Celal Bayar University Journal of Science

Spectroscopic (FT-Raman, FT-IR, UV-Vis, and NMR) and Theoretical Analysis of 1-Methylindole: Structural Characterization, Non-Covalent Interactions, and Electronic Properties



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> Received: September 21, 2024 Accepted: December 3, 2024 DOI: 10.18466/cbayarfbe.1554031

Abstract

The structural and spectroscopic characterization of 1-Methylindole (1MI) by favors of FT-Raman (4000-200 cm⁻¹), FT- IR (4000-400 cm⁻¹), UV-Vis, and ¹H and ¹³C NMR techniques is presented. The experimental observations were enlightened by density functional theory (DFT) calculations at the B3LYP/6-311G(d,p) level of theory. Geometrical structure of the molecule was obtained, and bond order analysis was performed based on the optimized structure. Non-Covalent Interactions (NCIs) were analyzed by using the Reduced Density Gradient (RDG) with energy density descriptors to visualize the limiting regions of these interactions. Furthermore, molecular charge distribution and isosurface mappings with local extrema were obtained and the critical regions on the molecular surface were visualized. The vibrational spectra were calculated, and the normal modes were assigned based on total energy distribution (TED) calculations. The electronic properties of 1MI were explored experimentally through UV-Vis spectroscopy and analyzed in detail via Atoms in Molecules (AIMs) methodology. Total and partial density of state (TDOS and PDOS) and overlap population density of state (OPDOS) diagrams were calculated and fractional contributions of nonpolar methyl group and aromatic indole to frontier molecular orbitals were obtained through this methodology. Theoretical NMR chemical shifts were assigned based on DFT calculations that use the gauge-invariant atomic orbital (GIAO) method. Inclusion of solvents effect in NMR calculations produces twice less dispersive data and better fitting results to experimental observations. Nonlinear optical properties: polarizability, anisotropy of polarizability, and first hyperpolarizability of the molecule were also computed to explore the potential of 1MI as nonlinear spectroscopy agent.

Keywords: 1-methylindole, DFT, UV, IR and Raman, NMR, Non-Covalent Interactions, Orbital Fragmentation.

1. Introduction

Indole is a heterocyclic aromatic organic compound which occur in nature [1–4] as a five-membered ring with the formula of C9N1H8. The indole family has significant distribution in the central nervous system and thus has shown an extensive range of biological effects [5,6] such as antibacterial, antifungal, anticonvulsant, antiviral, and antiproliferative activities [7–10]. An important indole derivative tryptophan for example is an extremely important biomolecule because it carries a vital amino acid essential in human nutrition found in a vast number of proteins across the biosphere [11,12]. Anticancer activity of indole derivatives is another critical perspective; some indole based compounds exhibit significant antiproliferative/cytotoxic activity against human cancer cells [13]. Methyl-indole inhibits pancreatic cancer cell viability by down-regulating ZFX expression and targeting the P13K/AKT pathway, suggesting potential as a therapeutic agent for pancreatic cancer [14]. Besides, electro synthetical production of polyindoles with low electrical conductivity is another important characteristic of indole containing compounds [15–18].

Based on studies showing great potential of indole-based compounds, structural properties of indole molecule have been studied extensively in experiments and theoretical works. Roychowdhury [19] performed X-ray diffraction studies of indole in the orthorhombic space group, and Catalan [20] carried out the molecular geometry of indole theoretically.



1MI consists of a six-membered benzene ring fused to five-membered pyrrole ring in which a methyl group substituted on to the nitrogen. The methyl group can donate electrons through the C-N σ bond, and its hydrogen atoms can interact with the nearby π electrons in the aromatic ring through hyper conjugation. Thus, Nmethyl substitution can lead to a change in the electron density of the molecular species, the electronic transition energy, and the frequency of some vibrations [21]. 1methylindole shows improved stability in hydrogen storage reactions compared to indole [22]. Mourik et. al. have performed high-level ab initio calculations on indole and 1-methylindole-water system because of the importance of water in the solvation processes of the biologically active indole derivatives [23]. Muñoz et. al. [24] reported to FT-IR and fluorescence studies on the ground and excited state hydrogen-bonding interactions 1-methylindole and water in waterbetween triethylamine mixtures, and hydrogen-bonding interactions between 1-methylindole and alcohols [25]. Semi-empirical analysis was brought by Mons et al. [26] on modelled indole-water and 1-methylindole-water complexes. Absorption and emission energies in seven step methodology followed in our previous work [27] for both formalisms have been obtained using TD-DFT calculations with B3LYP/6-311G(d,p) model chemistry based the ground and first excited state optimized geometries obtained.

To the best of our knowledge, no literature has been yet available on description of the structural and spectroscopic behaviors of the 1MI compound by utilization of broad range of spectral techniques and tools of quantum chemical calculations. Therefore, we have focused on both experimental and theoretical exploration of 1MI by using FT-IR, Raman, UV-Vis, and NMR spectral techniques along with DFT and TD-DFT calculations. The geometrical structure investigations were enriched by bond order analysis and non-covalent interaction visualizations. Besides, further informative properties such as the dipole moment, nonlinear optical (NLO) properties, chemical hardness, electronegativity, chemical potential, and electrophilicity index were determined, and their relations with the structure of the molecule were discussed.

2. Materials and Methods

2.1. Experimental Details

The FT-IR spectrum of the 1MI was recorded between 4000 and 400 cm⁻¹ on an Agilent Cary 660 FT-IR spectrometer with ATR objectives. The spectrum was recorded at room temperature, with a scanning speed of 8 cm⁻¹ min⁻¹ and the spectral resolution of 4.0 cm⁻¹. FT-Raman spectrum of the sample was recorded at 4000-200 cm⁻¹ region on a Bruker RFS 100/S FT-Raman instrument, which uses a liquid nitrogen-cooled Ge detector, using 1064 nm excitation from an Nd: YAG

laser. Five hundred scans were accumulated at 4 cm⁻¹ resolution using a laser power of 100 mW. The ultraviolet absorption spectra of the 1MI in water and ethanol were examined in the range 200–400 nm by using Shimadzu UV–2101PC spectrometer. 1H and 13C Nuclear magnetic resonance spectra were recorded on a Bruker-Spectroscopy Advance DPX 400 MHz Ultra-Shield in dimethyl sulfoxide (DMSO-d6) with TMS as internal reference.

