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Research Paper

Vibrational spectroscopy (FT-IR, FT-Raman and UV) studies of E-[1-Methyl-2,6-diphenyl-3-(propan-2-yl)piperidin-4-ylidene]amino 3-methylbenzoate] using DFT method

Physics

KEYWORDS :

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ABSTRACT

The FT-IR and FT-Raman spectra of E-[1-Methyl-2,6-diphenyl-3-(propan-2-yl)piperidin-4-ylidene]amino 3-methylbenzoate] (AMB) were recorded in the region 4000–400 cm–1 and 3500–100 cm–1, respectively. The geometrical structure, harmonic vibrational frequency, IR intensity, Raman activity and bonding features of this compound was carried out by DFT method with 6-31G basis set. The electric dipole moment (μ) and the first-order hyperpolarizability (β_0) values had been computed quantum mechanically. The calculated HOMO and LUMO energies showed that, the charge transfer occured within the molecule. The charge delocalization of this molecule had been analyzed using NBO analysis. The solvent effects had been calculated using TD-DFT in combination with the polarized continuum model and the results were in good agreement with experimental measurements. The other molecular properties like Mulliken population analysis, MEP and thermodynamic properties of the title compound had been calculated. Finally, the calculated results were applied to simulate FT-IR and FT-Raman spectra of the title compound which showed good agreement with observed spectra.

INTRODUCTION

Methyl benzoate, derivative of benzoic acid is an essence or oil of Niobe with colourless, oily transparent liquid with a pleasant odor. It has boiling point 198.6°C and flash point 82.7°C. It is insoluble in water, miscible with alcohol, ether and methanol. It is stable against oxidation and easily saponified by a strong base. Methyl benzoate is obtained by heating methyl alcohol and benzoic acid in presence of sulfuric acid and passing dry hydrogenchloride through a solution of benzoic acid in methanol. It occurs naturally in oils of dove, ylang-ylang and tuberose. It is used as a perfume and dye carrier. It is also used as solvent for cellulose esters, ether, resins, rubber and flavoring.

Vibrational spectra of benzoic acid and substituted benzoic acids have been studied by various authors [1-3]. Verma et al., [1] recorded the IR absorption spectrum of *m*-flurobenzoic acid in the region 4000–250 cm^{-1}. The activation energies and relaxation times of some substituted benzoic acids and their esters have been determined in the 3 cm microwave region at 20°C in dilute solutions of benzene . Korobkov and Kharkov [4] reported the low-frequency Raman spectra of benzoic acid and some of its derivatives. Abdullin and Furer [5] studied the calculation of band intensities in IR spectrum and conformation of aromatic esters.

Based on the literature survey, neither the vibrational analysis nor the quantum mechanical calculations for the molecule AMB have been reported so far. In this present study, a complete vibrational analysis of AMB is performed by combining the experimental (FT-IR and FT-Raman) data and theoretical information using Pulay's DFT based scaled quantum mechanical (SQM) method. The redistribution of ED in various bonding, anti-bonding orbital and E^2 energies have been calculated by NBO analysis to give clear evidence of stabilization originating from the hyper conjugation of various intra-molecular interactions. The UV-Vis spectroscopic studies along with HOMO and LUMO analysis has been used to elucidate information regarding charge transfer within the molecule. Finally, the thermodynamic properties of the optimized structures were obtained theoretically from the harmonic vibrations.

EXPERIMENTAL DETAILS

Synthesis Procedure

3-Isopropyl-2,6-diphenylpiperidin-4-one was synthesized by Mannich condensation using benzaldehyde (2 mol), ammonium acetate (1 mol) and isobutyl methyl ketone (1 mol) in absolute ethanol, warmed for 30 min and stirred over night at room temperature. The product was treated with methyl iodide (1.5 mol) in the presence of potassium carbonate (2 mol) in acetone (10 ml) and refluxed for two hours yielding (4E)-1-methyl-3-isopropyl-2,6-diphenylpiperidin-4-one. The oximation was done by hydroxylamine hydrochloride (2 mol) in the presence of sodium acetate (2 mol) in ethanol (10 ml) and refluxed for two hours. The resulting oxime (0.5 g, 1.55 mmol) was stirred with dry pyridine (5 ml), added 3-methylbenzoic acid (0.23 g, 1.7 mmol) followed by the dropwise addition of phosphorus oxychloride (0.21 mL, 2.3 mmol) and stirred at ambient temperature for 15 min; the progress of the reaction was monitored by thin layer chromatography. Upon completion of the reaction, saturated sodium bicarbonate solution (8 ml) was added to the reaction mixture. The product was filtered and dried to get a white solid (0.62 g, 91%) which was recrystallized from ethanol to yield crystals suitable for X-ray crystallographic studies.

FT-IR, FT-Raman and UV–Vis spectra

The FT-IR spectrum of MPPDO was recorded in the spectral region between 400–4000 cm^{-1} using the KBr pellet technique. The spectrum was recorded at room temperature with a scanning speed of 10 cm^{-1} per minute and at the spectral resolution of 2.0 cm^{-1} in the Department of Chemistry, Jamal Mohamed College, Trichy, Tamilnadu, India. The FT-Raman spectrum of title compound was recorded using the 1064 nm line of an Nd:YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on Bruker model IFS 66V spectrophotometer equipped with an FRA 106 FT-Raman module accessory and at spectral resolution of 4 cm^{-1}. The FT-Raman spectral measurement was carried out from SAIF Laboratory, IIT Madras, Tamilnadu, India. The UV-Vis absorption spectrum of MPPDO was recorded in the range of 200–500 nm using a Shimadzu – 2600 spectrometer in the Department of Chemistry, Jamal Mohamed College, Trichy-20. The UV pattern was taken from a 10^{-5} molar solution of MPPDO dissolved in benzene.

COMPUTATIONAL DETAILS

For meeting the requirements of both accuracy and computing economy, theoretical methods and basis sets should be considered. DFT had proved to be extremely useful in treating electronic structure of molecules. The density functional three parameter hybrid model (DFT/B3LYP/6-311++G(d,p) basis set was adopted to calculate the properties of the title molecule in this work. All the calculations were performed using the Gaussian 03W program package [6] with the default convergence criteria without any constraint on the geometry [7] It should be noted that Gaussian 03W package did not calculate the Raman intensities. The Raman activities were transformed into Raman intensities using Raint program [8] by the expression:

RESULTS AND DISCUSSION

Molecular Geometry

The optimized geometrical structure of the title compound is shown in Fig. 1. The molecular structure of the AMB belongs to a C_s point group of symmetry. The optimized structural parameters for this compound was calculated by B3LYP method with 6-31G basis set is listed in Table 1. The calculated geometrical parameters can be used as the foundation to calculate other parameters for the compound. The molecule AMB has one piperidine ring, four methyl groups and 3 benzene rings. The optimized geometrical parameters of AMB are compared with XRD data [9] . The C–C and C–H bond lengths of the molecule AMB are approximately (except little difference) equal to experimental values [9]. The calculated C–C bond length in ring varies from 1.581 to 1.397Å.

According to Aydin et al., [10] the piperidine ring in the chair conformation has the endocyclic bond angles closer to tetrahedral geometry (110.3(3)-111.8(3)°) and the average endocyclic torsion angle is 54. 93(13)°. In this study the calculated endocyclic bond angles vary in the range of 106.95-115.65° and the average endocyclic torsion angles by DFT method is ~53.30°. In piperidine moiety the bond distances varies between 1.491-1.581Å. These values are supported by literature [11]. The bond angles between C_4-C_{37}-N_{38}, C_{40}-C_{42}-C_{43} and C_3-C_{37}-N_{38}, C_{40}-C_{42}-C_{44} are respectively differed by 12.09°, 5.25°, which are due to conformations. Gundersan et al., [12] calculated the C-N bond distance for piperidine as 1.469Å, which is moderately in agreement with our data (1.491Å/C_2-N_{36}). In the piperidine ring, the C-N (1.491/1.495Å) bond distances are moderately shorter than C-C (1.496-1.581Å) bond distances while C-C-N (111.23/113.38°) bond angles are slightly shorter than C-N-C (114.29°) bond angle. This trend is supported by earlier studies [13]. It should be mentioned here that the shortening of bond length C47-C62 (1.513Å) from its normal value (1.44Å) [14], which is due to the hyperconjugation interaction occurs with the releasing of electronic charge from C-H to C-C bond in the phenyl ring.

Vibrational Analysis

The title compound consists of 65 atoms and has 189 normal modes of vibrations. These normal modes of AMB are distributed with 127 in-plane vibration and 62 out-of-plane vibration. The vibrational modes are assigned on the basis of TED analysis is carried out using VEDA4 program [15 ,16]. Vibrational frequencies are calculated using B3LYP/6-31G level of basis set. Table .2 shows that scaled frequencies, observed frequencies in the FT-Raman and FT-IR spectra with their intensities, force constants, reduced masses and proposed normal modes of the title compound. To understand the analysis of spectral features, the comparison of stimulated and observed FT-IR and FT-Raman spectra of AMB are presented in Figs.2 and .3, respectively.

C–H Vibrations

The AMB molecule is a tetra-substituted aromatic structure. It has one isolated and three adjacent C–H moieties and hence Five C–H stretching vibrations, five in-plane / out-of-plane bending vibrations are possible. The hetero aromatic structure shows the presence of the C–H stretching vibration in the range 3100–3000 cm^{-1}, which is the characteristic region for the ready identification of the C–H stretching vibrations [17], and typically exhibit weak bands compared with the aliphatic νC-H mode [18]. In the present work, the C–H stretching vibrations belong to piperidine and benzene ring moieties are respectively assigned to wavenumbers 3053, 2963, 2955, 2934, 2800, 2782 cm^{-1} and 3127-3072, 3071-3063 cm^{-1} (Mode nos: 17, 24, 25, 27, 31, 32 and 1-10, 12-15). As showed by the TED, these modes involve approximately 90% contribution suggesting that these are pure CH stretching modes, which are further supported by observed bands: FTIR: 3090, 3066, 2962 & 2772/FT-Raman: 3067 & 2966 cm^{-1}.

The aromatic C–H in-plane bending vibrations occur within the region 1300–1000 cm^{-1} and out-of plane bending vibrations in the region 1000–700 cm^{-1} [19]. The C–H in-plane bending vibrations belong to piperidine ring are computed at 1382, 1361, 1324, 1282 & 1223 cm^{-1}. The calculations show that the bands corresponding to the β_{CH} modes of benzene moieties: Two, Three and four are located at 1494, 1492, 1455, 1188, 1078 cm^{-1} (mode nos: 42, 44, 54, 79, 93); 1599, 1458, 1182, 1175, 1175 cm^{-1} (mode nos: 36, 53, 82-84) and 1489, 1311, 1184, 1097 cm^{-1} (mode nos: 46, 69, 81, 91), respectively. These results are supported by literature [20] and also find support from FT-Raman bands: 1084 (FTIR), 1183 & 1313 cm^{-1} in addition to TED output (>22%). The harmonic bands at 1463, 1348, 1317, 1279, 1276 cm^{-1} (mode nos: 52, 62, 68, 73, 74) and at 982, 973, 925, 923, 856, 771 cm^{-1} (mode nos: 108, 109, 115, 116, 122, 128) are designated as Γ_{CH} modes of piperidine and benzene moieties, respectively. The mode nos: 52, 73 & 128 are in consistent with the observed FTIR bands: 1465 (FT-Raman), 1279 & 772 cm^{-1}. These assignments are further supported by literature [21] in addition TED results (>24%). The mode nos: 77/167: are belong to $\beta C_{54}H_{58}/\Gamma C_{54}H_{58}$ modes.

Methyl Vibrations

The title compound AMB possesses four CH_3 group on the side substitution chain. For the assignment of CH_3 group frequencies, nine fundamentals can be associated with each CH_3 group, namely: two asymmetric νCH_3, one symmetric νCH_3, two asymmetric βCH_3, one symmetric βCH_3, two ρCH_3 and one τCH_3 modes[22]. The ν_{asy} and ν_{sy} modes of CH_3 group attached with benzene moiety are usually downshifted due to electronic effects [23] and are expected near 2925 and 2865 cm^{-1} for asymmetric and symmetric stretching vibrations, respectively. The CH stretching vibration in CH_3 occurs at lower frequencies than those of aromatic ring (3100–3000 cm^{-1}). Moreover, the asymmetric stretch is usually at higher frequencies than the symmetric stretch. In CH_3 group, the ν_{sym} and ν_{asy} modes appeared in the ranges 2860-2935 cm^{-1} and 2925-2985 cm^{-1}, respectively [24]. In the present work, the CH_3 asymmetric and symmetric stretching modes are assigned at 3072, 3057, 3021, 3017, 3014, 3004, 2988 & 2982 cm^{-1} (mode nos: 11, 16, 18-23) and 2936, 2926, 2924 & 2841 cm^{-1} (mode nos: 26, 28-30), respectively. These assignments are in line with observed FTIR/FT-Raman bands (3021, 2879/3021, 2872 cm^{-1}) and also supported by literature [25] in addition to TED output (>80%).

The asymmetric and symmetric bending vibrations of methyl groups normally appear in the regions 1465–1440 cm^{-1} and 1390–1370 cm^{-1}, respectively [26 , 27]. In accordance with above conclusion, the harmonic bands at 1500, 1493, 1492, 1491, 1489, 1486, 1480, 1477 & 1476 cm^{-1} (mode nos: 41, 43-50) are assigned to β_{asy} CH_3 deformations, whereas mode nos: 57-59 (1419, 1408 & 1395 cm^{-1}) are assigned to β_{sym} CH_3 deformations. These modes are very well within the expected region and also find support from the observed bands (FT-IR: 1479, 1402, 1406/FT-Raman: 1489, 1417 cm^{-1}). These (βCH_3) modes are mainly coupled with the in-plane bending vibrations. In AMB the rocking vibrations of the CH_3 groups are appeared as mixed vibrations. These modes usually appear in the region 1070–900 cm^{-1} [28 ,29]. The (mode nos: 45, 47, 51, 77, 85, 86, 88, 89 and 90, 92, 96, 101, 105, 111, 113, 114 are assigned to in-plane and out-of-plane rocking vibrations of CH_3 groups, in which (modes nos: 77, 88, 92 & 113 are in agreement with observed FTIR bands (1237, 1140, 1091: FT-Raman & 935 cm^{-1}). The τCH_3 mode is expected to occur below 400 cm^{-1} [30] · According to the literature the harmonic bands at 248, 227, 209, 203 cm^{-1} (mode nos: 165, 167, 169, 170) are attributed to τCH_3 modes.

