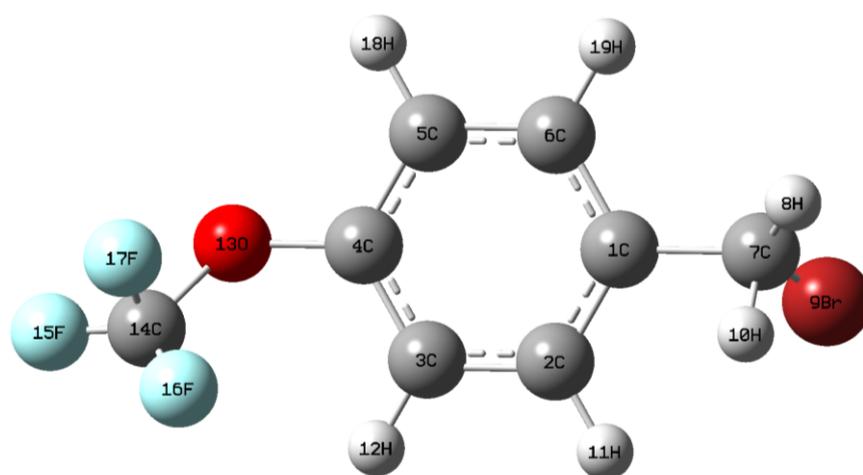


CHAPTER - 6



UV-Vis AND NMR SPECTRAL ANALYSIS OF 4-(TRIFLUOROMETHOXY) BENZYL BROMIDE USING DFT CALCULATIONS

CHAPTER - 6

6.1 INTRODUCTION

The production of benzyl bromide is widely used as a foaming and frothing agent and also involved in the organic synthesis which ultimately released in the environment through various waste streams. Benzyl bromide maybe released in air through automobile exhaust from vehicles using leaded gasoline containing ethylene dibromide (a lead scavenger). If released to air, a vapour pressure of 0.45 mm Hg at 25°C indicates benzyl bromide which will exist solely as a vapour in the ambient atmosphere. Benzyl bromide in its vapour-phase will be ruined in the atmosphere by reaction with photochemical-produced hydroxyl radicals and the half-life period for this reaction in air is estimated to be 7 days. If released to soil, benzyl bromide is expected to have low mobility based upon an estimated K_{oc} of 920. Moreover, mobility in soil may be mitigated based on the hydrolysis of benzyl bromide in water.

Benzyl bromide is expected to undergo a chemical hydrolysis in water and moist soil based on the hydrolysis with the half-life of 79 minutes, thus volatilization from water surfaces, bio concentration in aquatic organisms and adsorption to suspended solids and sediment are not expected to be a significant fate processes. Industrial exposure to benzyl bromide may happen through inhalation and skin contact with this compound at workplaces where benzyl bromide is manufactured or used. Data monitoring is represented that the normal population may have been uncovered to benzyl bromide through inhalationof automobile exhaust from vehicles using leaded gasoline.

Bromophenyl methane is alternatively known as a benzylbromide or bromotoluene. This compound is water immiscible liquid that is corrosive clear with a distinctive smell of paint thinners, redolent of the sweet smell of the associated compound benzene. It is chiefly produced by the bromination of toluene at stable room

temperature in air, using manganese (IV) oxide as a heterogeneous catalyst. It is mainly used in organic synthesis for the involvement of the benzyl protecting group for alcohols and carboxylic acids. It is basically an aromatic hydrocarbon that is extensively used as a feed stock and as a solvent in industries. It is also a general solvent, which has the capacity to dissolve paints, various chemical reactants, paint thinners, painting ink, rubber, glues, lacquers, leather tanners, and many disinfectants with a functional raw material for certain imperative products such as poly urethane foam, phenol and TNT.

In addition, toluene can be used as fullerene indicator and an octant booster in gasoline fuels used in internal combustion engine. Industrial utilization of toluene is dealkylation of benzene and is disproportionate to a mixture of benzene and xylene. In several clinical tests, it is used to break red blood cells in order to take out hemoglobin. Towards electrophilic aromatic substitution, toluene reacts as a normal aromatic hydrocarbon (Wade., 1992; Furnell and Vogel., 1989). To the best of our knowledge, neither quantum chemical calculations nor the ^{13}C and ^1H NMR and UV-Vis spectra have not yet been reported.

