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Synthesis, molecular structure, FT-IR, FT-Raman and XRD spectroscopic investigations of (E)-1-(5-((4bromophenyl)diazenyl)-2- hydroxyphenyl)ethanone: A comparative DFT study

Erbil Agar^a, Ozgur Alver^b, Ahmet Koroglu^{c,}, Sedat Gumus^{c, *}, Canan Kazak^c

^a Ondokuz Mayis University, Faculty of Arts and Sciences, Department of Chemistry, 55200, Atakum, Samsun, Turkey

^bAnadolu University, Science Faculty, Department of Physics, 26470, Eskişehir, Turkey ^cOndokuz Mayis University, Faculty of Arts and Sciences, Department of Physics, 55200, Atakum, Samsun, Turkey

Abstract

The (E)-2-acethyl-4-(4-bromophenyldiazenyl) phenol compound was synthesized and analysed by elemental analysis, single-crystal X-ray diffraction (XRD), FT-IR and FT-Raman spectroscopies. Furthermore, vibrational spectra of this compound have been assigned by using scaled quantum mechanical force field approximation from density functional method (B3LYP) with 6-31G(d) basis set. A well-agreement has been attained between the calculated and observed spectra. Morever, NBO analysis indicates there are strong conjugate interactions inside the molecule. Apart from this, the single-crystal sturucture from X-ray study has showed that this compound has a strong intramolecular O-H. . . O hydrogen bond and $\pi - \pi$ stacking.

Keywords: Azo compounds; Bromophenyl; X-ray structure determination; Vibrational assignment; Density functional method.

1. Introduction

Azobenzenes are chemical compounds considered as derivatives of organic diazenes. As containing π -congugation in the structure, they absorb light efficiently. Therefore, they have been mainly used as dyes and pigments in various fields of the industry such as couloring in polyester fiber, textile materials and food additives [1-8]. In addition, they have also other potential applications in science and tecnology as reaction initiators, fluorescant indicators,

^{*} Corresponding author. *E-mail address:* <u>sedatg@omu.edu.tr (S. Gumus)</u>.

therapeutic agents, drug delivery, biosensor systems and biomedical materials [9,10]. One of the most important reasons of studying azobenzenes and its derivatives are probably to be able to adjust their properties easily and precisely [11]. Moreover, azobenzene derivatives upon photo-irradition with UV light show isomerisation over reversal between their trans and cis forms [12-18] and resistance to thermal decomposition [19-21]. This fact enables azobenzenes to control the motion of different moities in molecules containing them [22] and so to use as a photoswitch in smart surfaces [23] and biochemical systems [24]. For instance, in biological systems, photo-induced dynamics of azo compounds changes enzyme activity and function of proteins [24,25]. Nowadays, azobenzene based-polymers have given promise in using as storage devices of optical data as consequence of significant non-linear optics feature [26-29]. For all these reasons, they have recently attracted a lot of attention in experimental and theoretical studies because of undergoing cis-trans photoisomerization in photoexcited state. Some spectroscopic and molecular structure characterizations of some azo derivatives of some 2-hydroxyacetophenone were reported previously [30]. However, novel compound "(E)-1-(5-((4-bromophenyl)diazenyl-2-hydroxyphenyl) ethanone" presented here is a derivative of azo benzene group and providing insight into some structural properties of title compound may be of importance for researchers studying azo compounds.

In this study we present vibrational analysis of FT-IR and FT-Raman spectra by using scaled quantum mechanical procedure (SQM) of normal coordinate analysis at the density functional theory level of B3LYP/6-31G(d), and also report syntesis, results of single crystal X-ray diffraction technique and elemental analysis of this title compound.

