Computational Studies on C₃H₄N₂ Isomers

E.E. Etim*, U. Lawal, C. Andrew, I.S. Udegbunam

Department of Chemical Science, Federal University, Wukari Nigeria

*Corresponding Author: *E.E. Etim, Department of Chemical Science, Federal University, Wukari Nigeria*

Abstract: *The $C_3H_4N_2$ isomers comprising of thirteen members were subjected to computational calculations using the Gaussian 4 compound method. Important parameters including dipole moment, bond distance and angle, standard enthalpy of formation, rotational constants and vibrational frequencies were obtained from the optimized geometries of these isomers and compared with experimental results where available. Imidazole was found to be the most stable among the $C_3H_4N_2$ isomers with the least standard enthalpy of formation of 26.641 kcal/mol. The bond distances and angles for Imidazole and Pyrazole were observed to be in excellent agreement with the measured experimental values. Additionally, the computationally calculated rotational constants; A=9.7740943, B=9.4123152, C=4.7948970 and A=12.4751355, B=3.8580794, C=3.0007692, and dipole moments of 3.8535D and 2.2268D for Imidazole and Pyrazole respectively were accurately determined when compared with experimental results. Thus, the high accuracy obtained from this quantum chemical calculation indicates that other $C_3H_4N_2$ isomers with no experimental values are well predicted with the Gaussian-4G4 compound model.*

Keywords: *Isomer, Computational, Gaussian-4, Experimental, Accuracy.*

1. INTRODUCTION

Quantum Mechanics forms the bedrock of computational chemistry, which is primarily concern with the numerical computation of the molecular electronic structures and its interactions. Quantum Mechanics compliments the classical mechanics because it takes into consideration additionally the wavelike nature property of matter when providing solutions to chemical problems. Quantum and classical mechanics, statistical physics and thermodynamics are the foundation of most computational theories and programs software. This is because they use mathematics to model atoms and molecular compounds. [1, 2] The versatility of computational chemistry in enhancing our knowledge of chemical phenomena within chemical specie or reaction path is ever on the increase. Quantum chemical calculations were only true for a few molecules until recently. The ever widening computational power has increased the complexity and rigor of quantum mechanical (QM) calculations.

Computational chemistry has increasingly evolve to impact several aspects of chemistry and has found usefulness in study important properties of atoms and molecules which are not limited to electronic structure determinations, geometry optimization, frequency calculations, definition of transition structure and reaction paths, protein calculations, potential energy surface calculations, docking, rates constants. [3, 4]

By far the most important computational techniques are the ab-initio (Latin word "from scratch") a set of approaches in which molecular structures are calculated with Schrodinger equations, Semi-empirical techniques uses approximations from experimental data to provide inputs into mathematical models and lastly the Molecular Mechanics uses classical physics and semi-empirical force field to explain and interpret the behavior of atoms or molecules.

G4 compound model methods used in this research is one of the popular procedures for computing the total energies of molecular species at their equilibrium geometries; unlike its DFT counterpart that consist of a single job, compound methods consist of several component calculations whose result are assembled in a prescribed manner. G4 method runs both Hartree-fock and Post SCF method whose main advantage is giving highly accurate result at less computational cost. The Gaussian theory 4 (G4

and G4MP2) with analogous have been widely used for thermodynamic property calculations for most systems. G4 level of calculations are mostly used for geometry optimization, Zero Potential Energy ZPE, Single Point calculations etc. [5-7]

C$_3$H$_4$N$_2$ isomeric group consists of important biological molecules; the imidazole ring structure occurs in fundamental biological molecules such as histidine (an amino acid) and purines; imidazolium and pyrazolium-based ionic surface are now receiving attention of researches as good materials for biosensing; pyrazole and its derivatives are important constituents of many drugs because of their muscle relaxing, antidiabetic, analgesic, anti-inflammatory, and other biological activities. [8, 9] As important as the molecules are, some of them have not really been studied experimentally partly due to their unstable nature and as such some of their potential applications are still not known. Thus, there is dearth of information regarding some to the chemical properties/parameters of some of these isomeric species. Computational chemistry has the advantage of treating these set of molecules irrespective of their stability. In the present studies, we aim to use computational methods in investigating the C$_5$H$_5$N isomers and predicting some parameters of interest such as the IR frequencies and intensities, dipole moment, rotational constants, bond length and angles, standard enthalpy of formation, etc. The predicted parameters will also be compared with the available experimental data from literature.
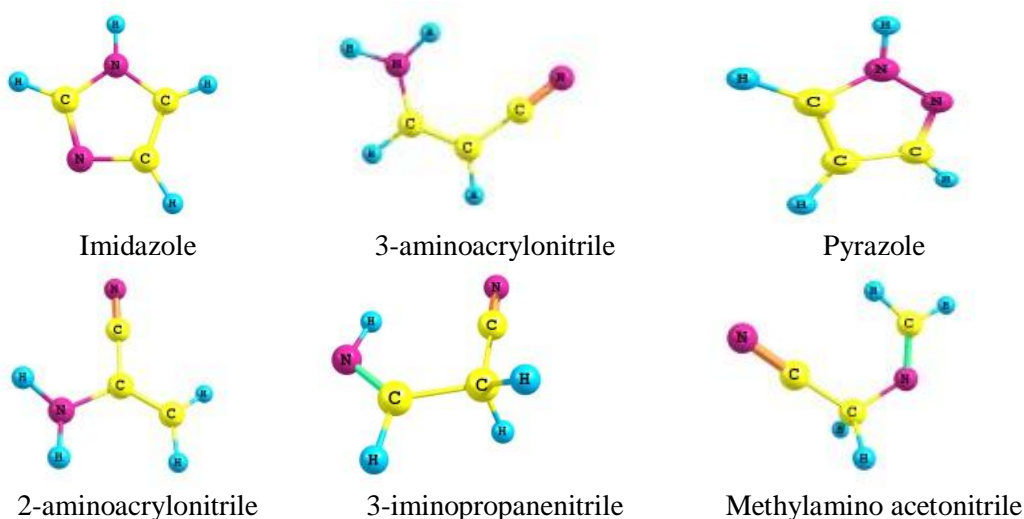
2. COMPUTATIONAL METHOD