6.2 METHODOLOGY

The compound under investigation is 4-(Trifluoromethoxy)benzylbromide (TMB), purchased from Sigma-Aldrich chemicals, USA with spectroscopic grade and it was used as such without any further purification. The absorption spectrum of the compound was analyzed with the instrument from Shimadzu UV-Visible (UV-Vis) spectrometer. The band width on halfheight is 3.0 nm. ^{13}C (100 MHz: CDCl_3) and ^1H (400 MHz: CDCl_3) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker HC400 instrument. Proton chemical shifts were reported in parts per million scales (δ scale) with the downfield from tetramethylsilane (TMS).

6.3 COMPUTATIONAL DETAILS

The quantum chemical calculations (QCC) was done using local spin density approximation (LSDA) methods with 3-21G basis set using the Gaussian 09W program. The electronic absorption spectra for a standardized molecule computed with time dependent density functional theory (TD-DFT) at LSDA/3-21G level of theory. The LSDA method allows calculating the shielding constants with accuracy. The ^{13}C and ^1H NMR isotropic shielding were computed by GIAO method with the help of the standard parameters obtained from LSDA/3-21G method and also includes the effect of solvent on the theoretical NMR parameters by PCM model. The isotropic shielding of stable values was used to compute the isotropic chemical shifts δ with respect totetramethylsilane (TMS).

6.4 RESULTS AND DISCUSSION

The optimized structure and the atom numbering scheme are shown in Figure 6.1.

6.4.1 Analysis of Electronic Structure

The TMB molecule time dependent density functional theory (TD-DFT) employed electronic spectra were calculated on the optimized structure at 6-311+G(d,p) basis set (Perdew *et al.*, 1996; Vijay Solomom *et al.*, 2014). The experimental UV-Visible spectrum of TMB has given in Figure 6.2(a) and the calculated UV-Vis spectrum given in Figure 6.2(b). Experimental and theoretical results were listed in Table 6.1. The calculated result consists of wavelengths, excitation energies and the oscillator strengths. LSDA/3-21G method have predicted two electronic transition in both water and methanol solvents. The maximum absorption in the UV-Visible spectrum was observed at 310 nm and 200 nm in experimentally. The theoretical absorption bands for the title molecule predicted to produce intense bands with ($f=4.9089$) at 280 nm in water, ($f=4.9084$) at 284 nm in methanol, respectively. These bands can be easily assigned to the π/π^* transitions. This conversion involves the

transfer of charge density from methyl group to the benzene ring. The observed band was congruent with the computed values.

6.4.2 Analysis of NMR Spectrum

The experimental NMR spectra of ^{13}C and ^1H of TMB were taken using CDCl_3 as solvent and the recorded spectrum are given in Figure 6.3 (a and b). Also, the theoretical NMR spectra of the title molecule are recreated by LSDA method with 3-21G basis set. Experimentally, the obtained data are compared with the theoretically predicted values and explored the chemical shifts of title molecule from both data. In general, the chemical shifts of aromatic carbons are predicted in the spectrum between 100 ppm and 150 ppm (Kalinowski *et al.*, 1988)

6.4.3 ^{13}C NMR

From the observed spectrum in the experiment, the carbon signals are elevated at 124 to 26 ppm which is assigned for aromatic ring carbons C_1 to C_6 . The C_7 carbon of the benzyl group could be identified easily from the carbon rings by their downfield absorption at 130 ppm. The signals appeared at 142 ppm are appropriate for the methoxy carbon C_{14} in the benzene ring.

6.4.4 ^1H NMR

A coupling constant of 4 and 6.8 ppm yields a doublet of doublet for H_8 and H_{10} . The multiplets were observed for the protons H_{11} , H_{12} , H_{18} and H_{19} with coupling constants between 6.5 and 9.9 ppm. The calculated values were appeared in the region of 6 to 9.6 ppm with four protons having the integral value which is assigned to the aromatic ring protons. The predicted and experimentally observed ppm values are correlated well which are given in Table 6.2.

