TEST Engineering & Management

November /December 2020
ISSN: 0193-4120 Page No. 321-336

Investigation on Structural, Spectroscopic, DFT and Biological Activity of 4, 5 – Dimethyl-O-Phenylene Diamine

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Article Info
Volume 83
Page Number: 321 - 336
Publication Issue:
November /December 2020

Article History
Article Received :*25 October 2020*
Revised: *22 November 2020*
Accepted: *10 December 2020*
Publication: *31 December 2020*

Abstract

The structure of 4,5-dimethyl-o-phenylene diamine (DMPDA) was investigated on the basis of spectroscopic data and theoretical calculations, The spectroscopic data and theoretical calculations. The structure was determined by FT-IR, FT-Raman, ^{1}H and ^{13}NMR spectra.An experimental study and a theoretical analysis were associated by using the B3LYP method with Gaussian 09 package program.FT-IR and FT-Raman spectra were recorded in the region of 4000cm^{-1}-400 cm^{-1} and 4000 cm^{-1} - 100cm^{-1} respectively. The vibrational spectra were calculated by DFT method and the Total Energy Distribution (TED).The chemical reactivity and hardness of the molecule in terms of HOMO-LUMO energy gap have been implemented to reactivity parameters. Moreover, the molecular docking witha predictedtarget has been performed to check the binding interactionsas well as sites of the molecule.

INTRODUCTION

Amine derivatives are molecule that are found in the body of any living organism at Milli molar concentrations, and are produced by decarboxylation of amino acids. Phenyl amine and its derivatives, which have been used in commercial purposes and industrial,

including pesticide, pharmaceuticals manufacturing and chemical dye industries have been studied extensively[1-3].Some of Para-substituted derivatives of aniline are commonly used local anesthetics and among these molecules the amino group plays an important role in the interaction with the receptor. The inclusion of a substituent group in aniline also leads to the variation of charge distribution in the molecule, and the therefore this greatly affects the structural, electronic and vibrational parameters.

Phenyl amine is the starting material in the dye manufacturing industry and important in the manufacture of rubber processing chemicals, explosives, plastics, antioxidants and varnishes, organic di amines are now widely used as a hole transport materials in applications ranging from the Xerox process to multi layer organic light emitting diode [4].Extensive experimental and theoretical investigation have focused on elucidating the structure and normal vibrations of aniline and its methyl derivatives.The methyl and amine groups are generally referred as electron donating substituent's in aromatic ring systems. The substituted amine derivatives with high optical non-linearly are very promising materials for future optoelectronics and non-linear optical applications. Many spectroscopic studies with regard to aniline and its derivations have been reported.

In the present investigation, an experimental and theoretical analysis of DMPDA has been carried out by recording FT-IR and FT-RAMAN spectra which are subjected to normal coordinate analysis, for the assignment of the vibrational fundamentals. To understand the substitution effect of methyl and amine to provide the complete informationabout the molecular dynamics.

EXPERIMENTAL METHODS

The compound 4,5-dimethyl-O-phenylenediamine(DMPDA) was purchased from Lancaster chemical company, UK.Thesampletakenas such foranalysis to obtain FT-IRand FT-Ramanspectra at roomtemperature. In the analysis, BRUKER IFS-66V instrument was employed to originating FT-IR spectrum. In which,Globar Arc source isused to generate the Mid IRradiation and get processed throughKBr beamsplitter to induce the analyze. The resulted absorption band is processed by the MCT detector and delivered the digitalized output spectrum within region of 4000–400cm^{-1}at a resolution of ±1cm^{-1}. The FT-Raman analysis carried out on the same BRUKER IFS-66V model interferometer by engaging additional FRA-106 FT-Raman accessory.

The laser sourceNd:YAG laser with 1064 nm line is used to irradiate the analyte. The spectrum was obtained in the 4000–50 cm^{-1} stokes region by using the excitation operation at 200Mw power with the accuracy of ±1 cm^{-1} of wave number.

METHODS OF COMPUTATION

The theoretical values of the various properties of the 4,5-dimethyl-O-phenylenediamine(DMPDA) has been computed using GAUSSIAN-09W software package for the comparison with the experimental values. The properties like molecular geometry optimizations, energy and vibrational frequency calculations are derived for theanalyte on the theories of B3LYP functions [5] combined with the standard6-311+G (d, p) and6-311++G (d, p) basis sets. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming it as having C_1point group symmetry. The vibrational assignments for the title compound, referring the symmetry group of molecule, made precisely using the in-built feature of Gaussian program software[6]. The comparison of DFT theory results with the experimental results reveals that the computation using B3LYP functional is the most promising one in providing exact vibrational wavenumbers.The molecules were explored through molecular docking using Auto Dock Vina software.