Ring Vibrations

The C–C aromatic stretching vibration gives rise to characteristic bands in both the observed FT-IR and FT-Raman spectra, covering the spectral range from 1600–1400 cm^{-1} [31]. The observed bands (FTIR: 1607, 1084, 1071/FT-Raman: 1597, 1313 cm^{-1}) have weak intensities with considerable TED values are designated as ν_{C-C} modes of benzene moieties of AMB. The harmonic wavenumbers for this mode fall within the range of 1601-1073 cm^{-1} (mode nos: 35-40, 54, 56, 65, 66, 69, 70, 79, 80, 91, 93, 94). These results are supported by the literature [32]. The C-C stretching is observed at 1051 cm^{-1} for piperidine [33]. The ring stretching vibrations are observed as medium to weak bands in all the recorded spectra. Accordingly, in piperidine moiety, the ν_{C-C} modes are observed at 1091(w)/935(m) cm^{-1} (FT-Raman/FTIR). These results are further supported by harmonic wavenumbers in the range (1093-939 cm^{-1}/mode nos: 92, 100, 111, 113) in addition to TED results. The bands observed at 1156 and 1204 cm^{-1} in FTIR spectrum can be assigned to the νC_{40}-C_{42}, νC_{47}-C_{62} and νC_1-C_{10} modes, respectively, which are in agreement with harmonic bands at 1160, and 1196 cm^{-1} (mode nos: 87 and 78). These assignments are further supported by TED.

The harmonic bands at 1026, 999, 628 cm^{-1} (mode nos: 98, 102, 140); 1026, 999, 998 cm^{-1} (mode nos: 99, 102, 103); 664, 545, 532 cm^{-1} (mode nos:137, 144, 145) are assigned to β_{CCC} modes and the bands at 710, 416 cm^{-1} (mode nos: 133, 154); 764, 701, 411 cm^{-1} (mode nos: 129, 135, 155); 674, 492, 427 cm^{-1} (mode nos: 136, 148, 152) are assigned to Γ_{CCC} modes of phenyl rings (Ring 2;3;4) for AMB, respectively. These assignments are agreeable with literature [31] and also find support from observed FTIR bands: 999 cm^{-1}/FT-Raman and 763, 694, 680, 482, 433 cm^{-1} in addition to TED values. In AMB the mode no: 100 is attributed to β_{CCC} mode of piperidine moiety and the mode no: 121 belongs to νC_{53}-C_{54} mode.

C=N, C-N Vibrations

The identification of C=N and C-N vibrations is a very difficult task, since the mixing of several bands are possible in the region [33]. In liquid phase FTIR spectrum of the 2 and 3-methylpiperidine molecules Erdogdu et al.,[22] assigned the C-N stretching at 1085 and 1055 cm^{-1}. Based on the above literature data, in this study weak bands are found in FTIR/FT-Raman spectra at 1071, 1049/1047 cm^{-1} are assigned to C-N stretching modes, the TED also predicts that these vibrations are mixed vibrations and is evident from Table 2. The harmonic wavenumbers corresponding to this mode 1073, 1032 cm^{-1} (mode nos: 94, 97) are in agreement with recorded as well as above mentioned literature data. The C=N stretching appears in the region 1600-1670 cm^{-1} [22] Kolev et al., [34], also assigned C=N stretching mode at 1641 cm^{-1} (FTIR). In our present study, the strong band is observed in FTIR spectrum at 1689 cm^{-1} and weak band in FT-Raman spectrum at 1688 cm^{-1} is assigned to C_{37}=N_{38} stretching mode. For the same mode the calculated frequency is 1618 cm^{-1} (mode no: 34) and this assignment is further supported by TED (74%) value. In AMB, the βC_2-N_{36}-C_{32}, βC_3-C_{37}=N_{38} and $\tau C_2C_3C_{37}N_{38}$ modes are assigned to mode nos: 150, 139 and 186, respectively, in which mode nos: 150, 139 are supported by observed bands (446 cm^{-1}: FTIR, 638 cm^{-1}: FT-Raman) in addition to TED value.

C=O, C-O, N-O Vibrations

The $\nu_{C=O}$ vibrations in ketones are expected to occur in the region 1680-1715 cm^{-1}. The intensity of carbonyl bands will increase because of conjugation, which leads to the intensification of the Raman lines as well as the increased IR band intensities [35]. It can be seen from the Table .2 the FTIR band with very strong intensity (IR relative intensity: 49.74) and it is observed at 1768 cm^{-1} belongs to the C_{40}=O_{41} stretching mode in conformity with the TED (78%) distribution, whereas the calculated frequency 1661 cm^{-1} (mode no: 33) shows a negative deviation of ~107 cm^{-1}. The difference in stretching frequency is observed for carbonyl group and it may be due to the existence of different conformers of the target molecule probably in the solid state the hydrozone moiety existing in *syn* orientations. But during the theoretical calculation are hydrozone moiety may be existing in the anti-orientations.

Normally the νC-O modes occur in the region 1000-1260 cm^{-1} [36]. The force constant of the C=O bond is increased by the electron-attracting nature of the adjacent oxygen (O_{39}) atom due to inductive effect [37]. The C-O next to the carbonyl is stiffer than the other single bonds due to resonance which tends to localize the high vibration in the C-O bond. Based on the facts, the harmonic band at 1065 cm^{-1} in IR spectrum with maximum (100) relative intensity is assigned to νC_{39}-O_{40} vibration for AMB. This mode is not pure but contains significant contributions from other modes. (ν_{CC} (22%)+β_{CCO} (28%)). This assignment is in the expected range and also find support from TED (32%). The mode no: 131, (736 cm^{-1}) with significant TED value (64%) is undoubtedly assigned to N_{38}-O_{39} stretching vibration. The $\beta_{C=O}$/$\Gamma_{C=O}$ modes are reported at 900/523 cm^{-1} theoretically and at 567 cm^{-1} ($\Gamma_{C=O}$) experimentally by [38]. The bands calculated at 1065, 638, 638 cm^{-1} (mode nos: 95,139,139) and 674, 375 cm^{-1} (mode nos: 136, 156) are assigned as deformation bands of $\beta C_{42}C_{40}C_{41}$, $\beta C_{37}N_{38}O_{39}$, $\beta C_{42}C_{40}O_{39}$ and $\tau C_{43}C_{42}C_{40}O_{41}$, $\tau C_3C_{37}N_{38}O_{39}$, respectively. These assignments are supported by observed bands at 638 cm^{-1} (FT-Raman), 680 cm^{-1} (FT-IR) and in addition to TED value.

NLO Property

In this work, the dipole moment, molecular polarizability, anisotropy of polarizability and first order hyperpolarizability of AMB molecule are calculated using B3LYP/6-31G basis set and are listed in Table 3. The calculated values of dipole moment (μ) are found to be 0.366, 1.441 and –0.257 Debye. The highest value of dipole moment is observed for component μ_y. In this direction, this value is equal to 1.509 Debye. The calculated polarizability α_{ij} have non-zero and zero values and are dominated by the diagonal components. Total polarizability (α_{tot}) calculated as 819.899×10^{-24}, esu for title molecule. The first hyperpolarizability values β_0 of the title compound is $1.7472\ \times10^{-30}$ esu which is ~5 times greater than that of urea. The magnitude of the molecular hyperpolarizability β_0, is one of important key factors in a NLO system.

NBO Analysis

The NBO analysis is performed using B3LYP/6-31G basis set to study the stabilization originating from the hyper conjugation of various intra-molecular interaction in AMB molecule. The calculated second-order interaction energies ($E^{(2)}$) between the donor-acceptor orbital in AMB molecule are listed in Table 4. Generally more energy transfer takes place during σ to σ* transition. In AMB, the σ bonds of C_{11}-C_{13}, C_{11}-H_{14}, C_{15}-H_{19}, C_{22}-C_{24}, C_{24}-H_2 transfer more energy 87.4, 84.27, 85.81, 80.46 KJ/mol to the anti-bonding acceptor orbitals. On the other hand the π bonds C_{10}-C_{12}, C_{11}-C_{13}, C_{15}-C_{17}, C_{22}-C_{23}, C_{24}-C_{26}, C_{25}-C_{28} also transfer energy 80.17, 85.94, 84.22, 86.99, 83.72, 87.78 KJ/mol to the anti-bonding acceptor orbitals. Similarly LP O_{39} transfer the (E^2) energy 39.62 and 31.51 KJ/mol to its anti-bonding orbitals σ*(C_{40}-O_{41}) and π*(C_{40}-C_{41}), respectively. The maximum stabilization energy (168.07 KJ/mol) is associated with hyperpolarizability interaction is (n-σ*) LP O_{41}→O_{39}-C_{40}, which may be due to lone pair electron of carbonyl group.

Homo-Lumo Analysis

Many organic molecules that contain conjugated π electrons are characterized as hyperpolarizabilities and are analyzed by vibrational spectroscopy [39, 40]. According to the DFT calculated electronic absorption spectra, the maximum absorption wavelength corresponding to the electronic transition is from the HOMO to the LUMO. These molecular orbitals for AMB is shown in Fig. 4. The lowest singlet→singlet spin-allowed excited states of title molecule were taken into account for the B3LYP/6-31G calculation to investigate the properties of electronic absorption. The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity.

The HOMO energy is 5.991 eV and the LUMO energy 1.303 eV. The energy gap of HOMO–LUMO explains the eventual charge transfer interaction within the molecule, and the frontier orbital energy gap of AMB is found to be 4.688 eV. The HOMO is located over the pyridine ring and N-methyl and the LUMO is located over methyl benzene. The HOMO→LUMO transition implies an ED transfer to C–H group from the benzene ring. The hardness and softness are the important properties to measure the molecule stability and reactivity. The various quantum chemical parameters such as ionization potential, electron affinity, electrophilicity index, etc., were calculated and are listed in Table .5. In addition the frontier molecular orbital energies are also listed in Table .6

UV-Vis Spectra

All the molecular structure allows strong **π→π*** or σ→σ* transition in the UV–Vis region with a high extinction coefficients. The UV–Vis spectrum of AMB is recorded in ethanol solution as shown in Fig. 5. To support experimental observations, the electronic absorption spectral calculation using TD-DFT/6-31G basis set for the title compound in ethanol and water solution is performed. The experimental and computed electronic features such as the absorption wavelength (λ), excitation energies (E) and oscillator strengths (f) major contributions of the transitions and assignments of electronic transitions are listed in Table 7. TD-DFT methods are computationally more expensive than semi-empirical methods but allow easily study the medium-size molecules [41,42]. The calculated maximum absorption (λ_{max}) values 331.71, 321.70, 285.49, 276.98, 266.08 and 256.04 nm (in ethanol) and 331.41, 321.18, 285.39, 276.57, 265.65 and 255.30 nm (in water), show good agreement and their experimental absorption values are 320 nm and 221 nm (in ethanol). These excitations correspond **π to π* transition.**

MEP Analysis

MEP have been found to be a very useful tool in the investigation of correlation between molecular structures with its physiochemical property relationship, including biomolecules and drugs [43]. The MEP is calculated with B3LYP/6-31G basis set and the MEP map is shown in Fig. 6. The different electrostatic potential values of the surface are represented by different colors, the maximum negative region, which is the preferred site for electrophilic attack as shown in red colour. The maximum positive region, which is the preferred site for nucleophilic attack as shown in blue colour and green represent by zero potentials. In the present work, the calculated result shows that the negative potentials are mainly over the electron negative oxygen atoms and positive potential are over the nucleophilic reactive hydrogen atoms. This result gives information for the region from where the compound can have inter-molecular interactions.

Mulliken Atomic Charges

Mulliken [44] atomic charge calculation has an important role for the application of quantum chemical calculation of the molecular system. Atomic charge affects dipole moment, polarizability, electronic structure and other molecular properties of the system. The Mulliken atomic charge (e) values are calculated using B3LYP/6-31G basis set and are listed in Table .8 and are shown in Fig. 7. It is clearly shown that the carbon atom attached with hydrogen atom is negative, whereas the remaining carbon atoms are positively charged in the title compound. The carbon, oxygen and nitrogen atoms have more negative charge whereas all the hydrogen atoms have the positive charges. Generally the hydrogen connected methyl carbon having more negative charges (C_{62}:-0.481, C_{57}:-0.415, C_{53}:-0.413, C_{32}:-0.271) due to the accumulation of electronic charge oweing to the higher electronegative character than the hydrogen atoms. Similarly the more negative charge of carbon atoms are C_{57}: -0.415 and C_{62}: -0.481, The O_{39} atom has more negative charge (-0.483 au), which is due to more electronegativity of O_{39} than N_{38}.

Thermodynamic Properties

Scale factors have been recommended for an accurate prediction in determining the zero-point vibration energies, heat capacities, entropies, enthalpies, Gibbs-free energies. All these thermodynamic parameters and dipole moment at room temperature (298.15 K) are also presented in Table 9. The variations in zero point vibrational energies seem to be insignificant. The standard statistical thermodynamic functions: standard heat capacities ($C^0_{p,m}$), standard entropies (S^0_m) and standard enthalpy changes (H^0_m) for AMB are obtained from the theoretical harmonic frequencies calculation using B3LYP/6-31G level and are listed in Table 10. It should be noted here, that the thermodynamic functions are increasing with temperature ranging from 50 to 250k and it is due to the fact that the molecular vibrational intensities is increased with temperature [45]. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures are fitted by quadratic formulas and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9989, 0.9999 and 0.9995, respectively. The correlation graphs are shown in Fig. 8. and their corresponding fitting equation are:

$$C^0_{p,m} = 14.2352 + 0.0601T + 5.3097 \times 10^{-5} T^2 \quad (R^2 = 0.9989)$$

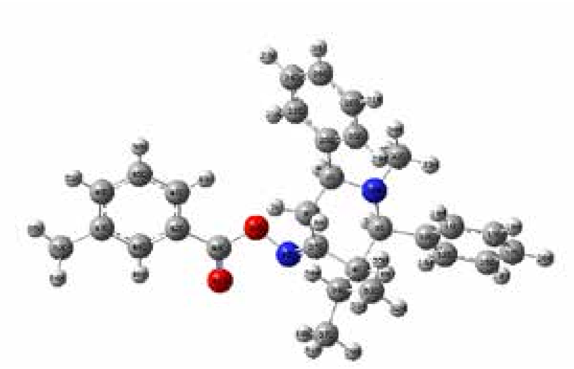
$$S^0_m = 2.4039 + 0.01015T + 8.9666 \times 10^{-5} T^2 \quad (R^2 = 0.9999)$$

$$\Delta H^0_m = 6.67875 + 0.02819T + 2.49101 \times 10^{-5} T^2 \quad (R^2 = 0.9995)$$

CONCLUSION

For the first time a complete vibrational analysis had been performed for the molecule AMB. The optimized geometric parameters (bond lengths, bond angles and dihedral angles) were theoretically determined and compared with XRD data. The predicted first hyperpolarizability value was ~5 times greater than that of urea which implies that the molecule AMB might become a kind of good NLO material. The NBO result reflected the charge transfer within the molecule. The HOMO-LUMO energy gap (4.678 eV) indicated the stability and reactivity of the title molecule. A good correlation between the UV-Vis absorption maxima and calculated electronic absorption maxima were found. MEP of AMB showed that the negative potential site was on the electronegative oxygen atoms, while the positive potential site around all the hydrogen atoms. Mulliken atomic charges of the title compound had been calculated and also plotted. The calculation results were applied to simulate the vibrational spectra of the molecule AMB, which showed good agreement with the experimental spectra.

