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Investigation of NLO Properties of Pyridine Benzimidazole Derivatives: Ab-Initio Approach

Ayhan UNGORDU

Cumhuriyet University, Faculty of Science, Department of Chemistry, 58140 Sivas, TURKEY

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Abstract: Quantum chemical calculation analyses of pyridine benzimidazole and their derivatives are done at HF/6-31+G(d) level in gas phase. Geometric parameters, IR spectrum, ^{1}H- and ^{13}C-NMR spectrum are calculated at HF/6-31+G(d) level in gas phase and examined in detail. In addition to these analyses, some quantum chemical descriptors which are related to non-linear optical (NLO) properties are calculated. Substituent effect on NLO properties are examined in detail and it is found that methyl group increases the NLO activity.

Keywords: Crossed square, Cornered crossed module, fibration

Piridin Benzimidazol Türevlerinin NLO Özelliklerin İncelenmesi: Ab-Initio Yaklaşımı

Özet: Piridin benzimidazol ve türevlerinin kuantum kimyasal hesaplama analizleri, gaz fazında, HF/6-31+G(d) seviyesinde yapıldı. Bu bileşiklerin geometrik parametreleri, IR spektrumları, ^{1}H- ve ^{13}C-NMR spektrumları detaylı şekilde incelendi. Bu analizlere ek olarak, lineer olmayan optik (NLO) özellikler ile ilgili kuantum kimyasal parametreler de hesaplandı. Ayrıca, NLO özellikler üzerine sübstitüent etkisi incelendi ve metil gruplarının NLO aktivitesini artırdığı bulundu.

Anahtar Kelimeler: Piridin benzimidazole, NLO özellikler, Moleküler modelleme, Ab-initio çalışması, Sübstitüent etkisi

1. INTRODUCTION

Common computational and experimental studies have been carried out on the structural, spectral and electronic properties of nonlinear optical (NLO) materials over the past two decades due to their potential applications in optoelectronic and a lot of optical devices [1-9].

The search determining new and good NLO materials has become an important research area so as to provide the requirements of developing technology. For this purpose, particularly, the π-conjugated molecular systems are satisfactory in terms of their NLO features due to they can treat as a donor and an acceptor [10-13].

It is reported that donor and acceptor molecules demonstrate high NLO features. Also, it is well known that proton or electron transfer compounds have a significant role in the field of magnetic, electrical conductivity and optical properties [14-17].

Substituted pyridine benzimidazole compounds which have π-conjugated system are synthesized by Kathleen et al. (Scheme 1) [18]. Detailed

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* Corresponding author. *Email address: aungordu@cumhuriyet.edu.tr*
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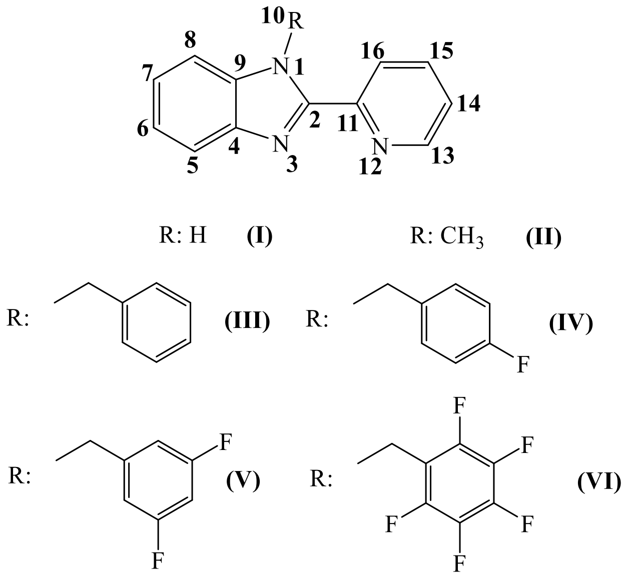
quantum chemical study on structural, spectroscopic properties and NLO property of these compounds are not yet available. Therefore, quantum chemical calculation with ab-initio method has been used to examine different aspects of mentioned molecules.

Optimized molecule structures are obtained at HF/6-31+G(d) level in vacuo. Then IR, UV-VIS and NMR spectrum are calculated and examined in detail. Especially, four area (chloroform, DMSO, gas phase and water) are taken into account in calculation of UV-VIS spectrum. In these calculations, conductor polarized continuum model (C-PCM) is used to explain the solute – solvent interaction. Additionally, substituent effect over the NLO properties is investigated.



