

Structure, Spectroscopic Measurement of 4-(Diethoxymethyl) benzaldehyde

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ABSTRACT

The structural of 4-(Diethoxymethyl)benzaldehyde (DTMB) are determined by B3LYP method with 6-311++G** basis set. The fundamental vibrations are analyzed with the help of FT-IR (4000-400 cm⁻¹) and FT-Raman (3500-100 cm⁻¹) spectra. The theoretically calculated vibrational frequencies are compared with experimental FT-IR and FT-Raman frequencies. The ¹H and ¹³C NMR spectra have been analyzed and compared with theoretical ¹H and ¹³C NMR chemical shifts calculated by gauge independent atomic orbital (GIAO) method.

Keywords: DTMB, NMR, B3LYP

I. INTRODUCTION

Benzaldehyde does not possess α -hydrogen, therefore, benzaldehyde cannot form enolate (enol) reaction intermediates. This precludes intermolecular aldol condensation reactions. The electronic character of phenyl ring is perfectly suited for the benzoin condensation. Electron donating substituents on the phenyl ring inhibit benzoin condensation because the carbanion intermediate is destabilized. Conversely, electron withdrawing groups on the phenyl ring stabilize the analogous carbanion and subsequent nucleophilic addition reaction will not occur.

Benzaldehyde is the simplest aromatic aldehyde and the substitution of a functional group in benzaldehyde changes the spectra markedly. The vibrational spectra of benzaldehyde and its derivatives have been extensively investigated by many earlier researchers [1, 2]. In the present study 4-(Diethoxymethyl)benzaldehyde have been discussed.

II. EXPERIMENTAL DETAILS

The compound under investigation namely 4-(Diethoxymethyl)benzaldehyde (DTMB) is purchased from Sigma-Aldrich chemicals, U.S.A with spectroscopic grade and it was used as such without any further purification. The band width on half height is 3.0 nm. ¹³C (100 MHz: CDCl₃) and ¹H (400 MHz: CDCl₃)

nuclear magnetic resonance (NMR) spectra were recorded on a Bruker HC 400 instrument. Chemical shifts for protons are reported in parts per million scales (δ scale) downfield from tetramethylsilane (TMS).

III. COMPUTATIONAL DETAILS

Quantum chemical calculations (QCC) were carried out for DTMB with Gaussian 09W program package [3] using the Becke's three-parameter (B3) hybrid functional with Lee-Yang-Parr (LYP) correlation functional [4, 5] with the standard 6-311++G** basis set. We have scaled the numbers with standard scaling factor 0.965.

The Raman activities (S_i) calculated by the Gaussian 09W program was converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [6, 7].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i / KT)]} \quad (1)$$

where ν_0 is the laser exciting wavenumber in cm⁻¹ (in this work, we have used the excitation wavenumber $\nu_0 = 9398.5$ cm⁻¹, which corresponds to the wavelength of 1064 nm of a Nd:YAG laser), ν_i is the vibrational wavenumber of the i^{th} normal mode (cm⁻¹), while S_i is the Raman scattering activity of the normal mode ν_i , f (is a constant equal to 10^{-12}) is a suitably chosen common

normalization factor for all peak intensities h , k , c and T are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.

3.1. Result and Discussion

The maximum number of potentially active observable fundamentals of a non-linear molecule which contains N atoms is equal to $(3N-6)$, apart from three translational and three rotational 6 degrees of freedom [8, 9]. The DTMB molecule (Figure 1), that was planar, has 17 atoms with 45 normal modes of vibrations and considered under $C1$ point group symmetry. All vibrations are active both in Raman and infrared absorption. The experimental and theoretical FT-IR and FT-Raman spectra of title molecule are shown in Figure 2 and 3, respectively.

