

## Investigations of FT-IR, FT-Raman, UV-Visible, FT-NMR Spectra and Quantum Chemical Computations of Diphenylacetylene Molecule

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## Abstarct

FT-IR and FT-Raman spectra of Diphenylacetylene were recorded and analyzed in the region 3700–0 cm<sup>-1</sup>. Molecular modeling of the compound was completed by the density functional theoretical (DFT) method using Becke's three parameter exchange functional combined with the Lee–Yang–Parr correlation functional with 6-311++G(d,p) as basis set. The computed values of frequencies were scaled using a suitable scale factor to yield good coherence with the observed values. The linear polarizability ( $\alpha$ ) and the first order hyperpolarizability ( $\beta$ ) values and its related properties ( $\alpha_0$ ,  $\mu$  and  $\Delta \alpha$ ) of the investigated molecule have been computed using DFT quantum mechanical calculations. The energy and oscillator strength calculated by time-dependent density functional theory (TD-DFT) results complements with the experimental findings. The <sup>1</sup>H nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by GIAO method. The thermodynamic functions of the title compound have been performed.

## Introduction

Diphenylacetylene is the molecule consists of phenyl groups attached to both ends of analkyne<sup>[1]</sup>. It is a colorless crystalline material with molecular weight 178.23g/mol. This molecule is widely used as a building block in organic and as a ligand in organo metallic chemistry and in the pharmaceutical field. Jim et.al., were study the Production of 6-Phenylacetylene Picolinic Acid from Diphenvlacetylene by a Toluene-Degrading Acinetobacter Strain<sup>[2]</sup>. Their result shows the potential for using the normal growth substrate to provide energy and to maintain induction of the enzymes involved in biotransformation during preliminary stages of biocatalyst development. Rahmat Hidayat *et* al. were studied the Photoluminescence and Electroluminescence in Polymer Mixture of Poly (alkylphenylacetylene) and Poly (Diphenylacetylene) Derivatives<sup>[3]</sup>. Han, Dong Cheul et al., were reported the Improvement of Operation Lifetime in Organic Solar Cell Coated with Diphenylacetylene Polymer Film. The Diphenylacetylene polymer film significantly improved the operation lifetime of the Organic Solar Cell by efficiently absorbing the UV light, while reducing the UV-light energy loss to a minimum by converting the UV light to visible light through a down-conversion process<sup>[4]</sup>.

To the best of our knowledge, neither quantum chemical calculation, nor the vibrational spectra of Diphenylacetylene (DPA) have been reported. Therefore, the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various modes with greater wavenumber accuracy. Density functional theory (DFT) and Hartree Fock (HF) calculations have been performed to support our wavenumber assignments. Hence, in the present work, a detailed vibrational analysis,



chemical shifts, HOMO–LUMO, Mulliken atomic charge, thermodynamic studies, NMR spectral analysis and UV-Visible spectral analysis has been attempted using DFT/B3LYP and HF methods at 6-311++G(d,p) basis set by recording FT-IR and FT-Raman spectra of the compound.

## **Experimental details**

The samples Diphenylacetylene was purchased from Sigma-Aldrich Company (USA) with a stated purity 98% and it was used as such without further purification. The FTIR spectrum of Diphenylacetylene was recorded in the region  $3700-0 \text{ cm}^{-1}$  recorded by KBr pellet on a Burkerr 1 FS 66 v Spectrometer equipped with a global source, Ge/KBr beam splitter and a TGs detector. The FT-Raman spectrum of the compound also recorded in the range 0-3700 cm<sup>-1</sup> using the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source. The frequencies of all sharp bands are accurate to 2 cm<sup>-1</sup>. The ultraviolet absorption spectrum of the tested molecule has been examined in the range 200-400 nm using Shimadzu UV-1800 PC, UV-Vis recording Spectrometer. Data are analyzed by UV PC personal spectroscopy software, version 3.91. NMR experiments were performed in Bruker DPX 400 MHz at 300 K. The compound was dissolved in CDCl3. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for <sup>1</sup>H NMR spectra of Diphenylacetylene.

