

Full Length Research Paper

Quantum chemical calculations on molecular structures and solvents effect on 4-nitropicolinic and 4-methoxypicolinic acid

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The density functional theory (DFT) (B3LYP) was used to study the solvents effect on electronic properties of 4-methoxypicolinic acid (4MOPIC) and 4-nitropicolinic acid (4NPIC). The calculated vibration frequencies at DFT/6-311++G** were compared to that of un-substituted picolinic acid to know the effect of donor/acceptor substituent on the molecules. Five solvents namely acetone, ethanol, diethyl ether, N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) were used to study solvents effect. The methoxyl (OCH₃) group in 4MPIC pushed electrons into the picolinic acid ring thereby resulted in upfield resonance as compared to 4NPIC in which nitro (NO₂) group brought about downfield in ¹HNMR. The solvents increased the minimum energy required to remove an electron for 4MOPIC whereas it was lower in 4NPIC. The HOMO and LUMO energies calculated in the solvents revealed that both HOMOs and LUMOs experienced stabilization in 4NPIC but LUMOs were destabilized in 4MOPIC as compared to gas phase.

Key words: 4-methoxypicolinic acid, 4-nitropicolinic acid, solvents effect, density functional theory (DFT).

INTRODUCTION

Picolinic acid and its substituents are of interest to many researchers mainly because of their usefulness as ligands; the availability of some donor atoms on the compounds which can serve as binding sites to various metals in forming various monomeric and polymeric complexes (Yurovskaya et al., 1998). Picolinic acid is the body's prime natural chelator of vital trace elements such as chromium, zinc, manganese, copper, iron and molybdenum (Evan and Johnson, 1980). Picolinic acid is biosynthesized in the liver and kidneys from the amino acid tryptophan, and stored in the pancreas during digestion, secreted into the intestine (Fernandez-Poi et al., 2001).

The vibrational frequencies, UV-Visible, ¹H and ¹³C NMR spectra of picolinic acid with its metal complexes of Fe(III), Ni(II), Cu(II), Zn(II) and Ag(I) were recently

reported (Kalinowska et al., 2007; Goher and Abu-Youssef, 1996). The 3-methylpicolinic acid and 6-methylpicolinic acid with their cobalt complexes were synthesized and characterized by spectroscopic techniques and thermal characterization in the solid state (Kukovec et al., 2009).

In the past the chemical behaviour of ambident ligands such as mercaptobenzothiazole and mercaptobenzimidazole ligands has been investigated using density functional theory (AlHokbany and AlJammaz, 2011). This is with a view of understanding the coordination chemistry of the metal complexes to be formed. Density functional theory has been employed over the years to obtain thermochemical data, molecular structure force fields frequencies assignment of nuclear magnetic resonance (NMR), photoelectron, erythrocyte

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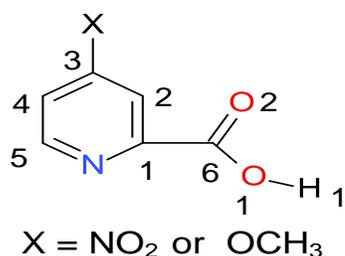


Figure 1. Schematic structures of the studied molecules: 4-nitropicolinic acid for X = NO₂ and 4-methoxypicolinic acid for X = OCH₃.

sedimentation rate (ESR) and ultra violet (UV) spectra, activation barriers, dipole moments and other one electron properties (Koczon et al., 2003; Parajón-Costal et al., 2004; Ziegler, 1991).

The effect of protic and aprotic solvents on the reactivity of picolinic, nicotinic and isonicotinic acid as well as of some substituted nicotinic acids with diazodiphenylmethane has been investigated (Dimitrijević et al., 1974; Drmanic et al., 2012; Marinkovi, 2005). In one of our recent work, DFT/B3LYP with various basis sets (6-31G*, 6-31G**, 6-311G**, 6-311+G**, 6-311++G**) was used to study solvents effect on geometry and electronic properties of picolinic acid. The results revealed that solvent-molecule interactions are more prominent around the heteroatoms in the case of the polar solvents. Therefore, this was a greater shielding/de-shielding on carbon nuclei around nitrogen and oxygen atoms of picolinic acid in the case of the polar solvents (Adeoye and Semire, 2013). The aim of this study is to employ density functional theory to study the effect of solvents on molecular structures and electronic properties of two 4-substituted picolinic acid namely 4-nitropicolinic acid and 4-methoxypicolinic acid as shown in Figure 1. The solvents employed are acetone, Ethanol, Diethyl ether, N,N-Dimethylformamide (DMF) and Tetrahydrofuran (THF) (Figure 1).

COMPUTATIONAL METHODS

The 4MOPIC and 4NPIC were optimized without symmetry constraint using density functional theory Beckes's three-parameter hybrid functional (Becke, 1988) employing the Lee, Yang and Parr correlation functional B3LYP (Lee et al., 1988) with 6-31G*, 6-31G** and 6-311G** basis sets. The vibration frequencies, electronic properties and NMR were calculated. In the calculation of vibration frequency, no imaginary frequency modes were obtained for the two molecules, therefore it was believed that true minimum on the potential energy surface were found for the molecules. The absorption transitions were calculated from the optimized geometry in the ground state S₀ using configuration interaction (CI) theory using density functional theory (DFT with 6-31G* in five different solvents namely acetone, ethanol, diethyl ether, N,N- Dimethylformamide (DMF) and tetrahydrofuran (THF). The convergence criteria for the energy calculations and geometry

optimizations used in the density functional methods were default parameters in the Spartan 06 program (Table 1).

