Synthesis, Experimental and Theoretical Studies by DFT on Molecular, Electronic, IR, NMR Analysis of 3-[(4-Methylbenzylidene)amino]phenol

S. Anbuselvi[1], V. Jayamani[1,*], R. Mathammal[2] and R. Sangeetha[1]

[1]Department of Chemistry, Sri Sarada College for Women (Autonomous), Salem-636 016, India
[2]Department of Physics, Sri Sarada College for Women (Autonomous), Salem-636 016, India

*Corresponding author: E-mail: jayamani@gmail.com

Synthesis and structural characterization by physical constants, IR, NMR and UV study of 3-[(4-methylbenzylidene)amino]phenol (4MBAP) was carried out. In order to present a full description, DFT calculations were carried out using B3LYP/6-31G(d,p) to obtain geometry, vibrational frequency and NMR data. The theoretical electronic spectra have been calculated by using CIS method. NBO analysis of 3-[(4-methylbenzylidene)amino]phenol was carried out. The observed and theoretical IR data of 3-[(4-methylbenzylidene)amino]phenol are compared. The FT-IR spectrum of the title compound was recorded in solid phase.

Key Words: Density functional theory, FT-IR, Vibrational frequencies, ^{1}H and ^{13}C NMR spectra, HOMO, LUMO and NBO.

INTRODUCTION

Schiff bases[1] contain carbon-nitrogen double bonds in which nitrogen atoms are connected to an aryl or alkyl group. Schiff base ligands have been used in different areas such as electrochemistry, bioinorganic catalysis, metallic deactivators, separation process, environmental chemistry and pharmaceutical, dye, plastic industries as well as in the field of liquid-crystal technology[1-4]. Several Schiff bases possess antiinflammatory allergic inhibitors reducing activity[5], radical scavenging[6], analgesic[7], antioxidative action and antiulcer activity[8]. The computational methods[9-12] are widely used for the calculation of frequencies and intensities of spectral bands. DFT calculations leads to more accurate molecular structure and frequencies when compared to HF and MP2 calculations[13-15]. Here we present besides the experimental determination of molecular structure[16,17]calculation of IR, NMR, electronic and other quantum chemical parameters such as HOMO, LUMO energies, softness and hardness, atomic charges calculated using optimized geometry.

EXPERIMENTAL

Commercially available AR grade *p*-tolualdehyde, 3-amino phenol and ethanol were used without further purification. 3[(4-Methylbenzylidene)amino]phenol (4MBAP) synthesized from *p*-tolualdehyde and 3-amino phenol. A solution of *p*-tolualdehyde (0.1 m mol) in alcohol was added in drop wise to an alcoholic solution of 3-amino phenol (0.1 m mol). The reaction mixture was heated under reflux for 5 h, cooled and then poured into water. The product (3[(4-methylbenzylidene)-amino]phenol) was collected by filtration, washed with water and dried. Crystallized from ethanol. Brownish yellow. Yield: 1.9 g, m.p. 174 ºC. C, H, N analysis were performed by using CHNSO elemental analyser. IR spectra were obtained with ModelX99 IR spectrometer and UV studies were carried out by using Microprocessor UV/VIS spectrometer model 1371. CV studies were carried out by using electrochemical analyzer CH instruments INC' with a platinum working electrode, platinum wire counter electrode and Ag/AgCl reference electrode.

IR and UV measurement: The FT-IR spectrum of the synthesized material was recorded in the range 4000-400 cm^{-1} by KBr pellet technique (Thermo Nicolet avatar 370 DTGS FT-IR spectrometer). Theoretical methodology DFT calculations were carried out using the Gaussian 09 program package[9]. Initial geometry generated from standard geometrical parameters was minimized without any constant in the potential energy surface at B3LYP level adopting the standard 6-31 G(d, p) basis set. All calculations, which include geometry optimizations, energies, reduced masses, electronic, vibrational and NMR spectra were performed on isolated system using the Backe's three parameter B3LYP exchange correlation method. The 6-31G (d, p) basis set was chosen as a compromise between accuracy and applicability to large molecules. Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of

statistical mechanics. By combining the results of the GAUSS VIEW program with symmetry considerations, vibrational frequencies assignments were made with a high degree of accuracy. NMR calculations also done using optimised structure with the same level of theory. The theoretical electronic spectra have been calculated using CIS method.^{1}H and ^{13}CNMR chemical shifts were calculated by using gauge invarient atomic orbital method(GIAO). Also HOMO, LUMO energies, softness and hardness, atomic charges were calculated.

