

***Ab initio* and DFT study on molecular structure, reactivity indices and nonlinear properties of 4-(4-aminophenylethynyl)picolinic acid and 4-(3-aminophenylethynyl)picolinic acid.**

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Abstract

Ab initio and density functional theory methods were used to study chemical shifts and global reactivity index of 4-(4-aminophenylethynyl)picolinic acid and 4-(3-aminophenylethynyl)picolinic acid. The calculated chemical shifts for the two molecules correlated to the experimental data. The regression factor (R^2) for chemical shifts calculated at HF/6-31G* and B3LYP/6-31G* were 0.940 and 0.964 for 4APPA and 0.929 and 0.953 for 3APPA respectively. The absorption maxima for 4APPA were 302.81 and 341.52 nm and 292.12 and 346.95 nm for 3APPA. Global reactivity indexes (hardness, chemical potential and nucleophilicity) revealed that 4APPA should be a better nucleophile than 3AAPA. The first hyperpolarizability calculated for 4APPA and 3APPA were 8.84×10^{-30} and 3.41×10^{-30} esu respectively.

Keywords: 4-(4-aminophenylethynyl)picolinic acid, 4-(3-aminophenylethynyl)picolinic acid molecular properties, nonlinear properties, DFT

1.0 Introduction

Picolinic acid is the body's prime natural chelator of vital trace elements such as chromium, zinc, manganese, copper, iron and molybdenum [1]. It is biosynthesized in the liver and kidneys from the amino acid tryptophan, and stored in the pancreas during digestion, secreted into the intestine [2]. 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 [3]. A number of substituted picolinic acid have been synthesized as ligands for transition metal complexation such as aminopicolinic acid [4], 3-methyl and 4-methylpicolinic acid [5] and other derivatives [6-9]. Some derivatives of picolinic acid have been identified to play roles as diverse as reaction partners in industrial processes [10] and as building blocks in photovoltaic devices [11,12].

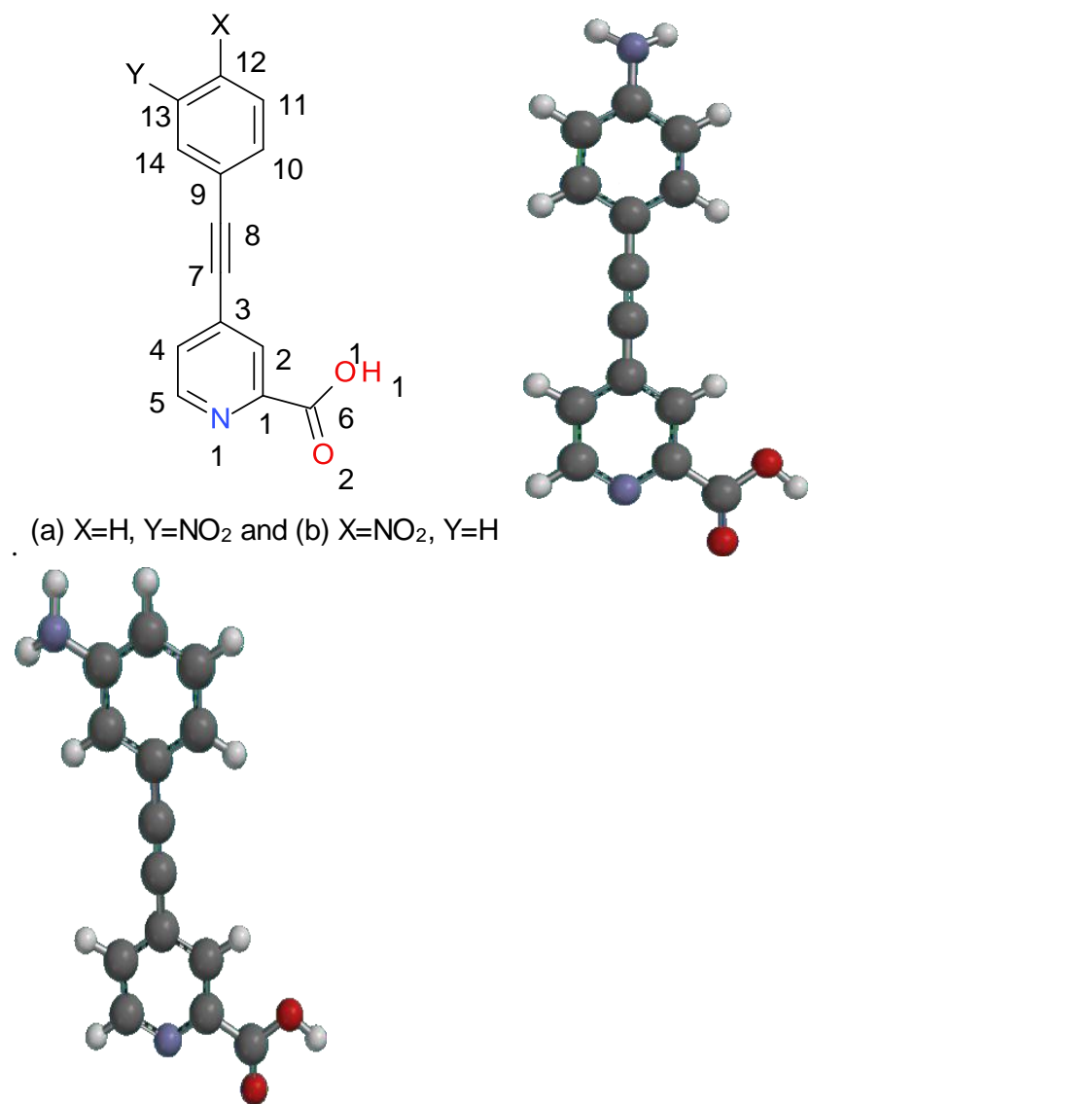


Figure 1: The structure of studied 4-aminophenylethynylpicolinic acid: (a) optimized structure of 4-(4-aminophenylethynyl)picolinic acid and (b) optimized structure of 4-(3-aminophenylethynyl)picolinic acid

In our recent work, DFT/B3LYP was used to study solvents effect on geometry and electronic properties of picolinic acid [13], 4-nitropicolinic acid, 4-

methoxypicolinic acid [14], 3-methylpicolinic acid, 4-methylpicolinic acid and 4-phenylpicolinic acid [15]. The purpose of the present paper is to evaluate the performance of *ab initio* (HF/6-31G*) and density functional theory (B3LYP) in calculating chemical shifts and vibrational frequencies of 4-(4-aminophenylethynyl)picolinic acid (4APPA) and 4-(3-aminophenylethynyl)picolinic acid (3APPA) which were recently synthesized [16]. The predicted structures for 4APPA and 3APPA are shown in Figure 1. The theoretical results are compared the experimental values, also chemical reactivity descriptors of these molecules are compared to each other.

