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DFT and MP2 Study of Geometry, IR and UV-Visible Spectroscopy and First Hyperpolarizability of 2-Aminopyridine, 3-Aminopyridine and 4-Aminopyridine in Gas Phase and in Solvents

NUHA AHMED WAZZAN

Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

Corresponding author: Fax: +966 12 695 2000/63170; Tel: +966 561404754; E-mail: nwazzan@kau.edu.sa

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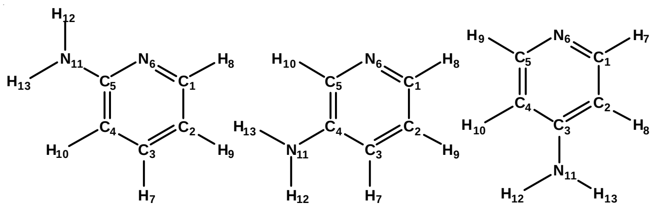
The electronic geometries, IR vibrational modes, the electronic absorption spectra and the quantum chemical parameters of 2-aminopyridine, 3-aminopyridine and 4-aminopyridine have been investigated at DFT/B3LYP and MP2 methods with different basis sets, *viz.* 6-31++G(d,p), 6-31++G(2d,2p), 6-311++G(d,p) and 6-311++G(2d,2p) and compared to experimental results. Also the solvent effects on these parameters have been investigated. A good agreement between the calculated and the experimental parameters was found.

Keywords: Aminopyridines, Quantum mechanical calculations, Quantum chemical parameters, NLO activity.

INTRODUCTION

Aminopyridine as a parent molecule of a huge class of compounds that have extensively studied because of their wide useful applications in pharmacology, medicine, chronic toxicity and carcinogenetic activity, as well as reagents in analytical chemistry. Chao *et al.* studied the crystal structures of 2-aminopyridine, 3-aminopyridine and 4-aminopyridine[1-4]. These compounds have received intensive experimental and theoretical studies; the quantum mechanical calculations have been used to study the electronic structures, spectroscopic information and dimerization. Büyükmurat and Akyüz[5] in a combined experimental and theoretical (force field refinement method together with *ab initio* (4-31G*) and semi-empirical (AM1) quantum chemical calculations) work studied the IR spectra of 3-aminopyridine. Their results indicated a qualitative agreement in the IR normal modes assignments[5]. Boyed *et al.*[6] in a combined experimental (^{1}H NMR) and theoretical (*ab initio* methods) work studied the self-association of 2-aminopyridine and 3-aminopyridine. At 291 K, they calculated the association constants for the two molecules in three deuterated solvents, the *ab initio* methods were used to demonstrate the dimer structures, also the polarized continuum model (PCM) solvation model was applied to 2-aminopyridine association model[6]. Raczyúska *et al.*[7] performed a B3LYP/6-311G(d,p) studies on all tautomers of 2-aminopyridine and 4-aminopyridine and their oxidized and reduced forms. They concluded that the one-electron oxidation has no significant effect on the stabilities of the 2-aminopyridine tautomers, while the one-electron oxidation increases the satiability of imine NH tautomer. For 4-aminopyridine, the oxidation increases the stability of both the amine and imine NH tautomers[7]. In case of a similar heterocyclic aromatic compound, *i.e.* 2-aminopyrimidine, Awad *et al.*[8] studied the conformational stability, relative IR intensities and harmonic vibrational wavenumbers of the electronic ground state of this molecule at two *ab initio* methods, namely MP2 and DFT-B3LYP with different extended basis sets. They found a good agreement between the theoretical and experimental data.

The aim of this work can be summarized into the following: (1) Study of the structural parameters, normal modes of vibration and electronic excitation properties of 2-aminopyridine, 3-aminopyridine and 4-aminopyridine molecules, (2) Study the effect of the type of calculation and the basis set used on these parameters and (3) Study the effect of solvent polarity on the UV-visible absorption spectra. The numeration of atoms of the studied aminopyridines is given in Fig. 1.



2-Aminopyridine 3-Aminopyridine 4-Aminopyridine

Fig. 1. Atoms numeration of aminopyridines molecules

COMPUTATIONAL METHODS

Calculations were performed using the Gaussian 09 suite programs[9]. Geometry optimizations were conducted at two levels of theory; (1) density functional theory (DFT) using Becke's three parameter exchange functional[10], the Lee-Yang-Parr correlation functional (B3LYP)[11] and (2) Møller-Plesset second-order perturbation theory (MP2)[12], with two types of basis sets; (1) the split-valence double zeta basis set (6-31G) and (2) the split-valence triple zeta basis set (6-311G). Each basis set was enlarged with two polarized basis functions (*d*- and *p*-orbitals), where a *d*-type orbital was added to all atoms except the hydrogen atoms and *p*-type orbital was added to all hydrogen atoms. Also each basis set was enlarged by two types of diffuse functions; (1) *sp*-type diffuse function was added to all atoms (heavy atoms) except the hydrogen atoms and (2) *s*-type diffuse function was added to all hydrogen atoms. Adding the higher angular momentum orbitals (polarization orbitals) in the basis set that are empty in the separated atoms was essential for improved representation of the electron density of the molecule and adding the diffuse function was also essential for better representation of the broad electrons distributions. The solvation effects were studied by applying the implicit solvation model, *viz.* polarized continuum model (PCM)[13]. In the polarized continuum model of solvation the solvent is treated as a continuum dielectric medium and the solute is considered as a trapped molecules in a cavity surrounded by solvent.

In geometry optimizations every bond length, bond angle and dihedral angle was allowed to relax and free of constraints. The nature of the stationary points, *i.e.* minima points on the potential energy surface (PES), was confirmed by vibrational frequency analysis, to verify that only real frequency (*i.e.* no imaginary frequency) values were obtained for all geometries. Solvation was carried out by re-optimized the geometries in the gas phase at the desired method and basis set, also the optimizations were carried out free of any constraints and the vibrational frequency analysis verified that the obtained solvated geometries are corresponding to minima points on the potential energy surface, since no imaginary frequencies were obtained. Molecular data insertion and visual inspection was carried out using the GuassView program (version 5.0.8) and Chemcraft program version 1.7 (build 365)[14,15].

Quantum chemical parameters (QCP) such as the frontier molecular orbitals (FMO), *i.e.* the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), energy gap (E.G.), total energy (T.E.), dipole moment (μ), sum of the total negative charges (TNC), electronegativity (χ), hardness (η), softness (σ) and electrophilicity index (ω) were calculated. The QCPs were used as effective parameters to predict the reactivity reasoning of different molecules toward the formation of the charge transfer complexes (CTC). The importance of the CTCs arises from their wide applications such applications are: corrosion inhibition of metals[16,17], solar cells[18,19] and optical devices[20,21]. The energies of HOMO and LUMO orbitals of a molecule are related to ionization potential (IE) and electron affinity (EA), respectively, by the following two equations:

$$\text{Ionization potential} = -E_{\text{HOMO}} \qquad (1)$$

$$\text{Electron affinity} = -E_{\text{LUMO}} \qquad (2)$$

Absolute electronegativity, χ and absolute hardness (η), are given as[22]:

$$\chi = \frac{\text{IE} + \text{EA}}{2} \qquad (3)$$

$$\eta = \frac{\text{IE} - \text{EA}}{2} \qquad (4)$$

According to Koopman's theorem[23], the softness (σ) is the inverse of the hardness[22]:

$$\sigma = \frac{1}{\eta} \qquad (5)$$

The absolute electrophilicity index is given as[24]:

$$\omega = \frac{\mu^2}{2\eta} \qquad (6)$$

RESULTS AND DISCUSSION

Gas phase

Optimized geometries: The optimized geometries in the gas phase of 2-aminopyridine at B3LYP and MP2 with different basis sets, *viz.* 6-31++G(d,p), 6-31++G(2d,2p), 6-311++G(d,p) and 6-311++G(2d,2p) are summarized in Table-1. The average absolute and percent errors in the geometrical parameters for all the studied aminopyridine molecules at different methods & basis sets compared with the X-ray crystal structures reported in literature[1-4] are summarized in Table-2.

Table-1 summarizes the B3LYP and MP2 optimized geometrical parameters, *i.e.* bond lengths (R), bond angles (A) and dihedral angles (D) using different basis sets for 2-aminopyridine. At the two methods and different basis sets, 2-aminopyridine geometry is non-planner; the two hydrogen atoms of the amino group are come out of the plane of the pyridine moiety. The deviation from planarity is demonstrated by the dihedral angles (D) between C4-C5-N11-H12 and N6-C5-N11-H13 that range from -15.9 to 33.6° instead of zero° for planner geometry. The calculated bond lengths (R), bond angles (A) and dihedral angles (D) were affected by the type of the method and the size of the basis set used in the calculation and showed a general trend. Most bond lengths are elongated at the MP2 compared to those at the B3LYP method keeping the basis set the same, for instance, the C5-N11 bond length equal to 1.383 and 1.384 Å at the B3LYP method and 1.392 and 1.394 Å at the MP2 method with differences range 0.009 to 0.01 Å. In contrast, the bond angles and dihedral angles were become smaller in MP2 method for some angles and become larger for another angles, for instance, the bond angles between N6-C5-N11 are larger (range 0.064 to 0.092°) in B3LYP compared to those angles by the MP2 method and the dihedral angles between N6-C5-N11-H13 are larger (range by the MP2 than those angles by the B3LYP method. Generally, the bond lengths are decreased as the size of the basis set increased more obvious at the B3LYP method. For instances, C1-C2 bond lengths decreased as the basis set become larger,

TABLE-1
OPTIMIZED GEOMETRY PARAMETERS OF 2-AMINOPYRIDINE CALCULATED AT B3LYP AND MP2 USING DIFFERENT BASIS SETS IN GAS PHASE

