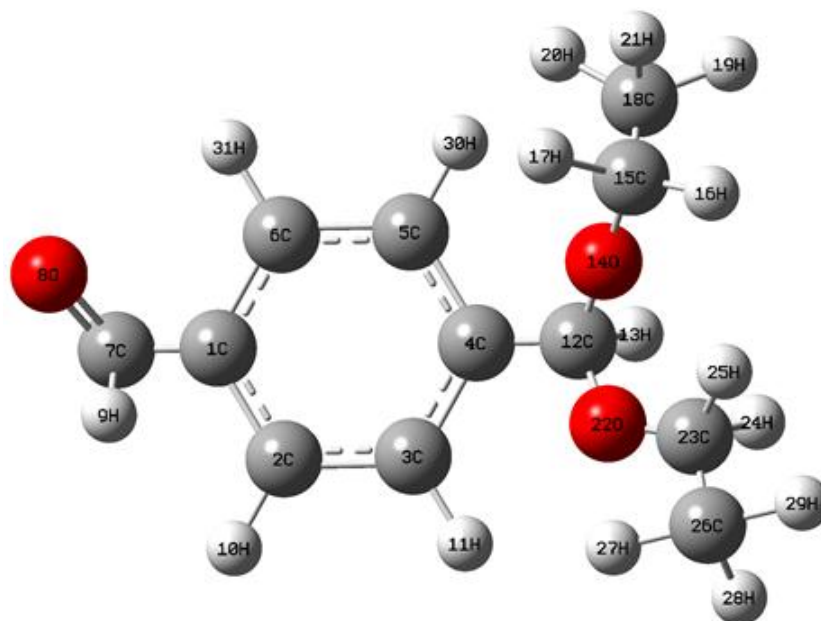


CHAPTER - 8



EVALUATION OF THE STRUCTURE AND SPECTROSCOPIC MEASUREMENT OF 4-(DIETHOXYMETHYL)BENZALDEHYDE

CHAPTER – 8

8.1. INTRODUCTION

Benzaldehyde does not possess α -hydrogen, and therefore, benzaldehyde cannot form enolate (enol) reaction intermediates. This precludes intermolecular aldol condensation reactions. The characteristic feature of electrons in phenyl ring perfectly suits for the benzoin condensation. Electron donating substituents on the phenyl ring inhibiting benzoin condensation because the carbanion intermediate is destabilized. On the other hand, the electron withdrawing groups on the phenyl ring stabilize the analogous carbanion and subsequent nucleophilic addition reaction which will not take place.

Benzaldehyde is one of the essential aromatic aldehyde and the substitution of a functional group in benzaldehyde that changes the spectra markedly. The vibrational spectra of benzaldehyde and its derivatives have been extensively investigated by many earlier researchers (Katti *et al.*, 1992; Mathew *et al.*, 1993). In the present study, 4-(Diethoxymethyl)benzaldehyde have been discussed.

8.2 METHODOLOGY

The compound under investigation namely 4-(Diethoxymethyl)benzaldehyde (DEMB) is purchased from Sigma-Aldrich chemicals, USA with spectroscopic grade and it was used as such without any further purification. The band width and 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 HC 400 instrument. Chemical shifts for protons are reported in parts per million scales (δ scale) downfield from tetramethylsilane (TMS).

8.3 COMPUTATIONAL DETAILS

Quantum chemical calculations (QCC) were carried out for DTMB with Gaussian 09W program package (Frisch *et al.*, 2004) using the Becke's three-parameter (B3) hybrid functional with Lee-Yang-Parr (LYP) correlation functional with the standard 6-311++G** basis set (Becke., 1993; Lee and Yang., 1998). We have scaled the numbers with standard scaling factor of 0.965.

The activities of Raman (S_i) calculated by the Gaussian 09W program was converted to the relative Raman intensities (I_i) using the subsequent relationship obtained from the intensity theory of Raman scattering (Keresztury *et al.*, 1993; 2002).

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i / KT)]} \quad (8.1)$$

Where ν_0 is the laser exciting wave number in cm^{-1} (we have used the excitation wave number $\nu_0 = 9398.5 \text{ cm}^{-1}$) which relates to the wavelength of 1064 nm of a Nd:YAG laser), ν_i is the vibrational wave number 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 that are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.