Fig. 1. The optimized molecular structure of AMB



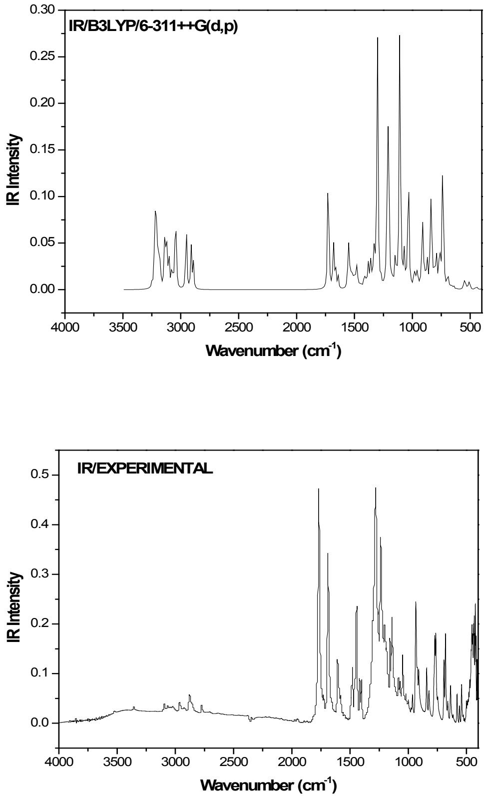
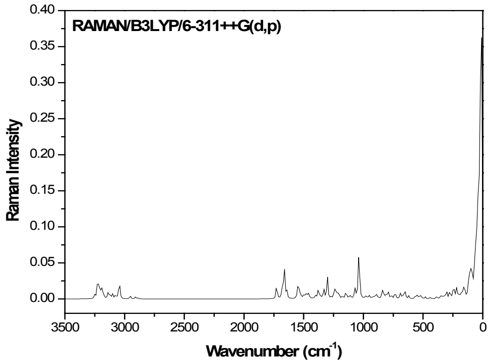


Fig.2. The combined theoretical and experimental FT-IR spectra of AMB



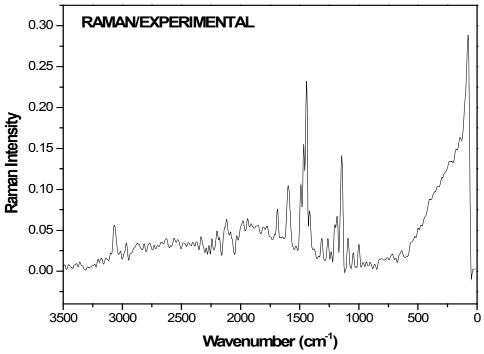
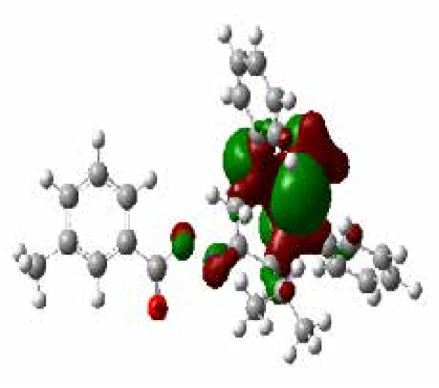
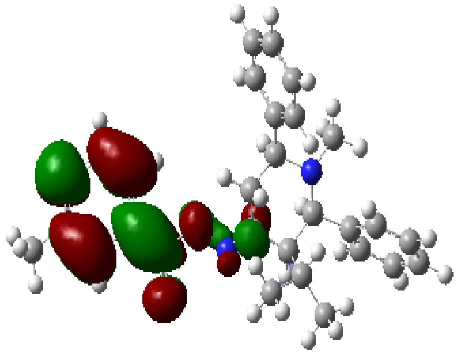


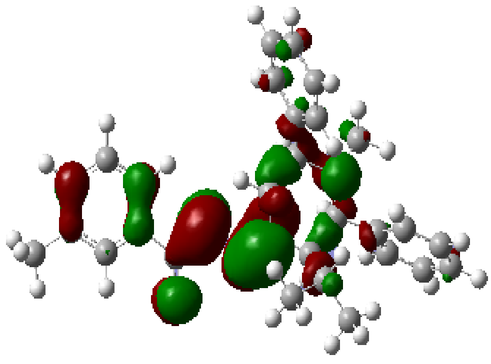
Fig. 3. The combined theoretical and experimental FT-Raman spectra of AMB



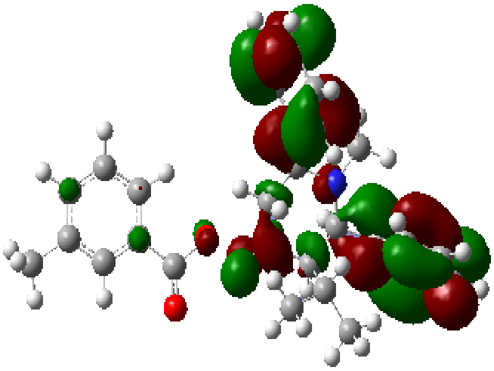
Homo = -5.991 eV



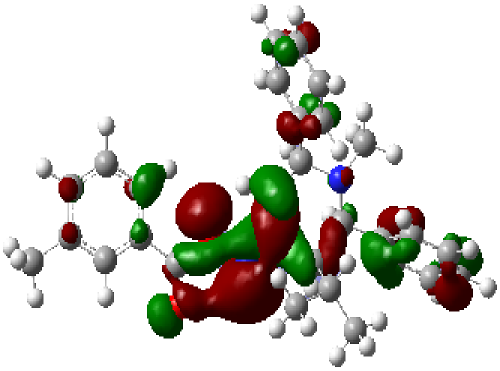
Lumo = -1.304 eV
Energy gap = 4.678 eV



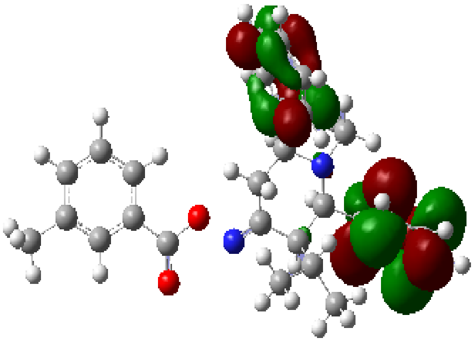
Homo -1 = -5.763 eV



Lumo +1 = -1.023 eV



Homo -2 = -5.212 eV



Lumo +2 = -0.823 eV

Fig.4. The frontier molecular orbitals of AMB

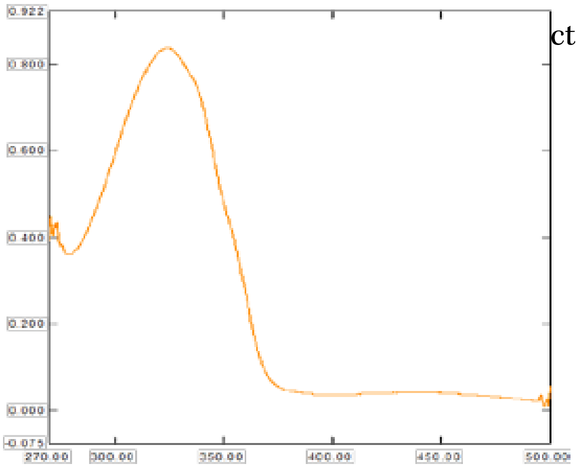


Fig. 5. Experimental UV-Vis spectrum of AMB

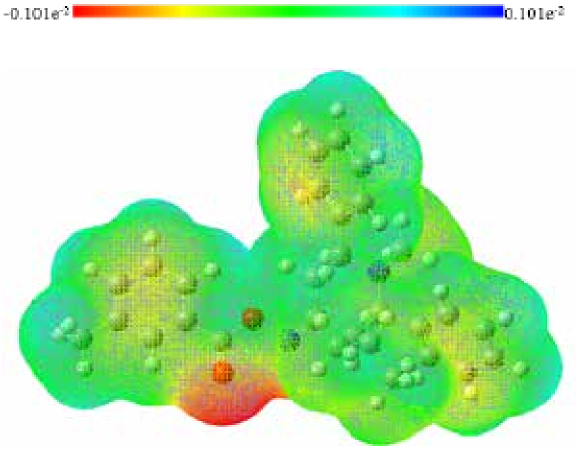


Fig.6. The molecular electrostatic potential map of AMB

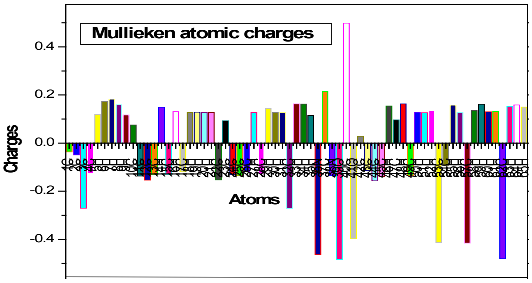
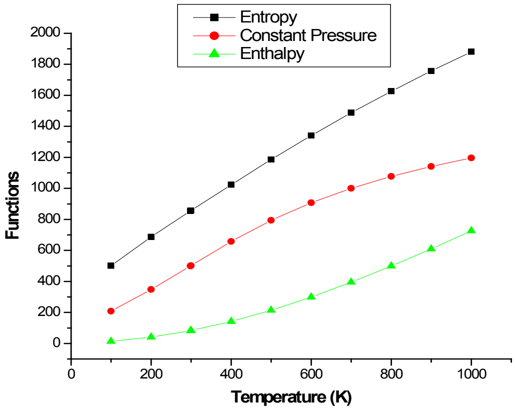


Fig.7. The Mulliken atomic charges of AMB



ctrum of AMB

Fig. 8. The thermodynamic properties of AMB at different temperatures

Table 1. The optimized bond parameters of AMB using B3LYP/6-31G basis set

Parameters	B3LYP/ 6-31G	XRD	Parameters	B3LYP/ 6-31G	XRD
Bond Lengths (Å)			Dihedral Angles (°)		
C1-C4	1.581	1.551 (2)	H5-C1-C4-H8	46.95	
C1-H5	1.110	0.980	H5-C1-C4-C37	-66.94	
C1-C10	1.525	1.516 (2)	H5-C1-C4-C54	166.20	
C1-N36	1.496	1.487 (17)	C10-C1-C4-H8	-68.15	
C2-C3	1.550	1.530 (2)	C10-C1-C4-C37	177.96	

Parameters	B3LYP/ 6-31G	XRD	Parameters	B3LYP/ 6-31G	XRD
C2-H9	1.109	0.980	C10-C1-C4-C54	51.10	
C2-C23	1.525	1.515 (19)	N36-C1-C4-H8	164.92	
C2-N36	1.491	1.470	N36-C1-C4-C37	51.03	
C3-H6	1.096	0.970	N36-C1-C4-C54	-75.83	
C3-H7	1.090	0.970	C4-C1-C10-C11	-89.97	
C3-C37	1.497	1.491	C4-C1-C10-C12	88.18	
C4-H8	1.097	0.980	H5-C1-C10-C11	156.39	
C4-C37	1.513	1.504 (2)	H5-C1-C10-C12	-25.46	
C4-C54	1.577	1.539 (19)	N36-C1-C10-C11	38.05	
C10-C11	1.406	1.384 (2)	N36-C1-C10-C12	-143.80	
C10-C12	1.404	1.381 (2)	C4-C1-N36-C2	-52.71	
C11-C13	1.398	1.383 (2)	C4-C1-N36-C32	-176.74	
C11-H14	1.084	0.930	H5-C1-N36-C2	62.82	
C12-C15	1.400	1.386 (2)	H5-C1-N36-C32	-61.21	
C12-H16	1.087	0.930	C10-C1-N36-C2	-179.92	
C13-C17	1.401	1.369 (3)	C10-C1-N36-C32	56.05	
C13-H18	1.086	0.930	H9-C2-C3-H6	-173.38	
C15-C17	1.399	1.365 (3)	H9-C2-C3-H7	-55.81	
C15-H19	1.086	0.930	H9-C2-C3-C37	67.48	
C17-H20	1.085	0.930	C23-C2-C3-H6	-56.77	
C21-C22	1.087	0.930	C23-C2-C3-H7	60.80	
C22-C23	1.403	1.380 (2)	C23-C2-C3-C37	-175.91	
C22-C24	1.400	1.386 (3)	N36-C2-C3-H6	66.90	
C23-C25	1.406	1.381 (2)	N36-C2-C3-H7	-175.53	
C24-C26	1.399	1.359 (3)	N36-C2-C3-C37	-52.24	
C24-H27	1.086	0.930	C3-C2-C23-C22	-100.85	
C25-C28	1.398	1.389 (3)	C3-C2-C23-C25	75.91	
C25-H29	1.085	0.930	H9-C2-C23-C22	15.35	
C26-H28	1.401	1.366 (3)	H9-C2-C23-C25	-167.89	
C26-H30	1.085	0.930	N36-C2-C23-C22	135.88	
C28-H31	1.086	0.930	N36-C2-C23-C25	-47.36	
C32-H33	1.089	0.960	C3-C2-N36-C1	52.00	
C32-H34	1.090	0.960	C3-C2-N36-C32	176.94	
C32-H35	1.107	0.960	H9-C2-N36-C1	-66.47	
C32-N36	1.485	1.465 (19)	H9-C2-N36-C32	58.47	
C37-N38	1.292	1.274 (2)	C23-C2-N36-C1	173.84	
N38-C39	1.499	1.452 (16)	C23-C2-N36-C32	-61.22	
O39-C40	1.395	1.347 (19)	C2-C3-C37-C4	56.98	
C40-O41	1.232	1.187 (19)	C2-C3-C37-N38	-120.21	
C40-C42	1.485	1.486 (2)	H6-C3-C37-C4	-61.27	
C42-C43	1.404	1.384 (2)	H6-C3-C37-N38	121.54	

