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# Spectroscopic (FT-IR, FT-Raman and UV) investigation, NLO, NBO, molecular orbital and MESP analysis of 2-{2-[(2,6-dichlorophenyl)amino]phenyl}acetic acid

# P. Govindasamy<sup>a,\*</sup>, S. Gunasekaran<sup>a,b</sup>

<sup>a</sup> Department of Physics, Karpagam University, Eachanari, Coimbatore 641021, TN, India <sup>b</sup> Research and Development St. Peter's Institute of Higher Education and Research, St. Peter's University, Avadi, Chennai 600054, TN, India

# HIGHLIGHTS

- A detailed interpretation of infrared, Raman and UV-Vis spectra of 2DCPAPAA were reported.
- Density plot of HOMO-LUMO energy surface were plotted to identify the donor and acceptor.
- The temperature dependence of the thermodynamic properties were investigated.
- Second order perturbation theory analysis by NBO method was carried out.
- MESP surface has been plotted to obtain electrophilic and nucleophilic sites of the molecule.

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## G R A P H I C A L A B S T R A C T



# ABSTRACT

In this work, FT-IR and FT-Raman spectra of 2-{2-[(2,6-dichlorophenyl)amino]phenyl}acetic acid (abbreviated as 2DCPAPAA) have been reported in the regions 4000–450 cm<sup>-1</sup> and 4000–50 cm<sup>-1</sup>, respectively. The molecular structure, geometry optimization, intensities, vibrational frequencies were obtained by the ab initio and DFT levels of theory B3LYP with 6-311++G(d,p) standard basis set and a different scaling of the calculated wave numbers. The complete vibrational assignments were performed on the basis of the potential energy distribution (PED) of the vibrational modes calculated using vibrational energy distribution analysis (VEDA 4) program. The harmonic frequencies were calculated and the scaled values were compared with experimental FT-IR and FT-Raman data. The observed and the calculated frequencies are found to be in good agreement. Stability of the molecule arising from hyper conjugative interactions, charge delocalization has been analyzed using natural bond orbital (NBO) analysis. The thermodynamic properties of the title compound at different temperature reveal the correlations between standard heat capacities (*C*) standard enthalpy changes ( $\Delta H$ ). The important non-linear optical properties such as electric dipole momentum, polarizability and first hyperpolarizability of 2DCPAPAA have been computed using B3LYP/6-311++G(d,p) quantum chemical calculations. The Natural charges, HOMO, LUMO, chemical hardness ( $\eta$ ), chemical potential ( $\mu$ ), Electro negativity ( $\chi$ ) and electrophilicity values ( $\omega$ ) are calculated and reported.

The oscillator's strength, wave length, and energy calculated by TD-DFT and 2DCPAPAA is approach complement with the experimental findings. The molecular electrostatic potential (MESP) surfaces of the molecule were constructed.

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\* Corresponding author. Tel.: +91 9976735346. *E-mail address:* pgovindasamy1985@gmail.com (P. Govindasamy).

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# Introduction

The 2-{2-[(2,6-dichlorophenyl)amino]phenyl}acetic acid is also referred diclofenac belongs to non-steroidal anti-inflammatory drugs (NSAIDs). 2DCPAPAA is an acetic acid NSAIDs with analgesic and antipyretic properties. It is a widely used as the counter analgesic (pain reliever) and antipyretic (fever reducer). 2DCPAPAA is commonly used for the relief of painful diseases, fever, dysmenorrhea, ocular inflammation, osteoarthritis, rheumatoid arthritis, ankylosing, spondylitis and actinic keratosis.

Rezaei et al., studied matrix effect and drugs were first extracted from the samples by Solid phase extraction (SPE). The extracted analytes were then eluted from the sorbent with tetrahydrofuran (THF), and the elate were subjected to Supra molecular solvent (SUPRAS) formation (SUPRASF) process [1]. Determination of NSAID can be performed by various techniques, such as highperformance liquid chromatography (HPLC) [2], gas chromatography-mass spectrometry (GC-MS) [3], micellar electro kinetic capillary chromatography (MEKC) and capillary electro chromatography (CEC) [4]. Cao et al., evaluated the potential use of a drug delivery system, drug-layered double hydroxide (LDH) nanocomposites for ocular delivery. 2DCPAPAA were successfully intercalated into Zn–Al–NO3-LDH by co precipitation method [5]. Haikova et al., studied quantification and a stability of the compounds in the pharmaceutical formulation 2DCPAPAA emulgel [6]. Patil et al., attempts at an isocratic separation of acetaminophen, methocarbamol and 2DCPAPAA sodium using supercritical fluid carbon dioxide doped with methanol and a simultaneous quantification of the drugs from solid dosage form using internal standard method with exhaustive evaluation of chromatographic figures of merit [7]. Szostak and Mazurek, studied the results of 2DCPAPAA sodium (DS) quantification in commercial tablets and capsules obtained by Partial Least Squares (PLS) treatment of DRIFTS data [8].

Laxman Kole et al., studied to assess the feasibility of the SBSE approach for the selective extraction of DIC from paediatric urine samples [9].

Literature survey reveals that to the best of our knowledge no HF and DFT/B3LYP with 6-311++G(d,p) basis set calculations of 2DCPAPAA have been reported so far. Therefore an attempt has been made in present study the detailed theoretical HF and DFT methods and experimental (FT-IR, FT-Raman and UV) spectral investigation of 2DCPAPAA. The FT-IR and FT-Raman spectra of this compound have been simulated with the use of the standard



Fig. 1. Structure of 2DCPAPAA.

### Table 1

Optimized geometrical parameters for 2DCPAPAA.

1 8	· · · · · · · · · · · · · · · · · · ·	- •	
Parameter	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Experimental
	/ ////		1
Bond length (A)			
$C_1 - C_2$	1.3946	1.4100	1.4050
$C_1 - C_6$	1.3970	1.4108	1.4070
$C_1 - N_{12}$	1.3989	1.3967	1.3952
$C_2 - C_3$	1.3823	1.3893	1.3810
$C_2 - Cl_{10}$	1.7449	1.7576	1.7438
$C_3 - C_4$	1.3800	1.3905	1.3850
C	1 0732	1 0821	0.9500
	1 3830	1 3012	1 3860
$C_4 C_5$	1.07/2	1.0921	0.0500
$C_4 - H_8$	1.0745	1,0051	1.2070
$C_5 - C_6$	1.3797	1.3895	1.3870
$C_5 - H_9$	1.0732	1.0822	0.9500
$C_6 - Cl_{11}$	1.7412	1.7545	1.7354
$N_{12}$ — $H_{13}$	0.9976	1.0164	0.9000
$N_{12}-C_{14}$	1.4216	1.4158	1.4160
$C_{14} - C_{15}$	1.3965	1.4097	1.4030
$C_{14} - C_{16}$	1.3863	1.3995	1.3970
C15-C17	1.3864	1.3959	1.3970
	1 5108	1 5174	1 5160
	1 3846	1 3903	1 3870
$C_{16} C_{18}$	1.0742	1.024	0.0500
$C_{16} - \Pi_{19}$	1.0745	1,0034	1,2050
$C_{17} - C_{20}$	1.3032	1.5924	1.3630
$C_{17} - H_{21}$	1.0764	1.0852	0.9500
$C_{18} - H_{20}$	1.3814	1.3927	1.3880
C <sub>18</sub> —H <sub>22</sub>	1.0754	1.0842	0.9500
C <sub>20</sub> —H <sub>23</sub>	1.0749	1.0835	0.9500
C <sub>24</sub> —H <sub>25</sub>	1.0817	1.0891	0.9900
$C_{24} - H_{26}$	1.0873	1.0952	0.9900
$C_{24} - C_{27}$	1.5101	1.5146	1.5160
$C_{27} - O_{29}$	1 1853	1 2103	1 2070
Car-Oaa	1 3266	1 3499	1 3344
0 -4	0.0465	0.0702	1,5544
029-1130	0.9405	0.9702	
Bond angle (°)			
$C_2 - C_1 - C_6$	116.2721	115.8588	115.3600
$C_2 - C_1 - N_{12}$	122.4061	121.6723	121.2300
$C_{e} - C_{1} - N_{12}$	121.2572	122.3624	123,1900
$C_{1} - C_{2} - C_{2}$	122 3769	122,5980	122 9700
$C_1 = C_2 = C_3$	110 6136	110 0/38	118 9/00
$C_1 C_2 C_{10}$	119,0100	119.2590	118.0000
$C_3 - C_2 - CI_{10}$	118.0094	110,5564	118.0900
$c_2 - c_3 - c_4$	119.6192	119.5564	119.6500
$C_2 - C_3 - H_7$	119.4106	119.3753	120.2000
$C_4 - C_3 - H_7$	120.9664	121.0622	120.2000
$C_3 - C_4 - C_5$	119.7277	119.8431	119.5900
$C_3 - C_4 - H_8$	120.1609	120.0967	120.2000
C <sub>5</sub> -C <sub>4</sub> -H <sub>8</sub>	120.1095	120.0561	120.2000
$C_4 - C_5 - C_6$	119.8701	119.8923	119.9600
$C_4 - C_5 - H_9$	120.8096	120.9173	120.0000
C <sub>6</sub> -C <sub>5</sub> -H <sub>9</sub>	119.3100	119.1712	120.0000
$C_1 - C_c - C_5$	122,1082	122.2022	122,2900
$C_1 - C_2 - C_{111}$	119 9691	119 8400	120 3300
CCCl	117 9125	117 9198	117 3600
$C_1 = N_{10} = H_{11}$	113 4708	114 9529	113 5000
$C_1 = N_1 = C_1$	121 0775	173 5380	173 0/00
$U_1 = N_{12} = U_{14}$	121,0773	123.3303	123,3400
$H_{13} - N_{12} - C_{14}$	111.1803	113.1237	113.0000
$N_{12} - C_{14} - C_{15}$	118.3145	118.9127	118.6600
$N_{12} - C_{14} - C_{16}$	121.9927	121.8080	121.6900
$C_{15} - C_{14} - C_{16}$	119.6905	119.2781	119.6500
$C_{14} - C_{15} - C_{17}$	118.7978	119.0596	118.5000
$C_{14} - C_{15} - C_{24}$	121.6714	121.0837	121.5100
$C_{17} - C_{15} - C_{24}$	119.4832	119.8250	119.9800
C <sub>14</sub> -C <sub>16</sub> -C <sub>18</sub>	120.6770	120.7477	120.6700
C14-C16-H19	119.6678	119.3283	119,7000
$C_{18} - C_{1c} - H_{10}$	119.6549	119.9219	119,9000
	121 5500	121 4590	121 7800
$C_{15} = C_{17} = C_{20}$	110 10/2	118 8526	110 1000
$C_{15} - C_{17} - H_{21}$	110,1042	110.0320	113,1000
$C_{20} - C_{17} - H_{21}$	119.33/3	119.0773	119.1000
$C_{16} - C_{18} - C_{20}$	120.0816	120.2668	119.2500
$C_{16}-C_{18}-H_{22}$	119.5553	119.4613	119.9000
$C_{20}$ — $C_{18}$ — $H_{22}$	120.3594	120.2678	120.4000
$C_{17}$ — $C_{20}$ — $H_{18}$	119.1923	119.1753	121.7800
C <sub>17</sub> -C <sub>20</sub> -H <sub>23</sub>	120.1641	120.2072	120.4000
C <sub>18</sub> -C <sub>20</sub> -H <sub>23</sub>	120.6422	120.6161	120.4000
C15-H24-H25	110.5148	110.2347	109.4000
C	100 0902	100 2202	100 4000