8.4 RESULTS 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 degrees of freedom (Silverstein *et al.*, 1991; Socrates., 2001). The 4-(diethoxymethyl)benzaldehyde molecule (Figure 8.1), that was planar, has 17 atoms with 45 normal modes of vibrations and considered under C_1 point group symmetry. All vibrations are mostly active that are both in Raman and infrared absorption. The experimental and theoretical FT-IR and FT-Raman spectra of title molecule are shown in Figure 8.2 and 8.3, respectively.

8.4.1 C–H Vibrations

The carbon and hydrogen atoms are only bonded by single covalent bonds in DCDNB. It 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 predicts the presence of C–H stretching vibration in the region 3100–3000 cm^{-1} which is the featuristic region for the complete identification of C–H stretching vibration (Saravanan *et al.*, 2017). In this region, the bands are not affected substantially 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} are assigned to C–H stretching vibration of hetero cyclic group. The counter part of the FT-Raman spectrum at 2715 cm^{-1} is 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 (Varsanyi., 1969). 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} (Sebastian *et al.*, 2011). 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} is well correlated with theoretically calculated values.

8.4.2 CH₃ Vibrations

The title compound DEMB possesses one CH₃ group on the side substitution chain. For the assignment of CH₃ group frequencies, nine fundamentals 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} . In addition, the asymmetric stretch is normally at a better frequencies than the symmetric stretch. The asymmetric and symmetric bending vibrations of methyl groups generally come into view in the region 1390–1370 cm^{-1} and 1470–1440 cm^{-1} respectively. In the present work, the CH₃

asymmetric vibrations are assigned at 3450 (vw) and 3400 (s) cm^{-1} in FT-IR spectrum. These assignments were also supported by literature (Saravanan *et al.*, 2017) in besides to PED output. The bands at 1356 and 1345 cm^{-1} in B3LYP method are assigned CH_3 bending vibration, and these vibrations are observed in FT-IR spectrum at 1456 cm^{-1} . The band in FT-IR spectrum at 1400 (vsm) cm^{-1} and FT-Raman spectrum at 1425 (vs) cm^{-1} are assigned with CH_3 symmetric deformation vibration. The rocking vibrations of the CH_3 group in title molecule appear at 1125 (s) cm^{-1} in FT-IR spectrum. These modes generally appear in the region 1070 – 900 cm^{-1} (Dollish *et al.*, 1997). All these calculated values are in good agreement with the observed values (Table 8.1).

8.4.3 Analysis of NMR Spectrum

The ^{13}C and ^1H NMR chemical shifts are calculated within gauge independent atomic orbital (GIAO) method using B3LYP /6-311++G** method. An assessment of the investigational and theoretical spectra can be very functional in making proper 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 Figure 8.4 ((a) ^{13}C and (b) ^1H). In Table 8.2, 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 which reveals that the influences of the electronegative nitrogen and methyl group atoms are negligibly small and their signals 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 8.2, theoretical ^{13}C and ^1H chemical shift results in the title compound that 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.

8.5 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 wavenumber 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.