RESULTS AND DISCUSSION

Molecular geometry

The optimized geometry by B3LYP with 6-311+G (d,p)and 6-311++G(d, p) of the DMPDA with atom numbering is shown in Fig .1. The values of the optimized bond lengths and bond angles of title compound are in Table .1. The obtained stable configuration of the molecule obtained from the conformer analysis which has been used for the structural analysis is shown in Fig.1.The calculated bond length, bond angle, and dihedral angle were obtained using B3LYP methods with 6-311++G (d, p) basis sets in Table .1. The CC bond lengths of the aromatic ring are expected to be 1.39Å by, but in the phenyl ring, C3-C4 is much lengthened by 1.54 Å because of the attachment of methyl functional groups with C3 and C4 respectively. Similarly, C5-C6 is also lengthened by 1.54 Å due to the attachment of the nitro group [7]. But C1-C2 & C4-C5 are affected anyway by the attachment of the nitro group. The structure of the phenyl ring is much distorted by the substitution of the nitro,

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methyl functional groups. In the case of the CN bond lengths, C4-N17 &C5-N20 are found to be 1.47 & 1.47 Å, here bond lengths with a nitro group are shortened and lengthened with a methyl group. This shortening and lengthening of the bond lengths affected the bond length in the phenyl ring. The bond lengths of CH, NH are observed in the literature.

In the case of the bond angles, where nitro and methyl group attached, are 118^o - 122^o respectively, it is observed that angles are lies from the expected range 120^o[8]. It signifies that the structure of the phenyl rings is distorted due to the attachment of the methyl and nitro group, but no disturbance is found either in bond length or bond angle due to the nitro group.

Table 1

Optimized geometrical structural parameter of 4,5-dimethyl-O-phynelenediamine obtained by density functional calculations.

Bond Length (Å)	B3LYP/ 6-311+G (d,p)	B3LYP/ 6-311+G (d,p)
C1-C2	1.29	1.32
C2-C3	1.35	1.39
C2-C13	1.54	1.51
C3-C4	1.54	1.39
C3-H7	1.07	1.08
C4-C5	1.35	1.41
C4-N17	1.47	1.39
C5-C6	1.54	1.39
C5-N20	1.47	1.42
C6-H8	1.07	1.08
C9-H10	1.07	1.09
C9-H11	1.07	1.09
C9-H12	1.07	1.09
C13-H14	1.07	1.09
C13-H15	1.07	1.09
C13-H16	1.07	1.09
N17-H18	1.01	1.04
N17-H19	1.02	1.03
N20-H21	1.01	1.03

N20-H22	1.01	1.01

Bond Angle	B3LYP/ 6-311+G (d,p)	B3LYP/ 6-311+G (d,p)
C2-C1-C6	122.7	118.3
C2-C1-C9	118.9	121.3
C6-C1-C9	122.2	120.2
C1-C2-C3	118.9	118.9
C1-C2-C13	119.9	121.1
C3-C2-C13	117.5	119.9
C2-C3-C4	117.6	122.5
C2-C3-H7	120.1	119.1
C4-C3-H7	120.2	118.3
C3-C4-C5	122.2	118.4
C3-C4-N17	120.4	120.8
C5-C4-N17	120.5	120.6
C4-C5-C6	120.7	118.8
C4-C5-N20	120.4	118.8
C6-C5-N20	121.6	122.2
C1-C6-C5	120.3	122.7
C1-C6-H8	119.4	118.9
C5-C6-H8	119.1	118.3
C1-C9-H10	110.4	111.8
C1-C9-H11	110.4	111.8
C1-C9-H12	109.4	110.9
H10-C9-H11	107.4	106.7
H10-C9-H12	109.4	107.6
H11-C9-H12	109.4	107.5
C2-C13-H14	109.4	111.7
C2-C13-H15	109.4	111.7
C2-C13-H16	109.4	111.7
H14-C13-H15	109.4	106.7
H14-C13-H16	109.4	107.6
H15-C13-H16	109.4	107.6
C4-N17-H18	109.4	117.4
C4-N17-H19	109.4	117.1
H18-N17-H19	109.4	114.6
C5-N20-H21	109.4	112.7
C5-N20-H22	109.4	112.1