6.5 CONCLUSION

The UV-Vis spectral analysis, the LSDA method with 3-21G basis set provided an insight into the wave numbers, excitation energies and oscillator strengths which were predicted predominantly with the electronic transitions that makes an outstanding agreement with the experimental data. ^{13}C and ^1H NMR spectra were recorded and the ^{13}C and ^1H NMR isotropic chemical shifts were calculated. The assignments were compared with the experimental values.

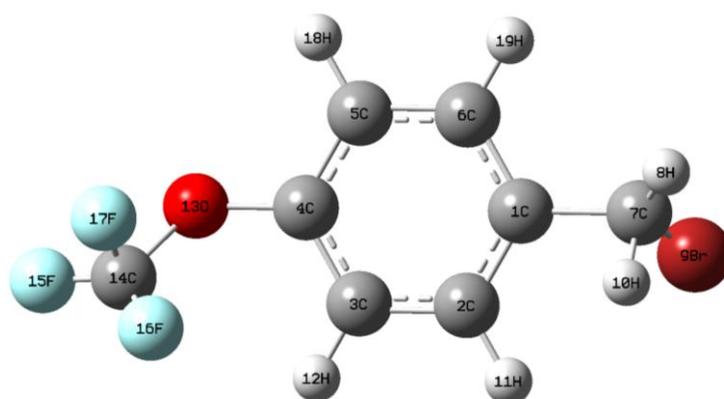


Figure 6.1 The optimized structure of TMB

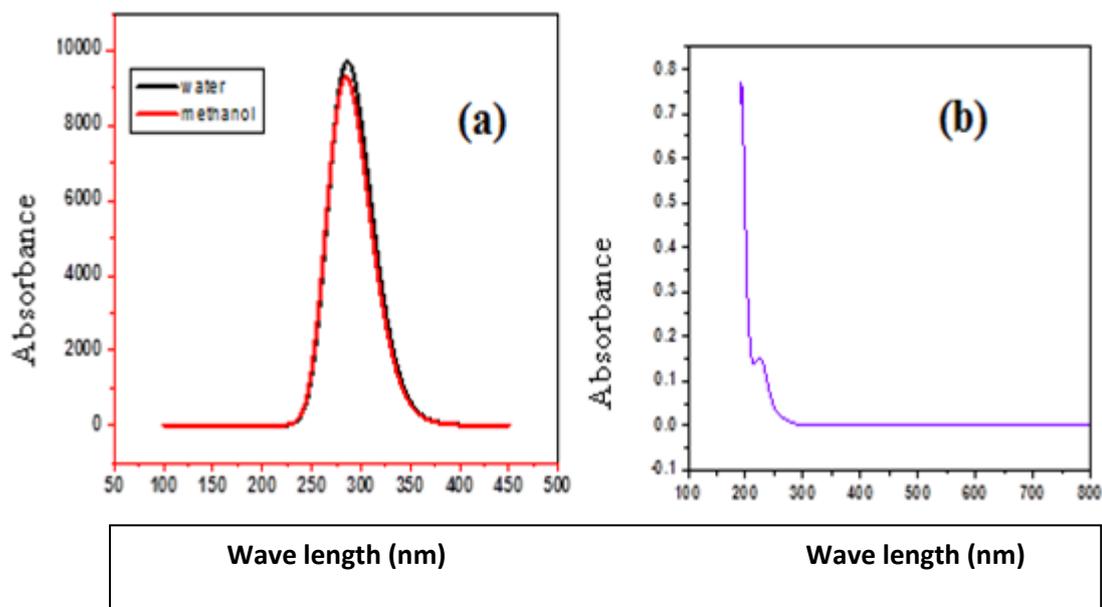
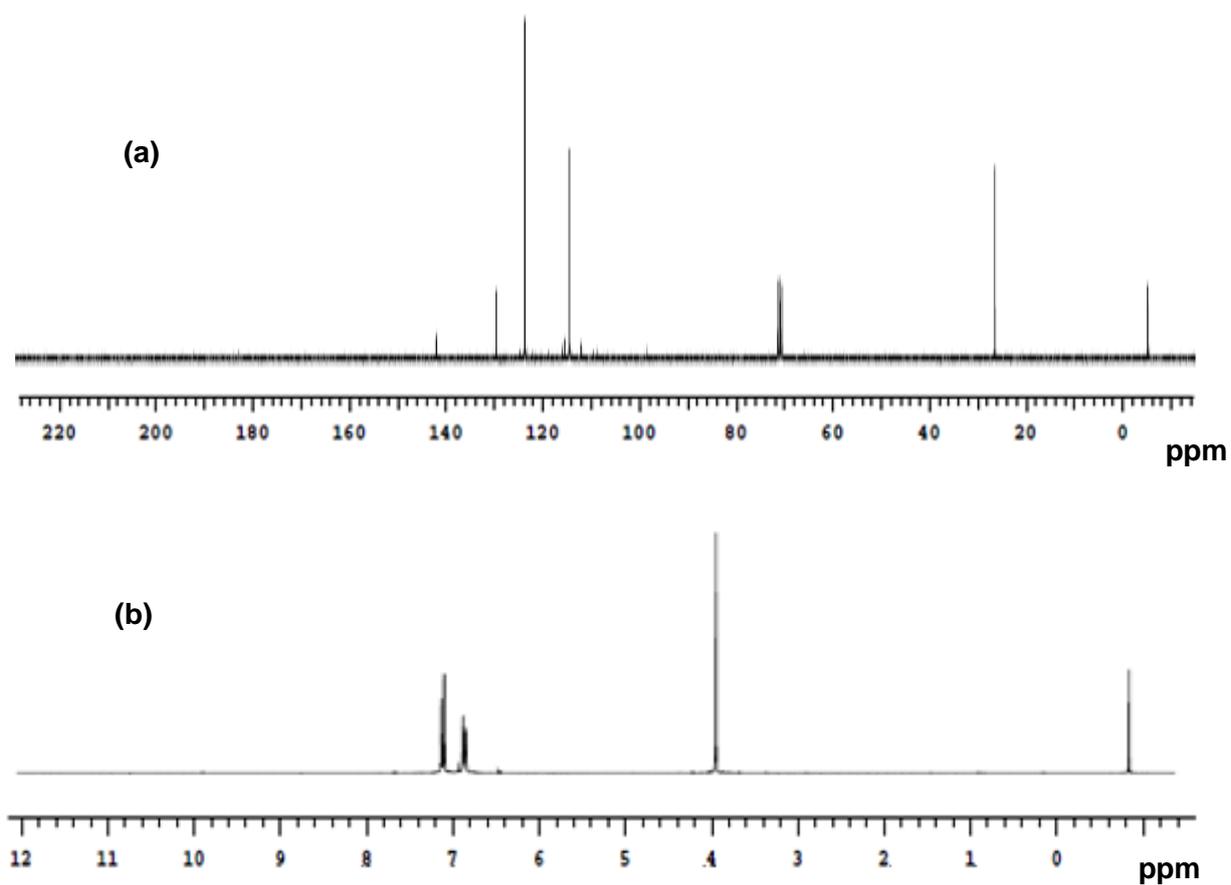