Parameters	B3LYP/ 6-31G	XRD	Parameters	B3LYP/ 6-31G	XRD
C42-C44	1.406	1.386 (2)	H7-C3-C37-C4	179.11	
C43-C45	1.397	1.389 (2)	H7-C3-C37-N38	1.92	
C43-H46	1.082	0.930	C1-C4-C37-C3	-54.85	
C44-C47	1.400	1.389 (2)	C1-C4-C37-N38	122.72	
C44-H48	1.085	0.930	H8-C4-C37-C3	-168.08	
C45-C49	1.399	1.361 (3)	H8-C4-C37-N38	9.49	
C45-H50	1.085	0.930	C54-C4-C37-C3	74.55	
C47-C49	1.407	1.387 (3)	C54-C4-C37-N38	-107.88	
C47-C62	1.513	1.509 (3)	C1-C4-C54-C53	-88.79	
C49-H51	1.087	0.930	C1-C4-C54-C57	150.48	
H52-C53	1.098	0.960	C1-C4-C54-H58	30.70	
C53-C54	1.546	1.517 (3)	H8-C4-C54-C53	29.83	
C53-H55	1.090	0.960	H8-C4-C54-C57	-90.90	
C53-H56	1.097	0.960	H8-C4-C54-H58	149.32	
C54-C57	1.547	1.528 (3)	C37-C4-C54-C53	147.08	
C54-H58	1.098	0.980	C37-C4-C54-C57	26.35	
C57-H59	1.096	0.960	C37-C4-C54-H58	-93.42	
C57-H60	1.094	0.960	C1-C10-C11-C13	177.47	
C57-H61	1.096	0.960	C1-C10-C11-H14	-3.20	
C62-H63	1.094	0.960	C12-C10-C11-C13	-0.69	
C62-H64	1.098	0.960	C12-C10-C11-H14	178.63	
C62-H65	1.096	0.960	C1-C10-C12-C15	-177.12	
			C1-C10-C12-H16	2.68	
Bond Angles (°)			C11-C10-C12-C15	1.09	
C4-C1-H5	104.40	108.30	C11-C10-C12-H16	-179.11	
C4-C1-C10	111.88	111.47 (11)	C10-C11-C13-C17	-0.13	
C4-C1-N36	113.38	111.65 (11)	C10-C11-C13-H18	179.91	
H5-C1-C10	106.77	108.30	H14-C11-C13-C17	-179.45	
H5-C1-N36	108.56	108.30	H14-C11-C13-H18	0.59	
C10-C1-N36	111.35	108.67 (11)	C10-C12-C15-C17	-0.67	
C3-C2-H9	107.36	109.90	C10-C12-C15-H19	179.75	
C3-C2-C23	108.73	108.34 (11)	H16-C12-C15-C17	179.53	
C3-C2-N36	111.23	110.59 (11)	H16-C12-C15-H19	-0.05	
H9-C2-C23	108.01	108.60	C11-C13-C17-C15	0.57	
H9-C2-N36	109.45	108.60	C11-C13-C17-H20	-179.87	
C23-C2-N36	111.91	112.04 (12)	H18-C13-C17-C15	-179.48	
C2-C3-H6	107.75	109.90	H18-C13-C17-H20	0.09	
C2-C3-H7	109.62	109.90	C12-C15-C17-C13	-0.17	
C2-C3-C37	110.33	108.92 (12)	C12-C15-C17-H20	-179.73	
H6-C3-H7	108.23	108.30	H19-C15-C17-C13	179.41	

Parameters	B3LYP/ 6-31G	XRD	Parameters	B3LYP/ 6-31G	XRD
H6-C3-C37	109.21	109.90	H19-C15-C17-H20	-0.16	
H7-C3-C37	111.60	109.90	H21-C22-C23-C2	-3.64	
C1-C4-H8	106.00	108.30	H21-C22-C23-C25	179.54	
C1-C4-C37	106.95	106.81 (11)	C24-C22-C23-C2	176.57	
C1-C4-C54	116.76	114.42 (12)	C24-C22-C23-C25	-0.25	
H8-C4-C37	106.98	105.80	H21-C22-C24-C26	-179.55	
H8-C4-C54	107.17	105.80	H21-C22-C24-H27	0.13	
C37-C4-C54	112.40	117.24 (12)	C23-C22-C24-C26	0.25	
C1-C10-C11	121.99	121.36 (14)	C23-C22-C24-H27	179.93	
C1-C10-C12	119.30	120.62 (13)	C2-C23-C25-C28	-176.82	
C11-C10-C12	118.68	117.98 (14)	C2-C23-C25-H29	4.48	
C10-C11-C13	120.56	120.85 (16)	C22-C23-C25-C28	-0.02	
C10-C11-H14	119.01	119.60	C22-C23-C25-H29	-178.72	
C13-C11-H14	120.42	119.60	C22-C24-C26-C28	0.03	
C10-C12-C15	120.85	120.91 (17)	C22-C24-C26-H30	179.81	
C10-C12-H16	119.42	119.50	H27-C24-C26-C28	-179.65	
C15-C12-H16	119.74	119.50	H27-C24-C26-H30	0.12	
C11-C13-C17	120.31	120.31 (18)	C23-C25-C28-C26	0.29	
C11-C13-H18	119.70	119.80	C23-C250-C28-H31	-179.68	
C17-C13-H18	119.99	119.80	H29-C25-C28-C26	178.98	
C12-C15-C17	120.05	120.25 (17)	H29-C25-C28-H31	-1.00	
C12-C15-H19	119.80	119.90	C24-C26-C28-C25	-0.30	
C17-C15-H19	120.15	119.90	C24-C26-C28-H31	179.67	
C13-C17-C15	119.54	119.67 (17)	H30-C26-C28-C25	179.93	
C13-C17-H20	120.23	120.20	H30-C26-C28-H31	-0.10	
C15-C17-H20	120.22	119.90	H33-C32-N36-C1	-57.93	
H21-C22-C23	119.45	119.70	H33-C32-N36-C2	175.21	
H21-C22-C24	119.86	119.70	H34-C32-N36-C1	-177.33	
C23-C22-C24	120.69	120.61 (19)	H34-C32-N36-C2	55.81	
C2-C23-C22	120.27	120.19 (15)	H35-C32-N36-C1	62.68	
C2-C23-C25	120.75	121.24 (14)	H35-C32-N36-C2	-64.18	
C22-C23-C25	118.91	118.47 (15)	C3-C37-N38-O39	0.40	
C22-C24-C26	120.05	120.70 (19)	C4-C37-N38-O39	-176.79	
C22-C24-H27	119.82	119.70	C37-N38-O39-C40	-153.92	
C26-C24-H27	120.13	119.60	N38-O39-C40-O41	12.72	
C23-C25-C28	120.47	120.04 (19)	N38-O39-C40-C42	-168.93	
C23-C25-H29	118.98	120.00	O39-C40-C42-C43	6.78	
C28-C25-H29	120.53	120.00	O39-C40-C42-C44	-173.68	
C24-C26-C28	119.64	119.22 (18)	O41-C40-C42-C43	-174.90	
C24-C26-H30	120.19	119.60	O41-C40-C42-C44	4.65	
C28-C26-H30	120.17	120.40	C40-C42-C43-C45	179.65	
C25-C28-C26	120.24	120.9 (2)	C40-C42-C43-C46	0.09	
C25-C28-H31	119.78	119.50	C44-C42-C43-C45	0.12	
C26-C28-H31	119.98	119.50	C44-C42-C43-C46	-179.44	
H33-C32-H34	108.52	109.50	C40-C42-C44-C47	-179.85	
H33-C32-H35	108.30	109.50	C40-C42-C44-H48	0.00	
H33-C32-N36	110.47	109.50	C43-C42-C44-C47	-0.29	
H34-C32-H35	108.37	109.50	C43-C42-C44-H48	179.55	
H34-C32-N36	109.40	109.50	C42-C43-C45-C49	0.02	
H35-C32-N36	111.70	109.50	C42-C43-C45-H50	-179.72	
C1-N36-C2	114.29	108.29 (11)	C46-C43-C45-C49	179.58	
C1-N36-C32	110.94	108.89 (11)	C46-C43-C45-H50	-0.16	
C2-N36-C32	109.23	108.29 (11)	C42-C44-C47-C49	0.32	
C3-C37-C4	115.65	112.59 (12)	C42-C44-C47-C62	-178.95	
C3-C37-N38	128.64	127.95 (14)	H48-C44-C47-C49	-179.53	
C4-C37-N38	115.65	119.25 (13)	H48-C44-C47-C62	1.21	
C37-N38-O39	110.05	108.37 (11)	C43-C45-C49-C47	0.01	
N38-O39-C40	113.08	113.56 (11)	C43-C45-C49-H51	-179.81	
O39-C40-O41	123.71	124.53 (15)	H50-C45-C49-C47	179.75	
O39-C40-C42	111.17	109.46 (13)	H50-C45-C49-H51	-0.07	
O41-C40-C42	125.10	125.98 (15)	C44-C47-C49-C45	-0.17	
C40-C42-C43	122.66	122.52 (15)	C44-C47-C49-H51	179.65	
C40-C42-C44	117.41	118.00 (15)	C62-C47-C49-C45	179.09	
C43-C42-C44	119.92	119.46 (16)	C62-C47-C49-H51	-1.09	
C42-C43-C45	119.37	119.28 (19)	C44-C47-C62-H63	-16.80	
C42-C43-H46	119.82	119.30	C44-C47-C62-H64	103.01	
C45-C43-H46	120.81	119.30	C44-C47-C62-H65	-137.41	
C42-C44-C47	121.11	121.47 (18)	C49-C47-C62-H63	163.95	
C42-C44-H48	118.31	120.40	C49-C47-C62-H64	-76.23	
C47-C44-H48	120.58	119.30	C49-C47-C62-H65	43.34	
C43-C45-C49	120.36	120.68 (19)	H52-C53-C54-C4	-66.17	
C43-C45-H50	119.82	119.70	H52-C53-C54-C57	57.64	
C49-C45-H50	119.83	119.70	H52-C53-C54-H58	175.05	
C44-C47-C49	118.26	117.63 (19)	H55-C53-C54-C4	54.69	
C44-C47-C62	120.97	120.4 (2)	H55-C53-C54-C57	178.50	
C49-C47-C62	120.77	120.0 (2)	H55-H53-C54-H58	-64.09	
C45-C49-C47	120.99	121.45 (18)	H56-C53-C54-C4	175.52	
C45-C49-H51	119.66	119.30	H56-C53-C54-C57	-60.67	
C47-C49-H51	119.35	119.30	H56-C53-C54-H58	56.74	
H52-C53-C54	109.81	109.50	C4-C54-C57-H59	55.86	

Parameters	B3LYP/ 6-31G	XRD	Parameters	B3LYP/ 6-31G	XRD
H52-C53-H55	108.15	109.50	C4-C54-C57-H60	-65.29	
H52-C53-H56	107.62	109.50	C4-C54-C57-H61	174.88	
C54-C53-H55	113.03	109.50	C53-C54-C57-H59	-66.67	
C54-C53-H56	110.08	109.50	C53-C54-C57-H60	172.18	
H55-C53-H56	107.98	109.50	C53-C54-C57-H61	52.35	
C4-C54-C53	110.78	115.51 (14)	H58-C54-C57-H59	175.41	
C4-C54-C57	112.87	110.75 (14)	H58-C54-C57-H60	54.26	
C4-C54-H58	107.98	105.80	H58-C54-C57-H61	-65.57	
C53-C54-C57	107.59	111.31 (16)			
C53-C54-H58	109.17	106.20			
C57-C54-H58	108.37	106.20			
C54-C57-H59	110.85	109.50			

Parameters	B3LYP/ 6-31G	XRD	Parameters	B3LYP/ 6-31G	XRD
C54-C57-H60	113.28	109.50			
C54-C57-H61	109.50	109.50			
H59-C57-H60	107.66	109.50			
H59-C57-H61	107.97	109.50			
H60-C57-H61	107.39	109.50			
C47-C62-H63	111.31	109.50			
C47-C62-H64	111.25	109.50			
C47-C62-H65	111.46	109.50			
H63-C62-H64	107.46	109.50			
H63-C62-H65	107.98	109.50			
H64-C62-H65	107.18	109.50			

[a] Vinuchakkaravarthy .T., Sivakumar, R., Acta Cryst. E 69 **(2013)** o1276.

