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Quantum Chemical and Spectroscopic (FT-IR, FT-Raman) Study, First Order Hyperpolarizability, NBO, Analysis HOMO and LUMO Analysis of Selegiline by abinitio HF and DFT Method

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ABSTRACT

The FT-IR and FT-Raman vibrational spectra of selegiline were recorded. The optimized geometry and wavenumbers in the ground state were calculated using density functional (B3LYP) method with standard 6-31G(d,p) basis set. The computed B3LYP/6-31G(d,p) results show the best agreement with the experimental values over the other methods. Natural bond orbital analysis of selegiline is also carried out, which confirms the occurrence of strong intermolecular bonding, stability of the molecule arising from hyperconjugative interactions, and charge delocalization. The electric dipole moment (α), polarizability (α), and first hyperpolarizability (β_0) which results also show that the selegiline might have microscopic non-linear optical behavior with non-zero values. The calculated HOMO and LUMO energies show that charge transfer occur in the molecule. The results of the calculations were applied to simulated spectra of the title compound, which show excellent agreement with observed spectra.

Key words: FTIR; FTRaman, DFT, HOMO and LUMO, NBO, First hyperpolarizability, Selegiline.

INTRODUCTION

In the past two decades quantum chemical computational methods have proven to be an essential tool for interpreting and predicating vibrational spectra[1-2]. A significant advance in this area was made by combination of empirical and ab initio information in the scaled quantum mechanical (SQM) force field method[3-6]. In the SQM approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules[2-7]. In the present study, vibrational spectroscopic analysis of selegiline has been carried out and discussed in detail. The Chemical is called methyl(1-phenylpropan-2-yl)(prop-2-yn-1-yl)amine. Selegiline is the original product of chinoin, which is widely used in the treatment of Parkinsonism. Investigation of metabolism of this drug is still in progress nowadays. One of the possible routes of metabolism of selegiline-as a tertiary amine-is the oxidation of the nitrogen atom followed by further chemical or enzymatic transformations.

Modern vibrational spectroscopy has proven to be an exceptionally powerful technique for solving many chemistry problems. Density functional theory (DFT)[8-10] has been accepted by the ab initio quantum chemistry community as a cost effective general procedure for studying physical properties of the molecules. In the framework of DFT approach, different exchange and correlation functionals are routinely used. Among those the B3LYP combination is most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. The use of B3LYP functional and standard basis set 6-31G (d,p) provides an excellent balance between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The vibrational frequencies obtained by quantum chemical calculations are typically larger and they have to be scaled by empirical scaling factors. These scaling factors depend on both the method and basis sets and they are determined from the mean deviation between the calculated and experimental frequencies[11–14]. The aim of this work is to check the performance of B3LYP density functional force field for simulation of the IR and Raman spectra of the title compounds with the use of standard 6-31G (d,p) basis set. The simulated and observed spectra were analyzed in detail.

EXPERIMENTAL

The compound selegiline was purchased from Sigma Aldrich Chemical Company, USA with more than 98% purity and was used as such without further purification to record FTIR and FT Raman spectra. The FTIR spectrum of the compound is recorded in the region 4000 – 400 cm^{-1} in evacuation mode on Bruker IFS 66V spectrophotometer using KBr pellet technique(solid phase) with 4.0cm^{-1} resolution. The FT Raman spectrum is recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 3500 – 100 cm^{-1} on Bruker IFS 66V spectrometer equipped with FRA 106 FT Raman module accessory. The spectral measurements were carried out at SAIF, IIT, Chennai, India. The experimental FTIR and FT Raman spectra of selegiline are presented in the Fig. 2 and 3.

Quantum chemical calculations

The entire calculations conducted in the present work were performed at Hartree–Fock (HF) and B3LYP levels included in the Gaussian 03W package[15] program together with the 6-31G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization[16]. The geometries were first determined at the Hartree Fock level of theory employing 6-31G (d,p) basis set. All the geometries were then optimized using 6-31G (d,p) basis sets using density functional theory (DFT)[17] employing the Becke's three-parameter hybrid functional[18] combined with Lee–Yang–Parr correlation[19] functional (B3LYP) method. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of selegiline were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. Finally, calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. Zero point vibrational energy was also calculated in the present work. By combining the results of the Gaussview program[20] with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the Gaussview program.

RESULTS AND DISCUSSION

Molecular Geometry

The optimized structure parameters of selegiline calculated by ab initio HF and DFT-B3LYP levels with the 6-31G(d,p) basis set are listed in the Table 1 in accordance with the atom numbering scheme given in Fig. 1. Table 1 compares the calculated bond lengths and angles for selegiline with those experimentally available from X-ray diffraction data[21].

Table 1: Optimized geometrical parameters of Selegiline bond length(Å), Interaxial angles(°)