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Table 1 (continued)

Parameter	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Experimental
C <sub>15</sub> —H <sub>24</sub> —C <sub>27</sub>	115.1280	112.4932	111.3100
$H_{25}$ — $H_{24}$ — $H_{26}$	107.0544	108.7175	108.0000
$H_{25} - H_{24} - C_{27}$	108.1705	109.3499	109.4000
$H_{26} - C_{24} - C_{27}$	105.5849	106.6822	109.4000
$C_{24} - C_{27} - O_{28}$	125.9626	124.9937	123.6200
$C_{24} - C_{27} - O_{29}$	111.8660	112.8549	112.9000
$0_{28} - C_{27} - 0_{29}$	122.1384	122.1509	123.4700
$C_{27} - O_{29} - H_{30}$	108.7948	107.3120	

6-311++G(d,p) basis set. The result of the theoretical and spectroscopic studies is reported here in. Detailed interpretations of the vibrational spectra of 2DCPAPAA have been made on the basis of the calculated potential energy distribution (PED). The redistribution of electron density (ED) in various bonding, antibonding orbitals and E(2) energies had been calculated by natural bond orbital (NBO) analysis to give clear evidence of stabilization originating from the hyper conjugation of various intra-molecular interactions. The important non-linear properties such as electric dipole momentum, polarizability and first hyperpolarizability of 2DCPA-PAA have been computed. The energy, wavelength and oscillator strength are calculated at TD-DFT calculations with the experimental findings. In this study of HOMO, LUMO analyses have been used to elucidate information regarding charge transfer within the molecule. The natural charge and physico-chemical properties title of the molecule have been calculated and reported. Furthermore molecular electrostatic potential (MESP) surface of the molecule have been constructed.

# Experimental

The powder form of 2DCPAPAA was procured from leading pharmaceutical company in Chennai and used as such without further purification. Fourier transform infrared spectrum of the title compound is measured at the room temperature recorded in the range 4000–450 cm<sup>-1</sup> on Bruker IFS 66 V spectrophotometer using KBr pellet technique with 4.0 cm<sup>-1</sup> resolution. The FT-Raman spectrum recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the 4000–50 cm<sup>-1</sup> region on Bruker IFS 66 V spectrophotometer with FRA 106 Raman module which was used as an accessory. The UV–Visible spectral measurements were carried out using a Varian Cary 5E UV–NIR spectrophotometer. The spectral measurements were carried out at Sophisticated Analysis Instrumentation Facility, IIT Madras, India.

## **Computational details**

The quantum chemical calculation employed vibrational spectroscopic studies are of paramount importance in the understanding of fundamental modes of vibrations of the chemical



Fig. 2. Experimental and simulated FT-IR spectra of 2DCPAPAA.



Fig. 3. Experimental and simulated Raman spectra of 2DCPAPAA.

compounds. The molecular geometry optimizations, calculations of energy, vibrational frequencies, IR intensity and Raman intensity were carried out for 2DCPAPAA with the GAUSSIAN 09 software package [10] using HF and DFT/B3LYP functional combined with the standard 6-311++G(d,p) basis set. The geometries were first optimized at the HF level of theory employing the 6-311++G(d,p)basis set. DFT employed the B3LYP keyword which invokes Becke's three parameter hybrid method [11] using correlation function of Lee et al. [12]. The optimized structural parameters were used in the vibrational frequency calculations at both HF and DFT levels to characterize all stationary points as minima. The optimized structural parameters were used in the vibrational frequency calculations. The assignments of calculated wave numbers are aided by the animation option of Gauss View 5.0 graphical interface [13]. Furthermore, theoretical vibrational spectrum of the title compound is interpreted by means of PEDs using the VEDA 4 program [14]. UV absorption energies, wave length, oscillator strengths of this compound were calculated by TD-DFT method in gas phase, solution DMSO and acetone. The Natural Bonding orbital (NBO) calculations were performed using DFT/B3LYP with 6-311++G(d,p) basis set [15]. The calculation as implemented in the Gaussian 09W package at the above said level in order to understand various second order interactions, between the filled orbital of one subsystem, which is a measure of the intermolecular and intra-molecular dislocation or hyper conjugation. The MESP analysis have been made at B3LYP level using 6-311++G(d,p) basis set [16]. The HOMO-LUMO energy gap have been calculated using HF and B3LYP level with 6-311++G(d,p) basis set.

# **Result and discussion**

### Molecular geometry

The molecular structure of 2DCPAPAA belongs to  $C_1$  point group symmetry. The structure of the molecule with numbering scheme for the atoms is shown in Fig. 1. The interaction of carboxyl, choloro, hydroxyl and amine groups substituent's on the ring is of great importance in determining its structural and vibrational properties.

The optimized structure parameters of 2DCPAPAA calculated by HF and DFT/B3LYP level with 6-311++G(d,p) basis set are presented in Table 1. This molecule has eight C—C, six C=C, two C—Cl, one C=O, one C—O, one N—H, two C—N, one O—H and ten C—H bond lengths. The experimental data on the geometric structure of the related molecule was compared with theoretical values [17]. The bond distances calculated by B3LYP method are larger than by HF method. From theoretical values we can find that most of the optimized bond angles and bond lengths are slightly larger than experimental values and comparing of 2DCPAPAA at B3LYP/6-311++G(d,p) basis set lead to geometrical parameter which are much closer to experimental values. The small differences between experimental and theoretical bond lengths and bond angles may be attributed to intermolecular hydrogen bonding.

The calculated C—C bond lengths vary from 1.3895 Å to 1.5174 Å at B3LYP with 6-311++G(d,p) basis set. The computed C—C bond lengths  $C_{15}$ — $C_{24}$ ,  $C_{24}$ — $C_{27}$  are larger and  $C_5$ — $C_6$ ,  $C_{16}$ — $C_{18}$  are shorter. Further the result of our calculations very high

# Table 2

Vibrational band assignments of 2DCPAPAA.