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H21-N20-H22	109.4	108.4

Dihedral angle	**B3LYP/ 6-311+G (d,p)**	**B3LYP/ 6-311+G (d,p)**
C6-C1-C2-C3	0	1.6
C6-C2-C2-C13	180	-179.16
C9-C1-C2-C3	180	-179.147
C9-C1-C2-C13	0	0.0843
C2-C1-C6-C5	0.0001	-0.9047
C2-C1-C6-H8	-180	178.226
C9-C1-C6-C5	-180	179.8427
C9-C1-C6-H8	0.0001	-1.0266
C2-C1-C9-H10	-30	-58.7475
C2-C1-C9-H11	90	60.9532
C2-C1-C9-C12	-150	-178.975
C6-C1-C9-H10	150	120.4821
C6-C1-C9-H11	-90	-119.817
C6-C1-C9-H12	30	0.2543
C1-C2-C3-C4	0	-0.3995
C1-C2-C3-H7	180	177.7087
C13-C2-C3-C4	180	-179.64
C13-C2-C3-H7	0	-1.5318
C1-C2-C13-H14	-30	-58.8274
C1-C2-C13-H15	90	60.683
C1-C2-C13-H16	-150	-179.086
C3-C2-C13-H14	150	120.397
C3-C2-C13-H15	-90	-120.093
C3-C2-C13-H16	30	0.138
C2-C3-C4-C5	0	-1.5506
C2-C3-C4-N17	180	175.6611
H7-C3-C4-C5	-180	-179.673
H7-C3-C4-N17	0	-2.4615
C3-C4-C5-C6	0.0001	2.2297
C3-C4-C5-N20	-180	179.7966
H17-C4-C5-C6	-180	-174.989
H17-C4-C5-N20	0.0001	2.5777
C3-C4-N17-H18	90	34.7644
C3-C4-N17-H19	-150	177.2085
C5-C4-N17-H18	-90	-148.085
C5-C4-N17-H19	30	-5.6408
C4-C5-C6-C1	-0.0001	-1.0469
C4-C5-C6-H8	179.9	179.8171
N20-C5-C6-C1	179.9	-178.528
N20-C5-C6-H8	-0.0001	2.3356