Parameters	Expt.	HF/6-31 G(d,p)	B3LYP/ 6-31G(d,p)
$H_{31}-C_{14}$	1.113	1.081	1.092
$H_{30}-C_{14}$	1.113	1.093	1.106
$H_{29}-C_{14}$	1.113	1.085	1.096
$H_{28}-C_{13}$	1.100	1.077	1.088
$H_{27}-C_{12}$	1.100	1.076	1.086
$H_{26}-C_{11}$	1.100	1.076	1.086
$H_{25}-C_{10}$	1.100	1.076	1.086
$H_{24}-C_{9}$	1.100	1.077	1.087
$H_{23}-C_{7}$	1.113	1.086	1.096
$H_{22}-C_{7}$	1.113	1.084	1.093
$H_{21}-C_{7}$	1.113	1.084	1.093
$H_{20}-C_{6}$	1.113	1.083	1.095
$H_{19}-C_{5}$	1.113	1.086	1.096
$H_{18}-C_{5}$	1.113	1.087	1.097
$H_{17}-C_{3}$	1.090	1.057	1.065
$H_{16}-C_{1}$	1.113	1.085	1.098
$H_{15}-C_{1}$	1.113	1.093	1.109
$C_{14}-N_{4}$	1.438	1.449	1.458
$C_{13}-C_{12}$	1.420	1.383	1.394
$C_{13}-C_{8}$	1.420	1.393	1.404
$C_{12}-C_{11}$	1.420	1.387	1.397
$C_{11}-C_{10}$	1.420	1.383	1.395
$C_{10}-C_{9}$	1.420	1.387	1.396
$C_{9}-C_{8}$	1.420	1.389	1.401
$C_{8}-C_{5}$	1.497	1.515	1.513
$C_{7}-C_{6}$	1.523	1.529	1.532
$C_{6}-C_{5}$	1.523	1.548	1.558
$C_{6}-N_{4}$	1.438	1.466	1.476
$N_{4}-C_{1}$	1.438	1.450	1.465
$C_{3}-C_{2}$	1.212	1.187	1.208
$C_{2}-C_{1}$	1.470	1.474	1.466
$N_{4}-C_{14}-H_{29}$	109.50	109.36	109.26
$N_{4}-C_{14}-H_{30}$	109.44	113.85	114.26
$N_{4}-C_{14}-H_{31}$	109.46	110.35	110.12
$H2_{9}-C_{14}-H_{30}$	109.44	107.68	107.48
$H_{29}-C_{14}-H_{31}$	109.46	107.35	107.46
$H_{30}-C_{14}-H_{31}$	109.52	108.02	108.01
$H_{28}-C_{13}-C_{12}$	120.00	119.48	119.72
$H_{28}-C_{13}-C_{8}$	120.00	119.54	119.31
$C_{12}-C_{13}-C_{8}$	120.00	120.98	120.97
$H_{27}-C_{12}-C_{13}$	120.00	119.75	119.76
$H_{27}-C_{12}-C_{11}$	120.00	120.03	120.05
$C_{13}-C_{12}-C_{11}$	120.00	120.02	120.19
$H_{26}-C_{11}-C_{12}$	120.00	120.27	120.26
$H_{26}-C_{11}-C_{10}$	120.00	120.32	120.27
$C_{12}-C_{11}-C_{10}$	120.00	119.40	119.47
$H_{25}-C_{10}-C_{11}$	120.00	120.09	120.11
$H_{25}-C_{10}-C_{9}$	120.00	119.71	119.74
$C_{11}-C_{10}-C_{9}$	120.00	120.19	120.05
$H_{24}-C_{9}-C_{10}$	120.00	119.44	119.68
$H_{24}-C_{9}-C_{8}$	120.00	119.55	119.30
$C_{10}-C_{9}-C_{8}$	120.00	121.01	121.02
$C_{5}-C_{8}-C_{13}$	120.00	120.38	120.26
$C_{5}-C_{8}-C_{9}$	120.00	121.42	121.53
$C_{13}-C_{8}-C_{9}$	120.00	118.19	118.20
$C_{6}-C_{7}-H_{21}$	109.50	109.75	110.07
$C_{6}-C_{7}-H_{22}$	109.44	110.35	110.13
$C_{6}-C_{7}-H_{23}$	109.46	112.35	112.26
$H_{21}-C_{7}-H_{22}$	109.44	108.62	108.75
$H_{21}-C_{7}-H_{23}$	109.46	108.27	108.29
$H_{22}-C_{7}-H_{23}$	109.52	107.38	107.23
$N_{4}-C_{6}-C_{5}$	109.50	114.08	114.39
$N_{4}-C_{6}-C_{7}$	109.44	110.49	110.73
$N_{4}-C_{6}-H_{20}$	109.46	105.52	104.99
$C_{5}-C_{6}-C_{7}$	109.44	112.06	111.89
$C_{5}-C_{6}-H_{20}$	109.46	107.54	107.20
$C_{7}-C_{6}-H_{20}$	109.52	106.61	107.07
$C_{6}-C_{5}-C_{8}$	109.50	113.67	113.40
$C_{6}-C_{5}-H_{18}$	109.44	109.06	108.69
$C_{6}-C_{5}-H_{19}$	109.46	109.70	109.51
$C_{8}-C_{5}-H_{18}$	109.44	108.44	108.73
$C_{8}-C_{5}-H_{19}$	109.46	109.24	109.67
$H_{18}-C_{5}-H_{19}$	109.52	106.48	106.60
$C_{1}-N_{4}-C_{6}$	109.50	115.04	114.40
$C_{1}-N_{4}-C_{14}$	109.44	110.78	110.21
$C_{6}-N_{4}-C_{14}$	109.44	116.01	115.55
$C_{2}-C_{3}-H_{17}$	179.99	179.47	178.99
$C_{1}-C_{2}-C_{3}$	180.00	178.26	178.11
$C_{2}-C_{1}-N_{4}$	109.50	113.49	113.82
$C_{2}-C_{1}-H_{15}$	109.44	108.15	108.34
$C_{2}-C_{1}-H_{16}$	109.46	107.55	108.40
$N_{4}-C_{1}-H_{15}$	109.44	113.23	113.04
$N_{4}-C_{1}-H_{16}$	109.46	107.83	107.30
$H_{15}-C_{1}-H_{16}$	109.52	106.19	105.52

Table 2 Vibrational Wavenumbers obtained for selegiline at B3LYP/ 6-31G(d,p) [wavenumber (cm^{-1}) IR intensities(km mol^{-1}), Raman scattering activities (Å amu $^{-1}$), reduced mass (amu), force constants (m dyne Å $^{-1}$) and Raman depolarisation ratio]