2.2. Quantum Calculations

The DFT and TD-DFT ab initio calculations were carried out using Gaussian 16 program [28]. Molecular geometries of the singlet ground state of the 1MI was fully optimized in the gas phase at the B3LYP/6-311G(d,p) level of theory [29-31]. All spectroscopic properties were calculated on the basis of optimized structure. The harmonic vibrational wavenumbers were computed and scaled with 0.983 and 0.958 for up to 1700 cm⁻¹ and greater than 1700 cm⁻¹, respectively, to correct overestimations [32]. The TED calculation, which showed the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule, thus enable us numerically to describe the character of each mode, was carried out by the scaled quantum mechanical (SQM) method [33] by using Parallel Quantum Solutions (PQS) program and visualized using GaussView 6 [34]. In this method, the output files created at the end of the frequency calculations are used to compute vibrational energies of each mode.

The contributions of each fragment to total molecular orbital was calculated using Mulliken population analysis. GaussSum 3.0 [35] was used to calculate group contributions to the molecular orbitals to determine the partial density of states and overlap population density of states (OPDOS) diagrams. The OPDOS diagram was created by convoluting the molecular orbital information with gaussian curves of unit height and FWHM of 0.3 eV.

The quantum theory of Atoms in Molecules proposed by Bader [36] allows one to partition a molecular space into atomic basins. It provides a route for consistent description of atoms (e.g. atomic volume and electron population, dipole moment) and interactions between atoms (i.e. covalent, ionic, and hydrogen bonds, van der Waals interactions) in terms of the topological properties of the electron density $\rho(r)$. Reduced Density Gradient (RDG) and Mayer Bond Order (MBO) [37,38] was calculated with use of Multiwfn program [39,40].

3. Results and Discussion

3.1. Geometrical Structure and Bond Order

The geometrical structure obtained by DFT calculations and atom labelling of 1MI are shown in Figure 1, and the



optimized parameters are gathered in Table 1 in comparison with the experimental values from literature along with the MBO values. Because the crystallographic data on 1MI has not been recorded in literature, we compared geometric parameters obtained in calculations to that of methylindole available from experiments of indole [19]. This comparison also allows exploration of variations in bond lengths and angles differs due to substitution of methyl group to MI.

The calculated bond lengths of C–C in benzene group in range from 1.388 to 1.42 Å for B3LYP with 6-311G(d,p) basis set which are in good agreement with experimental values reported between 1.372 and 1.411 Å for indole [19,20].



Figure 1. The optimized geometrical structure of 1MI. Blue: Hydrogen, Yellow: Carbon, and Pink: Nitrogen.

Table 1. The geometric parameters (bond lengths (Å), angles (°)) and MBO of 1MI obtained by DFT/B3LYP/6-311G(d,p) comparison of experimental indole parameters.

Parameters						
Bond Lengths (Å)	Calculated	X-Ray ^[19]	MBO	Bond Angles (⁰)	Calculated	X-Ray ^[19]
C_1 - C_2	1.423	1.411	1.2589	$C_2-C_1-C_6$	122.141	116.4
C_1 - C_6	1.398	1.395	1.3282	C_2 - C_1 - N_{15}	107.767	
C1-N15	1.381	1.374	1.0878	$C_6-C_1-N_{15}$	130.092	
C ₂ -C ₃	1.403	1.398	1.3404	C_1 - C_2 - C_3	118.839	
C ₂ -C ₈	1.434	1.436	1.2990	C_1 - C_2 - C_8	106.722	
C ₃ -C ₄	1.387	1.381	1.4921	$C_3-C_2-C_8$	134.439	
C ₃ -H ₉	1.085	1.087	0.9729	C_2 - C_3 - C_4	119.130	
C4-C5	1.408	1.396	1.3727	$C_3-C_4-C_5$	121.112	
C_4-H_{10}	1.084	1.087	0.9690	$C_4-C_5-C_6$	121.220	124.8
C5-C6	1.388	1.372	1.4896	C_1 - C_6 - C_5	117.559	119.7
C ₅ -H ₁₁	1.084	1.087	0.9690	$C_8-C_7-H_{13}$	129.858	
$C_{6}-H_{12}$	1.084	1.088	0.9596	C8-C7-N15	110.262	111.5
C7-C8	1.368	1.358	1.5879	H ₁₃ -C ₇ -N ₁₅	119.880	
C ₇ -H ₁₃	1.079	1.082	0.9627	C_2 - C_8 - C_7	106.875	105.5
C7-N15	1.383	1.381	1.1566	C_2 - C_8 - H_{14}	127.219	
$C_{8}-H_{14}$	1.079	1.082	0.9783	$C_7-C_8-H_{14}$	125.906	
N15-C16	1.449	-	0.9589	C_1 - N_{15} - C_7	108.373	
C ₁₆ -H ₁₇	1.094	-	0.9604	C_1 - N_{15} - C_{16}	125.528	
C ₁₆ -H ₁₈	1.094	-	0.9604	C7-N15-C16	126.100	
C ₁₆ -H ₁₉	1.090	-	0.9707	N15-C16-H17	111.063	

The variation, due to substitution of methyl group to indole, in the bond length of C_1 – N_{15} bond is only 0.007 Å while we expect much higher deviations. Average deviation of bond lengths from experimental values is nearly 0.006 Å already. This is a preliminary indication that the methyl group is not dominant in determination of characteristics of the ring systems. Bond angle calculations also well correlated with experimental results with only average of 2.8° deviations. The maximum drift, 5.7°, is observed in C_2 – C_1 – C_6 bond angle indicating that the substitution plays a significant role in distortion of the benzene ring despite creating no effect on bond lengths. The C–H bond lengths are in a good agreement with indole [19]. For example, the calculated average of C–H bond lengths, 1.084 Å and 1.079 Å, are in good agreement with experimental reports of 1.087 Å and 1.082 Å for in the rings, respectively.