Table .2. The experimental and calculated frequencies of AMB using B3LYP/6-31G level of basis set [harmonic frequencies (cm^{-1}), IR, Raman intensities (Km/mol), reduced masses (amu) and force constants ($mdynA^{o-1}$)]

Mode No.	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥10% (TED)
	Un Scaled	Scaled	FT-IR	FT-Raman	Abs.	Rel.	Abs.	Rel.			
1	3250	3127			4.99	1.54	47.54	1.26	1.09	6.81	$\nu C_{43}H_{46}$(94)
2	3228	3105			13.31	4.10	117.77	3.11	1.10	6.74	$\nu C_{11}H_{14}$(88)
3	3225	3103			18.48	5.70	136.65	3.61	1.10	6.73	$\nu C_{24}H_{27}$(96)
4	3222	3099			4.14	1.28	24.72	0.65	1.09	6.67	$\nu C_{43}H_{46}$(98)
5	3219	3097			35.71	11.01	49.26	1.30	1.09	6.68	$\nu C_{11}H_{14}$(78)
6	3216	3094			32.51	10.02	14.00	0.37	1.09	6.67	$\nu C_{24}H_{27}$(90)
7	3211	3089	3090 w		25.55	7.88	55.27	1.46	1.09	6.64	$\nu C_{43}H_{46}$(94)
8	3206	3084			25.50	7.86	47.35	1.25	1.09	6.61	$\nu C_{12}H_{16}$(97)
9	3204	3082			23.50	7.24	42.80	1.13	1.09	6.60	$\nu C_{22}H_{21}$(93)
10	3194	3072			6.51	2.01	48.12	1.27	1.09	6.55	$\nu C_{11}H_{14}$(88)
11	3193	3072			11.86	3.65	23.96	0.63	1.10	6.59	$\nu C_{32}H_{34}$(96)
12	3193	3071			0.04	0.01	38.38	1.01	1.09	6.53	$\nu C_{24}H_{27}$(86)
13	3188	3067	3066 w	3067 w	11.25	3.47	43.96	1.16	1.09	6.51	$\nu C_{43}H_{46}$(99)
14	3185	3064			6.64	2.05	11.39	0.30	1.09	6.49	$\nu C_{12}H_{16}$(92)
15	3183	3063			7.75	2.39	12.83	0.34	1.09	6.49	$\nu C_{22}H_{21}$(96)
16	3177	3057			14.31	4.41	28.31	0.75	1.09	6.50	$\nu C_{53}H_{55}$(83)
17	3174	3053			4.20	1.29	25.68	0.68	1.09	6.50	$\nu C_{3}H_{6}$(89)
18	3141	3021	3021 w	3021 vw	23.09	7.12	55.72	1.47	1.07	6.22	$\nu C_{32}H_{34}$(90)
19	3136	3017			36.15	11.14	19.53	0.52	1.10	6.36	$\nu C_{57}H_{60}$(95)

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Mode No.	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥10% (TED)
	Un Scaled	Scaled	FT-IR	FT-Raman	Abs.	Rel.	Abs.	Rel.			
20	3133	3014			14.22	4.38	30.00	0.79	1.10	6.36	$\nu C_{62}H_{63}(90)$
21	3122	3004			48.50	14.95	42.60	1.13	1.10	6.31	$\nu C_{57}H_{61}(89)$
22	3106	2988			15.95	4.92	17.86	0.47	1.10	6.25	$\nu C_{53}H_{52}(80)$
23	3100	2982			23.09	7.12	55.60	1.47	1.10	6.20	$\nu C_{62}H_{63}(88)$
24	3080	2963	2962 w	2966 w	12.76	3.93	29.56	0.78	1.07	5.96	$\nu C_{3}H_{6}(89)$
25	3072	2955			9.96	3.07	21.20	0.56	1.08	6.03	$\nu C_{3}H_{6}(76)$
26	3052	2936			36.19	11.16	62.26	1.65	1.04	5.70	$\nu C_{57}H_{60}(95)$
27	3050	2934			6.86	2.11	36.89	0.98	1.08	5.90	$\nu C_{1}H_{5}(75)$
28	3042	2926			20.59	6.35	35.89	0.95	1.04	5.68	$\nu C_{53}H_{52}(80)$
29	3040	2924			35.76	11.03	125.59	3.32	1.04	5.65	$\nu C_{62}H_{63}(97)$
30	2953	2841	2879 w	2872 vw	77.66	23.94	47.73	1.26	1.06	5.45	$\nu C_{32}H_{35}(94)$
31	2910	2800			44.97	13.86	25.06	0.66	1.08	5.39	$\nu C_{2}H_{9}(96)$
32	2892	2782	2772 w		32.85	10.13	16.42	0.43	1.08	5.32	$\nu C_{1}H_{5}(96)$
33	1726	1661	1768 vs		161.34	49.74	217.11	5.74	12.40	21.77	$\nu O_{41}C_{40}(78)$
34	1682	1618	1689 s	1688 w	51.44	15.86	131.48	3.47	8.55	14.24	$\nu N_{38}C_{37}(74)$
35	1664	1601	1607 w		19.97	6.16	313.56	8.29	5.68	9.27	$\nu C_{43}C_{45}(61)+\nu C_{42}C_{44}(42)$
36	1662	1599			2.33	0.72	108.44	2.87	5.54	9.03	$\nu C_{22}C_{23}(55)+\beta H_{27}C_{24}C_{26}(40)$
37	1661	1598		1597 w	6.58	2.03	138.23	3.65	5.53	8.99	$\nu C_{10}C_{12}(66)$
38	1644	1581			1.85	0.57	24.00	0.63	5.39	8.58	$\nu C_{22}C_{23}(57)+\beta C_{22}C_{24}C_{26}(16)$
39	1641	1579			0.78	0.24	20.18	0.53	5.35	8.49	$\nu C_{10}C_{12}(44)$
40	1641	1579			11.48	3.54	63.69	1.68	5.36	8.51	$\nu C_{43}C_{45}(29)+\nu C_{42}C_{43}(22)+\nu C_{47}C_{49}(30)+\beta H_{46}C_{43}C_{42}(21)$
41	1559	1500			8.23	2.54	6.27	0.17	1.05	1.50	$\beta H_{52}C_{53}H_{55}(47)+\beta H_{60}C_{57}H_{61}(37)$
42	1553	1494			5.32	1.64	2.77	0.07	1.96	2.78	$\beta H_{14}C_{11}C_{13}(62)+\beta H_{16}C_{12}C_{15}(24)$
43	1552	1493			24.91	7.68	36.19	0.96	1.47	2.09	$\beta H_{52}C_{53}H_{55}(54)+\beta H_{52}C_{53}H_{55}(27)$
44	1551	1492			3.59	1.11	48.08	1.27	1.33	1.88	$\beta H_{14}C_{11}C_{13}(32)+\beta H_{52}C_{53}H_{55}(24)+\beta H_{52}C_{53}H_{55}(27)$
45	1549	1491			7.34	2.26	40.78	1.08	1.09	1.54	$\beta H_{33}C_{32}H_{34}(31)+\Gamma C_{32}H_{34}N_{36}H_{33}(38)$
46	1548	1489		1489 w	7.98	2.46	10.49	0.28	1.57	2.21	$\beta H_{50}C_{45}C_{43}(20)+\beta H_{46}C_{43}C_{45}(26)+\beta H_{63}C_{62}H_{64}(29)$
47	1544	1486			3.60	1.11	45.78	1.21	1.05	1.48	$\beta H_{34}C_{32}H_{35}(38)+\Gamma C_{32}H_{34}N_{36}H_{35}(41)$
48	1538	1480	1479 w		1.91	0.59	60.70	1.60	1.05	1.46	$\beta H_{33}C_{32}H_{34}(23)+\beta H_{52}C_{53}H_{55}(13)+\beta H_{52}C_{53}H_{55}(29)+\beta H_{60}C_{57}H_{61}(37)$
49	1535	1477			11.53	3.56	9.91	0.26	1.43	1.99	$\beta H_{46}C_{43}C_{45}(36)+\beta H_{63}C_{62}H_{64}(29)$
50	1535	1476			3.47	1.07	11.44	0.30	1.06	1.47	$\beta H_{33}C_{32}H_{34}(23)+\beta H_{52}C_{53}H_{55}(53)$
51	1534	1476			8.84	2.73	63.04	1.67	1.05	1.46	$\beta H_{64}C_{62}C_{47}(25)+\tau H_{63}C_{62}C_{47}C_{49}(22)+\Gamma C_{62}H_{63}C_{47}H_{64}(37)$
52	1521	1463		1465 m	5.97	1.84	13.52	0.36	1.10	1.50	$\tau H_{6}C_{3}C_{2}N_{36}(37)+\Gamma C_{3}C_{2}C_{37}H_{7}(46)$

Mode No.	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥10% (TED)
	Un Scaled	Scaled	FT-IR	FT-Raman	Abs.	Rel.	Abs.	Rel.			
53	1516	1458			8.48	2.61	14.97	0.40	1.83	2.47	$\beta H_{20}C_{17}C_{13}(27)+\beta H_{27}C_{24}C_{26}(31)+\beta H_{27}C_{24}C_{26}(21)$
54	1512	1455			6.56	2.02	4.58	0.12	2.00	2.69	$\nu C_{10}C_{12}(28)+\beta H_{20}C_{17}C_{13}(37)+\beta H_{27}C_{24}C_{26}(21)$
55	1499	1442	1444 m	1441 s	9.55	2.94	39.16	1.03	1.24	1.65	$\Gamma C_{32}H_{33}H_{35}H_{34}(64)$
56	1484	1427			27.69	8.54	84.80	2.24	2.64	3.42	$\nu C_{42}C_{44}(42)+\beta H_{46}C_{43}C_{42}(31)$
57	1475	1419	1416 w	1417 w	11.86	3.66	4.31	0.11	1.19	1.53	$\beta H_{52}C_{53}H_{55}(29)+\beta H_{60}C_{57}H_{61}(37)$
58	1464	1408	1402 w		3.95	1.22	109.21	2.89	1.22	1.54	$\beta H_{63}C_{62}H_{64}(51)$
59	1450	1395			3.15	0.97	17.67	0.47	1.19	1.47	$\beta H_{33}C_{32}H_{34}(23)+\beta H_{52}C_{53}H_{55}(44)$
60	1436	1382			4.62	1.42	8.21	0.22	1.37	1.66	$\beta H_{5}C_{1}N_{36}(44)+\beta H_{9}C_{2}C_{23}(31)$
61	1415	1361			17.77	5.48	8.92	0.24	1.32	1.55	$\beta H_{27}C_{24}C_{26}(31)+\beta H_{5}C_{1}N_{36}(24)+\beta H_{9}C_{2}C_{23}(31)$
62	1402	1348			6.55	2.02	41.65	1.10	1.27	1.47	$\beta H_{8}C_{4}C_{54}(46)+\Gamma C_{1}C_{10}N_{36}H_{5}(42)$
63	1387	1334			7.33	2.26	11.17	0.30	1.41	1.60	$\beta H_{14}C_{11}C_{10}(29)+\beta H_{27}C_{24}C_{26}(21)+\beta H_{8}C_{4}C_{54}(26)+\Gamma C_{2}C_{23}N_{36}H_{9}(26)$
64	1381	1329			6.51	2.01	23.14	0.61	1.49	1.67	$\Gamma C_{54}C_{4}C_{53}H_{58}(68)$
65	1378	1326			9.61	2.96	20.86	0.55	2.04	2.28	$\nu C_{22}C_{23}(32)+\Gamma C_{54}C_{4}C_{53}H_{58}(38)$
66	1378	1326			3.96	1.22	16.06	0.42	3.44	3.85	$\nu C_{42}C_{43}(49)+\beta H_{48}C_{44}C_{42}(37)$
67	1376	1324			7.55	2.33	74.13	1.96	1.36	1.52	$\beta H_{6}C_{3}C_{2}(31)+\Gamma C_{2}C_{23}N_{36}H_{9}(26)+\Gamma C_{54}C_{4}C_{53}H_{58}(28)$
68	1369	1317			0.72	0.22	21.85	0.58	1.91	2.11	$\beta H_{58}C_{54}C_{53}(40)+\Gamma C_{1}C_{10}N_{36}H_{5}(32)$
69	1363	1311		1313 w	0.57	0.18	1.46	0.04	1.69	1.85	$\nu C_{47}C_{49}(20)+\beta H_{48}C_{44}C_{42}(27)+\beta H_{46}C_{43}C_{45}(36)$
70	1359	1307			26.65	8.22	22.04	0.58	1.59	1.73	$\nu C_{22}C_{23}(32)+\beta H_{7}C_{3}C_{37}(17)+\beta H_{58}C_{54}C_{53}(30)$
71	1344	1293			13.85	4.27	22.70	0.60	1.85	1.97	$\beta H_{58}C_{54}C_{53}(60)$
72	1333	1282			10.20	3.14	31.11	0.82	1.77	1.85	$\beta H_{7}C_{3}C_{37}(47)$
73	1330	1279	1279 vs		6.11	1.88	82.55	2.18	1.48	1.54	$\beta H_{8}C_{4}C_{54}(26)+\beta H_{58}C_{54}C_{53}(30)+$ΓC4C37C54H8(37)
74	1327	1276			34.08	10.51	17.19	0.45	1.61	1.67	$\Gamma C_{4}C_{37}C_{54}H_{8}(47)$
75	1307	1258		1261 m	35.55	10.96	26.59	0.70	1.93	1.95	$\beta H_{9}C_{2}C_{23}(61)$
76	1301	1251			264.23	81.46	294.03	7.77	3.82	3.81	$\nu C_{40}C_{42}(20)+\nu C_{47}C_{62}(25)+\beta C_{40}C_{42}C_{43}(34)$
77	1271	1223	1237 s		7.65	2.36	19.06	0.50	2.06	1.96	$\nu C_{1}C_{10}(11)+\beta H_{6}C_{3}C_{2}(31)+\Gamma C_{32}H_{34}N_{36}H_{35}(41)$
78	1244	1196	1204 w		0.82	0.25	131.41	3.47	2.52	2.30	$\nu C_{1}C_{10}(33)$
79	1235	1188			1.75	0.54	48.31	1.28	1.45	1.30	$\nu C_{10}C_{12}(16)+\beta H_{14}C_{11}C_{10}(19)+\beta H_{27}C_{24}C_{26}(29)+\beta H_{14}C_{11}C_{13}(22)$
80	1234	1187			0.35	0.11	26.18	0.69	1.24	1.11	$\nu C_{22}C_{23}(13)+\beta H_{16}C_{12}C_{15}(24)$
81	1231	1184			1.45	0.45	18.07	0.48	1.15	1.03	$\nu C_{43}C_{45}(21)+\beta H_{50}C_{45}C_{43}(20)+\beta H_{46}C_{43}C_{45}(36)$
82	1229	1182		1183 w	2.31	0.71	14.96	0.40	1.58	1.41	$\nu C_{1}C_{10}(20)+\beta H_{21}C_{22}C_{24}(22)$
83	1222	1175			0.03	0.01	23.86	0.63	1.09	0.96	$\beta H_{18}C_{13}C_{17}(12)+\beta H_{27}C_{24}C_{26}(47)$
84	1221	1175			0.83	0.26	21.24	0.56	1.13	1.00	$\beta H_{18}C_{13}C_{17}(22)+\beta H_{27}C_{24}C_{26}(57)$