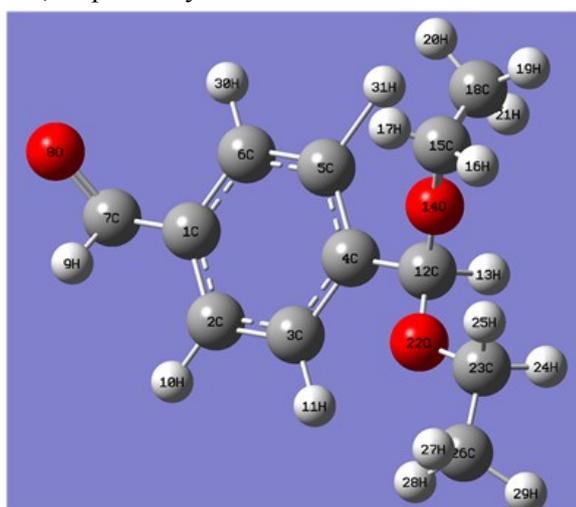


Figure 1. Molecular structure of 4-(Diethoxymethyl) benzaldehyde.

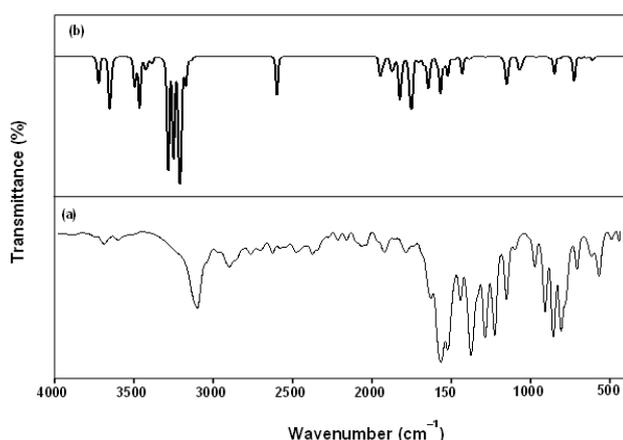


Figure 2. The FT-IR spectra of DTMB (a) Experimental (b) Calculated by B3LYP/6-311++G** method.

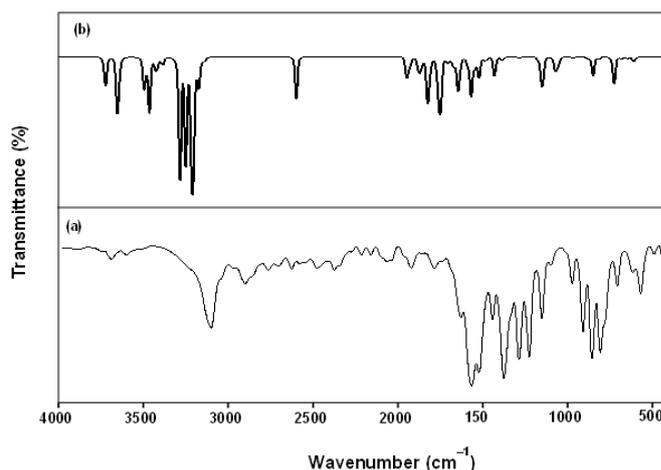


Figure 2. The FT-IR spectra of DTMB (a) Experimental (b) Calculated by B3LYP/6-311++G** method.

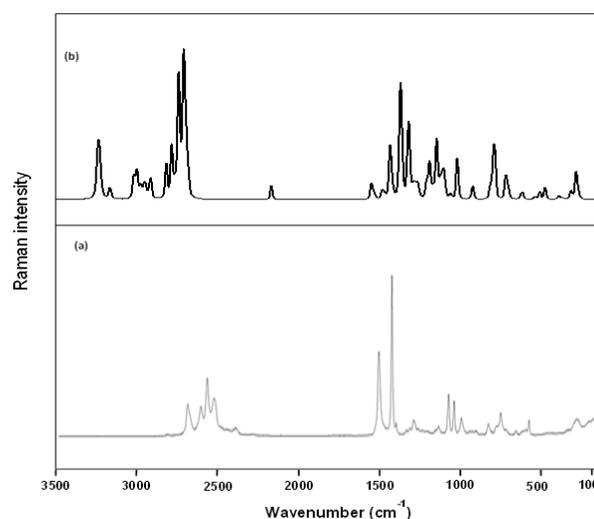


Figure 3. The FT-Raman spectra of DTMB (a) Experimental (b) Calculated by B3LYP/6-311++G** level of theory.