The GAUSSIAN 09 suite of programs was used for all the quantum chemical calculations reported in this work. Among the different composite quantum chemical methods that are now in use to accurately calculate several chemical parameters of interest, the G4 method has been found to be very effective in predicting these parameters in many molecules as reported in literatures. The molecules were optimized at the G4 level of theory. The optimized structures were found to be stable with no imaginary frequency as shown from the frequency calculations. [10-20]
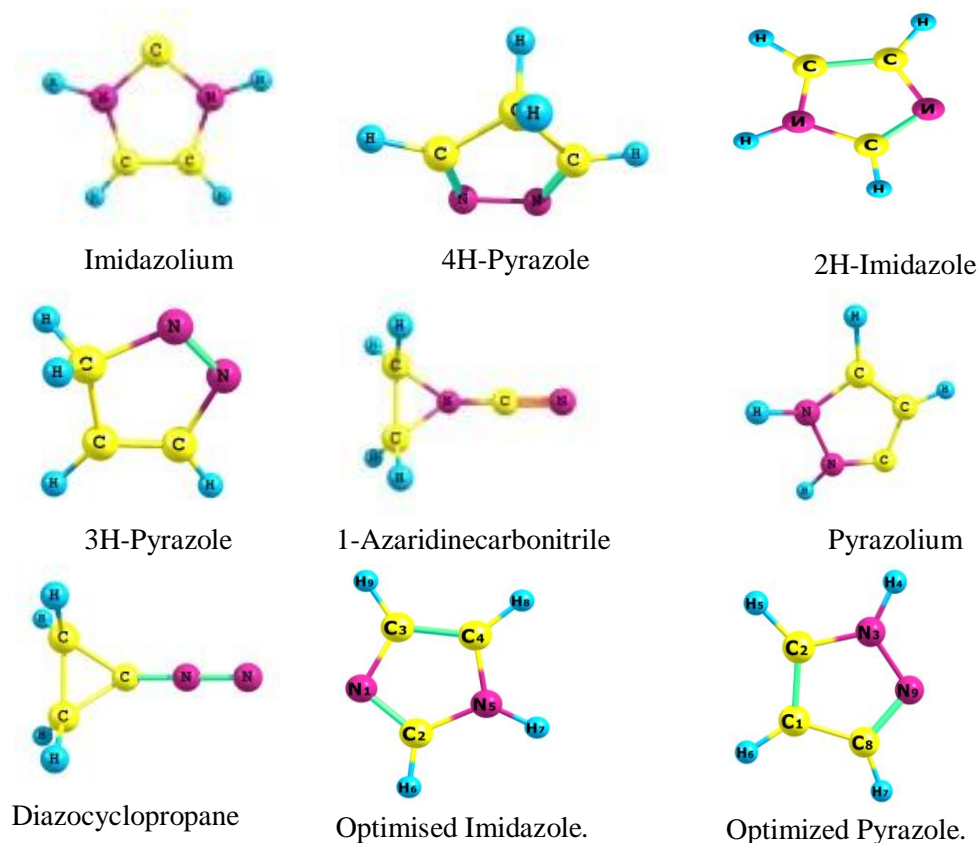
3. RESULTS AND DISCUSSION

The quantum chemical calculations carried out in this study for C$_3$H$_4$N$_2$ isomers or the Imidazole group (Imidazole, 3-aminoacrylonitrile, Pyrazole, 2-aminoacrylonitrile, 3-iminopropanenitrile, Methylamino acetonitrile, Imidazolium, 4H-Pyrazole, 2-Azaridinecarbonitrile, 3H-Pyrazole, 1-Azaridinecarbonitrile, Pyrazolium, Diazocyclopropane) was based on G4 computational method described above are discussed under the following separate sub-headings and the results are compared with literature experimental values where available.

