

# Vibrational (UV and NMR) Analysis of 4-(Trifluoromethoxy) benzylbromide by Density Functional Theory Calculations

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## ABSTRACT

The energy and oscillator strength are calculated by time-dependent density functional theory (TD-DFT) with the experimental findings for 4-(Trifluoromethoxy) benzylbromide (TMB). <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts results were also compared with the experimental values. Both UV and NMR shielding values calculated using LSDA method with 3-21G basis set.

**Keywords:** TMB, NMR, LSDA.

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## I. INTRODUCTION

Benzyl bromide's production and use as a foaming and frothing agent and in organic synthesis may result in its release to the environment through various waste streams. Benzyl bromide may be released to air in automobile exhaust from vehicles using leaded gasoline containing ethylene dibromide (a lead scavenger). If released to air, a vapor pressure of 0.45 mmHg at 25°C indicates benzyl bromide will exist solely as a vapor in the ambient atmosphere. Vapor-phase benzyl bromide will be degraded in the atmosphere by reaction with photochemical-produced hydroxyl radicals; the half-life 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<sub>oc</sub> of 920. However, mobility in soil may be mitigated based on the hydrolysis of benzyl bromide in water.

Benzyl bromide is expected to undergo chemical hydrolysis in water and moist soil based on a hydrolysis half-life of 79 min thus volatilization from water surfaces, bio concentration in aquatic organisms, and sorption to suspended solids and sediment are not expected to be important fate processes. Occupational exposure to benzyl bromide may occur through

inhalation and dermal contact with this compound at workplaces where benzyl bromide is produced or used. Monitoring data indicated that the general population may have been exposed to benzyl bromide via inhalation of automobile exhaust from vehicles using leaded gasoline.

Bromophenyl methane is also known as a bromotoluene or benzyl bromide. It is a corrosive clear, water insoluble liquid with a typical smell of paint thinners, redolent of the sweet smell of the related compound benzene. It can be prepared by the bromination of toluene at room temperature in air, using manganese (IV) oxide as a heterogeneous catalyst. It is used in organic synthesis for the introduction of the benzyl protecting group for alcohols and carboxylic acids. It is an aromatic hydrocarbon that is widely used as an industrial feed stock and as a solvent. It is also a common solvent, able to dissolve paints, paint thinners, many chemical reactants, rubber, painting ink, glues, lacquers, leather tanners, many disinfectants and a useful raw material for certain important 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 uses of toluene include dealkylation to benzene and disproportionate to a mixture of benzene and xylene. In biochemistry tests it is used to break open red blood cells in order to extract hemoglobin. Towards electrophilic aromatic substitution, toluene reacts as a normal aromatic hydrocarbon [1, 2]. To the best of our knowledge, neither quantum chemical calculations, nor the  $^{13}\text{C}$  and  $^1\text{H}$  NMR and UV-Vis spectra have been reported, as yet.

## II. METHODS AND MATERIAL

### 1. Experimental Details

The compound under investigation namely 4-(Trifluoromethoxy) benzylbromide (TMB) is purchased from Sigma-Aldrich chemicals, U.S.A with spectroscopic grade and it was used as such without any further purification. The absorption spectrum of the compound was also recorded with the Shimadzu UV-Visible (UV-Vis) spectrophotometer. The band width on half height is 3.0 nm.  $^{13}\text{C}$  (100 MHz:  $\text{CDCl}_3$ ) and  $^1\text{H}$  (400 MHz:  $\text{CDCl}_3$ ) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker HC 400 instrument. Chemical shifts for protons are reported in parts per million scales ( $\delta$  scale) downfield from tetramethylsilane (TMS).

### 2. Computational Details

The quantum chemical calculations (QCC) have been performed at local spin density approximation (LSDA) methods with 3-21G basis set using the Gaussian 09W program [23]. The electronic absorption spectra for optimized molecule calculated 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  $^{13}\text{C}$  and  $^1\text{H}$  NMR isotropic shielding were calculated by GIAO method using the optimized parameters obtained from LSDA/3-21G method. The effect of solvent on the theoretical NMR parameters was included using the PCM model. The isotropic shielding constant values were used to calculate the isotropic chemical shifts  $\delta$  with respect to tetramethylsilane (TMS).

## III. RESULTS AND DISCUSSION

The molecular structure and the atom numbering scheme are shown in Figure 1.

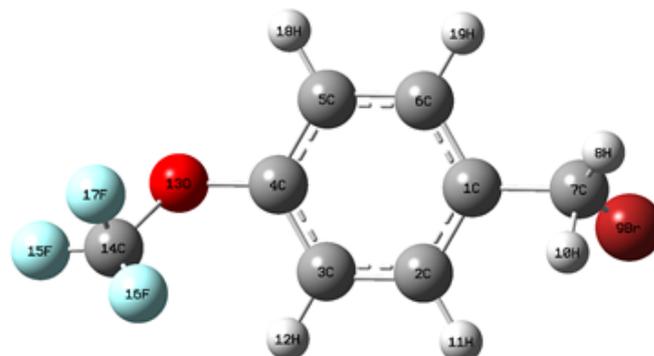
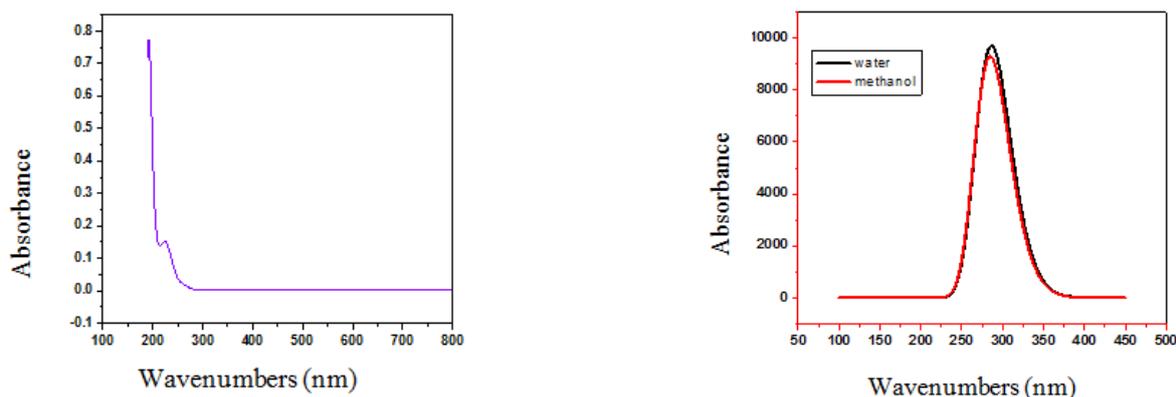