Mode No.	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥10% (TED)
	Un Scaled	Scaled	FT-IR	FT-Raman	Abs.	Rel.	Abs.	Rel.			
85	1216	1169			90.14	27.79	8.47	0.22	1.90	1.66	$\Gamma C_{32}H_{34}N_{36}H_{35}(41)$
86	1213	1166			35.41	10.92	18.09	0.48	1.80	1.56	$\beta H_{52}C_{53}C_{54}(37)+\Gamma C_{57}H_{59}C_{54}H_{61}(46)$
87	1206	1160	1156 w		188.04	57.97	81.64	2.16	1.94	1.66	$\nu C_{40}C_{42}(30)+\nu C_{47}C_{62}(25)$
88	1176	1131	1140 m	1145 m	10.16	3.13	41.86	1.11	1.64	1.34	$\Gamma C_{32}H_{34}N_{36}H_{33}(78)$
89	1154	1110			2.03	0.63	5.75	0.15	1.54	1.21	$\Gamma C_{32}H_{34}N_{36}H_{33}(38)+\Gamma C_{57}H_{59}C_{54}H_{60}(42)$
90	1149	1105			26.27	8.10	62.13	1.64	2.62	2.04	$\nu N_{3}6C_{1}(45)+\Gamma C_{32}H_{34}N_{36}H_{33}(38)$
91	1141	1097			5.25	1.62	25.50	0.67	1.61	1.24	$\nu C_{43}C_{45}(29)+\beta H_{46}C_{43}C_{42}(41)$
92	1136	1093		1091 w	5.72	1.76	17.70	0.47	2.00	1.52	$\nu C_{2}C_{3}(13)+\nu C_{2}C_{3}(19)+\Gamma C_{57}H_{59}C_{54}H_{60}(32)$
93	1121	1078	1084 vw		1.04	0.32	0.81	0.02	1.67	1.24	$\nu C_{10}C_{12}(18)+\nu C_{22}C_{23}(27)+\beta H_{20}C_{17}C_{13}(37)$
94	1115	1073	1071 vw		24.54	7.57	27.79	0.73	1.96	1.44	$\nu C_{10}C_{12}(28)+\nu N_{36}C_{1}(45)$
95	1107	1065			324.37	#####	28.59	0.76	3.01	2.17	$\nu C_{42}C_{44}(22)+\nu O_{39}C_{40}(32)+\beta C_{42}C_{40}O_{41}(28)$
96	1104	1062			15.08	4.65	6.54	0.17	1.54	1.10	$\beta H_{64}C_{62}C_{47}(35)+\Gamma C_{62}H_{63}C_{47}H_{64}(57)$
97	1073	1032	1049 w	1047 w	32.62	10.06	84.16	2.22	4.13	2.80	$\nu N_{36}C_{1}(42)$
98	1067	1026			7.09	2.18	69.97	1.85	2.29	1.53	$\beta H_{14}C_{11}C_{13}(32)+\beta C_{10}C_{12}C_{15}(52)$
99	1067	1026			9.20	2.84	17.85	0.47	2.29	1.54	$\nu C_{22}C_{23}(27)+\nu C_{26}C_{28}(18)+\beta C_{23}C_{25}C_{28}(40)$
100	1044	1004			12.48	3.85	72.34	1.91	3.24	2.08	$\nu C_{2}C_{3}(20)+\beta C_{1}C_{4}C_{37}(33)$
101	1039	1000			6.65	2.05	308.31	8.15	3.04	1.93	$\beta C_{23}C_{25}C_{28}(20)+\beta C_{40}C_{42}C_{43}(34)+\Gamma C_{62}H_{63}C_{47}H_{64}(37)$
102	1039	999		999 w	16.25	5.01	115.16	3.04	4.30	2.73	$\beta C_{23}C_{25}C_{28}(50)+\beta C_{10}C_{12}C_{15}(32)$
103	1037	998			9.09	2.80	61.88	1.64	4.18	2.65	$\nu C_{10}C_{12}(13)+\beta C_{23}C_{25}C_{28}(30)+\beta C_{10}C_{12}C_{15}(22)$
104	1035	996			13.77	4.25	46.06	1.22	2.43	1.53	$\nu C_{22}C_{23}(27)$
105	1032	993			61.23	18.88	127.89	3.38	1.97	1.24	$\nu C_{43}C_{45}(19)+\beta C_{40}C_{42}C_{43}(24)+\Gamma C_{62}H_{63}C_{47}H_{64}(37)$
106	1031	992			2.89	0.89	16.35	0.43	1.38	0.86	$\tau H_{27}C_{24}C_{26}C_{28}(42)+\tau$C22C24C26C28(38)
107	1031	991			31.73	9.78	11.93	0.32	1.89	1.18	$\tau H_{18}C_{13}C_{11}C_{10}(44)$
108	1021	982			1.56	0.48	2.15	0.06	1.35	0.83	$\Gamma C_{45}C_{43}C_{49}H_{50}(73)$
109	1011	973			0.60	0.19	1.61	0.04	1.37	0.83	$\tau H_{14}C_{11}C_{13}C_{17}(27)+\Gamma C_{12}C_{10}C_{15}H_{16}(41)$
110	1005	966			0.22	0.07	1.41	0.04	1.37	0.82	$\tau H_{27}C_{24}C_{26}C_{28}(25)+\tau H_{21}C_{22}C_{24}C_{26}(30)$
111	987	950			9.51	2.93	11.05	0.29	1.73	0.99	$\nu C_{2}C_{3}(39)+\Gamma C_{53}H_{52}C_{54}H_{55}(24)$
112	977	940			5.21	1.61	15.67	0.41	1.44	0.81	$\tau H_{48}C_{44}C_{47}C_{49}(33)+\Gamma C_{44}C_{40}C_{43}C_{42}(44)$
113	976	939	935 m		12.82	3.95	25.74	0.68	2.06	1.16	$\nu C_{2}C_{3}(33)+\Gamma C_{57}H_{59}C_{54}H_{60}(42)$
114	966	930			0.69	0.21	5.45	0.14	1.42	0.78	$\beta H_{52}C_{53}C_{54}(37)+\Gamma C_{57}H_{59}C_{54}H_{61}(46)$
115	962	925			12.47	3.84	5.93	0.16	1.57	0.86	$\Gamma C_{17}C_{13}C_{15}H_{20}(64)$
116	960	923			3.38	1.04	4.24	0.11	1.47	0.80	$\Gamma C_{17}C_{13}C_{15}H_{20}(34)+\Gamma C_{12}C_{10}C_{15}H_{16}(41)$
117	948	912			6.83	2.11	33.22	0.88	2.00	1.06	$\tau H_{21}C_{22}C_{24}C_{26}(60)$

Mode No.	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥10% (TED)
	Un Scaled	Scaled	FT-IR	FT-Raman	Abs.	Rel.	Abs.	Rel.			
118	947	911	910 vw		1.17	0.36	14.88	0.39	1.33	0.70	$\tau H_{46}C_{43}C_{45}C_{49}(73)$
119	925	890			7.06	2.18	22.69	0.60	3.47	1.75	$\nu O_{39}C_{40}(22)+\nu C_{53}C_{54}(31)$
120	913	878			92.60	28.55	27.57	0.73	3.68	1.81	$\nu O_{39}C_{40}(12)+\nu C_{53}C_{54}(41)$
121	896	862			24.31	7.50	50.94	1.35	2.81	1.33	$\nu C_{53}C_{54}(61)$
122	889	856			0.38	0.12	22.98	0.61	1.26	0.59	$\tau H_{14}C_{11}C_{13}C_{17}(22)+\Gamma C_{12}C_{10}C_{15}H_{16}(41)$
123	885	851			0.11	0.03	21.62	0.57	1.25	0.58	$\tau H_{27}C_{24}C_{26}C_{28}(24)+\tau H_{21}C_{22}C_{24}C_{26}(40)$
124	873	840	842 w		38.60	11.90	13.91	0.37	4.05	1.82	$\nu C_{1}C_{10}(30)$
125	843	811		824 vw	100.82	31.08	117.37	3.10	3.31	1.38	$\nu O_{39}N_{38}(24)+\tau H_{46}C_{43}C_{45}C_{49}(41)$
126	833	801			48.56	14.97	68.85	1.82	2.21	0.90	$\tau H_{46}C_{43}C_{45}C_{49}(21)+\Gamma C_{44}C_{40}C_{43}C_{42}(44)$
127	814	783			22.06	6.80	64.78	1.71	3.19	1.24	$\tau H_{46}C_{43}C_{45}C_{49}(61)$
128	801	771	772 w		6.12	1.89	35.82	0.95	2.28	0.86	$\Gamma C_{17}C_{13}C_{15}H_{20}(24)+\tau H_{18}C_{13}C_{11}C_{10}(44)$
129	795	764	763 w		18.67	5.76	9.94	0.26	2.08	0.77	$\tau H_{30}C_{26}C_{24}C_{22}(19)+\tau H_{27}C_{24}C_{26}C_{28}(22)+\tau C_{22}C_{24}C_{26}C_{28}(39)$
130	789	759			23.31	7.19	81.67	2.16	5.10	1.87	$\nu N_{36}C_{1}(24)+\nu O_{39}N_{38}(54)$
131	765	736			54.85	16.91	58.78	1.55	4.18	1.44	$\nu O_{39}N_{38}(64)$
132	740	712		716 vw	57.63	17.77	22.51	0.59	2.25	0.73	$\tau H_{46}C_{43}C_{45}C_{49}(21)+\tau C_{40}C_{42}C_{43}C_{45}(29)+\Gamma C_{44}C_{40}C_{43}C_{42}(34)$
133	738	710			58.02	17.89	24.92	0.66	1.65	0.53	$\tau C_{10}C_{11}C_{13}C_{17}(12)+\tau C_{1}C_{10}C_{12}C_{15}(26)+\tau C_{12}C_{15}C_{17}C_{13}(29)$
134	733	705			34.80	10.73	9.37	0.25	1.73	0.55	$\tau H_{30}C_{26}C_{24}C_{22}(19)+\tau C_{22}C_{24}C_{26}C_{28}(39)$
135	729	701	694 w		14.62	4.51	38.18	1.01	4.58	1.43	$\tau C_{22}C_{24}C_{26}C_{28}(59)$
136	701	674	680 w		5.91	1.82	6.64	0.18	4.05	1.17	$\tau C_{44}C_{47}C_{49}C_{45}(20)+\tau C_{40}C_{42}C_{44}C_{47}(32)+\tau C_{43}C_{42}C_{40}O_{41}(33)$
137	690	664			10.18	3.14	70.58	1.87	6.93	1.94	$\nu O_{39}N_{3}8(24)+\beta C_{42}C_{43}C_{45}(46)$
138	675	649			2.61	0.80	29.11	0.77	5.21	1.40	$\nu O_{39}N_{38}(54)$
139	663	638		638 vw	3.32	1.02	52.16	1.38	4.38	1.13	$\beta C_{3}C_{37}N_{38}(27)+\beta C_{42}C_{40}O_{39}(12)+\beta C_{37}N_{38}O_{39}(11)$
140	653	628			0.28	0.09	52.54	1.39	6.12	1.54	$\beta C_{10}C_{12}C_{15}(64)+\beta C_{10}C_{12}C_{15}(14)$
141	651	626			0.17	0.05	40.46	1.07	6.37	1.59	$\beta C_{22}C_{24}C_{26}(55)$
142	643	619			4.04	1.24	18.93	0.50	4.70	1.14	$\beta C_{22}C_{24}C_{26}(36)$
143	619	596			0.61	0.19	40.79	1.08	4.89	1.10	$\beta C_{22}C_{24}C_{26}(36)$
144	567	545			0.51	0.16	30.48	0.81	4.16	0.79	$\beta C_{42}C_{43}C_{45}(43)$
145	553	532			11.78	3.63	63.44	1.68	4.62	0.83	$\beta C_{42}C_{43}C_{45}(43)$
146	538	518			5.68	1.75	18.08	0.48	3.47	0.59	$\beta C_{42}C_{43}C_{45}(43)$
147	524	504			2.16	0.66	61.69	1.63	3.43	0.55	$\beta C_{42}C_{43}C_{45}(43)$
148	512	492	482 vw		7.59	2.34	12.38	0.33	3.85	0.59	$\tau C_{44}C_{47}C_{49}C_{45}(20)+\tau C_{43}C_{42}C_{40}O_{41}(23)+\tau C_{45}C_{49}C_{47}C_{62}(23)+\Gamma C_{44}C_{40}C_{43}C_{42}(34)$
149	500	481	471 w		3.64	1.12	5.88	0.16	4.21	0.62	$\Gamma C_{57}C_{4}C_{53}C_{54}(33)$
150	482	463	452 w		0.14	0.04	27.97	0.74	3.35	0.46	$\beta C_{2}N_{36}C_{32}(32)$

