Research Article

Theoretical Studies of Structure, Spectroscopy, and Properties of a New Hydrazine Derivative

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We will report a combined experimental and theoretical study on molecular structure, vibrational spectra, and energies of (E)-1-(2,4-dinitrophenyl)-2-[(4-methylphenyl)methylidene]hydrazine (1). The molecular geometry and vibrational frequencies and energies in the ground state are calculated by using HF and DFT levels of theory with 6-311G basis sets. The calculated HOMO and LUMO energies also confirm that charge transfer occurs within the molecule. The harmonic vibrational frequencies were calculated, and the scaled values have been compared with experimental FTIR and FT-Raman spectra. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed bar-type spectrograms.

1. Introduction

The properties of hydrazides and hydrazones are of interest due to their biological activities and their use as metal extracting agencies [1]. The hydrazones derivatives are used as fungicides and in the treatment of diseases such as tuberculosis, leprosy, and mental disorders. The complexes of various hydrazones are reported to act as inhibitors of enzymes [2]. Many substituted hydrazides are employed in the treatment of psychotic and psychoneurotic conditions. Carboxylic acid hydrazides are known to exhibit strong antibacterial activities which are enhanced by complexation with metal ions. Chemistry of Schiff bases has been intensively investigated in recent years, owing to their coordination properties and diverse applications. Schiff base hydrazones are widely used in analytical chemistry as a selective metal extracting agent as well as in spectroscopic determination of certain transition metals [3–6]. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions in the periodic table. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically

important species [7–11]. Schiff base metal complexes have been widely studied because they have industrial, fungicide, antibacterial, anticancer, and herbicidal applications [12, 13].

However, the detailed ab initio and DFT (LSDA) with 6-311G comparative studies on the complete FTIR spectra of compound (1) have not been reported so far. In this study, molecular geometry, optimized parameters, and vibrational frequencies are computed and the performance of the computational methods for the ab initio and DFT (LSDA) levels with the 6-311G basis sets is compared. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by the ab initio and DFT (LSDA) levels with the 6-311G basis sets.

2. Experimental

2.1. Computational Details. All calculations were performed using the Gaussian 03 program on a Windows-XP operating PC. The molecular structure of the title compound in the ground state is computed by performing the ab initio and DFT (LSDA) with the 6-311G basis sets.

FIGURE 1: Molecular structure and atom numbering scheme adopted in this study for (1).

FIGURE 2: Calculated infrared spectra of compound (1).

3. Results and Discussion

3.1. Molecular Geometry. The molecular structure of compound (1) belongs to C1 point group symmetry. The optimized molecular structure of title molecule is obtained from Gaussian 03W and Gaussview programs are shown in Figure 1. The optimized structural parameters of compound (1) calculated by the ab initio and DFT (LSDA) levels with the 6-311G basis sets are listed in Table 1.

3.2. Vibrational Analysis. Vibrational spectroscopy was extensively used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, reaction kinetics, and so forth. The observed and calculated data of the vibrational spectrum of compound (1) are given in Table 2. The suggested reason was that the result obtained by the calculation was harmonic oscillation frequency, while the experimental value contained the anharmonic oscillation frequency. Assignment of compound systems could be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamental modes. The calculated infrared spectra for different methods of compound (1) are presented in Figure 2. Correlation graphs between the scaled calculated

and observed results for the assigned fundamentals in the region $4000\text{--}500\text{ cm}^{-1}$ are shown in Figure 3.

Comparing the observed and calculated frequencies shows that the results of our computations are in good agreement with the experiment.

In the spectrum of ligand, the strong IR absorption at 3447 cm^{-1} is due to N-H frequency. The calculated stretching vibration modes of the N-H band for compound (1) with ab initio and DFT (LSDA) levels with the 6-311G basis sets are 3814 and 3353 cm^{-1} (unscaled), respectively. Obviously, LSDA functional gives results in closest agreement with the observed frequencies over the other methods surveyed. The experimental C=N bands were observed at 1591 cm^{-1} as sharp bands. The calculated stretching vibration mode of the C=N band for compound (1) with HF and LSDA methods at 6-311G basis set was somewhat shifted to the higher frequency appearing at 1792 and 1608 cm^{-1} , respectively.

The FT-IR spectrum showed absorption bands at 1092 cm^{-1} which were assigned to N-N and calculated theoretically by HF/LSDA at 1145 and 1066 cm^{-1} for compound (1).

As can be seen from Figure 3, experimental fundamentals have a good correlation with LSDA/6-311G.

TABLE 1: Optimized geometrical parameters for compound (1) at (HF/LSDA) methods by using 6-311G basis set.