## Quantum chemical calculations

The density functional theory <sup>[5]</sup> treated according to hybrid Becke's three parameter and the Lee–Yang–Parr functional (B3LYP) <sup>[6-8]</sup> functional were used to carry out ab initio analysis with the standard 6-311++G (d,p) basis sets to study the molecule Diphenylacetylene . All calculations were carried out using Gaussian 09 package<sup>[9]</sup>.Using the version 8 of Gaussian 09W (revision B.01) program ,the DFT calculation of the title compound was carried out on Intel Core2Duo/2.20 GHz processor. For the simulated IR and Raman spectra pure Lorentzian band shapes with the band width of 10 cm<sup>-1</sup> was employed using the Gabedit Version  $2.32^{[10]}$ . The animation option of the Gauss view 05 graphical interface for Gaussian program was employed for the proper assignment of the title compound and it was also used to visualize vibrational modes of the title compound and to check whether the mode was pure or mixed<sup>[11-14]</sup>. An empirical uniform scaling factor of 0.98 and 0.97<sup>[15, 16]</sup> were used to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity<sup>[17]</sup>.After scaled with scaling factor, the deviation from the experiments is less than 10cm<sup>-1</sup> with a few exceptions. The mean polarizability properties of tested molecule were obtained from the theoretical calculations to show the NLO property of the molecules. The thermodynamic properties of tested molecules, such as heat capacity, entropy, and enthalpy were investigated for the different terms from the vibrational frequency calculations of title molecule. The energy of highest occupied molecular orbit (E<sub>HOMO</sub>) and the energy of Lowest unoccupied Molecular Orbital (E<sub>LUMO</sub>) the dipole moment  $(\mu)$ , the ionization potential (I), the electron affinity (A), the electro negativity (X), the global hardness  $(\eta)$  were calculated for both the molecules and the comparison also discussed. The electronic absorption spectrum requires calculation of the allowed excitations and oscillator strengths. The theoretical UV-vis spectra have been compared with the experimental spectra for the molecule. These calculations are based on both TD-DFT methods with 6-311++G (d,p) basis set. <sup>1</sup>H NMR chemical shifts are calculated with gauge included atomic orbital (GIAO) approach <sup>[18, 19]</sup> by applying B3LYP/6-



311++G(d,p) method and compared with the experimental NMR spectra of DPA molecule.

# **Results and Discussion**

## Molecular geometry

The geometrical structure along with numbering of atoms of Diphenylacetylene is obtained from Gaussian 03W and GAUSSVIEW programs are shown in Fig.1.

The optimized geometrical parameters of DPA 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 3, it is observed that the various bond lengths are found to be almost same at HF and B3LYP levels. However, the B3LYP/6-31++G (d,p) level of theory, in general slightly over estimates bond lengths but it yields bond angles in excellent agreement with the HF method. The calculated geometric parameters can be used as origin to calculate the other parameters for the compound. The calculated C-C bond lengths of the ring vary from 1.39 to1.42 Å. In this study the C-H bond lengths were studied as 1.08 Å. The density functional calculation gives almost same bond angles in tested molecule. The dihedral angles of our title molecule show that our tested molecule was planar. In generally the optimized

bond length and bond angles are slightly smaller than the experimental values. This is due to the fact that all the theoretical calculations belongs to isolated molecule were done in gaseous state and the experimental results were belongs to molecule is in solid state.



Fig. 1: Optimized molecular structure of Diphenylacetaline.

Parameters	DFT(B3LYP)	HF 6-311++G	Parameters	DFT(B3LYP)	HF 6-
	6-311++G	(d-p)		6-311++G	311++G
	(d-p)			(d-p)	(d-p)
BOND			BOND		
LENGTH			LENGTH		
1C-2C	1.4073	1.3926	8C-9C	1.4233	1.4391
1C-6C	1.4073	1.3928	9C-10C	1.4073	1.3929
1C-7C	1.4233	1.4391	9C-14C	1.4073	1.3924
2C-3C	1.3902	1.3832	10C-11C	1.3902	1.3828
2C-15H	1.0834	1.0744	10С-23Н	1.0833	1.0745
3C-4C	1.3951	1.3858	11C-12C	1.395	1.3862
3C-17H	1.0842	1.0754	11C-21H	1.0842	1.0754
4C-5C	1.395	1.3859	12C-13C	1.3951	1.3855

Table1 (a): Comparison of the geometrical parameter bond lengths (in angstrom) of Diphenylacetaline



4C-19H	1.084	1.0755	12C-20H	1.084	1.0753
5C-6C	1.3902	1.3831	13C-14C	1.3902	1.3835
5C-18H	1.0842	1.0751	13С-22Н	1.0842	1.0752
6C-16H	1.0834	1.0745	14C-24H	1.0833	1.0745
7C-8C	1.2109	1.189			

Table1 (b): Comparison of the geometrical parameter bond angles (in degrees) of Diphenylacetaline.