Scheme 1. The structures of studied compounds with atomic labelling.

2. COMPUTATIONAL DETAILS

HF calculations of molecule **(I)** – **(VI)** were carried out by using GaussView 5.0.8 [19], Gaussian 09 AML64-G09Revision-D.01 programs [20] and ChemBioDraw Ultra Version (15.1.0.144) [21]. All calculations were performed at HF/6-31+G(d) level in vacuum. The vibration frequency analyses indicate that optimized structures of relevant molecules are at stationary points corresponding to local minima without imaginary frequencies. Gauge-including-atomic-orbital (GIAO) method with HF/6-31+G(d) level was used to calculate NMR spectra for studied molecules. Some quantum chemical parameters which are total static dipole moment (μ), the average linear polarizability (α), the anisotropy of polarizability ($\Delta\alpha$), the first hyperpolarizability (β), optical softness (σ_O), the biggest delocalization energy ($E_{Del.}$) and chemical potential (CP) are calculated by using following equations [22]:

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

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}{}^2 + 6\alpha_{xy}{}^2 + 6\alpha_{yz}{}^2]^{\frac{1}{2}} \tag{3}$$

$$\beta_0 = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{\frac{1}{2}} \tag{4}$$

$$\sigma_O = \frac{1}{E_{LUMO} - E_{HOMO}} \tag{5}$$

$$I = -E_{HOMO} \tag{6}$$

$$A = -E_{LUMO} \tag{7}$$

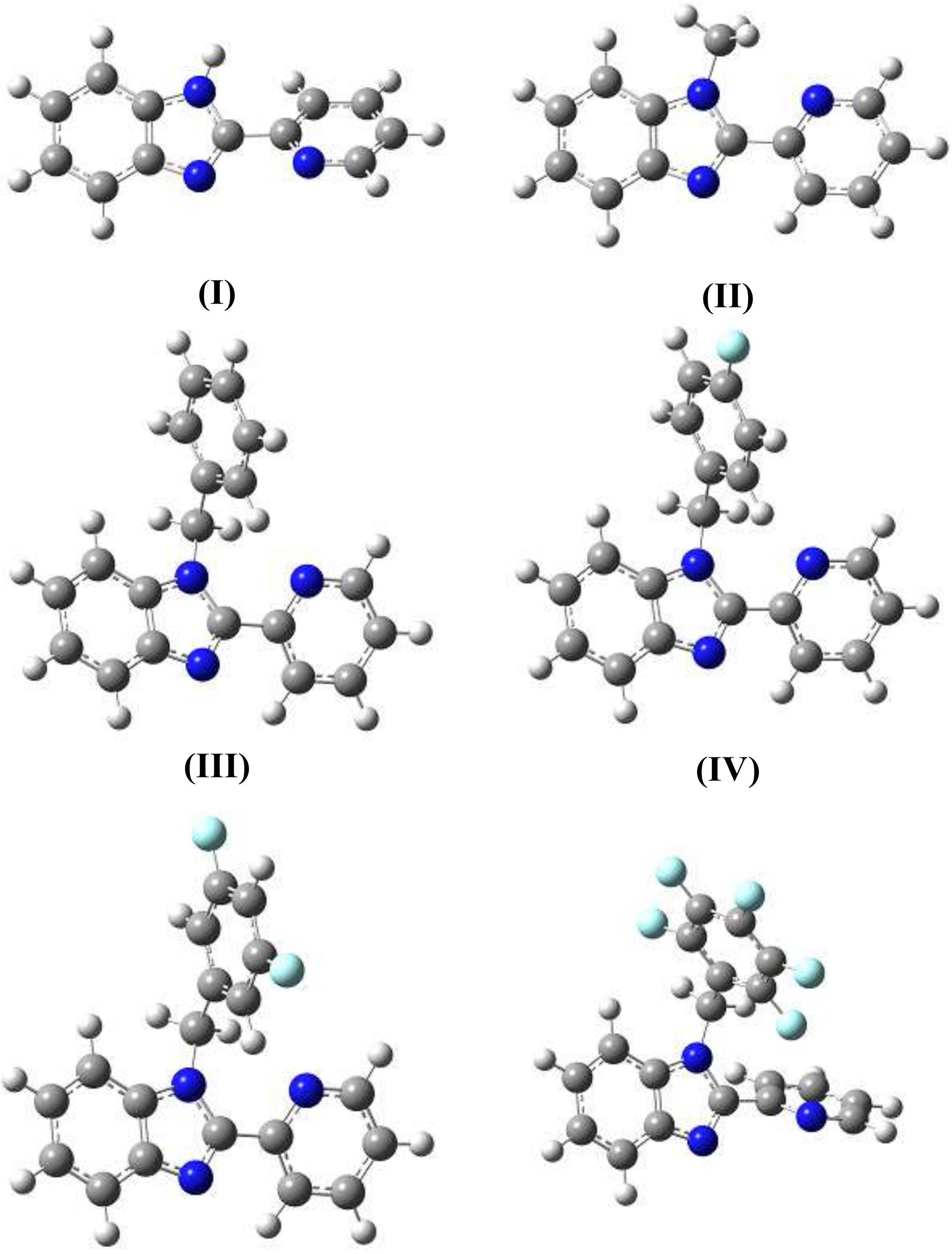
$$CP = -\left(\frac{2}{|I+A|}\right) \tag{8}$$

