

Spectral Investigations and *Ab Initio* Hartree-Fock Study of p-Toluenesulfonyl Isocyanate

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ABSTRACT

The molecular structure, electronic spectrum (UV-Vis) and NMR spectra (^{13}C and ^1H) of p-Toluenesulfonyl isocyanate (PTIS) have been studied by Hartree-Fock (HF) method with 6-311++G** basis set. The present calculations reproduce the both experimental spectral characteristics of the PTIS.

Keywords : UV-Vis, HF, PTIS

I. INTRODUCTION

p-Toluenesulfonyl isocyanate (PTIS) is a highly reactive sulfonyl isocyanate. The reactivity of PTIS with water introduced from pigments and solvents in the paints formulation generates carbon dioxide and soluble inert chemical products. This highly reactive sulfonyl isocyanate is also used as an intermediate in the synthesis of other useful chemical compounds [1]. The salts and ester of isocyanic acid are isocyanates. The isocyanate group reacts with the hydroxyl functional group to form a urethane linkage.

They are used in the synthesis for the target molecules such as pharmaceuticals, pesticides, textile softener, lubricants and industrial disinfectants. They can convert to polycyclic compounds such as hydrations and in imidazolons. They are used as plastic additives and as heat treatment salt formulations for metals [2].

The literature search has revealed that *ab initio* Hartree-Fock (HF), UV and NMR analysis have not been reported so far on PTIS. Therefore, the present investigation was undertaken to study the ultraviolet-visible (UV-Vis) and nuclear magnetic resonance (NMR) spectral details of this molecule completely using *ab initio* HF calculation.

II. METHODS AND MATERIAL

The sample p-Toluenesulfonyl isocyanate (PTIS) in the liquid form was purchased from the Lancaster Chemical Company, (UK) with a purity of greater than 98% and it was used as such without further purification. The absorption spectrum of the compound was also recorded with the Shimadzu UV-Visible spectrophotometer. ^1H (400 MHz; CDCl_3) and ^{13}C (100 MHz; CDCl_3) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-AV500 instrument. Chemical shifts for protons are reported in parts per million scales downfield from tetramethylsilane.

The molecular geometrical structure and frequency calculations were carried out for PTIS, with GAUSSIAN 09W software package [3] by HF method with standard 6-311++G** basis set (referred to as "large" basis). The HF method allows calculating the shielding constants with accuracy. The ^{13}C and ^1H NMR isotropic shielding were calculated using the gauge independent atomic orbital (GIAO) method [4, 5] using the optimized parameters obtained from HF/6-311++G** method. The effect of solvent on the theoretical NMR parameters was included using the polarizable continuum model (PCM). The isotropic shielding constant values were used to calculate the isotropic chemical shifts δ with respect to tetramethylsilane (TMS). Wavelengths (λ), oscillator strengths (f) and orbital energies are calculated using same method.

III. RESULTS AND DISCUSSION

The labelling of atoms in PTIS is given in Figure 1. The structure of spectral investigation obtained by *ab initio* HF level with the 6-311++G** basis set.

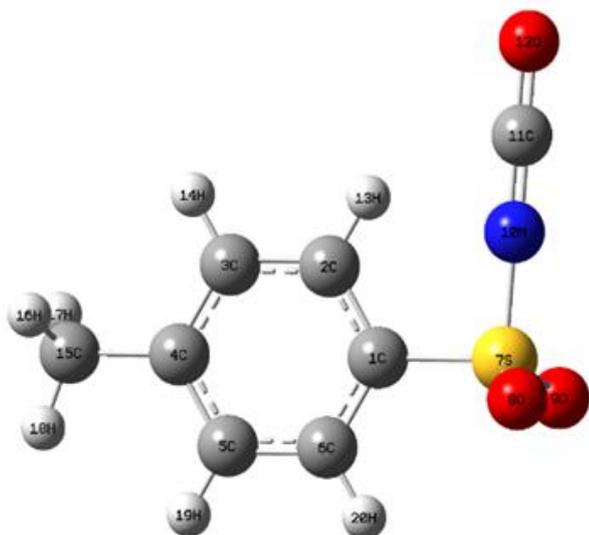


Figure 1. Molecular structure of PTIS

A. UV-Vis (Ultraviolet-Visible) Spectral Analysis

The energies of four important molecular orbitals (MO) of PTIS, the second highest and highest occupied MO's (HOMO and HOMO-1), the lowest and the second lowest unoccupied MO's (LUMO and LUMO +1) were calculated by considering CHCl₃ solvent effect are presented in Table 1. The lowest singlet→singlet spin allowed excited states were taken into account for the time dependent Hartree-Fock (TD-HF) calculation in order to investigate the properties of electronic absorption. The experimental λ_{max} values are obtained from the UV spectrum recorded in CHCl₃. The Figure 2 depicts the observed UV-Vis spectrum of PTIS. The calculated absorption wavelengths (λ_{max}) and the experimental wavelengths are also given in Table 1.

Table 1. Experimental and calculated absorption wavelength (λ), excitation energies (E), oscillator strength (f) and frontier orbital energies of PTIS by HF/6-311++G** method.

