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Quantum Chemical Studies on $C_4H_4N_2$ Isomeric Molecular Species

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Abstract

Quantum chemical calculations have been carried out on $C_4H_4N_2$ isomeric molecular species using the G4 method and compared with experimental values where available, probing parameters like thermochemistry, structural parameters (e.g. bond length, bond angles), rotational constants, vibrational spectroscopy and dipole moments. Pyrimidine was found to be the most stable of all the isomers with $\Delta_f H^0$ **=37.1 kcal/mol.** A critical analysis showed high correlation and consistency between the computed and experimental values of all the parameters under study and therefore providing the needed rationale to validate the values provided for the isomers which do not have available experimental data.

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1. Introduction

Quantum Chemistry is an area of computational chemistry which could reproduce experimental chemical phenomena mathematically, this branch of study avails one the opportunity to understand the electronic structures and model the nature of interactions molecules undergo not just for stable molecules as usually provided by experimental procedures but also for the short-lived intermediates or unstable analogues [1- 4]. It has been applied in different fields in chemistry where researchers have been able to make accurate predictions of future reactions [5, 6], physicochemical properties, docking, rate constants, protein calculations, calculations of potential energy surfaces, electronic structures of molecules and their isomers, molecules in the interstellar medium (ISM) [7].

$C_4H_4N_2$ has many isomeric species of wide spread relevance. Pyrazines ($C_4H_4N_2$) also known as 1,4-Diazines are heterocyclic aromatic organic compounds commonly distributed in nature such as in bacteria, fungi, insects and plants e.g. potatoes, coffee, nuts. They are responsible for the nutty and roasty smell which is reminiscent of cocoa and coffee. These compounds are used to improve aroma/flavor in food and cosmetic industries [8 – 11]. Nucleotides (such as cytosine, thymine), vitamin such as thiamine (i.e. vitamin B1), HIV drug Zidovudine and synthetic compounds like barbitutrates all contain the isomer pyrimidine [12]. The isomer pyridazine finds applications as herbicides (such as pyridafol, pyridate, credazine), as drugs such as minaprine, cadralazine, cefozopran[13].
It has been cumbersome studying certain molecules whose isomers or themselves are unstable molecules such as the present case. This challenge may be overcome to a certain level by the application of computational approach which has been shown

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Table 1: Standard enthalpy of formation of $C_4H_4N_2$ isomeric species

Molecules	$\Delta_f H^0$ (kcal/mol)
1,2-diisocyanoethane	92.4
1,3-butadiene-1,4-diimine	88.0
4-amino-2-butynenitrile	83.0
Iminopyrrole	62.3
2-methylene-2H-imidazole	60.1
Pyridazine	59.0
1,1-dicyanoethane	54.7
Pyrazine	41.0
Pyrimidine	**37.1**

to be a relative good substitute for experimental approach. Thus, the present study aims at using computational methods to investigate the isomers of the $C_4H_4N_2$ group by predicting the standard enthalpy of formation, bond length and angles, dipole moment, vibrational frequencies, rotational constants etc., and comparing their results with the available experimental values where available.

2. Computational Methods

GAUSSIAN 09 suite of program was employed in performing all the quantum chemical calculations reported in this study. The effectiveness of the G4 composite method has been reported in many literatures [14-16] in addition to experience from our previous studies [17- 23]; as such the molecule under study was optimized using the G4 level of theory.

3. Result and Discussion

The possible isomers of the $C_4H_4N_2$ isomeric group include; 1,2-diisocyanoethane, 1,3-butadiene-1,4-diimine, 4-amino-2-butynenitrile, iminopyrrole, 2-methylene-2H-imidazole, pyridazine, 1,1-dicyanoethane, pyrazine, pyrimidine. The results of the quantum chemical calculations carried out on the $C_4H_4N_2$ isomeric species using the G4 level of theory are presented and discussed below under the different subheadings:

3.1. Thermochemistry

The focal point of thermochemistry is energy changes such as enthalpy of formation and many other energy related parameters. Fig 1 shows the optimized geometries of the $C_4H_4N_2$ isomeric molecular species while the standard enthalpies of formation (ΔfH^O) computed for these isomeric species are presented in Table 1. Pyrimidine has the least enthalpy of formation of 37.1 Kcal/mol which corresponds to the most stable of all the isomers, 1,2-diisocyanoethane is shown to be the least stable of all the isomers of the $C_4H_4N_2$ isomeric group having the value of 92.4 Kcal/mol as the heat of formation. The experimentally reported standard heat of formation of pyrimidine ranges from 46.1±0.5 to 47.75± 0.4 [24-26], the disparity between the computed and experimental values point towards the possibility of an error in the experimentally reported value as Weisenburger and co-workers [27]. According to them, experimental measurement of heat of formation is always inaccurate and impractical. From previous studies, the G4 method has proven to be effective in predicting the enthalpy of formation that is in good accuracy with experimental results [14-23]. Standard enthalpy of formation is an important parameter that can be applied for safe and scaling up of chemical processes involving thermal stability. It helps researchers in predicting the spontaneity of a reaction, know whether a reaction can be favourable or not and the reactants and products quantities [27].

3.2. Vibrational Spectroscopy

Table 2 depicts the vibrational frequencies of pyrimidine (the most stable isomer of the $C_4H_4N_2$ isomeric group) with the corresponding spectrum in Figure 2. The vibrational frequencies and the corresponding spectra for other isomers of the $C_4H_4N_2$ isomeric group are presented in the appendix (Tables A1-A3 and Figure A respectively). Table 1 contains the calculated and experimental values of the vibrational frequencies of pyrimidine. The error between the values ranges between 0.3-4 cm^{-1}. The computed values are in excellent agreement with the reported experimental values. Thus, for the other isomers with no experimentally measured vibrational frequencies, the values computed at the G4 level (presented in the appendix) are believed to be accurate. The G4 composite method has also been reported to give accurate predictions for vibrational spectroscopic parameters for other molecular species with experimentally known values [14-23]. Among other applications, the vibrational spectroscopy parameters are useful in the chemical examination of the interstellar medium especially for the astronomical observation of interstellar molecular species with no dipole moment [17,20].

3.3. Rotational Constants

Rotational spectroscopy remains the most important spectroscopic technique employed in the astronomical observation of molecular species from different regions of the interstellar medium. The experimentally measured rotational constants (from the NIST Webbook) for pyrimidine and the values obtained at the G4 level are presented in Table 3 below. As shown in the Table, there is a good agreement between the experimental and the computed values of the rotational constant of pyrimidine. The Table also contains the rotational constants calculated for other isomers of the $C_4H_4N_2$ isomeric group at the G4 level of theory with no experimentally measured values. Analysis of the difference showed errors of 0.0261635, 0.0330026 and 0.0156889 GHz for the A, B and C rotational constants of pyrimidine respectively. This level of accuracy suggests a good level of accuracy for the rotational constants obtained for other isomers at the G4 level with no experimentally measured values.