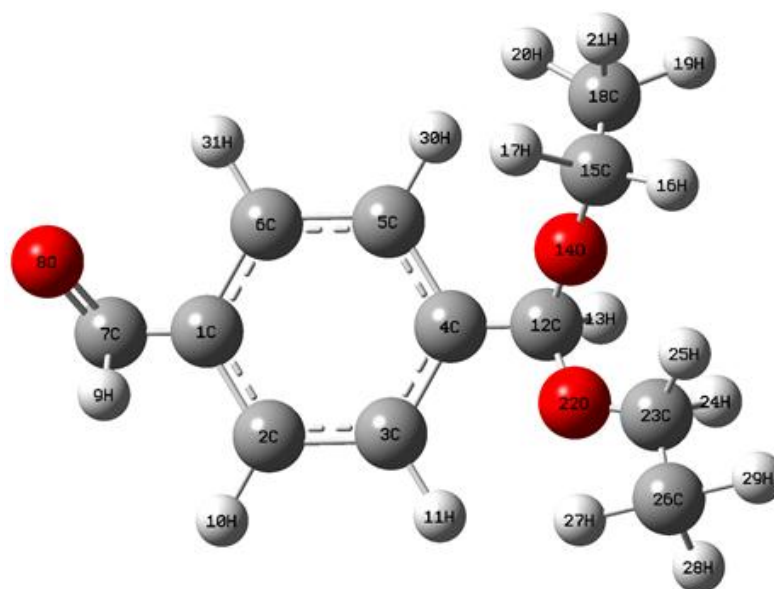


Figure 8.1 The optimized structure of DEMB

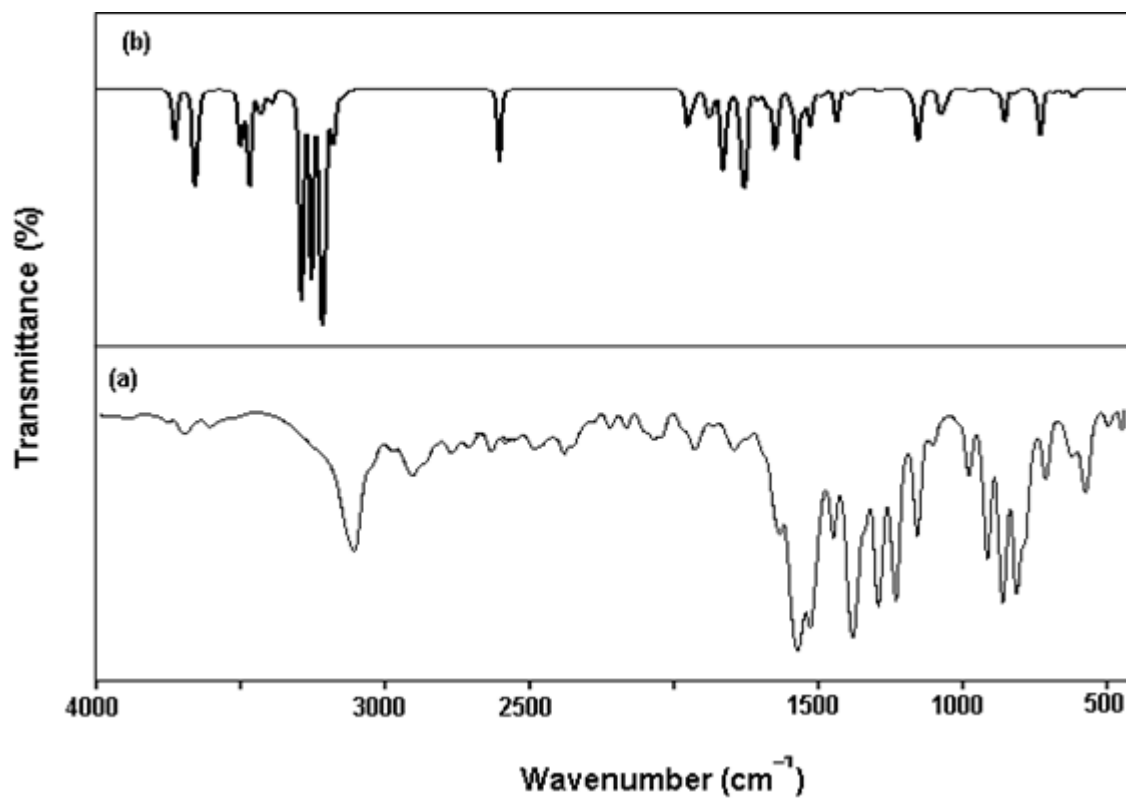


Figure 8.2 The FT-IR spectra of DEMB (a) experimental (b) calculated by B3LYP/6-311++G** method