3.1. Thermochemistry

The optimized structures of C$_3$H$_4$N$_2$ isomeric group figure 1 and the calculated standard enthalpies of formation ($\Delta_f H^O$) table 1 using the G4 method was illustrated. From Table 1 it is clear that the least calculated enthalpies of formation of the isomers of C$_3$H$_4$N$_2$ is Imidazole corresponding to the most stable isomer of the group while the highest calculated value of $\Delta_f H^O$ is Diazocyclopropane and the least stable isomer. [21]


| Imidazole | 3-aminoacrylonitrile | Pyrazole |
| 2-aminoacrylonitrile | 3-iminopropanenitrile | Methylamino acetonitrile |

Imidazolium   4H-Pyrazole   2H-Imidazole

3H-Pyrazole   1-Azaridinecarbonitrile   Pyrazolium

Diazocyclopropane   Optimised Imidazole.   Optimized Pyrazole.

Fig1. *Optimized geometry of C$_3$H$_4$N$_2$ isomers*

Table1. *Standard enthalpy of formation*

Molecules	Enthalpy of formation (kcal/mol)
Imidazole	26.641
3-aminoacrylonitrile	35.805
Pyrazole	36.958
2-aminoacrylonitrile	43.493
3-iminopropanenitrile	44.297
Methylamino acetonitrile	50.649
Imidazolium	53.781
4H-Pyrazole	59.291
2-Azaridinecarbonitrile	62.042
3H-Pyrazole	63.298
1-Azaridinecarbonitrile	65.786
Pyrazolium	86.986
Diazocyclopropane	91.710

3.2. Vibrational Spectroscopy

Table 2 contains the vibrational frequencies of pyridine and figure 2 depicts the corresponding spectrum. As shown in Table 2, the percentage error of the predicted vibrational frequencies of pyridine with known experimental values [22] ranges between 1-6% which is accurate and is within experimental accuracy from a spectroscopic point of view. Thus, our results of the calculated vibrational frequencies of pyridine using the G4 method which is in excellent agreement with the reported experimental values can be logically concluded that the other vibrational frequencies and the spectrums of C$_3$H$_4$N$_2$ isomers reported in this work (see appendix) are well predicted since they have no experimental determined results.
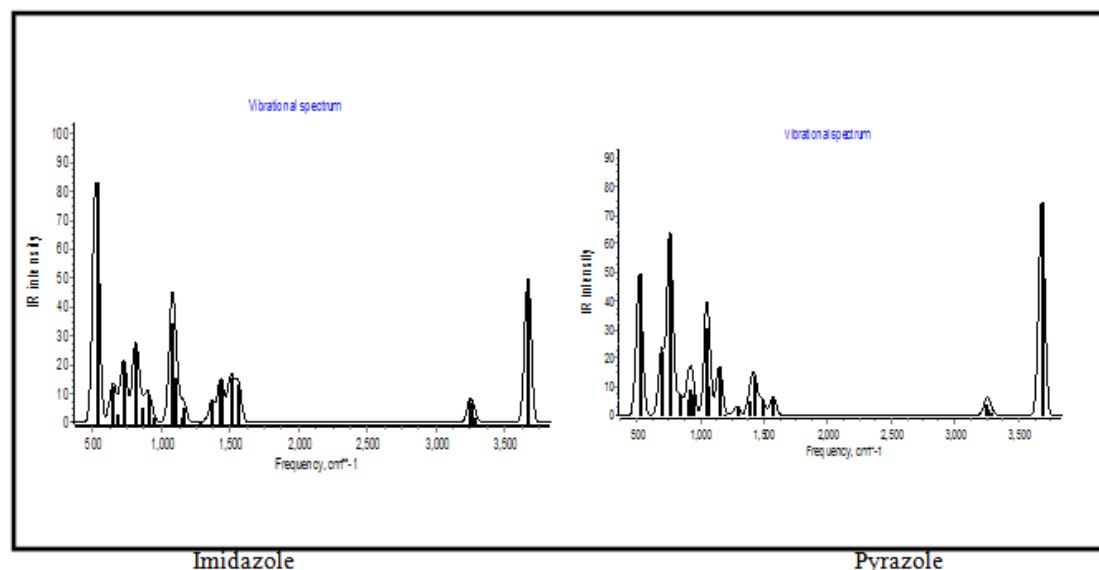
Figure2. *Calculated FT-IR Spectrum of Imidazole and Pyrazole*

Table2. *Calculated and experimental IR frequencies Imidazole and Pyrazole*

Cal. Frequency (cm^{-1}) Of Imidazole	Exp. Frequency (cm^{-1}) of Imidazole	% Error (cm^{-1})	Cal. Frequency (cm^{-1}) Of Pyrazole	Exp. Frequency (cm^{-1}) of Pyrazole	% Error (cm^{-1})
527	539	2.23	525	516	1.74
648	621	4.35	639	623	2.57
686	663	3.47	697	674	3.41
730	758	3.69	764	745	2.55
814	831	2.05	838	833	0.60
861	898	4.12	898	879	2.16
906	923	1.84	922	908	1.54
945	988	4.35	941	924	1.84
1080	1098	1.64	1053	1009	4.36
1102	1013	8.79	1062	1054	0.76
1153	1062	8.57	1150	1121	2.59
1165	1188	1.94	1186	1159	2.33
1287	1265	1.74	1286	1254	2.55
1369	1404	2.49	1388	1358	2.21
1435	1448	0.90	1423	1395	2.01
3250	3110	4.50	1485	1447	2.63
3253	3123	4.16	1571	1531	2.61
3283	3143	4.45	3246	3126	3.84
3669	3517	4.32	3260	3137	3.92
-	-	-	3281	3155	3.99
-	-	-	3678	3523	4.40

