Predicted Structures and Spectroscopic Characteristics of Hydrazine, Lithium-substituted Hydrazine and Their Higher Derivatives

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Calculation method.

Density functional theory, B3LYP hybrid exchange-correlation functional is employed to investigate a potential of molecules as novel propellant..

Dunning's aug-cc-pVDZ (5d) basis set is used for H, N, C, F elements, while 6-31G(d) basis set is used for Li atom, where aug-cc-pVDZ is not available.

Heat of formation is calculated as energy difference between a target molecule and constituent atoms in their standard state. Since H_2, O_2, F_2 are gas in their standard state,

Calculated value are used without modification, however standard state of C and Li are solid, thus experimental heat of formation of each atom 171.29 kcal/mol and 38.1 kcal/mol are used together with calculated total enthalpy.

Notation.

In the pictures of molecules, N,C,H and Li are given by skyblue, darkgreen, grey and brown, respectively.

Bond length between N,C and Li are given in Angstrom. Full molecular coordinate are available by request.

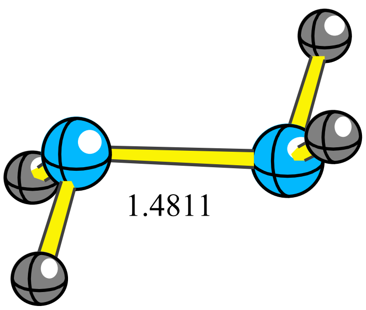
H_f denotes heat of formation and I_{sp} denotes specific impulse.

Investigation of HEDM molecules.

Propellants which are currently in use.

N_2H_4, Hydrazine (1_i)

C_{2h}, ^1A_g, H_f=15.7 kcal/mol, I_{sp}=185.7 sec.

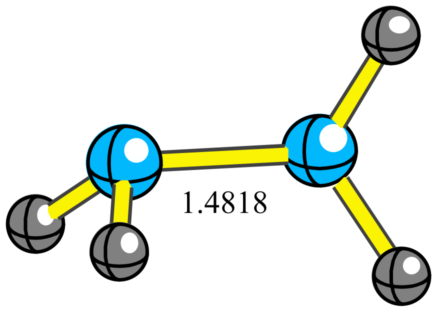


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	Au	-25.8	110.3	0.0	0.65
2	Ag	945.9	0.0	13.7	0.29
3	Bu	1034.4	160.8	0.0	0.61
4	Au	1104.7	1.1	0.0	0.61
5	Ag	1214.5	0.0	4.0	0.06
6	Bg	1475.7	0.0	3.1	0.75
7	Bu	1609.5	37.3	0.0	0.41
8	Ag	1671.4	0.0	6.1	0.64
9	Ag	3428.7	0.0	254.8	0.10
10	Bu	3446.2	2.6	0.0	0.51
11	Bg	3499.6	0.0	104.3	0.75
12	Au	3518.3	2.2	0.0	0.70

2.Dissociation into $2NH_2$.

N_2H_4, Hydrazine

C_2, ^1A

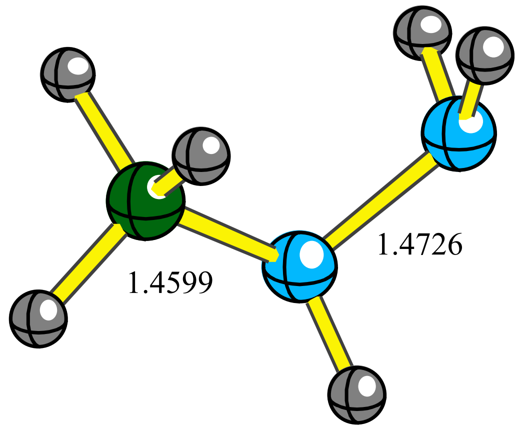


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	439.0	35.8	0.6	0.65
2	A	801.3	60.9	0.2	0.73
3	B	970.8	122.4	0.6	0.75
4	A	1112.7	11.3	11.2	0.11
5	B	1284.8	5.0	0.8	0.75
6	A	1320.2	3.0	1.2	0.72
7	B	1649.5	11.2	4.3	0.75
8	A	1665.9	8.5	6.3	0.48
9	B	3442.5	13.5	62.8	0.75
10	A	3451.0	3.2	229.9	0.01
11	A	3549.3	1.7	98.3	0.67
12	B	3554.1	2.8	21.8	0.75

2. Dissociation into $2NH_2$.

CN_2H_6, Monomethylhydrazine (MMH)

C_1, ${}^1A$, H_f=15.70 kcal/mol, I_{sp}=154.7 sec

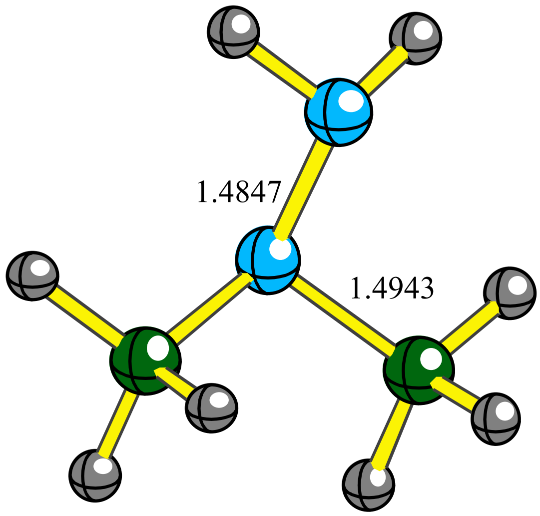


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	263.8	3.0	0.3	0.68
2	A	343.9	24.5	0.9	0.37
3	A	421.4	6.5	1.5	0.25
4	A	780.4	99.3	2.3	0.59
5	A	911.2	64.5	0.3	0.66
6	A	980.3	26.5	6.6	0.27
7	A	1124.8	6.7	1.8	0.46
8	A	1138.2	9.8	2.3	0.70
9	A	1215.2	4.1	3.3	0.29
10	A	1304.7	6.4	1.2	0.66
11	A	1423.0	0.3	2.1	0.75
12	A	1454.8	9.4	6.0	0.75
13	A	1470.2	3.0	3.7	0.71
14	A	1506.3	3.7	3.3	0.73
15	A	1659.5	13.0	5.2	0.63
16	A	2936.0	90.9	170.7	0.11
17	A	3056.7	37.4	116.1	0.23
18	A	3103.1	27.1	83.9	0.64
19	A	3378.6	18.6	156.8	0.11
20	A	3515.6	2.8	136.4	0.26
21	A	3532.3	0.9	28.3	0.75

8.Dissociation into CNH_4 + NH_2 or CH_3 + N_2H_3.

C$_2$N$_2$H$_8$, 1,1-Dimethyl hydrazine (UDMH)

C_s, $^1A'$, H_f=20.16 kcal/mol, I_{sp}=153.5 sec



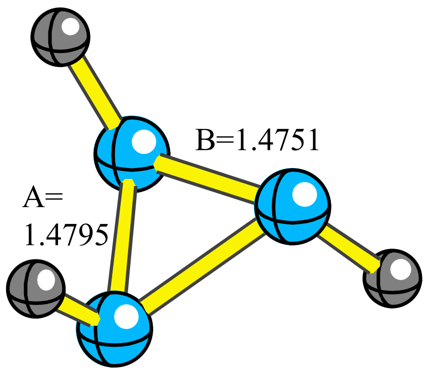
No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A"	154.5	35.0	0.2	0.75
2	A"	260.5	8.8	0.0	0.75
3	A'	277.9	0.1	0.9	0.72
4	A'	412.7	4.4	1.6	0.34
5	A"	438.4	1.6	1.3	0.75
6	A'	441.5	18.1	1.9	0.23
7	A'	818.6	15.0	13.1	0.37
8	A'	983.6	20.2	9.5	0.35
9	A"	1035.4	11.9	1.5	0.75
10	A"	1092.5	1.0	0.9	0.75
11	A'	1100.5	46.2	3.7	0.16
12	A"	1127.5	10.9	2.6	0.75
13	A'	1183.8	3.7	8.4	0.32
14	A'	1247.3	0.2	2.1	0.66
15	A"	1389.9	3.8	0.0	0.75
16	A"	1408.2	1.2	2.1	0.75
17	A'	1435.2	3.6	2.6	0.62
18	A"	1451.6	9.5	5.6	0.75
19	A'	1462.3	8.3	8.5	0.72
20	A"	1471.5	1.2	5.2	0.75
21	A'	1485.3	14.0	3.5	0.75
22	A'	1632.8	35.7	3.5	0.75
23	A"	2947.8	50.7	24.1	0.75
24	A'	2956.4	103.7	281.6	0.06
25	A"	3066.2	35.6	52.7	0.75
26	A'	3068.6	31.8	143.9	0.21
27	A"	3113.5	7.4	20.2	0.75
28	A'	3118.7	39.3	106.0	0.66
29	A'	3422.3	2.0	149.6	0.12
30	A"	3502.4	0.1	66.6	0.75

7.Dissociation into NH_2 + C_2NH_6.

