Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi
Iğdır University Journal of the Institute of Science and Technology

Theoretical Investigation of The Molecular Structure, Conformational and Nonlinear Optical Properties of Picolinic Acid and Its Derivatives

Güventürk UĞURLU[1]

ABSTRACT: In this paper, ab initio Hartree-Fock (HF) and Density Functional Theory (DFT), using Becke-3–Lee–Yang–Parr (B3LYP) hybrid density functional, calculations have been performed to characterize the ground state geometrical energy, the dipole moment (μ), polarizability (α), the hyperpolarizability (β) of picolinic acid (PA), picolinamide (PAA) and picolinic acid hydrazide (PAH) molecules using the 6-311++G (d, p) basis set. The ^{1}H and ^{13}C NMR chemical shifts were calculated by GIAO approach by using B3LYP/6-311+G (2d, p) and HF/6-31G (d) level of theory. Also, E_{HOMO} (the highest occupied molecular orbital energy), E_{LUMO} (the lowest unoccupied molecular orbital energy), HOMO-LUMO energy gap (ΔEg), the dipole moment (μ), polarizability (α) and the hyperpolarizability (β) are investigated as a function of the torsional angle, for each molecule. In addition, the trends in the calculated torsional potentials, barrier heights and energy differences between conformers are discussed. The trans-conformers of the studied molecules were found to be most stable among their conformers. The potential barrier height of cis- conformers are at 13.24, 10.69, and 9.56 with DFT/B3LYP level of the theory 6-311++G (d, p) basis set and at the HF/6-311++ G (d, p) 13.53, 10.94, and 10.55 kcal/mol, respectively. The structural parameters of the studied molecule compared with the data given in the literature.

Keywords Picolinic acid, DFT calculation, NMR, Non-linear optical properties

FBED İST

Pikolinik Asit ve Türevlerinin Moleküler Yapısının, Konformasyonel ve Doğrusal Olmayan Optik Özelliklerinin Teorik Olarak İncelenmesi

ÖZET: Bu çalışmada, Pikolinik asit (PAA), pikolinamid (PAA) ve pikolinik asit hidrazid (PAH) moleküllerinin taban (temel) durum geometrik enerjisini, dipol momenti (μ), polarizebilitesi (α) ve hiperpolarizebilitesini (β) belirlemek için *ab-initio* Hartree–Fock (HF) ve Becke-3-Lee-Yang-Parr (B3LYP) hibrit fonksiyonelli Yoğunluk Fonksiyoneli Teorisi (DFT) ile 6-311++G(d,p) temel seti kullanılarak hesaplamalar yapılmıştır. ^{1}H ve ^{13}C NMR kimyasal kayma hesaplamaları GIAO yaklaşımına göre B3LYP/6-311+G (2d, p) ve HF/6-31G (d) yöntemleri ile yapılmıştır. Ayrıca, her molekül için, E_{HOMO} (en yüksek dolu moleküler orbital enerjisi) ve E_{LUMO} (en düşük boş moleküler orbital enerjisi), E_{LUMO}-E_{HOMO} enerji gap (ΔEg), dipol momenti (μ), polarizebilite (α) ve hiperpolarizebilite (β) değerleri torsiyon açının fonksiyonu olarak araştırıldı. Bunlara ek olarak, Konformerler arasındaki hesaplanmış torsiyonal potansiyelleri, bariyer yükseklikleri ve enerji farkları tartışıldı. Çalışılan moleküllerin trans-konformerlerinin konformerler arasında en kararlı oldukları bulundu. Cis-konformers durumunda potansiyel bariyer yüksekliğinin DFT / B3LYP/6-311 ++ G (d, p) yönteminde 13.24, 10.69 ve 9.56 olduğu, HF / 6-311++G (d, p) yönteminde ise 13.53, 10.94 ve 10.55 kkal / mol olduğu sırasıyla bulunmuştur. Çalışılan molekülün yapısal parametreleri, literatürde verilen verilerle karşılaştırılmıştır.

Anahtar Kelimeler Pikolinik asit, DFT hesaplama, NMR, Nonlineer optik özellikler

Cilt/*Volume*: 8, Sayı/*Issue*: 1, Sayfa/*pp*: 75-83, 2018
ISSN: 2146-0574, e-ISSN: 2536-4618 DOI: 10.21597/jist.407838

[1] Güventürk UĞURLU (0000-0003-4171-7879), Kafkas Üniversitesi, Fen Edebiyat Fakültesi, Fizik Bölümü, Kars, Türkiye
Sorumlu yazar/Corresponding Author: Güventürk UĞURLU, gugurlu@kafkas.edu.tr