Above equations were used in determination of NLO properties. Tetramethylsilane and urea were used as reference substances for NMR spectrum and in determination of NLO properties, respectively. Additionally, UV-VIS spectrum of each compound is calculated by time dependent method. Four areas are selected for UV-VIS spectrum. Dielectric constants of gas phase, chloroform, dimethylsulfoxide (DMSO) and water are 1, 4.7113, 46.826 and 78.3553, respectively.In solvent calculations, conductor polarized continuum model (C-PCM) is used to explain the solute – solvent interaction.

3. RESULTS and DISCUSSION

3.1. Optimized Structures

Entitled compounds are optimized at HF/6-31+G(d) level in gas phase and optimized structures of mentioned molecules are given in Fig. 1. Some structural parameters of them are also given in Table 1.



(I) (II)

(III) (IV)

(V) (VI)

Figure 1. Optimized structures of studied compounds at HF/6-31+G(d) level in vacuo.

Table 1. Calculated some structural parameters of studied molecules

	Molecule **(I)**	Molecule **(II)**	Molecule **(III)**	Molecule **(IV)**	Molecule **(V)**	Molecule **(VI)**
Bond Lengths (Å)						
N1-C2	1.370	1.367	1.371	1.371	1.373	1.378
N1-C9	1.377	1.378	1.381	1.381	1.382	1.385
N1-C10	-	1.453	1.455	1.455	1.450	1.448
C2-N3	1.283	1.292	1.291	1.290	1.290	1.282
C2-C11	1.484	1.483	1.485	1.485	1.485	1.492
N3-C4	1.381	1.373	1.375	1.375	1.375	1.380
C4-C5	1.394	1.395	1.395	1.394	1.394	1.392
C9-C8	1.391	1.395	1.393	1.393	1.393	1.392
C11-N12	1.323	1.322	1.322	1.322	1.322	1.321
C11-C16	1.391	1.394	1.393	1.393	1.393	1.389
Bond Angles (º)						
C10-N1-C2	125.62	129.67	130.22	130.05	130.37	128.27
C10-N1-C9	126.47	124.63	123.59	123.70	123.48	125.91
N1-C2-C11	120.96	124.98	125.47	125.37	125.39	123.24
N3-C2-C11	125.79	121.46	121.01	121.10	121.25	122.97
Dihedral Angle (º)						
N1-N2-C11-N12	-39.08	-18.92	23.85	24.99	20.57	118.48
N1-N2-C11-C16	143.03	160.44	-155.18	-153.93	-158.32	-65.67
N3-N2-C11-N12	140.66	162.44	-157.93	-156.85	-161.11	-63.94
N3-N2-C11-C16	-37.21	-18.18	23.03	24.22	19.99	111.90
N1-N3-C16-N12	132.93	-18.64	23.54	24.66	20.41	105.41

There are not significant differences in bond lengths and the bond angles. Substituents are changed a little them. However, there are important differences in dihedral angles. Substituents which change dihedral angles are quite altered the main skeleton of molecules. According to Table 1, it is found that molecule **(I)** and **(VI)** deviate from planarity.

IR spectra is substantial in determination of functional groups of molecules. IR spectrum of mentioned compounds are calculated at the same level of theory in gas phase and represented in Fig. 2. Calculated frequencies in Fig. 2 are harmonic and some stretching frequencies are given in Table 2.

