39104

P.Chitradevi et al./ Elixir Vib. Spec. 92 (2016) 39104-39111

Available online at www.elixirpublishers.com (Elixir International Journal)

## **Vibrational Spectroscopy**



Elixir Vib. Spec. 92 (2016) 39104-39111

## Quantum chemical studies on structure, non-linear optical (nlo) properties and homo-lumo analysis of 6-amino-2, 3-dihydro-1, 4-phthalazinedione by *ab initio* and dft calculations

P.Chitradevi<sup>1</sup>, M. Arivazhagan<sup>2,\*</sup>, S. Manivel2 and E.Palanisamy<sup>3</sup> <sup>1</sup>Department of Physics, Rajah Serfoji Government College (Autonomous)- Thanjavur - 613005, TN, India. <sup>2</sup>Research Department of Physics, Government Arts College, Thiruverumbur, Trichy 22. <sup>3</sup>Research Department of Physics, Government Arts College, Karur -5, Tamil Nadu, India.

### **ARTICLE INFO**

Article history: Received: 16 February 2016; Received in revised form: 12 March 2016; Accepted: 17 March 2016;

#### Keywords

6-amino-2, 3-dihydro-1, 4-phthalazinedione, FT-IR, FT-Raman, HF, B3LYP.

#### ABSTRACT

In the present study, the FT-IR and FT-Raman spectra of 6-amino-2,3-dihydro-1,4phthalazinedione (ADHPD) have been recorded in the region 4000-400 cm-1 and 3500-50 cm-1, respectively. The fundamental modes of vibrational frequencies of ADHPD are assigned. Theoretical information on the optimized geometry, harmonic vibrational frequencies, infrared and Raman intensities were obtained by means of Hartree-Fock (HF) and density functional theory (DFT) gradient calculations with complete relaxation in the potential energy surface using 6-311+G(d,p) basis set. The vibrational frequencies which were determined experimentally from the spectral data are compared with those obtained theoretically from ab intio HF and DFT/B3LYP calculations. A close agreement was achieved between the observed and calculated frequencies by refinement of the scale factors. The predicted first hyperpolarizability also shows that the molecule might have a reasonably good non-linear optical (NLO) behaviour. The calculated HOMO-LUMO energy gap reveals that charge transfer occurs within the molecule. Unambiguous vibrational assignment of all the fundamentals was made using the total energy distribution (TED).

© 2016 Elixir all rights reserved.

#### 1. Introduction

6-amino-2,3-dihydro-1,4-phthalazinedione (ADHPD) is a versatile chemical that shows striking blue chemiluminescence in presence of certain metal ions when treated with appropriate oxidizing agent like hydrogen peroxide. This unique feature of ADHPD is often exploited by forensic investigators to detect trace amount of blood left in the crime scene. The biologists also use ADHPD as a cellular assay to detect copper, iron, etc. The use of ADHPD chemiluminescence has also been reported recently for facile detection of proteins, cancer biomarkers, as well as for reactive oxygen species produced by human neutrophils. An important aspect of ADHPD chemiluminescence is its different degrees of sensitivity from one substance to another. ADHPD shows higher sensitivity to animal or human blood, organic tissues and fluids than to other compounds containing metal ions, such as paints, metallic surfaces, household products, or vegetable enzymes.

The literature survey also reveals that no theoretical calculations or detailed vibrational infrared and Raman analysis have been performed on 6-amino-2,3-dihydro-1,4-phthalazinedione (ADHPD) molecule so far. So, in the present investigation, the vibrational wave numbers, geometrical parameters, modes of vibrations, minimum energy of ADHPD are investigated by using *ab initio* HF and B3LYP calculations with 6-311+G(d,p) basis set. Specific scale factors are also used and employed in the predicted frequencies.

#### 2. Experimentation

The pure compound 6-amino-2,3-dihydro-1,4phthalazinedione was purchased from Lancaster chemical

Tele: 9443189328					
E-mail address: jjmarivu@yahoo.co.in					
© 2016 Elixir all rights reserved					

company, U.K. and used as such without any further purification. The room temperature Fourier transform infrared (FTIR) spectrum of ADHPD is recorded in the range of 4000 - 400 cm<sup>-1</sup> at a resolution of  $\pm 1$  cm<sup>-1</sup> using a BRUKER IFS 66V FTIR spectrophotometer equipped with a cooled MCT detector. Boxcar apodization is used for the 250 averaged interferograms collected for both the samples and background. The FT-Raman spectrum is recorded on a computer interfaced BRUKER IFS model interferometer, equipped with FRA 106 FT-Raman accessories in the 3500 - 50 cm<sup>-1</sup> Stokes region, using the 1064 nm line of Nd:YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within  $\pm 1$  cm<sup>-1</sup>.