Coordinate	6-31++G(d,p)		6-31++G(2d,2p)		6-311++G(d,p)		6-311++G(2d,2p)		Crystal[2,3]
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	
R(1,2)	1.393	1.393	1.391	1.393	1.389	1.394	1.387	1.390	1.367
R(1,6)	1.340	1.348	1.338	1.346	1.337	1.346	1.336	1.344	1.340
R(1,8)	1.088	1.084	1.087	1.084	1.087	1.088	1.084	1.082	1.01
R(2,3)	1.401	1.400	1.399	1.401	1.398	1.401	1.395	1.397	1.380
R(2,9)	1.085	1.082	1.083	1.081	1.083	1.085	1.080	1.079	0.96
R(3,4)	1.388	1.389	1.386	1.391	1.384	1.391	1.381	1.387	1.364
R(3,7)	1.087	1.083	1.085	1.083	1.085	1.087	1.082	1.081	0.99
R(4,5)	1.412	1.407	1.409	1.407	1.409	1.409	1.406	1.404	1.405
R(4,10)	1.086	1.083	1.084	1.083	1.084	1.087	1.082	1.081	0.96
R(5,6)	1.342	1.344	1.339	1.341	1.338	1.341	1.336	1.339	1.345
R(5,11)	1.384	1.394	1.384	1.394	1.383	1.394	1.383	1.392	1.351
R(11,12)	1.009	1.010	1.008	1.008	1.008	1.011	1.006	1.006	0.96
R(11,13)	1.011	1.011	1.010	1.010	1.009	1.012	1.007	1.007	0.88
A(2,1,6)	124.061	123.837	124.038	123.919	124.026	123.964	123.972	123.769	124.2
A(2,1,8)	120.464	120.819	120.432	120.638	120.439	120.584	120.420	120.641	121
A(6,1,8)	115.475	115.343	115.529	115.443	115.534	115.451	115.607	115.590	115
A(1,2,3)	117.532	117.956	117.549	117.915	117.549	117.917	117.593	117.997	117.8
A(1,2,9)	120.765	120.507	120.738	120.480	120.765	120.492	120.730	120.467	119
A(3,2,9)	121.703	121.537	121.714	121.605	121.686	121.591	121.678	121.537	123
A(2,3,4)	119.547	119.224	119.493	119.052	119.534	119.044	119.521	119.089	120.2
A(2,3,7)	120.553	120.725	120.574	120.851	120.542	120.823	120.545	120.828	119
A(4,3,7)	119.900	120.048	119.934	120.096	119.923	120.131	119.935	120.083	121
A(3,4,5)	118.377	118.571	118.412	118.686	118.410	118.596	118.466	118.712	118.6
A(3,4,10)	121.190	121.100	121.216	121.077	121.169	121.127	121.158	121.013	124
A(5,4,10)	120.431	120.329	120.370	120.236	120.420	120.277	120.374	120.274	118
A(4,5,6)	122.523	122.820	122.509	122.795	122.453	122.908	122.404	122.675	121.6
A(4,5,11)	121.240	120.953	121.203	120.950	121.227	120.775	121.220	120.982	121.9
A(6,5,11)	116.199	116.107	116.245	116.177	116.283	116.204	116.335	116.271	116.5
A(1,6,5)	117.958	117.584	117.998	117.630	118.027	117.565	118.043	117.756	117.7
A(5,11,12)	117.914	115.523	117.234	115.242	117.879	115.077	117.179	115.398	120
A(5,11,13)	114.702	112.517	114.166	112.249	114.660	112.268	114.115	112.437	121
A(12,11,13)	115.289	112.894	114.646	112.637	115.269	112.641	114.580	112.892	117
D(6,1,2,3)	0.197	0.251	0.187	0.294	0.196	0.312	0.178	0.240	–
D(6,1,2,9)	-179.744	-179.612	-179.733	-179.671	-179.735	-179.638	-179.746	-179.700	–
D(8,1,2,3)	179.914	179.891	179.852	179.921	179.899	179.870	179.850	179.886	–
D(8,1,2,9)	-0.027	-0.028	-0.068	-0.044	-0.031	-0.080	-0.075	-0.054	–
D(2,1,6,5)	-0.450	-0.421	-0.478	-0.544	-0.461	-0.431	-0.479	-0.496	–
D(8,1,6,5)	179.821	179.921	179.842	179.811	179.823	179.991	179.835	179.842	–
D(1,2,3,4)	0.166	0.485	0.191	0.283	0.182	0.359	0.198	0.274	–
D(1,2,3,7)	179.999	179.800	-179.956	179.954	-179.995	179.831	-179.958	179.997	–
D(9,2,3,4)	-179.893	-179.654	-179.890	-179.753	-179.889	-179.692	-179.878	-179.788	–
D(9,2,3,7)	-0.060	-0.339	-0.037	-0.081	-0.066	-0.220	-0.034	-0.064	–
D(2,3,4,5)	-0.257	-1.003	-0.259	-0.574	-0.274	-0.863	-0.256	-0.503	–
D(2,3,4,10)	179.261	178.926	179.310	179.051	179.236	178.992	179.280	179.088	–
D(7,3,4,5)	179.910	179.677	179.887	179.752	179.902	179.662	179.899	179.772	–
D(7,3,4,10)	-0.573	-0.395	-0.545	-0.623	-0.588	-0.484	-0.566	-0.638	–
D(3,4,5,6)	0.000	0.859	-0.038	0.330	0.005	0.771	-0.051	0.250	–
D(3,4,5,11)	177.677	176.726	177.501	176.999	177.714	176.743	177.520	177.050	–
D(10,4,5,6)	-179.521	-179.070	-179.611	-179.298	-179.509	-179.085	-179.590	-179.344	–
D(10,4,5,11)	-1.845	-3.203	-2.071	-2.629	-1.800	-3.112	-2.020	-2.544	–
D(4,5,6,1)	0.344	-0.146	0.397	0.222	0.354	-0.124	0.409	0.243	–
D(11,5,6,1)	-177.442	-176.200	-177.256	-176.595	-177.461	-176.267	-177.273	-176.697	–
D(4,5,11,12)	25.392	33.488	26.931	33.176	25.561	33.635	27.077	32.402	–
D(4,5,11,13)	166.270	165.140	165.089	163.915	166.297	164.244	164.991	163.849	–
D(6,5,11,12)	-156.792	-150.379	-155.382	-149.944	-156.596	-150.133	-155.212	-150.602	–
D(6,5,11,13)	-15.913	-18.727	-17.225	-19.205	-15.859	-19.524	-17.297	-19.156	–

R: bond length; A: bond angle; D: Dihedral angle

TABLE-2
AVERAGE ABSOLUTE AND PERCENT ERRORS IN THE GEOMETRICAL PARAMETERS OF 2-AMINOPYRIDINE, REGULAR FONT, 3-AMINOPYRIDINE, BOLD FONT, 4-AMINOPYRIDINE, ITALICS FONT, AT B3LYP AND MP2 WITH DIFFERENT BASIS SETS IN GAS PHASE COMPARED TO EXPERIMENTAL DATA [Ref. 1-4]

Average	Bond length (Å)							
	6-31++G(d,p)		6-31++G(2d,2p)		6-311++G(d,p)		6-311++G(2d,2p)	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
<|Error|>	0.055	0.055	0.054	0.055	0.054	0.057	0.052	0.053
	0.063	**0.063**	**0.062**	**0.063**	**0.061**	**0.064**	**0.059**	**0.060**
	0.054	*0.054*	*0.053*	*0.054*	*0.053*	*0.055*	*0.052*	*0.052*
<%Error>	5.539	5.501	5.445	5.491	5.414	5.675	5.250	5.307
	6.492	**6.454**	**6.382**	**6.442**	**6.332**	**6.602**	**6.157**	**6.212**
	5.429	*5.401*	*5.361*	*5.384*	*5.322*	*5.541*	*5.200*	*5.253*
	Bond angle (°)							
<|Error|>	1.341	1.719	1.439	1.770	1.347	1.790	1.444	1.752
	1.247	**1.297**	**1.289**	**1.326**	**1.253**	**1.314**	**1.289**	**1.305**
	1.235	*1.598*	*1.378*	*1.637*	*1.265*	*1.639*	*1.395*	*1.633*
<%Error>	1.115	1.431	1.197	1.473	1.120	1.489	1.201	1.458
	1.056	**1.096**	**1.091**	**1.121**	**1.061**	**1.110**	**1.090**	**1.103**
	1.037	*1.343*	*1.158*	*1.376*	*1.062*	*1.377*	*1.172*	*1.372*

range 1.393 to 1.390 Å, C1-N6 bond lengths range is 1.340 to 1.336 Å, C5-N6 bond length range is 1.342 to 1.336 Å, while C5-N11 bond lengths are not affected by the size of the basis set, calculated values are 1.384 and 1.383 Å.

2-Aminopyridine is a non-symmetrical molecule since the substituted amino group is at C5 atom position, it is expected that each bond length and bond angle will have its unique value. At B3LYP/6-31++G(d,p) as a representative example, The longest bond lengths between the atoms in the pyridine moiety are for the pairs C4-C5 (1.412 Å), C2-C3 (1.401 Å) and C1-C2 (1.393 Å) indicating that these bonds have a higher single bond character, while the pairs C1-N6 (1.340 Å) and C5-N6 (1.342 Å) the bond lengths are the smallest indicating that these bond have a higher double bond character, this may be attributed to the higher electronegativity of the nitrogen atom that make the bonds with the atoms attached to it have a higher double bond character. The C5-N11 bond length is 1.384 Å, intermediate value between the longest and the shortest bond lengths. With respect to the C-H bond lengths, the longest C-H bond lengths are for the pairs C1-H8 (1.088 Å) and C3-H7 (1.087 Å), while the shortest for the pairs C4-H10 (1.086 Å) and C2-H9 (1.085 Å). Comparing the average of the calculated C-H bond lengths (1.087 Å) with the average experimental value from X-ray data (0.98 Å) shows a little disagreement between these data. The values of N11-H12/13 bond lengths are 1.009 and 1.011 Å and a little bit inconsistent with that obtained from X-ray data (0.96 and 0.88 Å).

The calculated bond angles between most atoms are larger by the B3LYP than those by MP2 method, for instance the bond angles between C5-N11-H12 and C5-N11-H13 are significantly larger by B3LYP (range 117.179 to 117.914 and 114.115 to 114.702°, respectively) compared to those by MP2 method (115.077 to 115.523 and 112.166 to 112.514°, respectively) keeping basis set the same. Also the bond angles between C1-N6-C5, N6-C5-N11, C4-C5-N11, C5-C4-H10, C3-C4-H10 and C2-C3-C4 as examples. Although some bond angles are larger by MP2 than by B3LYP method, for instance the bond angles for C4-C5-N6 and C3-C4-C5 are significantly larger at the MP2 (122.675 to 122.908° and 118.571 to 118.712, respectively) compared to their values at the B3LYP method (122.404 to 122.523 and 118.377 to 118.466 °, respectively). Also, the bond angles between C4-C3H7, C2-C3-H7 and C2-C1-H8 as examples. On the other hand, the bond angles not showed a specific trend with the size of used basis sets. Exceptions are: the bond angle for C2-C1-N6 is decreased as the basis sets become larger by B3LYP method, while they are increased by the MP2 method, the bond angle between N6-C5-N11 increased as the basis set enlarged by the two methods.

The calculated dihedral angles values for C4-C5-N11-H12 and N6-C5-N11-H13 determined the non-planarity of the molecule and depend on the basis set used. The values for these angles are 25.392, 26.931, 25.561 and 27.077 and -15.913, -17.225, -15.859 and -17.297 at the B3LYP method and 33.488, 33.176, 33.635 and 32.402° and -18.727, -19.205, -19.524 and -19.156° at MP2 method using 6-31++G(d,p), 6-31++G(2d,2p), 6-311++G(d,p), 6-311++G(2d,2p), respectively. Thus the largest values for these two dihedral angles were predicted by the MP2 method and with 6-31++G(d,p) and 6-311++G(d,p) basis sets, respectively. The calculated dihedral angles for the atoms of the pyridine ring are close to zero indicating that there is no deviation from planarity, *i.e.* C1-C2-C3-C4 (range 0.166 to 0.198 at the B3LYP and 0.283 to 0.485° at MP2 method), C2-C1-N6-C5 (range -0.450 to -0.479 at the B3LYP and -0.421 to -0.544° at MP2 method). Hydrogen atoms attached to the carbon atoms of the pyridine ring are also close to zero and thus indicating that the pyridine moiety is planner, this was find out from the calculated dihedral angles for H7-C3-C3-H10, H7-C3-C2-H9 and H9-C2-C1-H8 angles.