RESULTS AND DISCUSSION

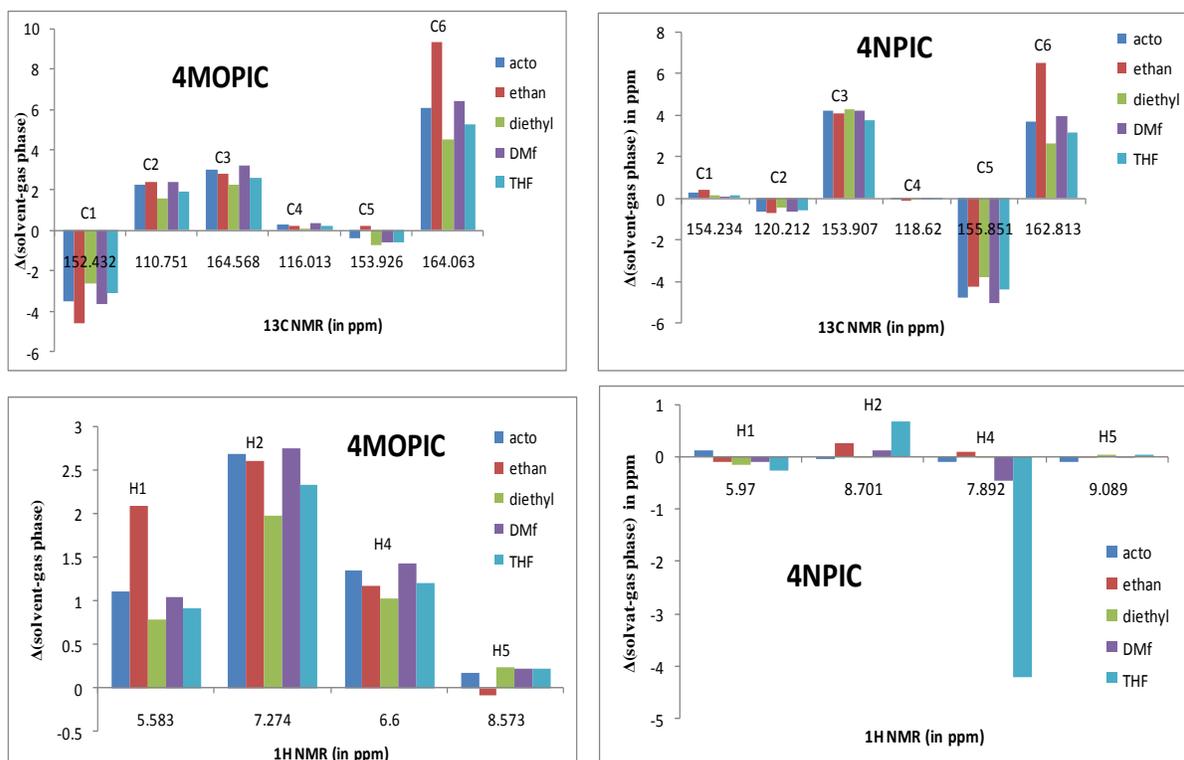
Chemical shifts and solvents effect

The molecular structure of the optimized 4MOPIC and 4NPIC using B3LYP method with 6-31G* basis set is used to calculate ¹³C and ¹H chemical shift calculations as shown in Table 1. It has been reported that ¹³C and ¹H NMR calculated using DFT are in good agreement with the experimental values (Teimouri et al., 2008; Karakurt et al., 2012; Cheeseman et al., 1996). Therefore, in the absence of experimental results the calculated ¹³C and ¹H NMR using DFT method can provide reasonable information that could assist in structural elucidation; thus the chemical shifts of the two isomers are compared. The results in Table 1 showed that ¹³C NMR chemical shifts for the two molecules are greater than 100 ppm which is the typical ¹³C NMR chemical shift for organic molecule (Kalinowski et al., 1988; Pihlaja and Kleinpeter, 1994). It has been reported that calculations based on the averaging of chemical shifts are in better agreement with the experimental values than plain calculations using optimized geometry (Stare et al., 2004). The chemical shifts of C2 and C4 are 109.373 and 115.541 ppm for 4MOPIC and 119.611 and 118.174 pmm for 4NPIC, therefore C2 and C4 experienced shielding effect because of its position in the molecules whereas other carbon atoms are de-shielded. C2 and C4 are more shielded in 4MOPIC because of higher electron density as a result of electron donating effect of CH₃ substituent. The chemical shifts of C3 are 165.388 and 155.204 ppm for 4MOPIC and 4NPIC respectively. The shielding/de-shielding of the substituent has no effect on C1, C5 and C6 of 4MOPIC as compared to un-substituted picolinic acid (Adeoye and Semire, 2013), although C1 and C5 in 4NPIC are slightly de-shielded. This is in agreement that the presence of electronegative atom attracts all electron clouds of carbon atoms towards itself, which in turn leads to de-shielding of carbon atoms and results in increase in chemical shift values (Varsanyi and Sohar, 1972). This de-shielding effect is noticed in 4NPIC molecule because of the attachment of NO₂ group.

The aromatic proton signals are observed at 5 to 7 ppm (Kalinowski et al., 1988; Pihlaja and Kleinpeter, 1994) and it has been found that presence of electrons on aromatic ring, double bonded atoms, and triple bonded atoms has been found to de-shield attached hydrogen (Varsanyi and Sohar, 1972). Its chemical shifts would be more susceptible to intermolecular interactions as compared to that for other heavier atoms. The methoxyl (OCH₃) group in 4MPIC pushed electrons into the picolinic acid ring thereby results in upfield resonance as compared to 4NPIC in which nitro (NO₂) group brought about downfield (Table 1). For instance, chemical shifts

Table 1. ^{13}C NMR and ^1H NMR (ppm) calculated at DFT/B3LYP level with various basis.