2.0 Computational details

The 4-(4-aminophenylethynyl)picolinic acid and 4-(3-aminophenylethynyl)picolinic acid were modeled and equilibrium geometry calculations were performed at density functional theory (Becke's three-parameter hybrid functional [17] employing the Lee, Yang and Parr correlation functional B3LYP [18]). Single point energy, vibration frequencies and chemical shifts calculations were performed on the optimized geometries of these molecules both at *Ab initio* and DFT level of theories. The vibrational frequencies calculated were scaled by 0.962 and 0.896 for B3LYP/6-31G* and HF/6-31G* respectively. These scaling factors were recommended by Merrick et al., [19] and they have been used by several researchers [20-23]. The absorption transitions were calculated from the optimized geometry in the ground state S_0 using TD-B3LYP/6-31G* in the gas phase. The convergence criteria for the energy calculations and geometry optimizations used in the density functional methods were default parameters in the Spartan 06 program.

The electronic properties of the molecules are calculated from the total energies and the Koopmans' theorem. The ionization potential (IP) is approximated to $-E_{HOMO}$ while the electron affinity (EA) is given as $-E_{LUMO}$, 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 [24-29] as shown in the following equations 1, 2 and 3.

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

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

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

3.0 Results and discussion

3.1 Molecular geometries

The schematic structure showing numbering system and optimized structures of the studied substituted picolinic acid were shown in Figures 1. The selected geometries from the optimized structures calculated at B3LYP/6-31G* were listed in Table 1. There were no significant differences in the bond distance calculated for 4PPA and 3APPA at each level of theoretical method used. The only major differences observed are around the position of attachment of amino group on aminophenyl subunit. For instance, C9-C14, C10-C11 and C11-C12 bond distances are 1.393Å, 1.379Å and 1.395Å for 4APPA and 1.391Å, 1.390Å and 1.383Å for 3APA respectively calculated at HF/6-31G* level. However, these bond distances are calculated to be 1.411Å, 1.386Å and 1.408Å for 4APPA and 1.408Å, 1.402Å and 1.393Å for 3APPA respectively calculated at DFT/6-31G* level. The effect of changing amino group from *para* to *meta* position on phenylethynyl subunit brought about lengthening of C3-C7 (C8-C9) and shortening of C7-C8 respectively in 4APPA as compared to 3APPA (Table 1).

The dihedral angles calculated at HF/6-31G*(DFT/6-31G*) for 4APPA are -63.58° (26.86°), 116.41° (-153.01°), 110.37° (83.31°), -69.61° (-96.57°) and 47.73° (70.53°) for C7-C8-C9-C10, C7-C8-C9-C14, C2-C3-C7-C8, C4-C3-C7-C8 and C3-C7-C8-C9 respectively. These are calculated to be -12.24° (-7.73°), 167.70° (172.16°), 170.30° (173.44°), -9.71° (-6.57°) and 19.13° (13.23°) respectively for 3APPA. Thus the aminophenyl unit rotated at about 90° (near perpendicular) to the picolinic acid unit in 4APPA as revealed by *ab initio* calculations compared to near planarity in 3APPA

Table 1: Selected bond distances (Å) and dihedral angles (°)

Bond distance	4APPA		3APPA	
	HF/6-31G*	DFT/6-31G*	HF/6-31G*	DFT/6-31G*
N-C1	1.323	1.343	1.322	1.343
C1-C2	1.383	1.395	1.383	1.395
C1-C6	1.503	1.503	1.503	1.504
C2-C3	1.394	1.409	1.394	1.408
C3-C4	1.386	1.407	1.387	1.405
C4-C5	1.388	1.394	1.387	1.395
C5-N	1.314	1.335	1.314	1.334
C3-C7	1.441	1.420	1.438	1.422
C7-C8	1.191	1.218	1.191	1.216
C8-C9	1.440	1.420	1.441	1.425
C9-C10	1.393	1.411	1.391	1.405
C10-C11	1.379	1.386	1.390	1.402
C11-C12	1.395	1.408	1.393	1.407
C12-C13	1.395	1.408	1.383	1.393
C13-C14	1.379	1.386	1.383	1.392
C9-C14	1.393	1.411	1.391	1.408
C7-C8-C9-C10	-63.58	26.86	-12.24	-7.73
C7-C8-C9-C14	116.41	-153.01	167.70	172.16
C2-C3-C7-C8	110.37	83.31	170.30	173.44
C4-C3-C7-C8	-69.61	-96.57	-9.71	-6.57
C3-C7-C8-C9	47.73	70.53	19.69	13.23

3.2 Chemical shifts (^1H MNR and ^{13}C NMR)

The experimental chemical shifts (NMR) data for 4APPA and 3APPA [16] were compared to the theoretical calculated values obtained using ab initio and DFT methods as listed in Table 2. The C3, C5, C7, C9, C11 and C12 chemical shifts calculated at HF/6-31G* (DFT/6-31G*) are 133.21 (132.51), 147.31 (153.29), 77.81 (90.50), 123.83 (123.06), 145.85 (145.48) and 112.86ppm (115.11ppm) for 4APPA respectively. These are calculated at HF/6-31G*(DFT/6-31G*) to be 133.53 (132.92), 147.20 (153.12), 74.63 (90.27), 107.20(111.44), 109.40 (112.68) and 148.72 ppm (146.72 ppm) respectively for 3APPA. The experimental reported NMR for C3, C5, C7, C9, C11 and C12 were 153.60, 139.90, 119.60, 143.70, 124.50 and 122.70 ppm for 4APPA and 147.60, 135.10, 121.00, 146.40, 122.80 and 134.10 ppm for 3APPA respectively. The ^{13}C NMR calculated are higher in values than that of experimental, although those DFT/6-31G* are closer to the observed values. In the experimental

report [16], C2, C4, C10 and C14 are assigned the same value (129.90 ppm), however calculations revealed that no two carbon atoms are in the same environment.

