bond parameters of PDHB molecule was compared with X-ray diffraction data of related molecule. To study the intra-molecular charge transfers within the molecule the Lewis (bonding) and Non-Lewis (anti-bonding) structural calculation was performed. The Non-linear optical behavior of the title compound was measured using first order hyperpolarizability calculation. In addition of Mulliken atomic charges and thermodynamic properties were also calculated and analyzed.

1. INTRODUCTION

Azo compounds represent the largest and most important group of synthetic dyes. These compounds have a basic structure of Ar-N=N-Ar' (where Ar and Ar' =aromatic groups). The -N=N-azo group is the chromophore responsible for the color of these compounds [1]. The azo compounds are most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibers, the coloring of different materials, colored plastics, biological and medical studies, and advanced application in organic synthesis [2–4]. Aromatic and heteroaromatic azo compounds constitute the largest and the most diverse group of synthetic dyes with application not only as textile colorants but in many other industrial fields for coloring different substrates, biological-medical studies, in the field of non-linear optics and optical data storage [5–7].

Azobenzenes have versatile applicability ranging from textile dyeing [8], leather dyeing [9], coloring of plastics and polymer [10] to advanced applications such as liquid crystal displays [11], biological and medical studies [12]. In this study, (*E*)-5-(2-phenyldiazenyl)-2-hydroxybenzaldehyde (PDHB) azo dyes were synthesized and geometrical parameters, and vibrational spectra were calculated. The calculated vibrational wavenumbers and chemical shifts were compared with the experimental data of the molecules. Furthermore, we interpreted the calculated spectra on the basis of total energy distributions (TED).

2. EXPERIMENTAL DETAILS

Synthesis

For synthesis of polyhydroxy azo–azomethine derivatives 6, substituted anilines 1 were first diazotized using sodium nitrite in the presence of hydrochloric acid, which coupled with salicylaldehyde 3 to afford 5-phenyldiazenylsalicylaldehyde dyes 4 in good yields. 5-Phenyldiazenylsalicylaldehydes 4 were purified by recrystallization from suitable solvents. The reaction of 4 with tris(hydroxymethyl)aminomethane (5) then afforded polyhydroxy azo–azomethine derivatives 6, which were purified by recrystallization from suitable solvents.

Computational details

The entire calculations were performed at DFT levels on a Pentium 1V/3.02 GHz personal computer using Gaussian 03W [13] program package, invoking gradient geometry optimization [14, 13]. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. Then, vibrationally averaged nuclear positions of PDHB were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. In this study, the DFT method (B3LYP/6-311++G(d,p)) was used for the computation of molecular structure, vibrational frequencies and energies of optimized structures. The vibrational modes were assigned on the basis of TED analysis using VEDA4 program [15].

It should be noted that Gaussian 03W package able to calculate the Raman activity. The Raman activities were transformed into Raman intensities using Raint program [16] by the expression:

$$I_i = 10^{-12} \times (\nu_0 - \nu_i)^4 \times \frac{1}{\nu_i} \times RA_i \quad (1)$$

Where I_i is the Raman intensity, RA_i is the Raman scattering activities, ν_i is the wavenumber of the normal modes and ν_0 denotes the wavenumber of the excitation laser [17]. The same formula (Eqn. 1) has been used to convert the Raman activity into Raman intensity.

3. Results and discussion

Geometrical Parameters

In this study, the optimized molecular structure of the title molecule is depicted in Fig. 1. The comparative optimized structural parameters such as bond lengths, bond angles and dihedral angles were performed using B3LYP/6-311++G(d,p) basis set are presented in Table. 1. These parameters are compared with X-ray data of the related molecule [18].

The calculated N=N bond distance of the title molecule is 1.2524 Å (at B3LYP/6-311++G(d,p)), where as the experimental value 1.2524 Å. The calculated C-N bond lengths C3-N12: 1.4174/1.4177 Å and C14-N13: 1.4161/1.4169 Å are belong to B3LYP (6-31G(d,p)/6-311++G(d,p) basis set, respectively. On comparing these values with the B3LYP/6-311++G(d,p) values are in agreement with literature [18]. The C21-O23 and O23-H24 bond distances calculated at B3LYP/6-311++G(d,p) are in agreement with X-ray data [18].

As it is evident from Table. 1. The azo benzene (1) ring moiety is coplanar [C2-C3-N12=N13=179.99 °] and [C4-C3-N12=N13=0 °] and phenol (2) ring is also coplanar with the azo chromophore [N13=N12-C14-C16=180 °] and [N13=N12-C14-C15=0 °]. Similarly, the OH and CHO groups are also coplanar with the benzene (2) ring [C19-C21-O23-H24=180 ° and C17-C21-O23-H24=0 °] and [C21-C17-C25=O27=179.99 ° and C15-C17-C25=O27=0 °] respectively. The angles between N12=N13 and both rings are almost 115 ° which shows the steric repulsion is absent in the present system.