Parameters	DFT	HF	Parameters	DFT	HF
	(B3LYP)	6-311++G		(B3LYP)	6-311++G
	6-311++G (d_n)	(d-p)		6-311++G (d-n)	(d-p)
Bond Angle	(u-p)		Bond Angle $\begin{pmatrix} 0 \\ \end{pmatrix}$	(u-p)	
			Donu Angle ()		
2C-1C-6C	118.7344	119.2529	10C-9C-14C	118.7338	119.2539
2C-1C-7C	120.638	120.365	9C-10C-11C	120.4424	120.2644
6C-1C-7C	120.6276	120.3822	9С-10С-23Н	119.1666	119.4379
1C-2C-3C	120.4429	120.2644	11С-10С-23Н	120.3909	120.2977
1C-2C-15H	119.166	119.4447	10C-11C-12C	120.3413	120.2164
3С-2С-15Н	120.3911	120.2908	10C-11C-21H	119.6121	119.6891
2C-3C-4C	120.3412	120.2167	12C-11C-21H	120.0466	120.0945
2С-3С-17Н	119.613	119.6818	11C-12C-13C	119.6982	119.7866
4C-3C-17H	120.0459	120.1014	11С-12С-20Н	120.1513	120.1014
3C-4C-5C	119.6988	119.7871	13С-12С-20Н	120.1505	120.1121
3С-4С-19Н	120.1504	120.1078	12C-13C-14C	120.3414	120.2149
5C-4C-19H	120.1508	120.1051	12С-13С-22Н	120.0466	120.1057
4C-5C-6C	120.3413	120.2143	14С-13С-22Н	119.612	119.6793
4C-5C-18H	120.0477	120.1005	9C-14C-13C	120.4429	120.2637
6C-5C-18H	119.611	119.6852	9C-14C-24H	119.1653	119.4488
1C-6C-5C	120.4414	120.2646	13С-14С-24Н	120.3918	120.2874
1C-6C-16H	119.1665	119.4434	1C-7C-8C-6C—1C	179.9991	180.0277
5C-6C-16H	120.3921	120.292	7C-8C-9C-14C-1C	179.9945	179.9884
8C-9C-10C	120.6332	120.3648	1C-7C-8C-6C—2C	180.004	180
8C-9C-14C	120.6331	120.3814	7C-8C-9C-14C—2C	179.9889	180

## Vibrational analysis

The vibrational spectrum is mainly determined by the modes of free molecule observed at higher wavenumbers, together with the lattice (translational and vibrational) modes in the low wavenumber region. In our present study, we have performed a frequency calculation analysis to obtain the spectroscopic signature of Diphenylacetylene. The DPA molecule consists of 24 atoms therefore they have 66 vibrational normal modes. All the frequencies are assigned. The measured (FTIR and FT-Raman) wavenumbers and assigned wavenumbers of the some selected intense vibrational modes



calculated at the B3LYP and HF levels using basis set 6-311++G(d,p) basis set and they are listed in Table 2. For B3LYP and HF with 6-311++G(d,p)basis set, the wavenumbers are scaled with 0.99 and 0.98 respectively<sup>[20]</sup>. This reveals good correspondence between theory and experiment in main spectral features. The experimental and theoretical FTIR and FT-Raman spectra are shown in Figs. 2 and 3.



Fig. 2: Experimental (top) and theoretical (bottom) FTIR spectra of Diphenylacetaline.

The C-C stretching modes of the phenyl group are expected in the range from 1650 to 1200 cm<sup>-1</sup>. The aromatic ring modes are influenced more C-C bands <sup>[21-23]</sup>. Therefore, the C-C stretching vibrations of the title compound are found at 1602,1575, 1456, 1386, 1288, 1243 cm<sup>-1</sup> in FTIR and 1572, 1460, 1382,1290, 1240 cm<sup>-1</sup> in the FT-Raman spectrum and these modes are confirmed by their TED values. The theoretically computed values for C-C vibrational modes by B3LYP/6-31+G(d,p) method gives excellent agreement with experimental data. In the present work the bands occurring at 1007 and 720 cm<sup>-1</sup> in Raman spectrum are assigned to the CCC in-plane trigonal bending and ring breathing vibrations, respectively. These frequencies appear in the respective range <sup>[24-26]</sup>. The C–C–C trigonal bending and ring breathing modes of benzene ring are attributed to the strong bands 923 and 848 cm<sup>-1</sup>. The normal coordinate analysis predicts that the C–C–C in plane bending vibrations significantly mixed with the C–H in-plane bending modes <sup>[27]</sup>. The ring C=C stretching vibrations, known as semicircle stretching usually occur in the region 1400-1625 cm<sup>-1[28, 29]</sup>.



Fig.3: Experimental (top) and theoretical (bottom) FT-Raman spectra of Diphenylacetaline



Table	2:	Comparison	of	the	experimental	and	calculated	vibrational	wavenumbers	and	proposed
assign	mer	ts of Dipheny	lace	etalir	ne						

