

Spectral (UV and NMR) Analysis Of 4-(Dimethylamino) Benzonitrile 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-(Dimethylamino) benzonitrile (4DMABN). ^{13}C and ^1H NMR chemical shifts results were also compared with the experimental values. Both UV and NMR shielding values calculated using B3LYP method with 6-31+G(d,p) basis set. The calculations have been performed to NLO studies also calculated by density functional theory (DFT-B3LYP) with same basis set.

Keywords: DFT, NMR, UV.

1. INTRODUCTION

Benzonitrile is the [chemical compound](#) with the formula $\text{C}_6\text{H}_5(\text{CN})$, abbreviated as [PhCN](#). This aromatic organic is a colorless liquid with a sweet almond odour. It is mainly used as a precursor to the resin benzoguanamine. Chlorothalonil is a halogenated benzonitrile fungicide with broad-spectrum activity against vegetable, ornamental, orchard and turf diseases. It is available in a wide variety of formulations including suspension concentrates, wet table powders, and water dispersible granules. 4-(Dimethylamino) benzonitrile (hereafter abbreviated as 4DMABN) is a fundamental molecule which attracts much attention in various aspects. One of the unique photophysical character of 4DMABN is the dual fluorescence in polar solvents [1, 2]. This phenomenon is interpreted as a result of simultaneous emission from the locally excited state and the intramolecular charge transferred excited state, the latter of which is stabilized in polar environment [2]. This compound has also attracted attention as a fundamental structure of nonlinear optical materials [3], since the molecule has electron donating (dimethylamino) and accepting (cyano) moieties in both ends of the conjugated π -electron system (benzene ring). The mechanism of the dual fluorescence is sometimes discussed in relation to the excited molecular structure and have been extensively studied by static and time resolved UV/VIS, fluorescence, and other means of spectroscopic methods [4, 5] as well as by theoretical calculations [6]. On the molecular structure of the intramolecular charge transferred state, twisted intramolecular charge transfer model has been proposed [1] and widely accepted until now. However, several other structural models for the intramolecular charge transferred state have also been

proposed recently [6, 7], and this point is still in controversy. Charge transfer reactions are among the most important processes in chemistry and biology. Intermolecular charge transfer in electronically excited states is conveniently studied with spectroscopic techniques. Over the past decades 4DMABN (Fig. 1) has received continuous interest from experimentalists [8] and theoreticians [9] alike. The striking feature of this donor-acceptor compound is the occurrence of dual fluorescence in polar solvents reflecting the existence of two distinct excited-state intermediates. To the best of our knowledge, neither quantum chemical calculations, nor the ^{13}C and ^1H NMR and UV-Vis spectra have been reported, as yet.

2. EXPERIMENTAL DETAILS

The compound under investigation namely 4-(dimethylamino) benzonitrile (4DMABN) 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}C (100 MHz: CDCl_3) and ^1H (400 MHz: CDCl_3) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker HC400 instrument. Chemical shifts for protons are reported in parts per million scales (δ scale) downfield from tetramethylsilane (TMS).

3. COMPUTATIONAL DETAILS

The quantum chemical calculations (QCC) have been performed at B3LYP methods with 6-31+(d,p) basis set using the Gaussian 09W program [10]. We have utilized the gradient corrected density functional theory [11] with the three parameter hybrid functional (B3) [12] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [13], accepted as a cost effective approach for the computation of optimized structures. The electronic absorption spectra for optimized molecule calculated with time dependent density functional theory (TD-DFT) at B3LYP/6-31+G(d,p) level of theory. The DFT method allows calculating the shielding constants with accuracy. The ^{13}C and ^1H NMR isotropic shielding were calculated by GIAO method using the optimized parameters obtained from B3LYP/6-31+G(d,p) level of theory. 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 (δ in ppm) with respect to tetramethylsilane

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(TMS).

4. RESULTS AND DISCUSSION

4.1. Non-Linear Optical Analysis

The molecular structure and the atom numbering scheme are shown in Figure 1. Non-linear optical deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wave number, phase or other physical properties [14]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing [15, 16]. Organic materials have been shown in recent years to possess superior second-order nonlinear optical properties compared to the more traditional inorganic materials. This property together with the inherent ultra-fast response time and enumerable structure variations of organic materials has drawn a sizeable amount of research interest in organic nonlinear optical (NLO) materials. In this context, the first hyperpolarizability was also calculated in the present study. First hyperpolarizability by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components to the Kleinman symmetry [17]. Since the value of polarizabilities and the hyperpolarizability of Gaussian output is reported in a atomic mass units (a.u.), the calculated values have been converted into electrostatic units (esu) (α : 1 a.u.= 0.14482×10^{-24} esu β : 1 a.u.= 0.0086×10^{-30} esu). The results of electronic dipole moment μ_i (i=x,y,z) polarizability α_{ij} and first order hyperpolarizability [18] β_{ijk} are listed in Table 3. The calculated first hyperpolarizability values of the all the three compounds are greater than that of the standard NLO materials urea [19] (0.13×10^{-30} esu), concluding that all the three compounds can be used as nonlinear optical material. Urea is the classical molecule used in the study of the NLO properties of the molecular systems and is used often as a threshold value for comparative purposes. The dipole moment of 4DMABN is calculated to be $\mu = 5.681$ Debye with maximum contribution from X direction. In Y and Z directions, dipole moment is practically negligible. The calculated dipole moment for title molecule is given in Table 1. The first static hyperpolarizability value is found to be appreciably higher 8.672×10^{-24} .