Higher derivatives of hydrazine: N_xH_y molecules.

N_3H_3, Cyclotriazane (c,t)

C_s, $^1A'$, H_f=85.66 kcal/mol, I_{sp}=365.4 sec.

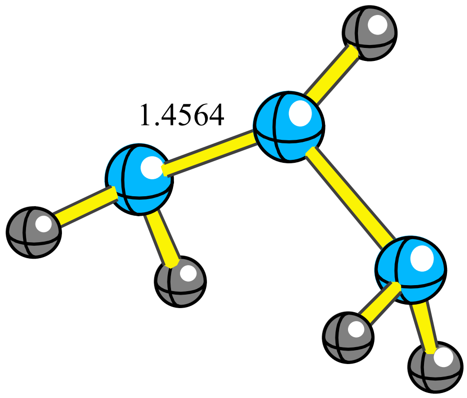


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A"	787.0	9.9	6.7	0.75
2	A'	790.7	8.1	6.8	0.74
3	A"	1099.9	28.6	2.3	0.75
4	A'	1121.8	55.0	2.0	0.39
5	A'	1166.4	17.7	22.9	0.08
6	A'	1281.1	42.7	5.4	0.32
7	A"	1288.5	41.7	0.2	0.75
8	A"	1424.5	12.8	4.9	0.75
9	A'	1459.6	0.3	13.2	0.10
10	A"	3371.2	0.0	68.9	0.75
11	A'	3398.0	1.0	197.0	0.14
12	A'	3426.1	1.4	53.1	0.37

1.Open ring at A.
2.Dissociation into NH + N_2H_2 (breaks two bonds A and B).
5.Dissociation into 3NH (breaks three bonds).

N_3H_5, Triazine

C_s, $^1A'$, H_f=32.2 kcal/mol, I_{sp}=219.1 sec.

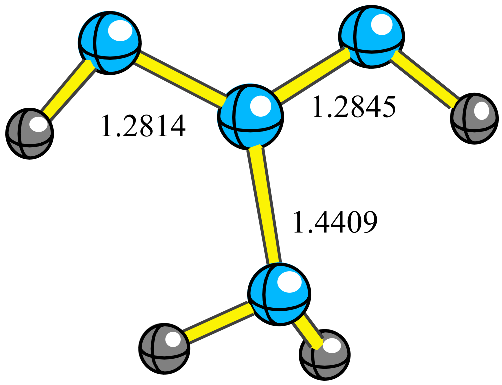


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A"	333.9	0.1	0.4	0.75
2	A'	437.1	52.2	1.8	0.20
3	A'	477.0	0.1	4.9	0.28
4	A'	785.1	45.4	3.6	0.40
5	A"	830.5	265.8	0.6	0.75
6	A'	956.6	28.8	2.6	0.50
7	A"	1091.0	0.8	1.2	0.75
8	A'	1154.1	21.4	10.4	0.33
9	A"	1230.1	3.5	1.8	0.75
10	A'	1344.5	11.3	0.3	0.25
11	A"	1507.8	0.1	1.7	0.75
12	A"	1640.6	0.5	6.0	0.75
13	A'	1666.7	27.9	3.7	0.55
14	A'	3367.6	30.5	278.9	0.10
15	A"	3380.5	2.4	18.5	0.75
16	A'	3516.3	0.3	179.6	0.32
17	A"	3532.6	1.0	22.7	0.75
18	A'	3545.3	6.2	16.0	0.41

7. Dissociation into NH_2 + N_2H_3.

N_4H_4 , 2-aminotriazene

C_1, ^1A, H_f=80.14 kcal/mol, I_{sp}=306.1 sec.



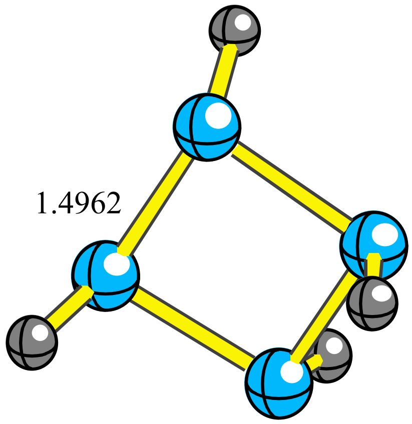
This structure is preferred over a structure with a three-member nitrogen ring structure.

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	103.8	32.3	0.2	0.69
2	A	506.7	1.6	0.6	0.30
3	A	563.9	5.7	3.1	0.74
4	A	618.7	10.8	4.6	0.26
5	A	655.2	27.6	1.9	0.34
6	A	778.4	92.5	0.3	0.11
7	A	810.0	130.8	3.6	0.16
8	A	990.0	58.3	17.8	0.11
9	A	1227.2	76.6	16.9	0.32
10	A	1256.4	54.4	33.0	0.23
11	A	1302.3	291.1	0.0	0.74
12	A	1494.5	85.7	4.8	0.06
13	A	1624.4	42.4	4.7	0.44
14	A	1690.3	132.2	5.4	0.72
15	A	3462.2	8.5	85.3	0.09
16	A	3466.9	16.4	35.2	0.75
17	A	3478.2	2.2	158.2	0.15
18	A	3568.2	15.7	42.7	0.75

7. Dissociation into NH_2 + N_3H_2.

N_4H_4 , Cyclotetrazane

C_2, ^1A, H_f=108.95 kcal/mol, I_{sp}=356.9 sec.

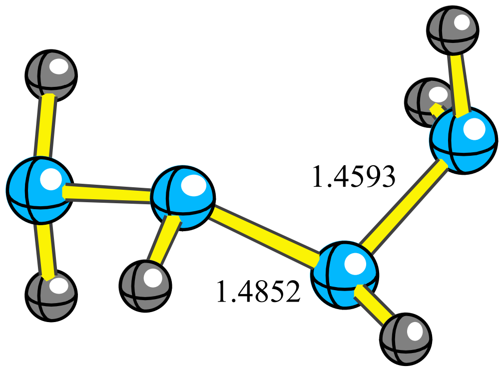


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	328.4	0.0	2.0	0.70
2	B	846.4	1.1	0.0	0.75
3	B	846.4	1.1	0.0	0.75
4	A	890.8	1.3	2.8	0.75
5	A	969.6	0.0	14.7	0.13
6	A	1024.0	0.0	10.1	0.75
7	A	1091.9	2.4	3.3	0.75
8	B	1119.2	153.1	0.7	0.75
9	B	1119.2	153.1	0.7	0.75
10	A	1271.6	0.0	0.0	0.07
11	A	1370.8	0.0	13.5	0.04
12	B	1451.1	2.3	4.9	0.75
13	B	1451.1	2.3	4.9	0.75
14	A	1491.0	0.0	0.8	0.75
15	A	3388.3	0.0	337.9	0.12
16	B	3414.9	0.3	56.4	0.75
17	B	3415.0	0.3	56.4	0.75
18	A	3429.1	0.1	6.6	0.75

2,3. Dissociation into NH + N_3H_3 (two bonds breaking).
5. Dissociation into 4NH. (four bonds breaking).
6. Dissociation into $2N_2H_2$ (two bonds breaking).

N_4H_6 , Tetrazine

C_2, ^1A, H_f=53.07 kcal/mol, I_{sp}=245.04 sec.