The chemical shifts for C1, C2 C3, C4 and C5 calculated at DFT/6-31G* for 4PPA(3APPA) are 150.95(150.70), 130.55(129.73), 132.51(132.91), 128.14(127.53) and 153.29 ppm (153.12 ppm) respectively compared to 151.71, 126.59, 150.28, 124.50 and 154.14 ppm in 4-phenylpicolinic acid [15]; thus C3/C2(C4) experienced shielding/de-shielding effect in both 4PPA and 3APPA as compared to 4-phenylpicolinic acid. The experimental chemical shifts show that pyridine carbon atoms (C1, C2 C3, C4 and C5) are shielded in 3APPA compared to 4APPA.

The proton chemical shifts calculated at both *ab initio* and DFT are higher than those observed experimentally, although that of *ab initio* calculations are closer to the experimental values. The calculated chemical shifts at HF/6-31G* (DFT/6-31G*) level for H2, H5, H10 and H14 are 8.45 (7.92), 9.13 (8.71), 6.93 (6.38) and 7.19ppm (6.75ppm) for 4APPA and 8.43 (7.84), 9.12 (8.64), 7.78 (7.20) and 7.78ppm (7.18ppm) for respectively. These protons were experimentally observed at 8.52, 8.75, 7.49 and 8.04 ppm for 4APPA and 8.43, 8.77, 8.06 and 7.76 ppm for 3APPA respectively. The amino hydrogen atom (H15/H16) is calculated at HF/6-31G*(DFT/6-31G*) to be 2.38 (2.57ppm) and 2.51 (2.76ppm) for 4APPA and 3APPA respectively. However, this proton was observed at 7.13 and 7.57ppm for 4APPA and 3APPA respectively. The theoretical methods used failed to reproduce or predict accurately amino hydrogen atoms of aromatic amines [30-32].

In order to compare the experimental and theoretical chemical shifts (^1H and ^{13}C NMR) for 4PPA and 3PPA, correlation graphics based on the calculations have been presented in Figures 2 and 3. The chemical shifts correlation values (R^2) are found to be 0.940 and 0.964 for 4APPA and 0.929 and 0.953 for 3APPA at *ab initio* and DFT respectively; thus chemical shifts predicted at DFT/6-31G* are closer to the experimental values.

Table 2: Experimental and calculated chemical shifts

Atom	4-(4-aminophenylethynyl)picolinic acid			4-(3-aminophenylethynyl)picolinic acid		
	HF/6-31G*	DFT/6-31G*	Expt. ^a	HF/6-31G*	DFT/6-31G*	Expt. ^a
C1	145.20	150.95	153.70	145.00	150.70	148.40
C2	127.20	130.55	129.90	128.25	129.73	126.10
C3	133.21	132.51	153.60	133.53	132.91	147.60
C4	125.89	128.14	129.90	127.25	127.53	125.60
C5	147.31	153.29	139.90	147.20	153.12	135.10
C6	153.54	164.14	161.90	153.67	164.35	164.40
C7	77.81	90.50	119.60	74.63	90.27	121.00
C8	88.11	99.21	121.60	88.12	99.81	122.40
C9	123.83	123.06	143.70	107.20	111.44	146.40
C10	115.16	118.08	129.90	136.10	135.23	130.30
C11	145.85	145.48	124.50	109.40	112.68	122.80
C12	112.86	115.11	122.70	148.72	146.37	134.10
C13	129.94	129.34	142.00	109.40	112.64	124.20
C14	119.99	123.95	129.90	136.10	135.20	122.80
H1	5.56	5.65	-	5.51	5.60	-
H2	8.45	7.92	8.52	8.43	7.84	8.43
H4	7.62	7.02	8.21	7.64	6.95	7.90
H5	9.13	8.71	8.75	9.12	8.64	8.77
H10	6.93	6.38	7.49	7.78	7.20	8.06
H11	6.77	6.28	7.76	6.63	6.23	7.53
H13/H12	7.54	7.00	7.76	6.63	6.22	7.32
H14	7.19	6.75	8.04	7.78	7.18	7.76
H15/H16	2.38	2.57	7.13	2.51	2.76	7.57

a is taken from reference 16.