Table-2 shows averages for the absolute and relative errors (<|Error|> and <%Error>) in gas phase for bond lengths and bond angles of 2-aminopyridine optimized at different methods and basis sets, as compared with their crystal structures[2,3]. There is excellent agreement between these data although the calculated values are for the gas phase geometries and the experimental values are for the solid phase geometries. On one hand, the intermolecular H-bonds in the crystal structure[6] may account in part for the minor differences. On the other hand, a good agreement between computed and observed geometrical values occurs because most bond lengths and angles are typical of sp^2 hybridized systems, *i.e.*, 2-aminopyridine is π-conjugated in nature and thus acquire rigid structures, same conclusion was derived in literature for similar molecules[25]. The average percent errors (<%Error>) in bond lengths are larger, range 5.25 to 5.67, than that for the bond angles, range 1.12 to 1.49. The best agreement between the calculated and experimental bond lengths was obtained by B3LYP/6311+G(2d,2p) (<%Error> = 5.250), while the best agreement for the bond angles was obtained by B3LYP/631+G(d,p) (<%Error> = 1.115),

Aminopyridines together: The differences between selected geometrical parameters for the three aminopyridine molecules at B3LYP/6-31++G(d,p) are given in Fig. 2. The main geometrical parameters found to have some changes due to different positioning of the substituted amino group. Dihedral angles between the two planes constructed from the four atoms.

Basis sets and quantum chemical parameters (QCPs)

Total and relative energy: For the three molecules, the B3LYP calculated total energy has a higher negative value compared with that of MP2 method at the same basis set, this result disagree with that reported in literature for 2-aminopyrmidine molecule[8]. For instance, at 6-311++G(2d,2p) basis set the differences in total energies obtained by the two methods are: 0.8293, 0.8276, 0.8293 au for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively. In addition, the larger the basis set used in the calculation, the more stabilized geometry, *i.e.* total energy become more negative value, by both B3LYP and MP2 methods, this result agree with that obtained for 2-aminopyrimidine molecule[8] (Table-3).

The B3LYP and MP2 calculated quantum chemical parameters (QCP) with different basis sets for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine are collected in Table-4.

Frontier molecular orbitals (FMO): For the three molecules, the MP2 calculations showed a lower HOMO level and a higher LUMO level compared to the B3LYP calculation. For instance, the E_{HOMO} values for 2-aminopyridine are in the range -6.069 to -6.138 eV and in the range -8.470 to -8.494 eV by the B3LYP and MP2 methods, respectively and the E_{LUMO} values are in the range -0.789 to -0.836 eV and 1.072 to 1.044 eV by the B3LYP and MP2 methods, respectively. By the same method, the larger basis set (from double zeta to triple zeta basis set) and the addition of polarization functions [from (d,p) to (2d,2p) polarization functions] to the basis set leads to lower HOMO and LUMO levels, thus stabilization of both HOMO and LUMO orbitals. For instance, for 3-aminopyridine the E_{HOMO} values decrease in the order: 6-31++G(d,p) (-6.087 eV) > 6-31++G(2d,2p) (-6.107 eV) > 6-311++G(d,p) (-6.147 eV) > 6-311++G(2d,2p) (-6.155 eV) and the E_{LUMO} values decreases in same order, *i.e.* 6-31++G(d,p) (-0.875 eV) > 6-31++G(2d,2p) (-0.885 eV) > 6-311++G(d,p) (-0.936 eV) > 6-311++G(2d,2p) (-0.928 eV) by the B3LYP method. For the three molecules, B3LYP calculations showed a significantly smaller LUMO-HOMO energy gap (in the order of ~ 5 eV) compared with the MP2 Method. For instance, 4-aminopyridine the energy gap values are in the range 5.829 to 5.902 eV and 10.012 to 10.050 eV by B3LYP and MP2 methods, respectively. In addition,

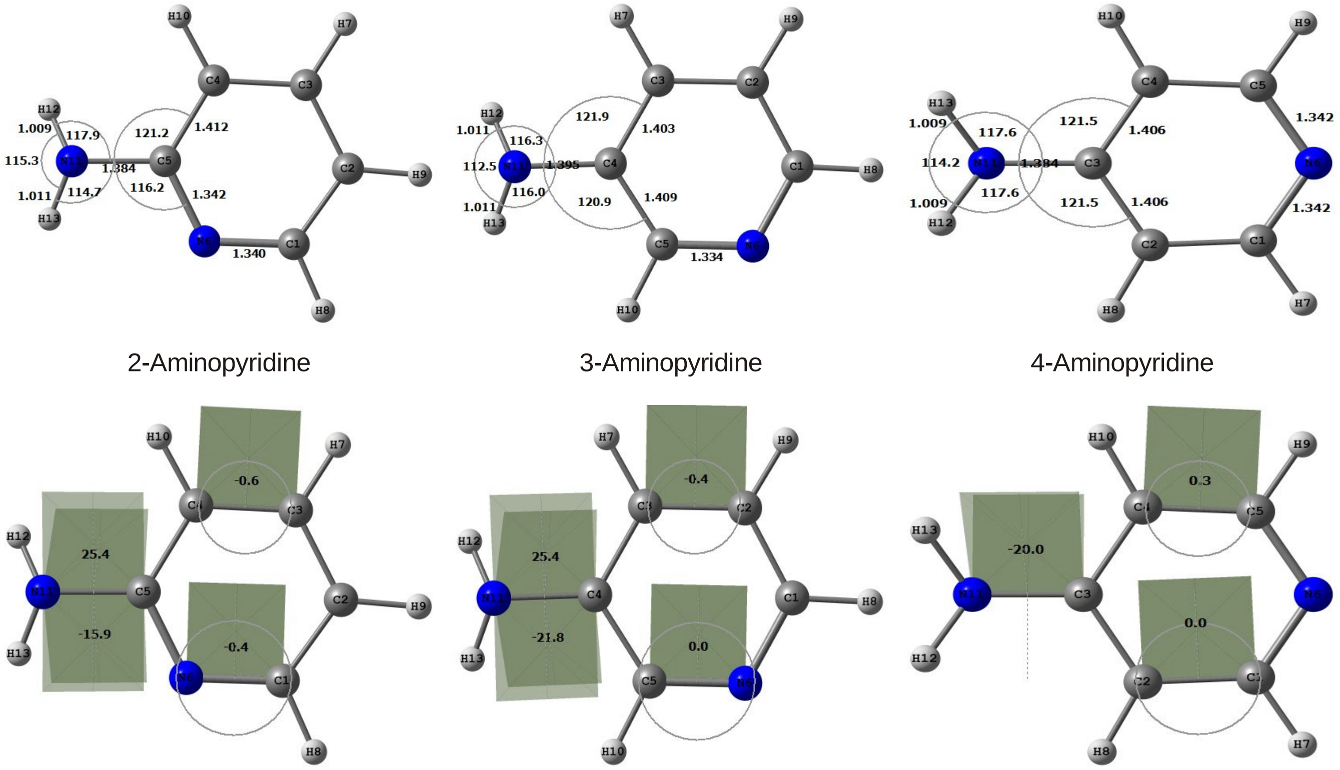

2-Aminopyridine
3-Aminopyridine
4-Aminopyridine

Fig. 2. Selected bond lengths, bond angles and dihedral angles for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine optimized at B3LYP/6-31++G(d,p) in the gas phase, along with the atomic numbering scheme used throughout this study

TABLE-3
CALCULATED TOTAL ENERGIES AND RELATIVE ENERGIES, FOR 2-AMINOPYRIDINE (REGULAR FONT), 3-AMINOPYRIDINE (BOLD FONT) AND 4-AMINOPYRIDINE (ITALICS FONT) BY B3LYP AND MP2 WITH DIFFERENT BASIS SETS IN GAS PHASE

Basis set	B3LYP		MP2	
	Total energies (au)	Relative energies (au)	Total energies (au)	Relative energies (au)
6-31++G(d,p)	-303.6766836	-0.0728	-302.7573684	-0.1629
	-303.6659954	**-0.0729**	**-302.7480909**	**-0.1632**
	-303.6709085	*-0.0728*	*-302.7513548*	*-0.1631*
6-31++G(2d,2p)	-303.6836566	-0.0659	-302.8299012	-0.0903
	-303.6731096	**-0.0658**	**-302.8208840**	**-0.0904**
	-303.6779126	*-0.0658*	*-302.8239882*	*-0.0905*
6-311++G(d,p)	-303.7383883	-0.0111	-302.8504103	-0.0698
	-303.7276114	**-0.0113**	**-302.8413623**	**-0.0700**
	-303.7325015	*-0.0112*	*-302.8445015*	*-0.0700*
6-311++G(2d,2p)	-303.7495107	0.0000	-302.9202415	0.0000
	-303.7389123	**0.0000**	**-302.9113226**	**0.0000**
	-303.7437259	*0.0000*	*-302.9144586*	*0.0000*

TABLE-4
B3LYP AND MP2 CALCULATED QCPs FOR 2-AMINOPYRIDINE (REGULAR FONT), 3-AMINOPYRIDINE (BOLD FONT) AND 4-AMINOPYRIDINE (ITALICS FONT), USING DIFFERENT BASIS SETS IN GAS PHASE

Method	Basis set	E_{HOMO} (eV)	E_{LUMO} (eV)	E.G. (eV)	μ (D)	χ (eV)	η (eV)	σ (eV^{-1})	ω (D^2/eV)
B3LYP	6-31++G(d,p)	-6.069	-0.789	5.280	2.040	3.429	2.640	0.379	0.788
		-6.087	**-0.875**	**5.212**	**3.362**	**3.481**	**2.606**	**0.384**	**2.169**
		-6.428	*-0.599*	*5.829*	*4.111*	*3.514*	*2.915*	*0.343*	*2.900*
	6-31++G(2d,2p)	-6.089	-0.796	5.292	1.994	3.443	2.646	0.378	0.751
		-6.107	**-0.885**	**5.222**	**3.256**	**3.496**	**2.611**	**0.383**	**2.030**
		-6.455	*-0.596*	*5.859*	*3.981*	*3.526*	*2.929*	*0.341*	*2.705*
	6-311++G(d,p)	-6.127	-0.844	5.282	2.025	3.486	2.641	0.379	0.776
		-6.147	**-0.936**	**5.212**	**3.327**	**3.541**	**2.606**	**0.384**	**2.123**
		-6.490	*-0.601*	*5.889*	*4.073*	*3.546*	*2.944*	*0.340*	*2.817*
	6-311++G(2d,2p)	-6.138	-0.836	5.301	1.987	3.487	2.651	0.377	0.745
		-6.155	**-0.928**	**5.226**	**3.242**	**3.542**	**2.613**	**0.383**	**2.011**
		-6.503	*-0.601*	*5.902*	*3.962*	*3.552*	*2.951*	*0.339*	*2.660*
MP2	6-31++G(d,p)	-8.470	1.072	9.542	2.142	3.699	4.771	0.210	0.481
		-8.385	**0.985**	**9.370**	**3.214**	**3.700**	**4.685**	**0.213**	**1.103**
		-9.080	*0.938*	*10.018*	*3.758*	*4.071*	*5.009*	*0.200*	*1.410*
	6-31++G(2d,2p)	-8.435	1.071	9.506	2.068	3.682	4.753	0.210	0.450
		-8.355	**0.986**	**9.341**	**3.134**	**3.684**	**4.670**	**0.214**	**1.052**
		-9.072	*0.941*	*10.013*	*3.692*	*4.066*	*5.007*	*0.200*	*1.361*
	6-311++G(d,p)	-8.494	1.048	9.542	2.129	3.723	4.771	0.210	0.475
		-8.405	**0.969**	**9.374**	**3.181**	**3.718**	**4.687**	**0.213**	**1.080**
		-9.121	*0.929*	*10.050*	*3.723*	*4.096*	*5.025*	*0.199*	*1.379*
	6-311++G(2d,2p)	-8.451	1.044	9.495	2.054	3.704	4.747	0.211	0.444
		-8.369	**0.967**	**9.336**	**3.125**	**3.701**	**4.668**	**0.214**	**1.046**
		-9.084	*0.928*	*10.012*	*3.685*	*4.078*	*5.006*	*0.200*	*1.356*

4-aminopyridine has the larger energy gap values and 3-aminopyridine has the smallest energy gap values by both method and with all basis sets, thus the order of the energy gap values for the three molecules is: 4-aminopyridine > 2-aminopyridine > 3-aminopyridine. Since, a more reactive molecule (toward charge transfer complex reactions for example) is always associated with small energy gap, thus the reactivity of these molecules is in the order: 3-aminopyridine > 2-aminopyridine > 4-aminopyridine (the reactivity of these molecules toward complexes formation with different π-acceptor molecules will be reported in future work).