The linearity between the experimental and calculated bond lengths of 1MI can be estimated from plotting the calculated versus experimental values. The relation



between experiment and calculation for bond lengths for 1MI can be described by the following equation.

$$\delta_{cal} = 0.9692\delta_{exp} + 0.0362, R^2 = 0.9992$$
 (3.1)

Bond order is an important concept for understanding the nature of a chemical bond. The MBO square with empirical bond order that is close to 1.0, 2.0, and 3.0 for single, double, and triple bond, respectively. In our study, the MBO calculated between C₁-C₂, C₁-C₆, C₂-C₃, C₂-C₈, C₃-C₄, C₄-C₅, and C₅-C₆ are 1.258, 1.328, 1.340, 1.299, 1.492, 1.372, and 1.489, respectively. These values fall into the region where the aromatic C-C bonds calculated from 1.229 to 1.455 [41]. The only MBO for C7-C8 was calculated to be 1.5879 that is slightly stronger than the other aromatic carbons. In order to find the reason behind this anormaly, orbital occupancy-perturbed Mayer bond orders (OOP-MBO) analysis [42] is performed using Multiwfn program to determine contributions of individual occupied molecular orbitals. If two electrons are replaced from HOMO, then Mayer bond order between C_7 and C_8 decrease from 1.5879 to 1.1538, and the contribution from HOMO-1 orbital is 0.20008. Therefore, we can state that HOMO orbital must be greatly beneficial for bonding and this orbital shows strong character of π -bonding between C₇ and C₈, which give higher bond order values than expected.

3.2. Electrostatic Potential and Weak Interaction Profile

Electrostatic potential (ESP) analysis is one of the most effective ways of proposing physicochemical properties, reactivity, and intermolecular interactions of molecules under study because the size and shape of molecular electrostatic potential and extremum positively/negatively charged regions can be visualized clearly by color-coding [39]. ESP is calculated directly from atomic coordinates obtained in geometrical optimization without any further second order mathematical derivations.



Figure 2. Electrostatic potential surface of 1MI with indications of extrema.

Here, we investigated quantitative electrostatic potential (ESP) analysis of molecular van der Waals (vdW) surface of 1MI. ESP obtained for 1MI is given in Figure 2 where it shows the most positive regions with red and the most

negative regions with blue in nearly 46 kcal/mol region. Extremum charged points are shown with dots and the values are given as well. The minimum -23.05 kcal/mol is the global minimum of the vdW surface. So the below and above of 1MI has abundant π electrons on the global minimum regions. We also calculated the ESP in the positive values ranging from +9.46 to +23.35 kcal/mol. Maximum value, +23.35 kcal/mol, is the global maximum rises from the positively charged H13 atom. Another important positive value is +17.35 kcal/mol due to presence of methyl group. We ultimately examine the molecular surface area in each ESP range due to its quantitatively fall out with ESP distribution on the whole molecular surface. From the Figure S1, it can be seen that there is a large portion of molecular surface having small ESP value, namely from -25 to +25 kcal/mol. Among these areas, the negative areas mainly correspond to the surface above and below the pyrrole region, and shows effect of the abundant π electron cloud while the positive part results from the positive charged the C-H hydrogens. This can be due to effect of van der Waals interactions between methyl groups and pyrrole hydrogen (H12), which keeps ESP value (+17.35 kcal/mol) smaller than global maximum region.

To understand and quantitatively describe the intramolecular weak interactions rather than estimate from their outcomes, Johnson and co-workers [43] developed an approach to investigate the weak interactions in real space based on the electron density and its derivatives. The reduced density gradient (RDG) is a fundamental dimensionless quantity formulated from the electron density and its first derivative, and described as follows.

$$RDG(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}}$$
(3.2)

The weak interactions can be specified in regions in terms of low electron density and low RDG value. The density values of the low-gradient spikes (in the plot of RDG versus ρ) appear to be an indicator of the interaction strength. The sign of λ_2 , which is the second largest eigenvalue of electron density Hessian matrix at position r, is utilized to distinguish the bonded ($\lambda_2 < 0$) from nonbonding ($\lambda_2 > 0$) interactions. The plot of the RDG versus the electron density ρ multiplied by the sign of λ_2 can allow analysis and visualization of a wide range of interaction types such as hydrogen bonding, van der Walls interactions, and steric effects. Large negative values of sign (λ_2) ρ are indicative of strong attractive interactions whereas the positive values correspond to repulsive interactions. Furthermore, these interactions can be visualized on the molecule using color-coding depending on the strength of interaction where the blue indicates the attraction and red is associated with repulsive effects. RDG calculations are obtained via



Multiwfn wavefunctions analyzer and visualization are plotted in VMD program [44,45]. The results of our analysis on 1MI are given in Figure 3.



Figure 3. Schematic view of a) RDG profile and b) visualization of weak interaction of 1MI.

Weak interactions in 1MI are only two kinds, either vdW or steric effects. The region marked by green-brown in Figure 3 b) can be identified as vdW interaction region which corresponds to the two central spikes below sign $(\lambda 2) \rho = 0.01$ and above sign $(\lambda 2) \rho = -0.01$ with nearly RDG=0.4 in Figure 3 a). We can also understand this effect from the extremum ESP points in Figure 2. The region between methyl group and the nearest hydrogen of the benzene ring is at under a positive ESP with the magnitude of +16.38 kcal/mol. Therefore, it is natural to have some attractive interaction in this region. Steric effects are observed in two levels. The first sharp spike is observed around sign ($\lambda 2$) $\rho = 0.02$ and characterized to be due to a weaker repulsion at the center of phenyl ring, which has also been observed in the structure [46]. A second tailing spike appears around sign ($\lambda 2$) $\rho = 0.05$ is associated with the repulsion centered at the middle of pyrrole ring and located above and below the molecular plane. This disruption is basically due to the unpaired electrons of the nitrogen on the ring.