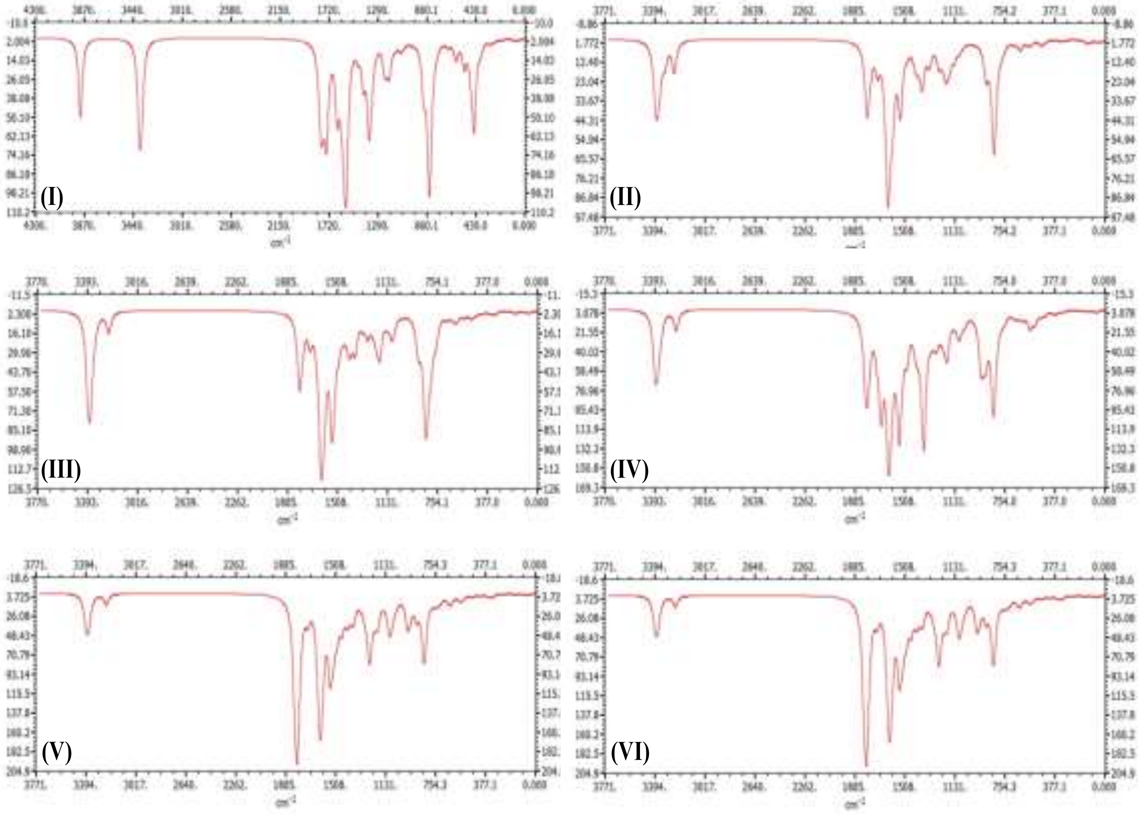


Figure 2. Calculated IR spectrum of studied compounds at same level of theory.

Table 2. Some calculated stretching frequencies (cm^{-1}) of related compounds at same level of theory.

Modes	Molecule **(I)**	Molecule **(II)**	Molecule **(III)**	Molecule **(IV)**	Molecule **(V)**	Molecule **(VI)**
ν_{NH}	3910	-	-	-	-	-
ν_{CH}	3374	3385	3373	3393	3386	3386
$\nu_{CH\ (aliphatic)}$	-	3252	3235	3235	3243	3278
$\nu_{C=C}$	1797, 1373	1796	1796	-	1795	1799
$\nu_{C=N}$	1747, 1571	1546	1555	1552	1554	1746
ν_{CF}	-	-	-	1367	1255	1246

Some functional groups which are (-NH), (-CF) and aromatic and aliphatic (-CH) frequencies are given in Table 2. There are some deviations from expected frequencies due to the fact that the given frequencies are harmonic. For instance, the range of NH stretching frequencies is between 3300 – 3500 cm^{-1}. However, it is calculated as 3910 cm^{-1}. Generally, harmonic frequencies can be corrected by scale factor. But, scale factor of HF/6-31+G(d) level is not available, yet.