Fig. 1. The molecular structure with atom numbering of 4DMABN

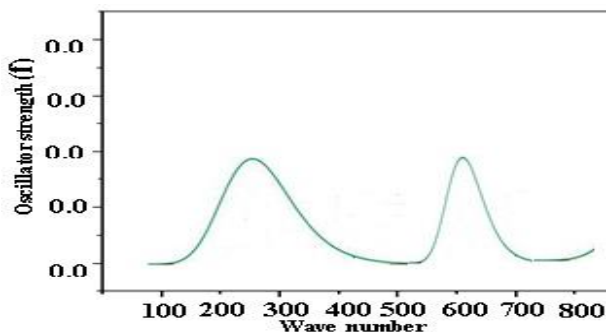


Table 1. Electric dipole moment (Debye), average polarizability ($\alpha_0 \times 10^{-24}$ esu), first hyper polarizability ($\beta_0 \times 10^{-24}$ esu) for 4DMABN calculated by B3LYP with 6-31+G(d,p) basis sets.

Parameters	6-31+G(d,p)	Parameters	6-31+G(d,p)
μ_x	-3.6124	β_{xxx}	-7.2043
μ_y	1.5418	β_{xyy}	-7.045
μ_z	-0.1565	β_{xyy}	-22.31
μ	5.681	β_{yyy}	45.79
α_{xx}	-99.245	β_{xzx}	6.567
α_{xy}	-1.487	β_{xzy}	-5.369
α_{yy}	106.653	β_{yyz}	4.987
α_{xz}	-1.451	β_{xzz}	8.987
α_{yz}	-3.943	β_{yzz}	-2.427
α_{zz}	-94.357	β_{zzz}	0.7056
α_0	-99.418	β_0	8.672

4.2. 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 6-31+G(d,p) basis set [20,21]. The recorded UV-Visible spectrum of 4DMABN has given in Figure 2. Experimental and theoretical results were listed in Table 2. The calculated result consists of wavelengths, excitation energies and the oscillator strengths. B3LYP method with 6-31+G(d,p) have predicted using water solvent. The maximum absorption in the UV-Visible spectrum was observed at 615 nm and 250 nm in experimentally. The theoretical absorption bands for the selected molecule predicted intense bands at 618.05 nm ($f=0.0885$) in water. These bands can be easily assigned to the π/π^* 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.

Table 2. Experimental and calculated absorption wavelength (nm), excitation energies (eV), oscillator strength (f) of 4DMABN by B3LTP/6-31+G(d,p) method.

Excitation states	Excitation energies (eV)	Wavelength (nm)		Oscillator strength (f)
		Experimental	Theoretical	
1	2.6524	615	618.05	0.0885
2	3.6588		534.86	0.0456
3	3.8997		412.27	0.0054
4	3.9865		366.35	0.0069
5	4.4029	250	258.77	0.0363
6	4.5230		235.67	0.0054

4.3. NMR Spectral Analysis

The experimental NMR spectra of ^{13}C and ^1H of 4DMABN were taken using 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 B3LYP method with 6-31+ (d, p)G 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 [22].

4.3.1. ^{13}C NMR

From the observed spectrum, the carbon signals are raised at 121 to 52 ppm which is assigned for aromatic ring carbons C1 to C6. The C7 carbon of the benzyl group could be identified

easily from the ring carbons by their downfield absorption at 125 ppm. The signals appeared at 131 and 145 ppm are assigned for the methyl carbon C12 and C16 in the benzene ring.

4.3.2. ^1H NMR

Doublet of doublet was observed for H17 and H20 by having coupling constant of 7.5 and 6.7 and ppm. The multiplets were observed for the protons H14 with coupling constant 3.3 ppm. The calculated values were appeared in the region of 7.51 to 6.57 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.

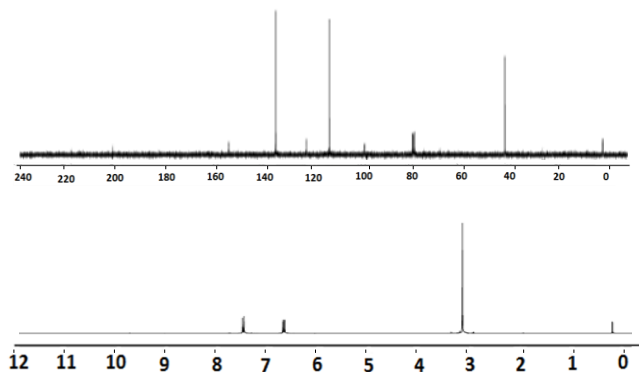


Table 3. Experimental and theoretical ^{13}C and ^1H chemical shift (δ in ppm) of 4DMABN.

Atoms	Theoretical Shift (ppm)	Experimenta - Shift (ppm)	Atoms	Theoretical Shift (ppm)	Experimenta - Shift (ppm)
C1	52	44	H9	6.57	
C2	88	78	H10	6.75	
C3	112	114	H13	7.29	
C4	105	103	H14	4.44	3.3
C5	121	-	H15	5.63	
C6	93	-	H17	6.74	6.7
C7	125	-	H18	4.58	
C12	145	156	H19	6.23	
C16	131		H20	7.51	7.5
			H21	6.92	

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