3.3. Vibrational Spectral Analysis

The title molecule has Cs symmetry when the planarity of the methyl group retained. There are 51 fundamental vibrational modes that can be distributed as 17A' + 34A" represented A' species in plane and A" species out-ofplane modes. To make a comparison between the results of the theoretical and experimental, the infrared and Raman spectra of the 1MI are shown in Figure 4 where the calculated intensity is plotted against the wavenumbers. The observed and calculated vibrational wavenumbers with proposed assignments generated from TED calculation for the 1MI are presented in Table 2. The last column contains a detailed description of the fundamental modes obtained from their TED. The results of theory obtained by DFT/ B3LYP/6-311G(d,p) basis set are generally higher than their experimental data. The deviation can be a consequence of the anharmonicity and the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. The other plausibility is the theoretical results have obtained in vacuum whereas experimental ones for solid phase. To minimize the overall deviation, the calculated frequencies were scaled by a scaling factor. After scaling, the results show better than older ones. The vibrational analyses of present molecule can supply helpful information about the fundamental bands, overtone, and combination bands. We also discuss following the fundamental modes of the molecule comparing their experimental data and similar structure.

The modes of C–H stretching are generally seen as multiply that in the region of $3000-3100 \text{ cm}^{-1}$ [47]. The C–H stretching modes of indole were observed in the region from 3140 to 3051 cm^{-1} and computed to be between 3135 and 3044 cm⁻¹ [48,49]. In this study, we observed (v1–v6) in the range of $3026-3121 \text{ cm}^{-1}$ and predicted in the range of $3027-3114 \text{ cm}^{-1}$ as pure modes by B3LYP functional of DFT as seen TED column in Table 2. C-H symmetric vibrations modes are seen higher than asymmetric ones in rings, while adverse situation is seen in methyl group.

The C–H modes of in plane and out-of-plane bending generally observed in aromatic compounds in the range of 1000–1300 cm⁻¹ and 750–1000 cm⁻¹, respectively [50]. The experimental C–H in-plane bending vibrations of 1MI are in the range of 1014–1488 cm⁻¹ and generally mixed with C–C stretching modes according to their TED results. The C–H out-of-plane bending vibrations are calculated at 711–959 cm⁻¹ region. The CH₃ group has nine fundamental vibrations, asymmetric and symmetric stretches, bending, rocking, and torsion modes [51]. The CH₃ asymmetric stretching vibrations are expected in the range of 3000–2925 cm⁻¹ and the symmetric CH₃ vibrations in the range of 2940–2905 cm⁻¹ [52].

The asymmetric stretch usually appears at higher wavenumbers than the symmetric stretching. Therefore, the CH₃ asymmetrical and symmetrical stretching occurs about 2900 cm⁻¹ and 2800 cm⁻¹, respectively [53,54]. In this study, the CH₃ stretching modes were observed at 2885 cm⁻¹ and 2941 cm⁻¹in FT-IR, and 2940 cm⁻¹ in FT-Raman. The methyl group stretching modes were predicted at 2893 cm⁻¹ (symmetric), and 2941 cm⁻¹and 2996 cm⁻¹ (Asymmetric.). The other methyl group assignments of the molecule determined using GaussView 6 [34] program as wagging, scissoring, wagging, rocking, twisting etc. are given in Table 2. Methyl deformations modes of in-plane as known scissoring were defined at 1394 cm⁻¹ and 1432-1460 cm⁻¹, and rocking at 247, and 1098 cm⁻¹.





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Table 2. Comparison of the calculated harmonic frequencies and experimental (FT-IR and FT-Raman) wavenumbers (cm^{-1}) using by B3LYP method 6-311G(d,p) basis set of 1MI molecule.

Modes	Sym.	Expe	rimental	Theoretical		TED ^b (10%)
No	Specie s	FT- IR	FT- Raman	Unscaled freq.	Scaled freq. ^a	
\mathbf{v}_1	A'	3121		3250	3114	vCH _{sym.} (100) _{ring2}
v_2	A'	3096		3231	3095	vCH _{asym.} (100) _{ring2}
V ₃	A'	3055	3053	3189	3055	vCH _{sym.} (100) _{ring1}
\mathbf{V}_4	A'			3178	3045	vCH _{asym.} (100) _{ring1}
V 5	A'			3168	3035	vCH _{asym.} (100) _{ring1}
V 6	A'	3026		3160	3027	vCH _{asym.} (100) _{ring1}
V 7	A'			3127	2996	vCH _{asym} (100) _{methyl}
V 8	A"	2941	2940	3069	2941	vCH _{asym} (100) _{methyl}
		2914				Overtone + Combination
		2906				Overtone + Combination
V 9	A'	2885		3020	2893	$\nu CH_{sym} (100)_{methyl}$
		2816				Overtone + Combination
		2770				Overtone + Combination
		2518				Overtone + Combination
		2492				Overtone + Combination
		1920				Overtone + Combination
		1888				Overtone + Combination
		1799				Overtone + Combination
		1766				Overtone + Combination
		1702				Overtone + Combination