Geliş tarihi / *Received:* 28.07.2017
Kabul tarihi / *Accepted:* 25.10.2017

INTRODUCTION

Picolinic acid, commonly known as PA, is pyridine derivative, which attracts great interest because of molecular properties biological and chemical. It is an isomer of nicotinic acid and isonicotinic acid with six membered ring structures. In recent years, pyridine and its derivatives have been widely investigated and analyzed owing to their interest in bioactivities and employment in pharmaceutical and in other industrial areas. (Pierrat et al., 2005). Picolinic acid is defined in varied biological environment as blood serum, mother milk, pancreatic juice and gastral homogenates (Dazzi et al., 2001; Rebello et al., 1982). During the digestion, it is secreted into the intestine and absorption of essential metals. (Evans, 1989). So, it is a body's chelator and acts as a chelating agent of elements such as chromium, zinc, manganese, copper, iron, and molybdenum in the body. It is used in food preservation, pharmaceutical and textile industry (Kiec et al., 2003; Ahren, 2001). It is known that 2-picolinic acid is terminal tryptophan metabolite, and its anion has been used as a valuable chelating ligand. Besides, 2-picolinic acid is not only a potential proton acceptor but also proton donor depending on deprotonated groups (Kukovec et al., 2008). Picolinic acid and its derivatives are used as building block in photovoltaic devices (Liu et al., 2014; Matsuda et al., 2004). Recently, nonlinear optical properties of picolinic acid complexes have been investigated. The nonlinear optical materials have received great interest because of advances in optical processing and opto-electronic technology. A great deal of research has been devoted to investigating different types of nonlinear optical (NLO) materials (Andraud et al., 1994; Lipscomp et al., 1981) to design excellent NLO materials which show potential application in modern communication technology, data storage and optical signal processing (Uyeda et al., 2002; Marder et al., 1983). In the particular, organic nonlinear optical materials have shown great promise around photonics due to their useful physical and optical properties. Theoretical study has been played a crucial role in designing and development of novel materials for nonlinear optics. The physical and chemical properties of a substance are strongly related to both its geometrical and electronic structures. In this work, molecular structure, dipole moment, relative energies, rotational barriers, polarizability, first static hyper polarizability, potential energy scan, the electronic structure and HOMO-LUMO energies of above-mentioned molecule have been studied. ^{1}H NMR and ^{13}C NMR chemical shifts calculations have been performed. The molecular structure using numbering scheme of the picolinic acid hydrazide is given in Figure 1. The cis-conformer is the structure in which the nitrogen (N_1) of pyridine and the carbonyl group are not on the same sides. In case of trans-conformer, they are in the same sides.

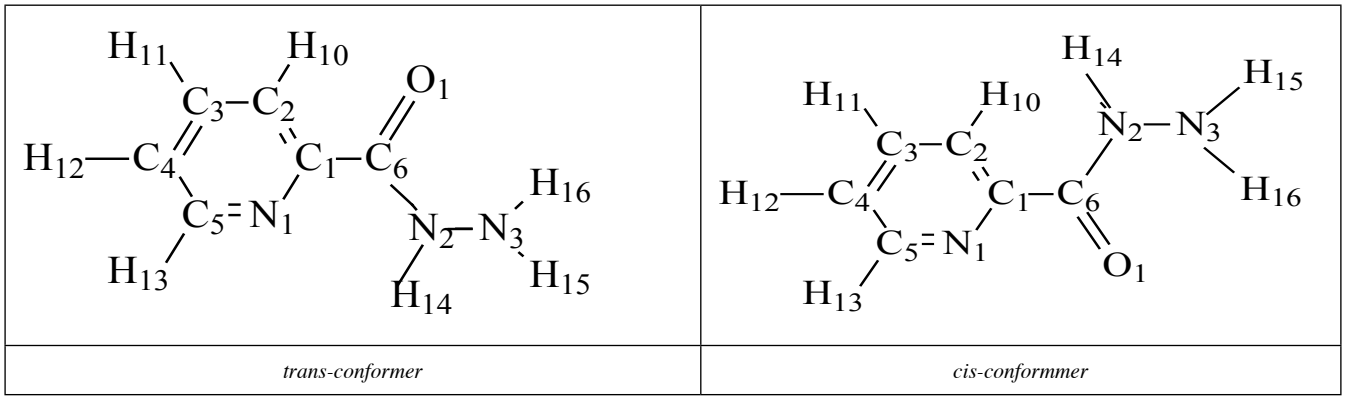


Figure 1. Molecular structure of picolinic acid hydrazide numbering scheme.