S.	Experime	ntal	B3LYP/6-3	11++G**			HF/6-311+	+G**			Assignment
no			Calculated		sity	ity an	Calculated		sity	ity it	
			wavenumb	er	IR Inten	Ram Activ	wavenumb	er	IR inten	Ram Activ	
	R	Raman	Unscale d	scaled			unscaled	scaled			
1			26	26	0	0	15	15	0	0	Lattice Vibration +Ring twisting
2			47	47	0.5562	0	51	51	0.6383	0	Lattice Vibration
3		81	51	51 140	1.1608	0	56	56	1.4769	0	Lattice Vibration+ Ring butterfly CCCβ+ring sciesoring
4			140		0	2.3553	158	153	0	2.0831	
5		153	156	153	0	5.5692	177	177	0	4.8243	CCCγ+ring rocking
6			260	260	0	0.2709	272	272	0	0.4487	Ring scissoring
7			286	286	0.1135	0	319	283	0.1647	0	Ring butterfly
8			410	410	0	0.0048	448	420	0	0.0002	Ring breathing
				448							Ring
9			448		0	8.3621	450	422	0.0001	0.0054	breathing
10	465		478	464	1.5379	0	461	461	0	7.374	ССНү
11	507		526	510	16.275	0.00000	510	505	2.2254	0	СССү+ ССН ү
12	534	539	566	538	0	11.3885	576	541	17.6349	0.00000	CCC β
13			577	577	0	20.644	584	549	11.0368	0.00000	ССН β
14			635	635	0.0031	0	646	646	0	24.1964	CCC β+Ring Asym.Deform ation
15			641	641	0	5.6451	648	648	0	32.6691	СССү
16	689	691	701	687	70.733	0.00000	678	678	0.0006	0	ССНβ+СН ОРВ
17			715	694	0.0014	0.0165	695	681	0	0.1708	CCHγ+CH OPB
18	755	755	766	758	0	14.4242	759	751	0	14.255	CCCγ+CH OPB
19			771	771	0.0032	10.5645	762	762	0.9472	1.1252	CCCγ+CH OPB
20			849	849	96.133	0.00040	763	763	74.241	0.01590	CH OPB+CCC bending
21	854		850	850	0	0.0011	848	848	71.551	9.63450	CHy+CCC
22			856	856	0	0.098	849	849	57.96	11.9076	C=C v+ CCC



											bending
											СНОРВ
23	916		927	018	1 2005	0	901	904	1 1552	0.0001	+CCC
23	310		521	310	1.2333	0	304	304	4.1332	0.0001	bending
				930							OPBCCC
24			930		0.0003	0.2487	946	918	0	0.0019	bending
25			980	980	7.0251	0	947	947	0.001	1.04	СН β
26			981	981	0	0.0002					СНү+СН ОРВ
27			995	995	0	0					HCCCT+CH OPB
28	997	996	996	996	0.167	0.0048					CCCβ+ CH OPB
29			1012	1012	0.0004	1.6088					CH β+CH IPB
30	1025	1026	1013	1013	0	439.412					CH y+CH IPB
31			1046	1025	0.0482	0.0193	1038	1027	0.0846	0.5084	CCCβ+CH IPB
32	1069		1048	1048	0.0003	38.7087	1039	1039	8.5217	0.005	CCCβ+CH IPB
											Ring
33							1080	1070	0	259.371	Sym.Deform
34			1099	1066	9.6909	0.001	1081	1081	0.1981	0.041	CC v+CH IPB
35	1101	1080	1101	1078	0.0002	0.012	1101	1101	0.0004	0.0045	CH IPB
36			1114	1103	12.216	0.00000	1114	1113	0.0198	2.6656	CH IPB
37			1115	1115	0	1210.74	1115	1115	0.0825	0.6768	CH IPB
38			1118	1118	0.0044		1119	1118	0.0001	26.9084	RingCH β+CH IPB
39	1156		1159	1148		16.4968	1168	1157	7.5725	0.0003	CH IPB
40		1141	1164	1150	0.0075	10.0018	1169	1146	0.0076	9.9686	CH IPB
41	1178		1182	1159	0.0653	0.001	1199	1175	4.8249	0.0171	CH IPB
42			1202	1202	0.1435	0.0003	1238	1238	6.8645	0.0739	CC v+CH IPB
43	1280		1309	1282	4.8597	0	1285	1285	0.0095	55.7815	CCv+CH Rock
44	1311		1312	1312	0.0003	25.871	1286	1286	0	509.237	CC v+CH IPB
45	1330		1340	1326	0.5422	0.0106	1318	1318	0.8497	0.0014	CC v +CH IPB
46	1386		1352	1352	0.0002	26.2704					CC v+CH IPB
47	1441	1442	1470	1381	8.4232	0.0006					C=C str
48	1492	1482	1472	1442	0	235.754					CC v + C=C
49			1514	1483	46.917	0.00010	1403	1333	0	55.0115	CC v +C=C
50	1532		1533	1533	0.0001	0.4318	1452	1394	0.0186	2.1671	Ring CC v
51	1571		1604	1572	3.2794	0.0007	1454	1440	1.4086	0.0311	CC v +C=C str
52							1587	1492	7.0886	0	C-H β+C=C
53	1598	1592	1605	1582	0.0001	2395.54	1589	1542	0.0001	10.2439	С-Н ү+С=С
54			1633	1600	32.364	0.00140	1641	1575	0.5643	0.0023	C=C v +CH Rock+C=C
55	1673		1643	1643	0	9459.75	1655	1588	0.0052	13.3889	CC v +C=C v