2. Experimental

2.1. Synthesis

The 4-bromoaniline (0.860 g, 5.0 mmol), water (50 ml) and concentrated hydrochloric acid (4.7 ml, 56 mmol) were mixed and stirred until a clear solution was obtained. This solution was cooled to 273-278 K and then sodium nitrite solution (1.8 g, 26 mmol) with water was added drop by drop to this mixture while the temperature was kept below 278 K. The resulting new mixture was stirred for 30 minutes in an ice bath. 2-hydroxyacetofenone (0.68 g, 5.0 mmol) solution (pH 9) was gradually added to a cooled solution of 4-bromobenzenediazonium chloride, prepared as described above, and resulting mixture was stirred at 273-278 K for 60 minutes in ice bath. The product was recrystallized from ethyl alcohol to obtain solid (E)-2-acethyl-4-(4-bromophenyldiazenyl) phenol. The crystal of (E)-2-acethyl-4-(4-bromophenyldiazenyl) phenol was produced by slow evaporation from ethyl

alcohol after one day (yield 76% m.p 457-459 K). The synthesis of compound is shown in Figure 1. Later on, the crystal of (E)-2-acethyl-4-(4-bromophenyldiazenyl) phenol was analysed by using elemental analysis technique. As a result, C, H, O and N were found 52.72, 3.35, 10.28 and 8.69 %, respectively.

2.2. X-ray diffraction analysis

Suitable single crystals were placed on a glass fiber and data collection were performed on a STOE IPDS(II) image plate detector using Mo K_a radiation (λ =0.71019 Å) at 298 K. Furthermore, the diffraction intensities were made the Lorentz-polarisation correction factor and the absorption correction was made by integration method via X-RED software and cell parameters were found by using X-AREA software [31]. The structure was solved by direct methods using SHELXS-9722 and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F2 using SHELXL-97 [32]. All carbon and hydrogen atoms were positioned geometrically and refined by a riding model with Uiso 1.2 times that of attached atoms and remaining hydrogen atoms were found by Fourier difference. Molecular drawings were obtained using ORTEP-III [33]. Details of the crystal data, data collection conditions, structure solution and refinement are given in Table 1.

2.3. FT-IR and FT-Raman analysis

FT-IR spectrum of the compound was recorded using Bruker Optics IFS66 vs. FT-IR spectrometer with the resolution of 2 cm⁻¹ in the spectral region of 4000–400cm⁻¹ with KBr pellet technique. The Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 785 nm excitation from a 3B diode laser of power 100 mW having 3 cm⁻¹ resolution.

2.4. Computational procedure

The molecular structure of title compound in the gas phase was optimised by using different hybrid DFT quantum mechanical methods implemented in the Gaussian Software 03W [34]. It is well-known that DFT methods accurately predict equilibrium geometries and quadratic harmonic force fields of molecules. Even if some theoretical models estimate accurate geometries, they may not provide a good quality of potential energy surface, leading to the wrong determination of vibrational spectra. The DFT methods (B3LYP, B3PW91 and PBEPBE) [35-39] preferred mostly in the computational chemisty were performed together

with 6-31G(d) base set [40]. In optimisation procedure, the geometric parameters from X-ray studies were taken as input for each quantum mechanical model. The ground-state energies for local minima on PESs over B3LYP, B3PW91 and PBEPBE were found as -3371.743 a.u, -3371.424 a.u. and -3370.397 a.u., respectively including the frequency key in the route section of the job. Then harmonic vibrational frequencies for optimized molecular structures were calculated and any imaginary vibrational frequency associated with a transition state of the molecular system was not encountered along with all the calculations. In addition to that, in order to investigate the portion distribution of each normal mode, TED calculations were carried out by the scaled quantum mechanical (SQM) program [41, 42] for which the necessary input data were extracted from the Gaussian output file of the opt+freq job. By the way, it should be stressed that SQM force field calculation of title molecule were based only on theory level of B3LYP/6-31G(d). In scaling procedure used to compansate systematic errors from quantum mechanical methods and to match between theoretical and observed frequencies, predefined scaling factors presented initially were refined with SQM and final scaling values were obtained (Table S1, see supplementary data). In order to match theoretical and observed frequency, two types of scaling were presented over dual scaling and multiscaling

In present work, all the infrared intensities were rescaled relative to 100 % the highest intensity peak and Raman scattering activities were converted into relative Raman intensities using the following formula [43, 44]:

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[\left(1 - \exp\left(-\frac{hc v_i}{kT}\right) \right) \right]}$$

In this equation v_0 is the laser exciting wavenumber (in present study, $v_0 = 12739 \text{ cm}^{-1}$), v_i the vibrational wavenumber of the ith normal mode and S_i is the Raman scattering activity of the normal mode v_i , f is a selected common normalization factor for all peak intensities. h, k, c and T are Planck and Boltzmann constants, speed of light and temperature respectively.