Computational Method

Computational calculations on the isolated molecules were performed by the aid of Gaussian 09W program package and Gauss view 5.0 molecular visualization programs (Frisch et al., 2010; Dennington et al., 2009) in the gas phase. The geometric parameters of picolinic acid (PA), picolinamide (PAA) and picolinic acid hydrazide (PAH) molecules in the equilibrium state were optimized at HF (Moller et al., 1934) and DFT with Becke's three parameter hybrid functional (B3) (Becke et al., 1988) and combined with gradient corrected correlation functional of Lee–Yang–Parr (LYP) (Lee et

al., 1988; Becke, 1993) and employing 6-311++G (d,p) basis set (Francl et al., 1982; Rassolov et al., 2001). In order to obtain the best stable structures, Conformational analysis of the optimized molecule was performed as a function of dihedral angle which was varied between 0 and 180° with increments of 10° both HF/6-31++G** and B3LYP/6-31++G** level of theory. The minimum of each PES was referred to as zero. Rotational barriers at 0° [ΔE_0 =E (ø=0°)-E (equilibrium)], at 90° [ΔE_{90} =E (ø=90°)-E (equilibrium)] and at 180° [ΔE_{180} =E (ø=180°)-E (equilibrium)] were calculated by using the energies of the respective optimized structures. After optimization, at all optimized structures of the title compounds obtained B3LYP/6-311++G (d,p) and HF/6-311++G (d,p) level of theory, the μ, α, β based on finite field approach and energy differences of E_{LUMO} - were calculated in the same as level of theory. The ^{1}H and ^{13}C NMR chemical shifts were calculated by GIAO approach by using B3LYP/6-311+G (2d, p) and HF/6-31G (d) level of theory (McLean et al., 1980; Krishnan .(et al., 1980

RESULTS AND DISCUSSION

Structural Results and Energies

The equilibrium state structures of picolinic acid, picolinamide and picolinic acid hydrazide molecules obtained by the HF/6-311++ G (d,p) and DFT/6-311++G (d,p) methods are compiled. It is found that, in three of the compounds, dihedral angle between the pyrimidine ring and carbonyl group is almost planar. The calculated values of the electronic, dipole moment, polarizability, hyperpolarizability, HOMO, LUMO energy and energy gap (ΔE_g) at the ground-state equilibrium geometry of studied molecules are listed in Table 1.

Table 1. The electronic, HOMO, LUMO energy, dipole moment, polarizability, hyperpolarizability, and energy gap (ΔE_g) of equilibrium conformers of title compounds

B3LYP/6-311++G (d. p)							
Electronic Energy (a.u)		μ (D)	α (a.u)	β (a.u)	E_{HOMO} (a.u)	E_{LUMO} (a.u)	*ΔEg (eV)*
PA	-436.9895188	5.96	80.09	40.85	-0.285578	-0.083905	5.4877
PAA	-417.1188787	3.42	85.57	41.95	-0.262983	-0.067039	5.3318
PAH	-472.4537888	3.12	95.67	86.03	-0.26462	-0.068704	5.3311
HH/6-311++G (d. p)							
PA	-434.4300319	6.03	73.07	67.73	-0.375896	0.027884	10.9873
PAA	-414.5965497	3.64	77.74	65.82	-0.361173	0.033023	10.7265
PAH	-469.6049508	3.36	86.23	84.74	-0.362946	0.0323	10.755

The X-ray crystal structures for these three molecules are available in the literature and the torsion angle obtained at X-Ray crystal structures is 4.8° (Takusagawa and Shimada, 1973) for PA and -18.1° (Gerzon et al., 2012) for PAA. In this analysis, calculations were done for PA, PAA and PAH of the studied molecule in the ground state and tabulated in the Table 2. At the B3LYP/6-311++G (d, p) and HF/6-311++G (d, p), the bond lengths C5-N1 of PA, PAA and PAH have been calculated as 1.334, 1.334, 1.334, 1.318, 1.318 and 1.317 *Å* whereas the corresponding reported value is 1.343 (Takusagawa and Shimada, 1973), 1.334 (Jose et al., 2006) (Gerzon et al., 2012). For C1-C6, as 1.511, 1.514, 1.511, 1.510, 1.512 and 1.511 *Å* whereas the corresponding reported value is 1.513 (Takusagawa and Shimada, 1973), 1.496 (Jose et al., 2006) (Gerzon et al., 2012) and for C6-O1 as 1.204, 1.222, 1.224, 1.180, 1.197 and 1.199*Å* whereas the corresponding reported value is 1.214 (Takusagawa and Shimada, 1973), 1.253 (Jose et al., 2006) (Gerzon et al., 2012) and 1.235 (Zareef et al., 2006), respectively. In both methods, the bond angles C2-C1-N1 of PA, PAA and PAH have been calculated as 123.5, 123.2, 123.3, 123.6, 123.3 and 123.4 Å whereas the corresponding reported value is 120.6 (Takusagawa and Shimada, 1973), 123.7 (Zareef et al., 2006).