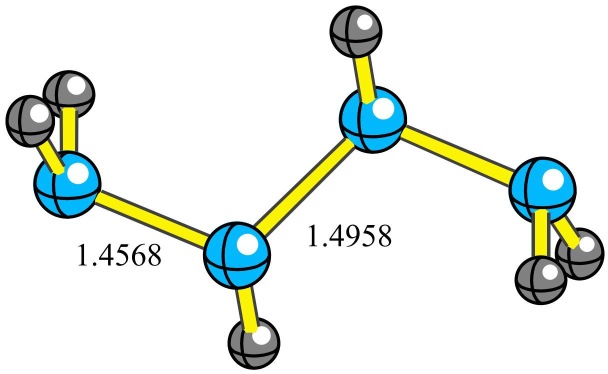
No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	99.0	2.4	1.1	0.72
2	B	340.0	49.0	0.0	0.75
3	A	362.3	31.4	0.5	0.74
4	A	469.8	1.2	8.4	0.15
5	B	550.5	81.6	0.6	0.75
6	A	783.6	3.0	5.1	0.75
7	B	867.2	161.6	0.8	0.75
8	A	881.9	15.0	0.5	0.69
9	B	978.4	159.6	1.8	0.75
10	A	994.6	2.1	9.1	0.20
11	A	1117.5	0.4	8.3	0.19
12	B	1200.2	10.4	1.1	0.75
13	A	1310.8	1.1	0.7	0.73
14	B	1324.9	19.2	0.5	0.75
15	A	1493.2	0.5	4.8	0.28
16	B	1506.7	0.3	3.0	0.75
17	A	1657.7	17.9	4.1	0.62
18	B	1659.8	11.2	5.7	0.75
19	B	3406.4	11.0	11.1	0.75
20	A	3409.2	3.7	308.3	0.07
21	B	3459.4	3.4	33.5	0.75
22	A	3479.4	0.1	204.1	0.21
23	B	3544.7	2.7	18.7	0.75
24	A	3545.7	2.7	59.5	0.64

5.Dissociation into $2N_2H_3$.

6.Dissociation into $NH_2 + N_3H_4$.

N_4H_6 , Tetrazine (t)

C_i, ^1A_g, H_f=54.02, I_{sp}=247.2 sec.



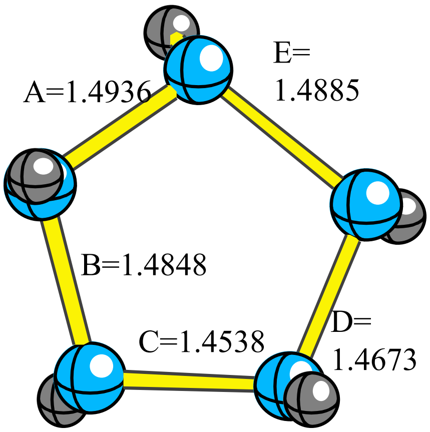
No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	Au	88.0	4.3	0.0	0.00
2	Au	310.8	25.0	0.0	0.00
3	Au	394.6	71.3	0.0	0.00
4	Ag	450.3	0.0	4.6	0.24
5	Ag	500.4	0.0	13.7	0.25
6	Ag	804.9	0.0	6.2	0.74
7	Au	880.1	275.8	0.0	0.00
8	Ag	909.9	0.0	12.7	0.52
9	Au	988.6	109.7	0.0	0.00
10	Ag	1073.7	0.0	3.9	0.75
11	Au	1112.1	23.5	0.0	0.00
12	Ag	1203.6	0.0	8.4	0.16
13	Au	1282.7	6.5	0.0	0.00
14	Ag	1351.7	0.0	2.1	0.17
15	Au	1471.4	7.4	0.0	0.00
16	Ag	1535.1	0.0	3.3	0.64
17	Au	1655.3	31.0	0.0	0.00
18	Ag	1655.6	0.0	10.1	0.62
19	Au	3397.6	20.8	0.0	0.00
20	Ag	3402.7	0.0	364.8	0.09
21	Ag	3439.7	0.0	151.5	0.36
22	Au	3459.4	4.5	0.0	0.00
23	Au	3542.7	8.0	0.0	0.00
24	Ag	3544.2	0.0	110.2	0.61

5.Dissociation into $2N_2H_3$.

11. Dissociation into NH_2 + N_3H_4.

N_5H_5 , Cyclepentazane

C_1, ^1A, H_f=103.16 kcal/mol, I_{sp}=310.6 sec.

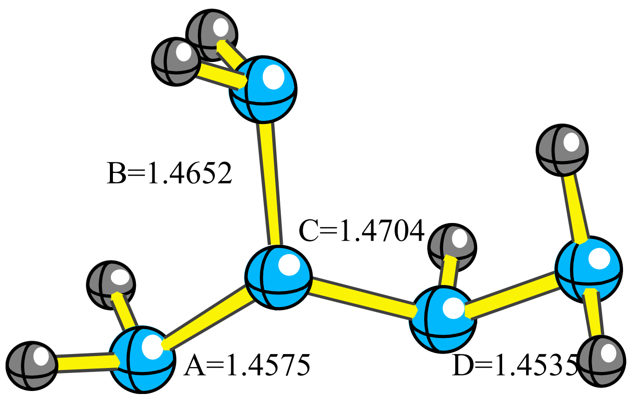


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	155.7	2.3	0.1	0.75
2	A	459.4	0.1	1.2	0.57
3	A	707.8	9.7	7.4	0.34
4	A	778.7	12.1	2.9	0.75
5	A	833.2	28.1	8.7	0.09
6	A	861.4	71.7	0.1	0.74
7	A	867.5	54.8	0.4	0.27
8	A	890.7	13.9	8.3	0.09
9	A	921.5	16.6	0.1	0.75
10	A	1035.8	15.5	1.0	0.67
11	A	1038.7	27.0	3.0	0.75
12	A	1079.8	98.6	2.6	0.41
13	A	1213.4	61.5	0.5	0.75
14	A	1259.5	26.7	15.4	0.04
15	A	1368.4	6.8	0.6	0.75
16	A	1426.0	2.9	5.1	0.08
17	A	1463.4	4.4	4.8	0.75
18	A	1528.5	0.5	1.9	0.75
19	A	1532.2	0.1	7.6	0.71
20	A	3410.9	0.2	20.8	0.75
21	A	3441.5	0.7	296.5	0.14
22	A	3457.8	0.2	57.0	0.40
23	A	3482.3	0.8	24.5	0.75
24	A	3490.4	6.0	24.9	0.36

3. Open ring at D.
4. Open ring at B.
5. Dissociation into NH + N_4H_4 (two bonds breaking at D and E).
6. Open ring at A or C.
7. Open ring at B or E.
8.Open ring at A or C.
9.Dissociation into N_2H_2 + N_3H_3 (two bonds breaking at A and C).

N_5H_7 , 2-aminotetrazine

C_1, ^1A, H_f=72.55 kcal/mol, I_{sp}=257.08 sec.

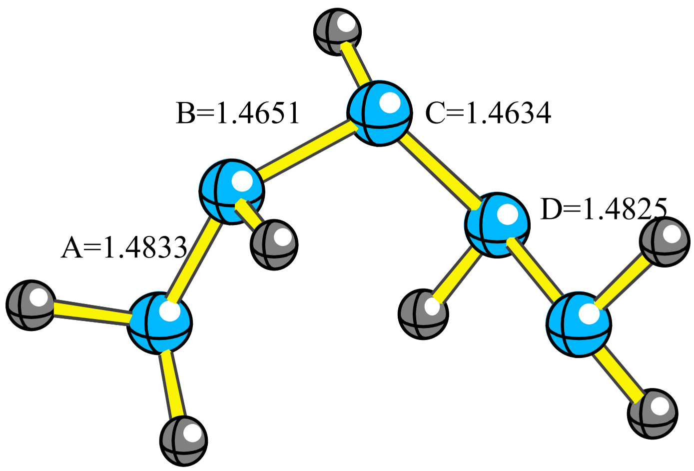


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	124.7	3.8	0.2	0.69
2	A	230.6	22.2	1.0	0.53
3	A	298.0	26.1	0.8	0.72
4	A	330.0	3.0	0.8	0.54
5	A	423.9	33.8	0.7	0.24
6	A	472.0	8.6	2.3	0.74
7	A	526.2	26.1	3.1	0.13
8	A	580.9	26.2	8.9	0.23
9	A	760.5	35.3	9.6	0.29
10	A	812.4	3.5	1.6	0.56
11	A	845.4	183.2	0.9	0.73
12	A	935.9	132.2	3.2	0.26
13	A	1010.4	67.9	4.5	0.30
14	A	1066.2	7.2	5.9	0.64
15	A	1161.8	17.6	4.2	0.75
16	A	1189.0	19.6	8.6	0.14
17	A	1242.1	1.9	2.5	0.47
18	A	1298.5	6.5	2.9	0.75
19	A	1365.2	14.9	0.7	0.62
20	A	1508.8	6.4	5.1	0.67
21	A	1615.0	1.7	5.4	0.75
22	A	1652.2	15.6	4.6	0.59
23	A	1659.5	30.4	7.1	0.75
24	A	3344.8	36.2	308.0	0.09
25	A	3355.4	1.6	26.0	0.73
26	A	3366.0	6.7	103.8	0.19
27	A	3409.8	9.1	87.2	0.10
28	A	3535.3	3.5	105.9	0.34
29	A	3540.2	4.8	66.2	0.55
30	A	3546.8	4.1	72.8	0.40

5.Dissociation into NH_2 + N_2H_2 + N_2H_3 (two bonds breaking at B and C).
12. Dissociation into N_4H_6 + NH_2 (bond breaking at D).
14. Dissociation into NH_2 + N_4H_6 (bond breaking at B).
15. Dissociation into N_3H_4 + N_2H_3 (bond breaking at C).