3.4. Structural Parameters

The bond lengths and bond angles of Pyrimidine are presented in Table 4 while Fig. 3 depicts the optimized geometry. As shown in the Table, there is an excellent agreement

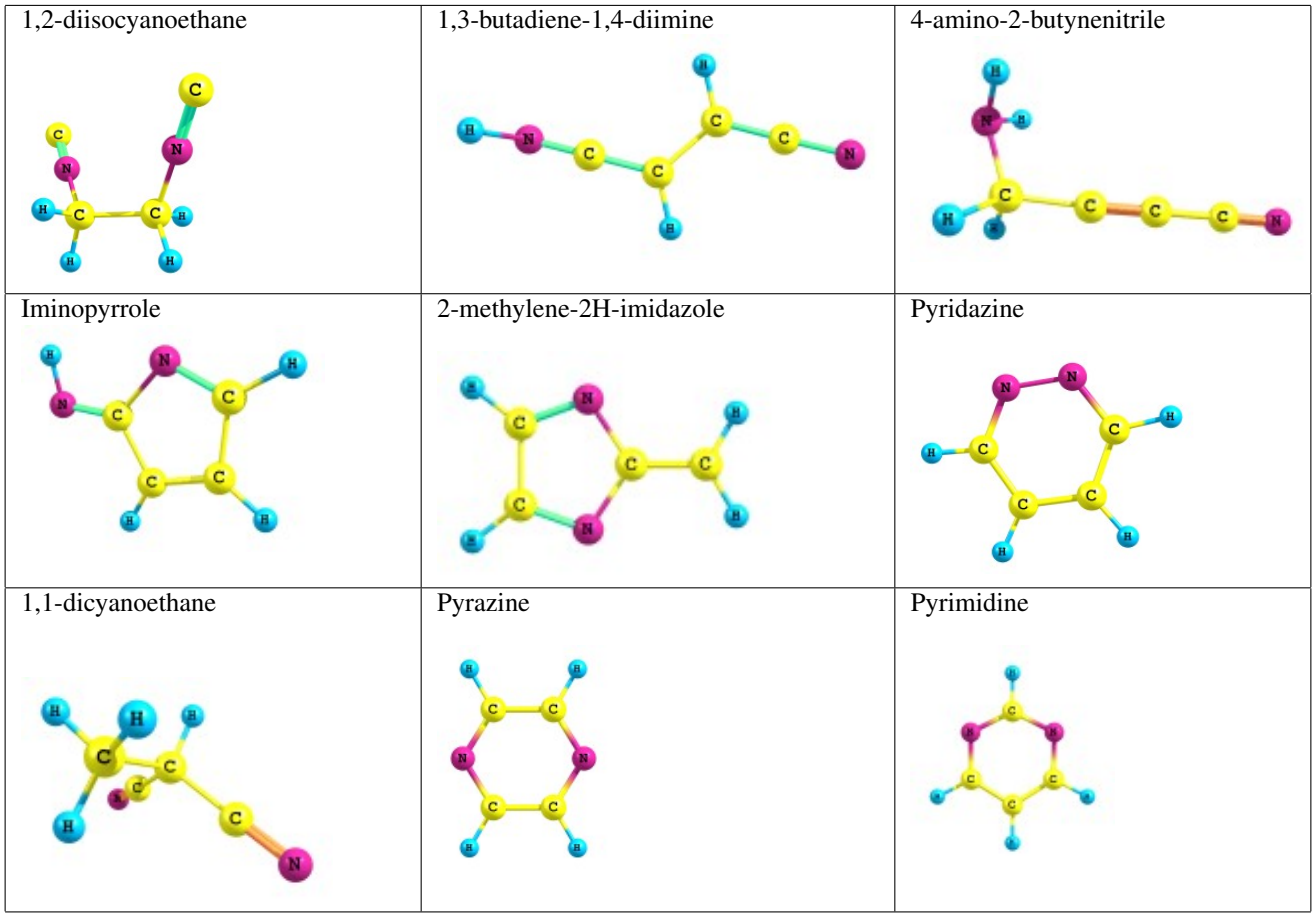

Figure 1: Optimized geometry of $C_4H_4N_2$ isomeric groups

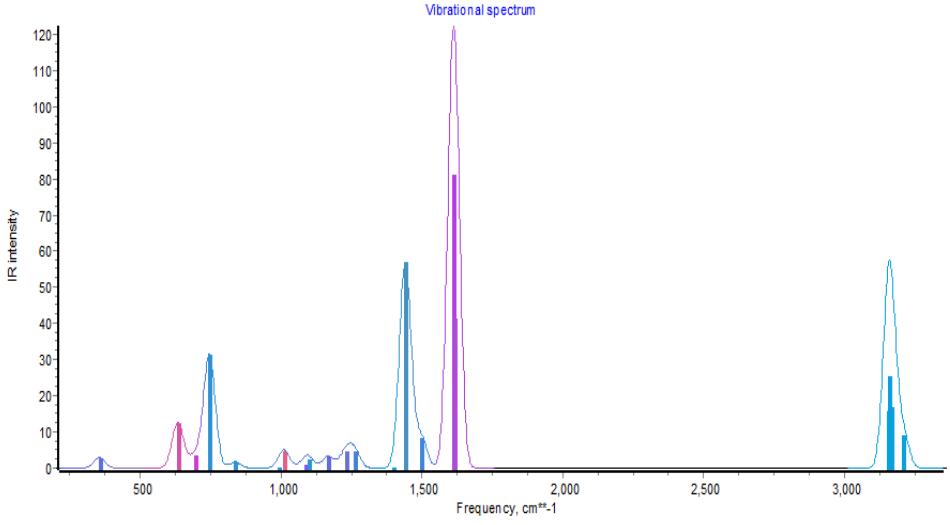

Figure 2: Calculated IR frequencies of pyrimidine

between the experimentally measured values and the computationally predicted values. For example, both the experimental (1.087Å) and the computational (1.087Å) values for rCH bond length. For the other bond lengths reported for pyrimidine, the difference between the experimental and the computational values range 0.36-0.46 Å while for the predicted bond angles, the difference between the experimental and the computational values range from 0.19-1.10 degrees. These findings suggest that

Table 2: Vibrational frequencies of pyrimidine

Calculated Frequency (cm^{-1})	ExperimentalFrequency (cm^{-1})	Error(cm^{-1})
353	347	1.69
411	398	2.9
632	621	1.58
693	679	1.45
744	719	3.36
835	804	3.59
988	960	2.74
1009	969	3.96
1011	980	2.97
1030	1033	-0.29
1083	1065	1.01
1095	1155	2.7
1165	1158	0.85
1227	1224	5.6
1260	1356	2.78
1395	1224	2.79
1439	1356	1.95
1496	1411	2.07
1610	1465	2.55
1612	1569	2.48
3154	1572	3.36
3157	3047	3.39
3165	3053	3.51
3207	3082	3.89

Table 3: Rotational Constant of $C_4H_4N_2$ isomers

Molecules		Rotation constants (GHz)		
		A	B	C
Pyrimidine	Calculated	6.3010414	6.0983826	3.0990279
	Experimental	6.2748779	6.06538	3.083339
	Error	0.0261635	0.0330026	0.0156889
1,2-diisocyanoethane	Calculated	7.4362588	2.5722569	2.0604923
1,3-butadiene-1,4-diimine	Calculated	23.1647044	1.3418215	1.2867453
4-amino-2-butynenitrile	Calculated	23.0996150	1.3419073	1.2868109
Iminopyrrole	Calculated	8.5048965	4.1234186	2.7770331
2-methylene-2H-imidazole	Calculated	8.7736412	4.2378633	2.8575861
Pyridazine	Calculated	6.4337599	5.9503379	3.0913068
Pyrazine	Calculated	6.4337599	5.9503379	3.0913068

the bond lengths and bond angles predicted with the G4 method for the other isomers of the $C_4H_4N_2$ isomeric group presented in the appendix (Tables A4-A6) with no experimental values will have a good level of accuracy and can be used when required.