Dipole moment: Fig. 2 represents the variation of the dipole moment values depending on the type of aminopyridine molecule and the type of applied basis set at the B3LYP and MP2 methods. MP2 calculations showed higher dipole moment values than those values by the B3LYP calculations at the same basis set. The calculated values of the former method are in the range of 2.054 to 3.758 Debye, while the calculate values for the later method are in the range of 1.987 to 4.111 Debye. B3LYP and MP2 methods showed that the dipole moment values were increased with the basis sets in the following order: 6-31++G(d,p) > 6-311++G(d,p) > 6-31++G(2d,2p) > 6-311++G(2d,2p), Fig. 2(a). For instance, the dipole moments for 2-aminopyridine by B3LYP method are: 2.040, 2.025, 1.994 and 1.987 Debye and by MP2 method are: 2.142, 2.129, 2.068 and 2.054 Debye at 6-31++G(d,p), 6-311++G(d,p), 6-31++G(2d,2p) and 6-311++G(2d,2p), respectively. The order of increasing the dipole moments for the three molecules by the two methods with different basis sets is: 2-aminopyridine < 3-aminopyridine < 4-aminopyridine, Fig. 2(b). For instance, at 6-31++G(d,p) basis set the dipole moment values by B3LYP are: 2.040, 3.362 and 4.111 Debye and by MP2 are: 2.142,.

3.214 and 3.758 Debye, for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively.

Other quantum chemical parameters (QCPs): Table-5 gives the average differences, <diff.>, in the calculated values of the QCPs for the three aminopyridine molecules by B3LYP and MP2 methods with different basis sets in the gas phase. MP2 calculations showed that the three aminopyridine molecules have more electronegativity and hardness values than those obtained from B3LYP calculations at the same basis set. <diff.> between those values are: 0.323 and 2.087 eV for the electronegativity and hardness values, respectively and thus they are more significant with respect to the hardness values. In addition, MP2 calculations showed that the three aminopyridine molecules have smaller softness and electrophilicity values than those obtained from B3LYP calculations at the same basis set, <diff.> between those values are: 0.160 eV^{-1} and 0.903 D^2/ eV for the softness and electrophilicity values, respectively. Since, such parameters were used to decide the reactivity and selectivity of a specific molecule toward specific reaction, B3LYP calculations showed higher reactivity for these three molecules as compared to MP2 calculations because of high values of softness and electrophilicity. Generally (with few exceptions), for the three molecules it can be observed that B3LYP calculations showed an increase of the calculated values of χ and η as the basis set increase, while the MP2 showed a reverse trend and no general trends were observed for the other two parameters, *i.e.* σ and ω.

TABLE-5
AVERAGE DIFFERENCES IN CALCULATED VALUES OF QCPS FOR THREE AMINOPYRIDINE MOLECULES BY B3LYP AND MP2 METHODS WITH DIFFERENT BASIS SETS IN GAS PHASE

	χ (eV)	η (eV)	σ (eV^{-1})	ω (D^2/eV)
<diff.>	0.323	2.087	0.160	0.903

Mulliken population analysis: The SD2 for complete list of the calculated Mulliken atomic charges on selected atoms and the total negative charges calculated at B3LYP and MP2 methods with different basis sets for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine. Fig. 3(a-c) and Fig. 4 summarize these data by graphical representations for easier comparison. From Fig. 3(a), it can be observed that net electronic accumulations mainly on C3, C5 and N6 atoms. By B3LYP method, C3 atom is the atom with the highest negative charge with 6-31++G(d,p) and 6-31++G(2d,2p) basis sets, C5 with 6-311++G(d,p) and N6 with 6-311++G(2d,2p) basis set. In contrast, by MP2 method, net electronic accumulations are on C3, N6 and N11 atoms. N11 atom is the atom with the highest negative charge with 6-31++G(d,p) basis set, N6 atom is the atom with the highest negative charge with 6-31++G(2d,2p) and 6-311++G(2d,2p) basis sets and C3 atom is the atom with the highest negative charge with 6-311++G(d,p) basis set. From Fig. 3(b), it can be observed that net electronic accumulations mainly on C1, C5 and N11 atoms. By B3LYP method, N11 atom is the atom with the highest negative charge with 6-31++G(d,p) basis set, C5 with 6-31++G(2d,2p) and C1 with 6-311++G(d,p) basis set. In contrast, by MP2 method, net electronic accumulations are on C1, N6 and N11 atoms. N11 atom is the atom with the highest negative charge with 6-31++G(d,p) and 6-31++G(2d,2p) basis sets, C1 and N11 atoms are the atoms with the highest negative charges with 6-311++G(d,p) basis set and N6 atom is the atom with the highest negative charge with 6-311++G(2d,2p) basis set. From Fig. 3(c), it can be observed that by B3LYP method net electronic accumulations mainly on C3 with all basis sets, in addition N6 has also comparable negative charge with 6-311++G(2d,2p) basis set. In contrast, MP2 method showed net electronic accumulations mainly on C3 with 6-31++G(d,p) and 6-311++G(d,p) basis sets, N11 with 6-31++G(2d,2p) and N6 with 6-311++G(2d,2p) basis set.

Fig. 4, at the same method and basis set, generally 4-aminopyridine shows the most negative atoms. For instance, with 6-31++G(d,p) basis set at B3LYP and MP2 method, C3 is the most negative atom in 2-aminopyridine and 4-aminopyridine molecules compared to the other atoms in these two molecules and it is more negative for 4-aminopyridine molecule, -0.574, 0.078 and -0.909e for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively at B3LYP and -0.399, 0.108 and -0.878e at MP2 method, but the effect of the method is that B3LYP gives more negative atom and less positive atom. To investigate the effect of going from double zeta (above) to triple set basis set, let us consider now the two cases; calculations at B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p), still C3 atom is the most negative atom for 2-aminopyridine and 4-aminopyridine, -0.534, 0.146 and -0.580e for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively at B3LYP and -0.407, 0.150 and -0.505e for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively at MP2, thus the effect of the triple zeta basis set depends on the applied method, *i.e.* it decreases the net negative charge at the B3LYP method and increases the net negative charge at the MP2 method. The atoms with the highest negative charges are mainly C3, N6 and N11 atoms. These changes in the calculated net atomic charges with different basis sets are compatible with different bonding multiplicity and degree of electronic delocalization, this conclusion was derived in literature[8].

The total negative charge on the whole skeleton of the three aminopyridine molecules were also affected by the type of method and basis set used. For 2-aminopyridine and 3-aminopyridine molecules the highest total negative charges were shown with 6-311++G(d,p) basis set, -1.803 and -1.733e for 2-aminopyridine and -1.257 and -1.457e for 3-aminopyridine by both B3LYP and MP2 calculations. However, for 4-aminopyridine the highest total negative charge was shown with 6-31++G(d,p) basis set, -2.483 and -2.103e by B3LYP and MP2, respectively. On the other hand, the lowest total negative charges were shown with 6-311++G(2d,2p) basis set by both B3LYP and MP2 calculations for the three molecules. The lowest total negative charges are: -1.090, -0.907 and -1.210e by B3LYP method and -1.185, -0.972 and -0.844e by MP2 for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively.

Basis sets and IR vibrational modes: The agreement between the calculated harmonic wave numbers by B3LYP and MP2 methods with different basis sets and the experimental wave numbers is very good, 3.02 < <%Error> < 5.16. Fig. 5 represents graphically this agreement for 3-aminopyridine, the correlation coefficients (R^2) is 0.998.

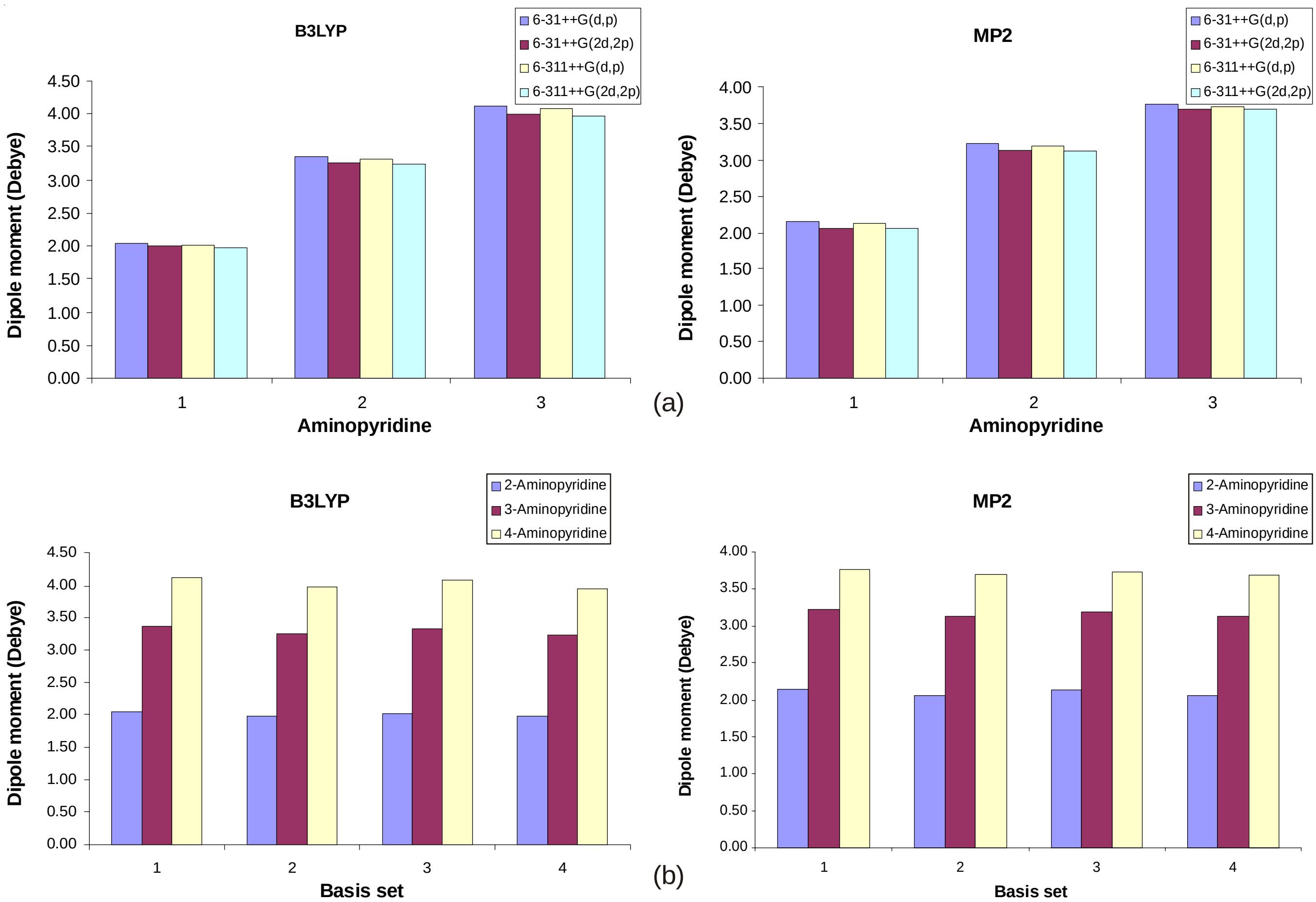


Fig. 3. Graphical representation of variation of the dipole moment values with the type of (a) aminopyridine molecule and (b) applied basis set at the B3LYP and MP2 methods