N_5H_7 , Pentazine (A)

C_1, ^1A, H_f=74.58 kcal/mol, I_{sp}=260.7 sec.

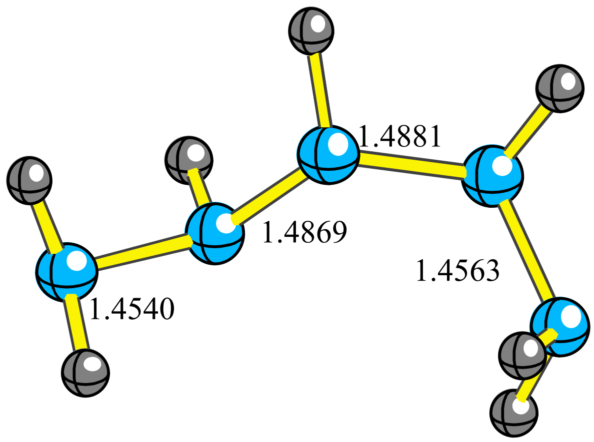


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	112.3	3.2	1.6	0.64
2	A	146.2	40.3	0.3	0.30
3	A	219.8	23.7	0.3	0.73
4	A	297.3	23.4	0.4	0.32
5	A	346.6	5.5	1.8	0.14
6	A	536.0	14.9	0.4	0.63
7	A	655.5	20.8	2.3	0.70
8	A	757.8	57.8	7.5	0.19
9	A	798.1	44.8	1.6	0.20
10	A	861.8	141.9	0.9	0.68
11	A	889.4	11.1	10.5	0.29
12	A	1021.6	8.0	2.1	0.24
13	A	1059.7	5.4	8.6	0.20
14	A	1096.7	126.9	1.0	0.74
15	A	1151.8	8.1	3.5	0.24
16	A	1172.2	26.6	6.8	0.26
17	A	1283.2	5.5	1.3	0.29
18	A	1332.0	8.6	2.8	0.50
19	A	1448.5	2.0	1.9	0.31
20	A	1522.7	3.2	3.5	0.67
21	A	1544.7	0.4	3.4	0.71
22	A	1619.5	27.6	4.3	0.73
23	A	1639.0	15.4	5.5	0.63
24	A	3359.1	15.0	64.4	0.16
25	A	3435.1	0.6	148.5	0.12
26	A	3462.0	1.3	135.9	0.12
27	A	3511.7	1.0	133.3	0.08
28	A	3517.8	2.4	67.7	0.69
29	A	3534.9	8.9	37.1	0.46
30	A	3564.1	8.6	71.3	0.67

8. Dissociation into N_2H_3 + N_3H_4 (bond breaking at B).
11. Dissociation into N_4H_5 + NH_2 (bond breaking at D).
13. Dissociation into NH_2 + N_4H_5 (bond breaking at A).

N_5H_7 , Pentazine (B)

C_1, ^1A, H_f=76.71 kcal/mol, I_{sp}=264.4 sec.

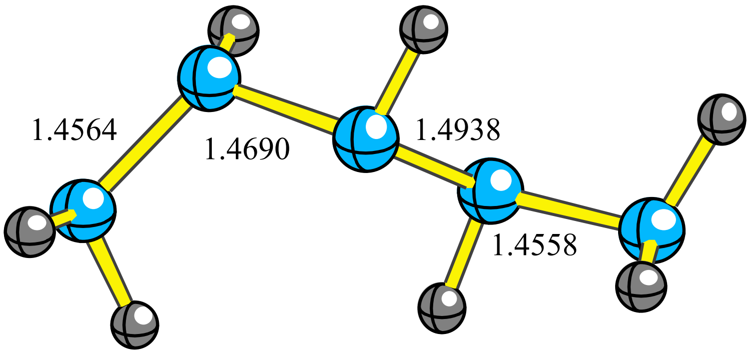


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	60.1	0.4	0.8	0.73
2	A	126.3	7.2	0.6	0.55
3	A	292.4	11.6	0.2	0.05
4	A	353.9	25.3	1.4	0.21
5	A	413.6	44.8	1.5	0.64
6	A	425.6	17.0	6.6	0.18
7	A	573.0	54.6	3.5	0.51
8	A	772.0	33.9	3.1	0.62
9	A	850.0	11.6	5.3	0.75
10	A	908.0	193.8	0.4	0.72
11	A	917.9	41.0	3.4	0.74
12	A	990.1	56.1	4.7	0.18
13	A	1033.3	14.2	11.0	0.10
14	A	1066.1	33.1	3.1	0.29
15	A	1180.5	13.6	2.6	0.62
16	A	1203.5	18.2	3.2	0.39
17	A	1307.3	5.9	3.1	0.69
18	A	1327.2	10.6	0.8	0.69
19	A	1462.3	2.1	5.3	0.40
20	A	1486.3	0.3	4.1	0.65
21	A	1510.2	0.2	3.0	0.56
22	A	1666.3	14.5	4.3	0.60
23	A	1669.8	14.7	6.0	0.61
24	A	3338.9	16.7	193.7	0.21
25	A	3396.5	9.7	124.4	0.13
26	A	3407.4	8.8	153.2	0.11
27	A	3460.7	0.8	141.9	0.25
28	A	3474.1	3.2	144.5	0.20
29	A	3536.1	1.6	48.0	0.58
30	A	3546.6	5.4	31.8	0.59

No frequency corresponds to N-N bond breaking.

N_5H_7 , Pentazine (C)

C_1, ^1A, H_f=52.27 kcal/mol, I_{sp}=218.2 sec.

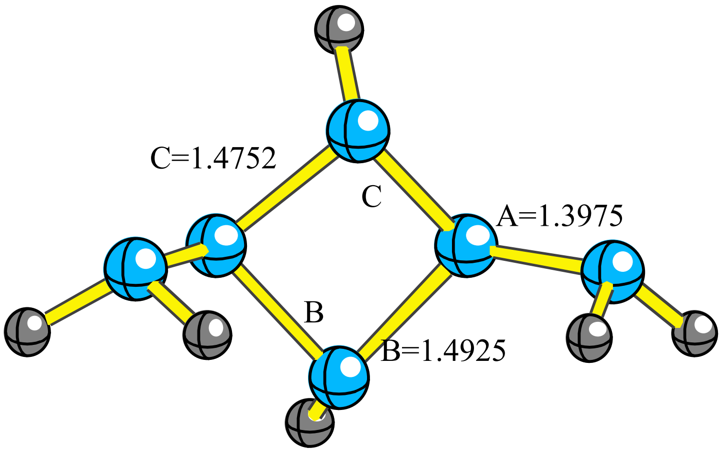


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	45.9	2.3	0.4	0.72
2	A	143.7	8.4	0.7	0.69
3	A	253.4	13.8	0.2	0.19
4	A	362.6	23.0	4.0	0.13
5	A	405.2	32.0	2.4	0.42
6	A	449.5	20.1	7.9	0.19
7	A	555.4	53.3	4.2	0.42
8	A	769.7	12.3	4.7	0.72
9	A	831.6	122.5	4.0	0.73
10	A	888.1	91.7	7.1	0.54
11	A	908.3	101.3	2.5	0.72
12	A	973.6	51.4	2.8	0.23
13	A	1058.9	15.7	3.4	0.40
14	A	1087.8	32.7	0.9	0.09
15	A	1156.5	13.9	9.8	0.10
16	A	1220.3	7.3	1.9	0.25
17	A	1305.9	1.3	0.5	0.72
18	A	1318.2	7.5	1.7	0.43
19	A	1450.1	10.0	0.3	0.71
20	A	1497.0	1.0	0.9	0.73
21	A	1533.2	1.3	4.1	0.74
22	A	1654.9	15.4	4.3	0.53
23	A	1666.2	14.3	6.2	0.69
24	A	3402.2	9.9	149.2	0.11
25	A	3419.0	7.9	144.5	0.04
26	A	3437.7	1.4	143.6	0.06
27	A	3441.0	3.8	104.4	0.62
28	A	3469.5	3.3	22.5	0.30
29	A	3543.7	5.4	55.3	0.65
30	A	3546.6	3.1	57.3	0.51

No frequency corresponds to N-N bond breaking.