Mode No.	Experimental	1	Calculated wavenumber (cm <sup>-1</sup> )		Vibrational		
	Wavenumber	r (cm <sup>-1</sup> )	HF/6-311++G(d	l,p)	B3LYP/6-311++	G(d,p)	Assignment (% PED)
	v(IR)	v(Raman)	Un scaled	Scaled	Un scaled	Scaled	
1	2207m	o(nunnun)	4112	2412	2744	2407	NOU(100)
2	3269m		3799	3267	3744	3281	NH(100)
3	5205111		3370	3080	3209	3119	υCH(100)
4			3364	3074	3203	3113	υCH(100)
5			3354	3066	3193	3104	υCH(98)
6			3345	3057	3185	3096	υ <b>CH(98)</b>
7			3342	3054	3185	3095	υCH(93)
8	3069w	3068vw	3338	3050	3170	3081	υCH(95)
9	3043w	3053vw	3329	3043	3151	3062	UCH(91)
10	2060.w	2061,004	3202	2908	3042	2055	UCH(88)
12	1795vw	2501000	1981	1811	1842	1791	0C(83)
13	175500		1792	1638	1642	1596	υCC(69)
14	1578vs	1580m	1743	1593	1623	1577	υCC(58) + υNH(22)
15			1738	1589	1614	1569	υCC(25)
16	1556vs		1722	1574	1598	1554	υCC(38) + υNH(12)
17	1502vs		1666	1522	1544	1501	$_{\delta}$ HNC(37)
18	1474s	1473vw	1634	1493	1512	1469	$_{\delta}$ HCC(17)
19	1448vs		1606	1468	1485	1443	$\upsilon$ CC(10) + $_{\delta}$ HCC(19)
20			1600	1463	1477	1436	$UCU(16) + {}_{\delta}HNC(25)$
21	1410vc	1/11/104	1580	1444	1470	1429	$_{\delta}$ HCH(70)
22	141003	1411000	1543	1425	1386	1347	$v_{0}C(15) + {}_{\delta}HCC(25)$
25			1545	1410	1500	1547	«HCC(26)
24	1300m	1305vw	1433	1310	1337	1300	vOC(22)
25	1285m		1417	1295	1324	1287	$vNC(32) + {}_{\delta}HCC(20)$
26	1278m	1275vw	1395	1275	1312	1276	vOC(16) + vNC(21)
27	1250w		1360	1243	1307	1270	$_{\delta}$ HOC(11) + $\tau$ HCCO(19)
28	1233w	1234vw	1349	1233	1281	1245	υCC(23)
29	1203w	1204vw	1320	1206	1258	1223	υ <b>NC(40)</b>
30	1196m	1189vw	1307	1194	1231	1197	$_{\delta}CH_{2}(25)$
31	1167m	1100	1290	1179	1215	1181	$\upsilon$ CC(13) + $_{\delta}$ HCC(34)
32		1160VW	1281	11/1	1199	1165	$UCC(23) + {}_{\delta}HCC(13)$
34			1210	1104	1173	1132	$_{\delta}$ HCC(32)
35			1200	1097	1149	1140	$\psi OC(23)$
36	1084m	1083vw	1190	1088	1114	1083	<sub>s</sub> CH <sub>2</sub> (22)
37		1068vw	1174	1073	1099	1068	υCC(32)
38	1062w	1063vw	1170	1070	1093	1062	<sub>δ</sub> CCC(30)
39	1041w	1042w	1140	1042	1069	1040	υCC(36) + <sub>δ</sub> HCC(10)
40			1104	1009	988	960	τHCCC(41)
41		952vw	1095	1000	972	945	$\tau$ HCCC(17) + $\tau$ CCCC(13)
42		927VW	10/2	980	959	932	THCCC(39)
45			1055	945	947	920	v(C(20))
45	884vw		986	901	907	882	$\tau HCCC(45)$
46	869vw	881vw	964	881	902	877	$\nu CC(10) + {}_{s}CCC(12)$
47			956	874	874	850	$\upsilon CC(11) + \tau HCCC(18)$
48		836vw	944	863	858	834	<sub>δ</sub> CCC(14)
49			910	832	847	823	$\upsilon$ CC(10) + $_{\delta}$ CCC(13)
50	760s	766vw	853	780	783	761	υ <b>ClC</b> (19)
51			845	772	775	754	$\tau$ HCCC(41) + $\tau$ CCCC(11)
52	744s	741vw	835	763	763	741	$\tau$ HCCC(13)
53	715.	71 / 100	822	751	740	725	$\tau U C C C (11)$
JH	71500	714000	700	721	750	715	.0000(17)
55			757	692	722	702	$\tau CCC(17)$
56	667vw		735	672	686	667	$\tau$ HNCC(20)
57	636w	638vw	693	633	654	636	$_{\delta}OCO(10) + \tau HOCC(58)$
58		604vw	674	616	622	604	$_{\delta}$ CCC(14) + $\tau$ HNCC(12)
59			656	600	610	593	<sub>δ</sub> OCO(24)
60	569w		636	581	590	574	<sub>δ</sub> OCO(22)
61	534vw	533vw	582	532	552	537	<sub>δ</sub> CNC(12)
62		518vw	581	531	536	521	$\gamma$ NCCC(17)
63 64		400	5/9	529	528	513	THULL(15)
04 65		490VW	558 540	510	522 ⊿87	5U8 474	$\gamma C(C(29))$ $\tau HOCC(16) + \gamma OCOC(15)$
66		441	491	494	407	4/4	$\gamma CCCC(10) = \gamma OCOC(15)$
67		1 1 1 7 77	478	437	441	429	sNCC(17)
68		403vw	441	403	413	401	$_{\nu}$ ClC(14) + $_{\delta}$ CH <sub>2</sub> (22)
69			398	364	402	391	<sub>δ</sub> OCC(24)

(continued on next page)

Table 2	(continued)	)
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Mode No.	Experiment	al	Calculated way	venumber (cm <sup>-1</sup> )			Vibrational	
	Wavenumb	er (cm <sup>-1</sup> )	HF/6-311++G(d,p)		B3LYP/6-311++	G(d,p)	Assignment (% PED)	
	υ(IR)	υ(Raman)	Un scaled	Scaled	Un scaled	Scaled		
70		365vw	383	350	362	352	<sub>ö</sub> CCC(16)	
71		309vw	354	323	318	309	$_{\delta}$ ClCC(13)	
72		284vw	316	289	287	279	$\tau CCCN(14) + {}_{\delta}CNC(11) + CLCCC(16)$	
73			300	274	274	267	$\gamma CCC(18)$ $_{\delta}CCC(18) + \tau CCCC(10)$	
74		223vw	251	229	228	221	$_{\delta}$ ClCC(30)	
75			226	207	205	199	$\tau$ CCCC(27)	
76		165vw	185	169	166	161	$_{\delta}$ ClCC(20)	
77		152w	177	161	162	157	$_{\delta}$ ClCC(11) + $_{\delta}$ CH <sub>2</sub> (20)	
78			114	104	112	109	τCCCC(10)	
79		96s	103	94	99	96	$\delta CNC(12)$	
80		74s	80	73	76	74	$\tau$ CCCC(41)	
81			61	56	55	54	τCCCN(38)	
82			43	39	43	42	$\tau OCCC(15) + \tau CNCC(47)$	
83			31	29	32	31	$\tau$ CCNC(16)	
84			23	21	24	23	$\tau OCCC(44) + \upsilon CLC(20)$	

m-Medium; w-weak; s-strong; vw-very weak; vs-very strong; υ-stretching; δ-bending; γ-out of plane bending; τ-torsion; potential energy distribution (PED).

bond length strong bond which is found to be  $C_2$ — $Cl_{10}$  (1.7576 Å) and smaller value of bond length weak bond  $O_{29}$ — $H_{30}$  (0.9691 Å). The experimental C=C bond length values of  $C_{14}$ = $C_{16}$ ,  $C_{15}$ = $C_{17}$ are same and C–C bond length values of  $C_3$ — $C_4$ = $C_{17}$ — $C_{20}$  = 1.3850 Å,  $C_5$ — $C_6$ = $C_{16}$ — $C_{18}$  = 1.3870 Å. It is clearly shown that from calculated CCC bond angle  $C_2$ — $C_1$ — $C_6 < C_{14}$ — $C_{15}$ — $C_{17} < C_{15}$ — $C_{14}$ — $C_{16} < C_2$ — $C_3$ — $C_4 < C_{17}$ — $C_{15}$ — $C_{24}$  are slightly increase by B3LYP/ 6-311++G(d,p) and experimental bond angles are  $C_2$ — $C_1$ — $C_6 < C_{14}$ — $C_{15}$ — $C_{17} < C_{16}$ — $C_{18}$ — $C_{20} < C_3$ — $C_4$ — $C_5 < C_2$ — $C_3$ — $C_4$ = $C_{15}$ — $C_{14}$ — $C_{16}$  are slightly differed [18].

The experimental C=O bond length in 2DCPAPAA is 1.2070 Å. The bond length calculated by B3LYP/6-311++G(d,p) is 1.4158 Å which is close to the experimental data. The C–Cl bond distances are calculated in the range 1.7545-1.7576 Å by B3LYP/6-311++G(d,p) method. The computed C–N (1.4158 Å) bond length is very close to the experimental value of 1.4160 Å. Although theoretical results coincide with the experimental values for the title compounds, it is generally accepted that bond lengths and bond angles depend on the method and the basis set used in the calculations. The calculated geometric parameters represent good approximation and can be used as a foundation to calculate the other parameters for the compound.

#### Vibrational analysis

The molecule has C1 symmetry and 84 normal modes of vibrations, all active in infrared and Raman spectra. The observed and simulated FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2 and 3, respectively. We have calculated the theoretical vibrational spectra of 2DCPAPAA by using HF and B3LYP level with 6-311++G(d,p) basis set. Normally, the vibrational frequencies obtained by quantum chemical calculations with unscaled HF and B3LYP force field are generally greater than the experimental values due to the facts of the electron correlation approximate treatment, the anharmonicity effect and basis set deficiency, etc. A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different regions of vibrations [19-22]. The calculated frequencies are scaled by 0.830(OH), 0.860(NH) and 0.914(other modes) for HF/6-311++G(d,p). For B3LYP/6-311++G(d,p) basis set is scaled with 0.910(OH), 0.940(NH) and 0.972(other modes). The resultant scaled frequencies are presented in Table 2. The scale factors used in this study minimized the deviations very much between the computed and experimental frequencies. The scale factors are all much closer to unity and produced the frequencies very much closer to the experimental values. The observed and calculated frequencies using HF and B3LYP level force fields along with their probable assignments and potential energy distribution (PED) of the title compound are summarized in Table 2. The maximum number of values determined by B3LYP/6-311++G(d,p) method is in good agreement with the experimental values and is also confirmed by the scale factors used to get the scaled frequencies.