2-Aminopyridine, 3-aminopyridine and 4-aminopyridine molecules have 33 normal modes of vibrations. Fig. 6 gives an illustration of each normal vibration mode of 2-aminopyridine molecule as a representative example. For 2-aminopyridine, the agreement with the experimental wave numbers[26] was best achieved with the MP2/6-311++G(d,p) level of theory, where and <|Error|> = 57.78 and <%Error> = 3.20. The assignments of different vibrational modes were straight forward for some vibrations and aided with the experimental data for another vibrations. For instance, the N-H bond stretching modes (symmetrical and asymmetrical) are in good agreement with the experimental assignments for these modes (3445 and 3302 cm^{-1}). The symmetrical (mode # 33) and asymmetrical (mode # 32) N-H bond stretching modes of 2-aminopyridine molecule to the strong bands observed at 3706.50 and 3587.80 cm^{-1}, respectively, at MP2/6-311++G(d,p) level of theory. The experimental wave number for the wagging vibration of the NH_2 was not recorded but in the calculated IR spectrum this vibration was obvious and appears at 460.79 cm^{-1} (mode # 5) at the previous level of theory. Also the C-H bond stretching modes were not recorded in experiment but confidently assigned in the calculated IR spectrum (modes # 28, 29, 30 and 31) at 3196.27, 3206.68, 3222.59 and 3240.45 cm^{-1}, in addition, the twisting of NH_2 angle bending was confidently assigned in the calculated spectrum (mode # 2) at 344.14 cm^{-1}. The ring breathing mode of vibration which is a characteristic mode for cyclic molecules, was assigned successfully to the band at 1007.90 cm^{-1} (mode # 15) is close to the experimental band at 1060 cm^{-1}. The in-plane C-H bending vibration (mode # 19) is also assigned easily and agreed well with the experimental wave number, 1443 and 1174.06 from experiment and from MP2/6-311++G(d,p) level of theory, respectively. The out-of-plane C-H angle bending vibrations (mode # 11, 13 and 14) is assigned bands observed at 828.12, 881.65 and 902.48 cm^{-1} and this was corresponding to the available experimental wave number at 855 cm^{-1}. The experimental assignment of the IR band at 1627 cm^{-1} as a ring starching and scissoring of the angle bending of NH_2 is in a very good agreement with the calculated wave number (mode # 25), 1622.30 cm^{-1}.

Table-12 listed the average absolute and percent errors in the IR data parameters of 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, at B3LYP and MP2 with different basis sets in the gas phase compared to experimental data[26-28]. As can be seen, the best agreement with the experimental IR data for 3-aminopyridine is achieved by applying the B3LYP/6-311++G(2d,2p), <%Error> = 3.00, B3LYP/6-31++G(d,p) and MP2/6-31++G(2d,2p) levels, <%Error> = 3.02 for both levels. In contrast, for 4-aminopyridine, B3LYP/6-311++G(d,p) level performed a better job in predicting the experimental IR data, <%Error> = 3.70. It seems that generally that B3LYP as a method and 6-311++G(d,p) and 6-311++G(2d,2p) as larger basis sets performed better in predicting the experimental IR data.

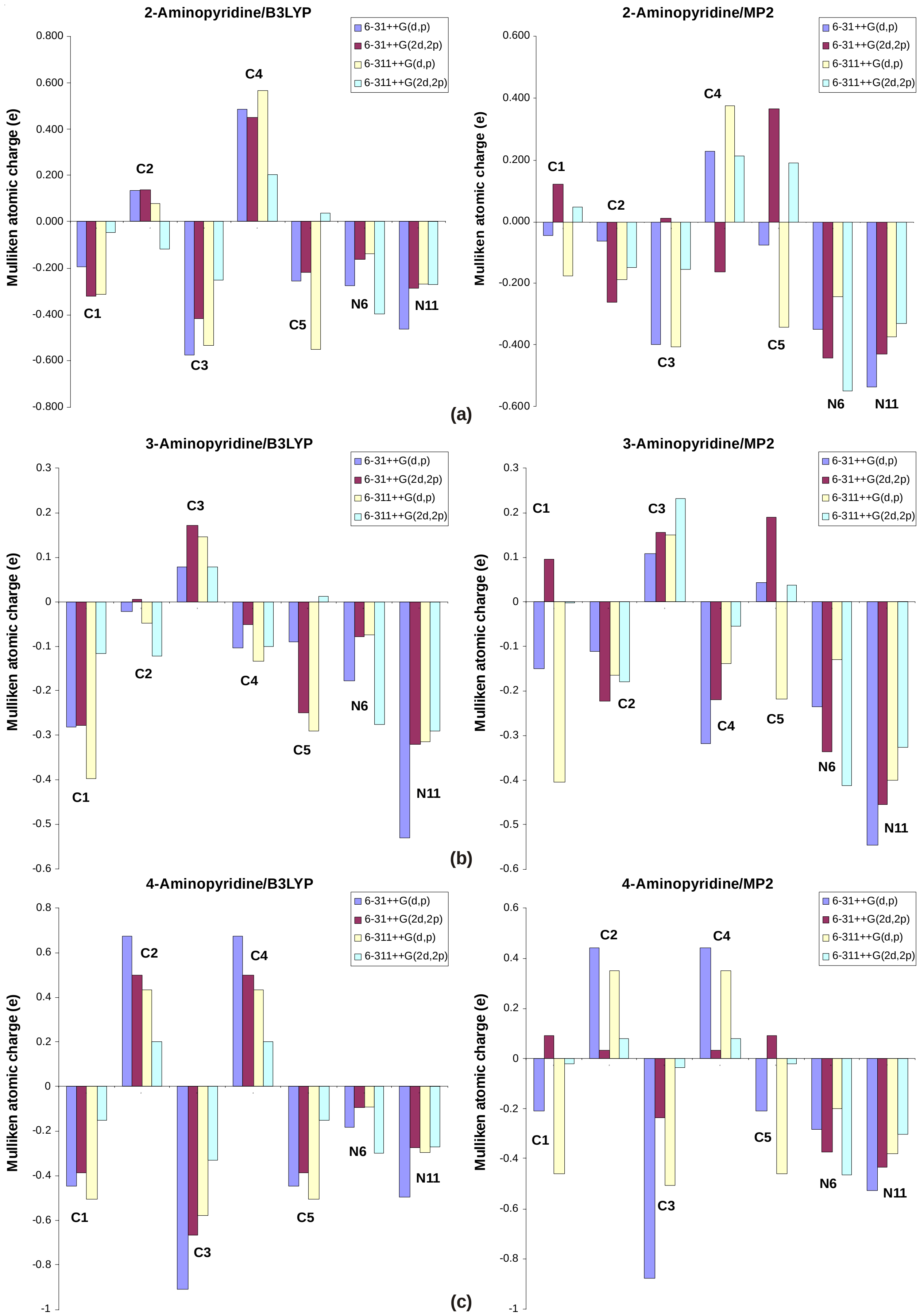
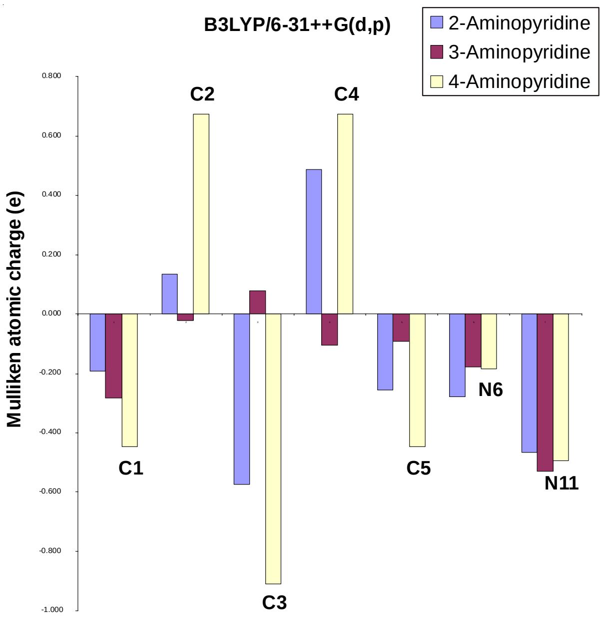
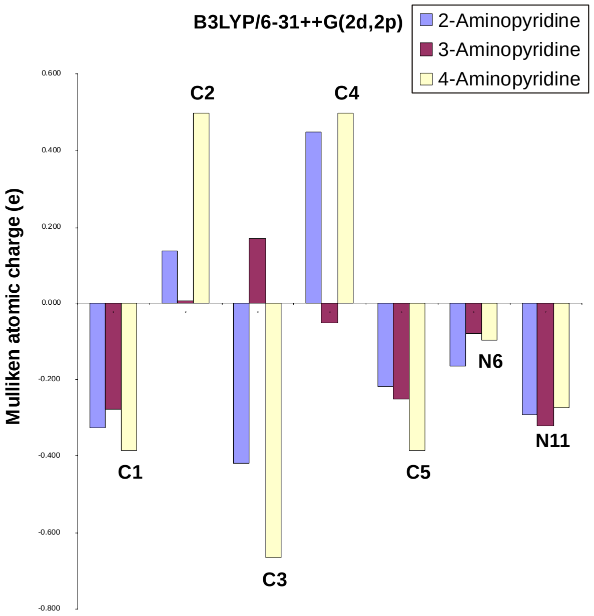
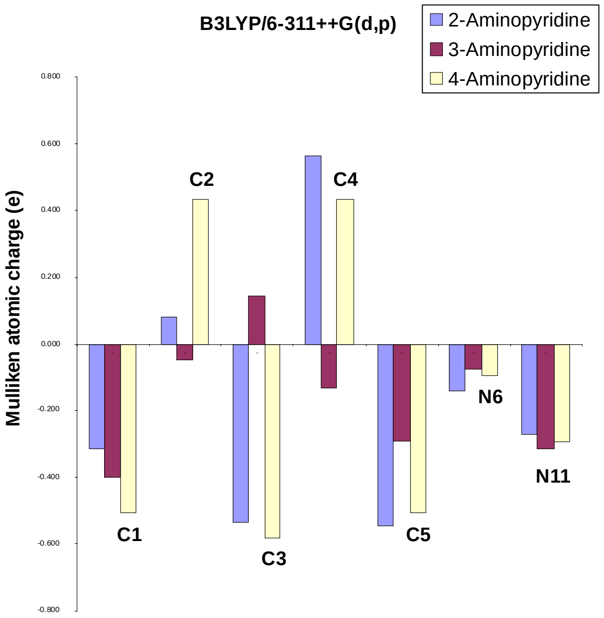
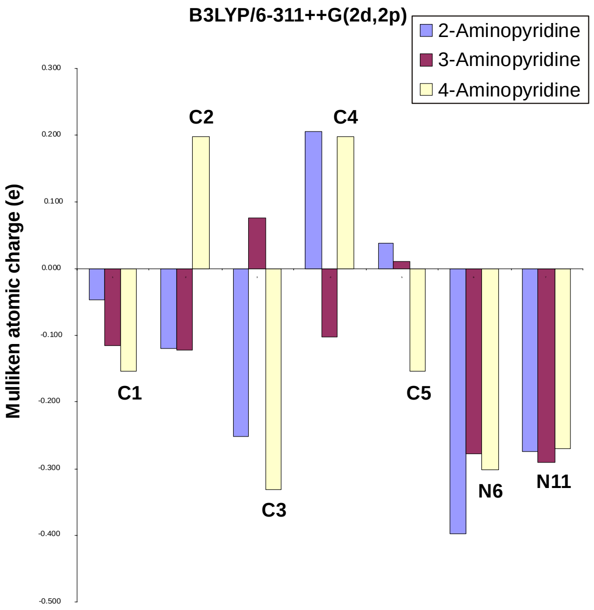