3.2. UV-VIS Spectra

UV-VIS spectrum of related compounds is calculated at the same level of theory in gas phase, chloroform, DMSO and water. The main band of related molecules in each area are given in Table 3. Additionally, distribution graphs are plotted and represented in Fig. 3.

Table 3. The main band of mentioned molecules in each area

Area	Molecule **(I)**	Molecule **(II)**	Molecule **(III)**	Molecule **(IV)**	Molecule **(V)**	Molecule **(VI)**
Gas Phase	166.7	168.2	172.5	166.0	164.2	156.4
Chloroform	174.8	175.7	173.3	170.4	168.9	160.6
DMSO	174.6	175.4	170.8	169.4	168.6	160.0
Water	172.8	174.5	172.8	169.1	167.6	159.8

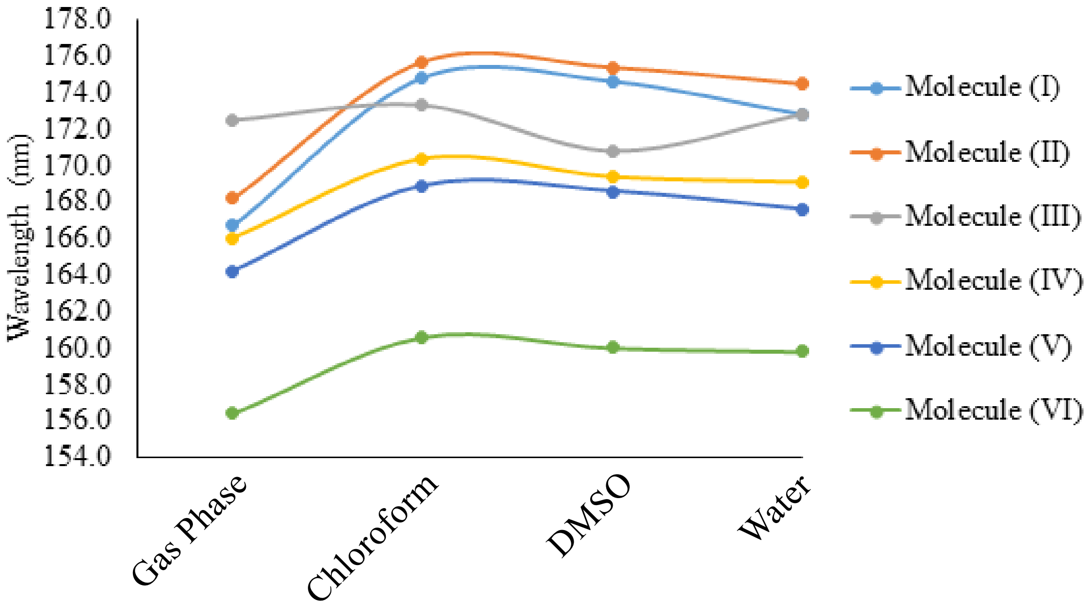


Figure 3. Distribution graph of main band of mentioned molecule for each area.

According to Fig. 3, the wavelength of the main band of molecule **(I)** increases in any solvent rather than gas phase expect molecule **(III)**. In addition to these results, the wavelength mainly decreases with increasing of dielectric constant except gas phase. Electronic mobility between molecular orbitals is more in any solvent area than gas phase. Because the wavelength of main band in any solvent is higher than gas phase. These results imply that required energy is lower in solvent area than gas phase. This situation increases some electronic properties which are NLO properties and chemical reactivity. Therefore, these properties increase in solvent area than those of gas phase.

3.3. NMR Spectra

Chemical shifts values of hydrogen and carbon atoms in studied molecule are calculated by using HF/6-31+G(d) level with GIAO method in gas phase. Additionally, these calculations, tetramethylsilane is calculated at same level of theory. Similarity of optimized structures are investigated by using chemical shift values of carbon and hydrogen atoms. Calculated ^{13}C-NMR and ^{1}H-NMR results are given in Table 4. Also, ^{13}C-NMR and ^{1}H-NMR spectrums are given in Fig. 4.

Table 4. Calculated NMR spectrum of related compounds at HF/6-31+G(d) level in gas phase.