RESULTS AND DISCUSSION

Molecular geometry: The molecular structure of 3[(4-methylbenzylidene)amino]phenol with C_1 symmetry is shown in Fig. 1.
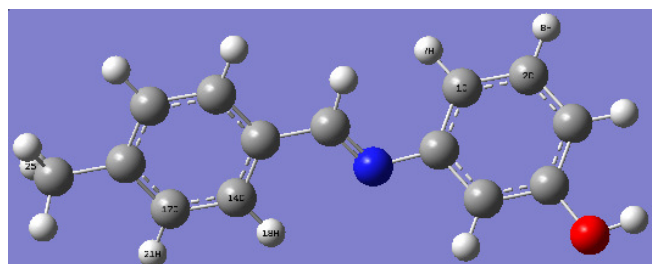

Fig. 1

The global minimum energy was obtained by the DFT structure optimization and was calculated as -671.3106 hartrees/particle and the corresponding zero point vibrational energy was calculated as 615989.9 joules/mol (141.22513 Kcal/mol). The most optimized structural parameters were also calculated (Table-1).

Vibrational assignments: 3[(4-Methylbenzylidene)-amino]phenol has 29 atoms and belongs to C_1 point group. It has 81 normal modes of vibration which includes 28 stretching vibrations, 53 bending vibrations. The 81 normal modes of

4MBAP are distributed among the symmetry species as vib = 55 [in plane (or) symmetry] + 26[out of plane (or) asymmetric] *i.e.*, 55 of this modes should be symmetric and 26 asymmetric with respect to the reflection on the symmetry plane for the atoms located in the plane of the molecule. The detailed FTIR experimental frequencies and calculated IR frequencies were reported in the Table-2. For the visual comparison, the observed and simulated FTIR was reported in the Fig. 2. The assignments based on the vibrational animations of fundamentals using the Gauss view package programme in the HF/ 6-31 G(d, p) calculations.
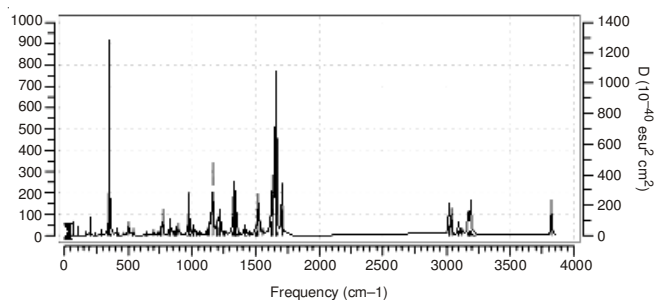

Fig. 2

Electronic spectra: The theoretical electronic absorption spectra calculated on the B3LYP/6-31 G(d,p) method level optimized structure are listed in the Table-3. Absorption Maxima (λ_{max}) for the compound was calculated by CIS method.

In order to characterize the excited state transitions presented in Table-4, we performed an analysis of all the molecular orbitals involved, taking into consideration that orbital 56 is the HOMO and orbital 57 is the LUMO for 4MBAP. The HOMO, LUMO energies are used to describe the dynamic stability, hardness and softness of a molecule. According to Koopman's theorem