3.5. Dipole Moments

Dipole moment is useful in determining the polar nature of the chemical bond. It is also useful in astrophysics and related areas such as astrochemistry and astrobiology as the dipole of a molecule plays an important role in the astronomical observation of such molecule [2]. The dipole moments obtained at the G4 level for all the isomeric molecular species in this study

Table 4: Bond Distances/ Angles of Pyrimidine and its Isomers

Description	Calculated Value (Å)	Exp. Value (Å)	Error	Connectivity		
				Atom 1	Atom 2	Atom 3
rCH	1.087	1.087	0	4	4	-
rCH	1.079	1.083	0.36	3	3	-
rCH	1.082	1.087	0.46	2	2	-
rCC	1.393	1.389	0.29	3	2	-
rCN	1.328	1.334	0.45	1	1	-
aCCC	117.8	116.5	1.10	4	3	2
aHCC	120.90	121.13	0.19	2	2	3
aCCN	121.20	122.37	0.97	3	4	2

Table 5: Dipole Moment of $C_4H_4N_2$ isomers

Molecule	Calculated Dipole moment (Debye)	Experimental Dipole moment (Debye)
1,2-diisocyanoethane	5.1506	-
1,3-butadiene-1,4-diimine	3.6290	-
4-amino-2-butynenitrile	3.7238	-
Iminopyrrole	3.2055	-
2-methylene-2H-imidazole	1.0758	-
Pyridazine	4.5926	-
1,1-dicyanoethane	4.5904	-
Pyrazine	0.0000	-
Pyrimidine	2.4133	2.33

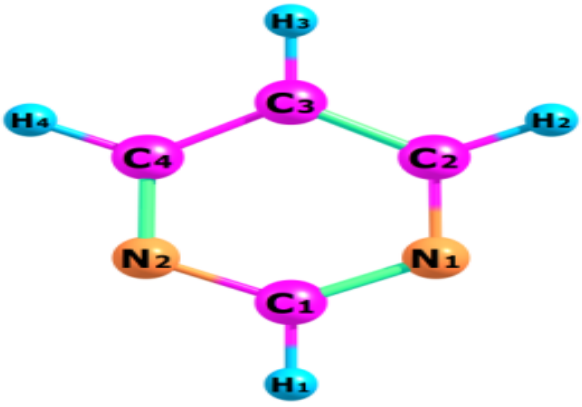

Figure 3: Optimized geometry of pyrimidine

are presented in Table 5. The experimental dipole moment of 2.33D [29] reported for pyrimidine is in good agreement with the value (2.41D) calculated at the G4 level. There are no experimentally reported dipole moments values for the other isomers of the pyrimidine isomeric group. However, the good agreement between the experinmentally measured and the computationally calculated values for pyrimidine suggest a good accuracy for the dipole moments predicted for those molecular species with no experimental values.

4. Conclusion

The Gaussian G4 compound model has been applied in computing some quantum chemical properties for the $C_4H_4N_2$ isomeric molecular species. Spectroscopic parameters (rotational and vibrational), bond distances, bond angles and dipole moments have been calculated for all the isomeric molecular species considered in this study. The results show a good agreement between the values obtained with the G4 method and the available experimentally measured values. This good agreement suggests a good accuracy for those the computationally predicted values with no experimental values. Thus, the predicted values at the G4 level of theory could serve as useful data where there are no experimental values.

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Appendix

Figure A: IR spectra of $C_4H_4N_2$ isomeric species.

Table A1: IR Frequencies and Intensities of $C_4H_4N_2$ isomers

Pyrazine		1,1-dicyanoethane		Pyridazine	
Frequency (cm^{-1})	IR Intensities	Frequency (cm^{-1})	IR Intensities	Frequency (cm^{-1})	IR Intensities
350.2454	0	142.6498	10.3325	377.4241	8.4376
436.8441	20.8309	212.9721	0.0061	378.1465	0
609.3268	0	217.325	10.417	629.7531	0.1251
718.6392	0	232.5641	0.1562	678.7734	3.7111
784.4478	0	390.8231	0.6653	773.826	26.977
813.6882	16.8768	501.3777	0.5045	784.7741	0
954.5671	0	577.079	2.0394	955.9237	0
995.7849	0	591.9736	0.0401	988.5043	0.0273
1004.4743	0	789.326	0.9436	1015.5701	6.7412
1032.2801	41.3863	924.1966	0.5222	1025.6928	0
1043.5004	0	1024.5549	3.0293	1057.3562	1.8513
1091.2542	11.3623	1077.6373	1.9773	1085.4055	1.9376
1168.3175	3.0353	1137.7852	11.4915	1094.3822	10.9875
1234.2883	3.3451	1293.1894	0.2956	1172.7042	0
1257.5615	0	1325.8192	10.5516	1198.4094	0.0296
1377.4992	0	1412.7563	0.8374	1315.9121	2.7813
1443.5577	32.5811	1489.6743	7.1366	1438.4468	17.1702
1516.3516	1.6121	1495.8979	2.9216	1480.3479	1.0699
1581.3618	0	2369.8219	1.4472	1604.0217	4.1776
1617.6288	0	2375.5886	1.0261	1608.3885	6.5778
3154.1328	0	3040.9897	0.0176	3171.291	11.3104
3154.5805	6.8491	3064.7956	7.0787	3175.4201	0.6737
3170.0288	69.5698	3150.5629	6.2676	3191.228	18.3941
3176.6122	0	3154.8613	4.5128	3205.5438	8.2119