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56	1757						1753	1682	12.589	0.00680	CH v s
57	1827						1754	1754	0.0001	57.5785	CH v s
58	1882						1783	1783	59.603	0.00010	CH v s
59	1951						1790	1790	0.0004	0.8889	СС ү+ СН ү
60		2220	2300	2231	3.6956	9.2921					СН ү
61		2478					2505	2480	0	5374.927	СС ү+ СН ү
62	3019		3164	3006	0.7331	49.7286					CH v
63	3031		3165	3038	0.0016	291.704					CH v s
64	3062		3173	3045	9.972	0.1707					CH v s
65		3064	3184	3056	32.364	0.34160	3319		1.2241	27.7374	CH v s
66	3077		3186	3186	0.0843	308.942	3320		1.471	31.6005	CH v s
67	3191		3191	3095	8.8598	7.5715	3331		2.2464	188.900	CH v s
68	3194		3195	3195	26.803	2.15520	3332		8.5872	51.0382	CH v s
69	3199		3197	3197	16.085	33.7378	3342		27.530	94.0274	CH v s
70	3346						3343		21.845	110.805	CH v <sub>as</sub>
71	3354						3352		7.4363	2.4271	CH v as
72	3356						3354		36.188	0.63240	CH v as
73	3358						3356		9.2253	181.102	CH v as
74	3359						3357		5.1797	363.177	CH v as

Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 cm<sup>-</sup> <sup>1</sup> due to aromatic C-H stretching vibrations<sup>[30]</sup>. The bands due to the C-H in-plane deformation vibrations, which usually occurs in the region 1390–990 cm<sup>-1</sup> are very useful for characterization and are very strong indeed<sup>[31]</sup>. When there is inplane interaction above 1200 cm<sup>-1</sup>, a carbon and its hydrogen usually move in opposite direction <sup>[32]</sup>. All the C-H stretching vibrations are very weak in intensity. The bands due to C-H in-plane bending vibrations are observed in the region 1000–1300 cm<sup>-1[33]</sup>. The C-H out-of-plane bending or wagging vibrations are appeared within the region 980-717 cm<sup>-1</sup> in naphthalene <sup>[34]</sup>.After scaling procedure, the theoretical C-H vibrations are in good agreement with the experimental values and literature <sup>[35]</sup>. The assignments for the tested molecule are listed in table 2 which shows analogous with the data from the above literature survey.

## Frontier molecular orbital analysis

The highest occupied molecular orbital (HOMO) and the lowest-lying unoccupied molecular orbital (LUMO) are named as frontier molecular orbitals (FMO). The FMO play an important role in the optical and electric properties, as well as in quantum chemistry and UV-Vis. spectrum <sup>[41]</sup>. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to the LUMO <sup>[36, 37]</sup>. Chemical hardness (g) and softness (s) can be used as harmonizing tools to describe the thermodynamic aspects of chemical reactivity. The Frontier orbital gap helps to characterize the chemical reactivity kinetic stability, chemical reactivity, optical polarizability, chemical hardness, softness of a molecule <sup>[38]</sup>. The



calculated HOMO and LUMO energy and the energy values of the frontier orbitals by B3LYP/6-311++G (d,p) are presented in Table 3. The ionization potential (I.P) values suggest how tightly an electron is bound within the nuclear attractive field of the systems. It is linearly related with the chemical hardness (g). By using HOMO and LUMO energy values for a molecule, the Ionization potential and chemical hardness of the molecule were calculated using Koopmans' theorem<sup>[39]</sup> and are given by  $\eta = (I_P - E_A)/2$  where  $I_P \sim E(HOMO)$ ,  $E_A \sim E(LUMO)$ ,  $I_P$  = Ionization potential (eV),  $E_A$  = electron affinity (eV)

## $\eta = \frac{1}{2} (\epsilon_{LUMO} - \epsilon_{HOMO}).$

The hardness has been associated with the stability of chemical system. Considering the chemical hardness, large HOMO-LUMO gap means a hard molecule and small HOMO-LUMO gap means a soft molecule. One can also relate the stability of molecule to hardness, which means that the molecule with least HOMO-LUMO gap means, it is more reactive. The hard molecules are not more polarizable than soft ones because they need big energy to excitation 3D plots of the HOMO, LUMO, orbitals computed at the B3LYP/6-311++G (d,p) level for the tested molecule are illustrated in Fig 4.The electron affinity can be used in combination with ionization energy to give electronic chemical potential,  $\mu = \frac{1}{2}$  ( $\varepsilon_{LUMO} + \varepsilon_{HOMO}$ ). Chemical  $softness(S) = 1/\eta$  describes the capacity of an atom or group of atoms to receive electrons and is the inverse of the global hardness <sup>[40]</sup>. The soft molecules are more polarizable than the hard ones because they need small energy to excitation. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule <sup>[41]</sup>. A hard molecule has a large energy gap and a soft molecule has a

small energy gap <sup>[42]</sup>. It is shown from the calculations that Diphenylacetylene has the least value of global hardness (0.063305eV) and the highest value of global softness (15.796540 eV) is expected to have the highest inhibition efficiency. The global electrophilicity index,  $\omega = \mu^{2}/2 \eta$  is also calculated and these values are listed in Table 3.