Geometrical parameters	6-311G	
	HF	LSDA
Bond length (Å)		
C1–C2	1.371	1.374
C2–C3	1.404	1.407
C3–C4	1.399	1.411
C4–C5	1.379	1.382
C5–C6	1.376	1.380
C6–C1	1.389	1.396
N13–C6	1.436	1.434
N13–O14	1.229	1.265
N13–O15	1.227	1.263
N10–C4	1.447	1.438
N10–O11	1.224	1.267
N10–O12	1.226	1.259
C3–N16	1.365	1.356
N16–N18	1.374	1.365
N18–C19	1.267	1.298
C19–C21	1.479	1.450
C21–C22	1.392	1.398
C21–C23	1.393	1.404
C22–C24	1.383	1.385
C26–C23	1.385	1.384
C28–C26	1.392	1.398
C24–C28	1.392	1.397
C28–N31	1.507	1.488
Bond angle (°)		
C1–C2–C3	121.4	120.6
C2–C3–C4	117.2	118.2
C3–C4–C5	121.7	121.0
C4–C5–C6	119.1	118.8
C5–C6–C1	120.9	121.5
C1–C6–N13	119.6	119.2
C5–C6–N13	119.4	119.1
O14–N13–O15	123.5	124.2
C3–C4–N10	122.3	121.5
C5–C4–N10	115.7	116.9
C4–N10–O11	118.1	117.8
C4–N10–O12	117.7	117.7
O11–N10–O12	124.0	124.1
C2–C3–N16	118.8	120.4
C4–C3–N16	123.8	121.3
C3–N16–N18	119.0	120.1
N16–N18–C19	120.7	118.0
N18–C19–C21	128.4	126.5
C19–C21–C22	119.5	121.1
C19–C21–C23	121.9	119.8
C21–C22–C24	120.7	120.4
C22–C24–C28	121.0	121.1
C24–C28–C26	118.0	118.2
C28–C26–C23	121.2	121.2
C26–C23–C21	120.5	120.1
C24–C28–C31	120.9	120.9
C26–C28–C31	120.9	120.8

(a)

(b)

FIGURE 3: Scaled calculated vibrational frequencies in comparison to the experimental obtained data and correlation coefficients for compound (1).

As a result, the fundamental vibrational are in good consistency with the experimental results and are found a good agreement above the predicated literature.

3.3. Orbital Analysis. The UV-Vis spectral analysis of compound (1) has been calculated by TD-HF/6-311G and TD-LSDA/6-311G methods along with measured UV-Vis data which are summarized in Table 3. The UV-Vis spectrum of compound (1) is shown in Figure 4 as measured in

TABLE 2: Observed and HF/DFT (LSDA) with 6-311G level calculated vibrational frequencies of compound (1).

Experimental	HF 6-311G	Int. (IR)	LSDA 6-311G	Int. (IR)	Vibrational assignments
3447	3814	66	3353	123	ν NH
3311	3410	2	3150	8	ν sCH
—	3361	8	3115	1	vasCH
3103	3356	3	3113	16	ν sCH
—	3345	11	3100	6	ν CH
—	3331	15	3080	1	vasCH
—	3242	23	3058	7	ν asCH ₃
—	3161	39	2954	13	ν sCH ₃
1615	1799	20	1642	113	ν sC–C + β CH
1591	1873	9	1615	4	ν sC–C + β CH + ν sC–N
1511	1792	382	1608	38	ν sC–N + β CH + β NH
1509	1741	7	1585	3	ν C–C + β CH + β NH
1419	1681	54	1552	25	β CH
1366	1607	196	1493	34	β NH + ν asNO ₂ + β CH
1331	1562	5	1450	76	ν asNO ₂ + β CH
1257	1489	544	1305	690	β NH + ν sNO ₂ + β CH
1092	1145	121	1066	61	ν N–N + β CH + β NH
1008	1136	1	1001	13	γ CH
908	890	16	795	8	δ NO ₂
831	873	7	759	8	γ CN + γ CH
740	811	23	713	8	ω NO ₂ + γ CH
705	720	1	655	4	β C–C–C + β C–NO ₂ + ω NO ₂
508	571	30	487	34	γ CH + γ NH

TABLE 3: Experimental and calculated absorption wavelength, energies, and oscillator strengths of compound (1) using the TD-HF/B3LYP/6-311G method.

Excitation energies		Wavelength cal. gas phase		Oscillator strength (f)		Expt.
HF/6-311G	LSDA/6-311G	HF/6-311G	LSDA/6-311G	HF/6-311G	LSDA/6-311G	
4.345	2.350	285	527	0.0080	0.0224	367
4.425	2.582	280	480	0.0005	0.4102	—
4.755	2.863	260	432	0.0522	0.0003	259
4.847	2.901	255	427	0.0008	0.0025	—
4.956	3.081	250	402	0.8317	0.0002	—
5.529	3.119	224	397	0.0604	0.0058	220

FIGURE 4: UV-Vis spectrum of (E)-1-(2,4-dinitrophenyl)-2-[(4-methylphenyl)methylidene]hydrazine.

acetonitrile solution. Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbitals that take part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by the ab initio and DFT (LSDA) levels with the 6-311G basis set Figure 5. This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular or orbital (LUMO). The HOMO is located over the group, and the HOMO $\rightarrow$ LUMO transition implies an electron density transfer to ring from chlorine and partially from ring.

The HOMO energy calculated by LSDA/6-311G method is higher than by HF method. The biggest LUMO energy value is 0.10537 a.u. obtained using HF/6-311G. The biggest value of energy gap (ΔE) between HOMO and LUMO

FIGURE 5: The atomic orbital compositions of the frontier molecular orbital for compound (1).

energies is -0.17595 a.u. obtained at LSDA/6-311G whereas the smallest one is -0.47583 a.u. obtained at HF/6-311G. The total energies are found to decrease with increase of basis set dimension.

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