3. Results and discussion

3.1. Molecular geometry, atomic net charges and NBO analysis

Figure 2 shows the labeled-atom scheme of title compound by means of ORTEP-3 plot [33]. The molecule $C_{14}H_{11}N_2O_2Br$ contains the azo group linking two aromatic rings to each other.

Some selected geometrical parameters of the molecular structure are given for comparison in Table 2.. The crystalographic results of the bond lengths N11-C3 and N12-C13 are 1.410 Å and 1.429 Å, respectively and the corresponding DFT results (B3LYP, B3BW91,PBEPBE) are (1.415,1.411,1.414 Å) and (1.408, 1.404,1.408 Å). These values were reported as 1.257 Å [45], 1,246 Å & 1.253 Å [46], 1.248 Å [47], 1.259 Å [48], 1.247 Å [49], 1.260 Å [50], 1.252 Å [51] and 1.263 Å [52] in the previous studies. However, NBO calculation indicates that hybridization state of N11-C3 bond is nearly close to single-bond character [0.64 C3(sp^{2.53})+ 0.76 N11 (sp^{2.13}) as in its own hybridization of the other N12-C13 [0.64* C13 (sp^{2.48})+ 0.76*N12(sp^{2.09})]. On the other hand, crystallographic N=N bond length (N11-N12) of 1.255 Å shows double bond character [41] and this case is supported with the N=N hybridization of [0.7061 N11 (sp^{2.31})+0.7081 N12 (sp^{2.29})] as well. Furthermore, hybridization states of nitrogen atoms differ a little in sp². Consequently, azo group may have a small dipole moment due to minor polarity between the nitrogen atoms.

The bond angles between aryl and azo groups are $115.0(4)^{\circ}$ for (N12-N11-C3) and $113.1(4)^{\circ}$ for (N11-N12-C13). As seen in Table 2, DFT calculations give a deviation from the experimental ones up to *ca*. 2° . However, torsinal bond angles related to azo group are nearly equal to 180° , which are consistent with DFT results. The molecule is nearly planar and its phenyl rings attached to azo group has trans-isomer conformation.

Natural population analysis (NPA) produces more convienent results than in the other atomic charge population analysis [53]. Therefore, NPA rather than the others is preferred to discuss atomic charges. NPA of DFT (B3LYP) displays that atoms O21 and O26 carry - 0.670e and -0.594e respectively and also have higher negative charges relative to other atoms as expected. Besides, bromine atom carries on a partial positive charge of 0.065e. The carbon atoms attached electronegative oxygen atoms in the molecule have partial positive charges and are susceptible to nucleophilic attack as well as bromine atom, whereas oxygen atoms are sensitive to electrophilic attack. Azo group (-N11=N12-) is an electron withdrawing group and have charges of -0.211e and -0.199e, respectively. Therefore, azobenzene shows resistant to electrophilic attacks [54].

NBO analysis indicates strong hyperconjugative/congugative interactions between electron donor orbitals (Lewis NBOs) and acceptor orbitals (non-Lewis NBOs) of the molecule. The azobenzene skeleton of the molecule results in strong congugative interactions (π - π^* delocalizations), which are in order of about 20 kcal/mol. Lone pairs of the bromine, the oxygens, the nitrogens and the carbon atoms C16 and C19 contribute strongly to stabilization

of molecule by transferring charge to π^* anti bonds in their own proximity. The larger interactions are in between lone pair of C16 and the anti-bond $\pi^*(C25-O26)$, and the anti-bond $\pi^*(C13-C14)$ by *ca*. 78 and 72 kcal/mol. Moroever, NBO analysis supports that charge transfer occurs from the lone pairs 1 and 2 of O26 to $\sigma^*(O21-H22)$ by the stabilization energies of *ca*. 5 and 27 kcal/mol, respectively. Therefore, the charge transfers from the donor NBO to the related acceptor bonds weaken those bonds in question, lowering the related bond order . It is expected to rise bond length of O21-H22 to some extent.

The crystal structure of title compound exists in strong intramolecular hydrogen bond between O21-H22 and O26 as in a common feature of (E)-2-Benzoyl-4-[(4methylphenyl)diazenyl]-phenol [55] and $\pi - \pi$ stacking. Geometrical parameters of the intra molecular hydrogen bonds are listed in Table 3. Furthermore, the single crystal structure of the title compound crystallized in monoclinic unit cell is illustrated in Figure 3 together with molecular arragenment.