#### **3.** Computational Methodology

Density functional theory calculations are carried out for ADHPD. The Hartree-Fock (HF) and DFT calculations using GAUSSIAN 09W program package [1] The geometry optimization was carried out using the initial geometry generated from the standard geometrical parameters is minimized without any constraint on the potential energy surface at Hartree-Fock level adopting the standard 6-311+G(d,p) basis set. This geometry is then re-optimized again at DFT level employing the B3LYP keyword, which invokes Becke's three-parameter hybrid method [2] using the correlation function of Lee *et al.* [3], implemented with the same basis set for better description of the bonding properties of amino group. All the parameters are allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The multiple scaling of the force constants are performed according to SQM procedure [4] using selective scaling in the natural internal coordinate representation [5]. Transformation of force field, the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the total energy distribution (TED) are done on a PC with the MOLVIB program (version V7.0 - G77) written by Sundius [6,7] The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wave numbers. The calculated geometrical parameters are compared with X-ray diffraction result [8]. Normal coordinate analysis were carried out for ADHPD to provide a complete assignment of fundamental frequencies.

#### 4. Results and Discussion

#### 4.1. Molecular geometry

The optimized molecular structure of ADHPD along with numbering of atoms is shown in Fig 1. The optimized structure parameters of ADHPD obtained by DFT-B3LYP/6-311+G (d,p) and HF/6-311+G(d,p) levels are listed in Table 1. From the structural data given in Table 1, it is observed that the various bond lengths are found to be almost same at HF/6-311+G(d,p) level of theory, in general slightly overestimates bond lengths but it yields bond angles in excellent agreement with the HF and B3LYP methods. The calculated geometric parameters can be used as foundation to calculate the other parameters for the compound.



Fig 1. Molecular structure of 6-amino 2,3-dihydro-1-4 phthalazinedione

Inclusion of CH group and NH atoms known for its strong electron-withdrawing nature, in N-heterocyclic position, is expected to increase a contribution of the resonance structure, in which the electronic charge is concentrated at this site. This is the reason for the shortening of bond lengths N14-H15 =N14-H16 = 0.995 Å obtained by HF 0.994 Å and method. The same bond lengths calculated by DFT method is found to be 1.009 Å and 1.010 Å. The carbon atoms are bonded to the hydrogen atoms with an -bond in heterocyclic ring and the substitution of hydrogen atoms for hydrogen reduces the electron density at the ring carbon atom. In ADHPD, the N-H bond lengths vary from 0.997 Å to 0.999 by HF method and from 1.013 to 1.014 B3LYP methods. The ring carbon atoms in substituted N-heterocyclic exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C-H force constants and a

decrease in the corresponding bond length. It is evident from the C-C bond lengths ranging from 1.375 Å to 1.489 Å by HF method and from 1.385 to 1.485 by B3LYP method in the Nheterocyclic rings of ADHPD, whereas the C-H bond lengths in ADHPD vary from 1.073 Å to1.076 Å and from 1.084 to 1.086 Å by HF and B3LYP methods, respectively. The heterocyclic rings appear to be a little distorted because of the NH<sub>2</sub> group substitution as seen from the bond angles C3-C4-C5 which are calculated as 118.96° and 118.76° respectively, by HF and B3LYP methods and they are smaller than typical hexagonal angle of 120°. From the theoretical values, it is found that most of the optimized bond lengths are slightly larger than the experimental values, due to that the theoretical calculations belong to isolated molecules in solid state. Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are bigger than the later and the B3LYP calculated values correlate well compared with the experimental data.