### **O**–H vibrations

The hydroxyl stretching vibrations bands can be identified by their broadness and the strength of the band, which is dependent on the extent of hydrogen bonding. The hydroxyl stretching vibrations are generally [23] observed in the region around 3500 cm<sup>-1</sup>. In bonded form, a broad and intense band appears in the region 3550–3200 cm<sup>-1</sup>. In the present investigation a medium absorption at 3397 cm<sup>-1</sup> (FT-IR) assigned to O—H stretching vibration. The PED of this mode is 100%. The PED for this mode suggests that this is a pure mode.

The theoretically computed O–H stretching vibrations scaled wavenumbers are at 3413 and 3407 cm<sup>-1</sup> by HF and B3LYP methods using 6-311++G(d,p) basis set respectively.

#### N—H vibrations

The title molecule possesses amine group with phenyl ring. It has been observed that the presence of N—H in various molecules may be correlated with a constant occurrence of absorption bands whose positions are slightly altered from one compound to another this is because of atomic group which vibrates independently from the other groups in the molecule and has its own frequency. In all the hetero cyclic compounds the N—H stretching vibrations occur in the region  $3600-3300 \text{ cm}^{-1}$  [24,25]. The position of absorption in this region depends upon the degree of hydrogen bonding and physical state of the sample. In the present case, the medium band N—H stretching vibration is found at  $3269 \text{ cm}^{-1}$  in FT-IR spectrum. The PED of this mode is 100%. The theoretically computed scaled values are 3267 and  $3281 \text{ cm}^{-1}$  by HF and B3LYP methods with 6-311++G(d,p) basis set respectively.

# C—H and CH<sub>2</sub> vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3100–3000 cm<sup>-1</sup>, which is the characteristic region for the ready identification of C—H vibrations

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#### Table 3

Calculated thermodynamic parameters of 2DCPAPAA.

Parameter	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
Zero-point		, , ,
Vibrational energy (kl/mol)	149 0331	139 0332
Rotational constant (GHz)	0 4114	0.4186
notational constant (Criz)	0.2393	0.2471
	0.2061	0.1913
Thermal energy (kJ/mol)		
Total	158.9270	149.5380
Translational	0.8890	0.8890
Rotational	0.8890	0.8890
Vibrational	157.1500	147.7600
Heat capacity constant (cal/mo	$bl^{-1} K^{-1}$ )	
Constant (cal/mol <sup><math>-1</math></sup> K <sup><math>-1</math></sup> )	,	
Total	59.2510	63.4990
Translational	2.9810	2.9810
Rotational	2.9810	2.9810
Vibrational	53.2900	57.5370
Entropy (cal/mol <sup>-1</sup> K <sup>-1</sup> )		
Total	132.4110	136.0010
Translational	42.9430	42.9430
Rotational	34.0260	34.0510
Vibrational	55.4420	59.0070

[26]. In this region, the bands are not affected, appreciably by the nature of the substituent's. "Since there is no dominated vibration of highly electronegative atoms in molecule, the entire C-H stretching vibrations formed in their characteristic region". The weak bands observed at 3069 and 3043 cm<sup>-1</sup> in FT-IR spectrum is assigned to C-H stretching vibration. The corresponding Raman peaks are observed at 3068 and 3053 cm<sup>-1</sup> respectively. These vibrations identified as pure mode with 95% PED values. The calculated scaled wavenumbers are at 3050, 3043 and 3081, 3062 cm<sup>-1</sup> by HF and B3LYP methods with 6-311++G(d,p) basis set respectively. The bands due to C-H in-plane bending vibrations are observed in the region  $1000-1300 \text{ cm}^{-1}$  [27]. For this compound, the C-H in-plane bending vibrations are found at 1285, 1167 and 1041 cm<sup>-1</sup> in FT-IR and at 1160 and 1042 cm<sup>-1</sup> in FT-Raman. The bands are observed at 952, 927, 884, 744 and 715  $cm^{-1}$  in FT-IR and at 714 cm<sup>-1</sup> in FT-Raman are assigned to C-H torsion vibrations for 2DCPAPAA.

The CH<sub>2</sub> stretching vibrations are normally observed in the region  $3100-2900 \text{ cm}^{-1}$  [28]. The CH<sub>2</sub> stretching vibration is observed as a weak band at 2960 cm<sup>-1</sup> in FT-IR and very weak band observed at 2961 cm<sup>-1</sup> in FT-Raman are assigned to CH<sub>2</sub> stretching vibrations. These vibrations identified as pure mode with 89% PED values. The calculated values are 2919 and 2957 cm<sup>-1</sup> by HF and B3LYP methods with 6-311++G(d,p) basis set respectively. The medium FT-IR bands are found at 1196 and 1084 cm<sup>-1</sup> and the very weak bands are found at 1189 and 1083 cm<sup>-1</sup> in FT-Raman due to CH<sub>2</sub> in-plane bending vibrations.

## C=O and C-O Vibrations

The position of the C=O stretching vibration is very sensitive to various factors, such as the physical state, electronic effects by substituent, and ring strains. Consideration of these factors provides further information about the environments of the C=O group. The most characteristic feature of carboxylic group is a single sharp band observed usually in the range of 1800–1700 cm<sup>-1</sup> [29] due to the C=O stretching vibration. This portion of the infrared and Raman spectra is quite sensitive to substitution effects and the geometry of the molecule. In this case, the very weak C=O stretching vibration is identified at 1795 cm<sup>-1</sup> in FT-IR spectrum. These vibrations identified as pure mode with 83% PED values. The calculated scaled wavenumbers are at 1811 and 1791 cm<sup>-1</sup> by HF and

#### Table 4

Thermodynamic properties at different temperatures at B3LYP/6-311G++(d,p) level for 2DCPAPAA.

T (K)	C (cal mol <sup>-1</sup> K <sup>-1</sup> )	$S (cal mol^{-1} K^{-1})$	$\Delta H$ (kcal mol <sup>-1</sup> )
100.0000	118.0800	371.9800	7.8900
200.0000	194.4000	476.6300	23.4300
298.1500	273.9900	569.1400	46.4300
300.0000	275.4600	570.8400	46.9400
400.0000	349.3100	660.4700	78.2700
500.0000	410.2900	745.2200	116.3600
600.0000	458.7800	824.4800	159.9100
700.0000	497.3500	898.2100	207.7900
800.0000	528.4900	966.7200	259.1300
900.0000	554.0700	1030.4900	313.3000
1000.0000	575.3900	1090.0100	369.8100



Fig. 4. Correlation graph of enthalpy and temperature of 2DCPAPAA.



Fig. 5. Correlation graph of heat capacity and temperature of 2DCPAPAA.



Fig. 6. Correlation graph of entropy and temperature of 2DCPAPAA.

B3LYP methods with 6-311++G(d,p) basis set respectively. Generally the C–O stretching vibrations occur in the region 1320–1210 cm<sup>-1</sup> [30]. In the present study, the medium bands observed at 1300 and 1278 cm<sup>-1</sup> in FT-IR and the very weak band observed at 1305 and 1275 cm<sup>-1</sup> in FT-Raman are assigned to C–O stretching

vibration. The calculated bands observed at 1310 and 1275 cm<sup>-1</sup> in HF and 1300 and 1276 cm<sup>-1</sup> in B3LYP level with 6-311++G(d,p) basis set respectively are in excellent agreement with experimental frequency (1300 cm<sup>-1</sup> in FT-IR and 1305 cm<sup>-1</sup> in FT-Raman). The C–O in-plane bending observed at 636 and 569 cm<sup>-1</sup> in FT-IR, and at 638 cm<sup>-1</sup> in FT-Raman. The C–O out-of-plane bending assigned at 715 and 714 cm<sup>-1</sup> in FT-IR and FT-Raman respectively.

# C=C and C-C vibrations

The C=C aromatic stretching vibrations give rise to characteristic bonds in both the observed FT-IR and Raman spectra, covering the spectral region ranging from 1650 to 1430 cm<sup>-1</sup> [31]. Therefore, the very strong C=C stretching vibrations of the title compound are found at 1578, 1556 and 1448  $\rm cm^{-1}$  in FT-IR spectrum. The medium C=C stretching vibrations observed at 1580 cm<sup>-1</sup> in FT-Raman spectrum and these modes are confirmed by the PED values as presented in Table 2. The calculated scaled wavenumbers are at 1593, 1574, 1468 and 1577, 1554, 1443 cm<sup>-1</sup> by HF and B3LYP methods with 6-311++G(d,p) basis set respectively. The ring C–C stretching vibrations normally occur in the region  $1590-1430 \text{ cm}^{-1}$  [32]. The present case, the very strong C--C stretching vibrations have been observed at 1410 cm<sup>-1</sup> in FT-IR and the very weak band observed at 1411 cm<sup>-1</sup> in FT-Raman are assigned to C-C stretching vibrations. The calculated scaled wavenumbers are at 1425 and 1410 cm<sup>-1</sup> by HF and B3LYP methods with 6-311++G(d,p) basis set respectively. The pecks observed at 1062 and 869 cm<sup>-1</sup> in FT-IR, and 1063, 881, 836 and 604 cm<sup>-1</sup> in FT-Raman spectrum are assigned to C--C in-plane bending. The C--C out-of-plane bending is found at 441 cm<sup>-1</sup> in FT-Raman spectrum. The C–C torsion vibrations are found at  $715 \text{ cm}^{-1}$  in FT-IR and at 952, 714 and 74 cm<sup>-1</sup> in FT-Raman spectrum.