Experimental and theoretical data in Table 2 obviously only slightly differ from each other and may be supposed to be in a good approximation. However, the stationary equilibrium geometry for the molecule was calculated in gas phase, not in solid phase.

3.2. Vibrational modes

This molecule of 30 atoms belongs to C_1 point group. Therefore, we have 84 vibrational modes but 16 of them falls into the region below 400 cm⁻¹. Vibrational analysis of this compound is presented in Table 4 together with theoretical mode assignments of observed Raman and IR bands, and the corresponding TED portions. Most of observed IR bands of this compound may be assigned to acetyl and azo groups while some of them to ring vibrations. However, as the molecule has low symmetry, band assignmens were checked by GaussView visualization program.in order to provide accuracy.

In this study, while v(O - H) stretching vibration appears Raman inactive, a broad band is seen in the infrared spectrum between 3600-3350 cm⁻¹ (see Figure S2) with an agreement with previously published results [46, 51]. It is calculated as 3347 cm⁻¹ with SQM method and a TED contribution of nearly 100 %. CH (ring) stretching vibrations as observed at 3085 (IR), 3073 (IR) cm⁻¹. These bands due to most probably weak polarization could not observed in the Raman spectrum and they are calculated as 3073, 3065 cm⁻¹ (dual scaling [56]) and 3083, 3075 cm⁻¹ (SQM) with total TED contributions in parenthesis v15-18 (88), v23-24 (8), v1-7 (80) and v2-8 (19). Methyl CH stretching is observed at 2933 cm⁻¹ (IR) and

calculated at 2908 cm⁻¹ (dual scaling) and 2918 cm⁻¹ (SQM) with a TED contribution of v27-30 (43), v27-28 (42) and v27-29 (15). These values are in agreement with previously published report [50]. v(C=O), stretching band or v(11-12) is found experimentally at 1639 cm⁻¹ and calculated as 1648 cm⁻¹ by both dual scaling factors and SOM method with a TED contribution of 61 %. The observed IR and Raman bands between 1491-1419 cm⁻¹, predominated by (N=N) azo group stretching bands, are theoretically found between 1496-1422 cm⁻¹ with the given TED contributions as shown in Table 4. The observed bands at 1170 (IR) cm⁻¹ and 1174 (R) cm⁻¹ is mostly governed by v(C-N) stretching vibrations in an agreement with previously reported data [46] and it is calculated as 1160 cm^{-1} (dual scaling), 1166 cm⁻¹ (SQM) with a TED contribution of 20 %. For the para substitued benzene moiety, two CH out-of-plane bendings are observed in IR bands at 970 and 833 cm⁻¹ and only one Raman band of 973 cm⁻¹. It is found as 960 cm⁻¹ for dual scaling. However, the IR band of 833 cm⁻¹ is diagnostic, and this band is usually expected at 860-790 cm⁻¹. On the other hand, in the 1,2,4 trisubstitued benzen ring, CH out-of-plane bendings are observed between 900- 870 cm^{-1} and $800-760 \text{ cm}^{-1}$ [57]. In this study, they appear at 897 and 818 cm⁻¹ only in the IR spectrum. Apart from this, scissoring vibration of methyl group is assigned to Raman band of 1369 cm⁻¹ and IR band of 1367 cm⁻¹ while it calculated at 1367 cm⁻¹ with TED portion of % 80. As can be seen from Table 4, there is a good agreement between experimental and theoretical vibration data for this study. This fact has also been verified by root mean square values (RMS) for the IR/Ramanspectra of this molecule as seen in Figure 4 and 5: 7.5 cm^{-1} (IR, dual scaling), 10.5 cm⁻¹ (Raman, dual scaling), 4.3 cm⁻¹ (IR, SQM), 5.5 cm⁻¹ (Raman, SQM). These assigned bands are well-correlated with those observed in previous studies [31, 46, 58-59].