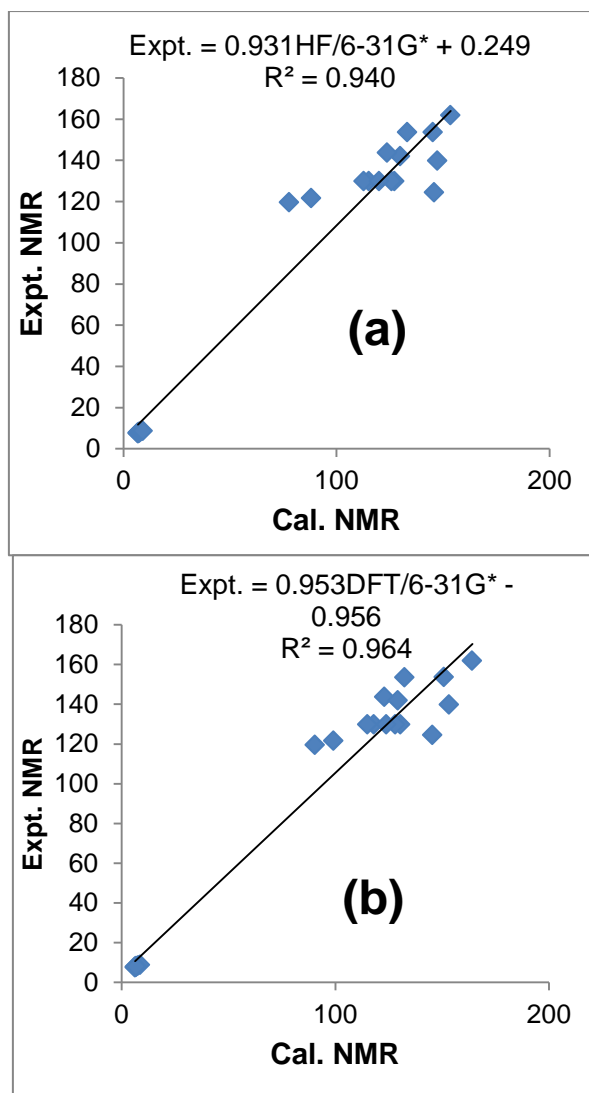


Figure 2: correlation between calculated and experimental NMR for 4-(4-aminophenylethynyl)picolinic acid: (a) = at HF/6-31G* and (b) = at B3LYP/6-31G*

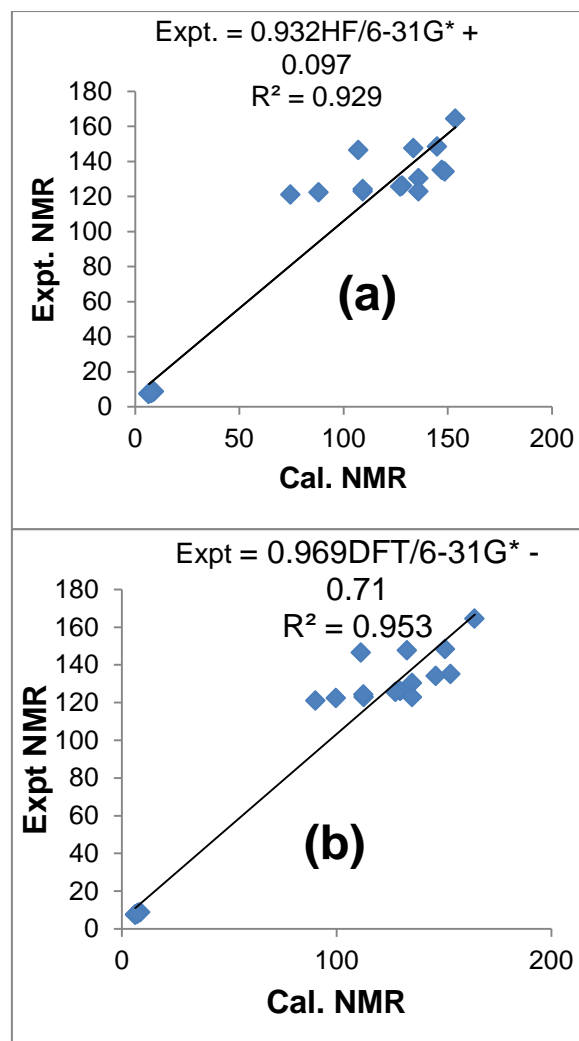


Figure 3: correlation between calculated and experimental NMR for 4-(3-aminophenylethynyl)picolinic acid: (a) = at HF/6-31G* and (b) = at B3LYP/6-31G*

3.3 Vibrational frequencies of 4APPA and 3APPA molecules

Spectroscopic methods especially vibrational spectroscopy has been extensively used for structural elucidation of organic molecules especially for functional groups identification and molecular distinction of conformers, tautomers and isomers [33]. Comparison of the experimental and theoretical vibration modes with proper assignment is helpful to understand a fairly complex system. In the absence of experimental data, theoretical simulated vibrational frequencies could be useful with reasonable degree of accuracy to understand the properties of molecules as well as effect of functional groups on molecules. It has been stated that accuracy of vibrational frequencies calculated could be improved by using scale factor. The scale factors recommended for better accurate prediction for IR frequencies calculated are

0.8953 and 0.9682 at HF/6-31G* and B3LYP/6-31G* respectively [34,35]; however the IR frequency values presented in this paper are in good agreement with the skeletal experimental data available, hence they are not un-scaled. The selected IR values and simulated spectra are shown in Table 2 and Figure 4 respectively.

The aromatic C–H stretching vibrations calculated at HF/6-31G* and B3LYP/6-31G* are in the regions 3083-3009 and 3131-3019 cm^{-1} for 4APP and 3083-3006 and 3128-3059 cm^{-1} for 3APPA respectively. These are observed experimentally at 3215 and 3187 cm^{-1} for 4APPA and 3APPA respectively [16]; this agreed well with 2009-3064 cm^{-1} assigned for aromatic stretching vibrations [36, 37]. The C–H in-plane bending vibrations (πCH) calculated theoretically are in-pure as calculated in the gas phase. They are calculated at HF/6-31G* and B3LYP/6-31G* to be in 1271-1050 and 1312-1047 cm^{-1} region respectively for 4APPA. For 3APPA, the πCH vibrations are in the region 1299-1044 and 1320-1061 cm^{-1} at HF/6-31G* and B3LYP/6-31G* respectively. The C–H out-of-plane bending vibrations (σCH) are calculated at HF/6-31G* to be in the region 1000-794 cm^{-1} and 999-794 cm^{-1} for 4APPA and 3APPA respectively. However, σCH vibrations are calculated at DFT/6-31G* to be 1312-1047 cm^{-1} and 1320-1061 cm^{-1} for 4APPA and 3APPA respectively.