Figure 6.2 UV-Vis Absorbance spectrum of TMB

(a) Experimental

(b) Calculated.



**Figure 6.3 (a) The experimental ^{13}C NMR spectrum of TMB
(b) The experimental ^1H NMR spectrum of TMB.**

Table 6.1 Absorption wavelengths (nm), excitation energies E (eV) and oscillator strengths (f) of its first and second excited state derived from calculation in different media using DFT/LSDA/3-21G method.

Wavelengths (λ in nm)			Excitation energy (eV)		Oscillator strength (f)	
Experimental	Calculated		Water	Methanol	Water	Methanol
	Water	Methanol				
310	280	284	4.9089	4.9084	0.0049	0.0043
200	211	215	4.9078	4.9071	0.0041	0.0038

Table 6.2 The experimental and calculated ^{13}C and ^1H isotropic chemical shifts (ppm) with respect to TMS of TMB.

Atoms	Experimental	Theoretical	Atoms	Experimental	Theoretical
C ₁	26	32	H ₈	4	3.5
C ₂	72	67	H ₁₀	4.2	4.7
C ₃	112	117	H ₁₁	6.8	7
C ₄	115	119	H ₁₂	6.5	6
C ₅	114	112	H ₁₈	7.2	7.5
C ₆	124	118	H ₁₉	9.9	9.6
C ₇	130	135			
C ₁₄	142	142			