Table A2: IR Frequencies and Intensities of $C_4H_4N_2$ isomers

2-methylene-2H-imidazole		Iminopyrrole		4-amino-2-butynenitrile	
Frequency (cm^{-1})	IR Intensities	Frequency (cm^{-1})	IR Intensities	Frequency (cm^{-1})	IR Intensities
231.2641	16.2028	222.6459	1.5177	102.9298	3.212
367.2831	5.0478	437.8852	15.624	136.5392	6.7159
545.8568	0	513.7051	0.5416	249.5854	0.2682
729.7105	0.9392	673.5182	13.329	273.9337	21.0114
757.4695	6.9218	709.63	1.5332	384.9431	30.924
778.714	0.0001	821.884	0.5162	500.8402	11.2464
893.0866	0.2762	839.2175	34.5306	575.9942	2.9544
912.9179	8.5062	878.6648	11.3524	582.7078	1.7895
915.8468	10.8072	926.5924	10.2062	699.5133	11.1841
954.3095	42.6853	967.2053	5.8961	889.2243	0.0003
961.4052	0.0001	969.8546	11.5774	895.8998	201.8104
979.8251	16.2158	993.4477	44.2831	1098.3395	26.2627
991.4666	31.7917	1058.7038	51.7342	1148.1344	4.2125
1202.2146	17.8701	1093.3592	5.4566	1183.4347	0.2291
1303.1681	6.2567	1280.4929	34.9662	1356.3555	33.0669
1346.2606	21.0282	1341.6019	75.8567	1383.0345	0.0121
1412.9732	17.8688	1353.3948	11.9765	1459.7535	5.1009
1496.1998	11.0291	1548.0035	19.6616	1669.8384	18.9874
1613.199	2.8089	1646.7243	11.3723	2258.8654	0.001
1714.8692	3.0856	1740.6104	20.5283	2396.7797	101.4735
3180.8768	0.0002	3175.7293	18.3444	3036.9215	13.0137
3196.1465	6.9809	3234.5262	3.2481	3070.8682	4.6604
3211.1464	15.5153	3266.179	1.1482	3496.6081	1.6966
3283.7487	0.0178	3434.2972	4.1245	3574.5662	3.4152

Table A3: IR Frequencies and Intensities of $C_4H_4N_2$ isomers

1,3-butadiene-1,4-diimine		1,2-diisocyanoethane	
Frequency (cm^{-1})	IR Intensities	Frequency (cm^{-1})	IR Intensities
83.6289	4.2328	78.7298	4.2564
127.629	1.9142	168.9156	0.5605
247.6388	0	192.4169	3.7141
413.9178	39.0839	262.623	0.1196
422.8897	0.0001	299.0842	0.3214
553.3442	90.5491	389.5249	0.2258
572.2602	0.0004	551.2205	13.3477
602.0439	17.4793	827.5204	7.2786
678.4837	0	859.6152	9.5185
879.0897	0.0004	1035.2344	3.9097
905.6999	99.6452	1041.9629	7.1071
1033.4248	0.0001	1091.3162	0.7493
1042.7608	612.5875	1268.8807	1.8639
1064.7913	0.0002	1304.1572	0.188
1144.81	40.0234	1384.277	13.328
1186.8856	0	1392.4053	22.9043
1291.0522	42.9681	1485.0234	17.2458
1485.9837	0	1486.765	0.1757
2123.9009	896.411	2224.3091	150.9267
2130.4724	0.1389	2226.309	166.4745
3174.8502	0.0003	3052.5648	3.5487

Table A4: Bond radius and angles of $C_4H_4N_2$ isomers

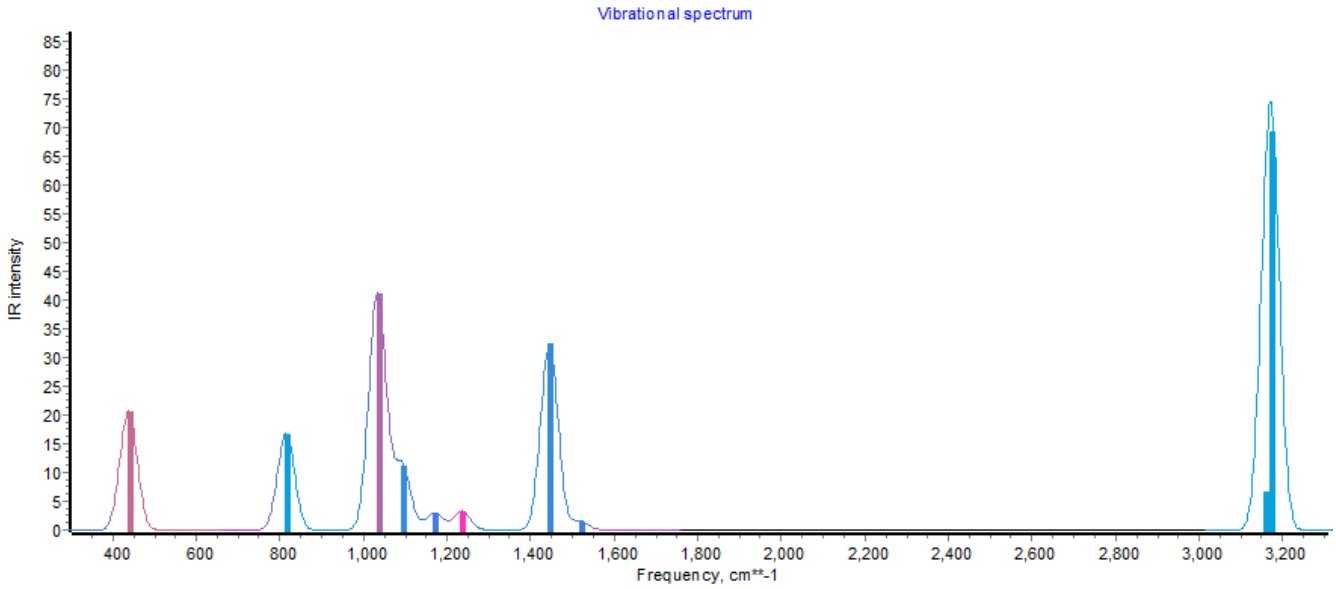
Pyrazine		1,1-dicyanoethane		Pyridazine	
Description	Cal. Value	Description	Cal. Value	Description	Cal. Value
R(1-2)	1.393	R(1-2)	1.154	R(1-2)	1.333
R(1-6)	1.334	R(1-3)	1.470	R(1-6)	1.332
R(1-7)	1.087	R(3-4)	1.470	R(2-3)	1.395
R(2-3)	1.334	R(3-6)	1.549	R(2-8)	1.086
R(2-8)	1.087	R(3-10)	1.098	R(3-4)	1.381
R(3-4)	1.334	R(4-5)	1.154	R(3-7)	1.084
R(4-5)	1.393	R(6-7)	1.092	R(4-5)	1.395
R(4-9)	1.087	R(6-8)	1.091	R(4-9)	1.084
R(5-6)	1.334	R(6-9)	1.092	R(5-6)	1.333
R(5-10)	1.087	A(2-1-3)	178.0	R(5-10)	1.086
A(2-1-6)	122.1	A(1-3-4)	110.7	A(2-1-6)	119.4
A(2-1-7)	120.8	A(1-3-6)	111.3	A(1-2-3)	123.8
A(1-2-3)	122.1	A(1-3-10)	107.3	A(1-2-8)	114.9
A(1-2-8)	120.8	A(4-3-6)	111.3	A(1-6-5)	119.4
A(6-1-7)	117.1	A(4-3-10)	107.3	A(3-2-8)	121.2
A(1-6-5)	115.9	A(3-4-5)	178.0	A(2-3-4)	116.8
A(3-2-8)	117.1	A(6-3-10)	108.9	A(2-3-7)	120.9
A(2-3-4)	115.9	A(3-6-7)	109.5	A(4-3-7)	122.3
A(3-4-5)	122.1	A(3-6-8)	110.5	A(3-4-5)	116.8
A(3-4-9)	117.1	A(3-6-9)	109.5	A(3-4-9)	122.3
A(5-4-9)	120.8	A(7-6-8)	109.0	A(5-4-9)	120.9
A(4-5-6)	122.1	A(7-6-9)	109.3	A(4-5-6)	123.8
A(4-5-10)	120.8	A(8-6-9)	109.0	A(4-5-10)	121.2
A(6-5-10)	117.1	R(1-2)	1.154	A(6-5-10)	114.9
R(1-2)	1.393	R(1-3)	1.470	R(1-2)	1.333
R(1-6)	1.334	R(3-4)	1.470	R(1-6)	1.332
R(1-7)	1.087	R(3-6)	1.549	R(2-3)	1.395
R(2-3)	1.334	R(3-10)	1.098	R(2-8)	1.086
R(2-8)	1.087	R(4-5)	1.154	R(3-4)	1.381
R(3-4)	1.334	R(6-7)	1.092	R(3-7)	1.084
R(4-5)	1.393	R(6-8)	1.091	R(4-5)	1.395
R(4-9)	1.087	R(6-9)	1.092	R(4-9)	1.084
R(5-6)	1.334	A(2-1-3)	178.0	R(5-6)	1.333
R(5-10)	1.087	A(1-3-4)	110.7	R(5-10)	1.086
A(2-1-6)	122.1	A(1-3-6)	111.3	A(2-1-6)	119.4
A(2-1-7)	120.8	A(1-3-10)	107.3	A(1-2-3)	123.8
A(1-2-3)	122.1	A(4-3-6)	111.3	A(1-2-8)	114.9
A(1-2-8)	120.8	A(4-3-10)	107.3	A(1-6-5)	119.4
A(6-1-7)	117.1	A(3-4-5)	178.0	A(3-2-8)	121.2
A(1-6-5)	115.9	A(6-3-10)	108.9	A(2-3-4)	116.8
A(3-2-8)	117.1	A(3-6-7)	109.5	A(2-3-7)	120.9
A(2-3-4)	115.9	A(3-6-8)	110.5	A(4-3-7)	122.3
A(3-4-5)	122.1	A(3-6-9)	109.5	A(3-4-5)	116.8
A(3-4-9)	117.1	A(7-6-8)	109.0	A(3-4-9)	122.3
A(5-4-9)	120.8	A(7-6-9)	109.3	A(5-4-9)	120.9
A(4-5-6)	122.1	A(8-6-9)	109.0	A(4-5-6)	123.8
A(4-5-10)	120.8	R(1-2)	1.154	A(4-5-10)	121.2
A(6-5-10)	117.1	R(1-3)	1.470	A(6-5-10)	114.9