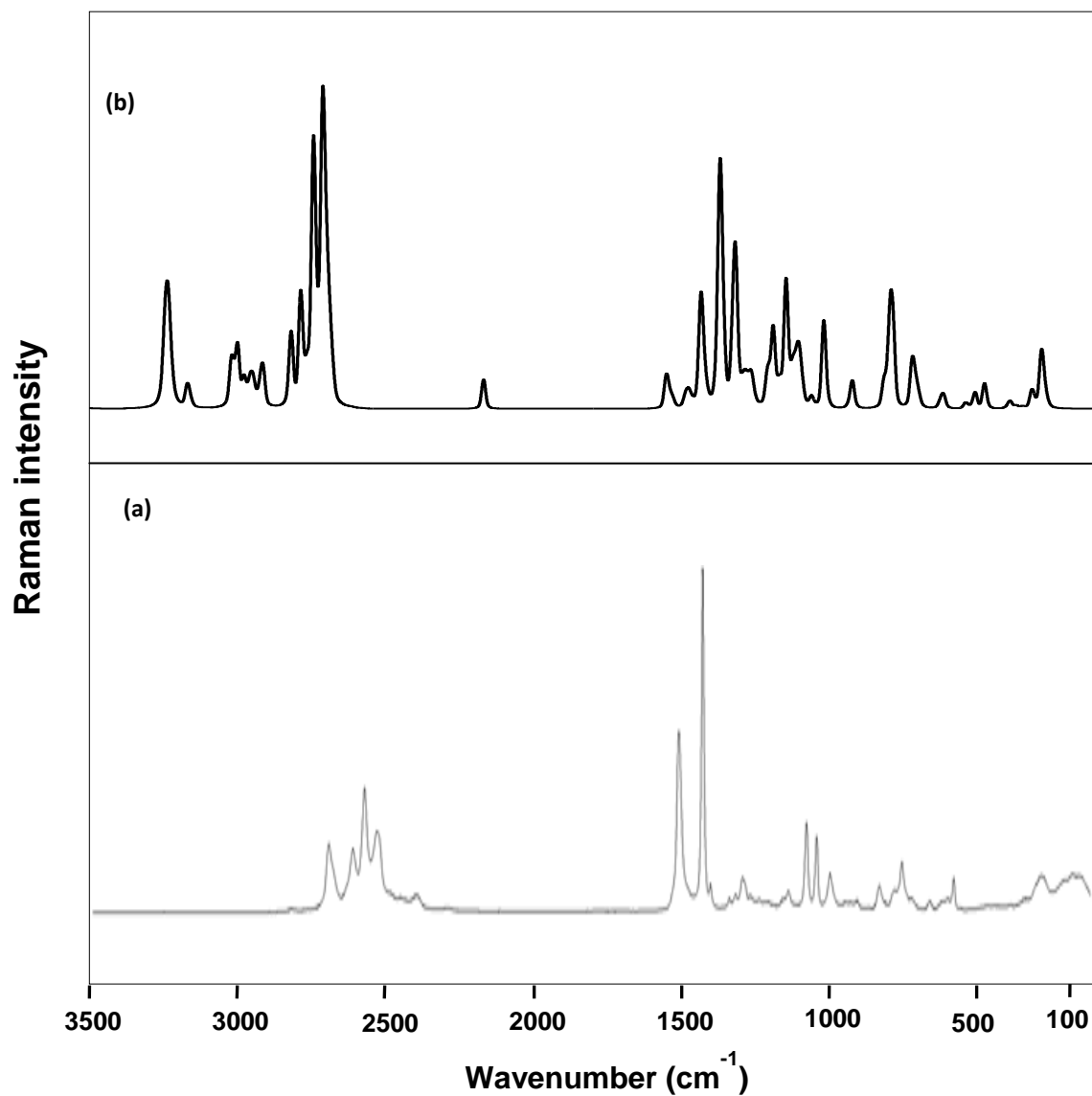


Figure 8.3 The FT-Raman spectra of DEMB (a) Experimental
(b) Calculated by B3LYP/6-311++G** level of theory.