	Molecule **(I)**	Molecule **(II)**	Molecule **(III)**	Molecule **(IV)**	Molecule **(V)**	Molecule **(VI)**
^{13}C-NMR results						
C2	132.159	132.802	133.405	133.39	132.897	135.321
C4	123.691	121.844	122.226	122.214	121.974	123.109
C5	105.206	104.015	103.592	103.76	103.98	104.958
C6	102.143	101.701	102.246	102.399	102.71	102.845
C7	105.206	104.731	104.753	104.932	105.387	104.958
C8	89.852	89.896	91.966	91.64	90.929	89.658
C9	113.938	117.162	117.061	116.888	116.716	113.667
C10	-	14.307	28.238	27.725	27.593	16.317
C11	134.307	134.667	134.583	134.487	133.931	134.514
C13	133.233	128.929	129.127	129.167	129.182	132.695
C14	101.436	101.273	101.517	101.678	101.847	101.563
C15	119.794	120.387	120.71	120.924	120.902	119.118
C16	100.123	104.522	105.031	105.105	104.896	102.605
^{1}H-NMR results						
N1*H*	25.275	-	-	-	-	-
C5*H*	24.397	24.538	24.557	24.545	24.491	24.509
C6*H*	25.254	25.286	25.309	25.297	25.233	25.237
C7*H*	25.176	25.164	25.35	25.324	25.251	25.208
C8*H*	25.187	25.234	25.438	25.453	25.473	25.237
C13*H*	23.484	23.716	23.834	23.809	23.921	23.426
C14*H*	25.332	25.364	25.341	25.313	25.337	25.216
C15*H*	24.558	24.502	24.459	24.439	24.45	24.52
C16*H*	25.185	23.753	23.772	23.806	23.705	25.321