Atom	4-methoxypicolinic acid				4-nitropicolinic acid			
	6-31G*	6-31G**	6-311G**	Aveg.	6-31G*	6-31G**	6-311G**	Aveg.
C1	152.432	145.375	154.018	150.608	154.234	147.115	155.407	152.252
C2	110.751	105.608	111.760	109.373	120.212	115.441	123.179	119.611
C3	164.568	158.971	172.625	165.388	153.907	150.061	161.643	155.204
C4	116.013	110.919	119.691	115.541	118.620	114.036	121.866	118.174
C5	153.926	145.624	155.270	151.607	155.851	147.514	156.685	153.350
C6	164.063	154.569	165.406	161.346	162.813	153.348	164.105	160.089
H1	5.583	6.757	5.511	5.950	5.970	7.166	5.868	6.335
H2	7.274	8.616	7.404	7.765	8.701	10.015	8.826	9.181
H4	6.600	7.867	6.862	7.110	7.892	9.198	8.015	8.368
H5	8.573	9.733	8.747	9.018	9.089	10.261	9.247	9.532

**Figure 2.** Solvents effect on ^{13}C NMR and ^1H NMR in ppm calculated at DFT/6-31G* level.

for H2 and H4 are 7.765 and 9.018 ppm for 4MOPIC and 9.181 and 9.532 ppm for 4NPIC respectively. The hydroxyl oxygen atom shows electronegative property hereby contributed to hydroxyl hydrogen atom (H) downfield resonance as reflected in the two molecules. The calculated chemical shifts of hydroxyl hydrogen atom are 5.950 and 6.355 ppm for 4MOPIC and 4NPIC respectively which shows that NO_2 substituent increased downfield resonance experienced by hydroxyl hydrogen atom of 4NPIC (Table 1).

Theoretically, the solvent effect is estimated by comparing calculated chemical shifts for solution and gas phase at a particular level of calculation. In this work, the ^{13}C NMR and ^1H NMR calculated at DFT/6-31G* are used to estimate effect of solvents on chemical shifts as shown in Figure 2. The effects of solvents on ^{13}C NMR chemical shifts for 4MOPIC are pronounced on C1, C2, C3 and C6. For instance, the differences calculated on C6 for 4MOPIC as compared to gas phase are 6.086, 9.301, 4.503, 6.379 and 5.256 ppm for acetone, ethanol, diethyl

Table 2. Selected vibrational frequencies calculated at B3LYP/6-311++G**.

4-methoxypicolinic acid			4-nitropicolinic acid		
Cal.	Int.	Assign.	Cal.	Int.	Assign.
3773	96.50	vOH	3773	115.25	vOH
3242			3246		
3204		vCH	3229		vCH
3160			3171		
1821	353.81	vC=O	1828	346.81	vC=O
1623	244.52		1651	40.40	vC=C +vC=N
1606	21.09		1604	28.18	vC=C +vC=N
1516		vC=C +vC=N	1595	251.34	vC=C +vC=N
1427	5.27	C=C + π CH	1495		vC=N + π CH
1355	110.82	C-O + π OH	1415		vC=C + π CH
1334	96.35	vC=N +C-OCH ₃	1375	199.19	vNO ₂
1317	30.00	vC-C + C-N	1360	79.29	C-O + π OH
1285	71.94	vC-OCH ₃ + π OH	1311		C-N + π OH+ π CH
1177	182.74	π CH + π OH	1301	30.91	vC=C-C=N+ π OH
1134	138.25	π CH + C-O	1206	87.52	vC-O + π OH +vC-NO ₂
1083	99.00	π CH + C-O	1139	203.08	vC-O+ π CH
1058	7.26	vC-OCH ₃	1087	71.93	vC-O+ π CH
1008	58.98	δ Ring	1012		ω Ring
998, 890, 860		σ CH	1001, 948, 880		σ CH
805		π (C=C-C)	734		π (C=C-C)
613		σ OH	660		ϕ (COOH)
572		ω Ring	608		σ OH
262		γ CH ₃	276		ω Ring
207		γ CH ₃	345		δ Ring
186		ω Ring	146		γ Ring
102		γ O-CH ₃	37		γ (NO ₂ + COOH)
36		γ COOH			

v, stretching; π , in-plane bending; σ , out-of-plane bending; τ , torsion, δ , breathing; ω , wagging; γ , rocking; ϕ , scissor.

ether, DMF and THF respectively. The effect of ethanol is felt more on C6 and C1 for 4MOPIC molecule (Figure 2). In case of 4NPIC, the solvent effects are pronounced on C3, C5 and C6. For C6, the differences calculated are 3.713, 6.562, 2.681, 3.961 and 3.169 ppm for acetone, ethanol, diethyl ether, DMF and THF respectively as compared to results from gas phase calculations.

The effects of solvents on ¹HNMR chemical shifts for 4MOPIC are felt by all hydrogen atoms although more on H1, H2 and H4. For 4NPIC, the only solvent that has much effect on the molecule is THF as it is reflected in ¹HNMR on H2 and H4. The differences in chemical as compared to gas phase calculation could be explained in terms of changes in free energy hypersurface of the nuclei (Jernej et al., 2004).

Vibration frequencies

The vibration frequencies calculated at B3LYP/6-

311++G** are shown in Table 2. The ring carbon hydrogen stretching vibrations calculated at B3LYP/6-311++G** are in the region 3242-3160 cm⁻¹ for 4MOPIC and 3246-3171 cm⁻¹ for 4NPIC. The C=O stretching vibration for 4MOPIC and 4NPIC are calculated to be 1821 and 1826 cm⁻¹ with 353.81 and 346.81 intensities respectively. However, C=O stretching vibration for un-substituted picolinic acid was calculated to be 1820 cm⁻¹ (Adeoye and Semire, 2013) and experimentally observed at 1717 cm⁻¹ (Varsanyi and Sohar, 1972) and 1719 cm⁻¹ (Gfeller et al., 1976). The OH stretching vibration is calculated for both molecules at 3773 cm⁻¹ with \approx 20% higher intensity in 4NPIC. This has been calculated at 3770 cm⁻¹ and experimentally observed at 3437 and 3464 cm⁻¹ for un-substituted picolinic acid (Varsanyi and Sohar, 1972; Gfeller et al., 1976). The C=C stretching coupled with C=N are calculated at 1623, 1606 and 1516 cm⁻¹ for 4MOPIC and 1651, 1604 and 1595 cm⁻¹ for 4NPIC. The C=C stretching coupled with C-H in plane deformation (π CH) are calculated to be 1427 and 1415 cm⁻¹ for

4MOPIC and 4NPIC respectively, this has been calculated at 1462 cm^{-1} and observed at 1439 cm^{-1} (Varsanyi and Sohar, 1972) and 1443 and 1719 cm^{-1} (Gfeller et al., 1976) for the un-substituted picolinic acid. The C-O stretching coupled with OH in plane deformation (πOH) is calculated at 1355 and 1360 cm^{-1} for 4MOPIC and 4NPIC respectively. Also, this has been calculated at 1358 cm^{-1} and observed experimentally at 1370 and 1347 cm^{-1} (Adeoye and Semire, 2013; Varsanyi and Sohar, 1972; Gfeller et al., 1976) un-substituted picolinic acid. The in-plane bending of C=C-C is calculated at 805 cm^{-1} for 4MOPIC and 734 cm^{-1} for 4NPIC.