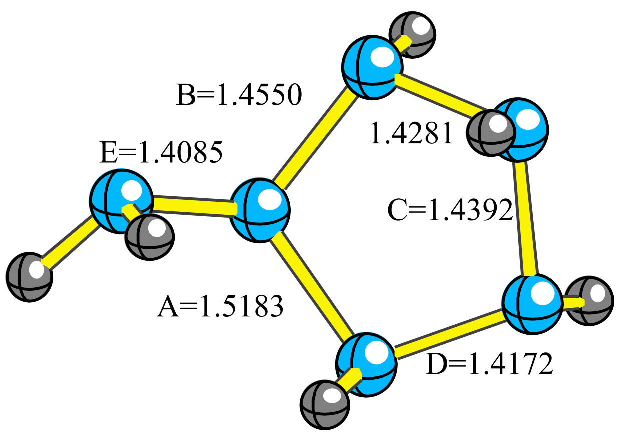
N_6H_6 , Paradiaminocyclotetrazane

C_1, ^1A, H_f=135.86 kcal/mol, I_{sp}=325.4 sec.



N_6H_6 , Aminocyclopentazane

C_1, ^1A, H_f=121.65 kcal/mol, I_{sp}=307.9 sec.



Vibrational frequency for N_6H_6, paradiaminocyclotetrazane.

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	118.1	0.1	2.6	0.38
2	A	281.3	29.7	0.6	0.75
3	A	318.3	38.5	2.7	0.54
4	A	402.7	11.5	2.4	0.25
5	A	468.9	99.8	2.9	0.75
6	A	520.8	0.8	3.5	0.19
7	A	546.5	2.0	0.5	0.75
8	A	704.7	12.6	11.2	0.26
9	A	796.4	68.3	0.3	0.75
10	A	814.3	132.0	4.3	0.75
11	A	829.2	105.6	7.3	0.11
12	A	907.0	9.3	17.6	0.20
13	A	937.6	14.2	10.5	0.75
14	A	960.5	60.0	0.8	0.33
15	A	1114.2	80.6	0.4	0.62
16	A	1130.3	32.2	2.9	0.75
17	A	1135.7	1.9	10.1	0.03
18	A	1252.0	6.9	6.2	0.05
19	A	1288.4	17.1	0.8	0.75
20	A	1319.7	0.6	0.7	0.75
21	A	1340.2	1.8	0.5	0.67
22	A	1389.6	10.3	0.6	0.75
23	A	1629.0	3.1	7.8	0.75
24	A	1637.3	47.2	3.3	0.58
25	A	3410.2	4.4	31.5	0.27
26	A	3410.7	6.8	288.1	0.06
27	A	3429.7	1.1	81.8	0.55
28	A	3440.3	5.1	126.1	0.21
29	A	3568.6	14.4	60.8	0.58
30	A	3568.7	5.0	107.1	0.41

5.Ring opening at B.
12.Dissociation into NH + N_5H_5 (two bonds breaking at B).
13.Dissociation into $2N_3H_3$ (two bonds breaking at B and C).
14. Dissociation into NH + N_5H_5 (two bonds breaking at C).

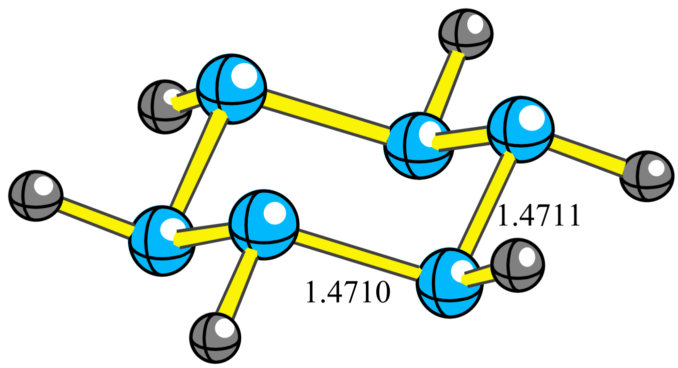
Vibrational frequencies for N_6H_6, aminocyclopentazane.

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	105.2	0.9	0.4	0.38
2	A	276.0	36.5	0.7	0.74
3	A	408.5	10.3	0.7	0.71
4	A	476.8	7.2	6.6	0.20
5	A	555.1	8.3	1.3	0.51
6	A	674.6	16.5	9.2	0.46
7	A	733.4	14.0	4.9	0.48
8	A	771.1	34.7	11.8	0.07
9	A	810.6	20.4	2.9	0.44
10	A	856.0	35.1	1.9	0.12
11	A	868.3	57.4	2.5	0.51
12	A	897.9	124.9	0.8	0.38
13	A	943.2	9.3	1.0	0.71
14	A	1019.0	20.4	1.4	0.61
15	A	1033.0	58.1	2.2	0.54
16	A	1097.0	52.3	1.2	0.75
17	A	1204.9	37.3	1.1	0.74
18	A	1265.0	35.3	15.5	0.04
19	A	1308.2	3.9	2.0	0.11
20	A	1370.8	3.5	0.2	0.75
21	A	1439.6	4.9	3.5	0.13
22	A	1515.1	1.3	5.6	0.73
23	A	1526.9	0.7	3.4	0.66
24	A	1637.7	19.2	6.0	0.55
25	A	3350.8	21.5	234.4	0.13
26	A	3365.6	0.2	16.2	0.38
27	A	3460.1	0.7	173.8	0.16
28	A	3482.2	1.0	23.6	0.73
29	A	3492.9	6.3	45.1	0.37
30	A	3567.7	13.4	77.5	0.41

6. Ring opening at A.
7. Ring opening at A or B.
8. Dissociation into N_2H_2 + N_4H_4 (two bonds breaking at A and B).
10. Ring opening at C.
11. Ring opening at A,B, or C.
12. Ring opening at D.
13. Ring opening at E.

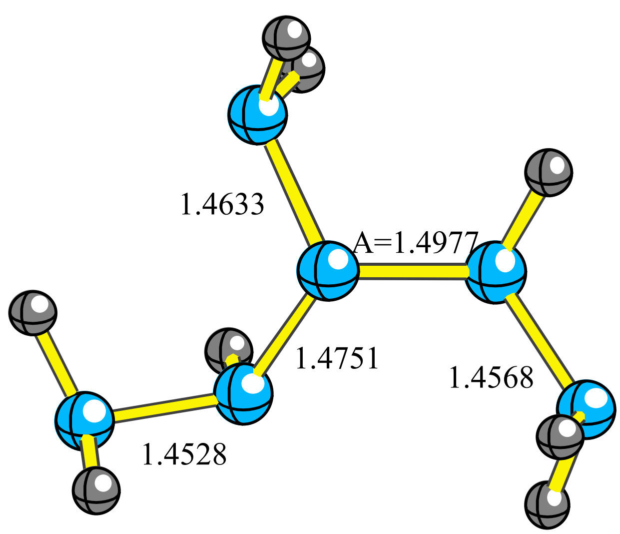
N$_6$H$_6$, Cyclohexazane

C_{2h}, ^1A_g, H_f=153.20 kcal/mol, I_{sp}=345.6 sec.



N$_6$H$_8$, 3-aminopentazine

C_1, ^1A, H_f=89.70 kcal/mol, I_{sp}=261.5 sec.



Vibrational frequecies of N_6H_6, cyclohexazane.