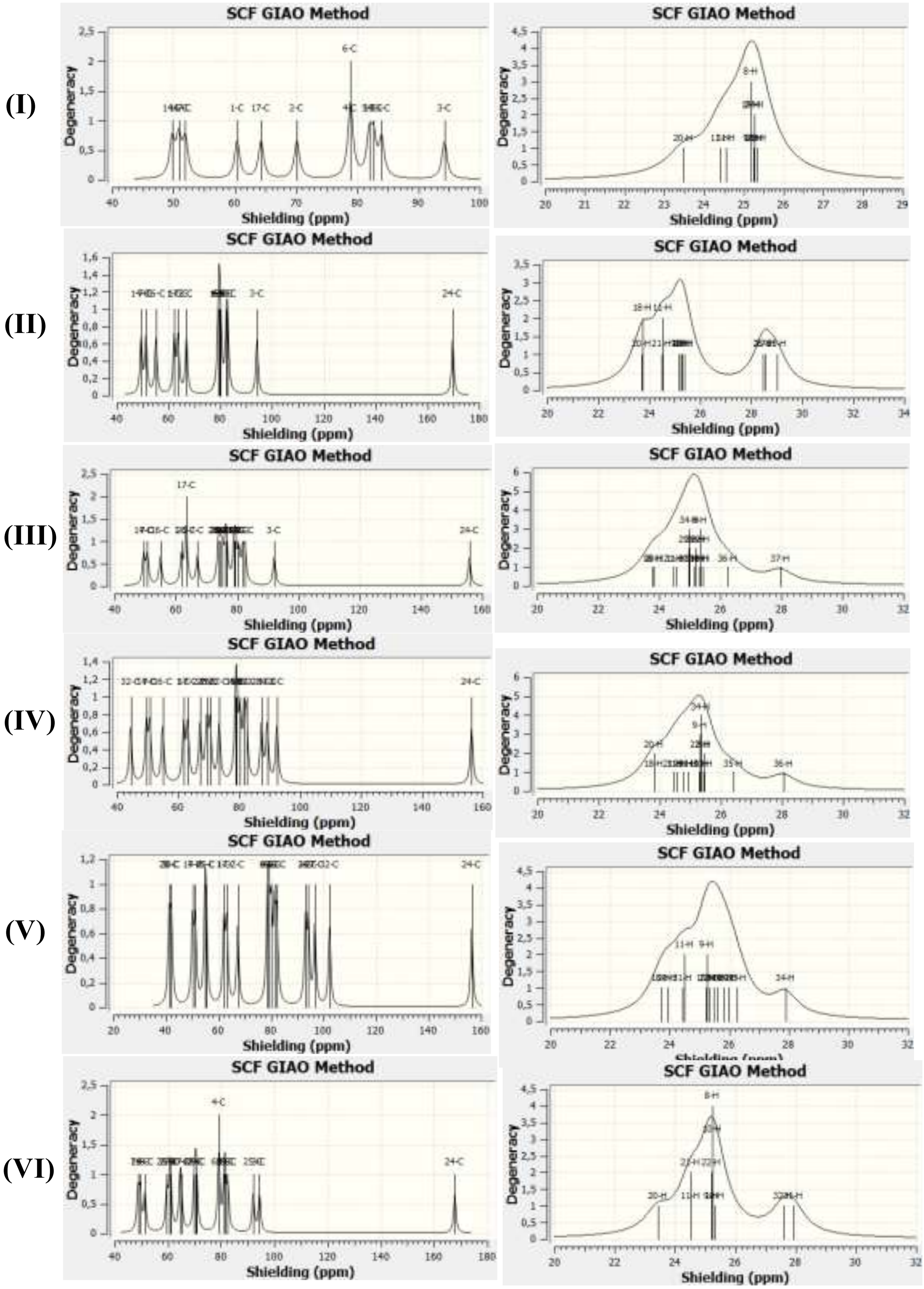


Figure 4. ^{13}C-NMR and ^{1}H-NMR spectrums of studied compounds at same level of theory.

Referring to Table 4, chemical shifts of aromatic carbon atoms are calculated in the range of 89-135 ppm. These results are appropriate with theoretical expectation. There are aliphatic carbon atoms in molecules and their chemical shifts values are within range of 14-29 ppm. These results are appropriate with theoretical expectations. As for the chemical shift values of hydrogen atoms, all results are quite compatible with each other.

3.4. Non-linear optical (NLO) properties

NLO is important feature in providing the key functions in technological areas. Thus, NLO is located in the foreground in current research. NLO properties can be affected by planarity of molecule, functional groups, π electron delocalization and area. Especially planarity and π electron delocalization are so important for NLO properties. Planarity and π electron delocalization increase the NLO properties of molecule. Some quantum chemical parameters which are total static dipole moment (μ), the average linear polarizability (α), the anisotropy of the polarizability (Δα), first hyperpolarizability (β) optical softness (σ_O), the biggest delocalization energy ($E_{Del.}$) and chemical potential (CP) are calculated by Eq. (1) – (11). In terms of planarity, molecule **(I)** and **(VI)** is significantly deviated from planarity. Dihedral angles belong to these molecules are given in Table 1. Due to the fact that molecule **(I)** and **(VI)** are neglected in determination of NLO properties. HOMO energy and calculated quantum chemical parameters are given in Table 5.

Table 5. Calculated quantum chemical parameters for mentioned molecule at same level of theory in vacuo

Molecule	μ^1	α^2	$\Delta\alpha^2$	β^3	$\sigma_O{}^4$	$E_{Del.}{}^5$	CP^4	$E_{HOMO}{}^6$
(II)	1.208	19.687	54.390	5.793×10^{-27}	9.632	160.19	-0.114	-0.291
(III)	1.185	26.505	54.142	4.513×10^{-27}	9.577	81.33	-0.116	-0.292
(IV)	1.405	26.403	55.062	5.596×10^{-27}	9.583	80.65	-0.120	-0.296
(V)	1.359	25.902	55.165	5.499×10^{-27}	9.636	78.96	-0.121	-0.298

^{1} in Debye, ^{2} in Å^3, ^{3} in cm^5/esu, ^{4} in eV^{-1},^{5} in kcal mol^{-1}, ^{6} in eV

NLO properties increase with increasing of all parameters. It is calculated that mentioned parameters of related molecules are higher than those of urea. Hence, NLO properties of studied molecules are better than urea. The ranking of NLO activity for each parameter is given as follow:

Molecule **(IV)** > Molecule **(V)** > Molecule **(II)** > Molecule **(III)** (in μ)

Molecule **(III)** > Molecule **(IV)** > Molecule **(V)** > Molecule **(1I)** (in α)

Molecule **(V)** > Molecule **(III)** > Molecule **(IV)** > Molecule **(I1)** (in Δα)

Molecule **(II)** > Molecule **(IV)** > Molecule **(V)** > Molecule **(III)** (in β)

Molecule **(III)** > Molecule **(IV)** > Molecule **(II)** > Molecule **(V)** (in σ_O)

Molecule **(II)** > Molecule **(IV)** > Molecule **(V)** > Molecule **(III)** (in $E_{Del.}$, CP, E_{HOMO})

According to these rankings, molecule **(II)** is the best candidate for NLO properties. Additionally, MEP maps of related compounds are given in Fig. 5.