The C-H out-of-plane deformation (σCH) for 4MOPIC is calculated at 998 , 890 and 860 cm^{-1} whereas this is calculated at 1001 , 948 and 880 cm^{-1} for 4NPIC. The OH out-of-plane deformation (σOH) is calculated to be 613 and 608 cm^{-1} for 4MOPIC and 4NPIC respectively. The COOH rocking vibration was at 36 cm^{-1} for 4MOPIC and 37 cm^{-1} for 4NPIC which is coupled with γNO_2 .

Global electrophilicity and Electronic properties

The electronic properties of the 4MOPIC and 4NPIC are calculated from the total energies and the Koopmans' theorem. The ionization potential (IP) is determined from the energy difference between the energy of the compound derived from electron transfer which is approximated; $\text{IP} \approx -E_{\text{HOMO}}$ while the electron affinity (EA) is given as; $\text{EA} \approx -E_{\text{LUMO}}$, respectively. The chemical potential (μ), chemical hardness (η), electrophilicity index (ω) and softness ($1/\eta$) of a molecule are deduced from IP and EA values (Takusagawwa and Shimada, 1976; Zhou and Navangul, 1990; Chamizo et al., 1993; Koopmans, 1734; Parr et al., 1999) as shown in the following Equations 1, 2 and 3.

$$\mu = \left(\frac{\partial E}{\partial N}\right) v(r) \approx -\left[\frac{\text{IP}+\text{EA}}{2}\right] \approx -\left[\frac{E_{\text{HOMO}}+E_{\text{LUMO}}}{2}\right] \quad (1)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right) v(r) \approx \left[\frac{\text{IP}-\text{EA}}{2}\right] \approx [E_{\text{HOMO}} - E_{\text{LUMO}}] \quad (2)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (3)$$

It is well known that when IP is small and EA is large and positive the molecule should be soft, therefore soft molecules are often more chemically reactive than hard molecules. Also, the electrophilicity index has being a useful structural depictor of the analysis of the chemical reactivity of molecules (Pearson, 1993; Bird, 1997; Chattaraj et al., 2003; Semire and Odunola, 2013; Semire, 2013). According to the definition, electrophilicity index measures the propensity of a species to accept electrons. As Domingo et al (Domingo et al., 2002) proposed the high nucleophilicity and electrophility of

heterocycles corresponds to opposite extremes of the scale of global reactivity indexes. A good, more reactive, nucleophile is characterized by a lower value of μ , ω and in opposite a good electrophile is characterized by a high value of μ , ω . The electronegativity and hardness are of course used extensively to make predictions about chemical behavior and these are used to explain aromaticity in organic compounds (De Proft and Geerlings, 2001). A hard molecule has a large HOMO–LUMO gap and a soft molecule has a small HOMO–LUMO. The LUMO represents electron(s) accepting ability and HOMO as electron donating ability of a molecule.

The HOMO, LUMO, energy band gap, dipole moment, energy of solvation, chemical potential, softness, electrophilicity/nucleophilicity index and UV-Vis adsorption maximum calculated are displaced in Table 3. The values of chemical hardness, chemical potential, softness, and electrophilicity index in gas phase for 4MOPIC are 5.46, -2.73, 0.183 and 0.6825 eV respectively and that of 4NPIC are 4.79, -2.40, 0.209 and 0.6013 eV respectively. Therefore, 4NPIC should be a better molecule to be involved in the interactions with electrophiles than for 4MOPIC. The dipole moment in a molecule is one of the important electronic properties when considering the interactions of molecules in solvents. The higher the value of dipole moment the stronger the intermolecular interactions would be expected, however the orientation of the dipole moment vector is also an important parameter. The calculated dipole moment values for 4MOPIC and 4NPIC in gas phase are 4.75 and 0.41 Debye respectively.

The HOMO and LUMO energies calculated in solvents revealed that both HOMOs and LUMOs experienced stabilization in 4NPIC but LUMOs are destabilized in 4MOPIC as compared to gas phase. In line with our recent report (Adeoye and Semire, 2013), the magnitude of solvation energies reflect the degree of polarity of the solvents used in these calculations (that is, Ethanol > acetone \approx DMF > THF \approx Diethyl ether). The absorption maxima calculated in solvents are shifted to longer wavelengths as compared to gas phase (Table 3). The absorption maxima calculated at DFT (B3LYP) level with 6-31G*, 6-31G**, 6-311G**, 6-311+G** and 6-311++G** basis sets are shown in Table 4. The absorption maxima are 218.79, 218.82, 219.81, 225.53 and 225.57 nm for 4MOPIC and 276.06, 276.01, 274.52, 281.45 and 281.47 nm for 4NPIC at 6-31G*, 6-31G**, 6-311G** and 6-311+G** basis sets respectively. Another indicator of electrophilic attraction apart of the electrostatic potential is provided by the local ionization potential energy surface which is an overlaying of the energy of electron removal (ionization) onto the electron density. The regions with red color represent regions in the molecular surface where electron removal goes (with minimal energy) most easily, therefore easy of electron removal. The local ionization potential energy for 4MOPIC and

Table 3. HOMO, LUMO, energy band gap, dipole moment, solvation energy, global electrophilicity index and UV-Vis adsorption maximum calculated in gas phase and in solvents at DFT/6-31G* level.