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V 10	A'	1616	1610	1654	1625	vCC(59) _{ring}
V11	A'	1578	1569	1612	1585	$vCC(60)_{ring}$
		1559				Overtone + Combination
V12	A'	1516	1513	1552	1526	νC=C(48), δNCH (11)
V13	A'			1525	1499	ωCH ₃ (63)
V14	A'	1488		1516	1490	ωCH ₃ (22), vCC(19), δCCH(19) ring1
		1478				Overtone + Combination
V15	A'	1465	1465	1495	1469	νCC(25), δCCH(35) _{ring1}
V16	A''			1485	1460	ρCH ₃ (89)
V17	A'	1423	1418	1457	1432	ρCH ₃ (81)
V ₁₈	A'	1390	1387	1418	1394	νCC(39), νCN(15), δCCH(16) _{ring2}
V19	A'		1357	1385	1362	νCC(25), νCN(28), δCCH(32) _{ring1}
V ₂₀	A'	1331	1331	1357	1334	vCC(53) _{ring1} , vCN(19)
V21	A'	1315		1348	1325	νCC(21), νCN(18), δCCH(37)
V22	A'	1243	1239	1268	1247	νCC(18), δCCH(41), δNCH(10)
V ₂₃	A'	1206	1205	1227	1206	νCC(26), δCCH(37)
V ₂₄	A'	1154		1177	1157	$vCC(18)_{ring1}, \delta CCH(69)_{ring1}$
V ₂₅	A'	1134	1135	1157	1137	$\nu CC(23)_{ring1}, \delta CCH(42)_{ring1}$
V26	A''			1144	1125	ωCH ₃ (98)
V27	A'	1098	1098	1117	1098	vCC(11), δCCC(11), δCCH(16), ΓCH ₃ (26)
V ₂₈	A'	1079	1077	1101	1082	νCC(11), δCCH(42) _{ring1} , δNCH(25)
V29	A'	1014	1010	1036	1018	$vCC(61)_{ring1}, \delta CCH(17)$
V30	A'			1023	1006	νCN(23), δCCH(20), ΓCH ₃ (23)
V31	Α"	959		973	957	γCH(88)
V32	Α"	923		932	916	γCH(91)
V33	A'	881	881	896	881	νCC(13), δCCC(40), δCCH(16)
V34	A''	842	844	857	842	γCH(75)
V35	A''			853	838	γCH(78)
V36	Α"			779	766	γCH(88)
V 37	A'	761	763	777	764	νCC(47), νCN(10), δCCC(13)
V38	A''	737		750	737	γCH(88)
V39	A'	711	711	723	711	νC ₁₆ -N(25), δCCC(23), δCCH(14)
V40	Α"			718	706	γCH(83)
V41	Α"			602	591	φPyrrole(62)
V42	Α"	573	573	583	573	φ Phenyl(44), τ CCCN(25)
V43	A'			581	571	νCC(12), δCCC(29), δCCN(26)
V 44	A'	533	534	544	535	$vCN(14), vCC(10), \delta CCC(35)_{ring1}$
V45	A'	467	468	478	470	$vCC(10), \delta CCC(34), \delta CNC(27)_{methyl}$
V46	A''	426	426	433	426	γCH(86))
V47	A''		261	266	261	ωCH ₃ (69)
V48	A'			251	247	1 CH ₃ (88)
V49	A"			219	215	Butterfly effect (71)
V 50	Α"			138	136	ωCH ₃ (88)
V51	A"			70	69	φCH ₃ (100)



^aWavenumbers in the ranges from 4000 to 1700 cm⁻¹ and lower than 1700 cm⁻¹ are scaled with 0.958 and 0.983, respectively.

^bTED: Total Energy Distribution v; stretching, γ ; out-of plane bending, δ ; in-plane-bending, τ ; torsion, ρ ; scissoring, ω ; wagging, ϕ ; twisting, Γ ; rocking.

Our previous study also supported this situation [55]. The twisting and wagging modes as known out-of-plane deformations of methyl group were determined at 69 $cm^{-1} \phi CH_3$ (twisting) and 261, 1125,1490 and 1499 cm^{-1} ω CH₃ (twisting) modes of the heading molecule. observed nearly the same region, showing agreement. The C–N stretching vibrations modes are generally very difficult to determine due to mixing of other several modes. Silverstein et al. [56] defined the C-N stretching modes in the region of 1386–1266 cm⁻¹ for aromatic amines. In the present work, the modes calculated at 535, 711, 764, 1006, 1325, 1334, and 1394 cm^{-1} have contribution from CN vibrations according to the TED analysis. These complex modes were observed at 533, 711, 761, 1014, 1315, 1331 and 1390 cm⁻¹ in FT-IR and 534, 711, 763, 1010, 1331 and 1387 cm⁻¹ in the FT-Raman experimentally. The theoretically scaled frequencies of C-N related bands by B3LYP method well correlates with experimental observation.

$$\delta_{\text{cal}} = 0.9692\delta_{\text{exp}} + 0.0362, \, R^2 = 0.9992 \tag{3.3}$$

$$\delta_{\rm cal} = 0.9692 \delta_{\rm exp} + 0.0362, \, {\rm R}^2 = 0.9992 \tag{3.4}$$

$$\delta_{cal} = 0.9692\delta_{exp} + 0.0362, R^2 = 0.9992$$
 (3.5)

The stretching vibrational modes of rings are highly important in the vibrational spectra of the aromatic compounds. The bands observed C-C stretching vibrations modes are of variable intensity and generally observed at 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380-1280 cm⁻¹ five bands in this region given by Varsányi [57]. Also ring carbon-carbon stretching vibrations appears in the region of 1400–1650 cm⁻¹ in benzene derivatives [32,55,57]. In this study, C-C stretching modes were computed in the region of 1625-1526 cm⁻¹, 1490 cm⁻¹, 1469 cm⁻¹, 1394–1137 cm⁻¹, 1098–1018 cm⁻¹, 881, 764 cm⁻¹, and 571–470 cm⁻¹ for the title molecule. The observed values are 1616-1516 cm⁻¹, 1488 cm⁻¹, 1465 cm⁻¹, 1390–1134 cm⁻¹, 1098– 1014 cm⁻¹, 881, 761 cm⁻¹, 533 and 467 cm⁻¹ in FT-IR spectra and 1610-1513 cm⁻¹, 1387-1135 cm⁻¹, 1098-1010 cm⁻¹, 881, 763, 534, and 468 cm⁻¹ in FT-Raman spectra. The highest contribution of the C-C stretching vibrations stem from v10 (%59) and v11 (%60) were assigned nearly pure modes of the 1MI.