Table 2. *S*elected structural parameters of picolinic acid and its derivatives.

Bond lengths (Å)									
		C1-C2	C2-C3	C3-C4	C4-C5	C5-N1	N1-C1	C1-C6	C6-O1
PA	DFT	1.393	1.391	1.393	1.394	1.334	1.339	1.511	1.204
	HF	1.382	1.384	1.383	1.385	1.318	1.320	1.510	1.180
	Exp[a].	1.382	1.391	1.366	1.386	1.343	1.344	1.513	1.214
PAA	DFT	1.394	1.391	1.393	1.394	1.334	1.340	1.514	1.222
	HF	1.384	1.383	1.383	1.385	1.318	1.321	1.512	1.197
	Exp[b].	1.386(2)				1.334(2)	1.370(2)	1.496(2)	1.253(2)
PAH	DFT	1.395	1.391	1.392	1.395	1.334	1.340	1.511	1.224
	HF	1.384	1.384	1.383	1.386	1.317	1.321	1.511	1.199
	Exp[c].								1.235

Bond angles (°)							
		C2-C1-C6	C2-C1-N1	C6-C1-N1	C1-C2-C3	C2-C3-C4	C3-C4-C5
PA	DFT	120.8	123.5	115.7	118.0	119.0	118.8
	HF	120.1	123.6	116.2	117.7	119.0	118.5
	Exp[a].	119.8	120.6	119.5	119.6	119.2	119.0
PAA	DFT	119.1	123.2	117.7	118.3	118.8	118.5
	HF	119.0	123.3	117.7	118.0	118.9	118.3
	Exp[b].			117.2(1)			
PAH	DFT	119.0	123.3	117.7	118.3	118.9	118.5
	HF	118.8	123.4	117.8	118.0	118.9	118.3
	Exp[c].		123.7		118.9	118.5	118.9

Torsion Angles (°)					
		C2-C1-C6-O1	N1-C1-C6-O1	C2-C3-C4-C5	C1-C2-C3-4
PA	DFT	0.0	180.0	0.0	0.0
	HF	0.0	-180.0	0.0	0.0
	Exp[a].	4.8			
PAA	DFT	0.0	-180.0	0.0	0.0
	HF	0.0	-180.0	0.0	0.0
	Exp[b].	-17.5	162.4(2)		
PAH	DFT	0.0	180.0	0.0	0.0
	HF	0.0	180.0	0.0	0.0
	Exp[c].				

[a]taken from Takusagawa and Shimada, 1973, [b]taken from Gerzon et al., 2012, [c]taken from Zareef et al., 2006.

For C6-C1-N1, as 115.7, 117.7, 117.7, 116.2, 117.7 and 117.8 Å whereas the corresponding reported value is 1.513 (Takusagawa and Shimada, 1973), 1.496 (Jose et al., 2006) (Gerzon et al., 2012) and for C6-O1 as 1.204, 1.222, 1.224, 1.180, 1.197 and 119.5 (Takusagawa and Shimada, 1973), 117.2 (Pierrat et al., 2005) Å (Gerzon et al., 2012), whereas the corresponding reported value is 1.214 (Takusagawa and Shimada, 1973), 1.253 (Jose

et al., 2006) (Gerzon et al., 2012) and 1.235 (Zareef et al., 2006), respectively. As the optimized structural parameters (bond length and bond angles) calculated by HF, DFT/B3LYP with 6-311++G (d,p) basis set are compared with the XRD experimental data (Takusagawa and Shimada, 1973; Zareef et al., 2006).

Conformational Analysis and Torsional Barriers

Conformational analysis of the optimized molecule was performed as a function of dihedral angle. The dihedral angle was defined as: ϕ= N1-C1-C6-O1. The dihedral angle ϕ is the C1-C6 single bond about which internal rotation forms clearly different conformations. This search focused on the alteration of ϕ torsional angle to determine the relative stabilities of the different conformers existing on PEY. To obtain potential energy surface of dihedral angles, ϕ= N1-C1-C6-O1 of the optimized molecular geometry (trans-conformer) was varied with increments of 10° starting from 0° throughout 36 steps while all other structural parameters were optimized and the result of potential energy surface is shown Figure 2 (a) and (b). Rotational barriers at 0° [ΔE_0 =E (ϕ=0°)-E (equilibrium)], at 90° [ΔE_{90} =E (ϕ=90°)-E (equilibrium)] and at 180° [ΔE_{180} =E (ϕ=180°)-E (equilibrium)] were computed by using the energies of the optimized structures. The results are shown in Figure 2 (a) and (b). As seen from Figure 2 (a) and (b), In both methods generated qualitatively parallel form of the torsion potential. The conformational analysis calculations at the HF/6-311++G (d,p) and B3LYP/6-311++G(d,p) showed that potential energy surface have two energy minima and a transition state structures.