Unscaled	Scaled	B3LYP/6-31G(d,p)				
ν_{cal} cm^{-1}	ν_{cal} cm^{-1}	IR intensity	Raman activity	Reduced mass	Force constant	r
332	319	0.98	1.07	2.64	0.17	0.57
349	336	3.24	9.98	2.86	0.20	0.69
360	346	0.30	0.99	2.11	0.16	0.39
413	397	0.29	1.61	2.62	0.26	0.28
431	415	8.06	1.67	3.63	0.39	0.74
466	448	0.25	3.72	3.56	0.45	0.20
517	497	11.34	2.08	3.06	0.48	0.40
577	555	0.20	1.93	4.29	0.84	0.74
605	582	51.30	0.33	1.20	0.25	0.71
617	594	3.62	4.32	4.37	0.98	0.51
652	627	40.02	0.75	1.23	0.31	0.47
715	688	15.82	0.91	2.11	0.63	0.58
752	724	33.39	7.25	1.70	0.56	0.10
793	763	1.49	3.19	2.94	1.09	0.64
841	809	0.86	9.39	3.33	1.39	0.17
869	836	8.32	4.66	2.04	0.90	0.61
929	894	3.81	1.79	1.47	0.74	0.74
957	921	3.41	2.98	3.08	1.66	0.22
973	936	0.05	0.09	1.34	0.75	0.58
995	958	5.69	2.00	1.85	1.08	0.68
997	960	1.24	0.93	1.33	0.78	0.70
1016	978	0.07	30.95	6.16	3.74	0.12
1024	986	9.64	5.70	1.75	1.08	0.26
1064	1024	31.25	5.55	1.98	1.32	0.67
1087	1046	19.43	3.80	1.75	1.21	0.68
1127	1085	14.72	0.55	1.51	1.13	0.63
1155	1112	15.01	6.78	1.36	1.07	0.71
1186	1142	0.55	5.53	1.10	0.91	0.74
1229	1183	4.28	21.49	2.50	2.22	0.12
1293	1245	31.61	6.19	1.49	1.47	0.74
1330	1280	10.60	32.79	1.44	1.50	0.37
1354	1303	1.61	2.05	2.04	2.20	0.65
1362	1311	0.30	3.33	2.04	2.23	0.69
1381	1329	6.31	23.63	1.27	1.43	0.52
1400	1348	37.85	10.43	1.46	1.69	0.60
1429	1376	8.05	9.59	1.34	1.61	0.74
1469	1414	0.59	10.09	1.16	1.48	0.73
1494	1438	3.71	4.67	1.59	2.09	0.74
1502	1446	8.44	7.93	1.13	1.51	0.73
1520	1463	0.28	5.71	1.06	1.44	0.71
1540	1483	14.53	1.81	2.24	3.13	0.38

1639	1578	0.86	8.02	5.49	8.70	0.74
1661	1599	9.97	57.35	5.62	9.15	0.50
2903	2795	50.60	71.36	1.07	5.33	0.15
2949	2839	79.16	87.01	1.06	5.43	0.17
3037	2924	26.40	78.04	1.05	5.75	0.03
3049	2936	13.04	114.25	1.04	5.69	0.00
3084	2969	20.30	17.58	1.09	6.15	0.53
3118	3002	31.03	39.59	1.09	6.28	0.36
3204	3085	22.47	294.94	1.09	6.64	0.11
3489	3359	57.98	39.66	1.16	8.32	0.23

From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values, due to the theoretical calculations belonging to isolated molecules in gaseous phase and the experimental results belonging to molecules in solid state. Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are on higher side than the latter and the HF calculated values correlate well compared with the experimental results. In spite of the differences, calculated geometric parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamic properties.

Vibrational Assignments

The vibrational analysis of selegiline is performed on the basis of the characteristic vibrations of amide, methyl, nitro and phenyl ring modes. The computed vibrational wave numbers, their IR and Raman activities, depolarization ratios, force constants and the atomic displacements as shown in fig.4 corresponding to the different normal modes are used for identifying the vibrational modes unambiguously. The harmonic vibrational frequencies calculated for selegiline at B3LYP levels using the 6-31G (d,p) basis set along with polarization functions have been summarized in Table 2. The force fields thus determined were used to calculate the vibrational potential energy distribution (PED) using the latest version of MOLVIB Program[22-23]. For visual comparison, the observed and calculated (simulated) FTIR and FT-Raman spectra of selegiline are presented in a common wave number scale in fig. 2 and 3. It can be noted that calculated results are harmonic frequencies while the observed frequencies contain anharmonic contribution. The later is generally lower than the former due to anharmonicity. The reproductions of observed fundamental frequencies are more desirable because they are directly observable in a vibrational spectrum. Comparison between the calculated and the observed vibrational spectra helps us to understand the observed spectral features.

The calculated vibrational wave numbers, measured infrared and Raman band positions and their assignments are given in the Tables.2 and 3. Comparison of the wavenumbers calculated at B3LYP with experimental values reveals the inclusion of electron correlation in density functional theory to a certain extent makes the wave numbers values in comparison with the experimental data.

C-H Vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3250cm^{-1} - 3000 cm^{-1} which is characteristic region for the ready identification of C-H stretching vibrations[24]. Hetero cyclic compound C-H vibration absorption bands are usually week, in many cases it is too weak for detection. In this region, the bands are not affected appreciably by the nature of substituents. In the present work, the bands observed at 3200 cm^{-1} both in FTIR and FT-Raman have been assigned to C-H stretching vibration. The B3LYP levels at 6-31G(d,p) gives the same frequency values at 3204 cm^{-1} as shown in Tables. 2 and 3. In general the aromatic C-H stretching vibrations calculated theoretically are in good agreement with the experimentally reported values[25] for trisubstituted benzene in the region 3250 cm^{-1} -3000 cm^{-1}.

Table 3: Vibrational wavenumbers observed using FTIR and FT Raman band positions (cm^{-1}) and vibrational assignments for Selegiline