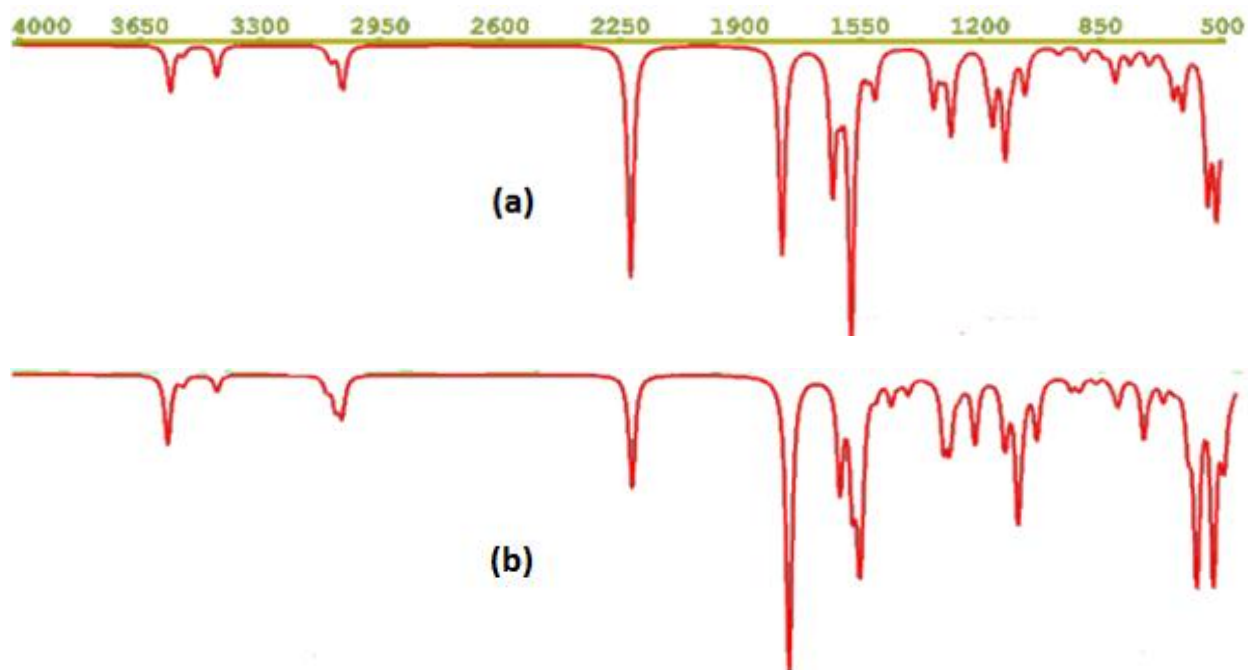


Figure 4: IR spectra simulated at B3LYP/6-31G* level: (a) 4-(4-aminophenylethynyl)picolinic acid and (b) 4-(3-aminophenylethynyl)picolinic acid

The C=C stretching are 1624, 1615 and 1583 cm^{-1} calculated at HF/6-31G*; 1608, 1576, 1551 and 1507 cm^{-1} for 4-PPA. For 3APPA, C=C stretching vibrations are 1619, 1615, 1597 and 1581 cm^{-1} at HF/6-31G* level of calculation; these are calculated at DFT/6-31G* to be 1598, 1579, 1571 and 1531 cm^{-1} . The C=C stretching coupled with were reported at 1668 and 1660 cm^{-1} [16]. The calculated CC triple bond stretching ($\nu_{\text{CC}_{\text{tri}}}$) at HF/6-31G* and DFT/6-31G* are 2271 and 2219 cm^{-1} for 4APPA and 2269 and 2229 cm^{-1} for 3APPA respectively. The experimental values were at 2258 and 2558 cm^{-1} for 4APPA and 3APPA respectively. Theoretically, *ab initio* and DFT calculations show $\nu_{\text{CC}_{\text{tri}}} + \pi\text{CH} + \nu_{\text{C-NH}_2}$ at 1516 and 1507 cm^{-1} for 4APPA and $\nu_{\text{CC}_{\text{tri}}} + \pi\text{CH}$ at 1499 and 1487 cm^{-1} for 3APPA respectively. The $\sigma_{\text{CC}_{\text{tri}}}$ is calculated at HF-31G* to be 574 and 594 for 3APPA respectively; this is calculated at DFT to be 539 and 544 for 4APPA respectively. The calculated benzene ring breathing (δ_{ring}) for 4APPA are displayed at 810 and 818 for HF/6-31G* and B3LYP/6-31G* calculations respectively. For 3APPA molecule, they are calculated at 971 and 973 or fHF/6-31G* and B3LYP/6-31G* calculations respectively.

The stretching vibrations of OH group for 4APPA and 3APPA are observed experimentally at 3558 and 3594 cm^{-1} respectively [16]. These are calculated at *ab initio* and DFT to be 3640 and 3561 cm^{-1} for 4APPA and 3639 and 3558 cm^{-1} for 3APPA respectively. The vibrations of OH in-plane (πOH) are predominantly at 1353 and 1336 for 4APPA and 3APPA respectively by HF/6-31G* and DFT calculations. The calculated out of plane (σOH) deformations are at 561 and 610 cm^{-1} for 4APPA and 547 and 611 cm^{-1} for 3APPA respectively.

The ν_{NH_2} stretching vibrations calculated for 4APPA are 3494 and 3403 cm^{-1} at HF/6-31G* and 3523 and 3425 cm^{-1} at B3LYP/6-31G*. These are calculated to be 3486 and 3397 cm^{-1} at HF/6-31G* and 3513 and 3417 cm^{-1} at B3LYP/6-31G* for 3APPA.