Mode No.	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥10% (TED)
	Un Scaled	Scaled	FT-IR	FT-Raman	Abs.	Rel.	Abs.	Rel.			
151	454	437	446 m		2.72	0.84	5.09	0.13	3.53	0.43	$\Gamma C_{57}C_{4}C_{53}C_{54}(33)$
152	444	427	438 w		0.16	0.05	11.95	0.32	2.74	0.32	$\beta C_{53}C_{54}C_{57}(44)+\tau C_{43}C_{45}C_{49}C_{47}(53)$
153	440	423	433 w		1.99	0.61	10.11	0.27	2.88	0.33	$\beta C_{53}C_{54}C_{57}(34)+\tau C_{43}C_{45}C_{49}C_{47}(43)$
154	433	416	428 w		0.03	0.01	2.64	0.07	2.87	0.32	$\tau H_{14}C_{11}C_{13}C_{17}(27)+\tau C_{1}C_{10}C_{12}C_{15}(26)+\tau C_{12}C_{15}C_{17}C_{13}(39)$
155	427	411			0.22	0.07	1.70	0.04	2.88	0.31	$\tau C_{22}C_{24}C_{26}C_{28}(58)$
156	390	375			3.43	1.06	17.48	0.46	4.39	0.39	$\tau C_{3}C_{37}N_{38}O_{39}(49)$
157	383	368			2.97	0.92	17.79	0.47	4.31	0.37	$\beta C_{42}C_{40}O_{41}(28)+\beta C_{42}C_{43}C_{45}(36)+\beta C_{49}C_{47}C_{62}(37)$
158	356	343			0.65	0.20	16.23	0.43	4.10	0.31	$\beta C_{1}C_{10}C_{12}(24)+\beta C_{2}C_{23}C_{22}(31)+\Gamma C_{32}C_{1}C_{2}N_{36}(37)$
159	350	337			0.77	0.24	18.57	0.49	3.66	0.26	$\beta C_{4}C_{54}C_{57}(14)+\beta C_{49}C_{47}C_{62}(37)+\Gamma C_{32}C_{1}C_{2}N_{36}(27)$
160	344	330			0.56	0.17	36.89	0.97	3.24	0.23	$\Gamma C_{32}C_{1}C_{2}N_{36}(37)$
161	325	312			1.95	0.60	48.79	1.29	3.27	0.20	$\beta C_{4}C_{5}4C_{57}(24)$
162	304	292			4.59	1.42	134.63	3.56	3.72	0.20	$\beta C_{3}C_{37}N_{38}(27)$
163	278	268			2.53	0.78	70.90	1.87	3.68	0.17	$\tau C_{22}C_{24}C_{26}C_{28}(38)$
164	272	262			0.93	0.29	36.70	0.97	3.61	0.16	$\beta C_{4}C_{1}N_{36}(13)+\tau C_{1}C_{10}C_{12}C_{15}(46)$
165	258	248			0.85	0.26	8.88	0.23	1.33	0.05	$\tau H_{34}C_{32}N_{36}C_{1}(27)+\tau H_{58}C_{54}C_{57}H_{59}(47)$
166	245	236			0.39	0.12	189.92	5.02	4.12	0.15	$\beta C_{1}C_{10}C_{12}(44)$
167	236	227			0.37	0.11	31.01	0.82	2.76	0.09	$\tau H_{58}C_{54}C_{57}H_{59}(77)$
168	221	212			1.43	0.44	122.64	3.24	2.87	0.08	$\tau C_{44}C_{47}C_{49}C_{45}(20)+\tau C_{45}C_{49}C_{47}C_{62}(43)$
169	217	209			0.84	0.26	12.79	0.34	1.19	0.03	$\tau H_{34}C_{32}N_{36}C_{1}(55)$
170	211	203			0.10	0.03	13.56	0.36	1.13	0.03	$\tau H_{34}C_{32}N_{36}C_{1}(27)+\tau H_{58}C_{54}C_{57}H_{59}(57)$
171	203	195			1.56	0.48	40.04	1.06	4.44	0.11	$\beta C_{40}C_{42}C_{44}(19)$
172	185	178			0.61	0.19	41.69	1.10	4.19	0.09	$\tau C_{40}C_{42}C_{43}C_{45}(69)$
173	175	169			1.13	0.35	62.05	1.64	4.15	0.08	$\beta C_{1}C_{10}C_{12}(44)$
174	166	160			0.78	0.24	35.17	0.93	3.99	0.07	$\beta C_{2}C_{23}C_{22}(31)+\Gamma C_{3}C_{23}N_{36}C_{2}(15)$
175	156	150			0.61	0.19	205.80	5.44	4.77	0.07	$\tau C_{40}C_{42}C_{43}C_{45}(29)+\tau C_{43}C_{42}C_{40}O_{41}(33)$
176	118	114			1.79	0.55	174.92	4.62	3.83	0.03	$\beta C_{1}C_{4}C_{54}(27)$
177	105	101			0.26	0.08	547.01	14.46	3.58	0.02	$\tau C_{1}C_{10}C_{12}C_{15}(22)+\tau C_{37}C_{4}C_{54}C_{53}(50)$
178	92	89			0.06	0.02	114.23	3.02	5.55	0.03	$\tau C_{1}C_{10}C_{12}C_{15}(12)+\tau C_{43}C_{42}C_{40}O_{41}(23)+\Gamma C_{37}C_{3}N_{38}C_{4}(12)$
179	86	83		75 s	0.48	0.15	234.55	6.20	3.73	0.02	$\tau C_{37}C_{4}C_{54}C_{53}(40)+\Gamma C_{2}C_{22}C_{2}5C_{23}(20)$
180	67	65			0.80	0.25	230.63	6.10	3.92	0.01	$\tau C_{37}C_{4}C_{54}C_{53}(50)$
181	63	60			0.14	0.04	448.49	11.85	4.18	0.01	$\tau C_{1}C_{10}C_{12}C_{15}(46)$
182	54	52			0.28	0.09	162.45	4.29	4.87	0.01	$\tau C_{40}C_{42}C_{44}C_{47}(12)+\tau C_{1}N_{36}C_{2}C_{23}(23)+\tau C_{43}C_{42}C_{40}O_{41}(33)$
183	45	44			0.23	0.07	1043.21	27.57	4.32	0.01	$\tau C_{1}N_{36}C_{2}C_{23}(43)$

Mode No.	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥10% (TED)
	Un Scaled	Scaled	FT-IR	FT-Raman	Abs.	Rel.	Abs.	Rel.			
184	37	36			0.71	0.22	446.81	11.81	4.72	0.00	$\tau C_{42}C_{40}O_{39}N_{38}(25)+\tau C_2N_{36}C_1C_{10}(26)+\tau C_{54}C_4C_1N_{36}(23)$
185	33	32			0.21	0.06	784.60	20.74	4.22	0.00	$\beta C_{23}C_2N_{36}(10)+\tau C_2N_{36}C_1C_{10}(42)$
186	25	24			0.17	0.05	513.46	13.57	2.00	0.00	$\beta C_{40}O_{39}N_{38}(11)+\tau H_{63}C_{62}C_{47}C_{44}(45)+\tau C_2C_3C_{37}N_{38}(12)$
187	22	21			0.17	0.05	690.38	18.25	1.49	0.00	$\tau H_{63}C_{62}C_{47}C_{44}(65)$
188	18	18			0.82	0.25	902.42	23.85	5.53	0.00	$\tau C_{42}C_{40}O_{39}N_{38}(55)+\tau C_2N_{36}C_1C_{10}(26)$
189	12	12			0.22	0.07	3783.82	100.00	4.17	0.00	$\tau C_{37}N_{38}O_{39}C_{40}(70)$

ν: Stretching, β: in-plane-bending, Γ: out-of-plane bending, τ: Torsion, vw: very week, w: week, m: medium, s: strong, vs: very strong,

[a] Scaling factor: 0.9608 (Radom et al., 1970 and Pople et al., 1993),

[b] Relative IR absorption intensities normalized with highest peak absorption equal to 100,

[c] Relative Raman intensities calculated by Equation (2.1) and normalized to 100,

[d] Total energy distribution calculated at B3LYP/6-31G level.

Table 3. The NLO measurements of AMB

Parameters	B3LYP/6-311++G(d,p)
Dipole moment (μ)	**Debye**
μ_x	0.3664
μ_y	1.4411
μ_z	-0.2575
μ	1.5091**Debye**
Polarizability (α_0)	***x10^{-30}esu***
α_{xx}	417.84
α_{xy}	-26.74
α_{yy}	328.85
α_{xz}	20.84
α_{yz}	0.9996
α_{zz}	219.63
α_o	0.8298**x10^{-30}esu**
Hyperpolarizability (β_0)	***x10^{-30}esu***
β_{xxx}	7.34
β_{xxy}	-185.89
β_{xyy}	-34.18
β_{yyy}	7.11
β_{xxz}	87.14
β_{xyz}	15.81
β_{yyz}	-9.94
β_{xzz}	27.37
β_{yzz}	1.05
β_{zzz}	19.42
β_0	1.7477x**10^{-30}esu**

Standard value for urea (μ=1.3732 Debye, β_0=0.3728x10^{-30}esu): esu-electrostatic unit

Table 4. Second order perturbation theory analysis of Fock matrix in NBO basis for AMB

Type	Donor NBO (i)	ED/e	Acceptor NBO (j)	ED/e	[a]**$E^{(2)}$** KJ/mol	[b]**E(j)-E(i)** a.u.	[c]F(i,j) a.u.
σ–σ*	BD(1) C1–C4	1.953	BD*(1) C1–C10	0.029	5.27	0.98	0.031
			BD*(1) C32–N36	0.011	10.71	0.61	0.038
			BD*(1) C37–N38	0.017	9.12	0.89	0.04
			BD*(2) C37–N38	0.110	6.82	1.13	0.039
			BD*(1) C54–C57	0.011	11.21	0.59	0.036
σ–σ*	BD(1) C1–H5	1.976	BD*(1) C4–C54	0.034	4.94	0.94	0.03
			BD*(1) C10–C11	0.024	15.73	0.83	0.05
σ–σ*	BD(1) C1–C10	1.971	BD*(1) C1–C4	0.032	15.61	1.06	0.056
			BD*(1) C2–N36	0.031	5.36	0.94	0.031
			BD*(1) C4–C37	0.029	9.83	0.93	0.042
			BD*(1) C10–C11	0.024	6.11	1.02	0.034
			BD*(1) C10–C12	0.022	10.46	1.18	0.049
			BD*(1) C11–C13	0.015	9.37	1.19	0.046
			BD*(1) C12–C15	0.017	8.54	1.2	0.044
σ–σ*	BD(1) C1–N36	1.981	BD*(1) C2–C23	0.034	8.7	1.19	0.045
			BD*(1) C10–C12	0.022	6.74	1.09	0.038
			BD*(1) C32–H34	0.008	6.36	1.26	0.039

Type	Donor NBO (i)	ED/e	Acceptor NBO (j)	ED/e	[a]$E^{(2)}$ KJ/mol	[b]**E(j)-E(i)** a.u.	[c]F(i,j) a.u.
σ–σ*	BD (1) C2–C3	1.954	BD*(1) C2–C23	0.0303	4.77	1.15	0.032
			BD*(1) C3–C37	0.038	5.31	0.99	0.032
			BD*(2) C22–C23	0.346	4.77	1.01	0.03
			BD*(1) C32–N36	0.016	11.42	0.62	0.04
			BD*(1) C37–N38	0.017	9.37	0.91	0.041
			BD*(2) C37–N38	0.116	10.25	1.15	0.048
σ–σ*	BD (1) C2–H9	1.979	BD*(1) C3–H6	0.015	13.77	0.6	0.04
			BD*(1) C23–C25	0.024	9.92	0.94	0.042
σ–σ*	BD (1) C2–C23	1.970	BD*(1) C1–N36	0.034	15.98	1.07	0.057
			BD*(1) C2–C3	0.025	10.17	0.93	0.042
			BD*(1) C3–C37	0.038	5.4	0.96	0.032
			BD*(1) C22–C23	0.022	8.58	1.03	0.041
			BD*(1) C22–C24	0.015	9.37	1.19	0.046
			BD*(1) C23–C25	0.024	8.62	1.19	0.044
			BD*(1) C25–C28	0.015	10.08	1.18	0.048
σ–σ*	BD (1) C2–N36	1.981	BD*(1) C1–C10	0.029	8.62	1.2	0.044
			BD*(1) C3–H7	0.011	6.65	1.09	0.037
			BD*(1) C22–C23	0.022	4.52	1.15	0.032
			BD*(1) C32–H33	0.009	5.48	1.26	0.036
σ–σ*	BD (1) C3–H6	1.964	BD*(1) C2–H9	0.037	5.48	1.16	0.035
			BD*(1) C37–N38	0.017	10.63	0.92	0.043
			BD*(2) C37–N38	0.110	11.05	1.06	0.047
σ–σ*	BD (1) C3–H7	1.977	BD*(1) C2–N36	0.031	21	0.51	0.046
			BD*(1) C4–C37	0.029	16.32	0.82	0.051
σ–σ*	BD (1) C3–37	1.975	BD*(1) C2–C23	0.030	16.32	0.9	0.053
			BD*(1) C4–H8	0.014	7.45	1.05	0.039
			BD*s(1) C4–C37	0.029	4.44	1.1	0.03
			BD*(1) C37–N38	0.017	6.32	1.05	0.036
σ–σ*	BD (1) C4–H8	1.979	BD*(1) C1N36	0.030	5.9	1.21	0.037
			BD*(1) C3–C37	0.038	17.28	0.8	0.051
			BD*(1) C54–H58	0.019	16.53	0.9	0.053
σ–σ*	BD (1) C4–C37	1.952	BD*(1) C1–C10	0.029	6.82	0.95	0.035
			BD*(1) C3–H7	0.011	8.91	1.03	0.042
			BD*(1) C3–C37	0.038	6.07	1.09	0.036
			BD*(1) C37–N38	0.017	4.27	1.04	0.029
			BD*(1) N38–O39	0.055	7.7	1.18	0.042
			BD*(1) C53–C54	0.016	31.3	0.74	0.066
σ–σ*	BD (1) C4–C54	1.962	BD*(1) C4–C37	0.029	4.35	1	0.029
			BD*(2) C37–N38	0.110	4.27	0.96	0.028
			BD*(1) C53–H56	0.005	12.13	0.58	0.037
			BD*(1) C57–H61	0.005	5.61	1.02	0.033
σ–σ*	BD(1) C10–C11	1.972	BD*(1) C1–C10	0.029	5.06	1.02	0.032
			BD*(1) C10–C12	0.022	9.46	1.09	0.044
			BD*(1) C11–C13	0.015	15.65	1.26	0.061
			BD*(1) C11–H14	0.014	12.47	1.27	0.055
			BD*(1) C12–H16	0.013	5.86	1.17	0.036
			BD*(1) C13–H18	0.012	9	1.15	0.045
σ–σ*	BD(1) C10–C12	1.974	BD*(1) C1–C10	0.029	8.62	1.16	0.044
			BD*(1) C1–N36	0.034	9.2	1.09	0.044
			BD*(1) C10–C11	0.024	5.06	1	0.031
			BD*(1) C11–H14	0.014	15.69	1.25	0.061
			BD*(1) C12–C15	0.015	8.87	1.17	0.045
			BD*(1) C12–H16	0.013	12.34	1.26	0.055
			BD*(1) C15–H19	0.011	5.82	1.16	0.036
π–π*	BD(2) C10–C12	1.666	BD*(1) C1–C4	0.032	8.49	1.16	0.044
			BD*(1) C1–N36	0.038	13.43	0.57	0.042
			BD*(2) C11–C13	0.323	7.82	0.56	0.031
			BD*(2) C15–C17	0.330	80.17	0.28	0.065