The low-energy conformers were obtained at = 180 and -180°(trans-conformer). Maxima energy conformers were seen at 0° dihedral angle (cis conformer). The trans-conformers of the studied molecules were found to be most stable among their conformers. The potential barrier height of cis- conformers are at 13.24, 10.69, and 9.56 with DFT/B3LYP level of the theory 6-311++G (d, p) basis set and at the HF/6-311++ G (d, p) 13.53, 10.94, and 10.55 kcal/mol, respectively.

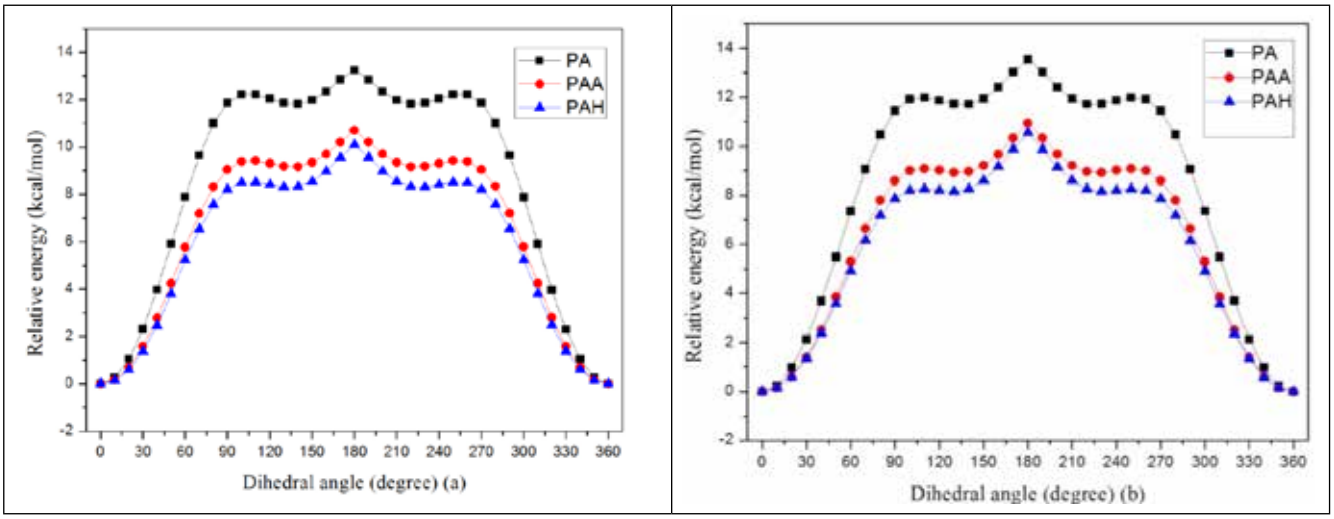


Figure 2. The potential energy surface (PES) (a) at the B3LYP/6-311++G (d,p), (b) HF/6-311++G (d,p).

Dipole Moment, Linear and Non-Linear Optical Effects (NLO)

Non-linear optics is the study of the interactions of light with matter under conditions in which the non-linear response of the atoms plays an important role. Some of the nitro substituted pyridine materials show efficient NLO properties that can be used in various non-linear optical devices. It is well known that the higher values of the μ, α and β are important for more active NLO properties. In this study dipole moment, polarizability and the second order polarizability or first hyperpolarizability of the titled molecule were investigated by using HF and B3LYP method at 6-311++G (d, p) basis set. The following equations (1, 2, 3) are used for calculating the magnitude of μ, α and β

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

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

$$\beta = \sqrt{\left(\beta_{xxx} + \beta_{yyy} + \beta_{zzz}\right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz}\right)^2 + \left(\beta_{zzz} + \beta_{xxz} + \beta_{yyz}\right)^2} \quad (3)$$

Where, the μ, α and β using the *x*, y, *z* components are defined as (Petek et al., 2006; Mol, 2010). The μ, ΔEg, α and β were calculated by using 6-311++G(d,p) basis set at the HF and DFT (B3LYP) of picolinic acid (PA), picolinamide (PAA) and picolinic acid hydrazide (PAH) molecules. The results are shown in Figure 3 (a), (b) and Figure 4 (a), (b), respectively. As results, the dipole moment in a molecule is very important electronic property and was used to study the intermolecular interactions involving the van der Waal type dipole-dipole forces.