Fig. 1. Optimized Structure of (E)-5-(2-phenyldiazenyl)-2-hydroxybenzaldehyde (PDHB)

Table. 1. The selected bond parameters of PDHB using B3LYP/6-311++G(d,p) level

Parameters	B3LYP/6-31G(d,p)	B3LYP/6-311++G(d,p)	XRD
Bond Lengths (Å)			
C3-N12	1.4174	1.4177	1.439 (3)
N12-N13	1.2609	1.2524	1.237 (2)
N13-C14	1.4161	1.4169	1.446 (3)
C14-C15	1.3948	1.3921	
C14-C16	1.4078	1.4055	1.401(3)
C21-O23	1.3579	1.3596	1.344 (3)
O23-H24	0.966	0.9628	
C25-O27	1.2162	1.2108	1.220 (3)
Bond Angles (°)			
C3-N12-N13	114.9212	115.596	113.4 (2)
N12-N13-C14	114.6928	115.2895	112.5 (2)
C19-C21-O23	115.9415	115.8629	117.7 (2)
C21-O23-H24	110.967	111.4827	
C17-C25-O27	124.9281	125.1213	124.5 (3)
H26-C25-O27	118.708	118.3659	
Dihedral Angles (°)			
C2-C3-N12-N13	179.9976	179.9998	177.2 (2)
C4-C3-N12-N13	-0.0022	0.0007	
N12-N13-C14-C15	0.008	0.003	
N12-N13-C14-C16	180.0029	180.0022	176.1 (2)
C15-C17-C21-O23	180.001	-180.0001	
C15-C17-C25-O27	-0.0118	0.0021	
C21-C17-C25-O27	179.9909	-179.9977	
C16-C19-C21-O23	-180.0026	180	
H22-C19-C21-C17	-179.998	180.0001	
H22-C19-C21-O23	-0.0025	0.0001	
C17-C21-O23-H24	-0.0027	-0.001	
C19-C21-O23-H24	-179.998	-180.001	

Vibrational Assignments

The title molecule belongs to C1 point group symmetry. It consist of 27 atoms and 75 normal modes of vibrations are distributed amongst the symmetry species as:

$$\Gamma_{3n-6} = 51' \text{ (in-plane)} + 24'' \text{ (Out-of-plane)}.$$

All these modes are found to be are active both in the Raman and IR absorption. To know the exact vibrational behaviour of this molecule the TED analysis was performed. The calculated wavenumbers were compared with recorded vibrational frequencies of FT-IR and FT-Raman spectra. Some discrepancies could be identified in between harmonic and observed frequencies, which were scaled down by proper scale factor [19]. The observed and calculated spectral results and their probable assignments are given in Table. 2 and the combined recorded and theoretical spectra are also shown in Figs. 2 and 3.s

O-H Vibrations

The O–H stretching vibrations are more sensitive to hydrogen bonding. The non-hydrogen bonded or a free hydroxyl group absorb strongly in the 3550–3700 cm⁻¹ region [20]. Intra-

molecular hydrogen bonding if present in six membered ring system would reduce the O–H stretching band to 3200–3550 cm^{-1} regions. In the present study, the OH stretching mode assigned at 3677 cm^{-1} while its corresponding vibrational bands are absent (mode no: 1). The in-plane bending vibrations calculated at 1130 cm^{-1} (mode no: 30). The OH out-of-plane deformation vibration in phenol lies in the region 517–710 cm^{-1} for associated OH [Varsanyi, 1974] [21].

In this study, the FTIR bands observed at 708 cm^{-1} and its corresponding harmonic value 692 cm^{-1} (mode no: 50) are assigned to Γ OH mode. This results show that the frequency increases with hydrogen bond strength because of the larger amount of energy required to twist the O–H bond out-of plane [22].

C=O Vibrations

The carbonyl stretching vibrations has been most extensively studied by IR spectroscopy. This multiply bonded group is highly polar and therefore gives rise to an intense IR absorption band. Because of the different electro negativities are distributed between the two atoms [23]. The lone pair of electrons on oxygen also determines the nature of the carbonyl group. In the present study, the very strong band observed at 1667 weak band at 1660 cm^{-1} in FTIR and FT-Raman spectra are assigned to C=O stretching vibration and its corresponding harmonic value is 1692 cm^{-1} (mode no: 11). This assignment is further supported by TED 88%. The β HCO / Γ HCO vibrations are ascribed to harmonic values 1402/966 cm^{-1} (mode nos: 20/37) with TED 74/64 % respectively. The ν C₂₁-O₂₃ mode is ascribed to FT-Raman band at 1201 cm^{-1} , this is supported by harmonic frequency 1196 cm^{-1} (mode no: 27) with TED 20%.

C-H Vibrations

In case of CH stretching modes they are expected to occur in the range 2900–3200 cm^{-1} [24, 25]. In this study, these vibrations are observed at 3064, 3041 cm^{-1} in FTIR spectrum and 3051 cm^{-1} in Raman spectrum. The harmonic frequencies in the range 3087-3041 cm^{-1} (mode nos: 2 to 9) are belong to the same mode. In which mode nos: 8 to 9 are in excellent agreement with experimental value and also find support from TED > 86%.