## NLO properties

Nonlinear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields <sup>[43]</sup>. The first hyperpolarizability  $(\beta_0)$  of this novel molecular system and related properties ( $\beta_{tot}$ ,  $\alpha$ ,  $\Delta \alpha$ ) of Diphenylacetylene are calculated using DFT/B3LYP method at 6-311G++ (d,p) basis set based on the finite field approach. NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical inter connections<sup>[44-46]</sup>.

In the presence of an applied electric field, the energy of a system is a function of the electric field. First order hyperpolarizability is a third rank tensor that can be described by  $3 \times 3 \times 3$  matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry <sup>[37]</sup>. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3 x 3 x 3 matrices is a tetrahedral. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field.



Figure 4: Atomic orbital composition of the frontier molecule for Diphenylacetaline.



Where  $E^0$  is the energy of the unperturbed molecules,  $F_{\alpha}$  is the field at the origin,  $\mu_{\alpha}$ ,  $\alpha_{\alpha}\beta$  and  $\beta_{\alpha\beta\gamma}$  are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively. DFT has been extensively used as an effective method to investigate the organic NLO materials<sup>[47-51]</sup>. The total static dipole moment ( $\mu$ ), the mean polarizability ( $\alpha_0$ ), the anisotropy of the polarizability ( $\Delta\alpha$ ) and the mean first order hyperpolarizability ( $\beta_0$ ), using the x, y, z components they are defined as:

$$\begin{aligned} \alpha_{\text{total}} &= \alpha_0 = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\ \Delta \alpha &= [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \alpha^2_{xz} + 6 \alpha^2_{yz}]^{1/2} \\ \beta_0 &= (\beta_x^2 + \beta_x^2 + \beta_x^2)^{1/2} \\ &= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2} \\ \Delta \alpha &= [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2/2]^{1/2} \end{aligned}$$

Polarizability is the property of a species and it is minimum for most stable species and is maximum for least stable species like transition state. The  $\alpha$  and  $\beta$  values of the Gaussian 05 output are in atomic units (a.u) and these calculated values converted into electrostatic unit (e.s.u) ( $\alpha$ : 1 a.u = 0.1482×10<sup>-24</sup>esu; for  $\beta$ : 1 a.u =8.639×10<sup>-33</sup> esu;) and these above polarizability values of Diphenylacetylene are listed in Table 4. The total dipole moment can be calculated using the following equation.  $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$ 

	0
Molecular properties	B3LYP/6-311++G(d,p)
$E_{LUMO+1}$ (eV)	-0.17641
E <sub>LUMO</sub> (eV)	-0.21409
E <sub>HOMO</sub> (eV)	-0.34070
E <sub>HOMO-1</sub> (eV)	-0.3738
$\Delta E_{\text{HOMO-LUMO}}$ (eV)	0.12661
$\Delta E_{\text{HOMO-LUMO+1}}(\text{eV})$	0.16429
$\Delta E_{\text{HOMO-1 - LUMO}}(\text{eV})$	0.15971
$\Delta E_{\text{HOMO-1}-\text{LUMO+1}}(\text{eV})$	0.19739
Global hardness(η)	0.063305
Chemical softness(S)	15.796540
Electronic chemical potential(µ)	0.277395
Global electrophilicity index(ω)	0.607755991

Table 3: Calculated energy values of Diphenylacetaline in its ground state.

To study the NLO properties of molecule the value of urea molecule which is prototypical molecule is used as threshold value for the purpose of comparison. The total molecular dipole moment of Diphenylacetaline from DFT–B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) basis sets are 9.2096 and 4.4375 Debye which are greater than that of urea and the first order hyperpolarizability DFT and HF with the same basis sets are 0.0118 and 0.0627 are lesser than that of urea ( $\mu$  and  $\beta$  of urea are 1.3732 Debye and 0.3728 x10-30 cm5/esu obtained by HF/6-311G(d,p) method[52]. These results indicate that the title compound is a good candidate of NLO material. The calculated dipole moment and hyperpolarizability values obtained from B3LYP/6-311G (d,p) and HF/6-31++G (d,p) methods are collected in Table 4. These results indicate that the title compound is a good candidate of NLO material. The theoretical calculation of  $\beta$  components is very useful as this clearly indicates the direction of charge delocalization. In  $\beta$ xyz direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The maximum  $\beta$  value may be due to  $\pi$  electron cloud movement from donor to acceptor which makes the molecule highly polarized and the intra molecular charge transfer possible.

Table 4: The electric dipole moment, polarizability and first order hyperpolarizability of

Diphenyl acetaline.