HOMO-LUMO energy differences, dipole moment, linear polarizability and the first hyperpolarizability values of PA, PAA and PAH are investigated as a function of the torsional angle using B3LYP/6-311++G (d,p) level of theory.

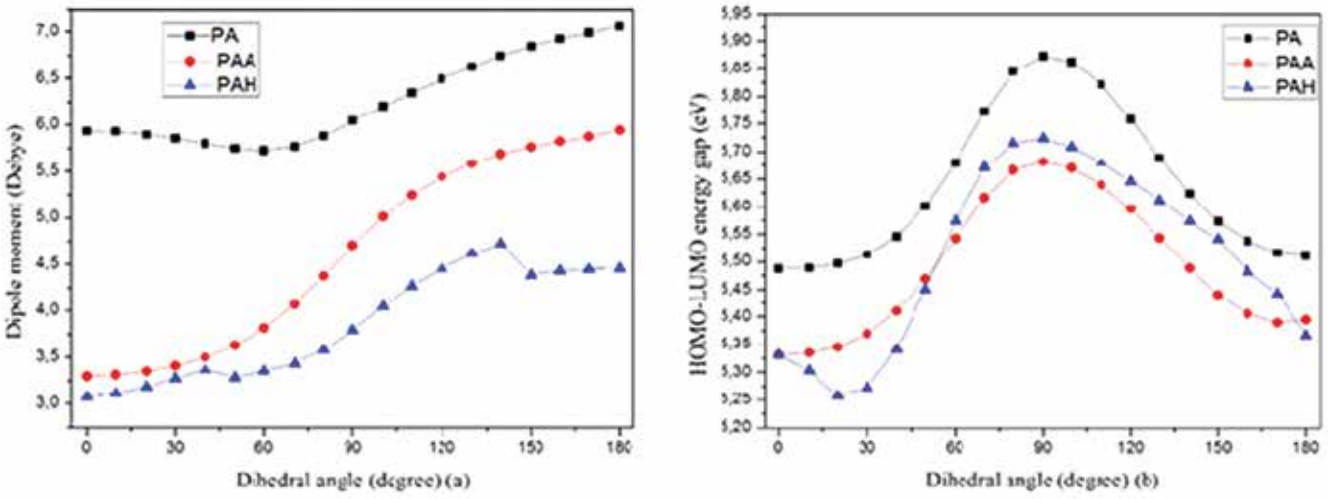


Figure 3. (a) The dipole moment (μ) and (b) the HOMO-LUMO energy gap at the B3LYP/6-311++G (d,p).

As seen from Figure 3 (a), dipole moment values of trans conformers of all the molecules are lower than that of cis-conformer. PA has the highest dipole moment value when comparing the other studied molecules. The calculation results showed that behavior of α of studied molecules as a function of torsion angle have the similar trend.

That is, according to the orthogonal conformation (90º) of the molecules, the polarizability curves are almost symmetric.

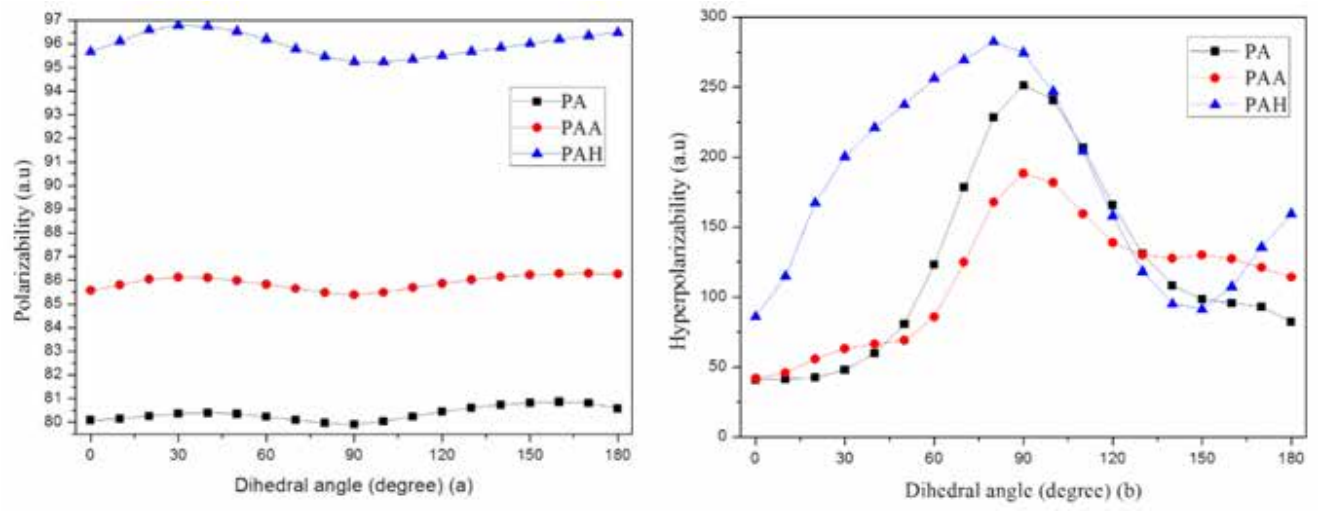


Figure 4. (a) Linear polarizability (α) and (b) first order hyperpolarizabilities (β) at the B3LYP/6-311++G (d,p).