Table 2: Experimental and calculated vibrational frequencies

4-(4-aminophenylethynyl)picolinic acid		4-(3-aminophenylethynyl)picolinic acid		
HF/6-31G*	DFT/6-31G*	HF/6-31G*	DFT/6-31G*	Assign.
3640	3561	3639	3558	ν_{OH}
3494	3523	3486	3513	$\nu_{\text{NH}_2_{\text{asy}}}$
3403	3425	3397	3417	$\nu_{\text{NH}_2_{\text{sv}}}$
3083-3009	3131-3019	3083-3006	3128-3059	$\nu_{\text{C-H}}$

2271	2219	2269	2229	$\nu\text{CC}_{\text{tri}}$
1838	1778	1839	1789	$\nu\text{C}=\text{O}$
1651	1630	1651	1634	ϕNH_2
1624, 1615, 1583	1608, 1576, 1551	1619, 1615 1597	1598, 1579 1571	$\nu\text{C}=\text{C}$
1581	1528	1581	1532	$\nu\text{C}=\text{C} + \nu\text{C}=\text{N}$
1516	1507	-	-	$\nu\text{C}-\text{C}_{\text{tri}} + \pi\text{CH} + \nu\text{C}-\text{NH}_2$
-	-	1499	1487	$\nu\text{C}-\text{C}_{\text{tri}} + \pi\text{CH}$
1492	1464	1489	1465	$\nu\text{C}-\text{C}_{\text{tri}} + \nu\text{C}=\text{N} + \pi\text{CH}$
1353	1336	1353	1337	πOH
1271	1312	1299	1320	$\nu\text{C}-\text{CC}_{\text{tri}}-\text{C} + \pi\text{CH}$
		1314	1317, 1294	$\nu\text{C}=\text{C} + \pi\text{CH}$
1293	1278	1287	1280	$\nu\text{C}=\text{N} + \pi\text{CH} + \pi\text{OH}$
-	1253	-	1253	$\nu\text{C}=\text{C} + \nu\text{C}=\text{N}$
-	-	1236	1247	$\nu\text{C}-\text{CC}_{\text{tri}} + \pi\text{CH} + \nu\text{C}-\text{NH}_2$
1194	1180, 1164	1187,	1164, 1159	$\nu\text{C}-\text{CC}_{\text{tri}} + \pi\text{CH} + \nu\text{C}-\text{COOH}$
1099	1128	1143	1124	$\nu\text{C}-\text{CC}_{\text{tri}} + \nu\text{C}-\text{O} + \pi\text{CH}$
	1120	1138	1111	$\gamma\text{NH}_2 + \pi\text{CH}$
	1107, 1070	1099	1071	$\nu\text{C}-\text{O} + \pi\text{CH}$
1050	1047	1044	1061	$\gamma\text{NH}_2 + \pi\text{CH}$
810	818	971	973	$\delta_{\text{ring}}(\text{benzene})$
981	971	980	972	$\delta_{\text{ring}}(\text{pyridine})$
1000, 994, 977, 968, 941, 877, 841, 827	953, 921, 914, 901, 896, 841, 806, 794	999, 988, 938, 896, 882, 874, 796, 794, 722	955, 932, 902, 850, 843, 936, 764, 710, 672	σCH
794	764	794	764	$\sigma\text{C}-\text{COOH} + \sigma\text{CH}$
650	637	651	638	ϕCOOH
594	512	655	615	ωNH_2
561	610	547	611	σOH
519	537	612	565	$\omega\text{NH}_2 + \sigma\text{OH}$
574	539	594	544	$\sigma\text{CC}_{\text{tri}}$
261	321	227, 223	308	γNH_2
31	47	31	39	γCOOH

ν , stretching; π , in-plane bending; σ , out plane bending; τ , torsion, δ , breathing; ω , wagging; γ , rocking; ϕ , scissor; a is taken from reference 16.

The ϕNH_2 is theoretically observed for both 4APPA and 3APPA molecules at 1651 cm^{-1} for HF/6-31G* calculations. For B3LYP/6-31G* calculations, it is observed at 1630 cm^{-1} for 4APPA and 1634 cm^{-1} for 3APPA. The ωNH_2 for both molecules are calculated at HF/6-31G*(B3LYP/6-31G*) to be 594 cm^{-1} (512 cm^{-1}) for 4APPA and 655 cm^{-1} (615 cm^{-1}) for 3APPA. ωNH_2 coupled with σOH is calculated at HF/6-31G*(B3LYP/6-31G*) to be 519 cm^{-1} (537 cm^{-1}) and 612 cm^{-1} (565 cm^{-1}) for 4APPA and 3APPA respectively. Pure γNH_2 vibrations are calculated at HF/6-31G* and B3LYP/6-31G* for 4APPA to be 261 and 321 cm^{-1} respectively. These are calculated

for 3APPA to be 227(223 cm^{-1}) and 308 cm^{-1} at HF/6-31G* and B3LYP/6-31G* respectively. γNH_2 coupled with πCH are also observed in the two molecules (Table 2).

3.4 Molecular reactivity and Electronic properties

The total energy, salvation energy, energy band gap, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), dipole moment, softness, chemical potential and nucleophilicity index calculated at B3LYP/6-31G* are displaced in Tables 3. The total energies calculated are -501548.33 and -501546.89 kcal/mol for 4APPA and 3APPA respectively, this shows that 4APPA is thermodynamically more stable by 1.44 kcal/mol. The HOMO and LUMO denote electron donating and accepting ability of a molecule. The HOMO, LUMO and energy band gap are -5.54 eV, -1.74 eV and 3.81 eV for 4APPA and -5.79 eV, -1.91 eV and 3.88 eV for 3APPA respectively. The frontier molecular orbital maps: HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1 and LUMO+2 for 4APPA and 3APPA are displayed in Figures 5a and 5b respectively. The chemical potential, chemical hardness and nucleophilicity index for 4APPA are -3.64, 1.918 and 3.48 eV respectively. For 3APPA, they are -3.85, 1.94 and 3.82 eV respectively, hence 4APPA should be a better nucleophile than 3APPA. The standard zero point energy (ZPE^o) calculated at 298 K and 1 atm using B3LYP/6-31G* method is 554.92 and 555.24 kJ/mol for 3APPA respectively. The standard enthalpy (H_m^o) and entropy (S_m^o) are 591.34 kJ/mol and 467.56 J/mol for 4APPA and 591.71 and 467.80 for 3APPA respectively.