#### 4.2. Non-Linear Optical (NLO) Properties

The potential application of the title compound in the field of nonlinear optics demands, the investigation of its structural and bonding features contribution to the hyperpolarizability enhancement, by analysing the vibrational modes using IR and Raman spectroscopy. Many organic molecules, containing conjugated electrons are characterized by large values of molecular first hyperpolarizabilities, are analysed by means of vibration spectroscopy [9] In most of the cases, even in the absence of inversion symmetry, the strongest band in the IR spectrum is weak in the Raman spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group through a -bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for a calculations in conjugated systems that predict exceptionally infrared intensities for the same normal modes. The first hyperpolarizability (B) of this novel molecular system is calculated using the *ab initio* quantum mechanical method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a  $3 \times 3 \times 3$  matrix [10]. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electrical field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_{i} \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \nu_{ijkl} F^i F^j F^k F^l + \dots$$
... (1)

where  $E_0$  is the energy of the unperturbed molecule;  $F_i$  is the field at the origin; and µi, ij, ijk and ijkl are the components of dipole moment, polarizability, the first hyperpolarizabilities and second hyperpolarizibilities, respectively. The calculated total dipole moment  $(\mu)$  and mean first hyperpolarizability ( $\beta$ ) of ADHPD are 1.1437 Debye and  $8.3541 \times 10^{-30}$  esu, respectively, which is comparable with the reported values of similar derivatives. The large value of hyperpolarizibilities, which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from the electron cloud movement through conjugated frame work from electron donor to electron acceptor groups.

Bond	Value (Å)		Exn <sup>a</sup>	Bond angle	Value (°)		Exn <sup>a</sup>	Value (°)		
length	HE/	B3LVP/	LAP	Dona ungie	HF/	B3LVP/	Lap	Dihedral angle	HF/	B3LVP/
	6-	6-			6-	6-		Dineurur ungie	6-	6-311+G(d,n)
	311+G(d,p)	311+G(d,p)			311+G(d,p)	311+G(d,p)			311+G(d,p)	0 0 11 1 O(u,p)
C1-C2	1.387	1.408	1.359	C2-C1-C6	118.96	118.78	120.3	C6-C1-C2-C3	-0.7074	-0.733
C1-C6	1.391	1.403	1.383	C2-C1-C7	120.94	121.27	121.7	C6-C1-C2-C10	-179.01	-178.91
C1-C7	1.474	1.472		C6-C1-C7	120.12	119.91	119.8	C7-C1-C2-C3	-178.77	-178.84
C2-C3	1.382	1.393	1.415	C1-C2-C3	121.22	120.88	121.6	C7-C1-C2-C10	2.916	2.972
C2-C10	1.489	1.485		C1-C2-C10	119.81	120.41		C2-C1-C6-C5	0.5978	0.5812
C3-C4	1.392	1.404	1.423	C3-C2-C10	118.93	118.67		C2-C1-C6-H12	-179.40	-179.50
C3-H11	1.074	1.085	0.917	C2-C3-C4	119.82	120.21	116.4	C7-C1-C6-C5	178.68	178.72
C4-C5	1.402	1.415	1.391	C2-C3-H11	119.05	118.47		C7-C1-C6-H12	-1.314	-1.3642
C6-N14	1.379	1.381	1.347	C4-C3-H14	121.11	121.30		C2-C1-C7-N8	-7.242	-6.9752
C5-C6	1.375	1.385	1.364	C3-C4-C5	118.96	118.76	121.1	C2-C1-C7-O17	173.28	173.70
C5-H13	1.076	1.086	0.884	C3-C4-N14	120.66	120.74	122.5	C6-C1-C7-N8	174.71	174.93
C6-H12	1.073	1.084	0.920	C5-C4-N14	120.33	120.45	119.8	C6-C1-C7-O17	-4.757	-4.3905
C7-N8	1.371	1.387		C4-C5-C6	120.72	120.77	119.6	C1-C2-C3-C4	0.436	0.539
C7-O17	1.201	1.229		C4-C5-H13	119.41	119.34	121.7	C1-C2-C3-H11	-179.78	-179.63
N8-N9	1.401	1.411		C6-C5-H13	119.85	119.88		C10-C2-C3-C4	178.75	178.75
N8-H18	0.997	1.014	0.872	C1-C6-C5	120.34	120.56		C10-C2-C3-H11	-1.465	-1.4214
N9-C10	1.363	1.378	1.460	C1-C6-H12	118.92	118.47	120.3	C1-C2-C10-N9	-7.406	-6.485
N9-H19	0.999	1.013	1.405	C5-C6-H12	120.73	120.96	123.3	C1-C2-C10-O20	173.11	174.06
C10- O20	1.199	1.229		C1-C7-N8	116.00	115.41		C3-C2-C10-N9	174.24	175.29
N14- H15	0.994	1.009	0.908	C1-C7-O17	124.04	125.00		C3-C2-C10-O20	-5.230	-4.158
N14- H16	0.995	1.010	0.887	N8-C7-O17	119.95	119.57		C2-C3-C4-C5	-0.049	-0.182
				C7-N8-N9	121.61	122.02	119.8	C2-C3-C4-N14	177.64	177.54
				C7-N8-H18	112.55	113.73	115.2	H11-C3-C4-C5	-179.82	179.99
				N9-N8-H18	111.85	113.08		H11-C3-C4-N14	-2.1264	-2.276
				N8-N9-C10	122.47	122.95		C3-C4-C5-C6	-0.052	0.0336

# Table 1. Optimized geometrical parameters of 6-amino 2,3-dihydro-1,4-phthalazinedione obtained by HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) methods and basis set calculations

For numbering of atoms refer Fig. 1<sup>a</sup>

Value taken from Ref [8].