The computed results demonstrate that the values of HOMO-LUMO energy differences and the first hyperpolarizability at the dihedral angle of 90° are maximum, whereas this condition does not obtain for the polarizability. As a result, behavior of MO energy gap of studied molecules as a function of torsion angle are of the similar trend.

NMR Spectral Investigations

^{1}H, ^{13}C NMR values of conformers picolinic acid, picolinamide and picolinic acid hydrazide molecules have been calculated and given in Tables 3. The atomic positions are numbered as given in Figure 1. Calculations performed with GIOA/DFT and GIOA/HF methods were used the B3LYP/6-311+G (2d, p) and HF/6-31G (d) level of theory. Comparison of the calculated and experimental ^{1}H, ^{13}C NMR values indicates that results of HF/ 6-31G (d) are in good agreement with experimental data (Gerzon et al., 2012).

Table 3 The theoretical ^{1}H, ^{13}C NMR chemical shifts values of PA, PAA and PAH molecules (Gerzon et al., 2012).

	B3LYP/6311+G (2d, p)			**HF/6-31G(d)**			
Atoms	C1	C2	Exp[b]	C3	C1	C2	C3
1-C	154.6	157.6	150	157	145.3	147.6	147
2-C	128.3	127.3	121.9	127	120.9	120	120
3-C	142.5	141.2	137.6	141.1	136.9	135.8	135.8
4-C	130.8	129.4	126.4	129.5	121.2	120.1	120.2
5-C	152.7	153	148.4	153.3	143.7	143.6	143.8
6-C	167.8	168.4	166	170	151	156.7	158.1
10-H	8.55	8.62	8.12	8.58	8.2	8.23	8.2
11-H	8.07	7.99	7.98	7.96	7.96	7.86	7.85
12-H	7.64	7.52		7.51	7.26	7.14	7.15
13-H	10.58	7.59	8.63	8.79	8.62	5.96	8.58
14-H	8.82	8.81	8.05	8.66	8.26	8.58	6.79
15-H		4.62		3.25		3.7	2.26
16-H				3.25			2.26

CONCLUSION

In this paper, the ground state geometrical energy, μ, α, β, E_{HOMO}, $E_{LUMO,}$ ΔEg and NMR and ^{13}C NMR chemical shifts of picolinic acid (PA), picolinamide (PAA) and picolinic acid hydrazide (PAH) molecules are examined as a function of the torsional angle both HF/6-311++G (d,p) and B3LYP/6-311++G(d,p) level of the theory, for each molecule.

The tendency in the calculated torsional potentials, barrier heights, and energy differences between conformers are discussed.

The trans-conformers of the studied molecules were found to be most stable among their conformers. The potential barrier height of cis- conformers are at 13.24, 10.69, and 9.56 with DFT/B3LYP level of the theory 6-311++G (d, p) basis set and at the HF/6-311++ G (d, p) 13.53, 10.94, and 10.55 kcal/mol, respectively. The computed results demonstrate that values of the ΔEg and the β at the dihedral angle of 90° are maximum, whereas this condition isn't obtained for the α. The calculation results showed that behavior of α of studied molecules as a function of torsion angle have the similar trend. That is, according to the orthogonal conformation (90º) of the molecules, the α curves are almost symmetric. The results show that the internal rotation behavior and ΔEg of all molecules is almost similar.

Comparison of the calculated and the experimental ^{1}H and ^{13}C NMR values indicates that results of HF/6-31G (d) and B3LYP/6-311++G (d,p) level of the theory are in a good agreement with experimental data for picolinamide.

REFERENCES

Ahren, B., 2001. Reducing plasma free fatty acids by acipimox improves glucose tolerance in high-fat fed mice. Acta Physiol. Scand. 171:161-167.

Andraud C., Brotin T., Garcia C., Pelle F., Goldner P., Bigot B., Collet A. 1994. Theoretical And Experimental Investigations Of The Nonlinear-Optical Properties Of Vanillin, Polyenovanillin, and Bisvanillin Derivatives. J. Am. Chem. Soc. 116, 2094-2102.