Table 3: Molecular energy and global reactivity parameters

parameters	4APPA	3APPA
Total energy (kcal/mol)	-501644.77	-5015642.82
Energy diff.	0.00	1.95
E _{HOMO} (ev)	-5.54	-5.79
E _{LUMO} (eV)	-1.73	-1.91
E _{HOMO-LUMO} (eV)	3.81	3.88
Sol. Energy (kJ/mol)	-58.49	-57.30
Diploe Moment	8.04	6.40
η (ev)	1.91	1.94
μ (ev)	-3.64	-3.85

ω (ev)	3.48	3.82
ZPE° kJ/mol	554.9149	555.2420
H° kJ/mol	591.3416	591.7050
S° J/mol	467.5618	467.7962

The absorption peaks, oscillator strength (f) and molecular orbital component involved in transition are listed in Table 4. In the present work, transitions arising from low absorption bands i.e. oscillator strength (f) values less than 0.005 are discussed. 4APPA has three strong absorption (i.e. $> 0.005f$) at 271.19, 302.82 and 341.49 nm with 0.0104, 0.6489 and 0.5350 f respectively. The 271.19 absorption peak arises from HOMO \rightarrow LUMO+2 (63%) and HOMO-3 \rightarrow LUMO (29%); 302.82 nm absorption peak arises from HOMO \rightarrow LUMO+1 (82%) is characterized as π - π^* transition and 341.49 nm absorption peak arises from HOMO \rightarrow LUMO (85%). However, 3APPA has four strong absorption peaks greater than 0.005 f at 272.17, 291.97, 303.32 and 346.67 nm. The 272.17 nm absorption peak is from HOMO-1 \rightarrow LUMO+1 (74%); 291.97 nm absorption arises from HOMO \rightarrow LUMO+1 (47%) and HOMO-1 \rightarrow LUMO (46%) is characterized as π - π^* and n- π^* transition; 303.32 nm absorption is from HOMO \rightarrow LUMO+1 (49%) and HOMO-1 \rightarrow LUMO (40%) and 346.67 nm absorption arises from HOMO \rightarrow LUMO (93%) (Table 4).

Table 4: Calculated transitions, oscillation strength and transitions generated calculated at TD-DFT B3LYP/6-31G(d)

λ_{\max} (nm)	OS	MO component involved in transition
4APPA		
271.19	0.0104	HOMO \rightarrow LUMO+2 (63%) HOMO-3 \rightarrow LUMO (29%)
293.00	0.0025	HOMO-1 \rightarrow LUMO (93%)
302.82	0.6489	HOMO \rightarrow LUMO +1 (82%)
341.49	0.5350	HOMO \rightarrow LUMO (85%)
3APPA		
272.17	0.2259	HOMO-1 \rightarrow LUMO+1 (74%)
291.97	0.5898	HOMO \rightarrow LUMO+1 (47%) HOMO-1 \rightarrow LUMO (46%)
295.27	0.0026	HOMO-2 \rightarrow LUMO (92%)
303.32	0.1135	HOMO \rightarrow LUMO+1 (49%) HOMO-1 \rightarrow LUMO (40%)
346.67	0.1283	HOMO \rightarrow LUMO (93%)

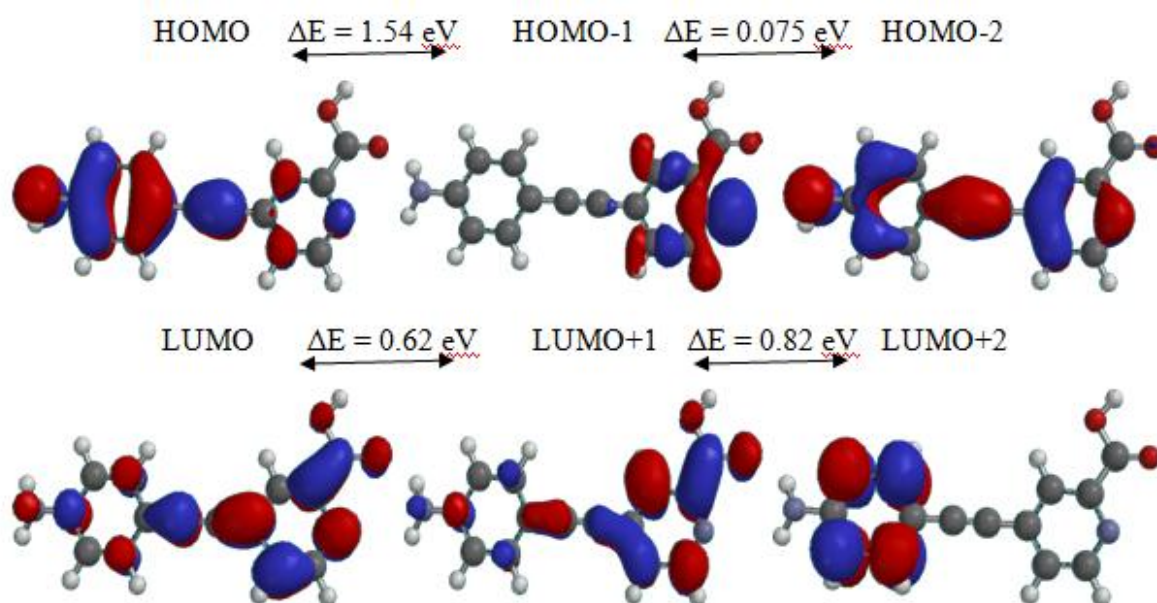


Figure 5a: The frontier molecular orbital maps of 4-(4-aminophenylethynyl)picolinic acid