4. Conclusion

In the present study, the equilibrum geometries of title molecule have been predicted by using various hybrid DFT (B3LYP, B3PW91 and PBEPBE) methods over the base set of 6-31G(d). It was seen that there was a good agreement between the crystal structure and the related results. Only at the theory level of DFT-B3LYP/6-31G(d), the intramolecular interactions and vibrational spectra of the compund have been interpreted in terms of NBO analysis and SQM method, respectively. NBO analysis showed that there were large delocalizations inside the present molecule. Morever, SQM-B3LYP/6-31G(d) is of an efficient capability to be able to clarify the correlation between the crystal structure–vibrational spectra of the azobenzene

compoud. Therefore, the scaling factors obtained here may be transferred to study vibrational spectra of azobenzene derivatives.

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Figure captions

Figure 1. Synthesis routes for the (E)-2-acethyl-4-(4-bromophenyldiazenyl)phenol.

Figure 2. An ORTEP-3 view of the title compound with the atomic numbering scheme.

Figure 3. Part of the crystal structure of the title compound.

Figure 4. Experimental (A) and theoretical (B) infrared spectrum of the title compound.

Figure 5. Experimental (A) and theoretical (B) Raman spectrum of the title compound.

Table captions

Table 1. Crystal data, data collection conditions and structure refinement for the title molecule.

Table 2. Some selected geometrical parameters of the title molecule.

Table 3. Geometrical parameters of the intra molecular H-bonds for the title molecule.

Table 4. Comparison of the experimental and calculated vibrational wavenumbers (cm-1) for the title molecule in gas phase.

Chemical Formula	$C_{14}H_{11}N_2O_2Br_1$
Formula Weight	319.15
Crystal System	Monoclinic
Space Group	P2 ₁
Z	2
Crystal Colour	yellow
a, b, c	4.02333(20) Å, 5.9537(4) Å, 26.7930(12) Å
β	94.182(4)°
V	640.08(6) Å ³
Calculated Density	1.656 Mg m^{-3}
Radition, λ	Mo K _α , 0.71073Å
μ	3.21 mm^{-1}
T(K)	296
T_{min}, T_{max}	0.4938, 0.8379
Scaning Mode	STOE IPDS II
Scan Range	ω
Crystal Size	0.14 0.28 0.36
$\theta_{min}, \theta_{max}$	26.0° 1.5°
Number of measured/independent reflections,	0.094
R _{int}	
Number of reflections with $2\sigma(I)$	2501
Number of refined parameters	172
S	0.90
$R[F2 > 2\sigma(F2)]$	0.041
wR(F2)	0.089
$\Delta \rho_{max}, \Delta \rho_{min}$	$0.55 \text{ e } \text{\AA}^{-3}$ -0.23 e \AA^{-3}

Table 1. Crystal data, data collection conditions and structure refinement for the title molecule.

Parameter	X-Ray	B3LYP / 6-31G(d)
Bond lengths(Å)		
Br—C6	1.899 (5)	1.915
C3—N11	1.410 (7)	1.415
N11—N12	1.255 (5)	1.256
N12—C13	1.429 (6)	1.408
C25—C27	1.484 (7)	1.513
O21—C19	1.347 (6)	1.332
O26 — C25	1.230 (7)	1.233
Bond angles (°)		
N11—N12—C13	113.1 (4)	115.32
N12—N11—C3	115.0 (4)	115.12
O26 — C25 — C16	119.6 (5)	120.87
O21—C19—C16	117.7 (5)	122.80
C1—C6—Br	120.0 (4)	119.46
Torsion angles (°)		\sim
C13 - N12 - N11 - C3	179.0 (4)	179.99
C2 — C3 — N11— N12	177.6 (5)	180.00
N11—N12—C13—C14	178.3 (4)	180.00
C14 - C16 - C19 - O21	178.4 (5)	180.00

 Table 2. Some selected geometrical parameters of the title molecule.

 Table 3. Geometrical parameters of the intra molecular H-bonds for the title molecule.