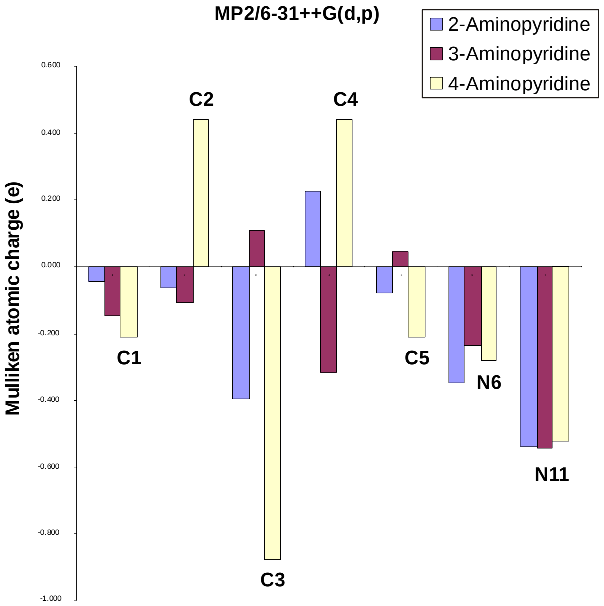
Fig. 4. Graphical representation of the Mulliken atomic charges for the three aminopyridine molecules according to the basis set effect (a) 2-aminopyridine, (b) 3-aminopyridine and (c) 4-aminopyridine by B3LYP and MP2 methods with different basis sets in the gas phase

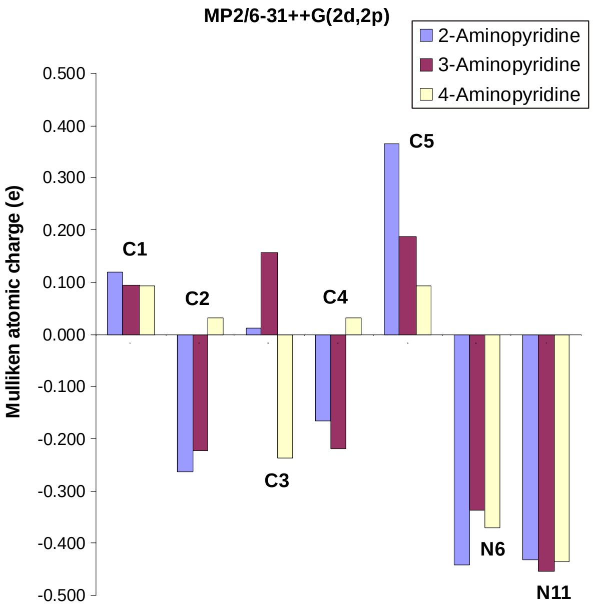

B3LYP/6-31++G(d,p)
2-Aminopyridine
3-Aminopyridine
4-Aminopyridine
Mulliken atomic charge (e)
0.800
0.600
0.400
0.200
0.000
-0.200
-0.400
-0.600
-0.800
-1.000
C1
C2
C3
C4
C5
N6
N11


B3LYP/6-31++G(2d,2p)
2-Aminopyridine
3-Aminopyridine
4-Aminopyridine
Mulliken atomic charge (e)
0.600
0.400
0.200
0.000
-0.200
-0.400
-0.600
-0.800
C1
C2
C3
C4
C5
N6
N11


B3LYP/6-311++G(d,p)
2-Aminopyridine
3-Aminopyridine
4-Aminopyridine
Mulliken atomic charge (e)
0.800
0.600
0.400
0.200
0.000
-0.200
-0.400
-0.600
-0.800
C1
C2
C3
C4
C5
N6
N11


B3LYP/6-311++G(2d,2p)
2-Aminopyridine
3-Aminopyridine
4-Aminopyridine
Mulliken atomic charge (e)
0.300
0.200
0.100
0.000
-0.100
-0.200
-0.300
-0.400
-0.500
C1
C2
C3
C4
C5
N6
N11


MP2/6-31++G(d,p)
2-Aminopyridine
3-Aminopyridine
4-Aminopyridine
Mulliken atomic charge (e)
0.600
0.400
0.200
0.000
-0.200
-0.400
-0.600
-0.800
-1.000
C1
C2
C3
C4
C5
N6
N11


MP2/6-31++G(2d,2p)
2-Aminopyridine
3-Aminopyridine
4-Aminopyridine
Mulliken atomic charge (e)
0.500
0.400
0.300
0.200
0.100
0.000
-0.100
-0.200
-0.300
-0.400
-0.500
C1
C2
C3
C4
C5
N6
N11

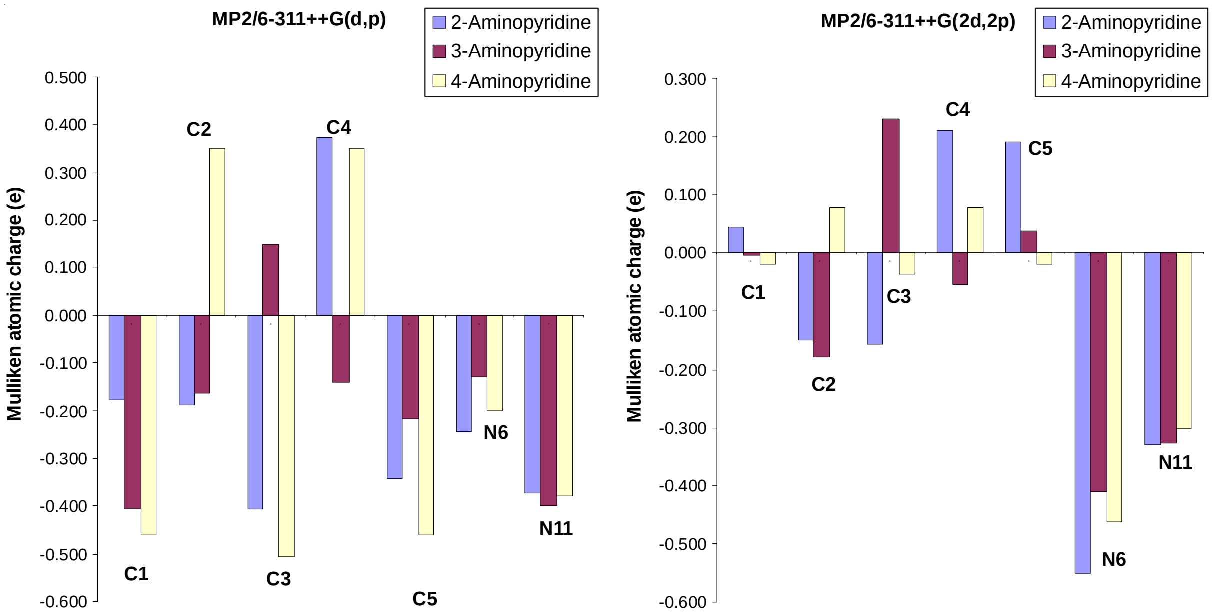


Fig. 5. Graphical representation of the Mulliken atomic charges for the three aminopyridine molecules according to the effect of type of aminopyridine molecule by B3LYP and MP2 methods with different basis sets in the gas phase

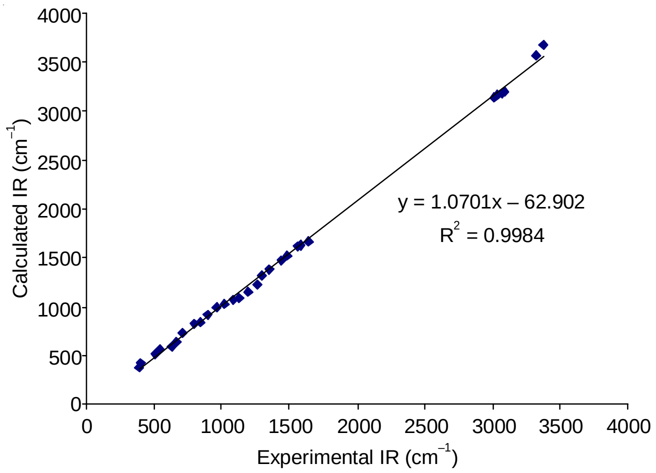


Fig. 6. A graphical representation of the comparison between the experimental and the calculated wave numbers of 3-aminopyridine calculated at B3LYP with 6-31++G(2d,2p) in the gas phase

Solvent effects

Quantum chemical parameters in different solvents: In order to investigate the energetic behaviour of the three aminopyridine molecules in solvent media, the optimizations were performed in solvents with different polarity, *i.e.* with different dielectric constant values (ε), ε range of 2-02 to 78.39, in the gas medium and in different solvent media (Table-8). The aminopyridine molecule becomes more stabilized in solvent phase than in gas phase and the stabilization increases with increasing of solvent polarity. The stabilization of the aminopyridine due to the solvent polarity is more obvious for 4-aminopyridine where the relative energy values (RE) are larger at the same solvent, for instance, the relative energy values in benzene are: -0.0047, -0.0059 and -0.0064 au for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively.

In order to investigate the effect of the medium of the studied molecules on the QCPs such as energy gap, μ and total negative charge, the optimizations were performed in the gas medium and in different solvent media. Table-9 listed the QCPs of 2-amino-pyridine, 3-aminopyridine and 4-aminopyridine in different solvents calculated at B3LYP/6-31++G(d,p) level using the PCM model of solvation. The energy gap values in the gas phase are: 5.2801, 5.2118 and 5.8293 eV for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively, the energy gap values were generally decreasing (with few exceptions) with increasing of the polarity of the solvent, for instance, the energy gap values for 3-aminopyridine are: 5.1746, 5.1699, 5.1441, 5.1215, 5.1201, 5.1185, 5.1155 eV in cyclohexane, benzene, chloroform, acetone, ethanol, acetonitrile and water, respectively. In addition, in going from the gas medium to solvent media, the η values decreasing, the σ values increasing, the ω values increasing analogous with the decreasing of the energy gap values, thus the aminopyridine molecule become more reactive as the polarity of the solvent increases. Moreover, total negative charges of the three aminopyridine molecules increase with the increasing polarity, this was combined with increasing the μ values. Similar conclusion was driven in literature for 2-aminopyrimidine molecule[8]. For instance, the total negative charge values for 3-aminopyridine are in the range of -1.205 to -1.347e and μ values are in the range of 3.3620 to 4.5329 Debye,

UV-visible spectra analysis: UV-visible electronic spectra of 2-aminopyridine, 3-aminopyridine and 4-aminopyridine molecules in gas and various solvents were calculated at TD-DFT/B3LYP/6-31++G(d,p) and the results are collected in Table-10. Similar to literature's observation for similar molecule, *i.e.* 2-aminopyrimidine, no absorption bands in and over 400 nm region in the gas phase or any solvent for all the studied aminopyridine molecules[29]. The calculated values of the band's wavelengths, λ_{calc}, in water solvent are in good agreement with the available experimental data in same solvent[29], the difference between the calculated and experimental wavelengths does not exceed 39 nm. According to the data from experiment in water, 2-aminopyridine exhibits absorption