In benzene like molecule the C–H in-plane bending vibrations are observed in the region 1000–1300 cm^{-1} and are usually weak. In this study the frequency of the β CH vibrations are calculated to be in the range 1453-1053 cm^{-1} (mode nos: 17 to 19, 24, 25, 29, 31, 34) for PDHB. These modes are observed in the FTIR: 1441, 1285, 1244, 1011 cm^{-1} /FT-Raman: 1466, 1429, 1244, 1142, 1000 cm^{-1} spectra with weak intensity.

The scaled frequencies in the range 965-754 cm^{-1} (mode nos: 39 to 43, 45, 46, 49) and FTIR bands at 944, 906, 837, 805 are assigned to Γ CH modes. These assignments are in the expected range and also find support from TED. Mode no: 10 (2715 cm^{-1}) belongs to ν C₂₅-H₂₆ mode.

Azo chromophoric group (–C–N=N–C–) vibrations

Azo chromophoric group contains two bands viz C–N and N=N. Each has its own well known characteristic vibrational wavenumber. The N=N stretching vibration has a very characteristic and intense band in the Raman and its difficult to observe in IR spectrum, which is due to its symmetry [26].

This molecule has two unequivalent C–N parts causes a change in dipole moment and hence the N=N stretching is IR active and is predicted to be medium strong. Literature survey reveals that the bands occurring between 1380 and 1450 cm^{-1} corresponds to the N=N stretching of an azo compound [27]. The ν C–N modes of azo compounds are expected to appear in the region 1200-1300 cm^{-1} [28, 29]. These bands shift in wavenumber and intensity in a complex fashion, depending on the neighbouring groups. Conjugation effects, H-bonding and molecular tautomerism [29]. Moreover, substituents on benzene ring 2 influence both the peak wavenumbers and intensity. The strong band at 1477 (FT-IR) and at 1482 cm^{-1} (FT-Raman) originate from the stretching vibration of (N=N) group fused in between the two rings. The observed FTIR: 1096/FT-Raman: 1106 cm^{-1} bands are assigned to ν C₁₄-N₁₃ mode. These two bands have contribution from β CH vibrations of their respective benzene rings. These assignments are in agreement with harmonic values 1485, 1170 and 1104 cm^{-1} (mode nos: 16, 28 and 32), respectively.

C-C vibrations

In general, the phenyl carbon-carbon (C-C) stretching vibrations are reported in the region of 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380-1280 cm^{-1} by Varsanyi (1974) [21]. In the present study the FTIR bands observed at 1570, 1530, 1303 and Raman band observed at 1591, 1570, 1380, 1314 cm^{-1} are assigned to C-C stretching vibrations and their corresponding harmonic values in the range of 1581-1296 cm^{-1} (mode nos: 12-15, 21-23). These assignments are in satisfactory agreement with literature [30]. The vC17-C25 mode predicted at 1059 cm^{-1} (mode no: 33) is in agreement with FTIR band observed at 1056 cm^{-1} .

Fig. 2. Theoretical and Experimental FT-IR spectra of PDHB

Fig. 3. Theoretical and Experimental FT-Raman spectra of PDHB

Homo = -6.51380 eV

Fig. 4. The frontier molecular orbital for PDHB

Fig. 5. Theoretical and Experimental UV-Visible spectra of PDHB

Table. 2. The experimental and calculated frequencies of PDHB using B3LYP/6-311++G(d,p) level of basis set [harmonic frequencies (cm^{-1}), IR, Raman intensities (Km/mol), reduced masses (amu) and force constants (mdynA^{-1})]