C4-C5-N20-H21	90	62.8063
C4-C5-N20-H22	-150	-174.415
C6-C5-N20-H21	-90	-119.712
C6-C5-N20-H22	30	3.0667

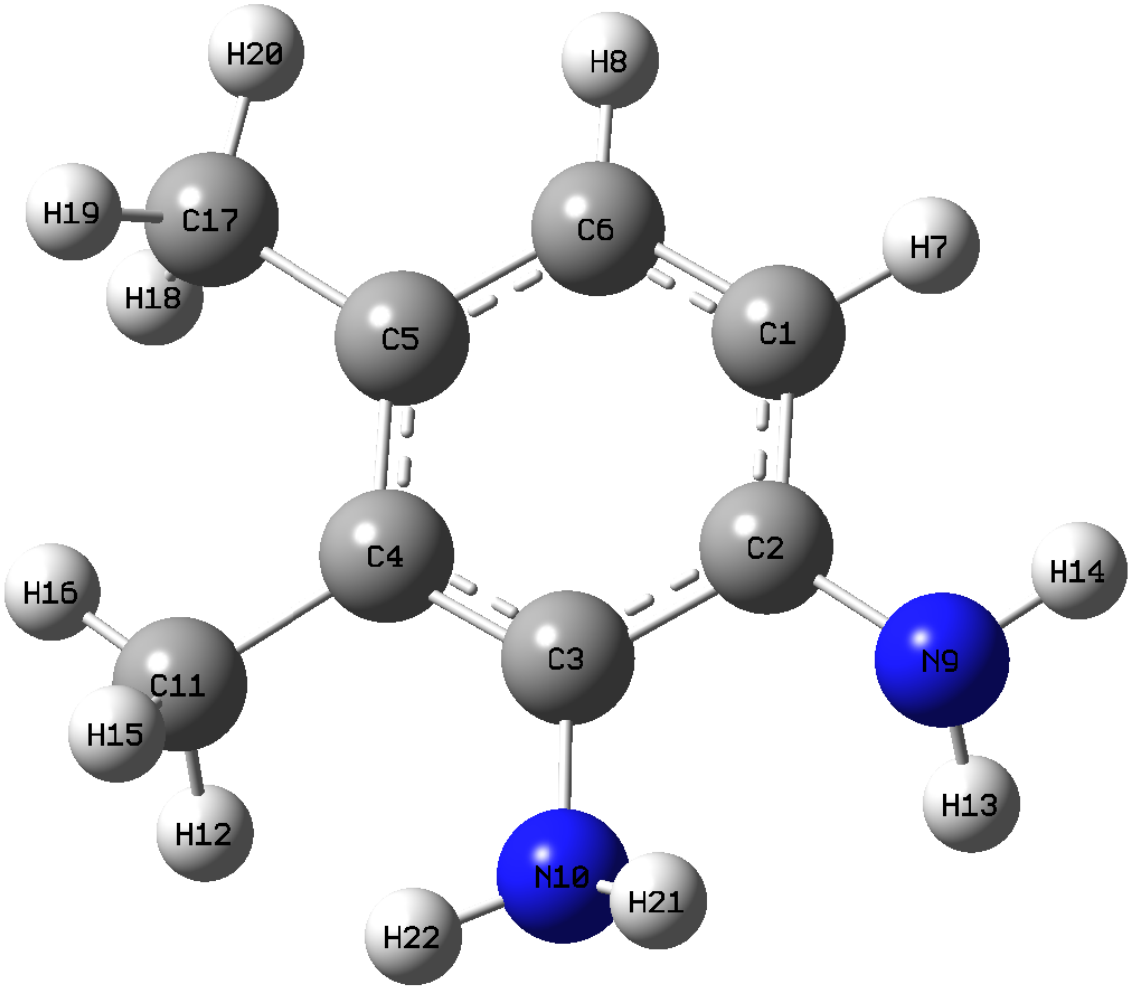

Fig. 1 : Optimized molecular structure of DMPDA

ASSIGNMENTS OF VIBRATIONAL SPECTRA

The observed vibrational assignments and analysis of DMPDA are discussed in terms of fundamental bands and combination IR bands. The FT-IR spectrum ofDMPDA molecule is shown in Fig. 2 and FT-Raman is shown in Fig.3. The observed and calculated frequencies using B3LYP/6-311++G (d, p) methods along with their probable assignments for DMPDA

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are given in Table 2.The calculated vibrational spectra using different methods and basis sets were calculated vibrational frequencies are in good agreement with experimental details.

Table2

Experimental and theoretical B3LYP with 6-311++G(d,p) and 6-311G+ (d, p) FT-IR and FT-Raman frequency of 4,5-dimethyl-O-phenylenediamine

Sl. No	Symmetry	Experimental frequency(cm^{-1})		Theoretical frequency(cm^{-1})				Assignment with TED
				B3LYP with 6-311++G(d, p)		B3LYP with 6-311+G(d, p)		
		FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled	
1.	A	-	3680	3703	3675	3712	3674	NH_2 asy(92)
2.	A	-	3550	3599	3545	3566	3544	NH_2 asy(92)
3.	A	-	3480	3595	3548	3580	3545	NH_2 symd(98)
4.	A	3360	-	3492	3446	3485	3485	NH_2 symd(99)
5.	A	-	3201	3146	3105	3140	3095	ν CH(99)
6.	A	-	3100	3138	3097	3135	3085	ν CH(98)
7.	A	-	3041	3097	3056	3075	3050	CH_3 ss(92)
8.	A	3010	3003	3093	3052	3025	3023	CH_3 ss(92)
9.	A	2985	-	3055	3015	3043	3014	CH_3 ips(94)
10.	A	-	2972	3050	3010	3025	2998	CH_3 ops(94)
11.	A	2927	-	3013	2973	2990	2970	CH_3 ops(90)
12.	A	-	2917	3010	2970	3005	2965	CH_3 ops(90)
13.	A	-	1642	1671	1649	1665	1630	ν CC(89)
14.	A	1624	-	1649	1627	1630	1624	ν CC(87)
15.	A	-	1617	1636	1614	1634	1615	ν CC(89)
16.	A	1592	-	1610	1589	1624	1585	ν CC(89)
17.	A	-	1580	1544	1523	1540	1520	ν CC(87)
18.	A	-	1550	1501	1481	1497	1487	ν CC(89)
19.	A	1516	-	1498	1478	1495	1476	ν CC(89)
20.	A	1459	-	1493	1473	1478	1470	ν CC(87)
21.	A	-	1445	1479	1459	1435	1424	ν NH_2sciss(86)
22.	A	-	1420	1447	1428	1425	1423	ν NH_2sciss(86)
23.	A	1383	1378	1423	1404	1420	1400	ν CN(81)
24.	A	1330	1329	1411	1392	1409	1387	ν CN(81)
25.	A	1297	1300	1348	1330	1345	1329	CH_3 ips(83)
26.	A	1237	-	1332	1314	1330	1310	CH_3 ips(83)
27.	A	1200	1204	1310	1292	1295	1290	CH_3 sb(84)
28.	A	-	1190	1254	1237	1245	1230	CH_3sb(84)
29.	A	-	1170	1219	1203	1210	1119	b CH(73)