	· ·	
Parameters (a.u)	DFT B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)
α <sub>xx</sub>	324.649023	147.763424
α <sub>xy</sub>	-0.00187608745	0.160182117
α <sub>yy</sub>	155.525453	266.581938
α <sub>xz</sub>	-0.000938377337	0.0221625953×10 <sup>-30</sup>
α <sub>yz</sub>	-0.000004235011055	-2.42340920×10- <sup>30</sup>
0. <sub>ZZ</sub>	84.3612923	83.9905152
α <sub>0</sub>	188.178	166.1119591
Δα	213.7817967	160.5061538

β <sub>xxx</sub>	0.00329884618	-0.0929418325
β <sub>xxy</sub>	0.0207528357	-0.00306912782
β <sub>xyy</sub>	0.00318870607	0.0380264257
β <sub>yyy</sub>	-0.0145490038	0.0505090201
β <sub>xxz</sub>	0.00443534185	-9.02248532×10 <sup>-29</sup>
β <sub>xyz</sub>	0.0723902843	1.76186305×10 <sup>-28</sup>
β <sub>yyz</sub>	0.00146952131	4.24573960×10 <sup>-29</sup>
β <sub>xzz</sub>	-0.00397387105	0.00221151415
β <sub>yzz</sub>	0.00461365515	-0.0134852216
β <sub>zzz</sub>	0.00265002629	1.22531942×10 <sup>-28</sup>
β <sub>0</sub>	0.011763718	0.062694655
μχ	-0.0000237661383	0.000122452807
μy	0.0000867565483	-0.0000426523936
μz	0.0000197539515	0.00306710389 ×10 <sup>-30</sup>
μ total (Debye)	9.209639842×10 <sup>-5</sup>	4.43753713×10 <sup>-5</sup> 1

## Mulliken charge analysis:

The charge distribution on a molecule has a significant influence on the vibrational spectra. The atomic charge in molecules is fundamental to chemistry. For instance, atomic charge has been used to describe the processes of electronegativity equalization and charge transfer in chemical reactions  $[^{53,54}]$ Mulliken net charges calculated at the HF and DFT level with the 6-311++G(d,p) atomic basis set in gas phase using Gaussian 09.The results are given in Table 5. The magnitudes of the carbon atomic charges, found to be either positive or negative, were noted to change from -1.092 to 1.236. All the hydrogen atoms have positive charges.

S.NO	ATOMS	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)
1	1 C	0.666426	0.758363
2	2 C	-1.09158	-1.31522
3	3 C	0.081044	0.142072
4	4 C	-0.61569	-0.77597
5	5 C	0.08105	0.141518
6	6 C	-1.0921	-1.31119
7	7 C	1.23643	1.464231
8	8 C	1.23647	1.464321
9	9 C	0.666385	0.758289
10	10 C	-1.09164	-1.31342
11	11 C	0.081001	0.141999
12	12 C	-0.61569	-0.77625
13	13 C	0.081057	0.142071

Table 5: Mulliken atomic charges of Diphenylacetaline calculated by DFT/B3LYP/6-311++G(d,p).



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14	14 C	-1.09204	-1.31318
15	15 H	0.10876	0.136967
16	16 H	0.108731	0.137172
17	17 H	0.178957	0.215896
18	18 H	0.178969	0.215743
19	19 H	0.159026	0.190463
20	20 H	0.159034	0.190372
21	21 H	0.178958	0.215873
22	22 H	0.17897	0.21578
23	23 H	0.108747	0.137008
24	24 H	0.108717	0.137099

## Thermodynamic properties:

The values of some thermodynamic parameters (such as zeropoint vibrational energy, specific heat capacity, rotational constants, entropy and dipole moment) of title molecule by B3LYP/6-311G (d,p) and HF/6-31++G (d,p) methods in ground state are listed in Table 6. On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity (C), enthalpy changes (H) and entropy (S) for the title molecule were obtained from the theoretical harmonic frequencies and listed in Table 6. All the thermodynamic data supply helpful information for the further study on the Diphenylacetylene. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics.

Table 6 : The calculated thermodynamic parameters of Diphenylacetaline employing B3LYP/ 6-

311++G(d,p) methods

Parameters	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)
	500579.4 (Joules/Mol)	534635.2 (Joules/Mol)
Zero point energy	119.64134 (Kcal/Mol)	127.78088 (Kcal/Mol)
Rotational temperature (Kelvin)		
	0.13672	0.13867
	0.01195	0.01203
	0.01099	0.01107
Rotational constants (GHZ)		
	2.84875	2.88935
	0.24891	0.25067
	0.22891	0.23066
Entropy (Cal/Mol-Kelvin)		
Total	107.629	105.595
Translational	41.438	41.438
Rotational	31.960	31.932
Vibrational	34.231	32.226
Thermal Energy (KCal/Mol)		



Total	126.589	134.247
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	124.811	132.469
Molar capacity at constant volume		
(Cal/Mol-Kelvin)		
Total	43.471	39.836
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	37.509	33.874

### UV-Visible studies and electronic properties:

Ultraviolet spectral analyses of Diphenylacetylene have been investigated 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 Diphenylacetylene. The electronic absorption spectrum of the title compound was recorded within the 200–400 nm range and representative spectra are shown in Fig. 6.