FT-IR	FT-Raman	Vibrational Assignments (%PED)
-	330	Rtrigd (27), CN (24), CC (9)
-	350	tRsym (17), Rsymd (15)
-	365	γCH (15)
-	410	tR (43), tCN (30)
-	435	γCC(30), nCC(6)
470	475	tR (48), bCN (27), tRasy (26)
520	-	βCN (38), CC (16)
570	570	γ CCC (61) ,gCNC (15)
608	605	βCN (19)
620	620	g CCC (40) ,n CC (16)
650	-	gCH(61)
720	720	g CN (27), tRrigd (15), gCH (6)
750	750	gCN (27), tRrigd (5)
800	-	γCH (86)
840	840	γCH (52),bCC (17)
870	-	R asymd(61), R symd(31)
930	930	CH3 opr (90)
957	957	γCH (89)
970	-	γCH (18), nCC (11)
995	-	βCC (16)
997	1002	νCC (16)
1025	1030	CH3 ipr (71)
1065	1065	CH2 twist (69), gCH (18)
1080	1080	R trigd(56), bCC(23)
1130	1125	βCC (23), gCH (14)
1160	1157	νCC (24)
1180	1185	CH2 twist (76)
1230	1230	νCC (66), bCH (16)
1290	1290	νCC (67)
1332	1330	CH2 wag (67)
1350	1350	νCN (89)
1360	1360	νCC(86)
1380	1380	νCN (41),b CH (18)
1400	1400	CH2 wag (84) ,nCC(17)
1430	1430	βCH3 (90) , nCC(16)
1470	1470	CH2 SCISS (51), nCC (19)
1495	-	CH2 SCISS (80), bCN (13)
1500	1502	$CH_{2\ \mathrm{SCISS}}$ (82), bCN (13)
1520	-	$CH_{2\ \mathrm{SCISS}}$ (84), bCN (12)
1542	-	$CH_{2\ \mathrm{SCISS}}$ (87), bCN (10)
1640	-	CCss (87)
1660	-	CCss (84)
2905	-	$CH_{2\ \mathrm{SS}}$(91)
2950	2950	νCH (98)
3035	3035	νCH (96)
3052	3050	νCH (98)
3080	3080	νCH (99)
3120	3120	CH3 ips (100)
3200	3200	νCH (99)
3480	-	νCH(99)

Abbreviations used: R - ring; b - bending; d - deformation; asym - asymmetric; sym - symmetric; g - wagging; t - torsion; trig – trigonal; ν - stretching, ips - inplane stretching; ops - out-of-plane stretching; ss - symmetric stretching; β - in-plane bending; γ - out-of-plane bending; sb - stretching bending; t- twisting; ipr – in-plane rocking; opr – out-of-plane rocking;

Table 4: Second order perturbation theory analysis of Fock matrix in NBO basis

Donor(i)	Type	ED(e)	Acceptor(j)	Type	ED(e)	E(2)[a] (kJ/mol)	E(j)–E(i)[b] (a.u.)	F(i, j)[c] (a.u.)
C_8-C_9	σ	1.97567	C_{10}-H_{25}	σ*	0.01213	2.09	1.16	0.044
			C_{13}-H_{28}	σ*	0.01323	2.22	1.16	0.045
C_8-C_9	π	1.65495	C_5-C_6	σ*	0.04303	3.31	0.60	0.043
			C_5-H_{18}	σ*	0.01347	1.81	0.69	0.035
			C_{10}-C_{11}	π*	0.33487	21.45	0.28	0.069
			C_{12}-C_{13}	π*	0.32691	19.34	0.28	0.066
C_8-C_{13}	σ	1.97482	C_5-H_{19}	σ*	0.01211	0.68	1.13	0.025
			C_9-H_{24}	σ*	0.01330	2.29	1.16	0.048
			C_{12}-H_{27}	σ*	0.01218	2.13	1.16	0.045
C_9-C_{10}	σ	1.97973	C_5-C_8	σ*	0.02012	3.44	1.12	0.055
			C_{11}-H_{26}	σ*	0.01227	2.34	1.17	0.047
C_9-H_{24}	σ	1.98226	C_8-C_{13}	σ*	0.2339	4.01	1.09	0.059
			C_{10}-C_{11}	σ*	0.01573	3.51	1.10	0.056
C_{10}-C_{11}	σ	1.98063	C_9-H_{24}	σ*	0.01330	2.35	1.16	0.047
			C_{12}-H_{27}	σ*	0.01218	2.36	1.17	0.047
C_{10}-C_{11}	π	1.67024	C_8-C_9	π*	0.34462	19.31	0.29	0.066
			C_{12}-C_{13}	π*	0.32691	20.70	0.28	0.068
C_{10}-H_{25}	σ	1.98283	C_8-C_9	σ*	0.02251	3.80	1.10	0.058
			C_{11}-C_{12}	σ*	0.01582	3.52	1.10	0.056
C_{11}-$C1_2$	σ	1.98069	C_{10}-H_{25}	σ*	0.01213	2.39	1.17	0.047
			C_{13}-H_{28}	σ*	0.01323	2.35	1.16	0.047
C_{11}-H_{26}	σ	1.98304	C_9-C_{10}	σ*	0.01491	3.54	1.10	0.056
			C_{12}-C_{13}	σ*	0.01475	3.51	1.11	0.056
C_{12}-C_{13}	σ	1.97981	C_5-C_8	σ*	0.02012	3.27	1.12	0.054
			C_{11}-H_{26}	σ*	0.01227	2.32	1.17	0.033
C_{12}-C_{13}	π	1.67607	C_8-C_9	π*	0.34462	20.75	0.29	0.069
			C_{10}-C_{11}	π*	0.33487	19.60	0.28	0.069
C_{12}-H_{27}	σ	1.98292	C_8-C_{13}	σ*	0.02339	3.81	1.09	0.058
			C_{10}-C_{11}	σ*	0.01573	3.49	1.10	0.055
C_{13}-H_{28}	σ	1.98180	C_8-C_9	σ*	0.02251	3.99	1.10	0.059
			C_{11}-C_{12}	σ*	0.01582	3.56	1.10	0.056
C_{14}-H_{29}	σ	1.98971	N_4-C_6	σ*	0.03366	3.58	0.87	0.050
N_4	LP(1)	1.87721	C_1-C_2	σ*	0.02074	1.16	0.73	0.027
			C_1-H_{15}	σ*	0.03973	8.54	0.68	0.070
			C_1-H_{16}	σ*	0.01826	1.03	0.70	0.025
			C_5-C_6	σ*	0.04303	8.89	0.62	0.068
			C_6-C_7	σ*	0.01735	1.73	0.65	0.031
			C_6-H_{20}	σ*	0.02115	0.54	0.74	0.18
			C_{14}-H_{29}	σ*	0.01025	1.56	0.71	0.031
			C_{14}-H_{30}	σ*	0.02919	8.60	0.69	0.070
			C_{14}-H_{31}	σ*	0.00854	0.78	0.72	0.022

[a] E(2) means energy of hyper conjugative interaction (stabilization energy).

[b] Energy difference between donor and acceptor i and j NBO orbitals.

[c] F(i, j) is the fork matrix element between i and j NBO orbitals.