D-HA	D-H	НА	DA	D-HA
O21-H22O26	0.82	1.81	2.534(6)	146.7
			(
			$ \rightarrow $	
)			
X Y				

	A		E			B3LYP/6-31G(d)		
Mode	Assignments	Experimental		Gas phase				
	TED (≥ 5 %)	IR	Raman	ν^{α}	ν^{β}	I _{IR}	I _R	
ν_1	v 15-18 (88) + v 23-24 (8)	3085	-	3073	3083	1.06	-	
v_2	v 1-7 (80) + v 2-8 (19)	3073	-	3065	3075	1.46	-	
V ₃	ν 25-26 (61) + δ 19-21-22 (5)	1639	-	1647	1648	100.00	-	
ν_4	v 13-14 (21) + v 19-23 (12) + v 25-26 (12)	1610	1615	1608	1611	16.82	33.66	
	ν 15-23 (10) + δ 16-14-17 (5)							
v_5	v 1-2 (19) + v 4-5 (19) + v 2-3 (13)	1582	1585	1578	1581	10.42	75.88	
	ν 11-12 (6) + ν 5-6 (6) + δ 3-2-8 (5)							
ν_6	δ 19-21-22 (24) + ν 15-23 (16) + ν 16-19 (12)	1573	1579	1567	1574	30.41	0.43	
	v 13-15 (11)							
v_7	ν 11-12 (37) + ν 13-15 (6) + δ 19-23-24 (6)	1489	1491	1491	1496	12.37	518.04	
	δ 19-21-22 (5)							
ν_8	δ 4-5-10 (9) + δ 6-5-10 (7) + δ 2-1-7 (7) + ν 5-6 (7)	1476	-	1467	1476	29.64	-	
	δ 5-4-9 (6) + v 3-4 (5) + δ 6-1-7 (5)							
v ₉	ν 11-12 (23) + δ 18-15-23 (6) + δ 13-15-18 (6)	1448	1452	1450	1457	2.59	625.53	
v_{10}	ν 13-14 (14) + ν 25-26 (13) + δ 19-21-22 (11)	1419	1423	1419	1422	0.40	116.98	
	v 14-16 (9) + v 11-12 (7) + v 13-15 (6)							
v_{11}	δ 19-21-22 (20) + υ 15-23 (15) + υ 14-16 (7)	1395	1397	1391	1398	44.13	6.03	
	v 1-2 (5)							
v_{12}	δ 28-27-30 (17) + δ 25-27-30 (15) + δ 25-27-28 (15)	1367	1369	1362	1367	13.00	10.42	
	$\delta 29-27-30(12) + \delta 28-27-29(12) + \delta 25-27-29(9)$							
	v 25-27 (6)	1000	1004	1000	1004	10.20	14.00	
v_{13}	v 16-19 (19) + v 16-25 (11) + v 13-14 (11)	1330	1334	1320	1324	10.30	14.09	
	V = 15-23 (6) S 2 1 7 (8) + S 4 5 10 (7) + S (1 7 (7) + S (5 10 (7)	1200	1200	1202	1201	0.04	(7.09	
v_{14}	0 2 - 1 - 7 (8) + 0 4 - 5 - 10 (7) + 0 0 - 1 - 7 (7) + 0 0 - 5 - 10 (0)	1306	1309	1293	1301	8.84	07.98	
	V 2-3 (6) + V 3-4 (6) + V 19-21 (6) + 0 3-2-8 (5)	1206		1200	1207	22.41		
V ₁₅	V 19-21 (20) + 0 18-15-25 (9) + 0 15-15-18 (5) 8 15 22 24 (5)	1290	-	1290	1297	22.41	-	