3.3. Rotational Constants

In Table 3, the equilibrium rotational constants for the C$_3$H$_4$N$_2$ isomers calculated at the G4 level of theory are shown. The error difference between the calculated and experimental rotational constants data [23] for Imidazole and Pyrazol reveal that there is consistency and therefore shows high accuracy in our findings. This work gives the rotational constant values of 9.7740943, 9.4123152, 4.7948970 GHz for pyridine and 12.4751355, 3.8580794, 3.0007692 GHz are consistent with reported experimental results of -, -, - GHz and -, -,- GHz. [24] Therefore, for the C$_3$H$_4$N$_2$ isomers with no experimental data, it is concluded that the G4 computational method has predicted the parameters with high accuracy.

Table3. *Rotational constants (GHz) for the C₃H₄N₂ isomers*

Molecules		Rotation constants (GHz)		
		A	B	C
Imidazole	Calculated	9.7740943	9.4123152	4.7948970
	Experimental			
	% Error			
3-aminoacrylonitrile	Calculated	9.6697127	9.4487871	4.7789869
Pyrazole	Calculated	12.4751355	3.8580794	3.0007692
	Experimental			
	% Error			
2-aminoacrylonitrile	Calculated	9.6338807	9.4116762	4.7607411
3-iminopropanenitrile	Calculated	9.6405275	9.4116300	9.6405275
Methylamino acetonitrile	Calculated	9.9930178	4.2951802	3.0129016
Imidazolium	Calculated	9.4487926	9.3420241	4.7160736
4H-Pyrazole	Calculated	11.9200528	3.7346109	2.8940953
2-Azaridinecarbonitrile	-	-	-	-
3H-Pyrazole	Calculated	18.8873495	3.6111591	3.2882130
1-Azaridinecarbonitrile	Calculated	17.6290216	3.7565371	3.4786160
Pyrazolium	Calculated	9.3456882	8.8697616	4.682251
Diazocyclopropane	Calculated	9.7730717	9.4153665	4.7954425

3.4. Structural Parameters

The optimized structural parameters such as bond length and bond angles for Imidazole and Pyrazole are presented in Tables 4 and 5 respectively. As shown in Table 4, the high consistency of these parameters calculated for Imidazole and Pyrazole which their experimental values have been determined [25] ranges between 0 – 0.399 Å. The high consistency of the bond distances angles determined shows that other C₃H₄N₂ isomers with no experimental measured results can presumed to be well foretold at the G4 level of theory.

Table4. *Bond distance and angles of Imidazole*

Description	Experimental Value (Å)	Calculated Value (Å)	Error	Connectivity		
				Atom 1	Atom 2	Atom 3
rNH	0.998	1.006	0.008	5	7	-
rCH	1.079	1.079	0	4	8	-
rCH	1.078	1.077	0.001	3	9	-
rCH	1.079	1.080	0.001	2	6	-
rCN	1.364	1.313	0.051	1	2	-
rCN	1.314	1.377	0.063	1	3	-
rCN	1.382	1.364	0.018	2	5	-
rCC	1.364	1.369	0.005	3	4	-
rCN	1.377	1.378	0.001	4	5	-
aNCN	111.99	111.722	0.268	1	2	5
aCNC	104.93	105.265	0.335	3	1	2
aCCN	110.69	110.717	0.027	1	5	3
aCCN	105.48	105.081	0.399	5	3	9
aCNC	106.9	107.215	0.315	3	9	8

Table5. *Bond distance and angles of Pyrazole*

Description	Experimental Value (Å)	Cal. Value (Å)	Error	Connectivity		
				Atom 1	Atom 2	Atom 3
rNN	1.351	1.346	0.005	3	9	-
rCN	1.332	1.355	0.023	2	3	-
rCC	1.417	1.412	0.005	1	8	-
rCC	1.374	1.379	0.005	1	2	-
rCN	1.360	1.330	0.03	8	9	-
rNH	1.002	1.005	0.003	3	4	-
rCH	1.083	1.078	0.005	2	5	-
rCH	1.080	1.078	0.002	1	6	-
rCH	1.082	1.080	0.002	8	7	-

aCNN	104.1	104.0	0.1	3	9	8
aCCN	112.0	112.0	0.0	1	8	9
aCCC	104.5	104.4	0.1	2	4	6
aCCN	106.4	106.2	0.2	1	2	3
aCNN	113.0	113.3	0.3	2	3	9
aHCN	119.3	119.5	0.2	5	2	3
aHCC	127.9	127.2	0.7	6	1	2
aHCN	121.4	121.7	0.3	5	2	3
aHNN	118.4	118.9	0.5	4	3	9

The reported C-C and C-N bond distance reported in this work compares favourably well with the studied once. [26] The C-N bond length was shorter in Imidazole (1.313 Å) and longer in Pyrazole (1.330 Å). As observed in Table 4 and 5, the calculated bond radius and angles are in good agreement with the determined experimental data for pyridine as reported by [25].