# C—N vibrations

The identification of C—N stretching frequency is a very difficult task, since the mixing of bands is possible in this region. The C—N stretching vibrations appear in the region of  $1285-1203 \text{ cm}^{-1}$  for aromatic amine [33]. In the FT-IR spectrum, the medium band observed at 1285 and  $1278 \text{ cm}^{-1}$  and the weak band at  $1203 \text{ cm}^{-1}$  are assigned to C—N stretching vibrations. The corresponding very weak Raman pecks are observed at 1275 and  $1204 \text{ cm}^{-1}$  respectively. The theoretically predicted scaled wavenumbers are at 1295, 1275, 1206 and 1287, 1276,  $1223 \text{ cm}^{-1}$  by HF and B3LYP methods with 6-311++G(d,p) basis set respectively. For this compound, the C—N in-plane bending vibrations are observed at  $534 \text{ cm}^{-1}$  in FT-IR, and at 533, 284 and  $96 \text{ cm}^{-1}$  in FT-Raman. The DFT/B3LYP method scaled values good correlation with the observed values presented in Table 2.

These assignments are in line with the literature [34]. The PED of this vibration suggests that this is a mixed mode with C—C stretching vibrations.

### C-Cl vibrations

The vibrations belonging to C–X (X = F, Cl, Br) bonds which are formed between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of molecular symmetry and the presence of heavy atoms [35,36]. When chlorine atoms are attached to one carbon atom, the band is usually more intense and at high frequency end of the assigned limits. In view of this, a strong band observed at 760 cm<sup>-1</sup> in FT-IR and the very weak band observed at 766 and 403 cm<sup>-1</sup> in FT-Raman spectrum are assigned to C–Cl stretching vibration. The theoretical scaled wavenumbers of C–Cl stretching vibrations are at 780, 761 and 403, 401 cm<sup>-1</sup> by HF and B3LYP methods with 6-311++G(d,p) basis set respectively. The very weak bands are observed at 309, 223, 165 and 152 cm<sup>-1</sup> in FT-Raman due to Cl—C in-plane bending vibrations. The Cl—C out-of-plane bending vibrations found at 284 and 490 cm<sup>-1</sup> in FT-Raman.

# Thermodynamic properties

The variation in Zero-Point Vibrational Energies (ZPVEs) seems to be important. The values of some thermodynamic parameters such as zero-point vibrational energy, thermal energy, specific heat capacity, rotational constants, entropy, and dipole moment of 2DCPAPAA by HF and DFT/B3LYP with 6-311++G(d,p) basis sets are listed in the Table 3 [37]. The ZPVE, energy is lower in the B3LYP method at 6-311++G(d,p) basis set than by HF method. The biggest value of ZPVE of 2DCPAPAA is 149.0331 kJ mol<sup>-1</sup> obtained at HF method. However, specific heat capacity and entropy were calculated the smallest values for HF but the highest values were obtained B3LYP method. The minimum value of thermal energy are calculated in 149.5380 at B3LYP/6-311++G(d,p) whereas the maximum one was calculated 158.9270 at B3LYP/6-311++G(d,p) in 2DCPAPAA molecule.

On the basis of vibrational analysis at B3LYP/6-311++G(d,p) level, the standard statistical thermodynamic functions: heat capacity (*C*), entropy (*S*), and enthalpy changes ( $\Delta H$ ) for the 2DCPAPAA compound were obtained from the theoretical harmonic frequencies and listed in Table 4. Figs. 4–6 depict the correlation of heat capacity (*C*) entropy (*S*), and enthalpy change ( $\Delta H$ ) with temperature along with the correlation equations. From Table 4, it can be observed that these thermodynamic functions are increasing with temperature ranging from100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures were fitted by quadratic formulas and the corresponding fitting regression factors ( $R^2$ ) for these thermodynamic properties are 0.9993, 0.9999 and 0.9992, respectively.

 $C = 19.1869 + 0.9927T - 4.3956 \times 10^{-4}T^2 \quad (R^2 = 0.9993)$  $S = 267.7189 + 1.0889T - 2.6770 \times 10^{-4}T^2 \quad (R^2 = 0.9999)$  $H = -12.3993 + 0.1313T + 2.5499 \times 10^{-4}T^2 \quad (R^2 = 0.9992)$ 

All the thermodynamic data supply helpful information for the further study on the 2DCPAPAA. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical





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## Table 5

Wavelength (nm)	, oscillatory	strength (f	) and	energy	(eV)	of 2DCPAPAA
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Calculated with B3LYP/6-311++G(d,p)						Exp			
Gas phase			DMSO			Acetone			
$\lambda_{\max}$ (nm)	<i>E</i> (eV)	f	$\lambda_{\max}$ (nm)	E (eV)	f	$\lambda_{\max}$ (nm)	<i>E</i> (eV)	f	$\lambda_{\max}$ (nm)
285.0400	4.3497	0.0200	281.9800	4.3969	0.0361	282.2000	4.3935	0.0336	
276.7900 258.7000	4.4793 4.7926	0.2426 0.0153	276.2400 258.4100	4.4882 4.7979	0.3172 0.0219	276.1900 258.3700	4.4892 4.7987	0.3094 0.0210	276.0000





Fig. 9. Density of state (DOS) spectrum of 2DCPAPAA.

reactions according to the second law of thermodynamics in thermo chemical field. Notice: all thermodynamic calculations were done in gas phase and they could not be used in solution.

# UV-Vis spectral analysis

UV-Vis spectra analyses of 2DCPAPAA have been investigated in DMSO, acetone and gas phase by theoretical calculation. On the basis of fully optimized ground-state structure, TD-DFT/ B3LYP/6-311++G(d,p) calculations have been used to determine the low-lying excited states of 2DCPAPAA. The experimental  $\lambda_{max}$ values are obtained from the UV–Visible spectrum recorded in acetone solution. The UV–Visible spectrum of 2DCPAPAA is shown in Fig. 7. The theoretical electronic excitation energies (*E*), oscillator strengths (*f*) and absorption wavelengths ( $\lambda$ ) are also listed in Table 5.

#### Table 6

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HOMO, LUMO and HOMO-LUMO energy values of 2DCPAPAA.

Parameters (eV)	HF/6-311++G(d, p)	B3LYP/6-311++G(d, p)
HOMO energy	8.3692	5.9218
LUMO energy	-1.0093	1.0408
HOMO-LUMO		
Energy gap	9.3785	4.8809

#### Table 7

Calculated physico-chemical properties for title molecule of 2DCPAPAA.

Chemical Parameters (eV)	HF/6-311++G(d, p)	B3LYP/6-311++G(d, p)
Ionization potential (I)	-8.3692	-5.9218
Electron affinity (A)	1.0093	-1.0408
Global hardness $(\eta)$	-4.6892	-2.4405
Global softness (S)	-0.2132	-0.4097
Chemical potential $(\mu)$	3.6799	3.4813
Electrophilicity $(\omega)$	-1.4439	-2.4829
Electro negativity ( $\chi$ )	-3.6799	-3.4813

The molecular orbital energy is calculated and shows that absorption maxima of this molecule correspond to electron transition between Highest Occupied Molecular Orbital (HOMO) to Lowest Unoccupied Molecular Orbital (LUMO). As can be seen from Table 5, the calculated absorption maxima values have been found to be 285, 276 and 258 nm for gas phase and 281, 276 and 258 nm for DMSO solution, and 282, 276 and 258 nm for acetone solution. The TD-DFT calculations on electronic absorption spectra in acetone solvent were performed. The absorption wavelength is calculated at 269 nm is in good agreement with the experimental absorption wavelength at 276 nm in the UV-Vis spectrum[38]. The observed transition from HOMO-LUMO is  $\pi \rightarrow \pi^*$ .

### Frontier molecular orbital's (FMO's)

The Highest Occupied Molecular Orbital's (HOMOs) and Lowest Unoccupied Molecular Orbital's (LUMOs) are named Frontier molecular orbital's (FMOs). The atomic orbital compositions of the frontier molecular orbital are shown in Fig. 8. The Gauss-Sum 2.1 Program [39] was used to calculate group contributions to the molecular orbital's (HOMO and LUMO) and prepare the density of the state (DOS) as shown in Fig. 9. The DOS spectra were created by convoluting the molecular orbital information with GAUSSION cures of unit height. The HOMO–LUMO energy gap of 2DCPAPAA was calculated at HF and B3LYP level with 6-311++G(d,p) basis set and is presented in Table 6. The LUMO as an electron acceptor represent the ability to obtain an electron, HOMO represents the ability to donate an electron [40]. The energy gap of HOMO–LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. The positive and negative phase is represented in red and green color, respectively.