Table A5: Bond radius and angles of $C_4H_4N_2$ isomers

2-methylene-2H-imidazole		Iminopyrrole		4-amino-2-butynenitrile	
Description	Cal. Value	Description	Cal. Value	Description	Cal. Value
R(1-2)	1.413	R(1-2)	1.437	R(1-2)	1.466
R(1-3)	1.295	R(1-3)	1.289	R(1-5)	1.465
R(2-5)	1.414	R(2-8)	1.484	R(1-9)	1.097
R(2-8)	1.339	R(2-9)	1.270	R(1-10)	1.097
R(3-4)	1.473	R(3-4)	1.486	R(2-3)	1.209
R(3-7)	1.084	R(3-7)	1.087	R(3-4)	1.365
R(4-5)	1.295	R(4-6)	1.081	R(4-6)	1.162
R(4-6)	1.084	R(4-8)	1.341	R(5-7)	1.016
R(8-9)	1.082	R(5-8)	1.079	R(5-8)	1.016
R(8-10)	1.083	R(9-10)	1.025	A(2-1-5)	115.2
A(2-1-3)	103.6	A(2-1-3)	104.8	A(2-1-9)	108.9
A(1-2-5)	113.0	A(1-2-8)	109.2	A(2-1-10)	108.9
A(1-2-8)	123.6	A(1-2-9)	125.3	A(1-2-3)	177.1
A(1-3-4)	109.9	A(1-3-4)	114.1	A(5-1-9)	108.7
A(1-3-7)	122.8	A(1-3-7)	121.5	A(5-1-10)	108.7
A(5-2-8)	123.5	A(8-2-9)	125.5	A(1-5-7)	109.7
A(2-5-4)	103.5	A(2-8-4)	106.2	A(1-5-8)	109.7
A(2-8-9)	120.3	A(2-8-5)	124.1	A(9-1-10)	106.0
A(2-8-10)	120.2	A(2-9-10)	108.7	A(2-3-4)	179.7
A(4-3-7)	127.2	A(4-3-7)	124.4	A(3-4-6)	180.0
A(3-4-5)	110.0	A(3-4-6)	125.4	A(7-5-8)	106.2
A(3-4-6)	127.2	A(3-4-8)	105.9	W1(A)	102.9
A(5-4-6)	122.8	A(6-4-8)	128.7	W2(A)	136.5
A(9-8-10)	119.5	A(4-8-5)	129.8	W3(A)	249.6
W1(A)	231.3	W1(A)	222.6	W4(A)	273.9
W2(A)	367.3	W2(A)	437.9	W5(A)	384.9
W3(A)	545.9	W3(A)	513.7	W6(A)	500.8
W4(A)	729.7	W4(A)	673.5	W7(A)	576.0
W5(A)	757.5	W5(A)	709.6	W8(A)	582.7
W6(A)	778.7	W6(A)	821.9	W9(A)	699.5
W7(A)	893.1	W7(A)	839.2	W10(A)	889.2
W8(A)	912.9	W8(A)	878.7	W11(A)	895.9
W9(A)	915.8	W9(A)	926.6	W12(A)	1098.3
W10(A)	954.3	W10(A)	967.2	W13(A)	1148.1
W11(A)	961.4	W11(A)	969.9	W14(A)	1183.4
W12(A)	979.8	W12(A)	993.4	W15(A)	1356.4
W13(A)	991.5	W13(A)	1058.7	W16(A)	1383.0
W14(A)	1202.2	W14(A)	1093.4	W17(A)	1459.8
W15(A)	1303.2	W15(A)	1280.5	W18(A)	1669.8
W16(A)	1346.3	W16(A)	1341.6	W19(A)	2258.9
W17(A)	1413.0	W17(A)	1353.4	W20(A)	2396.8
W18(A)	1496.2	W18(A)	1548.0	W21(A)	3036.9
W19(A)	1613.2	W19(A)	1646.7	W22(A)	3070.9
W20(A)	1714.9	W20(A)	1740.6	W23(A)	3496.6
W21(A)	3180.9	W21(A)	3175.7	W24(A)	3574.6
W22(A)	3196.1	W22(A)	3234.5	R(1-2)	1.466
W23(A)	3211.1	W23(A)	3266.2	R(1-5)	1.465
W24(A)	3283.7	W24(A)	3434.3	R(1-9)	1.097