The infrared and Raman correlation graphics were plotted individually (in Figure S2), to see the relations between theoretical and experimental data. Also, all wavenumbers are described as linear for total (together IR and Raman) in Figure S3. These states were showed following equations and showed linearity.

3.4. Electronic Properties



Figure 5. Theoretical and experimental UV spectra of 1MI in ethanol and water.

The experimental and calculated (using TD-DFT method) UV-Vis (electronic absorption) spectra predicted in gas phase, in water, and ethanol solvents, and measured in solvents were presented in Figure 5. The calculations were performed by using TD-DFT method, which is quite reasonable and computationally reliable, and suitable for medium size molecules [44,58]. Our theoretical calculations show that there should be five major transitions within the spectral range, the experimental spectra indicated four main peaks in the spectra. Simulated spectra can also reproduce the experimental spectra with embedded transition peaks underneath. Thus, the experimental UV-Vis spectra were quantified by multicomponent analysis method which been used successfully in explanation of has experimental UV spectra under the light of theoretical calculations [55,59]. In this method, the intensity, I, of the spectrum is modeled as a superposition of antisymmetrized Gaussian (AG) line shape functions given below, thus matches the peaks to major transition more accurately.

$$\delta_{\rm cal} = 0.9692\delta_{\rm exp} + 0.0362, \, {\rm R}^2 = 0.9992 \tag{3.6}$$

Table 3. Experimental and calculated wavelengths λ (nm), excitation energies (eV), oscillator strengths (f) and electronic transitions of 1MI for gas phase, in ethanol and water solutions.

		E (eV)	λ(nm)	f	Fitted-w	FWHM	Area	Major contributes
Gas Phase	α1	7.004	177.04	0.16	176.5	10.7	3.8	H-2→L (22%), H-1→L+4 (21%), H→L+4 (42%)
	α2	6.600	187.88	0.26	187.8	14.6	8.8	$H-2 \rightarrow L (27\%), H-1 \rightarrow L+1$ (36%), $H \rightarrow L+4 (25\%)$
	β1	6.274	197.64	0.29	196.6	10.5	1.4	H-2→L (28%), H-1→L+1 (40%), H→L+1 (13%)
	β2	5.983	207.24	0.37	204.8	18.6	18.8	H-1→L (26%), H-1→L+1 (11%), H→L+1 (47%)
	γ	4.646	266.89	0.08	264.5	29	5.4	H→L (85%)
	α1	6.989	177.42	0.15	177.6	11.7	3.2	H-2→L+1 (25%), H-1→L+3 (70%)
	α2	6.609	187.61	0.33	187.4	11.8	5.8	H-2 \rightarrow L (39%), H-1 \rightarrow L+1 (30%), H \rightarrow L+3 (22%)
Water Teo.	β1	6.216	199.5	0.25	196.3	11.5	2.5	H-2 \rightarrow L (24%), H-1 \rightarrow L+1 (58%)
	β2	5.897	210.26	0.63	209.1	17.9	18.9	H-1→L (30%), H→L+1 (57%)
	γ	4.570	271.33	0.09	268.6	31.6	4.8	H→L (90%)
	α	6.278			197.5	23	14.9	π-π*
Water Exn	β	5.649			219.5	15.4	14.1	π-π*
water Exp.	γ1	4.688			264.5	38.9	4.8	<i>n</i> - <i>n</i>
	γ2	4.351			285	23.8	2.8	<i>n</i> - π *
	α1	6.984	177.54		177.8	11.7	3.1	H-2→L+1 (25%), H-1→L+3 (70%)
Ethanol Teo.	α2	6.602	187.81	0.34	187.6	11.9	5.9	H-2→L (39%), H-1→L+1 (29%), H→L+3 (22%)
	β1	6.213	199.58	0.25	196.6	11.4	2.5	H-2→L (24%), H-1→L+1 (59%)
	β2	5.890	210.51	0.64	209.4	17.9	19	H-1→L (30%), H→L+1 (57%)
	γ	4.571	271.3	0.09	268.6	31.7	4.9	H→L (90%)
	α	6.064			204.5	20.5	10.4	π-π*
Ethanol Evp	β	5.624			220.5	13.9	13.3	π-π*
Etnanoi Exp.	γ1	4.550			272.5	30.7	5.3	<i>n</i> -π*
	γ2	4.283			289.5	14.8	1.2	<i>n</i> - π*

The calculated UV-Vis spectra (using ethanol and water solutions) which is fragmented into contributions from different transitions are plotted Figure 5. The experimental and theoretical absorption wavelengths (λ), excitation energies (E) determined with oscillator strength (*f*) and major contributions of counterparts from theory were listed in Table 3 for gas phase, water, and ethanol solvent. The peaks were located at 197.5, 219.5, 264.5 and 285.0 nm for water solution, and at 204.5, 220.5, 272.5 and 289.5 nm for ethanol solution, experimentally. After fitting procedure, the theoretical transitions are almost well agree based on the experimental results, so the major contributions noted are fully taken into account. The fitting of experimental data is also at acceptable level with R² values of 0.9881 and

0.9906 for the spectra taken in ethanol and water, respectively. This fitting operation applied is quite remarkable. In fact, some fitted peaks are located exactly at the same energy for both spectra.

An intuitive way of analyzing electronic properties of molecules is to investigate the population of states, partial contributions of fragmental sections in the molecule, and overlapping regions. The most important application of the DOS [60–62] plots is to demonstrate molecule orbital (MO) compositions and their contributions to chemical bonding through the OPDOS plots, which are also referred in the literature as Crystal Orbital Overlap Population (COOP) diagrams.





Figure 6. The OPDOS diagram of 1MI.