The physical properties of these conjugated molecules are governed by the high degree of electronic charge delocalization along the charge transfer axis and by the low band gaps. So the title compound is an attractive object for future studies of nonlinear optical properties.

#### 4.3. Frontier Orbital Energy

Many organic molecules that contain conjugated electrons are characterized hyperpolarizabilities and are analyzed by means of vibrational spectroscopy. In most cases, even in the absence of inversion symmetry, the weakest bands in the Raman spectrum are strongest in the IR spectrum and vice versa. But the intramolecular charge transfer from the donor to accepter group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. It is also observed in the title compound the bands in FTIR spectrum have their counterparts in Raman shows that the relative intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through conjugated frame work from electron donor to electron acceptor groups. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. Can determine the way the molecule interacts with other species; hence, they are called the frontier orbitals. HOMO, which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron

donor. On the other hand; LUMO can be thought the innermost orbital containing free places to accept electrons [11]. Owing to the interaction between HOMO and LUMO orbital of a structure, transition state transition of \* type is observed with regard to the molecular orbital theory. The calculated self-consistent field (SCF) energy of ADHPD is -623.9537 a.u. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbitals is called as energy gap that is an important stability for structures. In addition, the pictorial scheme of few MOs of ADHPD is shown in Fig 2. HOMO is localized on the central ring and has partially contribution from the substitution groups such as oxygen and amino group. LUMO is quite localized on the central ring and has strong contribution from the substituted electronegative oxygen and amino group. The energy gap between HOMO and LUMO is 0.1058 a.u., which shows that charge transfer may be taking place from the ring to oxygen atom. As seen from the Fig. 2, HOMO-1 is very similar to HOMO, rotated by 90°. HOMO-3 is mainly localized on ring carbon atom whereas LUMO+3 is localized on ring carbon atoms and oxygen atom.

#### 4.4. Global and local reactivity descriptors

Based on density functional descriptors global chemical reactivity descriptors of molecules such as hardness, chemical potential, softness, electronegativity and electrophilicity index



Fig 2. Electron density isocontour plots of few MOs of 6-amino 2,3-dihydro-1,4-phthalazinedione

as well as local reactivity have been defined. Pauling introduced the concept of electronegativity as the power of an atom in a molecule to attract electrons to it. The calculated value of electrophilicity index describes the biological activity of ADHPD. All the calculated values of hardness, potential, softness and electrophilicity index are shown in Table 2.

#### 5. Vibrational Spectra

The molecular structure of ADHPD belongs to C1 point group symmetry. For  $C_1$  symmetry there would not be any relevant distribution. The molecule consists of 20 atoms and

expected to have 54 normal modes of vibrations of the same species (A). The harmonic vibrational frequencies calculated for ADHPD at B3LYP level using the triple split valence basis set along with the diffuse and polarization functions,6-31+G(d,p) basis set. The maximum number of potentially active observable fundamentals of a non-linear compound that contains N atoms is equal to (3N-6). Accurate vibrational frequency assignment for aromatic and other conjugated system is necessary for characterization of compound.

Table 2. HOMO-LUMO energy gap and related molecular properties of 6-amino 2,3-dihydro-1,4-						
phthalazinedione						
Molecular Properties	B3LYP/6-311+G(d,p)					
	0.0000					

НОМО	-0.2839 a.u
LUMO	-0.1781 a.u.
Energy gap	0.1058 a.u.
Ionisation Potential (I)	0.2839 a.u.
Electron affinity (A)	0.1781 a.u.
Global softness (s)	18.9035 a.u.
Global Hardness	0.0529 a.u.
Chemical potential	-0.231 a.u.
Global Electrophilicity	0.5043 a.u.