Mode No	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Const.	Vibrational Assignments $\geq 10\%$ (TED) ^d
	Un Scaled	Scaled ^a	FT-IR	FT-Raman	Abs.	Rel. ^b	Abs.	Rel. ^c			
1	3827	3677			104.98	39.60	49.47	0.45	1.07	9.20	VO23H24(100)
2	3212	3087			4.46	1.68	6.23	0.06	1.09	6.63	VC15H18(100)
3	3209	3083			4.71	1.78	30.10	0.27	1.09	6.63	VC4H9(94)
4	3202	3077			4.21	1.59	92.13	0.83	1.10	6.62	VC19H22(92)
5	3196	3070			13.45	5.07	96.82	0.88	1.10	6.60	VC1H7(88)
6	3187	3062	3064w		0.97	0.37	28.00	0.25	1.09	6.51	VC16H20(92)
7	3186	3061			17.78	6.70	99.76	0.90	1.09	6.54	VC6H11(94)
8	3175	3051		3051 m	9.90	3.73	71.89	0.65	1.09	6.47	VC1H7(88)
9	3165	3041	3041 w		1.62	0.61	20.55	0.19	1.09	6.41	VC5H10(86)
10	2825	2715	2748 w		204.49	77.13	187.04	1.69	1.08	5.07	VC25H26(89)
11	1761	1692	1667 s	1660 w	265.12	100.00	280.24	2.54	10.67	19.51	VO27C25(88)
12	1645	1581		1591 m	166.98	62.98	661.49	5.99	6.89	10.99	VN12N13(12)+VC4C5(27)+VC14H16(23)
13	1636	1572	1570m	1570 w	67.83	25.59	249.18	2.26	5.87	9.26	VC2C3(36)+VC1H2(14)+ β H7C1C6(11)
14	1621	1558			13.68	5.16	31.60	0.29	5.89	9.12	VC3C4(27)+ β C1C6C5(19)+ β C1C2C3(14)
15	1619	1556			44.19	16.67	128.84	1.17	5.72	8.84	VC14C16(48)
16	1545	1485	1477 s	1482 m	40.24	15.18	11044.23	100.00	6.59	9.28	VN12N13(78)
17	1512	1453		1466 m	109.75	41.40	341.48	3.09	2.50	3.37	β H7C1C6(27)+ β H20C16C19(14)
18	1501	1442	1441 w		39.24	14.80	3049.11	27.61	2.37	3.14	β H7C1C6(22)+ β H18C15C17(10)+ β H20C16C19(16)
19	1480	1422		1429 s	0.96	0.36	2556.13	23.14	2.38	3.07	β H7C1C6(25)+ β H11C6C5(24)
20	1459	1402			14.24	5.37	103.27	0.94	1.35	1.70	β H26C25O27(74)
21	1456	1399	1380m	1380 w	26.25	9.90	3424.52	31.01	4.83	6.03	VC4C5(16)+VC14C16(16)
22	1361	1308	1303 w	1314 w	75.11	28.33	1089.56	9.87	4.44	4.84	VC4C5(35)+VC14C16(29)+ β H24O23C21(13)
23	1349	1296			5.05	1.91	67.85	0.61	3.99	4.27	VC1C2(42)+ VC3C4(18)
24	1336	1284	1285 s		2.12	0.80	485.03	4.39	1.64	1.73	VC3C4(13)+ β H7C1C6(62)
25	1309	1257	1244 w	1244 w	20.25	7.64	439.41	3.98	1.60	1.61	VO23C21(12)+ β H24O23C21(11)+ β H18C15C17(13)+ β H20C16C19(38)
26	1278	1228			76.87	28.99	366.98	3.32	5.11	4.92	VC4C5(10)+VC14C16(15)+VO23C21(15)+VN12C3(25)
27	1245	1196		1201 m	79.73	30.07	129.89	1.18	2.98	2.72	VO23C21(20)+ β H24O23C21(10)+ β H18C15C17(14)+ β C1C2C3(13)
28	1217	1170	1155 s	1157 m	71.26	26.88	3758.96	34.04	2.11	1.84	VN12C3(15)+ β H7C1C6(25)
29	1181	1135		1142 s	3.06	1.15	59.28	0.54	1.12	0.92	VC1C2(15)+ β H7C1C6(38)+ β H11C6C5(38)
30	1176	1130			216.43	81.63	29.53	0.27	1.26	1.02	β H24O23C21(19)+ β H7C1C6(24)+ β H20C16C19(18)
31	1169	1123			27.33	10.31	3045.58	27.58	1.43	1.15	β H7C1C6(23)+ β H20C16C19(30)
32	1149	1104	1096 w	1106 w	66.58	25.11	7102.29	64.31	2.18	1.70	VN12C3(23)+ β H24O23C21(10)+ β H18C15C17(13)
33	1103	1059	1056 w		18.13	6.84	1181.17	10.69	1.86	1.33	VC17C25(10)