v	0 13 - 23 - 24 (3) y 1 6 (25) + y 5 6 (21) + y 4 5 (8) + y 2 3 (7)	1283		1277	1270	0.50		
v 16	v 1-0 (25) + v 5-0 (21) + v 4-5 (0) + v 2-5 (7) v 3-4 (5)	1205	_	1277	1277	0.50	_	
N	$v = 14_{-16}(20) \pm v = 10_{-21}(12) \pm 8_{-13_{-14}}(12)$	1248	1252	1251	1254	15 42	45 12	
v 17	$v_{14-10}(20) + v_{12-21}(12) + v_{13-14-17}(12)$ $v_{12-13}(9) + \delta_{16-14-17}(8) + v_{16-25}(5)$	1240	1252	1231	1254	15.42	43.12	
Via	$v_{12-13}(0) + v_{10-14-17}(0) + v_{10-23}(0)$ $v_{19-23}(16) + v_{3-11}(10) + \delta_{19-23-24}(0)$	1217	1215	1208	1214	17 30	52.61	
v 18	v 19-25(10) + v 9-11(10) + 0 19-25-24(0) v 16-25(7) + v 25-27(6) + 8 19-21-22(6)	1217	1210	1200	1211	17.50	52.01	
	δ 15-23-24 (6)							
V10	$v 12 - 13(20) + \delta 16 - 14 - 17(9) + v 4 - 5(6)$	1170	1174	1160	1166	30.22	207.14	
. 19	δ 3-4-9 (5)							
V_{20}	$v 3-11 (18) + \delta 1-2-8 (12) + \delta 5-4-9 (8)$	1148	1151	1134	1142	0.97	699.57	
20	δ 3-2-8 (7) + ν 2-3 (6)							
V ₂₁	δ 18-15-23 (20) + δ 13-15-18 (17) + δ 15-23-24 (14)	1124	1127	1109	1117	11.18	112.66	
	ν 15-23 (10) + δ 19-23-24 (7) + ν 13-14 (6)							
v_{22}	$v 1-2 (17) + \delta 5-4-9 (14) + v 4-5 (12) + \delta 2-1-7 (10)$	1098	-	1090	1098	1.90	-	
	δ 1-2-8 (10) + δ 4-5-10 (7) + δ 3-2-8 (5) + δ 3-4-9 (5)							
v_{23}	v 5-6 (27) + v 1-6 (23) + v 6-20 (12) + v 1-2 (7)	1066	1069	1044	1045	8.47	26.78	
	v 4-5 (5)							
v_{24}	δ 25-27-28 (28) + δ 25-27-30 (28) + τ 26-25-27-29 (18)	1020	-	1019	1025	0.59	-	
	τ 16-25-27-30 (6) + τ 16-25-27-28 (6)							
v_{25}	$v 2-3 (11) + v 3-4 (11) + \delta 4-5-6 (10) + \delta 1-2-3 (9)$	1009	1012	991	1005	11.87	19.81	
	δ 3-4-5 (9) + δ 2-1-6 (9) + δ 3-2-8 (7) + δ 3-4-9 (7)							
	0 0 - 1 - 7 (0) + 0 0 - 5 - 10 (5) = 0 4 5 10 (41) + = 0 4 2 11 (17) + = 2 2 4 0 (10)	070	072	064	070	0.20	0.20	
v_{26}	τ 9-4-5-10 (41) + τ 9-4-5-11 (1/) + τ 2-3-4-9 (10)	970	973	964	970	0.20	0.20	
	10-3-4-9(9) + 110-3-0-20(0)							