3.5. Dipole Moment

Dipole moment is an important molecular property widely used to probe the infra-red spectroscopy of molecule. A molecule is IR active only when it is associated with change in dipole moments. Thus, provided that there is a dipole moment change during a normal molecular vibration, rotation and molecular rotation–vibration or from combinations, chemical compounds can absorb IR and are said to be IR active. Table 6 shows the dipole moments of C_5H_5N isomers at the G4 method. The highest calculated dipole moment was found to be 5.21 D for 1-cynao-1,3-butadiene and the lowest value was observed for azafulvene (1.02 D). The dipole moment of pyridine (2.33 D) in this study agrees well with the experimental reported literature data [24 and 26].

Table6. *Dipole moment (Debye) for C_5H_5N isomers*

Dipole Moment			
Molecules	Calculated Dipole Moment (Debye)	Experimental Dipole Moment (Debye)	% Error
Imidazole	3.8535		
3-aminoacrylonitrile	2.4286	-	-
Pyrazole	2.2268		
2-aminoacrylonitrile	2.9214	-	-
3-iminopropanenitrile	3.0205	-	-
Methylamino acetonitrile	4.3549	-	-
Imidazolium	4.9761	-	-
4H-Pyrazole	4.1976	-	-
2-Azaridinecarbonitrile	-	-	-
3H-Pyrazole	1.9403	-	-
1-Azaridinecarbonitrile	5.4213	-	-
Pyrazolium	3.6766	-	-
Diazocyclopropane	3.8517	-	-

4. CONCLUSION

This work have efficaciously used G4 level of theory to optimize the structures of thirteen $C_3H_4N_2$ isomers. Some important quantum chemical parameters were determined and compared with measured experimental values where available. The high correlation observed between the calculated and the known experimental data for some of the isomers studied in this work indicates that other $C_3H_4N_2$ isomers with no experimental values are predicted correctly based on the quantum chemical study using G4 method. 2-Azaridinec arbonitrile optimized file crashed providing no further computational information about the molecule.

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TableA1. *Bond radius and angles of C$_3$H$_4$N$_2$ isomers*

Methylaminoacetonitrile			Imidazolium		3- aminocerylonitrile	
Description	Exp. Value	Cal. value	Description	Cal. Value	Description	Cal. Value
R(1-2)	-	1.355	R(1-2)	1.379	R(1-2)	1.355
R(1-4)	-	1.086	R(1-6)	1.078	R(1-4)	1.086
R(1-7)	-	1.358	R(1-8)	1.412	R(1-7)	1.358
R(2-3)	-	1.081	R(2-3)	1.355	R(2-3)	1.081
R(2-5)	-	1.414	R(2-5)	1.078	R(2-5)	1.414
R(5-6)	-	1.162	R(3-4)	1.006	R(5-6)	1.162
R(7-8)	-	1.009	R(3-9)	1.346	R(7-8)	1.009
R(7-9)	-	1.004	R(7-8)	1.080	R(7-9)	1.004
A(2-1-4)	-	119.1	R(8-9)	1.330	A(2-1-4)	119.1
A(2-1-7)	-	126.2	A(2-1-6)	127.2	A(2-1-7)	126.2
A(1-2-3)	-	120.1	A(2-1-8)	104.4	A(1-2-3)	120.1
A(1-2-5)	-	121.2	A(1-2-3)	106.2	A(1-2-5)	121.2
A(4-1-7)	-	114.6	A(1-2-5)	132.1	A(4-1-7)	114.6
A(1-7-8)	-	118.7	A(6-1-8)	128.4	A(1-7-8)	118.7
A(1-7-9)	-	119.5	A(1-8-7)	128.4	A(1-7-9)	119.5
A(3-2-5)	-	118.7	A(1-8-9)	112.0	A(3-2-5)	118.7
A(2-5-6)	-	177.5	A(3-2-5)	121.7	A(2-5-6)	177.5
A(8-7-9)	-	116.3	A(2-3-4)	127.8	A(8-7-9)	116.3
-	-	-	A(2-3-9)	113.3	-	-
-	-	-	A(4-3-9)	118.9	-	-
-	-	-	A(3-9-8)	104.0	-	-
-	-	-	R(1-2)	1.379	-	-

TableA2. *Bond radius and angles of C$_3$H$_4$N$_2$ isomers*

2-aminoacrylonitrile			pyrazolium		3-iminopropanenitrile	
Description	Exp. Value	Cal. Value	Description	Cal. Value	Description	Cal. Vaue
R(1-2)	-	1.438	R(1-2)	1.370	R(1-2)	1.026
R(1-9)	-	1.157	R(1-7)	1.079	R(2-3)	1.262
R(2-3)	-	1.396	R(1-9)	1.448	R(3-4)	1.527
R(2-6)	-	1.342	R(2-3)	1.364	R(3-7)	1.094
R(3-4)	-	1.010	R(2-6)	1.080	R(4-5)	1.458
R(3-5)	-	1.010	R(3-5)	1.012	R(4-8)	1.098
R(6-7)	-	1.084	R(3-8)	1.402	R(4-9)	1.098
R(6-8)	-	1.080	R(4-8)	1.007	R(5-6)	1.155
A(2-1-9)	-	178.4	R(8-9)	1.336	A(1-2-3)	111.6
A(1-2-3)	-	114.1	A(2-1-7)	125.0	A(2-3-4)	128.5
A(1-2-6)	-	119.6	A(2-1-9)	110.2	A(2-3-7)	118.4
A(3-2-6)	-	126.1	A(1-2-3)	108.7	A(4-3-7)	113.0
A(2-3-4)	-	114.2	A(1-2-6)	132.3	A(3-4-5)	113.1
A(2-3-5)	-	115.0	A(7-1-9)	124.8	A(3-4-8)	109.2
A(2-6-7)	-	121.2	A(1-9-8)	101.4	A(3-4-9)	109.2
A(2-6-8)	-	120.7	A(3-2-6)	119.0	A(5-4-8)	109.6
A(4-3-5)	-	112.1	A(2-3-5)	124.2	A(5-4-9)	109.5
A(7-6-8)	-	118.1	A(2-3-8)	104.4	A(4-5-6)	177.6
-	-	-	A(5-3-8)	119.7	A(8-4-9)	106.0
-	-	-	A(3-8-4)	116.6	-	-
-	-	-	A(3-8-9)	114.9	-	-