				TABLE-1			
				OPTIMIZED GEOMETRICAL PARAMETERS OF 3[(4-METHYLBENZYLIDENE)AMINO]PHENOL			
Bond length value in (Å)				Bond angle value in (°)			
C_1-C_2	1.3922	C_{12}-C_{13}	1.4014	C_2-C_1-C_6	199.5781	C_{12}-C_{13}-C_{15}	120.6998
C_1-C_6	1.4083	C_{12}-C_{14}	1.4067	C_2-C_1-H_7	120.4561	C_{15}-C_{13}-C_{16}	119.487
C_1-H_7	1.0848	C_{13}-C_{15}	1.3939	C_6-C_1-H_7	119.9199	C_{12}-C_{14}-C_{17}	120.3363
C_2-C_3	1.395	C_{13}-H_{16}	1.0875	C_1-C_2-C_3	120.9971	C_{12}-C_{14}-H_{18}	118.4889
C_2-H_8	1.0863	C_{14}-C_{17}	1.3872	C_1-C_2-H_8	119.6907	C_{17}-C_{14}-H_{18}	121.1748
C_3-C_4	1.4004	C_{14}-H_{18}	1.0848	C_3-C_2-H_8	119.3109	C_{13}-C_{15}-C_{19}	120.8895
C_3-H_{27}	1.0877	C_{15}-C_{19}	1.3999	C_2-C_3-H_{27}	120.4893	C_{13}-C_{15}-H_{20}	119.5087
C_4-C_5	1.3949	C_{15}-H_{20}	1.0868	C_4-C_3-H_{27}	120.197	C_{19}-C_{15}-H_2	119.4635
C_4-O_{28}	1.3649	C_{17}-C_{19}	1.4066	C_3-C_4-C_5	120.3294	C_{14}-C_{17}-H_{19}	121.2636
C_5-C_6	1.4009	C_{17}-H_{21}	1.0874	C_3-C_4-O_{28}	122.4665	C_{14}-C_{17}-H_{21}	119.5087
C_5-H_9	1.0839	C_{19}-C_{22}	1.5093	C_5-C_4-O_{28}	117.2026	C_{19}-C_{17}-H_{21}	119.4635
C_6-N_{26}	1.4062	C_{22}-H_{23}	1.9054	C_4-C_5-C_6	120.1528	C_{15}-C_{19}-C_{17}	118.169
C_{10}-H_{11}	1.1006	C_{22}-H_{24}	1.0967	C_4-C_5-H_9	119.9874	C_{15}-C_{19}-C_{22}	121.2973
C_{10}-C_{12}	1.466	C_{22}-H_{25}	1.0932	C_6-C_5-H_9	119.8558	C_{17}-C_{19}-C_{22}	120.5348
C_{10}-N_{26}	1.2813	O_{28}-H_{29}	0.966	C_1-C_6-C_5	119.6033	C_{19}-C_{22}-C_{23}	111.3237
–	–	–	–	C_1-C_6-N_{26}	123.0676	C_{19}-C_{22}-C_{24}	111.5357
–	–	–	–	C_5-C_6-N_{26}	117.28	C_{19}-C_{22}-C_{25}	111.1693
–	–	–	–	H_{11}-C_{10}-C_{12}	115.5901	H_{23}-C_{22}-H_{24}	107.9521
–	–	–	–	H_{11}-C_{10}-N_{26}	121.7462	H_{23}-C_{22}-H_{25}	106.9473
–	–	–	–	C_{12}-C_{10}-N_{26}	122.6593	H_{24}-C_{22}-H_{25}	107.705
–	–	–	–	C_{10}-C_{12}-C_{13}	119.7091	C_6-N_{26}-C_{10}	119.9534
–	–	–	–	C_{10}-C_{12}-C_{14}	121.6491	C_4-O_{28}-H_{29}	108.9518
–	–	–	–	C_{13}-C_{12}-C_{14}	118.6417	–	–

TABLE-2
OBSERVED AND CALCULATED IR FREQUENCIES

Frequencies (cm⁻¹)					
Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
30.5939	–	655.7321	650	1161.8902	1161
30.5939	–	700.8978	700	1515.5942	1510
44.9733	–	729.7464	720	1523.3501	1520
61.5025		757.3462	755.16	1556.4458	1550
106.7540	–	771.5994	765	1619.6970	1626.06
170.2923	–	806.6004	800	1631.9340	1630
201.4483	–	833.4671	830	1657.5023	1663
238.8725	–	856.4495	856	1670.6949	1675
244.0902	–	862.8609	865	1706.5690	–
285.4906	–	878.0558	880	3020.0448	3024.51
340.0141	–	899.1212	888	3039.5359	3040
352.1679	–	956.3868	945	3095.3455	3100
366.9042	–	960.4032	–	3127.6740	3120
410.4455	408	975.4338	970.24	3168.3291	3165
421.8112	415	991.6674	985	3171.0894	3170
469.4104	470	1009.3242	1015	3175.8484	3175
500.9935	490	1012.1667	–	3188.9696	3180
503.6297	506.34	1018.5932	–	3190.0513	3190
535.3522	532	1036.6744	1030.03	3210.3961	–
542.3068	548	1064.0403	–	3216.4138	3218
629.4426	625	1118.9232	1118	3225.1710	3220sss
644.6980	645	1140.6278	1147.69	3824.1578	3820