Table A6: Bond radius and angles of $C_4H_4N_2$ isomers

1,3-butadiene-1,4-diimine		1,2-diisocyanoethane	
Description	Cal. Value	Description	Cal. Value
R(1-2)	1.316	R(1-5)	1.173
R(1-5)	1.226	R(2-3)	1.538
R(2-3)	1.461	R(2-5)	1.416
R(2-9)	1.085	R(2-7)	1.094
R(3-4)	1.316	R(2-8)	1.095
R(3-10)	1.085	R(3-6)	1.416
R(4-6)	1.225	R(3-9)	1.095
R(5-7)	1.023	R(3-10)	1.094
R(6-8)	1.023	R(4-6)	1.173
A(2-1-5)	173.7	A(1-5-2)	179.0
A(1-2-3)	124.3	A(3-2-5)	112.1
A(1-2-9)	116.9	A(3-2-7)	109.7
A(1-5-7)	115.8	A(3-2-8)	108.4
A(3-2-9)	118.8	A(2-3-6)	112.1
A(2-3-4)	124.3	A(2-3-9)	108.4
A(2-3-10)	118.8	A(2-3-10)	109.7
A(4-3-10)	116.9	A(5-2-7)	109.2
A(3-4-6)	173.7	A(5-2-8)	109.2
A(4-6-8)	115.8	A(7-2-8)	108.1
W1(A)	83.6	A(6-3-9)	109.2
W2(A)	127.6	A(6-3-10)	109.2
W3(A)	247.6	A(3-6-4)	179.1
W4(A)	413.9	A(9-3-10)	108.1
W5(A)	422.9	W1(A)	78.7
W6(A)	553.3	W2(A)	168.9
W7(A)	572.3	W3(A)	192.4
W8(A)	602.0	W4(A)	262.6
W9(A)	678.5	W5(A)	299.1
W10(A)	879.1	W6(A)	389.5
W11(A)	905.7	W7(A)	551.2
W12(A)	1033.4	W8(A)	827.5
W13(A)	1042.8	W9(A)	859.6
W14(A)	1064.8	W10(A)	1035.2
W15(A)	1144.8	W11(A)	1042.0
W16(A)	1186.9	W12(A)	1091.3
W17(A)	1291.1	W13(A)	1268.9
W18(A)	1486.0	W14(A)	1304.2
W19(A)	2123.9	W15(A)	1384.3
W20(A)	2130.5	W16(A)	1392.4
W21(A)	3174.9	W17(A)	1485.0
W22(A)	3183.6	W18(A)	1486.8
W23(A)	3422.3	W19(A)	2224.3
W24(A)	3422.6	W20(A)	2226.3
R(1-2)	1.316	W21(A)	3052.6
R(1-5)	1.226	W22(A)	3056.6
R(2-3)	1.461	W23(A)	3096.1
R(2-9)	1.085	W24(A)	3107.6
R(3-4)	1.316	R(1-5)	1.173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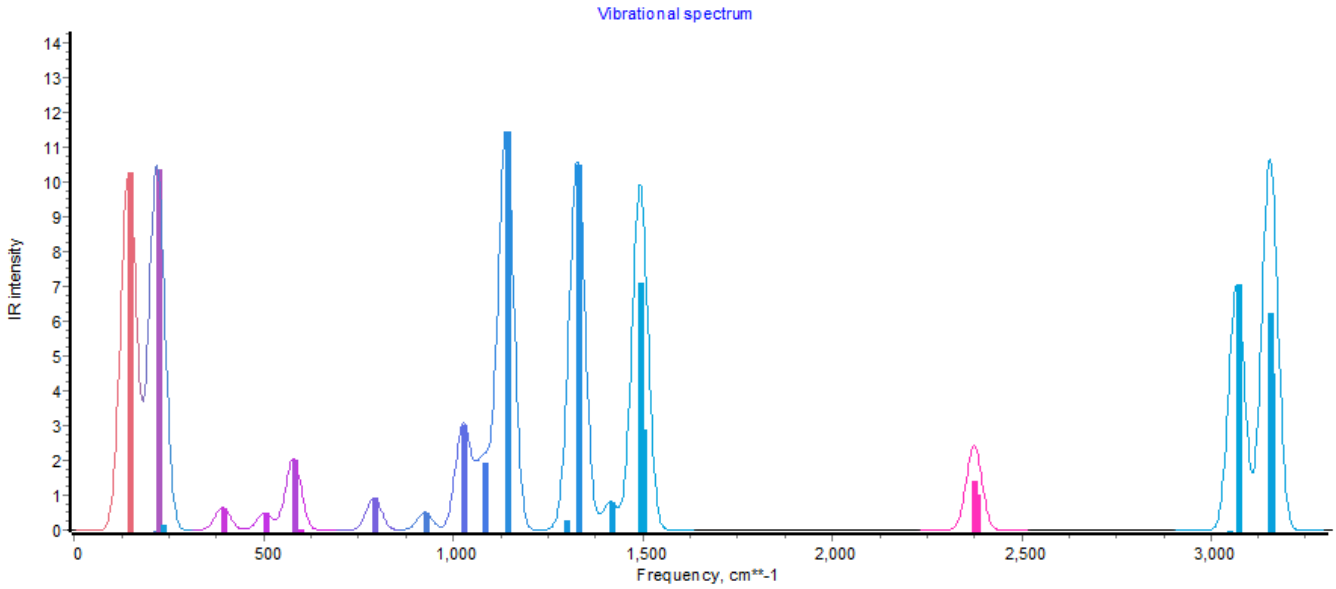
2,400
2,600
2,800
3,000
3,200

Pyrazine



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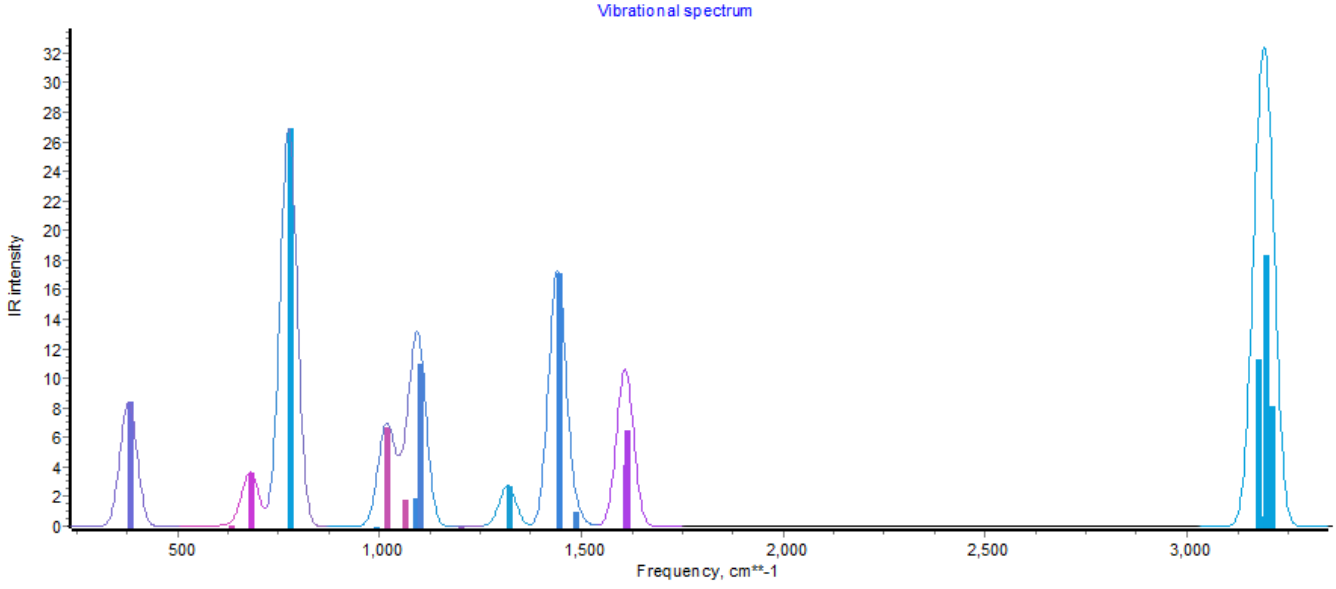