The computed HOMO energy values are 8.3692 and 5.9218 eV and LUMO energy values are -1.0093 and 1.0408 eV by HF and B3LYP levels with 6-311++G(d,p) basis set respectively. The HOMO–LUMO energy gap values are 9.3785 and 4.8809 eV by HF and B3LYP method. The most widely used theory by chemists is the molecular orbital (FMOs) theory. It is important that ionization potential (*I*), electron affinity (*A*), electrophilicity ( $\omega$ ), chemical potential ( $\mu$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ), and softness (*S*) be put into a MO framework.

We focus on the HOMO and LUMO energies in order to determine interesting molecular/atomic properties and chemical quantities. In simple molecular orbital theory approaches, the HOMO energy is related to the ionization potential (*I*) and the LUMO energy has been used to estimate the electron affinity (*A*) respectively by the following relations:  $I = -E_{HOMO}$  and  $A = -E_{LUMO}$ . Absolute electro negativity ( $\chi$ ), chemical potential ( $\mu$ ) and absolute hardness ( $\eta$ ) of the molecule are given by  $\eta = (I - A)/2$ ,  $\mu = -(I + A)/2$ ,  $\mu = -\chi$ . The softness is the inverse of the hardness  $S = 1/\eta$ . Parr et al. [41] introduced the global electrophilicity ( $\omega$ ) in terms of chemical potential and hardness as  $\omega = \mu^2/2\eta$ . The quantum chemical parameters of the molecule are presented in Table 7.

# NLO studies

The first order hyperpolarizability ( $\beta_o$ ), electric dipole moment ( $\mu$ ) and polarizability ( $\alpha$ ) are calculated using B3LYP/6-311++G(d,p) basis set on the basis of the finite-field approach. The complete equations for calculating the magnitude of total static dipole moment  $\mu_{tot}$ , the isotropic polarizability  $\alpha_o$ , the anisotropy of the polarizability  $\Delta \alpha$  and the mean first hyperpolarizability  $\beta_o$  using the *x*, *y*, *z* components from Gaussian 09W program output is given as follows,

The isotropic polarizability is defined as:

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

The polarizability anisotropy invariant is

$$\begin{aligned} \Delta \alpha = & \frac{1}{\sqrt{2}} \\ & \times \sqrt{\left(\alpha_{xx} + \alpha_{yy}\right)^2 + \left(\alpha_{yy} + \alpha_{zz}\right)^2 + \left(\alpha_{zz} + \alpha_{xx}\right)^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2} \end{aligned}$$

First hyperpolarizability is a third rank tensor that can be described by  $3 \times 3 \times 3$  matrix. The 27 components of 3D matrix can be reduced to 10 components due to the Kleinman symmetry  $\beta_{xyy} = \beta_{yyx} = \beta_{yyx} = \beta_{yyz} = \beta_{yyz} = \beta_{yyz}; \dots$  likewise other permutations

Table 8

The electric dipole moment $\mu$ ( <i>D</i> ) the average polarizability $\alpha$ (×10 <sup>-24</sup> esu) and the	e first hyperpolarizability $\beta_o$ (×10 <sup>-33</sup> esu) of 2DCPAPAA.
--	---

Parameters	Value	esu (×10 <sup>-24</sup> )	Parameters	Value	esu (×10 <sup>-33</sup> )
$\alpha_{xx}$	156.4960	23.1927	$\beta_{xxx}$	77.8897	672.9126
$\alpha_{xy}$	-5.8898	-0.8729	$\beta_{xxy}$	-92.0730	-795.4461
$\alpha_{\nu\nu}$	264.1374	39.1452	$\beta_{XYY}$	28.4503	245.7911
α <sub>xz</sub>	13.6367	2.0210	β <sub>γγγ</sub>	413.1094	3568.9759
$\alpha_{vz}$	-6.1047	-0.9047	β <sub>xxz</sub>	13.6174	117.6448
a.zz	202.6647	30.0349	$\beta_{XVZ}$	-91.6394	-791.7002
α0	207.7660	30.7909	$\beta_{VVZ}$	36.5807	316.0317
Δα	512.5283	75.9567	β <sub>xzz</sub>	-4.0783	-35.2338
$\mu_{x}$	-0.0065		β <sub>vzz</sub>	-8.3420	-72.0688
$\mu_{v}$	-0.1274		β777	51.2884	443.0955
$\mu_z$	0.0713		βο	344.2887	2974.4134
$\mu_{tot}$	0.1462		· -		

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#### Table 9

Second order perturbation theory analysis of Fock matrix in NBO basis by using B3LYP with 6-311++G(d,p) basis set method.