Type	Donor NBO (i)	ED/e	Acceptor NBO (j)	ED/e	$^{a}E^{(2)}$ KJ/mol	^{b}**E(j)-E(i)** a.u.	^{c}F(i,j) a.u.
σ–σ*	BD (1) C11–C13	1.978	BD*(1) C1–C10	0.029	87.4	0.28	0.068
			BD*(1) C10–C11	0.029	14.9	1.09	0.056
			BD*(1) C11–H14	0.014	14.31	1.25	0.059
			BD*(1) C13–C17	0.016	6.36	1.17	0.038
			BD*(1) C13–H18	0.012	11.46	1.26	0.053
			BD*(1) C17–H20	0.017	5.56	1.16	0.035
π–π*	BD (2) C11–C13	1.669	BD*(2) C10–C12	0.346	9.37	1.16	0.046
			BD*(2) C15–C17	0.330	85.94	0.28	0.068
σ–σ*	BD (1) C11–H14	1.980	BD*(1) C10–C11	0.024	84.27	0.28	0.066
			BD*(1) C10–C12	0.022	5.73	1.08	0.034
			BD*(1) C11–C13	0.015	16.95	1.08	0.059
			BD*(1) C13–C17	0.016	4.73	1.09	0.031
σ–σ*	BD (1) C12–C15	1.978	BD*(1) C1–C10	0.029	14.56	1.08	0.055
			BD*(1) C10–C12	0.026	14.35	1.09	0.055
			BD*(1) C12–H16	0.013	14.1	1.26	0.058
			BD*(1) C15–C17	0.016	5.94	1.15	0.036
			BD*(1) C15–H19	0.011	11.25	1.26	0.052
			BD*(1) C17–H20	0.012	5.48	1.16	0.035
σ–σ*	BD (1) C12–H16	1.981	BD*(1) C10–C11	0.024	9.5	1.16	0.046
			BD*(1) C10–C12	0.022	16.9	1.08	0.059
			BD*(1) C12–C15	0.015	5.27	1.09	0.033
			BD*(1) C15–C17	0.016	4.18	1.09	0.029
σ–σ*	BD (1) C13–C17	1.980	BD*(1) C11–C13	0.015	14.27	1.09	0.054
			BD*(1) C11–H14	0.014	11.72	1.27	0.053
			BD*(1) C13–H18	0.012	9.62	1.17	0.046
			BD*(1) C15–C17	0.016	5.52	1.16	0.035
			BD*(1) C15–H19	0.011	10.96	1.26	0.051
			BD*(1) C17–H20	0.012	9.75	1.16	0.046
σ–σ*	BD (1) C13–H18	1.982	BD*(1) C10–C11	0.024	5.56	1.16	0.035
			BD*(1) C11–C13	0.015	15.98	1.08	0.058
			BD*(1) C15–C17	0.016	4.39	1.1	0.03
σ–σ*	BD (1) C15–C17	1.980	BD*(1) C12–C15	0.015	14.43	1.09	0.055
			BD*(1) C12–H16	0.013	11.51	1.26	0.053
			BD*(1) C13–C17	0.016	9.75	1.15	0.046
			BD*(1) C13–H18	0.012	11	1.26	0.051
			BD*(1) C15–H19	0.011	9.62	1.16	0.046
			BD*(1) C17–H20	0.012	5.61	1.16	0.035
π–π*	BD (2) C15–C17	1.665	BD*(2) C10–C12	0.346	5.56	1.16	0.035
			BD*(2) C11–C13	0.323	84.22	0.28	0.067
σ–σ*	BD (1) C15–H19	1.982	BD*(1) C10–C12	0.022	85.81	0.28	0.067
			BD*(1) C13–C17	0.016	15.56	1.09	0.057
σ–σ*	BD (1) C17–H20	1.983	BD*(1) C11–C13	0.015	14.48	1.09	0.055
			BD*(1) C12–C15	0.015	14.52	1.1	0.055
σ–σ*	BD (1) H21–C22	1.982	BD*(1) C22–C23	0.022	14.56	1.09	0.055
			BD*(1) C23–C25	0.024	5.19	1.09	0.033
			BD*(1) C24–C26	0.016	17.03	1.08	0.059
σ–σ*	BD (1) C22–C23	1.974	BD*(1) C2–C23	0.036	14.14	1.09	0.054
			BD*(1) C2–N36	0.031	9.04	1.09	0.043
			BD*(1) H21–C22	0.016	4.18	1.01	0.028
			BD*(1) C22–C24	0.015	5.86	1.16	0.036
			BD*(1) C23–C25	0.024	12.34	1.26	0.055
			BD*(1) C24–H27	0.011	15.69	1.26	0.061
			BD*(1) C25–H29	0.014	8.54	1.16	0.044
π–π*	BD (2) C22–C23	1.663	BD*(1) C2–C3	0.025	8.62	1.17	0.044
			BD*(1) C2–N36	0.031	12.05	0.59	0.04
			BD*(2) C24–C26	0.328	11.63	0.56	0.038
			BD*(2) C25–C28	0.319	86.99	0.28	0.068
σ–σ*	BD (1) C22–C24	1.978	BD*(1) C2–C23	0.030	80.46	0.28	0.066

Type	Donor NBO (i)	ED/e	Acceptor NBO (j)	ED/e	[a]E$^{(2)}$ KJ/mol	[b]**E(j)-E(i)** a.u.	[c]F(i,j) a.u.
			BD*(1) H21–C22	0.013	14.81	1.09	0.055
			BD*(1) C22–C23	0.022	5.9	1.15	0.036
			BD*(1) C24–C26	0.016	14.06	1.26	0.058
			BD*(1) C24–H27	0.011	11.25	1.26	0.052

Type	Donor NBO (i)	ED/e	Acceptor NBO (j)	ED/e	[a]E$^{(2)}$ KJ/mol	[b]**E(j)-E(i)** a.u.	[c]F(i,j) a.u.
			BD*(1) C26–H30	0.012	5.44	1.16	0.035
σ–σ*	BD (1) C23–C25	1.973	BD*(1) C2–C23	0.030	9.5	1.16	0.046
			BD*(1) H21–C22	0.013	9.04	1.08	0.043
			BD*(1) C22–C23	0.022	9.08	1.15	0.045
			BD*(1) C25–C28	0.015	15.65	1.26	0.061
			BD*(1) C25–H29	0.014	12.22	1.27	0.054
			BD*(1) C28–H31	0.012	5.69	1.16	0.036
σ–σ*	BD (1) C24–C26	1.980	BD*(1) H21–C22	0.013	8.74	1.16	0.044
			BD*(1) C22–C24	0.015	9.79	1.15	0.046
			BD*(1) C24–H27	0.012	11.55	1.26	0.053
			BD*(1) C26–C28	0.016	5.65	1.16	0.035
			BD*(1) C26–H30	0.012	10.96	1.26	0.051
			BD*(1) C28–H31	0.012	5.56	1.16	0.035
π–π*	BD (2) C24–C26	1.668	BD*(2) C22–C23	0.346	9.54	1.16	0.046
			BD*(2) C25–C28	0.319	83.72	0.28	0.067
σ–σ*	BD (1) C24–H27	1.983	BD*(1) C22–C23	0.022	84.94	0.28	0.067
			BD*(1) C26–C28	0.016	15.44	1.09	0.057
σ–σ*	BD (1) C25–C28	1.978	BD*(1) C2–C23	0.030	14.52	1.09	0.055
			BD*(1) C23–C25	0.024	14.48	1.09	0.055
			BD*(1) C26–H30	0.012	11.34	1.26	0.052
			BD*(1) C28–H31	0.012	9.37	1.16	0.046
π–π*	BD (2) C25–C28	1.669	BD*(2) C22–C23	0.346	5.52	1.16	0.035
			BD*(2) C24–C26	0.328	87.78	0.28	0.068
σ–σ*	BD (1) C32–H33	1.989	BD*(1) C2–N36	0.031	4.23	1.1	0.03
σ–σ*	BD (1) C32–H34	1.988	BD*(1) C1–N36	0.034	11.88	0.82	0.043
σ–σ*	BD (1) C32–N36	1.983	BD*(1) C1–C4	0.032	13.26	0.81	0.046
			BD*(1) C2–C3	0.025	10.63	1	0.045
σ–σ*	BD (1) C37–N38	1.990	BD*(1) C3–C37	0.038	10.08	1.02	0.044
			BD*(1) C4–C37	0.029	9.12	1.35	0.049
			BD*(1) O39–C40	0.115	5.94	1.33	0.039
π–π*	BD(2) C37–N38	1.968	BD*(1) C1–C4	0.032	4.35	1.22	0.033
			BD*(1) C2–C3	0.025	7.95	0.66	0.032
σ–σ*	BD (1) N38–O39	1.978	BD*(1) C4–C37	0.029	12.8	0.67	0.041
			BD*(1) C40–C42	0.059	21.05	1.1	0.067
σ–σ*	BD (1) O39–C40	1.991	BD*(1) C42–C44	0.021	9.83	1.15	0.047
σ–σ*	BD (1) C40–O41	1.996	BD*(1) C40–C42	0.059	7.07	1.46	0.044
			BD*(1) C42–C43	0.023	7.28	1.51	0.046
π–π*	BD (2) C40–O41	1.980	BD*(2) C42–C43	0.376	4.73	1.63	0.039
σ–σ*	BD (1) C40–C42	1.973	BD*(1) N38–O39	0.055	20.84	0.4	0.044
			BD*(1) C40–O41	0.016	11.92	0.79	0.043
			BD*(1) C42–C43	0.023	4.52	1.22	0.033
n–σ*	LP (1) N36	1.880	BD*(1) C1–H5	0.035	7.87	0.53	0.031
			BD*(1) C2–H9	0.037	26.86	0.68	0.06
			BD*(1) C2–C23	0.030	27.99	0.69	0.062
			BD*(1) C32–H35	0.026	5.65	0.67	0.027
n–σ*	LP (1) N38	1.959	BD*(1) C3–C37	0.038	27.99	0.69	0.062
n–σ*	LP (1) O39	1.971	BD*(1) C40–O41	0.016	39.62	0.86	0.08
n–π*	LP (2) O39	1.587	BD*(2) C37–N38	0.110	23.14	1.18	0.072
			BD*(2) C40–O41	0.254	31.51	0.33	0.045
n–σ*	LP (1) O41	1.977	BD*(1) O39–C40	0.115	168.07	0.31	0.101
n–σ*	LP (2) O41	1.842	BD*(1) O39–C40	0.115	12.51	1.12	0.052

[a] E$^{(2)}$ means energy of hyper conjugative interaction (stabilization energy).

[b] Energy difference between donor (i) and acceptor (j) nbo orbitals.

[c] F(i,j) is the Fock matrix element between i and j nbo orbitals.

Table 5. The Physico-chemical properties of AMB

Parameters	Values
HOMO	-5.991 eV
LUMO	-1.303 eV
Energy gap	4.678 eV
Ionization potential (IP)	5.991 eV
Electron affinity (EA)	1.303 eV
Electrophilicity Index (ω)	2.837
Chemical Potential (μ)	4.678
Electronegativity (χ)	3.647
Hardness (η)	2.344
Softness S)	9.376

Table 6. The frontier molecular orbitals of AMB

Occupancy	Orbital energies (a.u)	Orbital energies (eV)	Kinetic energies (a.u)
O_{52}	-0.254	-6. 911	1.131
O_{53}	-0.249	-6.775	1.222
O_{54}	-0.246	-6.693	1.326
O_{55}	-0.244	-6.639	1.257
O_{56}	-0.220	-5. 986	1.649
V_{57}	-0.047	-1.278	1.690
V_{58}	-0.019	0.516	1.632
V_{59}	-0.005	-0.136	1.389
V_{60}	0.004	0.108	1.355
V_{61}	0.002	0.054	1.435

Table 7. The electronic transition of AMB

Excitation level	Wavelength λ (nm) Expt.	B3LYP/6-311++G(d,p)					
		Ethanol			Water		
		E (eV)	λ(nm)	(f)	E (eV)	λ(nm)	(f)
H−2→L+1 H→L		3.737	331.71	0.038	3.741	331.41	0.035
H−1→L	320	0.854	321.70	0.004	3.860	321.18	0.004
H→L+1 H→L+2		4.342	285.49	0.005	4.344	285.39	0.004
H−1→L+1		4.476	276.98	0.004	4.482	276.57	0.003
H−3→L H−1→L+2		4.659	266.08	0.005	4.667	265.65	0.004
H−4→L H−3→L H→L+1 H→L+2	221	4.842	256.04	0.215	4.856	255.30	0.015

Table 8. Mulliken atomic charges of AMB

Atoms	Charges	Atoms	Charges
C1	−0.036	H34	0.164
C2	−0.049	H35	0.114
C3	−0.270	N36	−0.464
C4	−0.127	C37	0.215
H5	0.118	N38	−0.135
H6	0.173	O39	−0.483
H7	0.183	C40	0.498
H8	0.159	O41	−0.398
H9	0.116	C42	0.028
C10	0.075	C43	−0.113
C11	−0.137	C44	−0.156
C12	−0.153	C45	−0.138
C13	−0.132	H46	0.154
H14	0.149	C47	0.096
C15	−0.129	H48	0.163
H16	0.137	C49	−0.134
C17	−0.119	H50	0.128
H18	0.129	H51	0.126
H19	0.128	H52	0.134
H20	0.127	C53	−0.413
H21	0.126	C54	−0.094
C22	−0.152	H55	0.158
C23	0.092	H56	0.127
C24	−0.129	C57	−0.415
C25	−0.136	H58	0.134
C26	−0.118	H59	0.161
H27	0.126	H60	0.129
C28	−0.130	H61	0.131
H29	0.143	C62	−0.481
H30	0.128	H63	0.152
H31	0.127	H64	0.158
C32	−0.271	H65	0.149
H33	0.162		

Table 9. The calculated total energy (a.u), zero point vibrational energies (Kcal/mol), rotational constants (GHz) and entropy (cal/mol K^{-1}) for AMB

Parameters	B3LYP/6-31G
Total Energies	-1383.906
Zero-point Energy	347.222 (Kcal/Mol)
Rotational constants (GHZ)	0.174
	0.069
	0.054
Entropy	
Total	204.231
Translational	44.136
Rotational	37.422
Vibrational	122.673

Table 10. Thermodynamic properties at different temperatures of AMB

T (K)	S (J/mol.K)	Cp(J/mol.K)	ddH (kJ/mol)
100.00	500.84	208.79	13.06
200.00	687.98	347.92	40.86
298.15	854.61	499.19	82.31
300.00	857.71	502.14	83.24

400.00	1023.74	657.60	141.32
500.00	1185.59	794.26	214.11
600.00	1340.75	907.50	299.38
700.00	1487.85	1000.42	394.93
800.00	1626.62	1077.33	498.94
900.00	1757.34	1141.74	609.98
1000.00	1880.53	1196.18	726.95

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