Table 4. Comparison of the experimental and calculated vibrational wavenumbers (cm⁻¹) for the title molecule in gas phase.

Table 4. (Continued)

	Assignments		Fynarimantal		B3LYP/6-31G(d)			
Mode	Assignments	Experimental		Gas phase				
	TED (≥ 5 %)	IR	Raman	ν^{α}	ν^{β}	I _{IR}	I _R	
v_{27}	v 25-27 (18) + δ 25-27-29 (16) + δ 25-27-28 (7)	937	940	940	945	7.47	3.67	
	δ25-27-30 (7) + v 13-15 (7)							
v_{28}	τ 12-13-14-17 (28) + τ 17-14-16-25 (23)	897	-	904	902	3.52	-	
	τ 17-14-16-19 (19) + τ 15-13-14-17 (14)							
V ₂₉	τ 3-4-5-10 (17) + τ 10-5-6-20 (12)	833	-	828	827	11.82	-	
	τ 9-4-3-11 (10) + τ 3-2-1-7 (10)							
	τ 1-6-5-10 (7) + τ 7-1-6-20 (7)							
	$\tau 8-2-3-11(6) + \tau 6-5-4-9(6)$							
v_{30}	τ 16-19-21-22 (50) + τ 22-21-19-23 (36)	818		817	815	26.31	-	
v_{31}	ν 19-21 (16) + ν 16-19 (9) + δ14-13-15 (9)	802	806	792	800	0.35	6.41	
	v 19-23 (7) + v 12-13 (5)							
v_{32}	$\tau 21-19-16-25 (10) + \tau 16-19-23-24 (9)$	738	742	726	734	4.55	3.32	
	τ 15-23-19-16 (8) + τ 13-15-23-24 (7)							
	τ 14-16-19-23 (7) + τ 22-21-19-23 (7)							
	τ 13-14-16-19 (6) + τ 17-14-16-19 (6)							
V ₃₃	τ 1-6-5-4 (10) + τ 2-1-6-5 (9) + τ 3-4-5-6 (9)	704	708	701	702	1.16	0.38	
	τ 3-2-1-6 (8) + τ 2-3-4-5 (8) + τ 1-2-3-4 (8)							
	τ 6-5-4-9 (7) + τ 6-1-2-8 (7) + τ 4-3-2-8 (6)							
	τ 2-3-4-9 (6)							
v_{34}	δ 15-23-19 (10) + δ 2-3-4 (7) + ν 6-20 (6)	670	674	659	669	1.93	3.89	
	δ 13-15-23 (5) + ν 12-13 (5)							
V ₃₅	$v 25-27 (14) + \delta 16-25-26 (12) + \delta 26-25-27 (12)$	644	645	629	639	7.60	2.22	
55	δ 21-19-23 (6)	Υ ΄						
v_{36}	δ 4-5-6 (9) + δ 1-2-3 (9) + δ 2-1-6 (9) + δ 3-4-5 (8)	626	631	622	632	1.74		
	δ 16-25-26 (8) + δ 26-25-27 (7) + v 25-27 (7)						9.30	
v_{37}	$v 3-11 (8) + v 6-20 (8) + \delta 12-13-15 (8) + \delta 4-3-11 (6)$	546	558	547	556	3.36	5.32	
	δ 11-12-13 (6) + δ 15-23-19 (6) + δ 14-16-25 (5)							
	δ 13-14-16 (5) + δ 2-3-4 (5)							
V ₃₈	τ 1-6-5-10 (9) + τ 5-6-1-7 (9) + τ 2-1-6-5 (8)	500	-	499	499	0.48	-	
	τ 1-6-5-4 (7) + τ 2-3-4-9 (6) + τ 4-3-2-8 (6)							
V ₃₉	δ 21-19-23 (20) + δ 16-19-21 (17) + δ 26-25-27 (15)	477	480	464	475	3.48	3.43	
	δ 11-12-13 (6) + δ 16-25-27 (6)							
v_{40}	τ 13-14-16-19 (14) + τ 14-16-25-26 (11)	439	441	438	439	0.20	0.01	
	τ 12-13-14-16 (10) + τ 14-16-19-21 (8)							
	τ 13-15-23-19 (7) + τ 15-13-14-16 (7)							
ν_{41}	τ 3-2-1-6 (19) + τ 3-4-5-6 (16) + τ 1-2-3-4 (8)	411	-	412	413	0.08	-	
	τ 1-2-3-11 (8) + τ 2-1-6-20 (7) + τ 1-6-5-4 (6)							
	τ 3-2-1-7 (6) + τ 6-5-4-9 (6)							

 v^{α} represents wavenumbers scaled by 0.955 above 1800 cm⁻¹ and 0.967 under 1800 cm⁻¹ while v^{β} does the ones by SQM methodology. I_{IR} and I_{R} are intensities of calculated infrared and Raman spectra. TED data are taken from SQM 1.0. Symbols used for vibrational modes are described by stretching (v) deformation (δ), torsion (τ). Number inside parenthesis shows TED portion of that mode.











Highlights

- The (E)-2-acethyl-4-(4-bromophenyldiazenyl) phenol was synthesized and analysed by different spectroscopic methods.
- Experimental values and theoretical calculations for this compound were compared with each other.
- These results were observed to approximately consistent with each other.
- This compound has strong intramolecular O-H. . . O hydrogen bonds and π - π stacking.

Parameter	Scaling type	Initial value	Optimization	Final value
Stre.	X-X	1.0000	Optimize	0.9284
Stre.	c-h	1.0000	Optimize	0.9180
Bend.	X-X-X	1.0000	Optimize	0.9889
Bend.	x-x-h	1.0000	Optimize	0.9541
Bend.	h-c-h	1.0000	Optimize	0.9331
Tors.	х-х-х-х	1.0000	Optimize	0.9425
Tors.	h-x-x-x	1.0000	Optimize	0.9304
Tors.	h-x-x-h	1.0000	Optimize	0.9688

Table S1. Predefined and final scaling parameters.

Initial value: Predefined scaling value; **Final value**: Scaling value after optimization; **x**: non-hydrogen atom.



Figure S2. FT-IR spectrum of the title coumpound in the region of $4000-400 \text{ cm}^{-1}$.