TableA3. *Bond radius and angles of C$_3$H$_4$N$_2$ isomers*

4H-Pyrazole			Diazocyclopropane			1-Aziridinecarnitrile		
Description	Exp. Value	Cal. Value		Exp. Value	Cal. Value		Exp. Value	Cal. Value
R(1-2)	-	1.497	R(1-2)	1.137		R(1-2)	1.484	
R(1-3)	-	1.497	R(2-3)	1.295		R(1-4)	1.085	
R(1-4)	-	1.098	R(3-4)	1.498		R(1-5)	1.479	
R(1-7)	-	1.098	R(3-5)	1.498		R(1-9)	1.085	
R(2-6)	-	1.084	R(4-5)	1.515		R(2-3)	1.085	
R(2-9)	-	1.282	R(4-7)	1.087		R(2-5)	1.478	
R(3-5)	-	1.084	R(4-9)	1.087		R(2-8)	1.085	
R(3-8)	-	1.282	R(5-6)	1.087		R(5-6)	1.344	
R(8-9)	-	1.447	R(5-8)	1.087		R(6-7)	1.161	
A(2-1-3)	-	97.6	A(1-2-3)	171.8		A(2-1-4)	118.0	
A(2-1-4)	-	113.2	A(2-3-4)	126.1		A(2-1-5)	59.9	
A(2-1-7)	-	113.2	A(2-3-5)	126.1		A(2-1-9)	120.1	
A(1-2-6)	-	125.9	A(4-3-5)	60.7		A(1-2-3)	118.0	
A(1-2-9)	-	112.9	A(3-4-5)	59.6		A(1-2-5)	59.9	
A(3-1-4)	-	113.2	A(3-4-7)	119.2		A(1-2-8)	120.1	
A(3-1-7)	-	113.2	A(3-4-9)	116.6		A(4-1-5)	117.1	
A(1-3-5)	-	125.9	A(3-5-4)	59.6		A(4-1-9)	115.9	
A(1-3-8)	-	112.9	A(3-5-6)	116.6		A(5-1-9)	113.7	
A(4-1-7)	-	106.7	A(3-5-8)	119.2		A(1-5-2)	60.3	
A(6-2-9)	-	121.2	A(5-4-7)	117.3		A(1-5-6)	118.6	
A(2-9-8)	-	108.3	A(5-4-9)	118.8		A(3-2-5)	117.1	
A(5-3-8)	-	121.2	A(4-5-6)	118.8		A(3-2-8)	115.9	
A(3-8-9)	-	108.3	A(4-5-8)	117.3		A(5-2-8)	113.8	
-	-	-	A(7-4-9)	114.5		A(2-5-6)	118.6	
-	-	-	A(6-5-8)	114.5		A(5-6-7)	176.2	

TableA4. *Bond radius and angles of C$_3$H$_4$N$_2$ isomers*

3H-Pyrazole			2H-Imidazole	
Description	Exp. values	Cal. Values	Description	Cal. Values
R(1-3)	-	1.476	R(1-2)	1.369
R(1-4)	-	1.098	R(1-4)	1.377
R(1-7)	-	1.488	R(1-6)	1.079
R(1-9)	-	1.098	R(2-5)	1.378
R(2-5)	-	1.080	R(2-7)	1.077
R(2-6)	-	1.433	R(3-4)	1.312
R(2-7)	-	1.338	R(3-5)	1.363
R(3-6)	-	1.258	R(3-9)	1.080
R(7-8)	-	1.079	R(5-8)	1.006
A(3-1-4)	-	108.5	A(2-1-4)	110.7
A(3-1-7)	-	104.4	A(2-1-6)	128.0
A(3-1-9)	-	108.4	A(1-2-5)	105.1
A(1-3-6)	-	109.4	A(1-2-7)	132.9
A(4-1-7)	-	114.4	A(4-1-6)	121.3
A(4-1-9)	-	106.5	A(1-4-3)	105.3
A(7-1-9)	-	114.4	A(5-2-7)	122.0
A(1-7-2)	-	105.3	A(2-5-3)	107.2
A(1-7-8)	-	126.2	A(2-5-8)	126.2
A(5-2-6)	-	118.8	A(4-3-5)	111.7
A(5-2-7)	-	130.7	A(4-3-9)	126.1
A(6-2-7)	-	110.5	A(5-3-9)	122.2
A(2-6-3)	-	110.4	A(3-5-8)	126.6
A(2-7-8)	-	128.5	-	-