TABLE-3
THEORETICAL ELECTRONIC ABSORPTION
SPECTRA VALUES CALCULATED λ_{max} (nm) CIS

Oscillator strength	Wavelength
0.5305	248.22
0.4478	219.55
0.0031	206.70

TABLE-4
CALCULATED QUANTUM CHEMICAL PARAMETERS OF
3[(4-METHYLBENZYLIDENE)AMINO]PHENOL

Parameters a.u.	B3LYP/6-31G**
HOMO	-0.21130(56)
LUMO	-0.05346(57)
ΔE	0.15784

$$E_{LUMO} = -|EA| = -0.05346$$
$$E_{HOMO} = -|IP| = -0.21130$$

where EA is the electron affinity and IP is the ionization potential. The hardness of the molecule is given by $\eta = (E_{LUMO} - E_{HOMO})/2 = 0.07892$. The softness is the reciprocal of hardness $\sigma = 1/\eta = 12.6711$. The atomic orbital compositions of the frontier molecular orbital are sketched in Figs. 3 and 4.
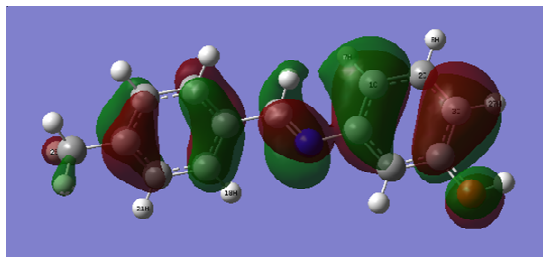

Fig. 3

NMR spectra: The molecular structure of the title compound is optimized. Then, gauge including atomic orbital
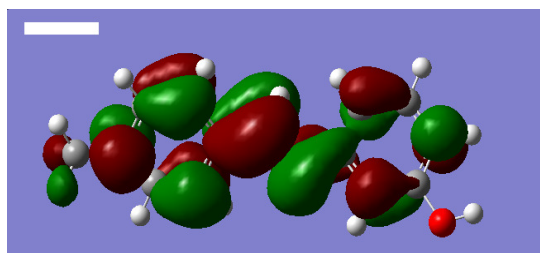

Fig. 4

(GIAO) ¹³C and ¹H NMR chemical shifts calculations of the title compound have been carried out by using B3LYP method with 6-31 G** basis set using Gaussian 09 programme package. Isotropic nuclear magnetic shielding tensors and ¹³C and ¹H NMR theoretical chemical shifts of 4MBAP were recorded and the obtained data are presented in Fig. 5 and 6. The calculated values are in excellent agreement with the expected chemical shift values. The range of ¹³C NMR chemical shifts for typical organic molecules usually is > 100 ppm and the accuracy ensures reliable interpretation of spectroscopic parameters. In the present study, the ¹³C NMR chemical shifts in the ring for 4MBAP are > 100 ppm as they would be expected. Thus it is possible to determine the preferred conformation and configuration of 4MBAP by NMR calculations at B3LYP with 6-31/ + G(d. p) basis set. ¹H NMR spectra of 4MBAP.
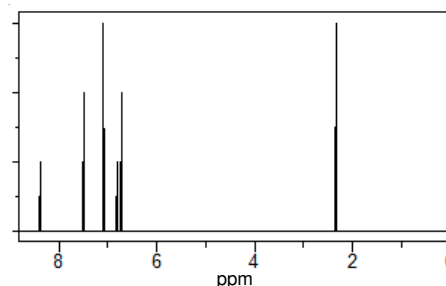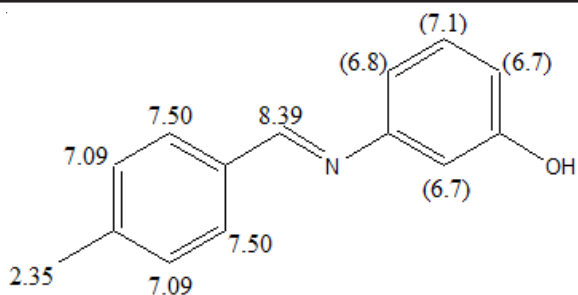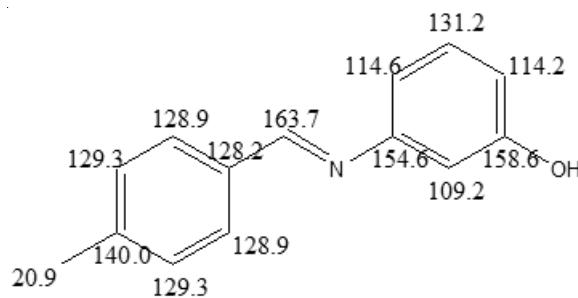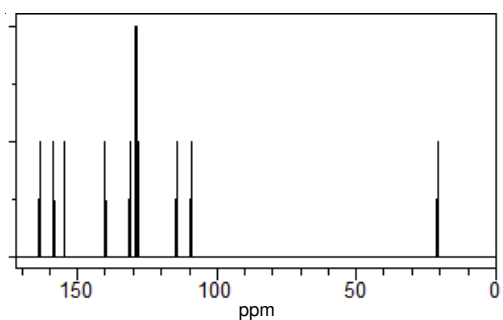
Fig. 5