4MOPIC						
	G. phase	Acetone	Ethanol	Diethyl ether	DMF	THF
HOMO (eV)	-6.96	-6.79	-6.88	-6.83	-6.78	-6.81
LUMO (eV)	-1.50	-1.52	-1.61	-1.51	-1.53	-1.51
$\Delta(H-L)$	5.46	5.27	5.27	5.32	5.25	5.30
Sol. E (kJ/mol)	-43.47	-51.68	-55.54	-43.32	-51.69	-46.18
D.M	4.73	6.18	6.47	5.78	6.16	5.97
UV	218.79	219.43	219.50	219.34	219.70	217.98
H	5.46	5.27	5.27	5.32	5.25	5.30
M	-2.73	-2.69	-2.64	-2.66	-2.63	-2.65
(1/2 η)	0.183	0.190	0.190	0.188	0.190	0.189
Ω	0.6825	0.6865	0.6613	0.6650	0.6588	0.6625
4NPIC						
HOMO (eV)	-7.96	-7.70	-7.75	-7.76	-7.69	-7.73
LUMO (eV)	-3.17	-2.99	-3.11	-3.03	-2.98	-3.00
$\Delta(H-L)$	4.79	4.71	4.64	4.73	4.71	4.73
Sol. E (kJ/mol)	-32.36	-50.38	-53.94	-43.41	-50.53	-45.93
D.M	0.41	0.55	0.39	0.49	0.64	0.55
UV	276.06	288.72	295.19	285.31	288.65	286.82
H	4.79	4.71	4.64	4.73	4.71	4.73
M	-2.40	-2.36	-2.32	-2.37	-2.36	-2.37
(1/ η)	0.209	0.212	0.216	0.211	0.212	0.212
Ω	0.6013	0.5913	0.5800	0.5938	0.5913	0.5938

Table 4. λ_{max} (in nm) calculated for 4-methoxyl and 4-nitropicolinic acid at DFT with various basis sets.

DFT/	4-methoxypicolinic acid		4-nitropicolinic acid	
	UV	Intensity	UV	Intensity
6-31G*	218.79	0.16	276.06	0.035
6-31G**	218.82	0.16	276.01	0.035
6-311G**	219.81	0.16	274.52	0.038
6-311+G**	225.53	0.17	281.45	0.039
6-311++G**	225.57	0.17	281.47	0.039

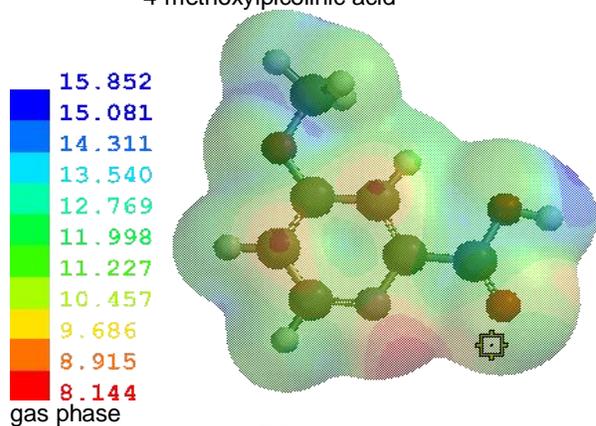
4NPIC are calculated in different solvents as displayed in Figure 3. The local ionization potential energy shows that solvents affect ionization potential of the molecules. The solvents increased the minimum energy required to remove an electron for 4MOPIC whereas the minimum energy required was lower in 4NPIC as compared to gas phase. Therefore, the minimum energy required to remove an electron in different solvents could be arranged as ethanol > acetone \approx DMF > THF > Diethyl ether > gas phase for 4MOPIC and gas phase > ethanol > diethyl ether > THF > acetone > DMF for 4NPIC. It could be suggested that increasing in electron density by electron donor substituent lowers the minimum energy required to remove an electron while decreasing in

electron density as a result of electron abstractor substituent raises the minimum energy required to remove an electron (Figure 3 and Table 5).