Table 7:	Theoretical	and expe	rimental	electronic	absorption	n spectra v	alues of L	Jiphenyl	lacetaline.

Experimenta	1	STATES Calculated by B3LYP/6-311++G(d		11++G(d,p)	
$\lambda$ (nm)	Absorbance		$\lambda$ (nm)	E (eV)	(f)
377.20	0.003	46 -> 48	378.33	3.2772	0.0000
320.60	0.006	47 -> 49	338.88	3.6586	0.0007
315.00	0.007	47 -> 50	332.62	3.7275	0.0000

From the table, the calculated absorption maxima values have been found to be 377,320 and 315 nm at TD-DFT/B3LYP/6-311++G(d,p) method. These values may be slightly shifted by solvent effects. The broad absorption bands associated to a strong  $\pi \rightarrow \pi^*$  and a weak  $\sigma \rightarrow \sigma^*$  transition characterize the UV–Vis absorption spectra. Natural bond orbital analysis indicates that molecular orbitals are mainly composed of  $\sigma$  and  $\pi$  atomic orbitals. The absorption bands at the longer wave lengths 377and 320 nm of Diphenylacetylene are caused by the  $n \rightarrow \pi^*$  transition. The absorption band at 315 nm is caused by  $\pi \rightarrow \pi^*$  transition. The  $\lambda_{max}$  is a function of substitution, the stronger the donor character substitution, the more electrons pushed into the molecules, the larger  $\lambda_{max}$ . These values may be slightly shifted by solvent effects. The role of substituents and solvent influences the UV-spectrum <sup>[55]</sup>. The theoretical electronic excitation energies, oscillator strengths and wavelength of the excitations were calculated and listed in Table 7.

### NMR studies

NMR spectroscopy is currently used to study the structure of organic molecules. The combined use of experimental and computer simulation methods offer a powerful way to interpret and predict the

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structure of large molecules. The optimized structure of Diphenylacetylene is used to calculate the NMR spectra at the DFT (B3LYP) method with 6-311++G(d,p) level using the GIAO(Gauge-Including Atomic Orbital) method. The NMR spectra calculations were performed by using the Gaussian03 program package. The theoretical <sup>1</sup>H NMR chemical shifts of Diphenylacetylene have been compared with the experimental data and listed in Table 8.



Fig.5: Experimental (top) and theoretical (bottom) UV spectra of Diphenylacetaline.



Fig. 6: Experimental (top) and theoretical (bottom) <sup>1</sup>H NMR spectrum of Diphenylacetaline.

Chemical shifts are reported in ppm relative to TMS for <sup>1</sup>H NMR spectrum. The <sup>1</sup>H atom is mostly localized on periphery of the molecules and their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solutions as compared to that for other heavier atoms. The calculated and experimental chemical shift values are given in Table 8 shows a good agreement between the experimental and theoretical approaches. The theoretical and experimental <sup>1</sup>H and NMR spectra are shown in Figure 6.

S.NO	ATOMS	Experimental NMR Chemical	Calculated chemical shift by	
		shift)	B3LYP method	
1	15 H	7.652	7.66427	
2	16 H	7.668	7.66427	
3	17 H	7.646	7.3875	
4	18 H	7.004	7.3875	
5	19 H	6.498	7.3875	
6	20 H	6.476	7.3875	
7	21 H	6.498	7.3875	
8	22 H	6.498	7.3875	
9	23 H	7.673	7.66427	
10	24 H	8.307	7.66427	

Table 8: The observed (in CDCl3) and predicted 1H and 13C NMR isotropic chemical shifts(with respect to TMS, all values in ppm) for Diphenylacetaline.

### Conclusions

The FTIR, FT-Raman, <sup>1</sup>H NMR spectra, UV-Vis spectral measurements have been made for the Diphenylacetylene molecule. The complete vibrational analysis and first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis and thermodynamic properties of the title compound was performed on the basis of DFT and HF calculations at the 6-311++G(d,p)basis set. The consistency between the calculated and experimental FTIR and FT-Raman data indicates that the B3LYP and HF methods can generate reliable geometry and related properties of the title compound. The difference between the observed and scaled wave number values of most of the fundamentals is very small. The theoretically constructed FTIR and FT-Raman spectra exactly coincide with experimentally observed counterparts. The Mulliken atomic charges and the natural atomic charges obtained are tabulated that gives a proper understanding of the atomic theory. The calculated dipole moment and first order hyperpolarizability results indicate that the title compound is a good candidate of NLO material. The calculated normal-mode vibrational frequencies provide thermodynamic properties by the way of statistical mechanics. The <sup>1</sup>H NMR chemical shift was calculated and compared with experimental one. The UV spectrum was measured experimentally and compared with the theoretical values by using TD-DFT/ 6-311++G(d,p) basis set. The energies of important MOs and the  $\lambda_{max}$  of the compounds were also evaluated from TD-DFT method

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