Fig. 6

Conclusion

Density functional theory calculations have been carried out to determine the electronic absorptions, vibrational frequencies, ^{1}H and ^{13}C NMR chemical shifts. IR data alone compared with experimentally observed spectral data. The theoretically computed values are found to be in reasonably good agreement with that obtained in the FT-IR spectrum of the 3[(4-methylbenzylidene)amino]phenol. Structure of 3[(4-methylbenzylidene)amino]phenol have been determined on the basis of the theoretically computed values and experimentally determined spectral data.

REFERENCES

1. H. Schiff, *Ann Chem.*, **13**, 18 (1864).
2. F. Shemirani, A.A. Mirroshandel, M. Salavati-Niasari and R.R. Kozani, *J. Anal. Chem.*, **59**, 228 (2004).
3. V.K. Gupta, A.K. Singh and B. Gupta, *Anal. Chim. Acta*, **575**, 198 (2006).
4. A. Nishinaga, T. Yama da, H. Fujisawa and K. Ishizaki, *J. Mol. Catal.*, **48**, 249 (1988).
5. D.N. Dhar and C.L. Traploo, *J. Sci. Ind. Res.*, **41**, 501 (1982).
6. L. Hadjipavlu, J. Dimitra, Geronikaki and A. Athina, *Drug Des. Discov.*, **15**, 199 (1998).
7. B. De and G.V.S. Ramasarma, *Indian Drugs*, **36**, 583 (1999).
8. X. Luo, J. Zhao, Y. Ling and Z. Liu, *Chem. Abstr.*, **138**, 247927 (2003).
9. Y. Gaowen, X. Xiaping, T. Huan and Z. Chenxue, *Chem. Abstr.*, **123**, 101089 (1995).
10. E.B. Wilson Jr., J.C. Decius and P.C. Cross, Molecular Vibrations, McGraw Hill, New York (1955).
11. S.J. Cyrin, Molecular Vibrations and Mean Square Amplitudes, Elseveir, Amsterdam (1968).
12. L.A. Gribov and M.J. Orille Thomas, Theory and Methods of Calculations of Molecular Spectroscopy, Wiley (1988).
13. P. Pulay, G. Forgarasi, X. Zhou and P.W. Taylor, *Vib. Spectrosc.*, **1**, 159 (1990).
14. H.A. Kramers and W. Heisenburg, *Z. Phys.*, **31**, 681 (1925).
15. J.M.L. Martin and C.V. Alsenoy, *J. Phys. Chem.*, **100**, 15538 (1996).
16. P.B. Nagabalasubramanian, S. Periandy, S. Mohan and M. Govindarajan, *Spectrochim. Acta A*, **73**, 277 (2009).
17. V. Krishnakumar, N. Surumbarkuzhali and S. Muthunatesan, *Spectrochim. Acta A*, **71**, 1810 (2009).