The title molecule selegiline has out-of-plane and in-plane aromatic C-H bending vibrations. The out of plane bending mode of C-H is found well with experimentally predicated[26] in the region 900 – 800 cm^{-1} at B3LYP /6-31G(d,p). The observed value of 840 cm^{-1} is in excellent agreement with 841 cm^{-1} of B3LYP/6-31 G(d,p) results. The C-H in plane bending vibrations assigned in the region 980-1260 cm^{-1} even though found to be contaminated by C- CH_3 stretch are found in literature[27-28], while the experimentally observed values are at 1065 and1263 cm^{-1}.

Methyl group vibrations

The title molecule selegiline under consideration possesses a CH_3 group in the side substitution chain. For the assignments of CH_3 group frequencies one can expect that nine fundamentals can be associated to each CH_3 group. The C-H stretchings are at lower frequencies than those of the aromatic ring. For CH_3 compound the mode appear in the region 3153 and 3050 cm^{-1} are assigned to CH_3 stretching mode of vibrations. The theoretically computed value shows an excellent agreement with experimental results. The CH_3 deformations are found in both FTIR and FT-Raman spectra are in good agreement with the calculated B3LYP results. The torsion vibrations are not observed in the FTIR spectrum because these appear at very low frequency. The FT-Raman experimental observations at 332 cm^{-1} show an excellent agreement with theoretical results. This assignment find support from the work of Singh and Prasad[29] and are with the frequency intervals given by Varsanyi[23].

C-C ring stretching

The C-C aromatic stretching vibrations give rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range from 1500 – 1300 cm^{-1}. The IR and Raman bands observed at 1470 and 1430 cm^{-1} have been assigned to C-C stretching vibrations. Of these bands, the band at 1400 cm^{-1} has appeared characteristically strong in the IR spectra respectively. The calculated bands at B3LYP levels in the same region are in excellent agreement with experimental observations of both in FTIR and FT-Raman spectra of selegiline[30]. The ring in plane vibrations has given rise to weak bands across the low region, that is to say 1000 cm^{-1}. The bands are 995cm^{-1} and at 840 cm^{-1} have been assigned to C-C in plane bending vibrations. As is seen from Table 2 and 3, the predicted frequencies by B3LYP agree well with the observed ones.

Table 5: The calculated electric dipole moments m (D) and dipole moment components for selegiline

	B3LYP/6-31G(d,p)
μ_x	0.0306
μ_y	-0.3110
μ_z	-0.1611
μ	0.351

Table 6: Calculated α and all β components of selegiline

	B3LYP/6-31G(d,p)			B3LYP/6-31G(d,p)	
	a.u	esu(X 10^{-24})		a.u	esu(X 10^{-33})
α_{xx}	166.126	24.6198	β_{xxx}	-508.253	4390.79766
α_{xy}	-4.472	-0.66275	β_{xxy}	31.4459	271.66113
α_{yy}	154.327	22.87126	β_{xyy}	-12.0221	-103.85892
α_{xz}	-12.056	-1.78669	β_{yyy}	-8.67348	-74.93019
α_{yz}	-8.614	-1.27659	β_{xxz}	-12.9266	-111.67289
α_{zz}	87.254	12.93104	β_{xyz}	-0.236889	-2.04648
α_{tot}	135.902	20.14067	β_{yyz}	-11.119	-96.057041
Δa	297.023	44.01880	β_{xzz}	22.3294	192.90368
			β_{yzz}	-8.52251	-73.62596
			β_{zzz}	-42.2698	-365.16880
			β_{tot}	493.7157561	4265.210417

C-N vibrations

The identification of C-N stretching vibration is a very difficult task since, the mixing of bands are possible in this region. The C-N stretching band is assigned at 1319 cm^{-1} in 2,6-dibromo-4-nitroaniline by Krishnakumar[31]. Xavier jesu Raja *et al.,*[31] have identified the FTIR band at 1342 cm^{-1} due to C-N in Theophylline. Hence in the present investigation the FTIR and FT-Raman bands observed at 1380 and 1350 cm^{-1} are assigned to C-N stretching mode of vibrations. The calculated value at 1381 and 1293 cm^{-1} are in excellent agreement with the observed value for the corresponding mode of vibrations.

Table 7: Mulliken atomic charges of selegiline at HF, B3LYP methods with 6-31G(d,p) basis set

Atoms	HF/ 6-31G(d,p)	B3LYP/6-31G(d,p)
C_1	-0.011283	-0.126697
C_2	0.114796	0.315022
C_3	-0.454163	-0.461495
N_4	-0.599162	-0.411568
C_5	-0.233543	-0.247930
C_6	0.064820	0.066101
C_7	-0.320760	-0.320366
C_8	-0.008553	0.120804
C_9	-0.161097	-0.125800
C_{10}	-0.142241	-0.084570
C_{11}	-0.156831	-0.088052
C_{12}	-0.142735	-0.085766
C_{13}	-0.154339	-0.123248
C_{14}	-0.132763	-0.156153
H_{15}	0.120878	0.095286
H_{16}	0.153906	0.127459
H_{17}	0.249216	0.162202
H_{18}	0.125861	0.095355
H_{19}	0.118609	0.089489
H_{20}	0.143979	0.116163
H_{21}	0.131422	0.123511
H_{22}	0.126012	0.118739
H_{23}	0.097348	0.092378
H_{24}	0.142665	0.075177
H_{25}	0.147266	0.083856
H_{26}	0.146612	0.084128
H_{27}	0.147844	0.083756
H_{28}	0.150185	0.085739
H_{29}	0.121483	0.105837
H_{30}	0.089490	0.074707
H_{31}	0.125077	0.115936

Other molecular properties

Natural bond orbital analysis

Natural bond orbital analysis gives the accurate possible natural Lewis structure picture of j, because all orbital are mathematically chosen to include the higher possible percentage of the electron density. Interaction between both filled and virtual orbital space information correctly explained by NBO analysis could enhance the analysis of intra and intermolecular interactions. The second-order Fock matrix was carried out to evaluate donor (i) and acceptor (j) i.e., donor level bonds to acceptor level bonds interaction in the NBO analysis[33]. The result of interaction is a loss of occupancy from the concentration of electron NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy E(2) associated with the delocalization i→j is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{{F_{(i,j)}}^2}{\varepsilon_j - \epsilon_i}$$

where *qi* is the donor occupancy, ε_j and ε_i are diagonal elements, and *F(i, j)* is the off-diagonal NBO Fock matrix elements.