34	1096	1053			6.97	2.63	647.53	5.86	1.59	1.13	VC1C2(23)+βH7C1C6(20)+ βH11C6C5(10)
35	1039	998	1011 w	1000 m	9.06	3.42	64.24	0.58	2.05	1.30	VC1C2(36)+βH7C1C6(34)+ βC1C2C3(10)
36	1015	975			0.90	0.34	1004.34	9.09	6.18	3.75	VC1C2(31)+βC4C5C6(44)
37	1005	966			1.35	0.51	11.69	0.11	1.74	1.04	ΓC15C14C17H18(19)+ ΓC25C17O27H26(64)
38	1005	965			3.30	1.24	54.93	0.50	2.97	1.76	VC4C5(14)+βC1C2C3(11)
39	1004	965			0.06	0.02	5.46	0.05	1.30	0.77	τH7C1C6C5(11)+τH9C4C3 C2(19)+ τH10C5C6H11(56)
40	991	952			0.00	0.00	0.31	0.00	1.37	0.79	τH8C2C3C4(78)
41	984	945	946 w		0.01	0.00	3.06	0.03	1.39	0.79	ΓC16C14C19H20(58)+ τH22C19C16C14(19)+ ΓC25C17O27H26(14)
42	952	914			15.91	6.00	8.10	0.07	1.47	0.78	ΓC15C14C17H18(60)+ ΓC25C17O27H26(13)
43	945	908	906 m		0.26	0.10	2.02	0.02	1.41	0.74	τH8C2C3N12(23)+ τH9C4C3C2(13)+ τH10C5C6H11(25)+ ΓC15C14C17H18(13)
44	901	866			6.09	2.30	7.20	0.07	6.48	3.10	β C3N12N13(15)+ β C14N13N12(17)
45	853	819	837 m		1.69	0.64	0.25	0.00	1.26	0.54	τH8C2C3N12(36)+ τH9C4C3C2(38)+ τH22C19C16C14(13)
46	852	819	805 w		28.32	10.68	1.46	0.01	1.45	0.62	τH9C4C3C2(11)+ ΓC16C14C19H20(18)+ τH22C19C16C14(47)
47	829	796		770 w	7.65	2.88	277.44	2.51	5.56	2.25	VC14C16(12)+ VO23C21(17)+ βC17C25O27(10)+ βC14C15C17(23)
48	787	756	759 m		17.70	6.67	11.27	0.10	6.54	2.39	VN12C3(14)+ βC1C6C5(10)+ βC1C2C3(10)
49	785	754			34.99	13.20	10.25	0.09	1.79	0.65	τH7C1C6C5(63)+ τH8C2C3N12(10)
50	720	692	708 m		11.07	4.17	17.73	0.16	3.80	1.16	τH22C19C16C14(10)+ τC14C16C19C21(62)+ ΓC19C21O23H24(20)
51	698	671	680 s		34.68	13.08	1.71	0.02	1.99	0.57	τH9C4C3C2(10)+ τC3C4C5C6(19)+ τC2C1C6C5(38)+ ΓN12C2C4C3(11)
52	660	634	639 w		3.15	1.19	89.70	0.81	7.24	1.86	βC1C2C3(25)+ βC1C6C5(24)
53	629	605			6.84	2.58	196.89	1.78	6.43	1.50	βC1C2C3(11)+ βC1C6C5(24)
54	626	601			25.63	9.67	52.28	0.47	6.39	1.47	βC4C5C6(11)+ βC17C21C19(10)+ βC17C25O27(26)+ βC1C6C5(10)
55	587	564	581 m		9.48	3.58	1.07	0.01	3.30	0.67	τC3N12N13C14(11)+ ΓC16C15N13C14(44)
56	563	541			21.66	8.17	37.37	0.34	4.97	0.93	βC15C14N13(18)+ βC19C21O23(20)
57	525	504	505 w		7.40	2.79	34.11	0.31	8.58	1.39	βC3N12N13(10)+ βC1C6C5(16)
58	512	492			1.63	0.62	0.10	0.00	3.19	0.49	τC2C1C6C5(16)+ ΓC16C15N13C14(17)+ ΓN12C2C4C3(34)
59	487	468			33.97	12.81	18.98	0.17	7.22	1.01	βC17C21C19(23)+ βC4C3N12(11)
60	448	430	449 m	447 w	7.31	2.76	4.87	0.04	3.14	0.37	τC15C14C16C19(66)
61	418	402			0.16	0.06	0.02	0.00	2.94	0.30	τC3C4C5C6(60)+ τC2C1C6C5(11)+ τC1C2C3C4(17)
62	401	386			4.95	1.87	15.48	0.14	5.28	0.50	τC19C16C14N13(30)+ τC16C19C21O23(30)
63	371	357			2.51	0.95	68.59	0.62	6.51	0.53	VC17C25(10)+ βC14C15C17(10)+ βC17C25O27(10)+ βC19C21O23(32)

64	323	310			104.11	39.27	38.99	0.35	1.18	0.07	τ H24O23C21C17(89)
65	291	279			5.12	1.93	31.51	0.29	5.67	0.28	β C15C14N13(13)+ β C19C21O23(17)+ β C4C3N12(14)+ β C21C17C25(15)
66	282	271			2.75	1.04	36.62	0.33	5.42	0.25	τ C2C1C6C5(18)+ τ C1C2C3C4(11)+ τ C3N12N13C14(13)
67	240	231		224 w	4.68	1.77	24.08	0.22	7.61	0.26	VN12C3(17)+ β C17C21C19(11)+ β C17C25O27(10)+ β C21C17C25(21)
68	203	195			0.66	0.25	39.06	0.35	6.59	0.16	τ C19C16C14N13(15)+ τ C16C19C21O23(23)+ τ C19C21C17C25(11)
69	162	156		150 w	5.03	1.90	105.14	0.95	7.08	0.11	β C3N12N13(15)+ β C15C14N13(10)+ β C4C3N12(21)+ β C21C17C25(27)
70	145	140			0.49	0.18	83.72	0.76	2.91	0.04	τ C15C14N13N12(14)+ τ C16C19C21O23(13)+ τ C19C21C17C25(52)
71	119	115			6.21	2.34	90.53	0.82	3.41	0.03	τ C15C17C25O27(81)
72	86	82		90 m	0.31	0.12	182.93	1.66	5.77	0.03	τ C2C3N12N13(42)+ τ C15C14N13N12(12)+ τ C1C2C3C4(11)+ τ C19C21C17C25(14)
73	63	61			0.84	0.32	219.56	1.99	6.28	0.01	β C3N12N13(22)+ β C15C14N13(26)+ β C14N13N12(30)
74	50	48			1.70	0.64	6.67	0.06	6.47	0.01	τ C19C16C14N13(29)+ τ C3N12N13C14(42)+ Γ N12C2C4C3(15)
75	21	20			0.10	0.04	494.46	4.48	4.27	0.00	τ C2C3N12N13(86)+ τ C15C14N13N12(50)