OPDOS is similar to DOS because it results from multiplying DOS by the overlap population. The OPDOS shows the bonding, anti-bonding, and nonbonding interaction of the two orbital's, atoms, or groups in a molecule. A positive value of the OPDOS indicates a bonding interaction, whereas negative value means an anti-bonding interaction, and zero value is for nonbonding interactions [63]. The OPDOS diagram for 1MI is shown in Figure 6 where the only overlapping between indole and methyl group is selected. Frontier occupied and virtual orbitals are shown in there. As can be seen from the OPDOS plot, a significant anti-bonding character is observed in the HOMO and HOMO-1/-2/-3/-4/-5 molecular orbitals, and a bonding character in the LUMO and LUMO+1/+2/+3. This is a very nature of the covalently bonded systems where the population overlaps show negative character in low energy states below HOMO and positive character in high energies above LUMO and further. The overlap population value of the HOMO for indole with methyl is -0.0093 and LUMO value is 0.0036. These values are relatively low compared to the fragmental interactions occur in molecules with electron donor/acceptor groups like carboxyl group [64]. Actually, this is an expected outcome if the molecular orbitals analyzed in terms of fractional contributions of each group. Fig. 7-a) shows the fragmental contributions to molecular orbitals, and Fig. 7-b) displays the combinations of fragmental orbitals of indole group and methyl group to create the molecular orbital. The indole orbitals play significant role in HOMO/-1/ and LUMO/+1 molecular orbital with 98/99 % and 99/95 % contributions, respectively. As for methyl orbitals, LUMO+2 orbital is localized with 30 % share as seen from Fig. 7-a). The HOMO orbital of the 1MI linked to indole's occupied frontier orbitals with 76% and 11% shares whereas no contributions from the occupied orbitals of the methyl group. On the other side, the LUMO orbital of 1MI accepts contributions from both groups. We infer that indole makes a larger contribution to the electron transfer in the ligand.



Figure 7. a) Molecular orbital energy levels of 1MI and fractional contributions from indole and methyl groups, b) Formation of frontier molecular orbitals of 1MI from fragmental combinations of indole and methyl groups.

The HOMO-LUMO energy is a critical parameter in determining molecular electrical transport properties because it is related to the electron conductivity [65]. The first most possible transition energies are also given in Fig 7-a) that ranges from 5.17 eV to 8.55 eV. Among these energy gaps, the $\Delta E_{(HOMO-LUMO)}$ is specifically important in determination of some physicochemical properties such as the order and the stability of molecular systems. The most prominent properties that can be calculated directly from the energy gaps are the chemical

potential (μ), electronegativity (χ), electrophilicity index (ω) and chemical hardness (η). These characteristic properties of 1MI in gas state and in water and ethanol solutions have been calculated using the formulas explained below and collated in Table S1 along with energies of molecular orbitals, energy gaps for first possible transitions.

The chemical hardness and the chemical potential are given by the following expression,

$$\begin{split} \delta_{cal} &= 0.9692 \delta_{exp} + 0.0362, \ R^2 &= 0.9992 \\ \delta_{cal} &= 0.9692 \delta_{exp} + 0.0362, \ R^2 &= 0.9992 \end{split} \tag{3.7}$$

Where, I and H are ionization potential and electron affinity of a molecular system. Electrophilicity index (ω) which is a measure of the stabilization energy in terms of electronic chemical potential and the chemical hardness is calculated by the following expression,

$$\delta_{cal} = 0.9692\delta_{exp} + 0.0362, R^2 = 0.9992$$
(3.9)

Finally, the electronegativity (χ) is given by

$$\delta_{\text{cal}} = 0.9692\delta_{\text{exp}} + 0.0362, \, R^2 = 0.9992 \tag{3.10}$$

These properties of the gas state are significantly different from that of solvents while they are nearly same for both solvents. This result is also consistent with the UV spectra being very similar in two solvents. Electron acceptation/donating properties for 1MI are found to be low in comparing to some other systems that contains other fractions rather than only methyl group [66].

Weak interactions in 1MI are only two kinds, either vdW or steric effects. The region marked by green-brown in Figure 3 b) can be identified as vdW interaction region

3.5. Nuclear Magnetic Resonance Spectral Analyses

The experimental ¹³C and ¹H NMR spectra of 1MI in chloroform were given in Figure 8 and Figure 9 with assignments to the appropriate nuclei. The molecule has nine carbon atoms give rise to nine distinct NMR peaks, and nine protons showed in seven peaks because the protons on the methyl group are indistinguishable experimentally. In order to make a deeper explain of these observations, ¹H and ¹³C NMR chemical shift values were calculated for the structure given in Figure 1 using a most widely used gauge including atomic orbital GIAO approach developed by Wolinski and Pulay [67] using the same method with the same level of theory used to optimize the structure. NMR calculations were performed for the gas state and chloroform solutions choosing IEFPCM for the solvent environment model. The isotropic chemical shifts, δ , values were calculated from the isotropic shielding values, σ , referencing to tetramethylsilane [TMS;(CH₃)₄Si] according to δ_{iso}^{x} = $\sigma_{iso}^{TMS} - \sigma_{iso}^{x}$. The calculated and experimental ¹³C and ¹H NMR chemical shifts values with determined assignments were collated in Table 4.



Figure 8. ¹³C NMR spectra of the of 1MI molecule in $CDCl_3$ solution.



Figure 9. ¹H NMR spectra of the of 1MI molecule in CDC13 solution.

DFT calculations of the magnetic properties of 1MI give quite good results to compare experimental recordings with only one deficiency. The protons on the methyl group actually cannot be differentiated in experiments, however, the calculations provide two peaks for these three protons assuming only the H_{17} and H_{18} were the same and the H_{19} differs from those. This is due to rigidity of the molecule in the calculations, which ignores the rotation of methyl group along its axes and breaking the symmetry during dynamic motion. Conformity of calculated results to experimental observations was analyzed and the correlation graphs in Figure S4 were created. ¹³C and ¹H chemical shifts calculated in solution and in gas phase compared to the experimental values. In



all cases, the calculated shift values are slightly higher than observations, resulting in the slope of the linear fit to be lower than one. However, these deviations are not more than 1 ppm for the ¹³C NMR and 0.1 ppm of the ¹H NMR calculated with the inclusion of solvent effect, as can be seen from the residual analysis at the top of each graph in Figure S4. These deviations doubles for the gas phase calculations despite seem to have the same trend in curves. This shows that the solvent effect in NMR calculations must be included to obtain reliable supportive data.