The observed FTIR and FT-Raman spectra of ADHPD are shown in Figs. 3 and 4 respectively. The detailed vibrational assignment of fundamental modes of ADHPD along with the calculated IR and Raman frequencies and normal mode descriptions (characterize by TED) are reported in Table 2. Comparison of frequencies calculated at HF and B3LYP with experimental values reveal the overestimation of the calculated vibrational modes due to neglect of harmonicity in real system. Inclusion of electrons correlation in DFT values smaller in comparison with the HF frequencies data. The calculated frequencies are slightly higher than the observed value for the majority of normal modes. The major factor which is responsible for these discrepancies between the experimental and computed value is related to the fact that the experimental value is an anharmonic frequency while the calculated value is harmonic frequency. While an harmonicity is the main factor of the discrepancies in the case of vibrations related to the NH<sub>2</sub> and C=O bonds, for other vibrations most of the discrepancies come from the approximate nature of the used computational technique, and probably also from the lattice effects in the substance.



Fig 3. FTIR spectrum of 2,3-dihydro-1-4-phthalazinedione



#### Fig 4. FT-Raman spectrum of 2,3-dihydro-1-4phthalazinedione

The comparative ADHPD of calculated vibrational frequencies by HF and DFT methods at HF/6-311+G(d,p), and B3LYP/6-311+G(d,p) basis sets for the ADHPD are given in Table 3. From the Table, it is found that the calculated (unscaled) frequencies by B3LYP with 6-311+G(d,p) basis sets are closer to the experimental frequencies than HF method with 6-311+G(d,p) basis set. This observation is supported by the literature report [12].

#### C-H vibrations

The hetero aromatic structure shows the presence of C-H stretching vibration in the region 3100 - 3000 cm<sup>-1</sup> which is the characteristic region for the ready identification of C-H stretching vibration [13]. In this region, the bands are not affected appreciably by the nature of substituents. The C-H stretching mode usually appears with strong Raman intensity and is highly polarized. May be owing this high polarization, Raman bands have not been observed in experimental spectra. In the FTIR spectrum of ADHPD, the weak bands at 3050, and 3000 cm<sup>-1</sup> are assigned to C-H stretching vibrations of hetrocyclic group. The counter part of the FT-Raman weak spectrum at 3015 cm<sup>-1</sup> is attributed to C-H stretching vibration. The theoretically computed wave number by B3LYP method falls in the range at 3056 - 3003 cm<sup>-1</sup> and is assigned to C-H stretching vibration as shown in Table 3. The C-H in-plane bending frequencies appear in the range 1000 -1300 cm<sup>-1</sup> and are very useful for characterization purpose [14] For ADHPD, the C-H in-plane bending vibrations appeared in FTIR spectrum at 1198 and 1082 cm<sup>-1</sup> and 1200 and 1196 cm<sup>-1</sup> in FT-Raman spectrum. The C-H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 1000 - 750 cm<sup>-1</sup> [15] for ADHPD, the C-H outof-plane bending vibrations are observed at 718 cm<sup>-1</sup> in FT-Raman and 735, 729 cm<sup>-1</sup> in FTIR spectrum.

#### C=O vibrations

The structural unit of C=O has an excellent group frequency, which is described as a stretching vibration. Since the C=O group is a terminal group, only the carbon is involved in a second chemical bond. This reduces the number of force constants determining the spectral position of the vibration.