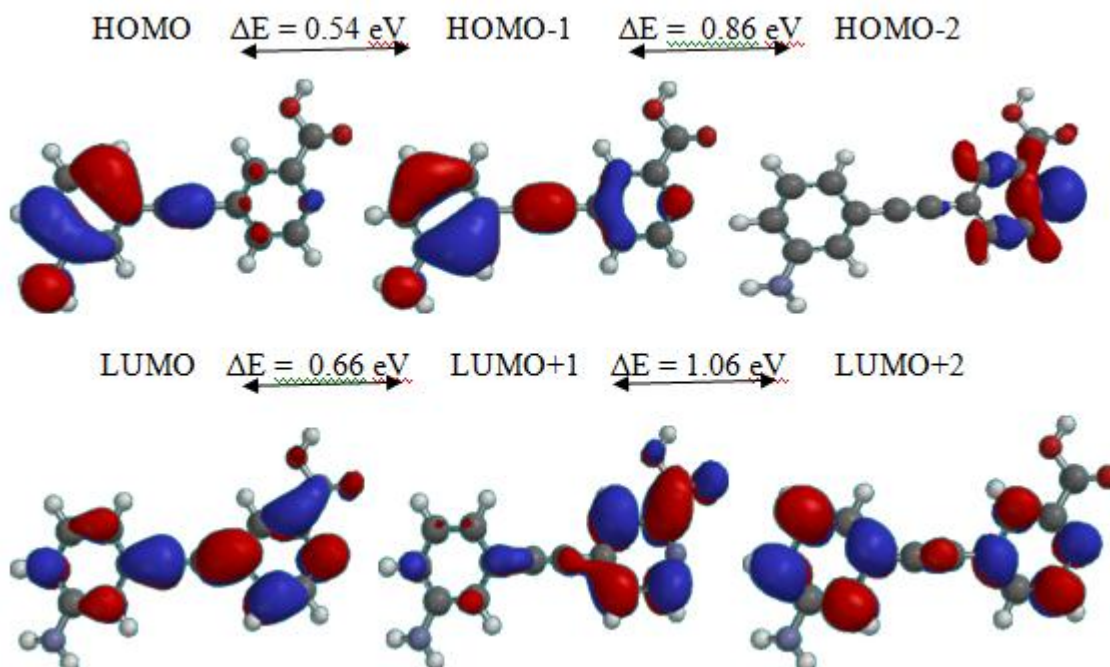


Figure 5b: The frontier molecular orbital maps of 4-(3-aminophenylethynyl)picolinic acid

3.4 Nonlinear properties

To determine non-linear optical (NLO) properties of the system, the strength of molecular interactions, as well as the cross-sections of different scattering and collision processes [38, 39], the Polarizability (α), hyperpolarizability (β) and the electric dipole moment (μ) of 4-(3-aminophenylethynyl)picolinic acid and 4-(4-aminophenylethynyl)picolinic acid an applied electric field were calculated at DFT/6-31G* based on the finite-field approach [40]. The total static dipole moment μ , the mean polarizability (α_0), the anisotropy of the polarizability ($\Delta\alpha$) and the mean first hyperpolarizability (β_0), using the x, y, z components they are defined as:

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

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\Delta\alpha = \frac{\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2 - 3\alpha_0^2}{6\alpha_0^2}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}}$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Table 4: The electric dipole moment μ (au), the average polarizability α_0 (esu) and the first hyperpolarizability β_0 (esu) of 4PPA and 3PPA.

Parameters	4APPA	3APPA
μ_x	-2.883795	2.131307
μ_y	0.048077	0.112349
μ_z	0.045799	0.067607
μ	2.885590	2.135336
μ (Debye)	7.331289	5.427092
α_{xx}	357.213616	308.74332
α_{xy}	17.516890	-9.649145
α_{yy}	148.070275	149.662606
α_{xz}	-6.403370	0.991346
α_{yz}	1.883214	9.458256
α_{zz}	47.553799	59.594992
$\Delta\alpha$	259.43	204.13
α_0	184.279230	172.666976
α_0 (esu)	5.461152×10^{-23}	5.117020×10^{-23}
β_{xxx}	-1876.387	477.973

β_{xyy}	142.958	201.314
β_{xzz}	26.151	-24.333
β_{yyy}	88.667	59.074
β_{yxx}	-396.809	-32.891
β_{zxx}	44.727	50.956
β_{yzz}	-26.358	-15.979
β_{zyy}	-7.856	2.374
β_{zzz}	17.197	7.507
β_x	-1024.366	392.972
β_y	-200.700	6.122
β_z	32.441	36.502
$\beta_0(\text{esu})$	8.841×10^{-30}	3.408×10^{-30}

The calculated values of dipole moment μ , the anisotropy of the polarizability ($\Delta\alpha$) and the mean polarizability (α_0) for 4APPA are 7.33Debye, 259.43 au and 5.46×10^{-23} esu respectively. For 3APPA, μ , $\Delta\alpha$ and α_0 quantities are calculated to be 5.43Debye, 204.13 au and 5.11×10^{-23} esu respectively. The magnitude of the molecular hyperpolarizability β is one of major factors in a nonlinear optics (NLO) system. The mean first hyperpolarizability (β_0) calculated for 3APPA and 4APPA are 8.84×10^{-30} and 3.41×10^{-30} esu respectively. These quantities are greater than those for urea calculated at the same theory [41]. The first hyperpolarizability of 4APPA and 3APPA are 24 and 9 times magnitude of urea, thus the two studied isomers are good candidate of NLO material; although 4APPA would be NLO superior material.

4.0 Conclusion

Ab initio and DFT methods were employed to study molecular properties, global reactivity index, chemical shifts, vibrational frequency and nonlinear optical properties of 4-(4-aminophenylethynyl)picolinic acid and 4-(3-aminophenylethynyl)picolinic acid. The HOMO, LUMO and nucleophilicity index suggested that 4-(4-aminophenylethynyl)picolinic acid would be a better molecule to be involved in the interactions with electrophiles. The chemical shifts calculated agreed with experimental data; thus molecular properties calculated could be used in the absence of experimental data. The calculated first hyperpolarizability for 4APPA and 3APPA showed that they are good candidate of NLO materials.

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