3.1.1 C–H Vibrations

The carbon and hydrogen atoms are only bonded by single covalent bonds in DCDNB. In this gives rise to two C–H stretching; two C–H in-plane bending vibrations and two C–H out-of-plane bending vibrations. The hetero aromatic structure shows the presence of C-H stretching vibration in the region $3100-3000\text{ cm}^{-1}$ which is the characteristic region for the ready identification of C-H stretching vibration [10]. In this region, the bands are not affected appreciably by the nature of substituents. The C-H stretching mode usually appears with strong Raman intensity and is highly polarized. In the FT-IR spectrum of title molecule, the strong and medium bands at 3118 and 2700 cm^{-1} is assigned to C-H stretching vibration of hetro cyclic group. The counter part of the FT-Raman spectrum at 2715 cm^{-1} are attributed to C-H

stretching vibration. The theoretically computed wavenumber by B3LYP method fall at 3063, 3042, 3011, 2975, 2942 and 2862 cm^{-1} are assigned to C-H stretching vibrations.

The C-H in-plane bending frequencies appear in the range 1000-1300 cm^{-1} and are very useful for characterization purpose [11]. For our title molecule, the C-H in-plane bending vibrations appear as a strong band in FT-IR spectrum at 1318, 1229 cm^{-1} and 1108 cm^{-1} as a very weak band in FT-Raman spectrum shows good agreement with calculated frequencies. The C-H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 1000-750 cm^{-1} [12]. The aromatic C-H out-of-plane bending vibrations are assigned in FT-IR and FT-Raman spectra at 1000, 620, 598, 525 cm^{-1} and 1040, 642, 580 cm^{-1} well correlated with theoretically calculated values.

3.1.2 CH₃ Vibration

The title compound DTMB possesses one CH₃ group on the side substitution chain. For the assignment of CH₃ group frequencies, nine fundamental can be associated with each CH₃ group. The CH stretching in CH₃ occurs at lower frequencies than those of aromatic ring at 3100-3000 cm^{-1} . Moreover, the asymmetric stretch is usually at higher frequencies than the symmetric stretch. The asymmetric and symmetric bending vibrations of methyl groups normally appear in the region 1470-1440 cm^{-1} and 1390- 1370 cm^{-1} , respectively. In the present work, the CH₃ asymmetric vibrations are assigned at 3450vw and 3400s cm^{-1} in FT-IR spectrum. These assignments were also supported by literature [10] in besides to PED output. The bands at 1356 and 1345 cm^{-1} in B3LYP method are assigned CH₃ bending vibration, these vibration is observed in FT-IR spectrum at 1456m. The band in FT-IR spectrum at 1400vsm cm^{-1} and FT-Raman spectrum at 1425vs cm^{-1} are assigned CH₃ symmetric deformation vibration. The rocking vibrations of the CH₃ group in title molecule appear at 1125s in FT-IR spectrum. These modes usually appear in the region 1070-900 cm^{-1} [13, 14]. All these calculated values are in good agreement with the observed values.

3.1.3. NH₂ Vibrations

The molecule under consideration possesses NH₂ group in pyrimidine ring and hence six internal modes of vibrations are possible such as: (i) the symmetric

stretching (ν_{sym}), (ii) asymmetric stretching (ν_{asym}), (iii) Scissoring (δ), (iv) Rocking (ρ), (v) wagging (ω), (vi) torsional mode (ϕ). In primary amines, usually the N-H stretching vibrations occur in the region 3500-3300 cm^{-1} [15]. The NH₂ group has two vibrations: one is being asymmetric and other symmetric. The frequency of asymmetric vibration is higher than that of symmetric one. In the present study, the asymmetric vibrations of N-H stretching are assigned in FT-IR and FT-Raman bands at 2420, 1750 and 2415 cm^{-1} . In the title molecule, theoretically calculated frequency agrees with experimental frequency. The N-H in-plane bending vibration (scissoring) are usually observed in the region 1630-1610 cm^{-1} [15] and the out-of-plane bending vibrations are normally identified in the region 1150-900 cm^{-1} [11].