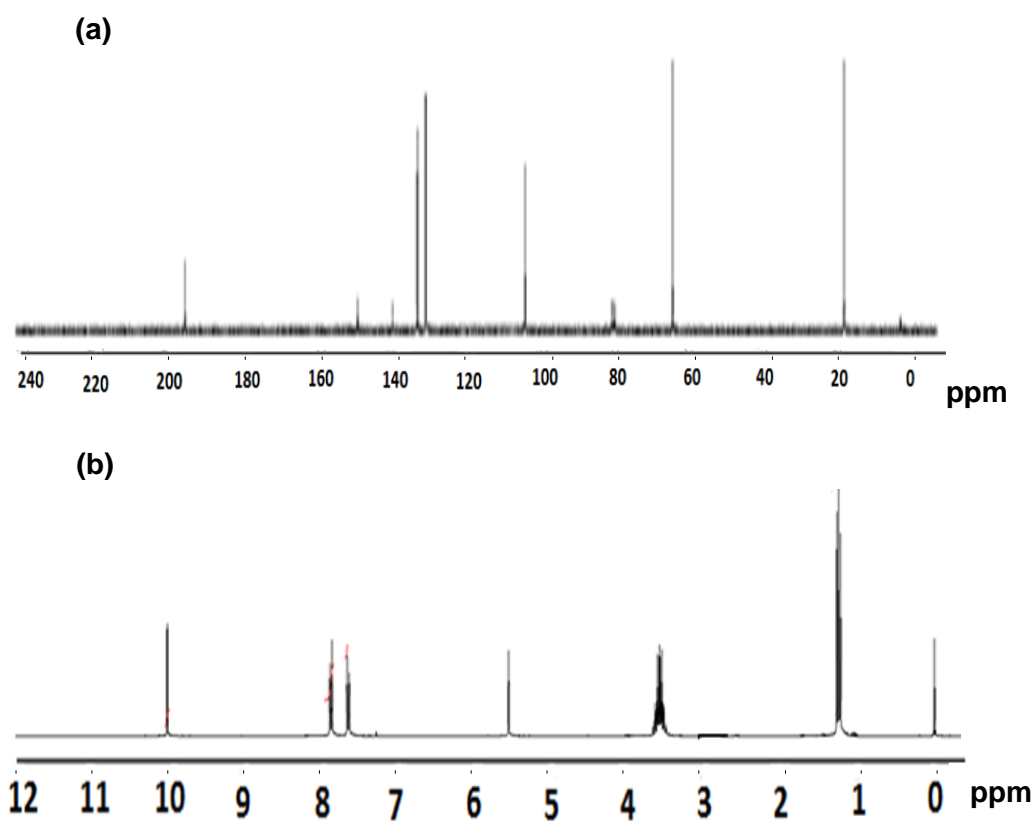


Figure 8.4 (a) The experimental ^{13}C NMR spectrum of DEMB

(b) The experimental ^1H NMR spectrum of DEMB

Table 8.1 Vibrational Assignments of fundamental frequencies are obtained for DEMB using B3LYP/6-311G** level of theories.

Experimental frequencies (cm ⁻¹)		Calculated frequencies (cm ⁻¹)		IR intensity	Raman activity	Vibrational assignments
FT-IR	FT-Raman	Unscaled	Scaled			
3450(vw)		3398	3299	57.492	79.694	vasym(CH ₃)(98)
3400(w)		3353	3250	110.941	132.821	vasym(CH ₃)(97)
		3316	3211	95.041	559.615	vasym(CH ₃)(94)
		3205	3195	240.218	43.138	vasym(CH ₃)(95)
		3167	3100	118.830	68.377	vsym(CH ₃)(91)
		3131	3092	170.208	377.585	vsym(CH ₃)(92)
3118(s)		3119	3063	73.421	69.667	vCH(83)
		3091	3042	33.944	80.679	vCH(81)
		3084	3011	309.268	71.257	vCH(82)
		3067	2975	252.849	96.205	vCH(80)
		3066	2942	226.152	246.945	vCH(78)
2700(m)	2715(m)	3051	2862	198.698	451.892	vCH(17)
2420(m)	2415(vw)	2470	2315	52.312	66.275	vasym(CH ₂)(85)
1750(m)		1773	1718	49.793	214.536	vasym(CH ₂)(72)
		1758	1668	6.654	117.043	vsym(CH ₂)(70)
		1701	1612	0.399	135.648	vsym(CH ₂)(75)
		1687	1595	11.777	38.029	vC=O(65)
1650(vw)		1645	1572	105.056	23.637	vCC(62)
		1639	1535	43.501	19.545	vCC(60)
		1626	1512	51.684	19.951	vCC(55)
		1584	1487	31.542	9.332	vCC(62)
		1572	1436	57.747	19.332	rock(61)
1560(s)	1550(s)	1560	1415	44.698	38.704	sciss(55)
		1516	1394	136.312	72.003	sciss(51)
1500(vw)		1509	1365	19.342	15.812	rock(54)
		1480	1356	18.415	9.732	ipb(61)
1456(m)		1459	1345	87.561	141.507	ipb(52)
1400(vs)	1425(vs)	1448	1232	92.900	37.189	sb(50)
		1386	1205	25.242	147.627	sb(57)
		1370	1293	0.552	42.610	βCH(63)
		1366	1279	42.536	34.928	opbCH ₃ (61)
		1342	1254	3.054	21.262	βCH(63)
1318(s)		1318	1242	139.266	22.323	βCH(59)
	1290(vw)	1291	1201	38.748	46.012	opbCH ₃ (61)
		1279	1125	34.145	11.568	βCH(63)
		1267	1116	79.176	40.266	iprCH ₃ (60)