Orbitals	Orbital Energies	λ (Expt In Nm)	λ (cal in nm)	E (ev)	Oscillator Strength (f)
E _{HOMO}	-0.282 eV	450	463	4.534	0.0562
E _{HOMO-1}	-0.291 eV		442	4.544	0.0324
E _{LUMO}	-0.061 eV		315	4.657	0.0286
E _{LUMO+1}	-0.052 eV	250	269	4.681	0.0184

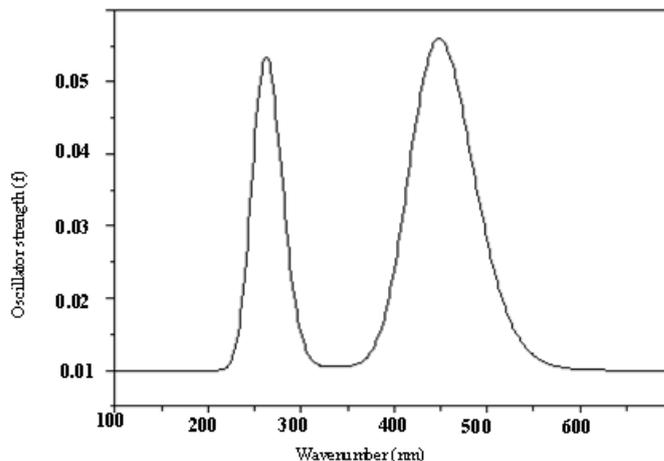


Figure 2. UV-Vis spectrum of PTIS

The strong absorption peak observed at 263.2 nm and the calculated wavelength 256.92 nm is caused by the $\pi \rightarrow \pi^*$ transitions and the other weak bands due to $n \rightarrow \pi^*$ transition are assigned at 301.2 and 291.4 nm and their calculated values are 273.44 and 263.98 nm, respectively [6]. A close agreement has been obtained between the experimental and calculated values of transition energies. TD-HF calculations predict three transitions in the near UV region for PTIS molecule. The strong transitions at 450 (0.0562) and 250 (0.0184) nm have been observed at 300.8 and 239.0 nm, respectively are assigned to a $\pi \rightarrow \pi$ transition. The numbers in parentheses represent oscillator strengths. On the basis of TD-DFT calculations, this shift may be explained as arising out of a larger decrease in the energy of the LUMO orbital (-0.061 eV) than the HOMO (-0.282 eV) and the HOMO-1 (-0.291 eV) orbitals, relative to their positions in PTIS molecule.

B. NMR Spectral Analysis

The observed ¹³C and ¹H NMR spectra of the compound PTIS are given in the Figure 3. The ¹³C and ¹H theoretical and experimental chemical shifts and isotropic shielding of title molecule are presented in Table 2. Aromatic carbons give signals with chemical shift values from 200 to 100 ppm [7, 8]. The observed experimental chemical shift positions of ring carbons of PTIS lie in 131–22 ppm. The effect of sulfur dioxide in the hetero ring of PTIS reduces the electron density of the carbon atom C1, thus its NMR signal is observed in the very downfield at 22 ppm.

Table 2. The experimental (Exp.), calculated (Cal.) ^1H and ^{13}C and isotropic chemical shifts (ppm) with respect to TMS of PTIS using HF level with 6-311++G** basis set.

^1H Assignment	σ_{iso}	Exp.	Cal.	^{13}C Assignment	σ_{iso}	Exp.	Cal.
H13	24.73	2.8	2.5	C1	11.86	22	27
H14	24.68		3.7	C2	26.39		35
H16	24.36	7.5	6.9	C3	63.91		46
H17	24.08		5.8	C4	65.74	80	89
H18	27.56	8.2	8.9	C5	56.79	140	135
H19	27.35		6.3	C6	35.51	145	142
H20	27.69		8.3	C11	125.32	125	118
				C15	135.52	131	129

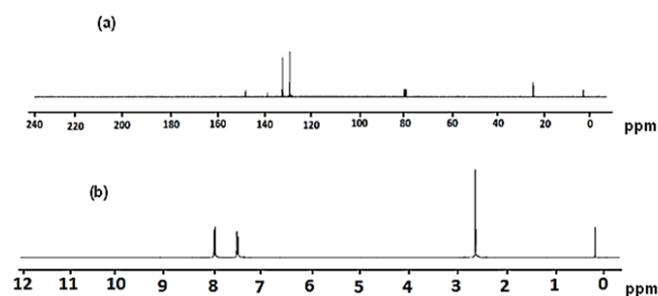


Figure 3. Experimental (a) CNMR and (b) HNMR spectrum of PTIS

Due to the influence of electronegative CH_3 group atoms of chemical shift value of C4 and C15 are also attributed to the upfield NMR signals 89 and 129 ppm, respectively. The carbon atoms C2, C3, C5 and C6 are significantly observed in the upfield with chemical shift values 35, 46, 135 and 142 ppm reveals that the influences of the electronegative hydrogen atoms are negligibly small and their signal are observed in the normal range.

^1H chemical shifts of PTIS were obtained by complete analysis of their NMR spectra and interpreted critically in an attempt to quantify the possible different effects acting on the shielding constant of protons. The hydrogen atoms H13 present in the benzene ring shows NMR peaks in the normal range of aromatic hydrogen atom is assigned to 2.8, The nucleus H13 form a triplet while the other three hydrogen atoms H14, H19 and H20 produced a doublet of doublet. The electron donating effect of methyl group is most pronounced on the chemical shifts of the ring protons H16, H17 and H18. The methyl group protons are put into the upfield at 7.5 and 8.2 ppm shows that these protons are under high magnetic shielding. The calculated and experimental chemical shift values are given in Table 2 shows a good agreement with each other.

IV. CONCLUSION

^{13}C and ^1H NMR spectra were recorded and the ^{13}C and ^1H NMR isotropic chemical shifts were calculated. The assignments made were compared with the experimental values. The UV-vis spectrum was also recorded and the energies of important MO's and the λ_{max} of the compound were also determined from TD-HF method using 6-311++G** basis set. The UV-vis wavelengths are in a good agreement with experimental data.

V. REFERENCES

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