#### P.Chitradevi et al./ Elixir Vib. Spec. 92 (2016) 39104-39111

Symmetry	Observe	d frequencies	Calculated frequ	encies (cm <sup>-1</sup> )	Scaling freq		Assignments (% TED)
C <sub>1</sub>	FTIR	FT-Raman	HF/ 6- 311+G(d,p)	B3LYP/ 6-	HF/ 6-311+G(d,	B3LYP/ p) 6-311+G(d,p)	-
A	3352ms	-	3936	3714	3400	3354	vNH2ass(99)
A	3270w	3272vw	3848	3598	3301	3275	vNH2ss(98)
A	3245ms	-	3845	3596	3288	3248	vNH(96)
A	3194w	3195vw	3820	3591	3220	3197	vNH(97)
A	3050w	-	3394	3219	3090	3056	vCH(93)
A	- 3000w	3015w	3382	3204	3068	3018	vCH(94)
A		-	1952	1749	1721	1698	vCH(93) vC=O(52) + C=O(35)
A	1672vs	-	1925	1734	1710	1678	vC=O(52) + C=O(55) vC=O(66)
А	-	1610s	1815	1669	1680	1616	vCC(65), NH2siss(33)
А	1550ms	1550ms	1786	1650	1590	1555	vNH2siss(64), C=O(31)
А	1492s	-	1763	1610	1534	1497	vCC(60), C=O(28)
А	-	1488vs	1677	1537	1520	1494	vCC(92)
A	1430s	-	1666	1518	1507	1435	vCC(91)
А	-	1410s	1615	1495	1488	1416	vCC(90)
A	1382ms	-	1569	1453	1440	1389	vCC(51). CN(23). bNH(19)
А	-	1352ms	1558	1399	1399	1358	vCC(52), CN(30), bNH(17)
A A	- 1301ms	1324w -	1459 1401	1354 1338	1370 1322	1329 1308	vCC(46), CN(35), bCH(16) vCN(48), NN(39), bCH(12)
А	-	1291w	1378	1321	1312	1297	vCN(42), bNH(31), bCH(26)
А	-	1273vw	1356	1317	1301	1279	vCN(67), bNH(33)
А	-	1250ms	1322	1301	1270	1258	vNN(51), bCH(32), R1asymd(13)
A	1231w	-	1301	1278	1255	1239	bNH(49), bCH(33), R1symd(17)
A	-	1212w	1231	1221	1225	1218	bNH(48), bCH(32), R1trigd(15)
A	-	1200vw	1225	1211	1239	1207	bCH (47), NH2rock(38), CN(12)
А	1198w	1196vw	1213	1206	1207	1199	bCH(46), R1asymd(31), CN(18)
А	1082w	-	1193	1189	1110	1087	bCH(45), R1symd(30), CN(22)
A	-	1064w	1175	1105	1100	1069	NH2rock(49), R1trigd(31), NH(18)
A A	-	1035vw 1010vw	1165	1099	1070	1038	R1asymd(45), bCO(32), NH(19) R1symd(47), NH(29), bCO(11)
A	080	10101	1125	1005	1010	0.85	$R_{1}$
A	980W	-	1123	10/4	1010	905	R1(11gd(44), RH(52), bCO(21)
A A	- 862vs	- 8/3W	1099	1069	899	<u>    877</u> 869	$R_2asymu(60), NH2wag(52)$ NH2wag(65), bCO(32)
A	_	821s	1087	1034	876	828	$R_{2}^{2}$ (69) CH(28)
A	790ms	-	1066	999	850	797	R2trigd(62), CH(29)
А	-	772s	1054	978	790	777	ωNH(51), R1asymd(31), CH(13)
A	761w	_	1024	921	783	768	ωNH(49), R1symd(32), CH(14)
A	753vw	_	1011	890	772	757	bCO(55), R1trigd(28), CH(17)
A	-	749w	1001	844	759	748	bCO(60) R2asymd(38)
A	735ms	-	982	827	748	739	$\omega$ CH(62), R2symd(28)
А	729vw	-	955	819	741	737	ωCH(63), R2trigd(33)
A	-	718ms	920	863	733	721	$\omega$ CH(64), tR1asymd(35)
А	-	552w	895	837	703	559	tR1asymd(72)
A	540w	-	872	809	689	549	tR1symd(71)
A	501ms	-	845	804	634	507	tR1trigd(69)
A A	491vw	491w 428vw	818	786	621	499	tR2asymd(74) tR2symd(70) CO(28)
A	-	400ms	738	649	589	406	bCN(52), tR1symd(30), CO(12)
А	-	392vw	703	572	532	399	tR2trigd(64)
А	-	300w	634	535	478	307	ωCO(51), tR2trigd(32), CN(15)
А	-	285vw	521	522	420	289	ωCO(66)
А	-	271vw	516	557	398	277	ωCN(72)
A	-	198w	413	309	334	203	NH2twist(52)
A	_	175w	393	222	211	179	Butterfly(61)

Table 3. The observed (FTIR and FT-Raman) and calculated (unscaled and scaled) frequencies (cm<sup>-1</sup>) and probable assignments (Characterized by TED) of 6-amino 2,3-dihydro-1,4-phthalazinedione using HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) methods and basis set calculations

Abbreviations: - stretching; b - in-plane bending; - out-of-plane bending; asymd - asymmetric; symd - symmetric; t - torsion; trig - trigonal; w - weak; vw-very week; vs - very strong; s - strong; ms - medium strong; ss - symmetric stretching; ass - asymmetric stretching; ips - in-plane stretching; ops - out-of-plane stretching; sb - symmetric bending; ipr - in-plane rocking; opr - out-of-plane rocking; opb - out-of-plane bending.