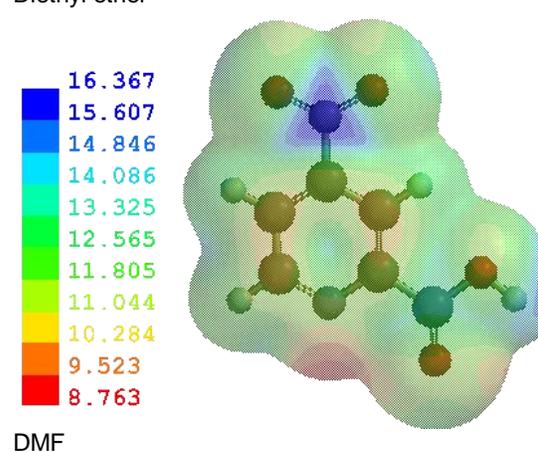
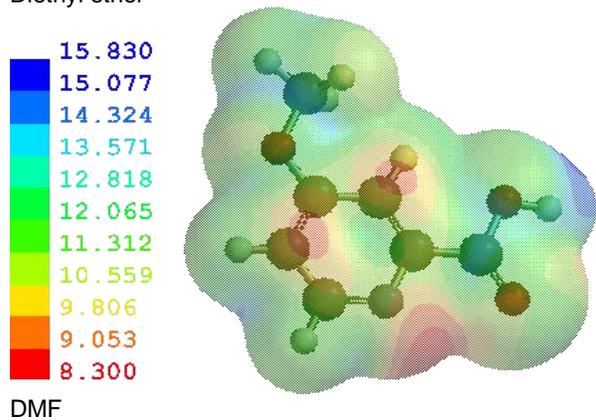
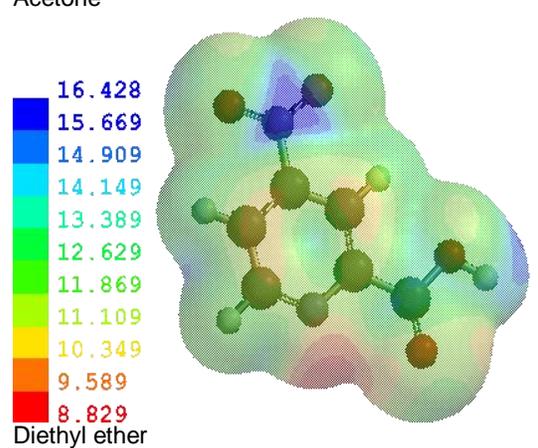
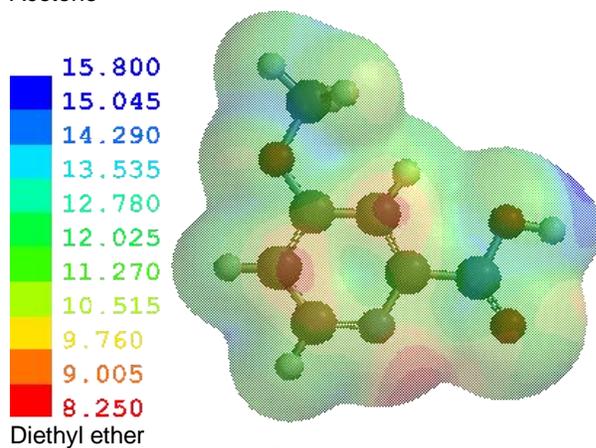
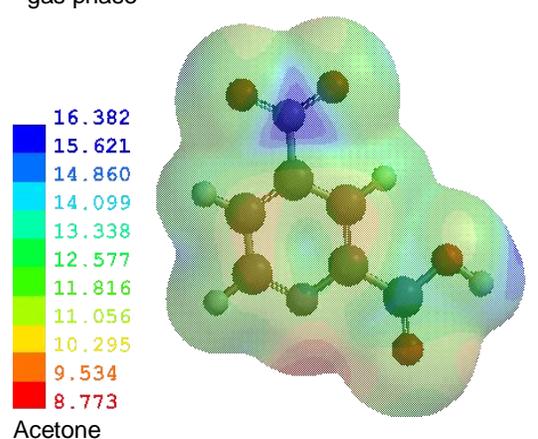
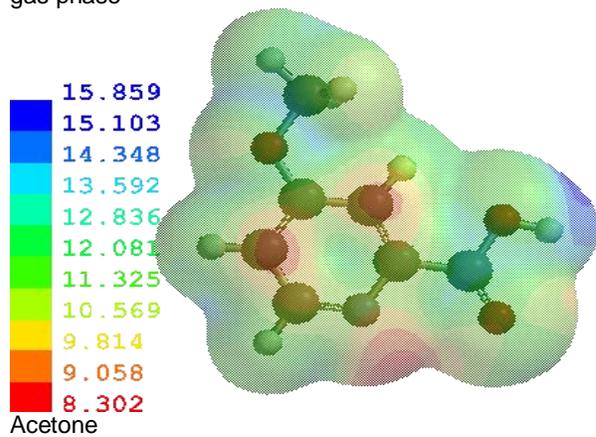
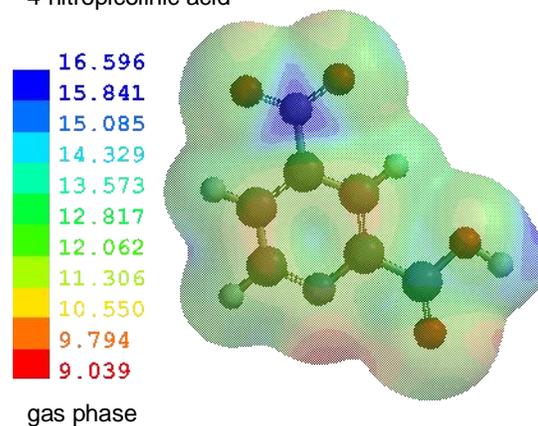
Thermodynamic properties

The standard enthalpy (H^0), standard entropy (S^0) and standard heat capacity at constant pressure (C_p^0) are 378.00, 372.77 and 138.63.94 J/mol for 4MOPIC; and 299.25, 373.34 and 136.75 J/mol for 4NPIC respectively. The thermodynamic functions such as heat capacity ($C_{p,m}^0$), entropy (S_m^0) and enthalpy (H_m^0) for 4MOPIC and 4NPIC are obtained from the theoretical harmonic frequencies as listed in Table 5. All the $C_{p,m}^0$, S_m^0 and H_m^0