Becke A.D., 1988. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A, 38(6):3098–310.

Becke, A. D., 1993. Density-Functional Thermochemistry .3. The Role of Exact Exchange. J. Chem. Phys., 98 (7): 5648-5652.

Dazzi, C, Candiano G, Massazza S, Ponzetto A, Varesio L. 2001. New highperformance liquid chromatographic method for the detection of picolinic acid in biological fluids. J Chromatogr, 751:61–68.

Dennington R., Keith T., Millam J., 2009. Semichem Inc., GaussView, Version 5, Shawnee Mission KS.

Evans., G. W. 1989. The effect of chromium picolinate on insulin controlled parameters in humans. International Journal of Biosocial and Medical Research, 11: 163-180.

Francl M.M., Pietro W.J., Hehre W.J., Binkley J.S., Gordon, M.S., DeFrees D.J., Pople, J.A, 1982. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. Chem. Phys, 77 3654-3665

Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J A, Vreven TJ., Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin N, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli CJ, Ochterski W, Martin LR, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox D J, 2010. Gaussian Inc., (Wallingford, CT).

Gerzon E. D., Aisle J. M., Marilia G.-G., Jeans W. R., Jines E. 2012. Contreras Crystal Structure. Theory and Applications, 1, 30-34

Jose, S.P., Mohan, S, 2006. Vibrational spectra and normal coordinate analysis of 2-aminopyridine and 2-amino picoline. Spectrochim. Acta A, 64, 240

Kiec-Kononowicz, K. and Szymanska, E, 2002. Antimycobacterial activity of 5-arylidene derivatives of hydantoin. Farmaco, 57, 909–916.

Krishnan, R., Binkley, J. S., Seeger, R. and Pople, J. A, 1980. Self-consistent molecular-orbital methods. 20. basis set for correlated wave-functions. J. Chem.Phys, 72: 650–654.

Kukovec B. M., Popović Z., Pavlović G., Linarić M. R., 2008. Synthesis and Structure of Cobalt(II) Complexes with Hydroxyl Derivatives of Pyridinecarboxylic Acids Conformation Analysis of Ligands in the Solid State, J. Mol. Struct., 882(1-3): 47–55.

Lee, C.T., Yang, W.T. and Parr, R.G, 1988. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. Phys. Rev. B, 37, 785-789.

Lipscomb G. F., Garito A. F., Narang R. S, 1981. An exceptionally large electro-optic effect in the organic solid MNA. J. Chem. Phys, 75 1509–1516.

Liu L. C., Xing F., Bai Y., Shao M., Li M., Zhu S., 2014 Synthesis, Structure, Thermal Stability and Luminescence of Five 2D Coordination Polymers Based on 4-(4-Oxypyridinium-1-yl) Phthalic Acid and Transition Metal Ions. J. Mol. Struct., 1067: 74–82.

Matsuda R., Kitaura R., Kitagawa S., Kubota Y., Kobayashi T. C., Horike S., Takata M., 2004. Guest Shape-Responsive Fitting of Porous Coordination Polymer with Shrinkable Framework, J. Am. Chem. Soc., 126(43): 14063–14070.

McLean AD, Chandler GS, 1980. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z= 11–18. J Chem Phys, 72:5639–5648

Moller C., Plesset M. S., 1934. Note on an approximation treatment for many- electron systems. Phys. Rev., 46 618-622.

Pierrat P, Gros P.C, Fort Y, 2005. Solid phase synthesis of pyridine-based derivatives from a 2-chloro-5-bromopyridine scaffold. J. Comb. Chem., 7; 879 886.

Rebello T. Lonnerdal B. Hurley L.S, 1982. Picolinic acid in milk, pancreatic juice, and intestine: inadequate for role in zinc absorption. Am J Clin Nutr., 35(1):1-5.

Rassolov V-A, Ratner M-A, Pople J-A, Redfern P-C, Curtiss L-A., 2001. 6–31G* basis set for third-row atoms. J Comp Chem., 22:976–984.

Takusagawa F., shımada A., 1973. The crystal structure of picolinic acid. Chem. Lett., 1089-1090.

Uyeda H. T., Zhao Y. X., Wostyn K., Asselberghs I., Clays K., Persoons A., Therien M. J. 2002. Unusual frequency dispersion effects of the nonlinear optical response in highly conjugated (polypyridil) metal- (porphinato)zinc(II) chromopores. J. Am. Chem. Soc. 124 13806-13813.

Zareef, M., Iqbal, R., Zaidi, J. H., Qadeer, G., Wong, W.-Y.,Akhtar, H. 2006. Crystal Structure of 2-Picolinic Acid Hydrazide", Z. Kristallogr. NCS, 221, 307–308.