The C=O stretching vibration usually appears in a frequency range that relatively free of other vibrations. For example, in many carbonyl compounds the double bond of the C=O has a force constant different from those of such structural units such as C=C, C-C, C-H etc., only structural units of C=C have force constants of magnitudes similar to that of the C=O group. The C=C vibration could interact with C=O if it is the same species, but generally it is not. Almost all carbonyl compounds have a very intense and narrow peak in the range of  $1800 - 1600 \text{ cm}^{-1}$  [16,17] or in other words the carbonyl stretching frequency has been most extensively studied by infrared spectroscopy [18]. The multiple bonded group is highly polar and therefore gives rise to an intense infrared absorption band in the region 1700 - 1800 cm<sup>-1</sup> [19]. The FT-Raman band observed at 1693 cm<sup>-1</sup> and IR band observed at 1672 cm<sup>-1</sup> is assigned to C=O stretching vibrations.

#### **N-H vibrations**

The hetero aromatic molecule containing an N–H group shows its stretching absorption in the region  $3500 - 3220 \text{ cm}^{-1}$ . This is usual range of appearance for NH<sub>2</sub> vibrations. The position of absorption in this region depends upon the degree of hydrogen bonding, and hence upon the physical state of the sample or the polarity of the solvent [20].

The vibrational bands due to the N-H stretching are sharper and weaker than those of C-O stretching vibrations by virtue of which they can be easily identified [21]. The N-H stretching fundamental of piperidine is observed in the vapor phase at 3364 cm<sup>-1</sup>. Gulluoglu *et al.* [22,23] observes in the liquid phase at 3340 cm<sup>-1</sup> for the N-H stretching of piperidine. In the present investigation, the FT-Raman and FTIR bands observed at 3195 cm<sup>-1</sup> and 3245 and 3194 cm<sup>-1</sup> is assigned for N-H stretching vibrations respectively. The in-plane and outof-plane bending vibration, of N-H group is also supported by the literature [24].

#### **NH2** Vibrations

The ADHPD molecule under consideration posses NH<sub>2</sub> group and hence six internal modes of vibration are possible such as symmetric stretching, asymmetric stretching, scissoring, rocking, wagging and torsional mode. The frequency of asymmetric vibration is higher than that of symmetric one. The frequencies of amino group in the region  $3500 - 3300 \text{ cm}^{-1}$  for NH stretching, 1700 - 1600 cm<sup>-1</sup> for 1150 - 900  $\text{cm}^{-1}$  for rocking deformation. scissoring and In the present investigation, the asymmetric and symmetric modes of  $NH_2$  group are assigned at 3352 cm<sup>-1</sup> for FTIR and 3270 and 3272  $cm^{-1}$  for both IR and Raman bands, respectively. The band observed at  $1550 \text{ cm}^{-1}$  for both FTIR and Raman spectrum is assigned to NH<sub>2</sub> scissoring mode. The rocking, wagging, twisting deformation vibrations of NH<sub>2</sub> contribute to several normal modes in the low frequency region. The band observed at 1064 cm<sup>-1</sup> in Raman is assigned to NH<sub>2</sub> rocking vibrations and the FTIR band observed at 862 cm<sup>-1</sup> is assigned to NH<sub>2</sub> wagging modes, and the band observed at 198 cm<sup>-1</sup> in Raman is assigned to NH<sub>2</sub> twisting modes [25].

#### C-C and C-N vibrations

Most of the ring vibrational modes are affected by the substitutions in the ring of the title molecule. The characteristic ring stretching vibrations are assigned in the region 1650 - 1300 cm<sup>-1</sup> [26, 27]. The presence of conjugate substituents such as C-C, C-N, C=O or the presence of heavy element causes a doublet formation. Therefore, the C-C stretching vibrations of ADHPD are found at 1610, 1488, 1410, 1352, 1324 cm<sup>-1</sup> in Raman and 1492, 1430, 1382 cm<sup>-1</sup> in

FTIR spectrum. The identification of C-N stretching frequencies is a rather difficult task, since the mixing of vibrations is possible in this region. The C-N stretching vibration is usually lies in the region 1400 - 1200 cm<sup>-1</sup>. The C-1301 cm<sup>-1</sup> N stretching is observed medium strong at and is mixed with C-O in-plane bending vibration. This frequency is also at the lower end of the expected range which may be also due to the interaction of C-C vibration, whose frequency extends up to this value. In the present investigation, the FTIR bands observed at 1301 cm<sup>-1</sup> and in FT-Raman 1291, 1273 cm<sup>-1</sup> of ADHPD have been designated to C-N stretching vibrations. Also, the bands ascribed at 980, 790 cm<sup>-1</sup> in the FTIR and bands found at 1035, 1010, 873, 821 cm<sup>-1</sup> in the Raman spectrum for the title molecule have been designated to ring in-plane bending modes by careful consideration of their quantitative descriptions. The ring outof-plane bending modes of ADHPD are also listed in Table 3. Conclusion