4-methoxypicolinic acid



4-nitropicolinic acid



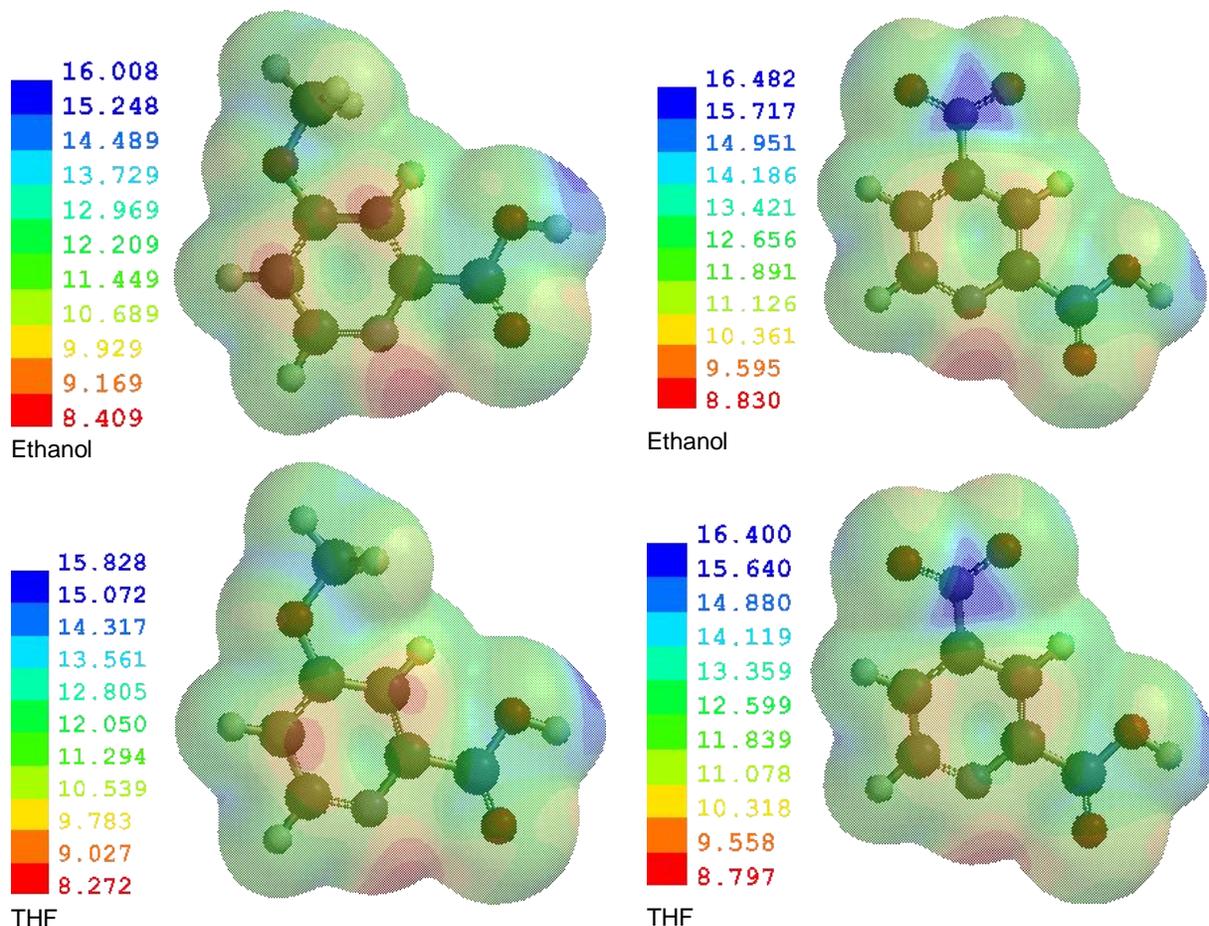


Figure 3. Local ionization energy surfaces on the molecular surfaces of 4MOPIC and 4NPIC with B3LYP/6-31G*. Color ranges, in kJ/mol.

Table 5. The thermodynamic properties obtained at different temperature for the 4-methoxyl- and 4-nitrocolinic acid at B3LYP/6-31++G** level.

Temp (K)	4MPIC			4NPIC		
	H ^o m (kcal/mol)	S ^o m (cal/mol)	Cp (cal/mol)	H ^o m (kcal/mol)	S ^o m (cal/mol)	Cp (cal/mol)
100	85.95	68.61	15.39	67.13	70.02	15.46
273	90.34	89.09	33.13	71.52	89.23	32.68
373	93.48	98.59	43.28	74.66	98.49	42.32
473	97.87	107.19	52.13	79.05	107.23	50.38
573	102.89	115.50	59.38	83.44	115.22	56.78
673	107.91	122.95	65.24	88.46	122.23	61.81
773	113.56	129.61	70.01	94.11	128.40	65.79
873	119.83	135.53	73.95	99.76	133.95	68.99
973	126.11	140.89	77.24	105.40	138.92	71.60

increases with the increase in temperature from 100 to 973K; this is due to the enhancement of molecular vibrations while temperature increases at constant pressure (1 atm). The correlations between these

thermodynamic parameters and temperature (T) are plotted and fitted by quadratic equations as shown in Figures 4, 5 and 6. The fitting factor (R^2) for these parameters for 4MOPIC and 4NPIC is found to be 0.999

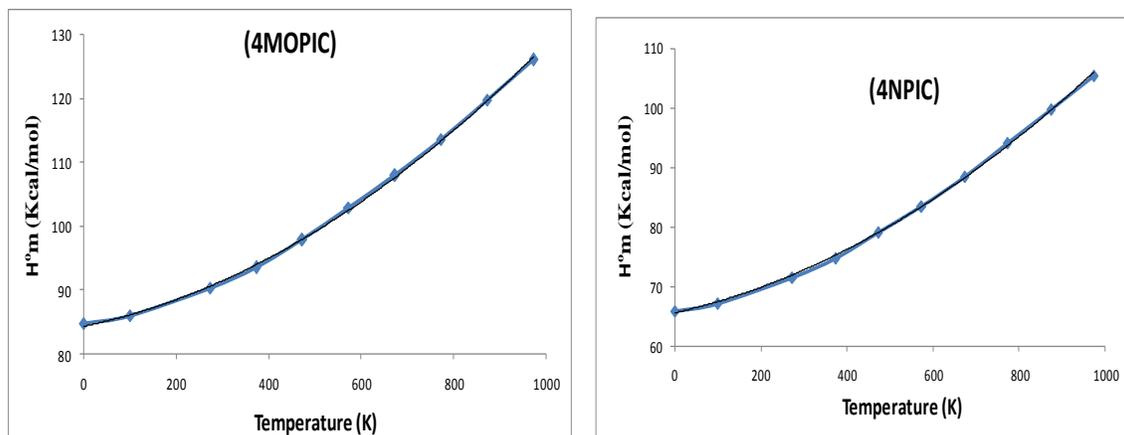


Figure 4. Correlation graph of enthalpy and temperature for 4-methoxypicolinic and 4-nitropicolinic.