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30.	A	-	1168	1134	1119	1130	1115	b CH(74)
31.	A	1157	-	1114	1099	1113	1097	NH_2rocking(78)
32.	A	1090	-	1092	1077	1087	1075	NH_2rocking(78)
33.	A	-	1050	1064	1050	1045	1047	R trigd 72
34.	A	1019	-	1041	1027	1024	1023	CH_3 opb(83)
35.	A	998	-	1018	1004	1016	986	CH_3 opb(83)
36.	A	-	960	1016	1002	1010	990	R symd(71)
37	A	-	908	877	865	870	860	R asymd(70)
38	A	869	-	868	856	855	850	b CC (70)
39	A	-	855	841	830	834	830	b CC (71)
40	A	845	-	791	780	787	775	ωNH_2wagging(72)
41	A	-	802	753	743	745	740	ωNH_2wagging(78)
42	A	-	760	724	714	725	710	bCN(58)
43	A	733	735	686	677	675	665	CH_3 ipr(75)
44	A	686	-	625	616	620	615	CH_3 ipr(75)
45	A	-	660	559	551	550	545	b CN(58)
46	A	-	642	516	509	510	505	CH_3opr(70)
47	A	-	620	461	455	460	448	CH_3opr(70)
48	A	-	549	439	433	434	423	ωCH(60)
49	A	508	512	413	407	410	398	ωCH(60)
50	A	452	-	369	364	367	360	R trigd (72)
51	A	-	440	308	303	309	304	R symd (72)
52	A	-	410	304	300	309	305	R asmyd (71)
53	A	-	375	289	285	280	287	ωCC(60)
54	A	-	305	271	267	275	260	ωCC(60)
55	A	-	285	259	255	257	259	ωCN(55)
56	A	-	205	186	183	180	185	ωCN(54)
57	A	-	187	173	170	176	167	NH_2twisting(53)
58	A	-	111	144	142	145	146	NH_2twising(53)
59	A	-	78	127	125	124	134	tCH_3(59)
60	A	-	54	116	114	113	110	t$CH_3$59)

Abbreviations: Abbreviation: ν- stretching; b - bending; symd – symmetric deformation; asymd - asymmetric deformation; trigd- trigonal deformation; δ-out of plane bending; t– torsion; twist-twisting.