Table Cont...

Table Cont...

Experimental frequencies (cm ⁻¹)		Calculated frequencies (cm ⁻¹)		IR intensity	Raman activity	Vibrational assignments
FT-IR	FT-Raman	Unscaled	Scaled			
1229(s)		1221	1105	22.521	12.826	βCH(59)
	1180(vw)	1175	998	56.709	84.314	βCH(54)
1125(s)		1160	983	2.380	42.182	iprCH ₃ (57)
		1086	977	12.693	17.536	oprCH ₃ (59)
		1079	962	4.391	57.099	oprCH ₃ (55)
		1070	957	67.841	8.628	waggCH ₂ (53)
1000(m)	1040(m)	1056	935	6.282	48.315	γCH(44)
	1000(w)	946	926	4.438	3.519	waggCH ₂ (52)
		911	908	1.639	19.803	γCH(41)
		836	801	1.566	1.109	γCH(43)
800(s)		821	798	6.514	14.341	βCOC(42)
725(s)	715(m)	724	718	7.842	41.356	βCOC(45)
620(s)	642(vw)	636	614	70.392	21.497	γCH(47)
598(m)	580(w)	602	597	23.101	34.765	γCH(45)
525(m)		562	546	54.167	45.095	γCH(43)
		470	431	35.740	16.465	γC=O(41)
		443	425	6.495	16.422	γCOC(43)
		418	408	4.005	2.855	twist(35)
		380	355	65.781	11.646	twist(35)
		344	326	5.992	13.191	tCH ₃ (23)
	215(m)	331	318	85.012	5.006	tCH ₃ (23)

Experimental relative intensities are abbreviated as follows: vs-very strong, s-strong, m-medium, w-weak, vw-very weak. asym-asymmetric stretching, sym-symmetric stretching, β-in-plane bending, γ-out-of-plane bending, sciss-scissoring, rock-rocking, wagg-wagging, twist-twisting, asymd-asymmetric deformation, t-torsion, sb-sym deformation, ipb-in-plane bending, opb-out-of-plane bending, ipr-in-plane rocking; opr-out-of-plane rocking.

Table 8.2 Experimental and theoretical ^{13}C and ^1H chemical shift (ppm) of DEMB

Atoms	Theoretical Shift (ppm)	Experimental Shift (ppm)	Atoms	Theoretical Shift (ppm)	Experimental Shift (ppm)
C1	157.613	150	H9	7.345	-
C2	78.639	66	H10	8.457	-
C3	143.395	142	H11	5.467	-
C4	112.649	106	H13	3.632	-
C5	137.919	132	H16	5.563	5.5
C6	85.289	80	H17	7.857	7.9
C7	33.354	18	H19	5.998	-
C12	71.432	-	H20	5.141	-
C15	183.651	195	H21	7.425	7.7
C18	89.654	-	H24	6.321	-
C23	98.362	-	H25	4.524	-
C26	137.125	134	H27	3.892	3.8
			H28	2.643	-
			H29	5.469	-
			H30	4.354	-
			H31	9.321	10.0