TableA5. *Vibrational frequencies of C₃H₄N₂ isomers*

2-aminoacrylonitrile		3-aminoacrylonitrile		3-iminopropanenitrile	
Frequency (cm⁻¹)	IR Intensities	Frequency (cm⁻¹)	IR Intensities	Frequency (cm⁻¹)	IR Intensities
525.0991	49.5264	575.9086	21.5883	202.9736	4.4959
639.277	0.0158	613.5534	0.0008	282.4279	19.7673
696.5904	22.2741	668.9532	0.0017	323.8778	13.1254
764.2045	63.6165	699.7175	1.1013	418.0543	4.6422
838.3296	7.0223	747.1274	171.6459	584.6423	181.5905
898.2095	5.0609	789.7703	0.0003	619.6409	53.7269
922.0133	9.375	920.1467	6.2397	683.7984	36.5688
941.0864	6.8674	926.291	3.98	725.3752	11.0116
1052.8633	30.536	1043.3008	22.0329	798.0997	2.2322
1061.9965	10.0182	1087.8465	9.5104	851.4581	52.6581
1150.2697	17.0397	1125.6724	10.3872	996.9491	6.3731
1185.6737	0.5771	1170.6652	0.0026	1133.078	3.4591
1286.2342	2.9288	1195.6093	0.287	1369.5018	58.8475
1387.5529	4.6676	1378.2362	3.6771	1446.071	1.5746
1422.958	13.6676	1393.1147	1.1407	1648.7204	32.8006
1485.1453	5.7641	1426.6761	28.4913	1688.3309	100.2896
1570.9814	6.3784	1617.7249	3.4538	2349.8673	11.8365
3246.0357	4.1271	3270.379	0.0859	3173.6549	3.9546
3260.4999	2.1455	3292.8518	1.5813	3276.721	1.2406
3280.5216	1.0434	3680.9036	97.2891	3561.3081	24.3418
3678.0259	74.4526	3682.1438	11.5568	3665.2661	21.0867
-	-	-	-	-	-

TableA6. *Vibrational frequencies of C₃H₄N₂ isomers*

Pyrazolium		Methylamino acetonitrile		Diazocyclopropane	
Frequency (cm⁻¹)	IR Intensities	Frequency (cm⁻¹)	IR Intensities	Frequency (cm⁻¹)	IR Intensities
393.399	185.1824	155.3421	7.0812	188.9509	9.2621
502.4211	65.0948	158.1273	5.8571	221.421	0.9945
601.4359	1.7357	379.2821	0.5801	553.0264	12.4105
657.4788	44.6608	423.363	1.5866	607.7282	0.7049
810.1463	35.6321	664.6791	5.2317	701.8706	16.0436
879.9919	4.9731	691.078	7.6882	800.3027	12.2606
905.5418	10.5093	848.3289	4.7301	906.6643	0.0691
917.7199	0.3647	984.8225	0.6734	963.0744	2.2665
973.5122	21.0466	988.6017	4.5255	1000.11	3.558
1071.757	11.5487	1147.7029	47.3786	1058.8602	1.209
1122.9111	22.8874	1219.9176	0.7249	1086.9585	47.469
1131.2264	5.617	1228.022	75.2103	1090.0172	5.5157
1266.927	21.6269	1330.6685	47.8396	1174.1022	0.0519
1348.2035	10.2814	1417.7048	17.6859	1433.0929	26.5465
1359.2695	6.6717	1445.8746	20.0989	1469.8808	0.1694
1491.006	10.6498	1741.3101	44.6298	1503.8835	46.6755
1513.2955	14.5404	2367.1923	4.2477	2205.7947	521.6628
3239.6069	1.71	3034.5872	0.9447	3110.1689	21.0886
3258.8842	5.9301	3067.4194	0.327	3110.4737	25.4667
3580.2733	24.6591	3091.5764	29.1032	3187.3116	0.0461
3647.1408	53.4047	3413.1022	1.2466	3201.1546	15.4516
-	-	-	-	-	-