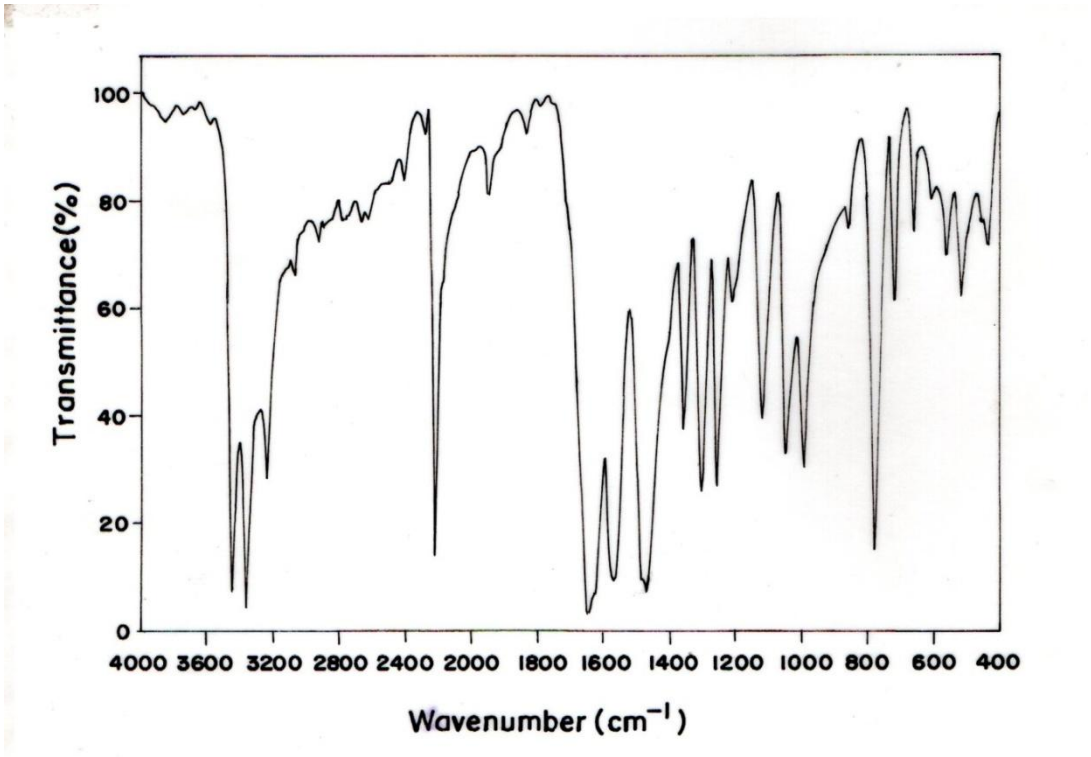

Fig. 2 FTIR spectrum of 4,5-dimethyl-O-phenylenediamine

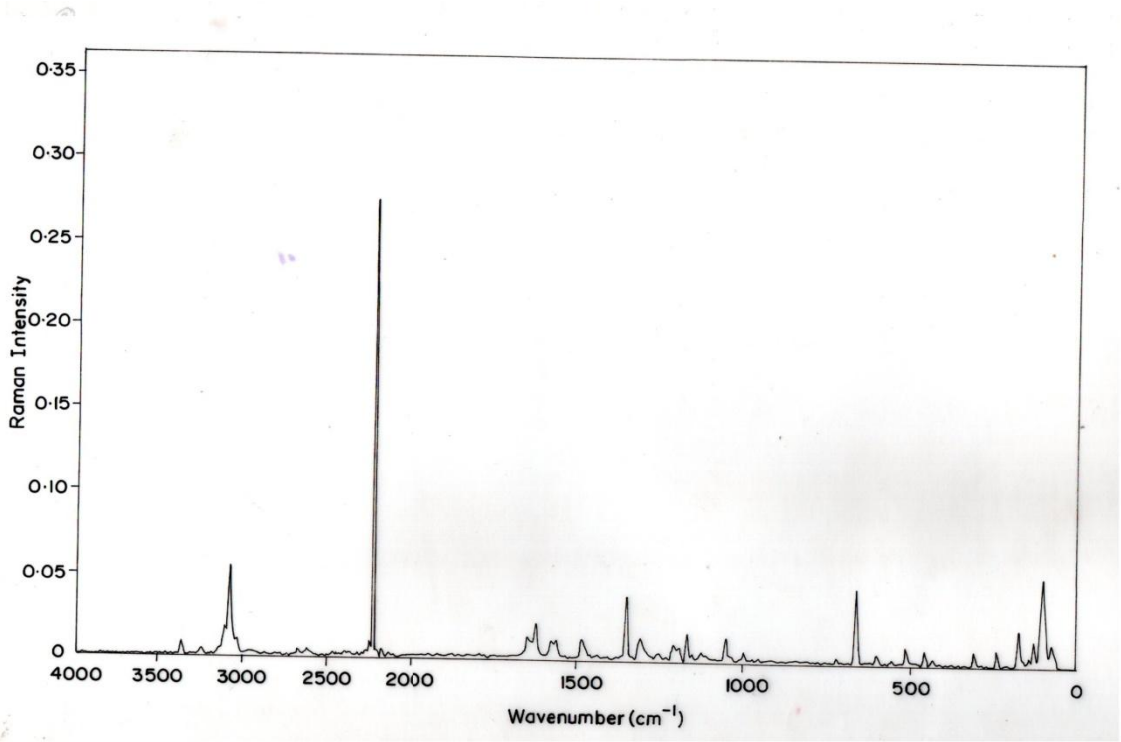

Fig. 3 FT-Raman spectrum of 4,5-dimethyl-O-phenylenediamine

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NH_2 VIBRATIONS

The DMPDA molecule, under consideration concrete with NH_2 group and posses six internal modes of vibraton viz. Symmetrystretching, asymmetric stretching,scissoring, rocking wagging and torsional mode.In NH_2 frequency value of asymmetric vibration is comparatively on higher side than that of symmetric one.The frequencies of amino group get spiked with the span of 3500-3300 cm^{-1} frequency for NH stretching 1700-1600 $cm^{-1}$for scissoring and 1150-900$cm^{-1}$for rocking deformation[9].In present investigation the asymmetric and symmetric modes of NH_2 group are evolved at 3680,3550,3480 cm^{-1} FT-IR and FT-Raman.

C-H vibrations

The C–H stretching vibrations of the phenyl ring are normally observed in the region 3200–3000 cm^{-1} which shows their uniqueness of the skeletal vibrations. In the present molecule stretching vibrations appear at 3201, 3100cm^{-1}in FT-Raman [10]. All the bands are well within the expected range which shows the slightly lesser than the aromatic nature of the phenyl ring is disturbed by the substitution group. All these vibrations are found active both in Raman.

Similarly, the C–H in-plane ring bending vibrations for aromatic CH occurs as strong to weak intensity bands in the region 1300–1000 cm^{-1}. In the present compound, the bands are observed at 1100 and 1168 cm^{-1} in FT-Raman. The last vibration 1047, 993, 856 cm^{-1} is observed in FT-IR with very strong intensity. Except for the one vibration, others are observed in the expected region. The C–H out-of-plane bending vibrations are expected in the region 1000–800 cm^{-1} [11]. But these vibrations are found at 549 cm^{-1} in the present case. All these CH vibrations are found in the expected range, the vibrations of the functional group have not in any way influence the CH vibrations.

C-C vibrations

The C-C stretching vibrations for phenyl ring are generally observed between 1600-1400 cm^{-1}, in which the bands between 1600-1500 cm^{-1} are assigned to C=C stretching and the rest to C-C stretching, even though no such distinction is present within the ring. In the present compound also, the bands observed at 1624, 1592,1516, 1459 cm^{-1} in FT-IR, and 1642, 1617,1580,1550 cm^{-1} in FT-Raman spectrum[12].

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These observations for the aromatic C-C are in agreement with literature values, which indicate that the skeletal vibrations are slightly affected by the substitution vibrations. The bands of C-C in-plane bending and out-of-plane bending vibrations are FT-IR and FT-Raman at 869cm^{-1} and 855, 375, 305 cm^{-1} respectively.