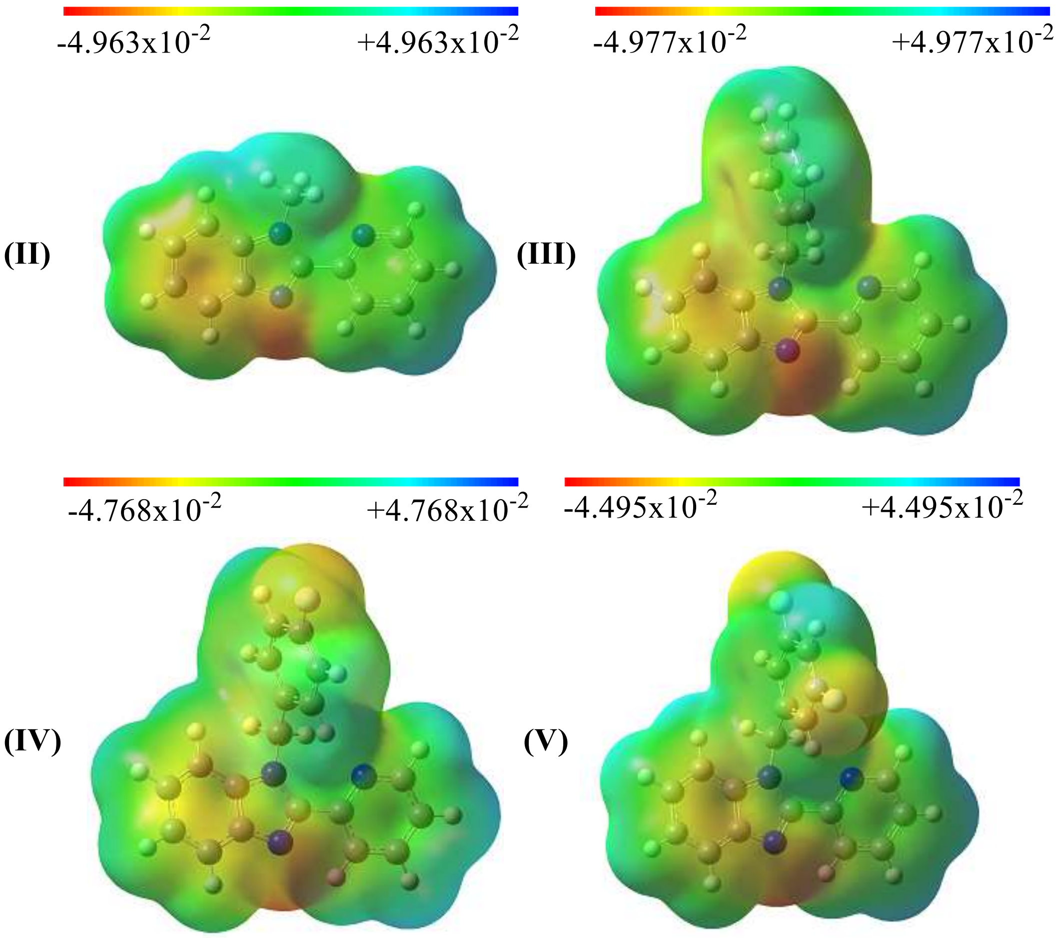


Figure 5. MEP maps of studied compounds except molecule **(I)** and **(VI)** at same level of theory.

According to Fig. 5, ESP charges are close to each other. However, molecular planarity of molecule **(II)** can easily see form this figure. Benzene and derivatives is distorted the whole molecular planarity. Methyl group is known as electron donating group and it increases the NLO properties of molecule. There are yellow regions on benzene ring due to the π electrons. It is implied that this delocalization increases the NLO activity of molecule.

4. CONCLUSIONS

Computational investigations of pyridine benzimidazole compound derivatives are performed at HF/6-31+G(d) level. Optimized structures, IR, UV-VIS, ^{1}H-NMR and ^{13}C-NMR are calculated and investigated. It is found that there is not molecular planarity in molecule **(I)** and **(VI)**. Similarities of mentioned molecules are supported by NMR spectrum. As for the UV-VIS spectrum, it is observed that electronic properties are more in solvent area. In addition to these results, NLO properties are investigated in detail and molecule **(II)** is the best candidate for NLO application.

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