Туре	Donor NBO (i)	ED ( <i>i</i> ) (e)	Туре	Acceptor NBO (j)	ED (j) (e)	E <sup>a</sup> (2) (kcal/mol)	$E(j) - E(i)^{b}$ (a.u)	<i>F</i> ( <i>i,j</i> ) <sup>c</sup> (a.u)
σ	$C_1 - C_2$	1.96817	$\sigma^*$	$C_1 - C_6$	0.04230	4.960	1.290	0.072
π	$C_1 - C_2$	1.67249	$\pi^*$	$C_2 - C_4$	0.33949	19.970	0.310	0.070
π	$C_1 - C_2$	1.67249	$\sigma^*$	N12-C14	0.03104	2.260	0.700	0.039
σ	$C_1 - C_c$	1.96643	$\sigma^*$	$C_1 - C_2$	0.04260	4.900	1.280	0.007
σ	$C_1 - N_{12}$	1.98346	$\sigma^*$	$C_1 - C_2$	0.04260	2.280	1.340	0.050
σ	$C_2 - C_2$	1.97760	$\sigma^*$	$C_1 - C_2$	0.04260	4.210	1.290	0.066
σ	$C_2 = C_{10}$	1 98579	$\sigma^*$	$C_1 - C_6$	0.04230	2 610	1 270	0.052
σ	$C_2 = C_1$	1 97033	σ*	$C_2 - C_{10}$	0.02947	4 970	0.860	0.058
π	$C_3 - C_4$	1 67303	π*	$C_2 = C_1$	0 38781	21 920	0.280	0.070
π σ	CH-	1 97751	σ*	$C_3 = C_0$	0.04260	4 670	1 080	0.064
σ	C-C-	1 97046	σ*	$C_1 = C_2$	0.02887	4 930	0.870	0.058
σ	$C_4 = C_5$	1 97872	σ*		0.02543	3 430	1 100	0.055
σ σ	$C_4 = C_8$	1.97810	σ*	$C_2 = C_3$	0.023 15	4 130	1 290	0.065
π	$C_5 = C_6$	1 69589	π*	$C_1 - C_2$	0.43983	20.970	0.280	0.003
π σ	CH	1,05505	π σ*	$c_1 - c_2$	0.4230	4 700	1 080	0.064
σ		1.97750	σ*	$C_1 = C_2$	0.04250	2 250	1.000	0.051
σ	C <sub>6</sub> Cl <sub>11</sub>	1,90501	0 (*	$C_1 = C_2$	0.04230	3.450	1.270	0.057
0 T	N _U	1.97222	υ π*	$c_1 - c_6$	0.04230	2 170	0.670	0.037
0	N U	1.97222	π π*	$C_{14} - C_{16}$	0.30303	2.070	1.260	0.045
0	$N_{12} - \Pi_{14}$	1.97652	-*	$C_{15} - C_{17}$	0.02127	2.070	1.500	0.047
0	$N_{12} - H_{14}$	1.97852	π*	$C_1 = C_2$	0.04230	1.350	0.770	0.032
6	$C_{14} - C_{15}$	1.90007	o. _*	$C_{14} - C_{16}$	0.02718	4.400	1.290	0.067
0	$C_{14} - C_{16}$	1.97222	<u>o</u> .	$C_{14} - C_{15}$	0.03290	5.080	1.290	0.072
π	$C_{14} - C_{16}$	1.65274	$\pi^*$	$C_{18} - C_{20}$	0.33933	21.320	0.290	0.071
π	$C_{14} - C_{16}$	1.65274	$\sigma^*$	N <sub>12</sub> —H <sub>13</sub>	0.02434	2.430	0.700	0.040
σ	$C_{15} - C_{17}$	1.97103	$\sigma^*$	$C_{14} - C_{15}$	0.03290	4.260	1.280	0.066
π	$C_{15} - C_{17}$	1.67711	$\pi^*$	$C_{14} - C_{16}$	0.36505	21.150	0.290	0.070
π	$C_{15} - C_{17}$	1.67711	$\sigma^*$	$C_{24} - C_{27}$	0.06987	3.990	0.620	0.048
σ	$C_{15} - C_{24}$	1.97145	$\sigma^*$	$C_{14} - C_{16}$	0.02718	3.050	1.220	0.054
σ	$C_{15} - C_{24}$	1.97145	$\pi^*$	$C_{27} - O_{28}$	0.21337	0.540	0.640	0.017
σ	$C_{16} - C_{18}$	1.97487	$\sigma^*$	$N_{12}-C_{14}$	0.03104	4.530	1.110	0.063
σ	$C_{16} - H_{19}$	1.97686	$\sigma^*$	$C_{14} - C_{15}$	0.03290	4.530	1.100	0.063
σ	$C_{17} - C_{20}$	1.97632	$\sigma^*$	$C_{15} - C_{24}$	0.02085	3.720	1.110	0.057
σ	$C_{17} - C_{21}$	1.97913	$\sigma^*$	$C_{14} - C_{15}$	0.03290	4.620	1.100	0.064
σ	C <sub>18</sub> -C <sub>20</sub>	1.97801	$\sigma^*$	$C_{17} - C_{20}$	0.01602	2.990	1.290	0.057
π	C <sub>18</sub> -C <sub>20</sub>	1.66929	$\pi^*$	C <sub>15</sub> -C <sub>17</sub>	0.34900	21.380	0.290	0.070
σ	C <sub>18</sub> -C <sub>22</sub>	1.97989	$\sigma^*$	$C_{14} - C_{16}$	0.02718	3.860	1.110	0.058
σ	C <sub>20</sub> -C <sub>23</sub>	1.98003	$\sigma^*$	C <sub>15</sub> -C <sub>17</sub>	0.02127	3.720	1.110	0.057
σ	C <sub>24</sub> —H <sub>25</sub>	1.97398	$\sigma^*$	$C_{27} - O_{28}$	0.02273	4.020	1.170	0.061
σ	C <sub>24</sub> —H <sub>25</sub>	1.97398	$\pi^*$	C <sub>27</sub> -O <sub>28</sub>	0.02273	1.690	0.520	0.028
σ	C24-H26	1.95087	$\pi^*$	C <sub>27</sub> -O <sub>28</sub>	0.21337	7.220	0.520	0.057
σ	C <sub>24</sub> -H <sub>26</sub>	1.95087	$\sigma^*$	C <sub>15</sub> -C <sub>17</sub>	0.02127	2.480	1.110	0.047
σ	C <sub>24</sub> —H <sub>27</sub>	1.97322	$\sigma^*$	O <sub>29</sub> —H <sub>30</sub>	0.01099	2.430	1.070	0.046
σ	$C_{24} - H_{27}$	1.97322	$\pi^*$	$C_{15} - C_{17}$	0.34900	1.830	0.070	0.035
σ	$C_{27} - O_{28}$	1.99598	$\sigma^*$	$C_{24} - C_{27}$	0.06987	1.730	1.510	0.046
π	$C_{27} - O_{28}$	1.99213	$\sigma^*$	C <sub>24</sub> -C <sub>26</sub>	0.01448	1.300	0.810	0.029
σ	C <sub>27</sub> -O <sub>29</sub>	1.99536	$\pi^*$	C <sub>27</sub> -O <sub>28</sub>	0.02134	0.900	0.420	0.018
σ	029-H30	1,98646	$\sigma^*$	C24-C27	0.06987	3.860	1.160	0.061
	$LP(1)Cl_{10}$	1.99240	$\sigma^*$	C2-C3	0.02543	1.610	1.510	0.044
	$LP(2)Cl_{10}$	1.96615	$\sigma^*$	$C_1 - C_2$	0.04260	4.720	0.880	0.058
	$LP(3)Cl_{10}$	1 92705	σ*	$C_1 - C_2$	0.04260	12 550	0 330	0.063
	$LP(1)Cl_{11}$	1 99236	σ*	$C_1 - C_2$	0.02468	1 720	1 500	0.046
	$LP(2)Cl_{11}$	1 96748	σ*	$C_3 = C_6$	0.04230	5 120	0.870	0.060
	$IP(3)C1_{11}$	1 02335	π*	$C_1 = C_2$	0.38781	12 700	0.330	0.000
	$IP(1)N_{10}$	1,92,555	π*	$C_5 C_6$	0./3083	16 330	0.330	0.065
	$ID(1)N_{-}$	1.01434	π σ*	$C_1 = C_2$	0.04220	10.000	0.200	0.005
	$IP(1)O_{0}$	1.01404	о с*	$C_1 = C_2$	0.04230	2.460	1 080	0.039
	$IP(2)O_{28}$	1.37330	۰ ۳	$C_{24}$ $C_{27}$	0.00307	2.400	0.650	0.047
	$LP(Z)U_{28}$	1.04820	0 <b>~</b> *	$c_{27} - c_{29}$	0.09472	54.200 7.270	1.000	0.150
	LP(1)U <sub>29</sub>	1.97070	<u>-</u> *	$C_{27} - O_{28}$	0.02273	/.3/0	1.270	0.08/
_*	LP(2)U <sub>29</sub>	1.818/0	σ.	$C_{27} - O_{28}$	0.02273	4/.560	0.360	0.118
π <sup></sup> _*	$L_1 - L_2$	0.43983	$\pi^{-}$	$L_3 - L_4$	0.33949	1/2./40	0.020	0.082
$\pi^{*}$	$L_1 - L_2$	0.43983	σ	N <sub>12</sub> -C <sub>14</sub>	0.03104	1.490	0.410	0.046
$\pi^{*}$	$C_5 - C_6$	0.38781	$\pi^{*}$	$C_3 - C_4$	0.33989	261.470	0.010	0.086
$\pi^*$	$C_{14} - C_{16}$	0.36505	$\sigma^*$	N <sub>12</sub> —H <sub>13</sub>	0.02434	1.140	0.410	0.044
$\pi^*$	$C_{15} - C_{17}$	0.34900	$\sigma^*$	C <sub>24</sub> —H <sub>27</sub>	0.06987	1.870	0.330	0.049
$\pi^*$	$C_{27} - O_{28}$	0.21337	$\sigma^*$	$C_{24} - H_{26}$	0.01448	1.110	0.390	0.055

<sup>a</sup> E(2) means energy of hyper conjugative interaction.

<sup>b</sup> Energy difference between donor and accepter *i* and *j* NBO orbitals.

<sup>c</sup> F(i,j) is the Fock matrix element between *i* and *j* NBO orbitals.

also take same value). The output from Gaussian 09W provides 10 components of this matrix as  $\beta_{XXX}$ ,  $\beta_{YXX}$ ,  $\beta_{XYY}$ ,  $\beta_{YXY}$ ,  $\beta_{ZXX}$ ,  $\beta_{XYZ}$ ,

 $\beta_{yyy}, \beta_{xzz}, \beta_{yzzz}, \beta_{zzz}$  respectively.

The components of the first hyperpolarizability can be calculated using the following equation. Using the *x*, *y* and *z* components

$$eta_0 = \sqrt{\left(eta_x^2 + eta_y^2 + eta_z^2
ight)}$$

calculated by:

of  $\beta$ , the magnitude of the first hyperpolarizability tensor can be

Та	ble	10

The natural charge distribution calculated by B3LYP/6-311++G(d,p) methods of 2DCPAPAA molecule.

Charges	Atoms	Charges
0.1053	C <sub>16</sub>	-0.2204
-0.0488	C <sub>17</sub>	-0.1806
-0.2159	C <sub>18</sub>	-0.1837
-0.1909	H19	0.2105
-0.2152	C <sub>20</sub>	-0.2105
-0.0388	H <sub>21</sub>	0.1990
0.2206	H <sub>22</sub>	0.2031
0.2112	H <sub>23</sub>	0.2036
0.2206	C <sub>24</sub>	-0.4980
0.0184	H <sub>25</sub>	0.2298
0.0250	H <sub>26</sub>	0.2542
-0.6548	C <sub>27</sub>	0.8174
0.4146	O <sub>28</sub>	-0.6120
0.1790	O <sub>29</sub>	-0.6756
-0.0486	H <sub>30</sub>	0.4815
	Charges 0.1053 -0.0488 -0.2159 -0.1909 -0.2152 -0.0388 0.2206 0.2112 0.2206 0.2112 0.2206 0.0184 0.0250 -0.6548 0.4146 0.1790 -0.0486	$\begin{tabular}{ c c c c } \hline Charges & Atoms \\ \hline 0.1053 & C_{16} \\ -0.0488 & C_{17} \\ -0.2159 & C_{18} \\ -0.1909 & H_{19} \\ -0.2152 & C_{20} \\ -0.0388 & H_{21} \\ 0.2206 & H_{22} \\ 0.2112 & H_{23} \\ 0.2206 & C_{24} \\ 0.0184 & H_{25} \\ 0.0250 & H_{26} \\ -0.6548 & C_{27} \\ 0.4146 & O_{28} \\ 0.1790 & O_{29} \\ -0.0486 & H_{30} \\ \end{tabular}$



Fig. 10. Natural charge distribution in 2DCPAPAA.