The strong FT-IR and FT-Raman bands at 1560 and 1550 cm^{-1} is assigned to the NH₂ group scissoring vibration. In our calculations, the theoretical values at 1415 and 1394 cm^{-1} corresponds well with the experimental results. In present investigation, the very weak FT-IR band at 1500 cm^{-1} is assigned to rocking vibration. The theoretically values at 1436 and 1365 cm^{-1} are agree with the experimental values. A noticeable deviation appeared between the scaled and experimental wavenumbers of the wagging vibration, likely due to its anharmonicity [16] or hydrogen bonding [17]. The wagging vibrations are assigned to the weak FT-Raman band at 1000 cm^{-1} for DTMB.

The torsion vibrations are calculated at 408 and 355 cm^{-1} . In accordance with the FT-Raman band at 344 and 265 cm^{-1} , those observed for aniline [16]. According to the literature, these assignments agree well with the literature [18]. The N-H vibrations of present molecule affect the other vibrational modes whereas the N-H vibrations themselves do not get affected by vibrations of other substitutions.

IV. NMR SPECTRAL ANALYSIS

The ¹³C and ¹H NMR chemical shifts are calculated within gauge independent atomic orbital (GIAO) method using B3LYP /6-311++G** method. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift molecular structure relationship.

The experimental ^{13}C and ^1H NMR spectra of the title compound are given in Fig. 4 ((a) ^{13}C and (b) ^1H). In Table 2, the experimental and the theoretical ^{13}C and ^1H isotropic chemical shifts in ppm for the title compound are presented. The ^{13}C chemical shift values for all calculations have the range from 183.657 to 33.354 ppm at B3LYP/6-311++G** level of theory for DTMB. Downfield and Upfield chemical shift values observed at 195 and 18 ppm of carbons C15 and C7 are due to electron donating effect of methyl group. The ring carbon atoms C1, C2, C3, C4, C5 and C6 are significantly observed in the upfield with chemical shift values 150, 66, 142, 106, 132 and 80 ppm, respectively reveals that the influences of the electronegative nitrogen and methyl group atoms are negligibly small and their signal are observed in the normal range.

The ^1H chemical shift values for all calculations have 9.321 to 2.643 ppm at B3LYP/6-311++G** method for DTMB molecule. As can be seen from Table 2, theoretical ^{13}C and ^1H chemical shift results of the title compound are generally closer to the corresponding experimental chemical shift data. The small shifts can be explained as a consequence of the change in the molecular environment.

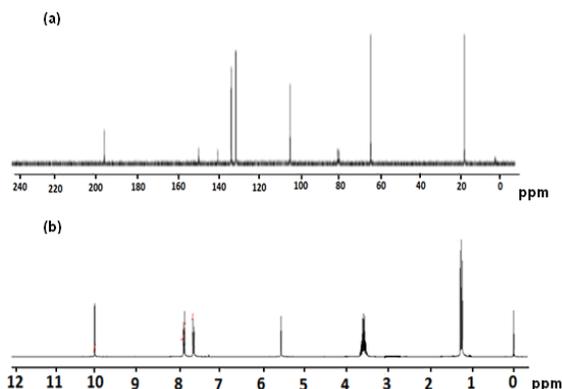


Figure 4. The experimental (a) ^{13}C and (b) ^1H NMR spectra of DTMB.

V. CONCLUSION

The FT-IR, FT-Raman and ^{13}C and ^1H NMR spectra of the compound DTMB have been recorded and analyzed. The detailed interpretations of the vibrational spectra have been studied. The observed wavenumbers are found to be in good agreement with the theoretically calculated values. The obtained optimized geometric

parameters, ^{13}C and ^1H NMR chemical shifts results seemed to be in a good agreement with experimental data.

VI. REFERENCES

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