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	Au	314.0	18.4	0.0	0.00
2	Bu	314.0	18.5	0.0	0.48
3	Ag	490.9	0.0	1.3	0.75
4	Bg	491.2	0.0	1.3	0.75
5	Ag	513.1	0.0	0.1	0.32
6	Bu	720.4	110.4	0.0	0.74
7	Au	843.5	50.8	0.0	0.73
8	Bu	843.5	50.8	0.0	0.75
9	Ag	843.6	0.0	5.5	0.73
10	Bg	843.9	0.0	5.4	0.75
11	Ag	845.7	0.0	29.5	0.17
12	Au	988.6	0.0	0.0	0.55
13	Au	1102.4	80.1	0.0	0.55
14	Bu	1102.6	80.1	0.0	0.74
15	Bg	1171.6	0.0	5.3	0.75
16	Ag	1171.7	0.0	5.4	0.75
17	Ag	1189.2	0.0	13.4	0.02
18	Bu	1241.4	83.8	0.0	0.58
19	Au	1353.6	0.0	0.0	0.62
20	Bg	1454.6	0.0	0.0	0.75
21	Ag	1468.9	0.0	4.7	0.75
22	Bg	1469.0	0.0	4.7	0.75
23	Bu	1498.0	38.5	0.0	0.60
24	Au	1498.2	38.5	0.0	0.21
25	Bu	3424.0	2.3	0.0	0.75
26	Bg	3428.0	0.0	107.6	0.75
27	Ag	3428.2	0.0	108.8	0.73
28	Au	3429.1	13.7	0.0	0.26
29	Bu	3429.4	13.7	0.0	0.75
30	Ag	3430.3	0.0	304.9	0.07

7. Open ring.
8. Dissociation into $NH + N_5H_5$ (two bonds breaking).
12. Dissociation into $3N_2H_2$ (three bonds breaking).

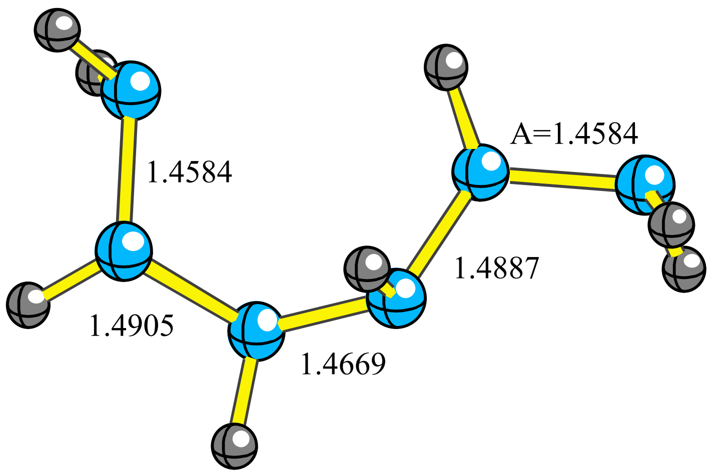
Vibrational frequecies of N_6H_8 , 3-aminopentazine.

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	120.8	2.9	0.8	0.75
2	A	158.6	2.0	0.4	0.68
3	A	269.0	8.2	0.2	0.75
4	A	304.2	15.4	1.9	0.19
5	A	345.7	20.2	0.9	0.75
6	A	373.9	63.4	0.8	0.65
7	A	431.0	16.5	2.9	0.32
8	A	491.6	0.7	11.8	0.23
9	A	540.6	18.6	6.4	0.08
10	A	601.0	49.2	4.9	0.67
11	A	783.6	24.7	7.2	0.51
12	A	808.1	51.8	5.1	0.36
13	A	906.2	233.4	0.7	0.36
14	A	917.9	32.8	4.2	0.49
15	A	946.3	34.5	9.2	0.50
16	A	1020.0	33.1	2.0	0.39
17	A	1042.2	10.8	5.2	0.64
18	A	1091.7	94.1	0.9	0.75
19	A	1189.2	8.9	10.7	0.14
20	A	1209.3	8.7	2.0	0.50
21	A	1275.6	2.6	2.2	0.73
22	A	1329.9	11.1	1.0	0.72
23	A	1353.9	4.3	1.0	0.53
24	A	1489.5	2.6	4.2	0.59
25	A	1505.9	4.4	2.0	0.69
26	A	1625.1	17.3	6.9	0.74
27	A	1656.4	18.3	5.3	0.63
28	A	1672.1	14.8	4.0	0.68
29	A	3365.8	11.9	170.0	0.11
30	A	3392.4	2.2	111.5	0.13
31	A	3405.4	6.4	173.3	0.12
32	A	3414.9	7.0	77.9	0.18
33	A	3478.2	3.4	86.9	0.25
34	A	3545.2	3.4	53.0	0.31
35	A	3546.7	7.4	91.4	0.57
36	A	3555.2	8.4	34.3	0.55

15. Dissociation into N_4H_5 + N_2H_3 (bond breaking at A).

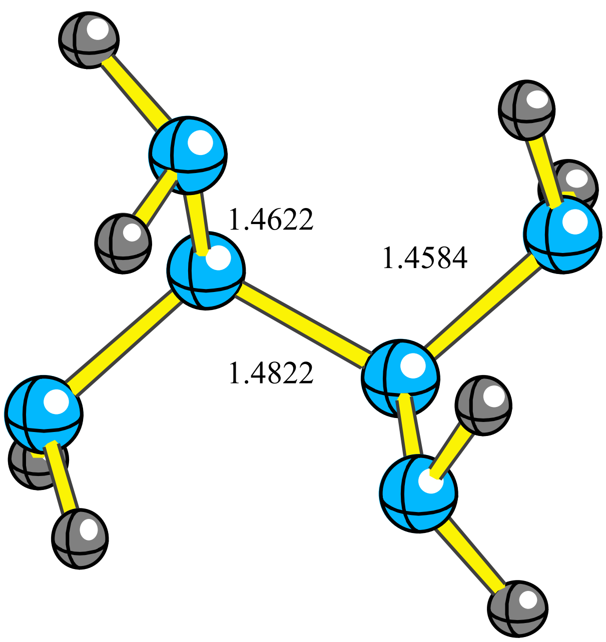
N_6H_8 , Hexazine (A)

C_1, ^1A, H_f=99.92 kcal/mol, I_{sp}=276.01 sec.



N_6H_8 , Tetraaminohydrazine (c,c)

C_2, ^1A, H_f=84.36 kcal/mol, I_{sp}=253.6 sec.



Vibrational frequecies of N_6H_8 , hexazine (A)

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	61.4	7.3	0.3	0.66
2	A	100.3	9.9	0.6	0.48
3	A	138.4	9.8	0.2	0.54
4	A	295.4	33.9	0.5	0.64
5	A	323.4	6.3	1.1	0.20
6	A	369.5	32.7	0.7	0.71
7	A	434.6	28.7	1.6	0.17
8	A	478.6	18.2	5.3	0.25
9	A	601.1	16.8	1.0	0.59
10	A	748.2	26.3	1.8	0.37
11	A	823.7	67.5	1.8	0.56
12	A	839.6	27.0	5.0	0.75
13	A	910.6	61.0	1.5	0.74
14	A	929.6	98.4	4.5	0.28
15	A	989.6	31.4	10.2	0.05
16	A	1057.4	35.5	7.6	0.04
17	A	1076.8	12.2	4.4	0.52
18	A	1127.9	53.9	3.3	0.50
19	A	1176.4	15.5	2.9	0.45
20	A	1201.3	18.4	3.4	0.38
21	A	1308.1	4.9	2.9	0.75
22	A	1312.1	5.0	1.3	0.75
23	A	1452.5	0.6	11.2	0.29
24	A	1469.1	1.5	3.0	0.70
25	A	1496.3	0.5	3.3	0.71
26	A	1514.4	0.7	2.8	0.75
27	A	1624.6	15.9	6.9	0.75
28	A	1666.3	14.3	7.0	0.58
29	A	3343.0	16.2	171.0	0.10
30	A	3369.0	9.7	141.2	0.52
31	A	3401.3	13.0	164.0	0.12
32	A	3416.4	6.4	231.0	0.09
33	A	3451.3	4.2	163.1	0.21
34	A	3489.3	1.4	100.5	0.16
35	A	3529.9	1.8	51.9	0.62
36	A	3574.8	7.5	75.7	0.57