v: Stretching, β : in-plane-bending, Γ : out-of-plane bending, τ - Torsion, vw: very week, w:week, m:medium, s:strong, vs:very strong,

a Scaling factor: 0.9608,

b Relative IR absorption intensities normalized with highest peak absorption equal to 100,

c Relative Raman intensities calculated by Equation (1) and normalized to 100., Total energy distribution calculated at B3LYP/6-311++G(d,p) level.

NLO property

The first-order hyper polarizability β is a third rank tensor that can be described by 3x3x3 matrix. The 27 components of 3D matrix can be reduced to 10 components due to the Kleinman symmetry [Kleinman, 1962] [31]. The output from Gaussian 03W provides 10 components of this matrix as β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} and β_{zzz} respectively. The components of the first-order hyper polarizability can be calculated using the following equations.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (2)$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (3)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

Since the values of the polarizabilities α and the first-order hyper polarizabilities (β) of Gaussian 03W output [13] are reported in atomic units (a.u), the calculated values have been converted in to electrostatic units (esu). The calculated value of dipole moment and first hyper polarizability values are 0.78768 Debye and 9.2446×10^{-30} esu, respectively and are listed in Table. 3. In which β value is 25 times that of urea. This shows that the molecule PDHB has good NLO property.

Table 3. The NLO properties of PDHB

Parameters	B3LYP/6-311++G(d,p)
Dipole moment (μ) Debye	
μ_x	0.0240
μ_y	-0.7873
μ_z	0.0001
μ	0.78768Debye
Hyperpolarizability (β_0) $\times 10^{-30}$ esu	
β_{xxx}	-1274.37
β_{xyy}	32.94
β_{xyy}	307.22
β_{yyy}	141.22
β_{xxz}	0.21
β_{xyz}	-0.17
β_{yyz}	-0.08
β_{xzz}	-94.03
β_{yzz}	-36.48
β_{zzz}	0.03
β_0	9.2446 $\times 10^{-30}$ esu

Standard value for urea ($\mu=1.3732$ Debye, $\beta_0=0.3728 \times 10^{-30}$ esu): esu-electrostatic unit

NBO analysis

NBO analysis has been performed to elucidate the intra-molecular interaction, rehybridization and delocalization. The second order perturbation analysis of Fock matrix of PDBH is summarized in Table. 4. The strong intra-molecular interactions are formed by the orbital overlap between $\sigma(\text{C-C})$, $\sigma^*(\text{C-C})$ and $\pi(\text{C-C})$, $\pi^*(\text{C-C})$ bond orbitals in the aromatic rings, which leads intra-molecular charge transfer (ICT) causing stabilization of the system.

Hyper conjugative interaction between electron donating O_{23} atom to $\text{C}_{17}\text{-C}_{21}$ anti-bonding orbitals in the benzaldehyde group are 128.62 KJ/mol. Similarly O_{27} atom ($n\text{-}\pi^*$) transfer energy to $\text{C}_{17}\text{-C}_{25}$ (74.14) and $\text{C}_{25}\text{-H}_{26}$ (99.75 KJ/Mol) orbitals.

The $\sigma(\text{N12-N13})$ band with ED stabilize the energy of 7.07 and 7.53 KJ/mol to its acceptor anti-bonding orbitals (C2-C3) and C14-C16). More energy transfer takes place during $\pi\text{-}\pi^*$ transition. In PDHB, the π bond of N12-N13 transfer 41.88 and 39.2 KJ/Mol energy to the anti-bonding orbitals (C2-C3) and C14-C15), respectively.

Table 4. The NBO analysis for PDHB

Type	Donor NBO (i)	ED/e	Acceptor NBO (j)	ED/e	$E^{(2)}$ KJ/mol	$E(j)-E(i)$ a.u.	$F(i,j)$ a.u.
$\sigma\text{-}\sigma^*$	BD (1) N12 -N13	1.98683	BD*(1) C2 - C3	0.02182	7.07	1.54	0.046
			BD*(1) C14 - C16	0.0225	7.53	1.52	0.047
$\pi\text{-}\pi^*$	BD (2) N12 - N13	1.91479	BD*(2) C2 - C3	0.37033	41.88	0.4	0.061
			BD*(2) C14 - C15	0.32793	39.2	0.4	0.058
			BD*(1) C16 - C19	0.01133	5.56	1.53	0.04
$n\text{-}\sigma^*$	LP (1) N12	1.95425	BD*(1) C3 - C4	0.03352	33.3	0.97	0.079
$n\text{-}\sigma^*$	LP (1) N13	1.95432	BD*(1) C14 - C15	0.03162	34.1	0.98	0.08
$n\text{-}\sigma^*$	LP (1) O23	1.97726	BD*(1) C17 - C21	0.03424	26.32	1.15	0.076
$n\text{-}\pi^*$	LP (2) O23	1.85595	BD*(2) C17 - C21	0.44127	128.62	0.35	0.1