Table 8: Comparison of HOMO, LUMO, energy gaps (*e*HOMO–LUMO), ionization potentials, Electron affinity, Global hardness and Electro negativity of selegiline

Basis set	ε HOMO εV	εLUMO εV	Energy gap (ε HOMO– ε LUMO)	Ionisation (I)εV	Electron affinity (A)εV	Global Hardness η = (I - A) / 2 eV	Electro negativity χ = (I + A) /2eV
HF	-8.554	3.907	-12.461	8.554	3.907	2.323	6.230
B3LYP	-5.639	0.065	-5.704	5.639	0.065	5.574	2.852

Natural bond orbital analysis of selegiline provides an efficient method for studying intramolecular bonding and interaction among bonds and also provides a convenient basis for investigating charge transfer or conjugation interaction in molecular systems. Some electron donor orbital, acceptor orbital, and the interacting stabilization energy results from the second-orders micro-disturbance theory are reported[34-35]. The larger the E(2) value the more intensive is the interaction between electron donors and acceptor, i.e., the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system[36]. Delocalization of electron density between occupied Lewis type (bond or lone pair) NBO orbital and formally unoccupied (antibond or Rydgberg) non-Lewis NBO orbital correspond to a stabilization donor-acceptor interaction. When the donor and the acceptor belong to different sub molecule in a title molecule, we call it intramolecular NBO interaction. It is the intramolecular NBO interaction that reveals the origin of intermolecular interaction. NBO analysis has been performed on the selegiline molecule at the DFT-B3LYP/6-31G(d,p) level in order to elucidate the intramolecular interaction within the molecule.

From Table 4, we can see that the intermolecular interaction is formed by the orbital overlap between s(C5 C8) and s(C13 H28) to the antibonding acceptor σ*(N4 C6) and σ*(C8 C9) bond orbital, which results intermolecular charge transfer causing stabilization energies 2.30 and 3.99 kcal/mol. The stabilization energy E(2) coupled with hyperconjugative interactions LP(1) N4→ σ*(C1 C2) and LP(1) N4→ σ*(C1 H15) are obtained as 1.16 and 8.54 kcal/mol, respectively (Table 4), which enumerate the extent of intramolecular hydrogen bonding. The maximum energy transfer occurs from LP(1) N4→ σ*(C5 C6) and LP(1)N4→ σ*(C14 H30) (8.89 and 8.60 kcal/mol), respectively as shown in Table 4. The differences in energies are reasonably owing to the fact that the accumulation of electron density in the C H bond is not only drawn from the LP(N) of hydrogen acceptor but also from the entire molecule.

Non linear optical effects

The first hyperpolarizability (β_0) of this novel molecular system, and related properties (β, α_0 and Δa) of selegiline are calculated using B3LYP/6-31G(d,p) method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by 3×3×3 matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry[37]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3×3×3 matrices is a tetrahedral. The components of b are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

Table 9: Theoretically computed energies (a,u), zero point vibrational energies (kcal mol^{-1}), rotational constants (GHz) entropies (cal mol^{-1} k^{-1}) and Dipole moment (D) (Kcal Mol^{-1} Kelvin^{-1}) of selegiline

Parameters	HF / 6-31G(d,p)	B3LYP / 6-31G(d,p)
Total energy	-556.289	-560.041
Zero point vibrational energy	180.124	168.164
Rotational constants	1.170	1.143
	0.390	0.399
	0.324	0.326
Entropy		
Total	188.54	177.186
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	186.768	175.409

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \ldots\ldots$$

where E^0 is the energy of the unperturbed molecules, F_a is the field at the origin, μ_a, α_{ab} and β_{abg} are the components of dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole momentm, the mean polarizability α_0, the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability β_0, using the x, y, z components are defined as:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}}$$

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

$$\Delta\alpha = 2^{-\frac{1}{2}}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{\frac{1}{2}}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}}$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$
$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Since the values of the polarizabilities (α) and hyperpolarizability (α) of the Gaussian 03 output are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) (α: 1 a.u. = 0.1482 × 10"24 esu; β: 1 a.u. = 8.639×10"33 esu). The total molecular dipole moment and first order hyperpolarizability are 1.5221 D and 4.5125 ×10"30 esu, respectively and are depicted in Tables 5 and 6. Total dipole moment of title molecule is approximately equal to those of urea and first hyperpolarizability of title molecule is 12 times greater than those of urea (μ and β of urea are 1.3732 D and 0.3728 ×10"30 esu obtained by HF/6-31G(d,p) method).

Mulliken population analysis

The total atomic charges of selegiline obtained by Mulliken population analysis by HF and B3LYP method with 6-31G (d,p) basis set are listed in Table 7. The charge distribution of the title compound shows that the carbon atom attached with hydrogen atoms is negative, where as the remaining carbon atoms (except C2 and C6) are positively charged. All the hydrogen atoms have positive charges. The maximum atomic charge is obtained for C2 when compared to other atoms. This is due to the attachment of negatively charged nitrogen (N4) atom. From the result it is clear that the substitution of aromatic ring leads to a redistribution of electron density (Figs. 5 and 6). The charge distribution on the molecule has an important influence on the vibrational spectra[38]. The corresponding plot of Mulliken's charges obtained by HF/6-31G (d,p) and B3LYP/6-31G (d,p) levels are shown in Figs. 5 and 6 respectively.

Homo–Lumo Band Gap

A deeper understanding of chemical reactivity can be gained by this electronic absorption corresponds to the transition from the ground to the first excited state and it is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)[39-40]. The HOMO represents the ability to donate an electron and LUMO represents the ability to obtain an electron. The HOMO is located almost over the nitrogen atom and also slightly delocalized in hydrogen atom as well as carbon atom. LUMO is mainly delocalized in carbon atoms of benzene ring and hydrogen atom. The frontier molecular orbitals of selegiline were shown in Fig. 7. The energy gap of the title molecule was calculated at B3LYP/6- 31 G (d,p) level, which reveals the chemical reactivity of selegiline and proves the occurrence of eventual charge transfer within selegiline.