Ç. Karaca

¹³ C NMR	Ca	lculated	Experimental	
Atom Label	Gas	Chloroform	Chloroform	
C16	32.7425	32.78	33.04	
C8	104.505	103.08	101.26	
C6	110.461	111.44	109.55	
C4	123.230	122.63	119.63	
C3	124.433	123.90	121.23	
C5	124.790	124.27	121.84	
C7	131.198	133.13	128.89	
C2	134.230	133.78	129.13	
C1	140.626	140.75	137.09	
¹ H NMR				
H19	3.4388	3.63	3.67	
H18	3.6115	3.67	3.67	
H17	3.6115	3.67	3.67	
H14	6.4173	6.46	6.45	
H13	6.7364	6.99	6.95	
H10	7.1749	7.22	7.08	
H11	7.1761	7.30	7.19	
H12	7.2414	7.37	7.24	
H9	7.6484	7.71	7.59	

Table 4. The experimental and calculated NMR chemical shifts (ppm) of 1MI.

3.6. Nonlinear optical properties

Nonlinear optical (NLO) properties are substantial in terms of determination and classification of materials whether they are considerable as candidates in the applications where the light matter interactions violates linear superposition principle such as second harmonic generations, birefringent effects, and optical Kerr effect [68,69]. The most essential characteristics to investigate in this regard are the electronic dipole moment, µ, molecular polarizability, α , anisotropy of polarizability, $\Delta \alpha$, and molecular first hyperpolarizability, β , of the material. These properties can be calculated from the dipole moment $\mu_x, \mu_y, \mu_z,$ the polarizability the first $\alpha_{xx}, \alpha_{xy}, \alpha_{xz}, \alpha_{yy}, \alpha_{yz}, \alpha_{zz},$ and hyperpolarizability

 $\beta_{xxx}, \beta_{xxy}, \beta_{xyy}, \beta_{yyy}, \beta_{xxz}, \beta_{xyz}, \beta_{yyz}, \beta_{xzz}, \beta_{yzz}, \beta_{yzz}$ tensors obtained at the end of frequency job directly via equations 11-14

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$
(3.11)

$$\alpha_{0} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta \alpha = \frac{1}{\sqrt{2}} [(\alpha_{xx} - \alpha_{yy})^{2} + (\alpha_{yy} - \alpha_{zz})^{2} + (\alpha_{zz} - \alpha_{xx})^{2} + 6\alpha_{xz}^{2} + 6\alpha_{xy}^{2} + 6\alpha_{yz}^{2}]^{\frac{1}{2}}$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^{2} + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^{2} + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^{2}]^{\frac{1}{2}}$$

$$(3.12)$$

$$(3.12)$$

$$(3.12)$$

$$(3.13)$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^{2} + (\beta_{yyy} + \beta_{yzz} + \beta_{yyz})^{2}]^{\frac{1}{2}}$$

$$(3.14)$$

The calculated values of the properties above for 1MI are tabulated in Table S2 and compared to that of urea as a limiting reference system for the materials to be considered as nonlinear optical in Table 5. A quick survey of the results shows that the title molecule has weak nonlinear optical properties; first hyperpolarizability of 1MI barely doubles that of urea, which is common for many organic compounds with any electron donor atom [55,59], and dipole moment of 1MI is even less than that of urea.



The average polarizability and the anisotropy of polarizability of 1MI, on the other side, are reasonably high, nearly four times larger than that of urea. The highest contribution to the polarizability comes from the α_{xx} component. Because the molecular plane is located on the xy-plane and x-axis is along the two rings, polarizability being high in this direction is very natural due to high charge mobility through π -bonds. Polarizability on the y- and z- directions mostly results from the presence of the unpaired electrons on the nitrogen. As a results, 1MI can be used as nonlinear optical material where the polarizability and anisotropy of polarizability are the main concerns rather than higher order properties.

Table 5. Comparison of optical properties of 1MI with Urea.

Optical Properties	1MI	Urea	Ratio
$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$	1188.66	605.999	2.0
$\mu = (\mu^2_x + \mu^2_y + \mu^2_z)^{1/2}$	0.9643	1.4249	0.7
$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$	15.1025	4.1496	3.6
Δα	38.0410	8.8998	4.3

4. Conclusion

Geometrical structure, electronic transitional, magnetic properties. and vibrational. identifier characteristics of 1MI were investigated experimentally and by DFT calculations. Theoretical results and experimental observations are found to be highly correlated. In this regard, UV-Vis and NMR calculations need to be done with the inclusion of solvent effect to produce more accurate and less dispersive data. Weak interactions in 1MI are found to be only two kinds, either vdW or steric effects, and steric effects in rings in two sides of the molecule are quite different from each other. The vdW interactions play a role only in the region between methyl group and the nearest hydrogen of the benzene ring as visualized in both RDG analysis and ESP surface mapping. Vibrational properties of the molecule are in well agreement with the literature of similar compounds with only one difference; the vibrational modes that have contributions CN modes are highly complicated. Electronic transitional properties found to be nearly same for 1MI dissolved in water or ethanol thus indicates that the 1MI is not much under the influence of the solvent. 1MI has some considerable nonlinear optical properties that can be taken into account in the applications involving the polarizability and anisotropy of polarizability

Ethics

There are no ethical issues after the publication of this manuscript.

Acknowledgement

The numerical calculations reported in this paper were fully/partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources). The experiments in this paper were fully/partially performed at Manisa Celal Bayar University (TURKEY)- Applied Science and Research Center (DEFAM).

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