In this present investigation, molecular structure, vibrational frequencies, HOMO, LUMO and polarizability analysis of ADHPD have been studied using *ab initio* HF and DFT (B3LYP/6-311+G(d,p)) calculation. On the basis of the agreement between the calculated and observed results, assignments of fundamental vibrational modes of ADHPD are examined and assignments are proposed. This study demonstrates that scaled DFT/B3LYP calculations are powerful approach for understanding the vibrational spectra of medium sized organic compound.

#### References

1 M.J. Frisch, G.W. Trucks, H.B. Schlegal, GAUSSIAN 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009

2 A.D. Becke, Journal of Chemical Physics, 98 (1993) 5648.

3 C. Lee, W. Yang, R.G. Parr, Phys. Rev., B37 (1988) 785.

4 P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, Journal Am. Chem. Soc.**105** (1983)7037

5 G. Fogarasi, P. Ulay, in: J.R. Durig (Ed.) Vibrational Spectra and Structure, Vol.14, Elsevier, Amsterdam, 1985, P. 125, Chapter 3.

6 T. Sundius, Journal of Molecular Structure, 218 (1990) 321.

7 MOLVIB (V.7.0): Calculation of Hormonic Force Fields and Vibrational Modes of Molecules, QCPE program No.807 (2002).

8 L. Wen, H. Yin, W. Li, K. Li, Acta Cryst., E 65 (2009) 2623

9 J. Karpagam, N. Sundaraganesan, S. Sebastian, S. Manoharan, M. Kurt, J. Raman Spectrosc. **41**(2010) 53.

10 D.A. Klein man, Phys. Rev. 126 (1962) 1977

11 P.L. Polavarapu, J. Phys. Chem. 94 (1990) 8106.

12 G. Keresztury, Raman spectroscopy theory, in: JM Chalmers, P, R. Griffiths (Eds.), Handbook of Vibrational Spectroscopy, Vol. 1, John Wiley & Sons Ltd., 2002, p. 71.

13 M. Arivazhagan, R. Kavitha, V.P. Subhasini Spectrochimia Acta Part A **130**(2014) 502

14 M. Elanthiraiyan B. Jayasudha M. Arivazhagan. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 134 (2015) 543–552

15 M. Arivazhagan J. Senthil kumar . Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 137 (2015) 490–502

16 N. Sundaraganesan, G. Elango, S. Sebastian, P. Subramani, Indian J. Pure Appl. Phys., **47** (2009) 481.

17 G. Varsanyi, Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives, Vols. 1–2, Academic Kiaclo, Budapet, 1973. 18 G. Socrates, Infrared and Raman, Characteristics Group Frequencies, 3<sup>rd</sup> edition, Wiley, New York, 2001

19 S. Sebastian, N. Sundaraganesan, B. Karthikeiyan, V. Srinivasan Spectrochim. Acta A78 (2011) 590-600.

20 R.M. Silverstein, C. Bassler, T.C. Morill, Spectrometric Identification of Organic Compounds, 5<sup>th</sup> ed., John Wiley & Sons, 1991.

21 A.J.A. Bienko, Z. Latajka, D.C. Bienko, D. Michalska, J. Chem. Phys., **250** (1999) 123.

22 J. Coates, R.A. Meyers, Interpretation of Infrared Spectra, A Practical Approach, John Wiley & Sons Ltd., Chichester, 2000.

23 S. Sebastian, N. Sundaraganesan Spectrochim. Acta A75 (2010) 941.

24 S. Gunasekaran, R.K. Natarajan, R. Rathikha, D. Syamala, Ind. J. Pure Appl. Phys., **43**(2005) 503.

25 M.T. Gulluoglu, S. Yurdakul, Vib. Spectrosc., 25 (2001) 205.

26 M. Arivazhagan, P. Muniappan, R. Meenakshi, G. Rajavel, Spectrochemica Acta, Part A **105** (2013) 497.

27 N. Sundaragnesan, S. Ayyappan, H. Umamaheswari, B.D. Joshua, Spectrochim. Acta **66 A** (2007) 17.