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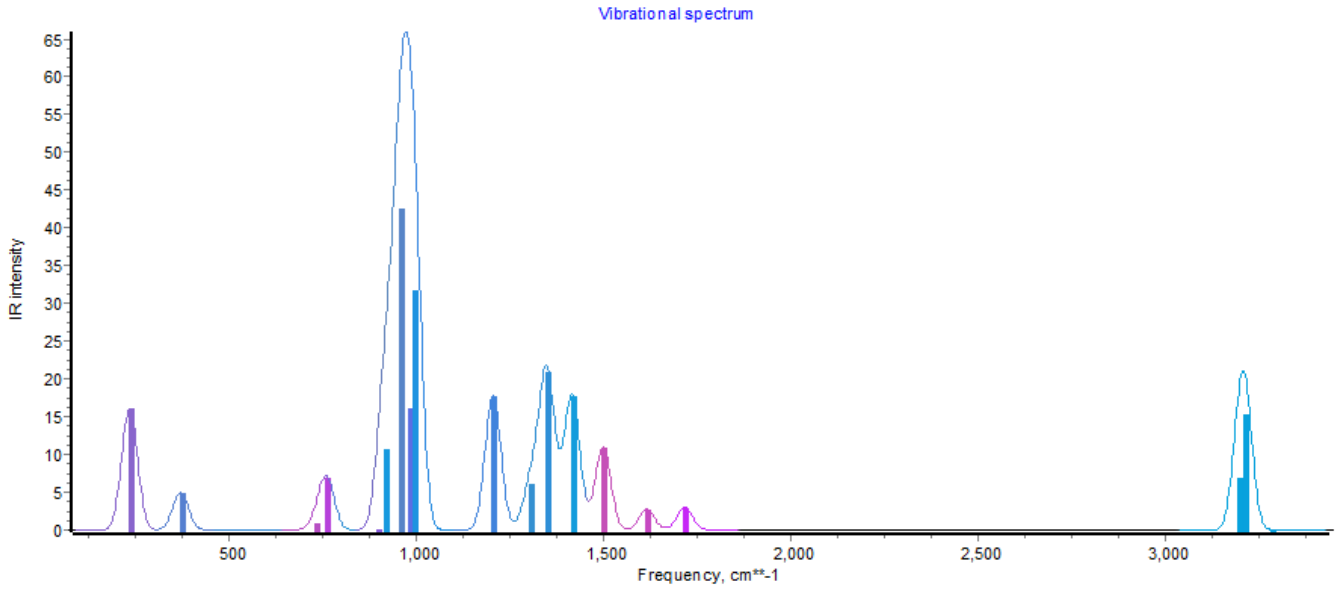

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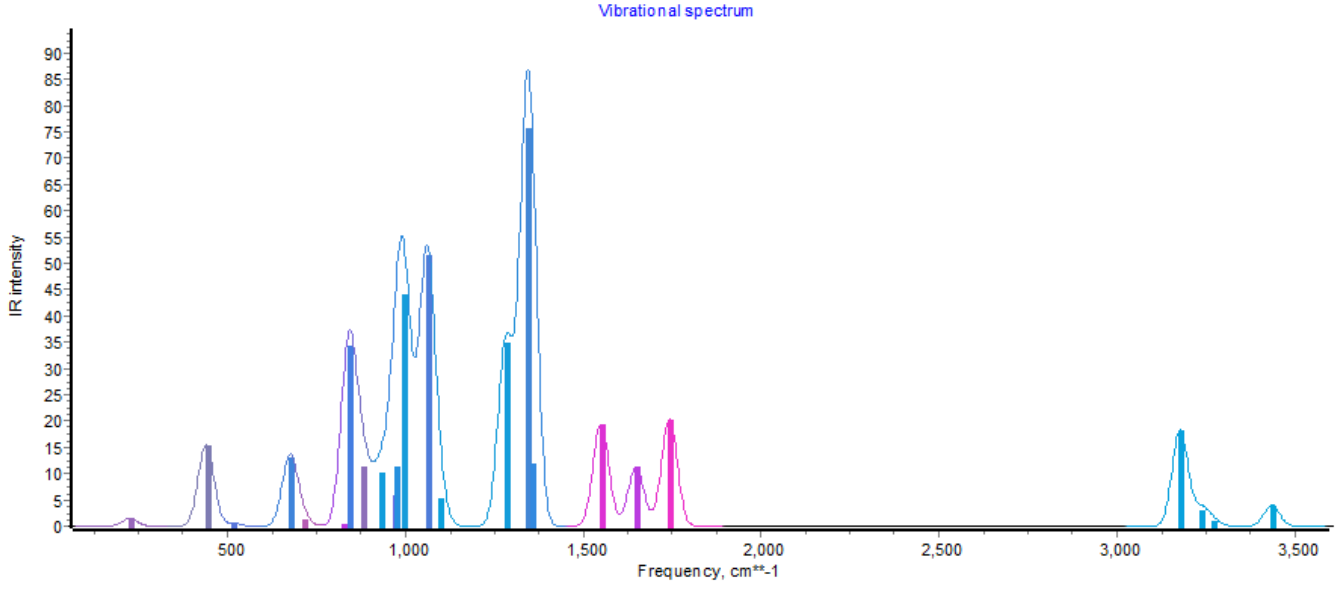
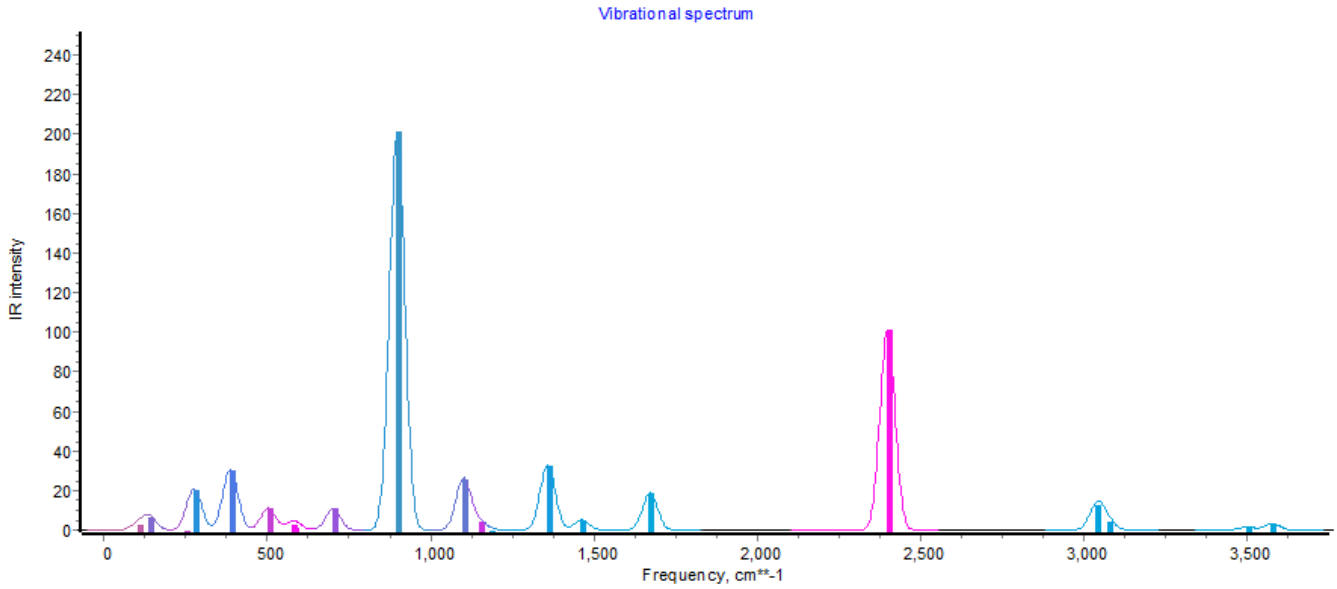