C-N vibrations

The mixing of several bands causes very difficultly in the identification of C-N vibrations in many molecules. The C-N stretching in the region 1382-1266 cm^{-1}.In the present molecule, the band is observed at 1383,1330cm^{-1} in FTIR and 1378 ,1329cm^{-1} in FT-Raman for C-N stretching vibrations[13]. In this case, it lies in between these two values, which may be due to the conjugation of electrons between the two adjacent NO bonds with these CN bonds. Similarly, the in-plane and out-of-plane vibrations are assigned at 760, 660 and 285,205 cm^{-1} respectively for this C-N which again has similar deviation noticed as in stretching, which may also be due to the conjugation of CN bonds.

Frontier Molecular Orbital Analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital are computed with B3LYP functional with 6-311+ G (d, p) basis set and the pictorial diagram of the HOMO-LUMO are shown in Fig.4. And the energies of the HOMO-LUMO, energy gap, and different reactivity descriptors of molecule in both optimized and electronic transition levels are presented in Table.3.The energy gap of the optimized benzene ring is 0.172 eV, where the energy flow is low [14]. On the contrary in the transition state, which shows the possibility of a high flow of energy from HOMO to LUMO. Similarly, other descriptors of the molecule do vary from the optimized to transition state and the values are presented in Table. 3. The electronegativity, which is a measure of the attraction of an atom for electrons in a covalent bond, has -0.36 eV in title molecule optimized and electronic states respectively. The chemical hardness of benzene is 1.42 eV in optimized and transition state respectively, which shows that the present molecule is less stable compared to the benzene ring. The electrophilicity index is a measure of lowering of total energy due to the maximal electron flow between the donors and the acceptors.

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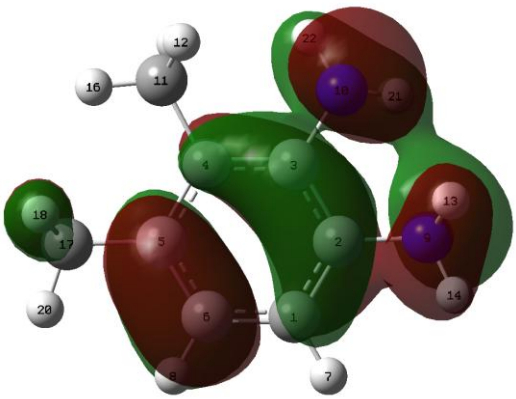
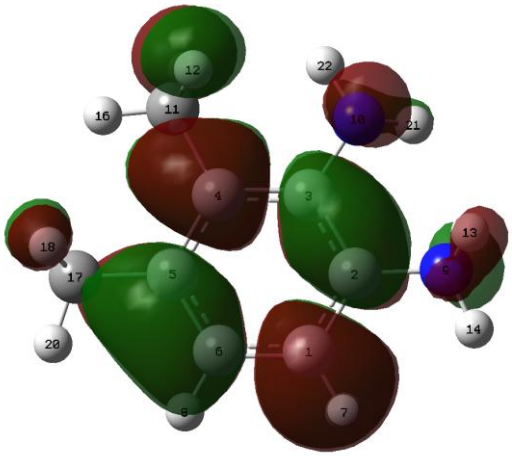
Table: 3- HOMO-LUMO analysis of 4,5-dimethyl-O-phenylenediamine

Molecular properties	values
E_{HOMO} (ev)	-0.016
E_{LUMO} (ev)	-0.188
$\Delta E_{HOMO\text{-}LUMO\ gap}$ (ev)	0.172
Electronegativity (χ)	-0.36
Global hardness (η)	0.532
Global softness (S)	-0.892
Chemical potential	1.424



LUMO=-0.188 eV



HOMO=-0.016 eV

Fig. 4. Frontier molecular orbital for 4,5-dimethyl-O-phenylenediamine

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Molecular docking analysis

Molecular docking is a powerful approach for predicting the molecular mechanism of protein-ligand interactions, bind to a receptor of known three-dimensional structures. Auto Dock suite 4.0 has been used to get inside into probable protein-ligand interactions and to identify the binding affinity of the molecules. For docking, the ligand was prepared by minimizing its energy at B3LYP/6-311G ++ (d,p) [15]. 3HSA was selected to be docked into the active site of the receptor 3HSA protein from the enzyme active site, which was downloaded from the RCSB protein data bank. Hydrogen atoms are added to the target protein and Kollaman atomic charges were calculated. Water molecules and other co-crystallized agents were removed. Lamarckian Genetic Algorithm (LGA) is used for molecular docking analysis. The binding protein of the target proton was specified using grid size 94 x95 x 91 A^0 with the aid of Auto grid. The resolution values i.e. the docking bond length values are 2.0, 2.1, 2.1, 2.3A^0. The ligand was docked into the functional site of the respective protein and its docking energy was examined to get a minimum value. Docked conformation which has the lowest binding energy was chosen to investigate the mode of binding. The result is shown in Table 4. The bond lengths are shown in Fig.6. Thus, a title molecule can interact with donor sites of residues in an enzyme active site. Consequently, this difference influences and explains the binding capacity of the compound enzyme active site and enzyme inhibition potency.