Table 8 lists the calculated values of the first ionization potentials, HOMO & LUMO, energy gaps, Electron affinity (A), Ionisation potential (I), Electro negativity (χ) defined by Mulliken[41] and Global Hardness (η) of selegiline. The hardness, defined as the second derivative of the total energy, together with the concept of electronegativity and the principle of quantization of electronegativities has been used to develop the principle of hard and soft acids and bases[42-43]. The lowest first ionization potential was obtained by HF/6-31G (d,p). The HOMO–LUMO energy gap is consistent for B3LYP methods and varies erotically to HF methods.

- HOMO energy = -5.6396041eV
- LUMO energy = 0.06530784eV

- HOMO–LUMO energy gap = -5.70491194 eV

Thermodynamic Properties

On the basis of vibrational analysis at B3LYP/ 6-31G(d,p) and HF/6-31G(d,p) levels, several thermodynamic parameters are calculated and are presented in Table 9 . The zero point vibrational energy (ZPVE) and the entropy, S_{vib} (T) are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in the total entropy of selegiline at room temperature at different methods are only marginal.

CONCLUSION

Attempts have been made in the present work for the proper wavenumber assignments for the compound selegiline from the FTIR and FT-

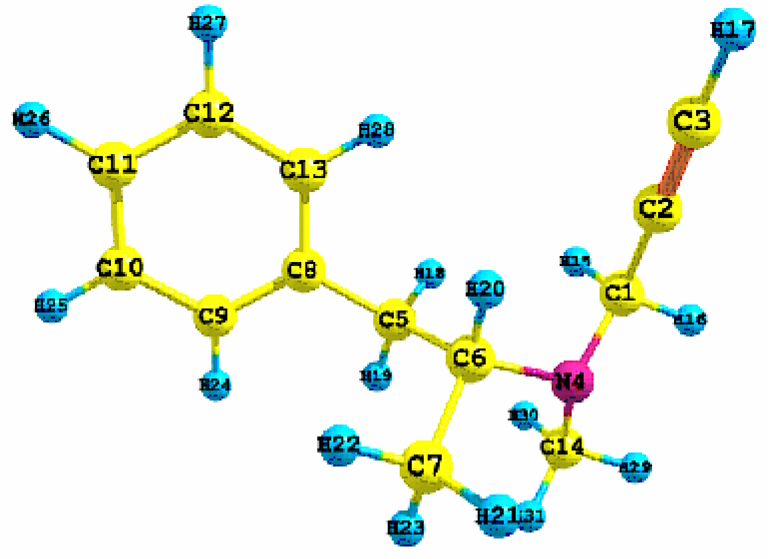


Fig. 1: Numbering system adapt in this study of Selegiline

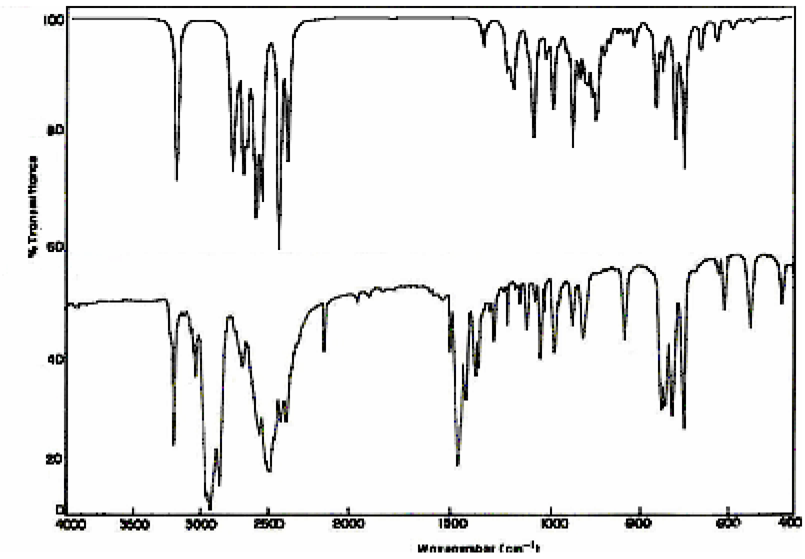


Fig. 2: FTIR spectrum of Selegiline (a) Observed and (b) Experimental

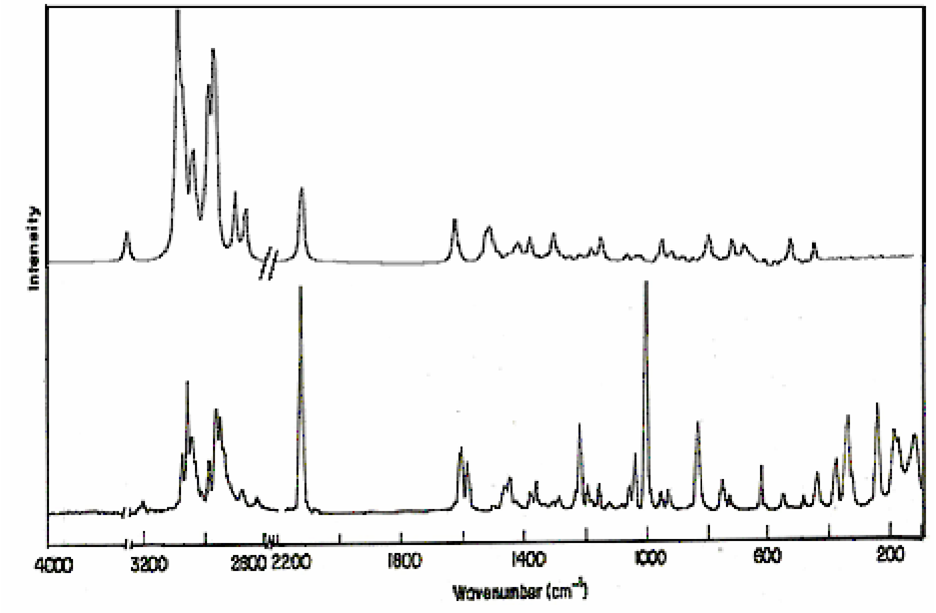
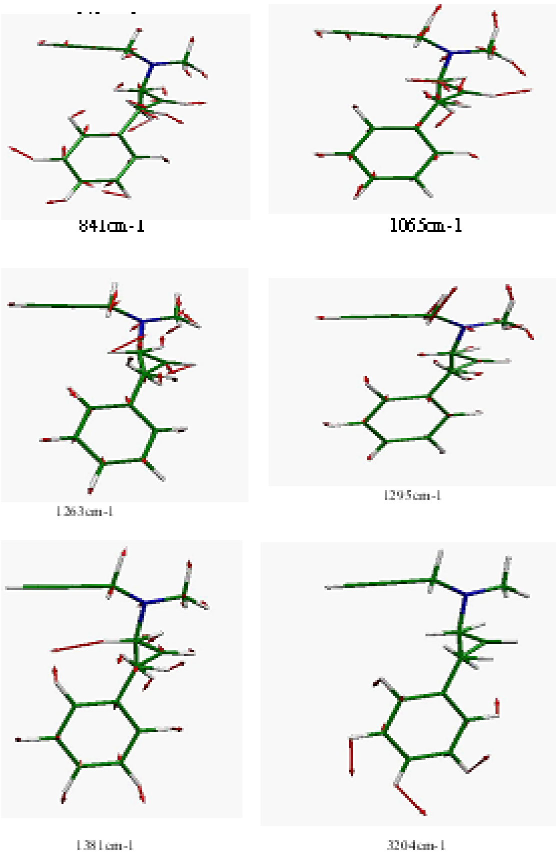