Figure 1. Optimized molecular structure of TMB

### 2.1.1. Electronic Structure Analysis

For the title molecule TMB, time dependent density functional theory (TD-DFT) employed electronic spectra were calculated on the optimized structure at 6-311+G(d,p) basis set [3, 4]. The recorded UV-Visible spectrum of TMB has given in Figure 2 (a) and the calculated UV-Vis spectrum given in Figure 2 (b). Experimental and theoretical results were listed in Table 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 intense bands at 280 nm ( $f=4.9089$ ) in water, at 284 nm ( $f=4.9084$ ) in methanol, respectively. These bands can be easily assigned to the  $\pi/\pi^*$  transitions. This transition involves the transfer of charge density from methyl group to the benzene ring. The observed band was good in agreement with the computed values.



**Figure 2.** Absorbance spectra of TMB (a) Experimental and (b) Calculated.

**Table 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.

Wavenumbers ( $\lambda$ 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

### 3. NMR Spectral Analysis

The experimental NMR spectra of  $^{13}\text{C}$  and  $^1\text{H}$  of TMB were taken using  $\text{CDCl}_3$  as solvent and the recorded spectrum are given in Figure 3 (a and b). Also the theoretical NMR spectra of the title molecule are recreated by LSDA method with 3-21G basis set. Experimentally 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 [5].

#### 3.1 $^{13}\text{C}$ NMR

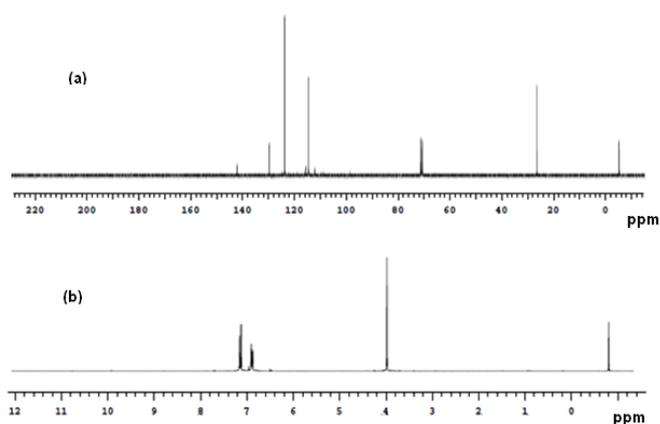
From the observed spectrum, the carbon signals are raised at 124 to 26 ppm which is assigned for aromatic ring carbons  $\text{C}_1$  to  $\text{C}_6$ . The  $\text{C}_7$  carbon of the benzyl group could be identified easily from the ring carbons by their downfield absorption at 130 ppm. The signals appeared at 142 ppm are assigned for the methoxy carbon  $\text{C}_{14}$  in the benzene ring.

#### 3.2 $^1\text{H}$ NMR

Doublet of doublet was observed for  $\text{H}_8$  and  $\text{H}_{10}$  by having a coupling constant of 4 and 6.8 ppm. The multiplets were observed for the protons  $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{18}$  and  $\text{H}_{19}$  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 is assigned to the aromatic ring protons. The predicted and experimentally observed ppm values are correlated well which are given in Table 2.

**Table 2.** The experimental and calculated  $^{13}\text{C}$  and  $^1\text{H}$  isotropic chemical shifts (ppm) with respect to TMS of TMB.

Atoms	Experimental	Theoretical	Atoms	Experimental	Theoretical
$\text{C}_1$	26	32	$\text{H}_8$	4	3.5
$\text{C}_2$	72	67	$\text{H}_{10}$	4.2	4.7
$\text{C}_3$	112	117	$\text{H}_{11}$	6.8	7
$\text{C}_4$	115	119	$\text{H}_{12}$	6.5	6
$\text{C}_5$	114	112	$\text{H}_{18}$	7.2	7.5
$\text{C}_6$	124	118	$\text{H}_{19}$	9.9	9.6
$\text{C}_7$	130	135			
$\text{C}_{14}$	142	142			



**Figure 3.** The experimental (a)  $^{13}\text{C}$  and (b)  $^1\text{H}$  NMR isotropic chemical shifts (ppm) spectra of TMB.

#### IV. CONCLUSION

The UV-Vis spectral analysis, the LSDA method with 3-21G basis set also provided insight the wavenumbers, excitation energies and oscillator strengths were predicted mainly the electronic transitions which were outstanding agreement with the experimental data.  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were recorded and the  $^{13}\text{C}$  and  $^1\text{H}$  NMR isotropic chemical shifts were calculated. The assignments were compared with the experimental values.

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