Table : 4

Docking analysis of 4,5-dimethyl-O-phenylenediamine

S. No	Protein	Binding energy (kcal/mol)	H-Bond interaction	Distance (Å)
1	3HS4	-5.42	VAL 55 ILE 102 LEU 22 SER 2	2.0 2.1 2.1 2.3

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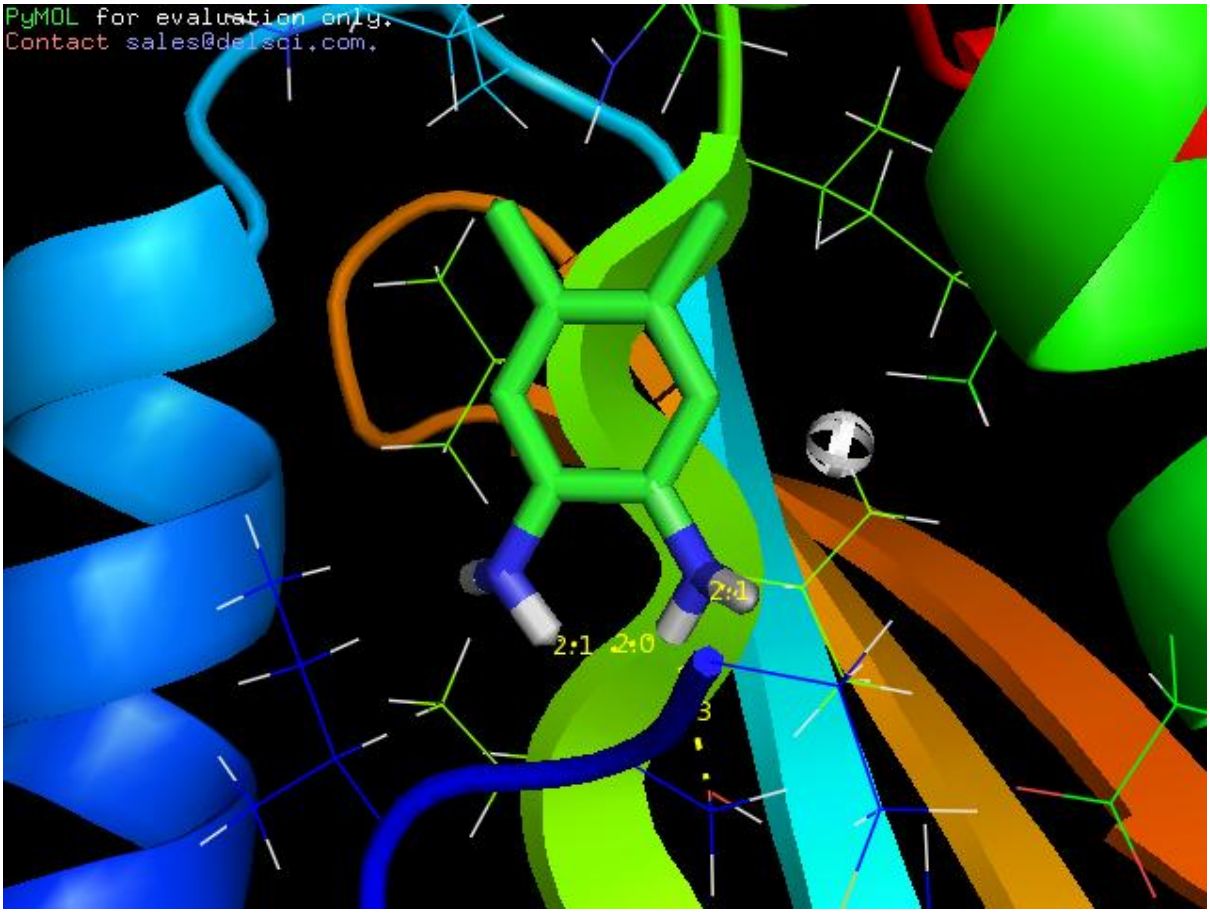

Fig. 5. Binding pose for 4,5-dimethyl-O-phenylenediamine

CONCLUSION

In the present investigation the density functional calculations on 4,5 dimethyl-o-phenylene diamine have been performed.Complete vibrational properties of DMPDA have been investigated FT-IR and FT-Raman spectroscopies respectively.The HOMO-LUMOenergy gap of the DMPDA molecule is evident that there is a significant influence on bioactivity of the molecule. The molecular docking study shows that DMPDA molecule can bind with protein induced with binding energy of -5.42 kcal/mol indicate the title molecule have pharmacological properties.

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