The complete equation for calculating the magnitude of  $\beta_0$  from Gaussian 09W output is given as follows:

$$\begin{split} \beta_{0} &= \sqrt{\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^{2} + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^{2} + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^{2}} \\ \beta_{x} &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_{y} &= \beta_{yyy} + \beta_{yzz} + \beta_{yxx} \\ \beta_{z} &= \beta_{zzz} + \beta_{zxx} + \beta_{zyy} \end{split}$$

In Table 8, the calculated parameters described above and electronic dipole moment { $\mu_i$  (i = x, y, z) and total dipole moment  $\mu_{tot}$ } for title compound were listed. The total dipole moment can be calculated using the following equation.

$$\mu_{\rm tot} = \sqrt{\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)}$$

It is well known that the higher values of dipole moment, molecular polarizability, and hyperpolarizability are important for more active NLO properties. The polarizabilities and hyperpolarizability are reported in atomic units (a.u), the calculated values have been converted into electrostatic units (esu) (for  $\alpha$ ; 1 a.u = 0.1482 × 10<sup>-24</sup> esu, for  $\beta$ ; 1 a.u = 8.6393 × 10<sup>-33</sup> esu). The

calculated value of the dipole moment ( $\mu_{tot}$ ) was found to be 0.1462 Debye. The highest value of dipole moment is observed for component  $\mu_z$ . In this direction, this value is equal to 0.0713 Debye and the lowest value of the dipole moment of the 2DCPA-PAA compound is  $\mu_x$  component (-0.1274). The calculated isotropic polarizability and anisotropy of the polarizability of 2DCPAPAA is 30.7909 × 10<sup>-24</sup> and 75.9567 × 10<sup>-24</sup> esu, respectively.

The B3LYP/6-311++G(d,p) levels, which are comparable with the reported values of similar derivatives [42,43]. The magnitude of the molecular first hyperpolarizability ( $\beta_o$ ), is one of important key factors in a NLO system. The B3LYP/6-311++G(d,p) calculated first hyperpolarizability value ( $\beta_0$ ) of 2DCPAPAA is equal to 2.9744 ×  $10^{-30}$  esu. Total dipole moment of title molecule is less than those of urea and first order hyperpolarizability of title molecule is greater than those of urea ( $\mu_{tot}$  and  $\beta_0$  urea are 1.5256 Debye and 0.7803 ×  $10^{-30}$  esu [44] respectively, obtained by B3LYP/6-311++G(d,p) method).

## NBO analysis

Natural bond orbital analysis has been carried out to explain the charge transfer or delocalization of charge due to the intra-molecular interaction among bonds, and also provides convenient basis for investigating charge transfer or conjugative interaction in molecular systems. NBO analysis provides the most accurate possible 'natural Lewis structure' picture, of ' $\phi$ ' because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. Another useful aspect of NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and intermolecular interactions. The second order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis [45,46]. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor NBO (i) and acceptor NBO (*j*), the stabilization energy associated with  $i \rightarrow j$  delocalization can be estimated as,

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F_{(ij)}^2}{\varepsilon_i - \varepsilon_i}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_j$  and  $\varepsilon_i$  are diagonal elements and  $F_{(i,j)}$  is the off diagonal NBO Fock matrix element. In NBO analysis large E(2) value shows the intensive interaction between electron donors and electron-acceptors and greater the extent of conjugation of the whole system, the possible intensive interactions are given in Table 9 as supporting information. The second-order perturbation theory analysis of Fock matrix in NBO basis shows strong intra-molecular hyper-conjugative interactions of  $\pi$  electrons.

In 2DCPAPAA, the interactions  $\pi^*(C_5-C_6) \rightarrow \pi^*(C_3-C_4)$  have the highest E(2) value around 261.470 kcal/mol. The other significant interactions giving stronger stabilization to the structure are

$$\begin{array}{rcl} \pi^*(C_1 - C_2) \to \pi^*(C_3 - C_4), LP(2)O_{29} & \to & \pi^*(C_{27} - O_{28}) \text{ and } LP(2)O_{28} \\ & \to & \pi^*(C_{27} - O_{29}). \end{array}$$

## Natural charge analysis

The Natural charge calculation has an important role in the application of quantum chemical calculation to molecular system. Because the atomic charges affect dipole moment, polarizability, electronic structure and more a lot of properties of molecular systems [47]. The natural charge distribution of the molecule are calculated at B3LYP level 6-311++G(d,p) basis set and is presented in

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Fig. 11. Molecular electrostatic potential contour surface of 2DCPAPAA.



Fig. 12. Molecular electrostatic potential surface of 2DCPAPAA.

Table 10. The charge distribution of 2DCPAPAA shows that the carbon atom  $C_{27}$ ,  $C_{14}$  and  $C_1$  atoms are attached with oxygen  $O_{28}$ ,  $O_{29}$  and nitrogen  $N_{12}$  atoms of the ring are positive because of the electron withdrawing nature of the N and O atoms, whereas the remaining carbon atoms are negatively charged. The oxygen  $O_{29}$  and nitrogen  $N_{12}$  atoms have more negative charges whereas all the hydrogen atoms have positive charges. The maximum positive charge is obtained for  $C_{27}$ ,  $H_{30}$  and  $H_{13}$  when compared with other carbon and hydrogen atoms. This is due to the attachment of negatively charged oxygen  $O_{28}$ ,  $O_{29}$  and nitrogen  $N_{12}$  atoms respectively. Illustration of natural charges plotted is shown in Fig. 10.

The negatively charged lone pair nitrogen N<sub>12</sub>, and oxygen O<sub>28</sub>, O<sub>29</sub> atoms show that the charge is transferred from N to H (N<sub>12</sub>  $\rightarrow$  H<sub>13</sub>), O to C (O<sub>28</sub>  $\rightarrow$  C<sub>27</sub>), (O<sub>29</sub>  $\rightarrow$  C<sub>27</sub>), and O to H (O<sub>29</sub>  $\rightarrow$  H<sub>30</sub>). The calculated natural charges of N<sub>12</sub> (-0.6548 eV), H<sub>13</sub> (0.4146 eV), O<sub>28</sub> (-0.6120 eV), C<sub>27</sub> (0.8174 eV), O<sub>29</sub> (-0.6756 eV), and H<sub>30</sub> (0.4815 eV), taking part in intra-molecular charge transfer is revealed in the natural bond orbital analysis. The minimum positive and negative charge is represented in Cl<sub>10</sub> and C<sub>6</sub>, and the maximum positive and negative charge is represented in C<sub>27</sub> and O<sub>29</sub> atoms respectively.

### MESP analysis

The molecular electrostatic potential surface (MESP) provides a visual method to understand the relative polarity of a molecula. The molecular electrostatic potential (MESP) and molecular electrostatic potential counter map are constricted by B3LYP/6-311++G(d,p) method using Gauss view 5.0 program. The molecular electrostatic potential contour surface of 2DCPAPAA is shown in the Fig. 11. The total electron density surface mapped with the molecular electrostatic potential of 2DCPAPAA is shown in

Fig. 12. Electrostatic potential correlates with dipole moment, electro negativity, partial charges and site of chemical reactivity of the molecule. Such surfaces depict the size, shape, charge density and site of chemical reactivity of the molecules. The different values of the electrostatic potential at the surface are represented by different colors [48,49]. The colors scheme for the MESP 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 is between -0.1510 a.u. (red) and 0.1290 a.u. (blue) title of the molecule. The negative regions are electrophilic regions around the chlorine, nitrogen, and oxygen atom represents the most negative potential region (red). Therefore total electron density surface mapped with electrostatic potential clearly reveals the presence of high negative charge on the oxygen atoms. The positive regions are the nucleophilic region and these are over the hydrogen atoms of the title molecule.

The negative electrostatic potential corresponds to an attraction of the proton by the concentrated electron density in the molecule and the positive electrostatic potential corresponds to repulsion of the proton by atomic nuclei in regions where low electron density exists and the nuclear charge is incompletely shielded. By definition, electron density isosurface is a surface on which molecule's electron density has a particular value and that encloses a specified fraction of the molecule's electron probability density. From these results it can be inferred that the H atoms indicates the strongest attraction and oxygen atom indicated the strongest repulsion. The dipole moment in a molecule is another important electronic property that results from non-uniform distribution of charges on the various atoms in a molecule.

It is mainly used to study the intermolecular interactions involving the Vander Waal type dipole–dipole forces, etc., because larger the dipole moment, stronger will be the intermolecular interactions.

# Conclusion

The present investigation thoroughly analyzed the vibrational spectra, both infrared and Raman spectra of 2DCPAPAA. The geometry of the title compound 2DCPAPAA was optimized with the HF and DFT-B3LYP methods using 6-311++G(d,p) basis set. The molecular structural parameters like bond length, bond angle and vibrational frequencies of the fundamental modes of the optimized geometry have been determined from ab initio and DFT calculations. The complete vibrational assignments of wave numbers are made on the basis of potential energy distribution (PED). Close

agreement between the experimental and computed scaled frequencies were achieved. The correlations between the statistical thermodynamics and temperature are also obtained. It was seen that the heat capacities, entropies and enthalpies increase with the increasing temperature owing to the intensities of the molecular vibrations increase with increasing temperature. UV-Vis spectral analyses of 2DCPAPAA have been done by theoretical calculations. The calculated HOMO and LUMO energies can be used to semi guantitatively estimate the ionization potential, electron affinity, electro negativity, electrophilicity, global hardness, global softness and chemical potential. The electronic dipole moment ( $\mu$ ), first hyperpolarizability ( $\beta_o$ ), and polarizability ( $\alpha$ ) of the title compound were calculated by B3LYP method using 6-311++G(d,p) calculated. The stability and intra molecular interactions have been interpreted by NBO analysis and the transactions give stabilization to the structure have been identified by second order perturbation energy calculations. The natural charge analysis reveals the charge distribution among the atoms and the MESP map shows the negative potential sites are on oxygen, chlorine and nitrogen atoms as well as the positive potential sites are around the hydrogen atoms.

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