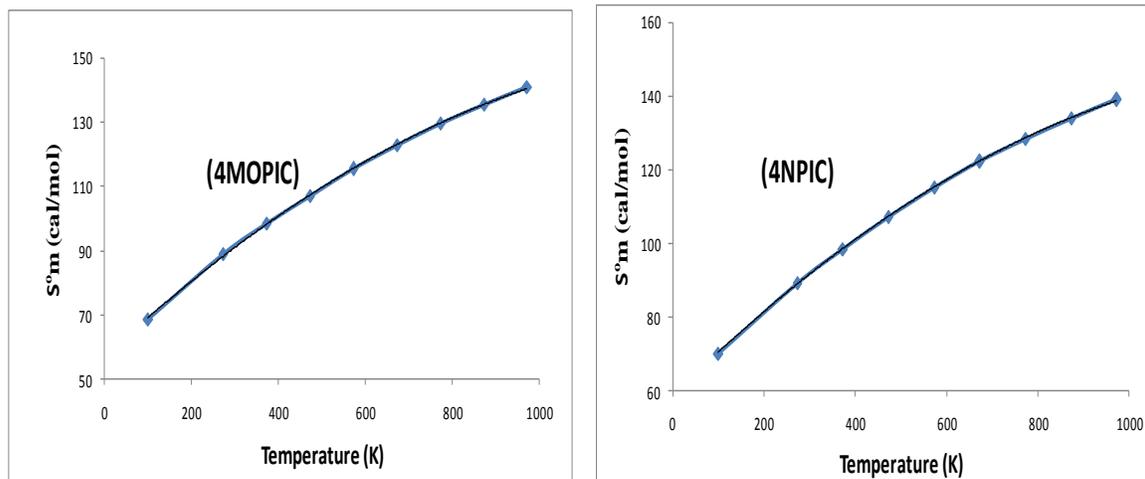


Figure 5. Correlation graph of entropy and temperature for 4-methoxypicolinic and 4-nitropicolinic.

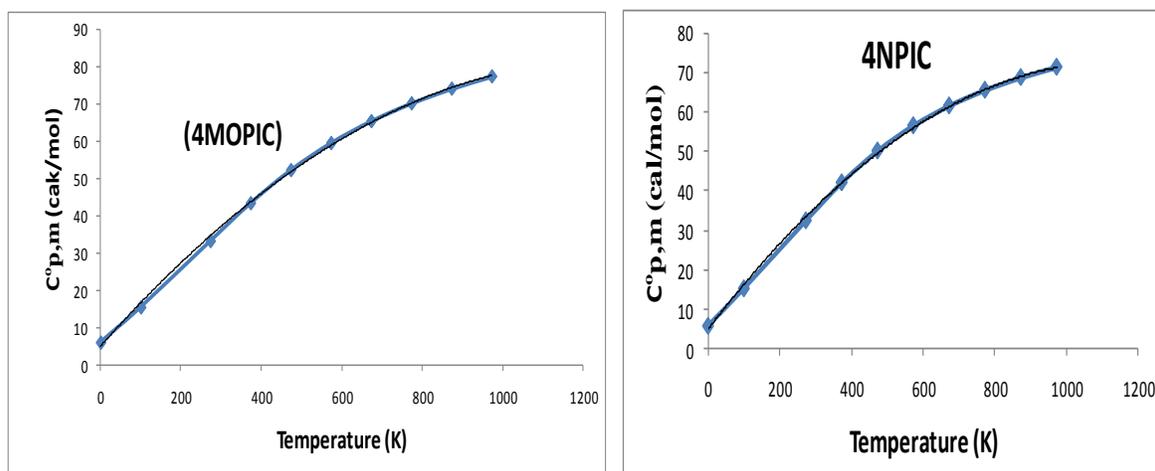


Figure 6. Correlation graph of heat capacity and temperature for 4-methoxypicolinic and 4-nitropicolinic.

Table 6. The fitting factor (R^2) for parameters for 4MOPIC and 4NPIC.

4MOPIC	4NPIC
$C_{p,m}^0 = 4.729 + 0.121T - 5.00T^2 \times 10^{-5}$; ($R^2 = 0.999$)	$C_{p,m}^0 = 4.98 + 0.119T - 5.00T^2 \times 10^{-5}$; ($R^2 = 0.999$)
$H_m^0 = 84.32 + 0.015T + 3.00T^2 \times 10^{-5}$ ($R^2 = 0.999$)	$H_m^0 = 65.44 + 0.016T + 3.00T^2 \times 10^{-5}$ ($R^2 = 0.999$)
$S_m^0 = 56.88 + 0.126T - 4.00 \times 10^{-5}T^2$ ($R^2 = 0.999$)	$S_m^0 = 58.37 + 0.123T - 4.00 \times 10^{-5}T^2$ ($R^2 = 0.999$)

for heat capacity, enthalpy and entropy as shown in Table 6.

All the thermodynamic calculations are performed in the gas phase; therefore scale factors have been recommended for better accurate prediction (Zhang et al., 2010). All these thermodynamic data would be helpful in providing information for further study of the two isomers which can be useful to determine the directions of chemical reactions according to the second law of thermodynamics (Yazıcı et al., 2011; Nataraj et al., 2013; Govindarajanaet al., 2012).

Conclusion

In this work, we have performed the quantum chemical calculations on geometry, vibrational frequency and electronic properties of 4MOPIC and 4NPIC using B3LYP with various basis sets. Solvents effect on the molecules are studied by using five solvents namely ethanol, acetone, diethyl ether, DMF and THF. The results show that the HOMO and LUMO energies experienced stabilization in the solvents for 4NPIC but LUMO is destabilized in 4MOPIC as compared to gas phase. The HOMO, LUMO, electrophilicity index and softness revealed that 4NPIC would be a better molecule to be involved in the interactions with electrophiles than for 4MOPIC. The absorption maxima calculated using B3LYP/6-31G*/CIS are shifted to longer wavelengths in solvents as compared to gas phase. The minimum energy required to remove an electron in different solvents could be arranged as ethanol > acetone \approx DMF > THF > Diethyl ether > gas phase for 4MOPIC and gas phase > ethanol > diethyl ether > THF > acetone > DMF for 4NPIC.

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