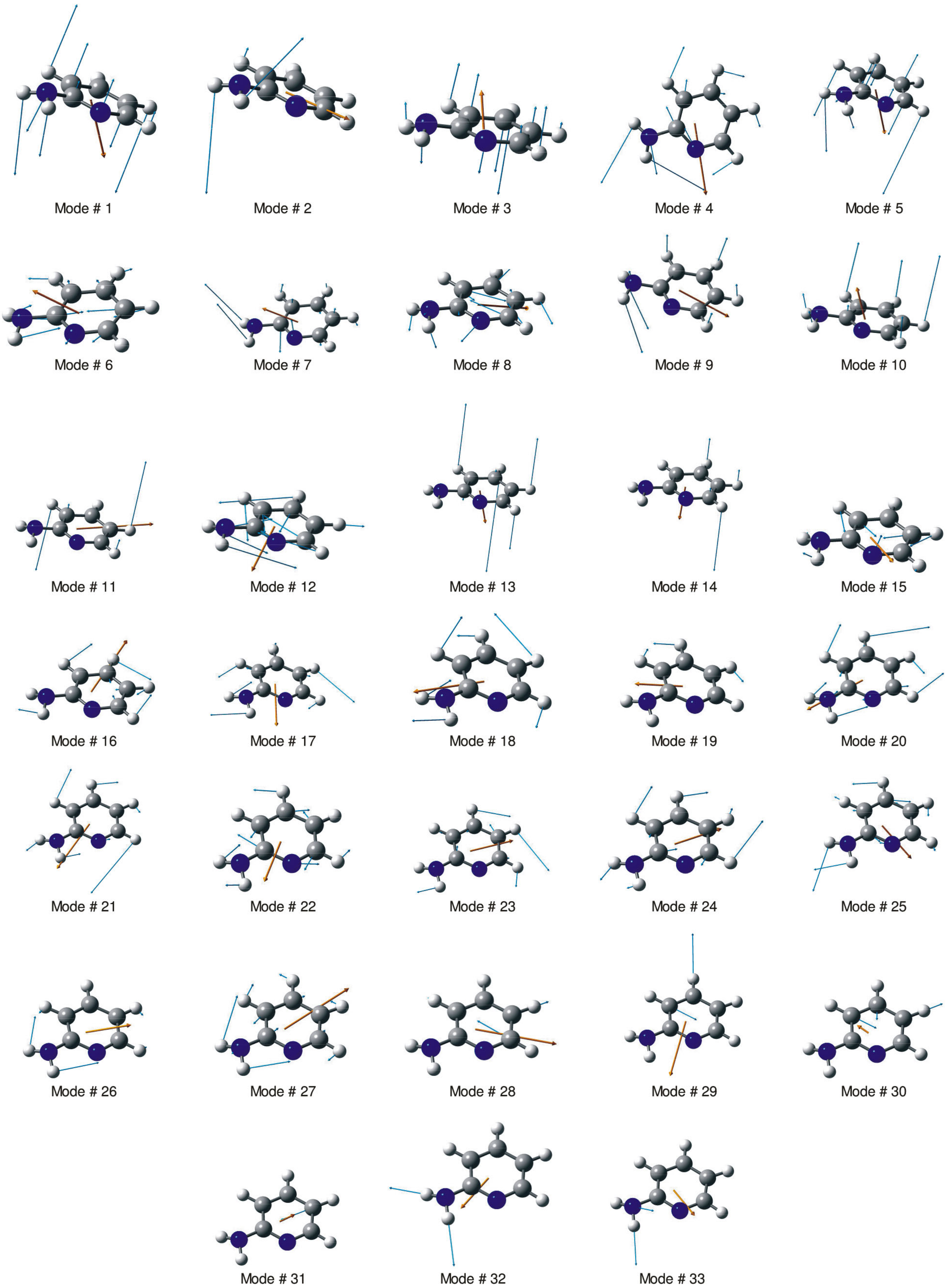


Fig. 7. Numeration and illustration of each vibrational mode of 2-aminopyridine (blue and orange arrows show displacement and dipole derivative unit vector, respectively)

TABLE-6
IR SPECTRAL DATA FOR 2-AMINOPYRIDINE CALCULATED AT B3LYP WITH DIFFERENT BASIS SETS IN GAS PHASE

Mode	Experimental[26]	Wave number (cm^{-1})				Assignment
		6-31++G(d,p)	6-31++G(2d,2p)	6-311++G(d,p)	6-311++G(2d,2p)	
1	3445	3710.50	3696.60	3694.00	3689.90	ν_{asy} (NH$_2$)
2	3302	3586.70	3579.20	3579.80	3580.10	ν_{sy} (N–H)
3	–	3216.10	3212.00	3199.10	3205.10	ν(C–H)
4	–	3197.00	3192.10	3180.00	3186.10	ν(C–H)
5	–	3181.50	3175.80	3164.40	3170.70	ν(C-H)
6	–	3167.50	3158.20	3147.30	3153.80	ν(C–H)
7	–	1657.50	1650.40	1649.30	1649.10	δ(NH$_2$)
8	1627	1633.60	1628.70	1628.70	1631.10	ν(C=C) + δ(NH$_2$)
9	1598	1618.90	1614.00	1610.20	1609.60	ν(C–C) + β(C–H)
10	1560	1517.70	1514.80	1511.30	1516.50	ν(C–C)
11	1490	1479.30	1475.30	1474.00	1479.70	ν(C–C)
12	1443	1352.60	1352.30	1349.60	1356.20	β(C–H)
13	1339	1340.50	1336.50	1335.40	1334.40	ν(C–NH$_2$) + β(C–H)
14	1325	1328.90	1323.10	1311.00	1303.20	β(C–H) + ν(C–NH$_2$)
15	1277	1175.70	1173.80	1173.30	1175.60	β(C–H)
16	1156	1144.50	1144.90	1143.10	1146.90	β(C–H) + β(NH$_2$)
17	1140	1068.70	1066.40	1065.80	1066.20	β(C–H)
18	1060	1055.00	1057.40	1054.00	1060.00	Ring breath
19	984	1000.50	1004.30	1001.30	1002.90	β(C–C–C)
20	–	994.80	1000.60	990.70	997.00	γ(C-H)
21	855	976.20	982.10	974.70	979.50	γ(C-H)
22	–	865.60	870.30	864.00	865.20	γ(C-H)
23	–	859.80	859.00	858.20	858.30	β(C–C–C) + ν(C–NH$_2$)
24	764	785.40	794.30	787.70	789.60	γ(C-H)
25	735	746.90	754.10	746.70	748.40	γ(C-H)
26	–	639.60	640.10	641.90	644.00	β(C–C–C)
27	–	571.30	577.00	572.60	581.50	ω(NH$_2$)
28	–	545.70	553.90	546.60	555.70	β(C–C–C) + ω(NH$_2$)
29	–	483.00	497.10	483.10	500.00	γ(C–C–C) + γ(C-H)
30	–	418.20	420.00	417.70	418.60	γ(C–C–C)
31	–	404.70	405.90	403.60	407.50	β(C–C–N)
32	–	367.10	366.00	366.70	366.90	τ(NH$_2$)
33	–	201.60	203.60	200.20	201.80	γ(C–NH$_2$) + γ(C–C–C)
<|Error|>	–	63.92	64.05	63.86	63.08	–
<%Error>	–	3.77	3.91	3.84	3.81	–

ν: stretching; ν_{sy}: symmetric stretching; ν_{asy}: asymmetric stretching; β: in-plane bending; γ: out-of-plane bending; ω: wagging; δ: scissoring; τ: twisting.

TABLE-7
AVERAGE ABSOLUTE AND PERCENT ERRORS IN IR DATA PARAMETERS OF 2-AMINOPYRIDINE (REGULAR FONT), 3-AMINOPYRIDINE (BOLD FONT) AND 4-AMINOPYRIDINE (ITALICS FONT), AT B3LYP AND MP2 WITH DIFFERENT BASIS SETS IN GAS PHASE COMPARED TO EXPERIMENTAL DATA [Ref. 26-28]

	6-31++G(d,p)		6-31++G(2d,2p)		6-311++G(d,p)		6-311++G(2d,2p)	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
<|Error|>	63.92 **57.23** *70.58*	64.55 **84.04** *105.57*	64.05 **54.87** *69.73*	59.87 **60.47** *84.70*	63.86 **52.06** *64.28*	57.78 **70.50** *86.54*	63.08 **52.98** *68.16*	59.42 **60.44** *84.52*
<%Error>	3.77 **3.27** *3.87*	3.55 **5.16** *6.50*	3.91 **3.17** *4.34*	3.40 **3.02** *5.63*	3.84 **3.02** *3.70*	3.20 **4.51** *5.66*	3.81 **3.00** *4.35*	3.29 **3.08** *5.70*

bands at 288, 233 and 230 nm, 3-aminopyridine exhibits absorption bands at 292 nm and 4-aminopyridine exhibits absorption bands at 288 and 230 nm. The results obtained by the TD-DFT calculations showed the above mentioned absorption bands for 2-aminopyridine at 271, 247 and 236 nm, 3-aminopyridine at 277 nm and 4-aminopyridine at 249 and 230 nm. For 2-aminopyridine and 3-aminopyridine in the gas phase and all solvents, the maximum absorption wavelengths are due to the electronic transition from the HOMO to the LUMO orbital, in addition to a considerable contribution from the electronic transition between HOMO-2 and LUMO+2. While, for 4-aminopyridine the maximum absorption wavelength is due to the

TABLE-8
CALCULATED ENERGIES AND RELATIVE ENERGIES FOR 2-AMINOPYRIDINE, 3-AMINOPYRIDINE AND 4-AMINOPYRIDINE BY B3LYP/6-31++G(d,p) IN GAS PHASE AND IN DIFFERENT SOLVENTS

Medium (ε)	2-Aminopyridine		3-Aminopyridine		4-Aminopyridine	
	Total energy (au)	Relative energy (au)	Total energy (au)	Relative energy (au)	Total energy (au)	Relative energy (au)
Gas phase (1.0)	-303.6766836	-0.0082	-303.6659954	-0.0102	-303.6709085	-0.0111
Cyclohexane (2.02)	-303.6797273	-0.0052	-303.6698009	-0.0064	-303.6750388	-0.0070
Benzene (2.25)	-303.6801707	-0.0047	-303.6703533	-0.0059	-303.6756402	-0.0064
Chloroform (4.90)	-303.6823480	-0.0026	-303.6730572	-0.0032	-303.6785791	-0.0034
Acetone (20.70)	-303.6843938	-0.0005	-303.6755771	-0.0006	-303.6813160	-0.0007
Ethanol (24.55)	-303.6845160	-0.0004	-303.6752688	-0.0010	-303.6814787	-0.0005
Acetonitrile (36.64)	-303.6846937	-0.0002	-303.6759442	-0.0003	-303.6817146	-0.0003
Water (78.39)	-303.6849206	0.0000	-303.6762220	0.0000	-303.6820170	0.0000

TABLE-9
QCPs CALCULATED FOR 2-AMINOPYRIDINE (REGULAR FONT), 3-AMINOPYRIDINE (BOLD FONT) AND 4-AMINOPYRIDINE (ITALICS FONT) AT B3LYP/6-31++G(d,p) IN GAS PHASE AND IN DIFFERENT SOLVENTS