n - σ^*	LP (1) O27	1.98435	BD*(1) C17 - C25	0.05927	6.19	1.14	0.037
n - σ^*	LP (2) O27	1.87453	BD*(1) C17 - C25	0.05927	74.14	0.71	0.102
			BD*(1) C25 - H26	0.07093	99.75	0.61	0.109
$\pi^*-\pi^*$	BD*(2) N12 - N13	0.20975	BD*(2) C2 - C3	0.37033	102.01	0.05	0.06
			BD*(2) C14 - C15	0.32793	132.21	0.05	0.067
$\pi^*-\pi^*$	BD*(2) C17 - C21	0.44127	BD*(2) C14 - C15	0.32793	518.82	0.02	0.08
			BD*(2) C16 - C19	0.28584	662.2	0.02	0.082

Homo-Lumo analysis

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are called frontier molecular orbitals as they lie at the outermost boundaries of the electrons of the molecules. The HOMO and LUMO are the main orbitals responsible for chemical stability. The HOMO–LUMO orbitals of the PDHB are as shown in Fig. 4. The positive and negative phases are represented in green and red colors, respectively. The calculated values of the HOMO and LUMO energy energies and band gap are given in Table. 5. HOMO represents the associated with the electron-donating ability of a molecule, whereas LUMO indicates its ability to accept electrons. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is generally associated with high chemical reactivity and low kinetic stability. In the present study, the HOMO/LUMO energies have been calculated using B3LYP/6-311++G(d,p) level are -6.514133/-2.695831 eV. In the most common case, ionization potential (I) and electron affinity (A) are related to HOMO and LUMO, respectively. The obtained values of I and A (Table. 5) were considered for the calculation of electronegativity (χ), global hardness (g) and softness (r). These quantum chemical parameters were evaluated using Eqs. (5) to (7) as below;

$$\chi = (I+A/2); \quad (5)$$

$$\eta = (I-A/2); \quad (6)$$

$$\sigma = 1/\eta \quad (7)$$

Table. 5. The Physico-Chemical properties of PDHB

Parameters	Values
HOMO	-6.514133 eV
LUMO	-2.695831 eV
Energy gap	3.818302 eV
Ionization potential (IP)	6.514133eV
Electron affinity (EA)	2.695831 eV
Electrophilicity Index (ω)	2.7768
Chemical Potential (μ)	4.604982
Electro negativity (χ)	-4.604982
Hardness (η)	-3.818302

Table. 6. The electronic transition of PDHB

Calculated at B3LYP/6-311++G(d,p)	Oscillator strength	Calculated Band gap (ev/nm)	Experimental Band gap (nm)
Excited State 1	Singlet-A (f=0.0000)	2.5756 eV/ 481.37 nm	
58 -> 60	0.6575	3.930672	
58 -> 61	-0.1035	-4.231629	
Excited State 2	Singlet-A (f=0.3393)	3.4326 eV/ 361.20 nm	
59 -> 60	0.56506	3.818289	
59 -> 61	0.33007	4.119246	
Excited State 3	Singlet-A (f=0.0000)	3.4558 eV/ 358.77 nm	336
56 -> 61	-0.15917	-5.258311	
58 -> 60	0.11221	3.930672	
58 -> 61	0.6693	4.231629	

UV-Visible analysis

The properties of azo benzene ($-N=N-$ group), have been mostly investigated by UV-Vis spectroscopy in various theoretical and experimental results have been reported [32]. The ($\lambda_{\max}$) of the title molecule were calculated by the TD-DFT/B3LYP/6-311++G(d,p) basis set. The observed and calculated UV-Visible absorption maxima of the molecule are given in Table. 6 and shown in Fig 5. The $\lambda_{\max}$ is a function of the electron availability. This band was due to electronic transition of the azo group.

The calculated results have three excited states namely ES₁, ES₂ and ES₃. The ES₁ appeared at 481.37 nm (2.5756 eV), ES₂ at 361.20 nm (3.4326 eV) and ES₃ lies at 358.77 nm (3.4558 eV). The calculated HOMO-LUMO energy gap 3.81826 eV/ band gap 3.4558 eV: 358.77 nm) are comparable with UV result 336 nm). This excitation corresponds to (π - π^*) transition.

Molecular electrostatic potential

The molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions [33, 34]. To predict reactive sites for electrophilic and nucleophilic attack of PDHB, MEP's were calculated at the B3LYP/6-311++G(d,p). The color scheme for the MEP surface is red, electron rich, partially negative charge; blue, electron deficient, partially positive charge; light blue, slightly electron deficient region; yellow, slightly electron rich region; green, neutral; respectively. The color code of the maps in the range -6.919 a.u. (deepest red) to 6.919 a.u. (deepest blue) in title molecule, where blue color indicates the strongest attractions and red indicates the strongest repulsion. The predominance of light green region in the MEP surfaces corresponds to a potential halfway between the two extremes red and dark blue color. It is obvious from Fig. 7 that the region around the oxygen atom of the OH group for represents the more negative potential regions (red) while there is a more positive charge around the hydrogen atoms of the PDHB.