TableA7. *Vibrational frequencies of C₃H₄N₂ isomers*

1-Azaridine carbonitrile		3H-Pyrazole		Imidazolium	
Frequency (cm^{-1})	IR Intensities	Frequency (cm^{-1})	IR Intensities	Frequency (cm^{-1})	IR Intensities
219.4103	4.4663	364.3905	10.3502	575.9086	21.5883
230.4277	3.3272	575.3528	5.1044	613.5534	0.0008
583.9591	3.6844	734.1264	13.1875	668.9532	0.0017
604.2676	0.6652	852.3408	0.5777	699.7175	1.1013
725.1352	22.4458	874.9645	0.055	747.1274	171.6459
823.3427	3.2726	914.5733	15.8186	789.7703	0.0003
843.9995	2.1245	939.0455	12.015	920.1467	6.2397
1033.5285	35.4058	946.4211	2.7426	926.291	3.98
1045.1415	0.2738	959.6332	5.4982	1043.3008	22.0329
1118.2427	1.8408	990.4822	15.5635	1087.8465	9.5104
1144.0223	2.0702	1120.8447	0.0684	1125.6724	10.3872
1184.7513	0.1063	1125.1653	9.224	1170.6652	0.0026
1190.8706	14.605	1258.2445	8.4671	1195.6093	0.287
1326.976	53.6226	1327.4239	20.0942	1378.2362	3.6771
1490.8011	1.2911	1390.6796	15.1938	1393.1147	1.1407
1515.507	10.418	1503.4348	12.7873	1426.6761	28.4913
2339.196	137.2211	1623.7317	2.9905	1617.7249	3.4538
3132.55	10.1578	3038.4585	0.4966	3270.379	0.0859
3135.8971	11.3025	3070.723	0.5829	3292.8518	1.5813
3223.9249	0.5287	3244.0255	1.5888	3680.9036	97.2891
3237.7969	5.5766	3269.242	3.3183	3682.1438	11.5568

TableA8. *Vibrational frequencies of C₃H₄N₂ isomers*

4H-Pyrazole		2H-Imidazole	
IR frequency	Intensities	IR frequency	Intensities
360.8472	0.0029	524.185	83.1349
525.1171	0	647.1016	12.3589
736.2805	12.1845	685.9971	3.1418
843.0621	0	729.2656	21.0757
846.8335	3.7602	814.8322	26.7511
871.3088	0.0263	861.6157	5.1441
893.5356	1.6014	905.6804	9.849
948.3713	0.9229	945.1978	1.2525
978.4525	14.4492	1078.5209	34.1322
986.5913	6.9645	1101.6394	15.3656
1123.285	0	1153.056	2.0436
1246.9104	0.4118	1164.9212	5.2322
1278.8229	18.2799	1287.1201	0.3966
1300.4942	9.3567	1369.3399	7.1738
1401.9305	23.4551	1434.8256	14.9076
1607.5964	15.8108	1508.9526	15.9976
1618.5266	3.6991	1562.7499	13.3686
3041.4076	0.2704	3249.4101	6.8253
3075.6116	0.6848	3252.3032	0.4411
3203.598	10.497	3282.7834	2.0618
3207.8204	0.2139	3671.9607	49.8887

APPENDIX B. *Vibrational spectra of C₃H₄N₂ isomers*

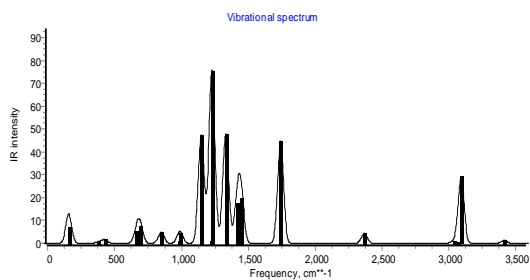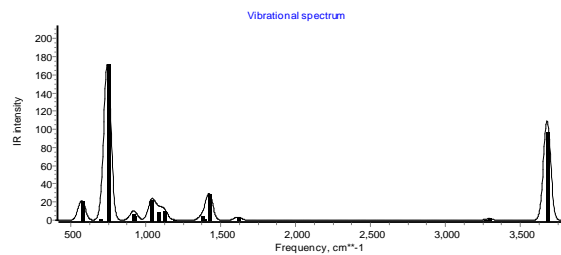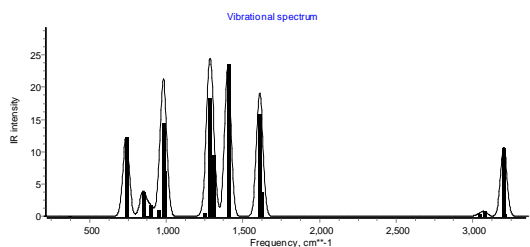2-aminoacrylonitrile
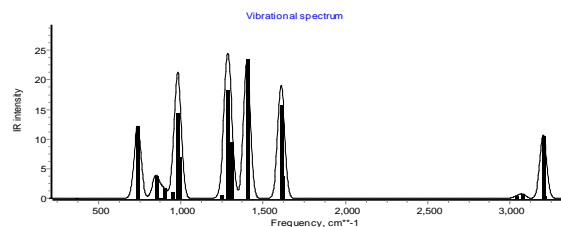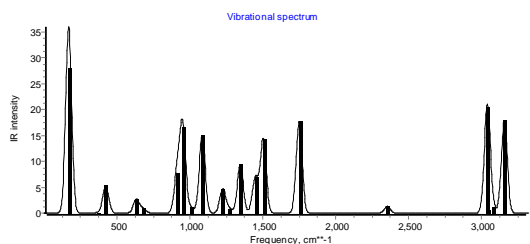

3-iminopropanenitrile

Methylamino acetonitrile

Vibrational spectrum

Imidazolium

Vibrational spectrum

4H-Pyrazole

Vibrational spectrum

3H-Pyrazole

Vibrational spectrum

1-Azaridinecarbonitrile

Vibrational spectrum

Pyrazolium

Vibrational spectrum

Diazocyclopropane

Vibrational spectrum

3-aminoacrylonitrile

Vibrational spectrum

2H-Pyrazole

Vibrational spectrum