Iminopyrrole



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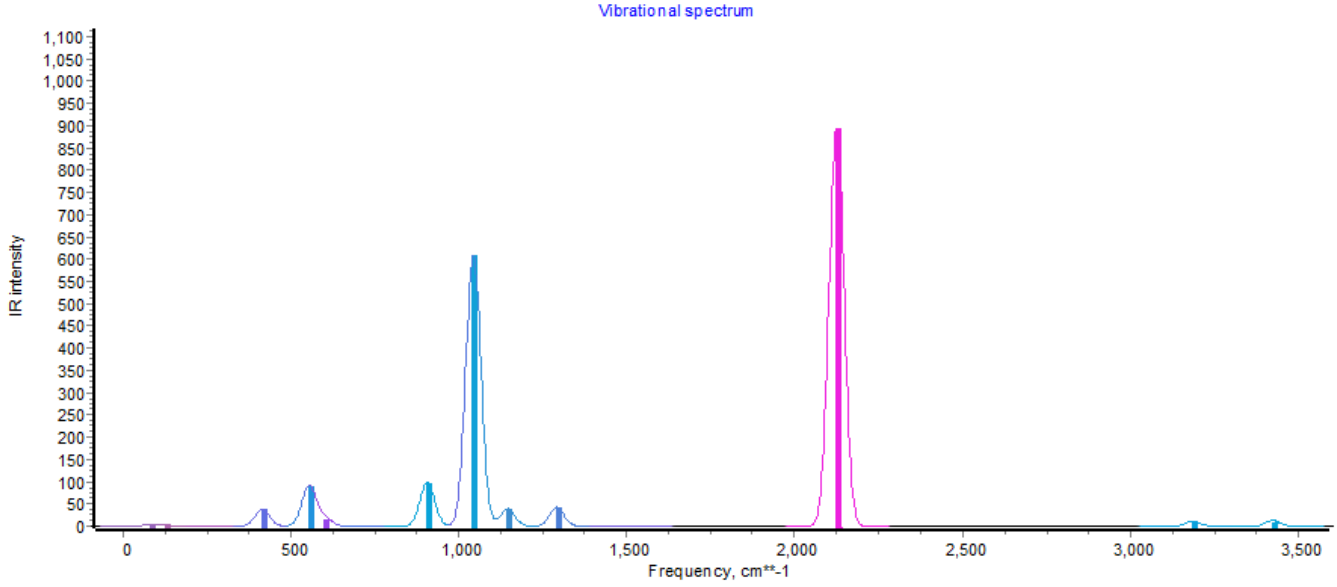

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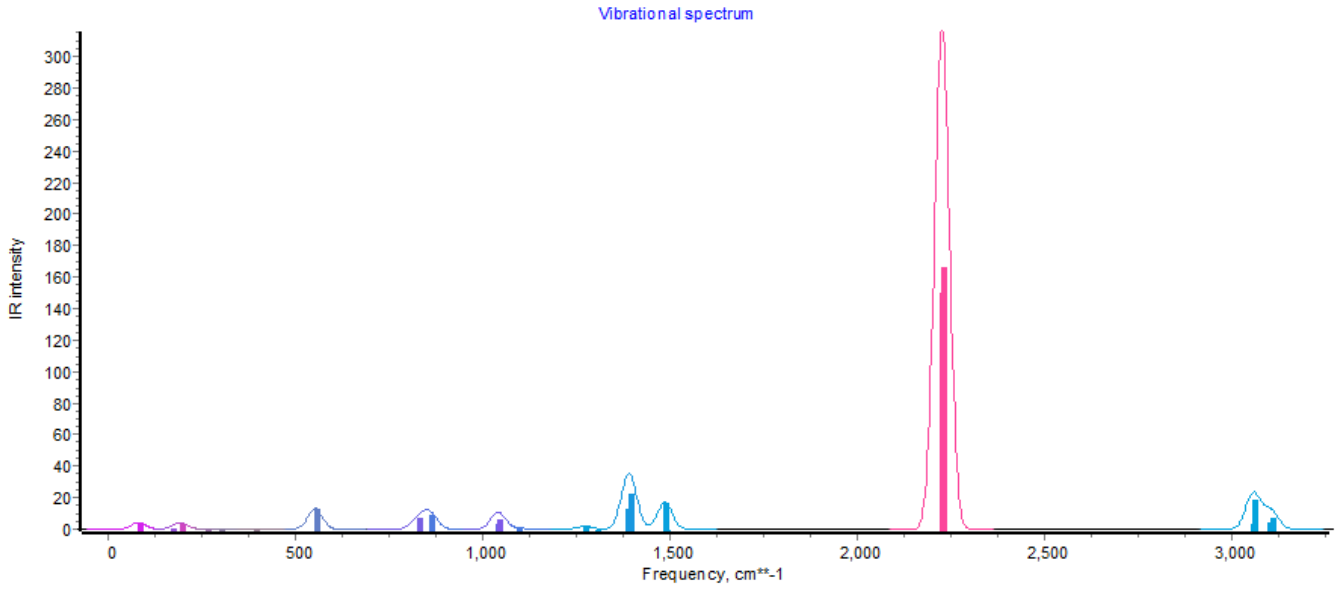

1,2-diisocyanoethane

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