Fig. 3: FT-Raman spectrum of Selegiline (a) Observed and (b) Experimental


841cm-1

1065cm-1

1263cm-1

1295cm-1

1381cm-1

3204cm-1

Fig. 4: Atomic displacements corresponding to selected vibrating modes of selegiline

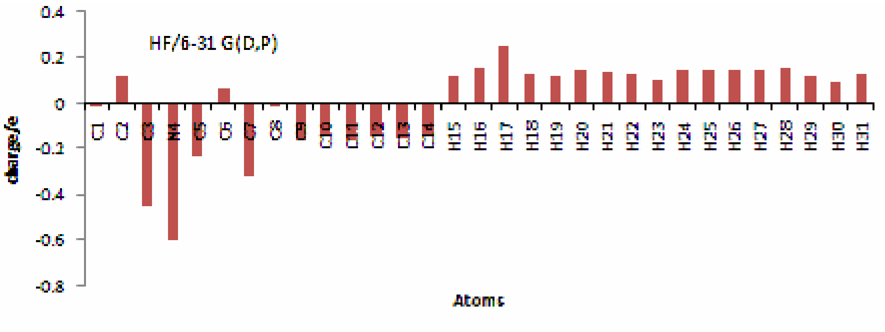


Fig. 5: Plot of Mulliken's charges obtained by HF/6-31G(d,p) method

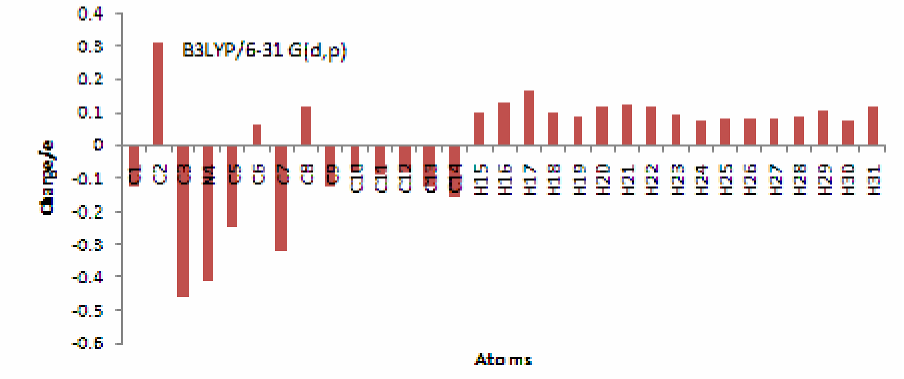


Fig. 6: Plot of Mulliken's charges obtained by B3LYP/6-31G(d,p) method

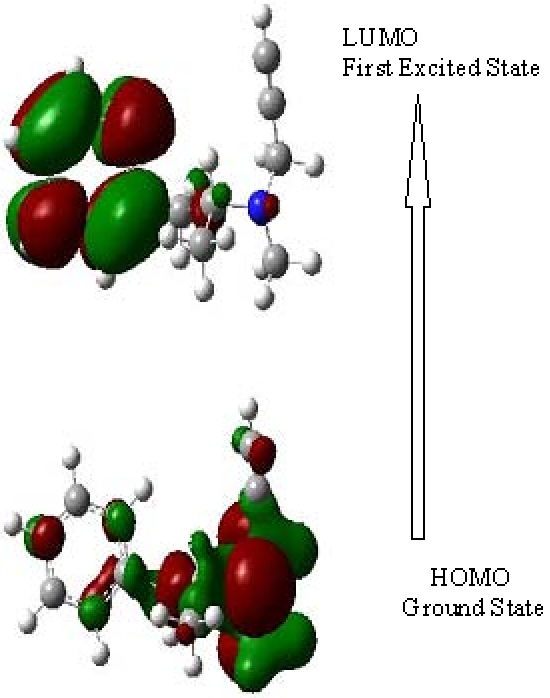


Fig. 7: The atomic orbital composition of the frontier molecular orbital of selegiline obtained by B3LYP/6- 31G(d,p) method

Raman spectra. The equilibrium geometries and harmonic frequencies of selegiline were determined and analyzed at DFT levels of theories utilizing 6-31G(d,p) basis set. The difference between observed and calculated wavenumbers' values of most of the fundamental modes is very small. The experimental and the simulated spectra of the title compound agree well. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignment made at higher levels of theory with only reasonable deviations from the experimental value seems to be correct. The potential energy distribution are made in this study also confirms the assignments proposed for various mode of the title compound.

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