19. Dissociation into N_5H_6 + NH_2 (bond breaking at A).

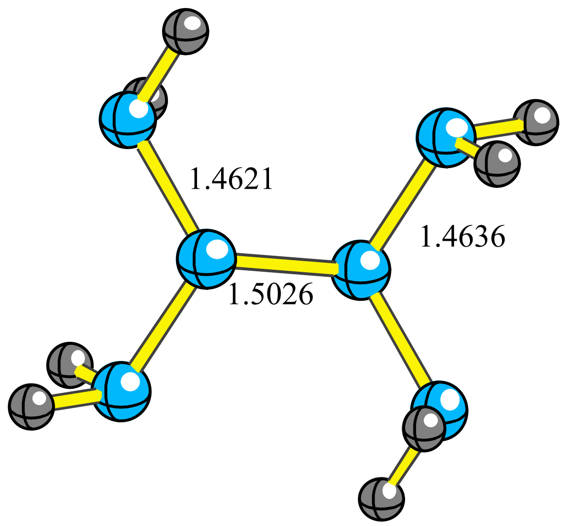
Vibrational frequecies of N_6H_8 , tetraaminohydrazine (c,c)

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	139.5	0.8	0.8	0.68
2	B	255.9	59.3	0.3	0.75
3	B	308.3	21.4	0.6	0.75
4	A	309.6	0.8	1.4	0.31
5	A	333.2	66.9	0.6	0.45
6	B	371.0	4.7	1.1	0.75
7	A	399.3	2.8	1.3	0.33
8	A	439.6	16.8	3.2	0.40
9	B	520.0	49.8	0.3	0.75
10	A	597.1	6.1	8.5	0.20
11	B	660.9	6.4	1.2	0.75
12	A	742.2	16.5	16.6	0.06
13	B	845.6	72.5	4.0	0.75
14	A	851.0	35.0	1.8	0.08
15	A	928.6	0.3	6.4	0.07
16	B	950.9	190.4	0.3	0.75
17	B	1075.3	35.2	3.5	0.75
18	A	1123.1	28.4	4.2	0.14
19	B	1181.0	103.0	2.3	0.75
20	A	1203.3	5.4	7.8	0.58
21	B	1268.2	0.9	1.5	0.75
22	A	1276.3	0.5	5.0	0.60
23	A	1354.9	8.7	1.2	0.40
24	B	1369.5	8.2	0.3	0.75
25	B	1624.9	25.5	4.1	0.75
26	A	1632.3	1.5	8.9	0.73
27	B	1639.7	34.0	5.4	0.75
28	A	1649.3	17.5	2.7	0.23
29	B	3374.9	13.7	4.5	0.75
30	A	3375.4	2.1	202.5	0.05
31	B	3416.6	0.3	39.1	0.75
32	A	3422.1	2.6	168.5	0.04
33	B	3531.4	3.7	71.3	0.75
34	A	3532.3	8.6	109.2	0.21
35	A	3555.4	0.6	169.2	0.43
36	B	3555.6	14.7	2.8	0.75

12. Dissociation into $2N_3H_4$.

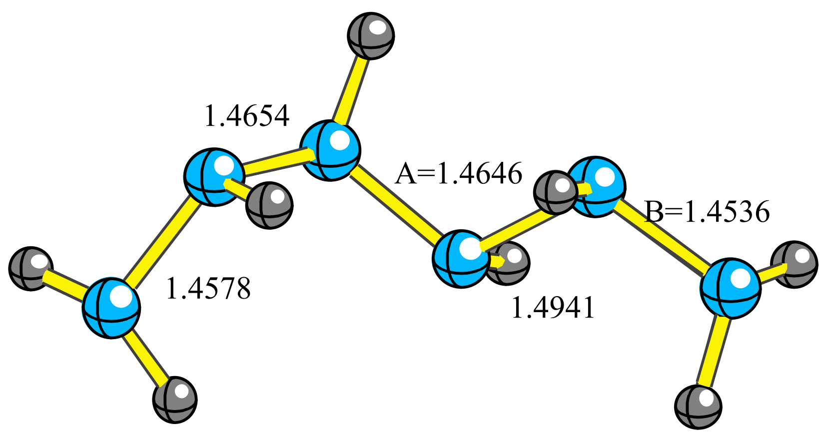
N_6H_8 , Tetraaminohydrazine (t,t)

C_i, ^1A_g, H_f=87.12 kcal/mol, I_{sp}=257.7 sec.



N_6H_8 , Hexazine (B)

C_1, ^1A, H_f=95.19 kcal/mol, I_{sp}=269.4 sec.



Vibrational frequecies of N_6H_8 , tetaaminohydrazine (t,t)

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	Au	112.7	7.3	0.0	0.00
2	Au	243.5	98.7	0.0	0.00
3	Ag	270.4	0.0	3.8	0.54
4	Au	277.7	19.9	0.0	0.00
5	Ag	285.3	0.0	4.2	0.66
6	Au	318.5	20.0	0.0	0.00
7	Au	426.8	12.5	0.0	0.00
8	Ag	430.7	0.0	6.8	0.23
9	Au	534.1	87.3	0.0	0.00
10	Ag	540.7	0.0	8.3	0.34
11	Ag	599.3	0.0	13.6	0.03
12	Ag	760.4	0.0	21.6	0.68
13	Ag	859.3	0.0	4.8	0.71
14	Au	876.7	80.1	0.0	0.00
15	Au	943.1	264.7	0.0	0.00
16	Ag	953.8	0.0	6.4	0.13
17	Au	1069.5	54.5	0.0	0.00
18	Ag	1103.9	0.0	12.4	0.56
19	Au	1186.8	109.4	0.0	0.00
20	Ag	1218.8	0.0	5.1	0.65
21	Ag	1285.4	0.0	4.4	0.64
22	Au	1294.1	8.8	0.0	0.00
23	Au	1365.8	22.2	0.0	0.00
24	Ag	1382.6	0.0	3.9	0.57
25	Au	1635.6	37.9	0.0	0.00
26	Ag	1638.9	0.0	12.3	0.74
27	Au	1650.3	37.7	0.0	0.00
28	Ag	1650.9	0.0	8.2	0.74
29	Au	3337.6	31.3	0.0	0.00
30	Ag	3343.7	0.0	335.0	0.12
31	Au	3376.1	15.6	0.0	0.00
32	Ag	3377.2	0.0	262.4	0.18
33	Au	3542.9	16.2	0.0	0.00
34	Ag	3544.6	0.0	112.8	0.40
35	Ag	3554.6	0.0	156.0	0.40
36	Au	3554.7	21.0	0.0	0.00

12. Dissociation into $2N_3H_4$.
13. Dissociation into $2N_3H_4$.

Vibrational frequecies of N_6H_8 , hexazine (B)

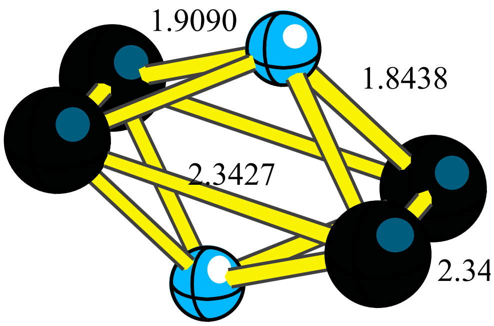
No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	35.1	4.1	0.7	0.73
2	A	85.9	2.0	0.8	0.54
3	A	148.3	5.4	0.4	0.74
4	A	291.2	21.5	0.8	0.10
5	A	339.9	11.8	2.4	0.12
6	A	397.0	14.3	7.0	0.25
7	A	428.1	35.8	0.8	0.39
8	A	543.2	35.7	5.4	0.33
9	A	585.7	49.7	2.7	0.29
10	A	749.3	9.6	4.8	0.73
11	A	796.7	74.2	3.6	0.73
12	A	867.2	139.8	0.5	0.73
13	A	894.3	38.2	12.4	0.57
14	A	932.9	115.5	0.6	0.20
15	A	972.5	32.2	1.7	0.69
16	A	1040.1	31.1	2.0	0.67
17	A	1081.2	26.3	4.8	0.05
18	A	1117.1	15.1	6.9	0.08
19	A	1191.4	19.7	2.4	0.65
20	A	1202.7	6.9	6.4	0.06
21	A	1304.8	4.7	1.9	0.52
22	A	1325.2	2.5	1.3	0.62
23	A	1441.6	6.5	1.3	0.74
24	A	1465.1	5.9	0.7	0.58
25	A	1500.7	0.7	2.0	0.67
26	A	1535.9	2.2	5.6	0.74
27	A	1654.6	1.1	5.2	0.70
28	A	1657.8	30.1	4.6	0.61
29	A	3404.9	9.1	131.3	0.10
30	A	3414.0	5.0	116.8	0.06
31	A	3424.2	1.9	194.2	0.10
32	A	3442.1	2.4	42.0	0.35
33	A	3447.4	1.2	162.4	0.24
34	A	3470.5	5.0	15.6	0.30
35	A	3538.5	3.7	62.4	0.51
36	A	3546.5	5.6	56.3	0.60

13. Dissociation into N_3H_4 + N_2H_2 + NH_2 (two bond breaking at A and B).

Lithium substituted hydrazine derivatives: N_xLi_y molecules.