Mulliken Charges

The Mulliken population analysis [35] provides a partitioning of either a total charge density or an orbital density. The Mulliken atomic charges were calculated at B3LYP/6-311++G(d,p) level are given in Table. 7. The mulliken charge plot is shown in Fig. 6. The charge distribution on the molecule has an important influence on the vibrational spectra. The carbon: C14 and C21 have the highest negative charge. Therefore, this might have been given C-C bond a greater ionic character. The C14 and C21 atoms bonded with N13 and O23 atoms. The C17 has highest positive charge, which is due to the attachment of CHO group with C17 atom. It is evident from the Table. 7 that the bond length between (C17-C21 1.4156 Å) and (C21-C19 1.398 Å) are differ by 0.0176 Å. This is due to C21/C17 atoms posses highest negative/positive changes.

Thermodynamic analysis

On the basis of vibrational analysis at B3LYP/6-311++G(d,p) level, the standard thermodynamic functions: heat capacity ($C_{p,m}^0$), entropy (S_m^0) and enthalpy changes (H_m^0) for the PDHB were obtained from the theoretical harmonic frequencies and are listed in Table. 8. Therefore, it can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 K due to the molecular vibrational intensities increase with temperature [36]. The correlation equations among heat capacity, entropy and enthalpy changes due to the temperature were fitted by quadratic, linear and quadratic formula and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.99957, 0.99997 and 0.99971. The corresponding fitting equations are as follows and the correlation graphs are shown in Fig. 8.

$$C_{p,m}^0 = -1.83066 + 0.1642T - 6.4227 \times 10^{-5} T^2 \quad (R^2 = 0.99957)$$

$$S_m^0 = 3.16547 + 0.14747T - 1.84592 \times 10^{-5} T^2 \quad (R^2 = 0.99997)$$

$$\Delta H_m^0 = 107.84214 + 0.00567T + 1.89583 \times 10^{-5} T^2 \quad (R^2 = 0.99971)$$

All the thermodynamic data are supportive information for further study of the PDHB. They can be used to compute other thermodynamic energies according to the relationship of thermodynamic functions and estimate of chemical reactions according to the second law of thermodynamics in thermo chemical field [37].

Table. 7. The Mulliken atomic charges of PDHB

Atoms	Charges	Atoms	Charges
1C	-0.22624	15C	-0.00184
2C	0.174061	16C	0.332857
3C	-0.36607	17C	1.818738
4C	-0.0236	18H	0.264383
5C	-0.19932	19C	-0.11844
6C	-0.31078	20H	0.196265
7H	0.184923	21C	-1.48676
8H	0.167961	22H	0.2055
9H	0.181698	23O	-0.17553
10H	0.189536	24H	0.260242
11H	0.15136	25C	-0.03432
12N	0.070018	26H	0.061518
13N	0.11474	27O	-0.24328
14C	-1.18762		

Table. 8. Thermodynamic properties at different temperatures of PDHB

T	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
100	342.85	101.31	6.77
200	433.05	167.53	20.16
300	514.31	238.18	40.44
400	592.12	304.48	67.64
500	666.25	360.16	100.97
600	736.02	404.85	139.31
700	801.21	440.57	181.64
800	862	469.49	227.19
900	918.71	493.26	275.37
1000	971.74	513.05	325.71

Fig. 6. The Mulliken atomic charges of PDHB **Fig. 7. Molecular electrostatic potential map of PDHB** **Fig. 8. The thermodynamic properties at different temperatures of PDHB**

4. CONCLUSION

A complete vibrational analysis has been performed for the first time for PDHB molecule. The detailed interpretations of the vibrational spectra have been carried out. The vibrational assignments are further justified with help of the TED. The optimized geometrical parameters were calculated and compared with the related XRD values. The angle between C3-N12=N13 and C14-N12=N13 have same value 115° , which shows that steric repulsion is absent in the present molecule. The $\nu_{\text{N12=N13}}$ mode appeared at higher wavenumber with strong intensity which is due to the neighbouring groups and conjugation effects. The β_0 value of PDHB is twenty five times greater than that of urea and hence the molecule (PDHB) has good NLO activity. In this study, the π - π^* interaction can make larger intra-molecular interaction and hence the polarizability of the molecule increases. The HOMO-LUMO energy gap is 3.8183 eV, which explain the eventual charge transfer occur within the molecule. MEP gives the visual representation of the chemically active sites and comparative reactivity of atoms. The Mulliken atomic charges of PDHB has been calculated and also plotted. The recorded UV-Visible spectral value agree well with calculated value. The absorption max (336 nm) is assigned to π - π^* type. Thermodynamic parameters have been calculated at different temperatures of PDHB molecule. The correlation between the statistical thermodynamics and temperature are also obtained.

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