Medium (ε)	E_{HOMO} (eV)	E_{LUMO} (eV)	E.G. (eV)	μ (D)	Total negative charge
Gas phase (1.0)	-6.0693	-0.7891	5.2801	2.0399	-1.765
	-6.0867	**-0.8749**	**5.2118**	**3.3620**	**-1.205**
	-6.4282	*-0.5989*	*5.8293*	*4.1113*	*-2.4830*
Cyclohexane (2.02)	-6.0940	-0.8283	5.2657	2.3217	-1.787
	-6.0834	**-0.9089**	**5.1746**	**3.7870**	**-1.256**
	-6.4143	*-0.5445*	*5.8698*	*4.6582*	*-2.4950*
Benzene (2.25)	-6.0998	-0.8357	5.2641	2.3651	-1.789
	-6.0848	**-0.9149**	**5.1699**	**3.8478**	**-1.263**
	-6.4138	*-0.5475*	*5.8663*	*4.7478*	*-2.4950*
Chloroform (4.90)	-6.1316	-0.8749	5.2567	2.5904	-1.804
	-6.0965	**-0.9524**	**5.1441**	**4.1613**	**-1.301**
	-6.4059	*-0.5695*	*5.8363*	*5.1882*	*-2.4990*
Acetone (20.70)	-6.1686	-0.9162	5.2524	2.8191	-1.818
	-6.1128	**-0.9913**	**5.1215**	**4.4570**	**-1.338**
	-6.4119	*-0.6011*	*5.8108*	*5.5720*	*-2.5100*
Ethanol (24.55)	-6.1705	-0.9187	5.2518	2.8316	-1.818
	-6.1136	**-0.9935**	**5.1201**	**4.4743**	**-1.341**
	-6.4127	*-0.6033*	*5.8094*	*5.5938*	*-2.5090*
Acetonitrile (36.64)	-6.1751	-0.9230	5.2521	2.8539	-1.820
	-6.1153	**-0.9968**	**5.1185**	**4.4993**	**-1.343**
	-6.4135	*-0.6063*	*5.8072*	*5.6255*	*-2.5100*
Water (78.39)	-6.1789	-0.9274	5.2516	2.8774	-1.821
	-6.1174	**-1.0019**	**5.1155**	**4.5329**	**-1.347**
	-6.4138	*-0.6087*	*5.8051*	*5.6780*	*-2.5110*

transition from the HOMO to the LUMO orbital, the contribution of transition between other orbitals is phase dependent, since in the gas phase there is a considerable contribution from the transition between HOMO and LUMO+2, in cyclohexane phase a considerable contribution from the transition between HOMO-2 and LUMO+1 and LUMO+2, in chloroform and ethanol phases a considerable contribution from the transition between HOMO-2 and LUMO+1. As in literature[29], the electronic transitions in such molecules are mainly derived from the contribution of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ band transitions. In addition, the second and third absorption bands show red shift (higher wavelength) in more polar medium, for instance, the second absorption bands for 3-aminopyridine appeared at 262, 254, 250, 248 and 247 nm in the gas phase, cyclohexane, chloroform, ethanol and water, respectively.

Electric moments: The various electric moments such as components of dipole moments, μ_{tot}, mean polarizability, $<\alpha>$ and first order hyperpolarizability, β_{tot}, of the studied aminopyridines calculated at B3LYP/6-31++G(d,p) in the gas phase are given in Table-11. The dipole moment of a molecule is an important property that frequently used to study the intermolecular interactions included the non-bonded type dipole-dipole interactions, thus as the dipole moment increases the intermolecular interactions strengthens. The component of the dipole moment with the highest value is the one along the x-axis (μ_x = 0.3929, 2.4975 and 4.0337 Debye for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively), this expects large opposite charge separation in these molecules along the line passing through the amino group, this is due to the presence of this group and the highly electronegative nitrogen atom (in the *o-/m-/p*-position). The μ_{tot} values are: 2.0400, 3.3619 and 4.1114 Debye for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively, indicating the separation of charge is more predominant (as expected) in

TABLE-10
CALCULATED WAVELENGTHS, EXCITATION ENERGIES, OSCILLATOR STRENGTHS AND ORBITALS CONTRIBUTION IN GAS PHASE AND IN DIFFERENT SOLVENTS FOR 2-AMINOPYRIDINE (REGULAR FONT), 3-AMINOPYRIDINE (BOLD FONT) AND 4-AMINOPYRIDINE (ITALICS FONT), AT TD-DFT/B3LYP/6-31++G(d,p). NOTE: EXPERIMENTAL VALUES ARE IN PARENTHESIS [Ref. 29]

Medium (ε)	λ_{calc} (nm)	E_{CT} (eV)	f	Major contribution
Gas (1.0)	267.72	4.631	0.0572	H-2 → L+2 & H→L
	270.30	**4.5868**	**0.0583**	**H-2 → L+2 & H→L**
	248.63	*4.9867*	*0.0045*	*H→L & H→L+2*
	252.77	4.905	0.0073	H→L+1 & H→L+2
	262.19	**4.7288**	**0.0048**	**H→L+1 & H→L+2**
	245.81	*5.0438*	*0.0096*	*H-2→L & H-2→L+2 & H-1→L+1 & H→L+1*
	242.11	5.121	0.0041	H-1→L
	256.35	**4.8365**	**0.0055**	**H-1→L**
	243.35	*5.0948*	*0.0015*	*H-2→L+2 & H-1→L+1 & H→L+1*
Cyclohexane (2.02)	270.38	4.5855	0.0812	H-2 → L+2 & H→L
	274.14	**4.5227**	**0.0816**	**H-2 → L+2 & H→L**
	247.28	*5.0140*	*0.0186*	*H-2 → L+1 & H-2→L+2 & H→L*
	247.10	5.0175	0.0085	H→L+1 & H→L+2
	254.12	**4.8790**	**0.0042**	**H-1→L & H→L+1 & H→L+2**
	240.72	*5.1505*	*0.0072*	*H→L+1 & H→L+2*
	240.08	5.11643	0.0054	H-1→L
	253.19	**4.8969**	**0.0078**	**H-1→L & H→L+1**
	238.99	*5.1879*	*0.0001*	*H-1→L*
Chloroform (4.90)	270.83	5.106	0.0072	H-2 → L+1 & H→L
	275.66	**4.4978**	**0.0826**	**H-2 → L+1 & H→L**
	248.34	*4.9925*	*0.0206*	*H-2 → L+1 & H→L*
	242.83	5.1058	0.0072	H→L+1 & H→L+2
	250.29	**4.9536**	**0.0051**	**H-1→L**
	235.05	*5.2748*	*0.0091*	*H→L+1 & H→L+2*
	237.97	5.2100	0.0061	H-1→L
	247.70	**5.0055**	**0.0061**	**H→L+1 & H→L+2**
	234.48	*5.2876*	*0.0000*	*H-1→L*
Ethanol (24.55)	270.85	4.5776	0.0814	H-2 → L+1 & H→L
	276.42	**4.4853**	**0.0787**	**H-2 → L+1 & H→L**
	249.13	*4.9767*	*0.0202*	*H-2 → L+1 & H→L*
	240.02	5.1656	0.0058	H-1→L & H→L+1 & H→L+2
	247.83	**5.0028**	**0.0053**	**H-1→L**
	231.40	*5.3581*	*0.0000*	*H-1→L*
	236.15	5.2503	0.0064	H-1→L & H→L+2
	243.32	**5.0955**	**0.0043**	**H→L+1 & H→L+2 & H→L+3**
	230.82	*5.3714*	*0.0132*	*H→L+1 & H→L+2 & H→L+3*
Water (78.39)	270.78 (288)	4.5789	0.0803	H-2 → L+1 & H→L
	276.51 (292)	**4.4839**	**0.0774**	**H-2 → L+1 & H→L**
	249.22 (288)	*4.9749*	*0.0199*	*H-1 → L+1 & H→L*
	239.57	5.1753	0.0056	H-1→L & H→L+1 & H→L+2
	247.42 (233)	**5.0111**	**0.0053**	**H-1→L**
	230.65	*5.3755*	*0.0000*	*H-2→L*
	235.80 (230)	5.2580	0.0065	H-1→L & H→L+2
	242.60	**5.1106**	**0.0039**	**H→L+1 & H→L+2 & H→L+3**
	230.15 (230)	*5.3871*	*0.0143*	*H→L+1 & H→L+2 & H→L+3*

H=HOMO; L=LUMO

4-aminopyridine followed by 3-aminopyridine 2-aminopyridine. Non-linear optical (NLO) activity was extensively investigated by calculating the first hyperpolarizability parameter. A large β_{tot} indicates a good NLO material[25,30,31]. Aminopyridines show significantly large β_{tot} values (3.0276×10^{-30}, 3.0441×10^{-30} and 1.6075×10^{-30} esu for 2-aminopyridine, 3-aminopyridine and 4-aminopyridine, respectively) comparable to those of NLO active molecules, for instance, ≈ 15 to 8 times more than that of urea (0.1947×10^{-30} esu), therefore, these molecules make good candidates as NLO materials.

Conclusion

The optimized geometries calculated at the B3LYP and MP2 levels of theory have a high accuracy and close to each other and showed a good agreement with the experimental data. It was shown that the higher basis set used in the calculations,

TABLE-11
DIPOLE MOMENT (IN DEBYE), MEAN POLARIZABILITY AND FIRST STATIC HYPERPOLARIZABILITY (IN au/esu × 10^{-30}) IN GAS PHASE FOR STUDIED AMINOPYRIDINES AT B3LYP/6-31++G(d,p) IN GAS PHASE

Polarizability	2-Aminopyridine	3-Aminopyridine	4-Aminopyridine	First static hyperpolarizability	2-Aminopyridine	3-Aminopyridine	4-Aminopyridine
α_{xx}	98.52561	97.42329	94.58247	β_{xxx}	-349.61799	-320.47897	-270.74197
α_{xy}	1.35097	-2.08017	-0.00001	β_{xxy}	-25.47780	26.17552	-0.00008
α_{yy}	78.65358	78.69351	80.77927	β_{xyy}	42.83690	1.55888	67.73568
α_{xz}	-0.37064	-0.33251	-0.28426	β_{yyy}	4.92097	22.06190	-0.00001
α_{yz}	0.08224	0.05589	-0.00000	β_{xxz}	14.48280	16.19101	12.98824
α_{zz}	440.26970	43.63695	43.73409	β_{xyz}	-1.60401	-0.47193	-0.00009
$<\alpha>$ (au)	205.816	73.251	35.857	β_{yyz}	5.54414	8.30709	6.62649
$<\alpha>$ (esu × 10^{-30})	1.7781	6.3284	3.0978	β_{xzz}	-43.55266	-23.91345	17.13488
μ_x	0.3929	2.4975	4.0337	β_{yzz}	17.71479	32.61409	0.00001
μ_y	1.8146	2.0386	0.0000	β_{zzz}	14.14309	18.49869	17.71067
μ_z	0.8453	0.9536	0.7956	β_{tot} (au)	350.4428	352.3603	186.0721

the more stabilized geometry is obtained using both the B3LYP and MP2 methods. Moreover, the B3LYP calculated total energy has a higher negative value compared with that obtained by MP2 at the same basis set. The un-scaled frequencies are completely in a good agreement with the experimental frequencies and thus in this case, no need for scaling the frequencies. Solvent effect on FMO were studied using DFT-B3LYP at the 6-31++G(d,p) using PCM model. TD-DFT calculations showed that the electronic transitions are mainly derived from the contribution of $\pi\rightarrow\pi^*$ or $n\rightarrow\pi^*$ types. First hyperpolarizability calculations demonstrated that these molecules are active NLO materials.

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