N_2Li_4

C_{2h}, ^1A, H_f=79.83 kcal/mol, I_{sp}=317.03 sec.



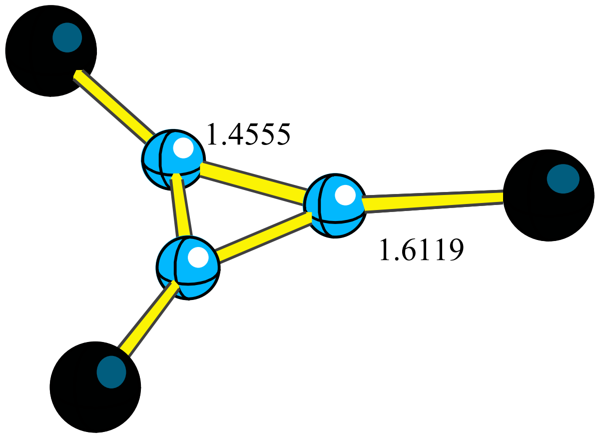
Initial geometry for geometry optimization was hydrazine type structure.

No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	Au	219.1	0.0	0.0	0.41
2	Au	375.3	40.7	0.0	0.46
3	Bu	376.0	40.8	0.0	0.75
4	Ag	472.8	0.0	973.4	0.00
5	Bg	484.5	0.0	196.0	0.75
6	Ag	485.3	0.0	149.2	0.75
7	Ag	486.3	0.0	58.0	0.73
8	Bu	514.5	299.0	0.0	0.75
9	Bg	597.6	0.0	143.9	0.75
10	Au	727.6	214.8	0.0	0.04
11	Bu	728.0	214.9	0.0	0.62
12	Ag	735.1	0.0	325.9	0.03

2.Li-Li-Li-Li ring opening.
3.Li-Li-Li-Li ring opening.
7. Li ring rupture (two bonds breaking).
10. Li-N bond breaking (two bonds breaking).
11.Li-N bond breaking (four bonds breaking).
12. Dissociation into 2Li + N_2Li_2.

N_3Li_3

C_{3h}, $^1A'$, H_f=173.50 kcal/mol, I_{sp}=440.3 sec.

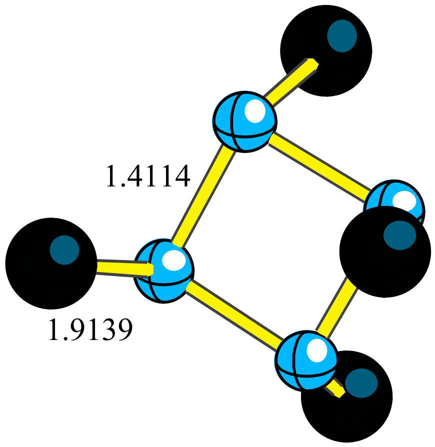


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	E'	62.8	54.1	913.8	0.74
2	A'	155.7	0.0	0.0	0.27
3	A"	158.0	60.0	10.0	0.75
4	E"	253.3	0.0	329.1	0.75
5	E'	560.5	81.7	> 1000	0.72
6	A'	638.2	0.0	> 1000	0.19
7	E'	848.5	23.4	> 1000	0.70
8	A'	1352.5	0.0	> 1000	0.17

5. Ring opening.
7.Dissociation into Li + N_3Li_2 .
8.Dissociation into 3NLi (three bonds breaking).

N_4Li_4

S_4, ^1A, H_f=138.48 kcal/mol, I_{sp}=340.7 sec.

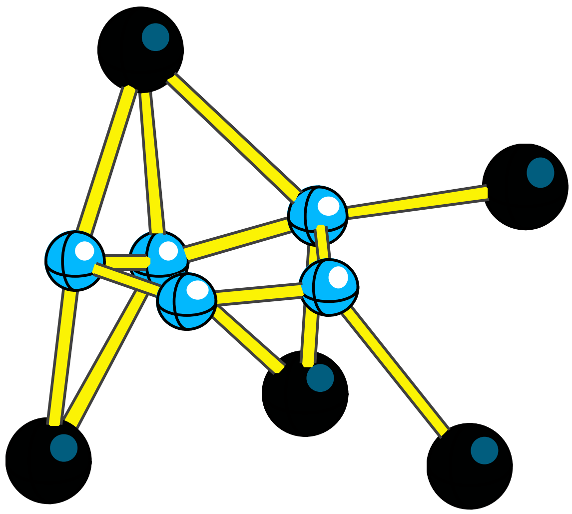


No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	34.5	10.1	60.3	0.75
2	A	34.5	10.1	60.3	0.75
3	A	53.9	2.7	409.1	0.75
4	A	55.5	0.0	206.0	0.00
5	A	108.8	1.8	389.8	0.75
6	A	108.8	1.8	389.8	0.75
7	A	236.2	0.0	> 1000	0.00
8	A	262.7	59.5	632.5	0.75
9	A	321.8	0.0	962.1	0.07
10	A	572.2	48.4	114.4	0.75
11	A	575.0	11.8	770.0	0.75
12	A	575.0	11.8	770.0	0.75
13	A	794.0	0.0	> 1000	0.10
14	A	878.6	5.1	9.5	0.75
15	A	878.6	5.1	9.5	0.75
16	A	1142.3	7.2	5.2	0.75
17	A	1143.7	0.0	801.2	0.01
18	A	1212.9	0.5	12.2	0.75

14.Dissociation into NLi + $N3LI_3$ (two N-N bonds breaking).
15. Dissociation into NLi + $N3LI_3$ (two N-N bonds breaking).
17. Dissociation into 4NLi (four N-N bonds breaking).
18. Dissociation into $2N_2Li_2$ (two N-N bonds breaking).

N_5Li_5

C_1, ^1A, H_f=141.11 kcal/mol, I_{sp}=307.6 sec.



No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	A	81.0	24.6	638.5	0.20
2	A	101.9	9.5	582.2	0.26
3	A	145.4	6.9	80.5	0.51
4	A	169.7	13.6	> 1000	0.16
5	A	204.0	41.2	988.3	0.40
6	A	210.8	9.9	75.8	0.25
7	A	260.8	25.3	> 1000	0.10
8	A	273.5	15.0	> 1000	0.05
9	A	311.2	9.0	935.9	0.12
10	A	343.7	86.6	300.6	0.74
11	A	406.5	5.0	416.1	0.57
12	A	422.2	4.7	> 1000	0.15
13	A	490.4	32.5	430.9	0.18
14	A	504.7	3.7	> 1000	0.07
15	A	532.0	0.8	> 1000	0.73
16	A	607.1	32.5	114.1	0.23
17	A	662.3	101.1	> 1000	0.23
18	A	716.2	3.4	146.1	0.72
19	A	741.2	4.1	778.7	0.19
20	A	848.6	6.0	100.2	0.32
21	A	920.0	8.9	161.6	0.14
22	A	1032.7	4.3	47.2	0.67
23	A	1069.2	36.9	458.8	0.15
24	A	1354.7	39.3	271.6	0.12

15,16,17,18,22,23,24. Ring opening.
19,21. Ring opening (two bonds breaking).

Conclusions.

1. Currently used propellants have calculated I_{sp} less than 200 sec, and the lowest dissociation mode vibrational frequency at more than 800 cm^{-1}.

2. Hydrazine derivatives, especially ring compounds, have I_{sp} about 300 to 360 sec, thus have potential as HEDM molecules. The lowest dissociation mode vibrational frequecy is at the similar range as the currently used molecules. Also, as ring compounds must involve two bond breaking for dissociation into two fragments, the activation barrier is expected to be higher than linear molecules of similar kind.

3. Lithium substitution on hydrogen position further increases I_{sp} without lowering of the lowest dissociation frequency. For example, I_{sp}=440 sec for N_3Li_3.

Acknowledgements
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