Experimental and Theoretical Study of 2,6-Difluorophenylnitrene, its Radical Cation, and of their Rearrangement Products in Argon Matrices.

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Supporting Information, Part 1

Table S1: Vertical excitation energies of difluoroazirine **3b** calculated by the CASPT2 method

Figure S1: Active space of molecular orbitals of **3b** referred to in the last column of Table S1.

Table S2: Vertical excitation energies of difluoroketeneinime **4b** calculated by the CASPT2 method

Figure S2: Active space of molecular orbitals of **4b** referred to in the last column of Table S2

Table S3: Vertical excitation energies of difluoroketeneinime radical cation $\mathbf{4b}^{\bullet+}$ calculated by the CASPT2 method

Figure S3: Active space of molecular orbitals of $\mathbf{4b}^{\bullet+}$ referred to in the last column of Table S3

Table S1: Vertical excitation energies of difluoroazirine **3b** calculated by the CASPT2 method [a].

state	ΔE_{CASSCF} eV	ΔE_{CASPT2} eV	reference weight [b]	λ nm	*F* [c]	Major configurations [d]
1	0.00	0.00	0.76	–	–	87% ground config.
2	4.57	3.78	0.75	328	3.9×10^{-3}	42% H-1→L 26% H→L+1
3	5.52	4.25	0.74	291	2.3×10^{-3}	35% H-1→L+1 +17% H→L +12% H→L+1
4	6.74	4.70	0.71	264	4.0×10^{-2}	18% H→L +1 +18% H-1→L
5	7.50	5.17	0.73	240	1.4×10^{-1}	50% H→L 20% H→L+1
6	6.43	5.58	0.74	222	1.2×10^{-4}	28% H-2→L +15% 2×[H→L]
7	7.88	6.06	0.71	205	9.6×10^{-3}	16% H-2→L+1

[a] based on a CASSCF(14,12)/ANO-S wavefunction at the B3LYP/6-3G(d) geometry; to eliminate intruder states, a level shift of 0.2 h was applied in the CASPT2 calculations; [b] weight of the zero-order CASSCF in the CASPT2 wavefunction; [c] oscillator strength for electronic transition; [d] Electron excitations within the active space of orbitals depicted in Figure S1.

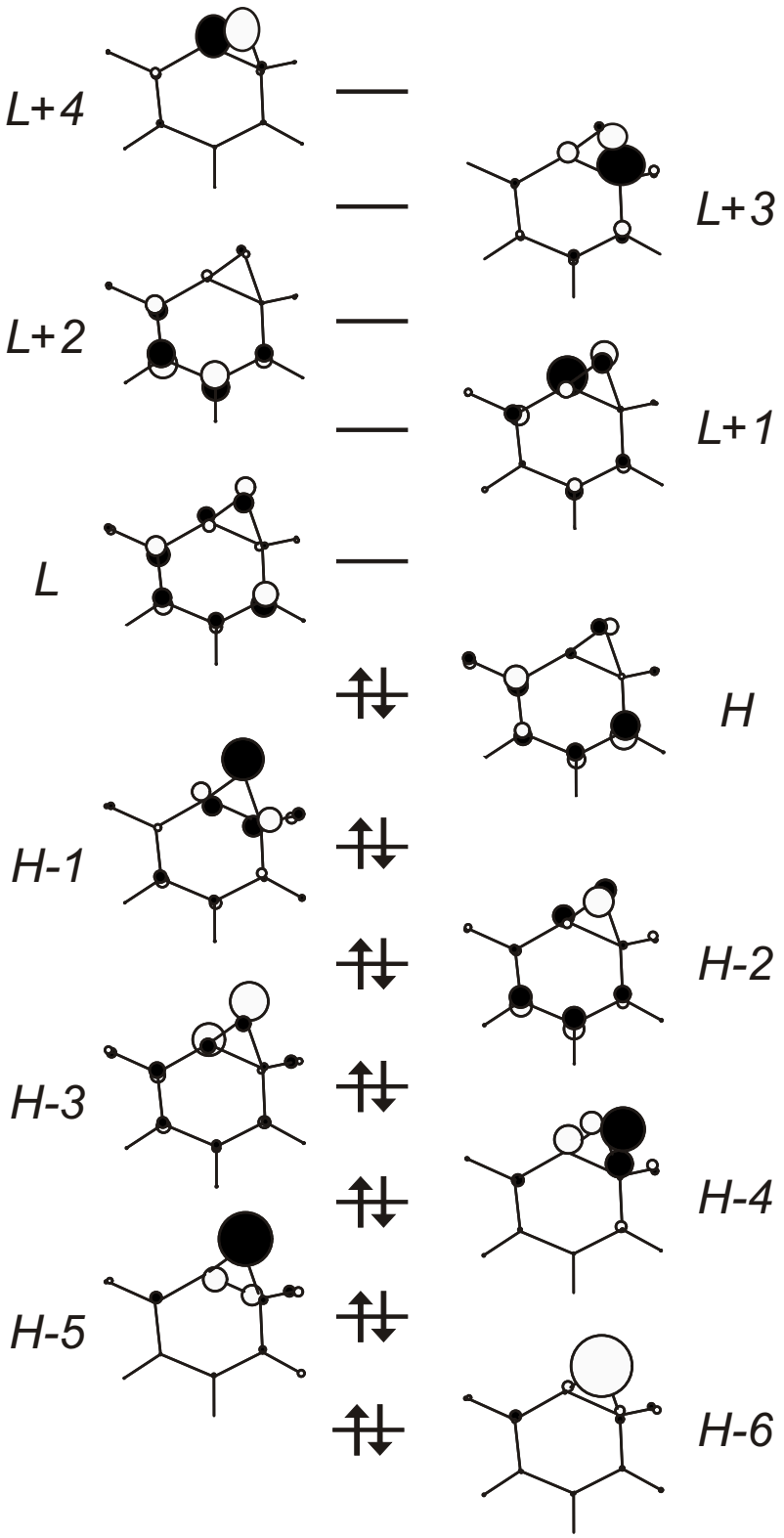

Figure S1

Table S2: Vertical excitation energies of difluoroketeneinime **4b** calculated by the CASPT2 method [a].

state	ΔE_{CASSCF} eV	ΔE_{CASPT2} eV	reference weight [b]	λ nm	*F* [c]	Major configurations [d]
$1A_1$	0.00	0.00	0.76	–	–	87% ground config.
$2A_1$	3.65	2.97	0.75	417	2.0×10^{-2}	60% H→L
$3A_1$	4.02	3.39	0.75	366	6.7×10^{-3}	50% H→L+1 11% [H →L+ H →L+1]
$4A_1$	5.21	4.27	0.74	290	1.6×10^{-2}	44% H-1→L
$6A_1$	6.31	4.56	0.70	271	4.8×10^{-3}	17% H →L+1 16% [H →L+ H→L+1
$5A_1$	5.61	4.93	0.74	251	3.8×10^{-3}	20% 2×[H→L]
$7A_1$	6.62	5.06	0.70	249	1.2×10^{-2}	22% H-2→L 16% 2× [H→L]

[a] based on a CASSCF(14,12)/ANO-S wavefunction at the B3LYP/6-3G(d) geometry; to eliminate intruder states, a level shift of 0.2 h was applied in the CASPT2 calculations; [b] weight of the zero-order CASSCF in the CASPT2 wavefunction; [c] oscillator strength for electronic transition; [d] Electron excitations within the active space of orbitals depicted in Figure S2.

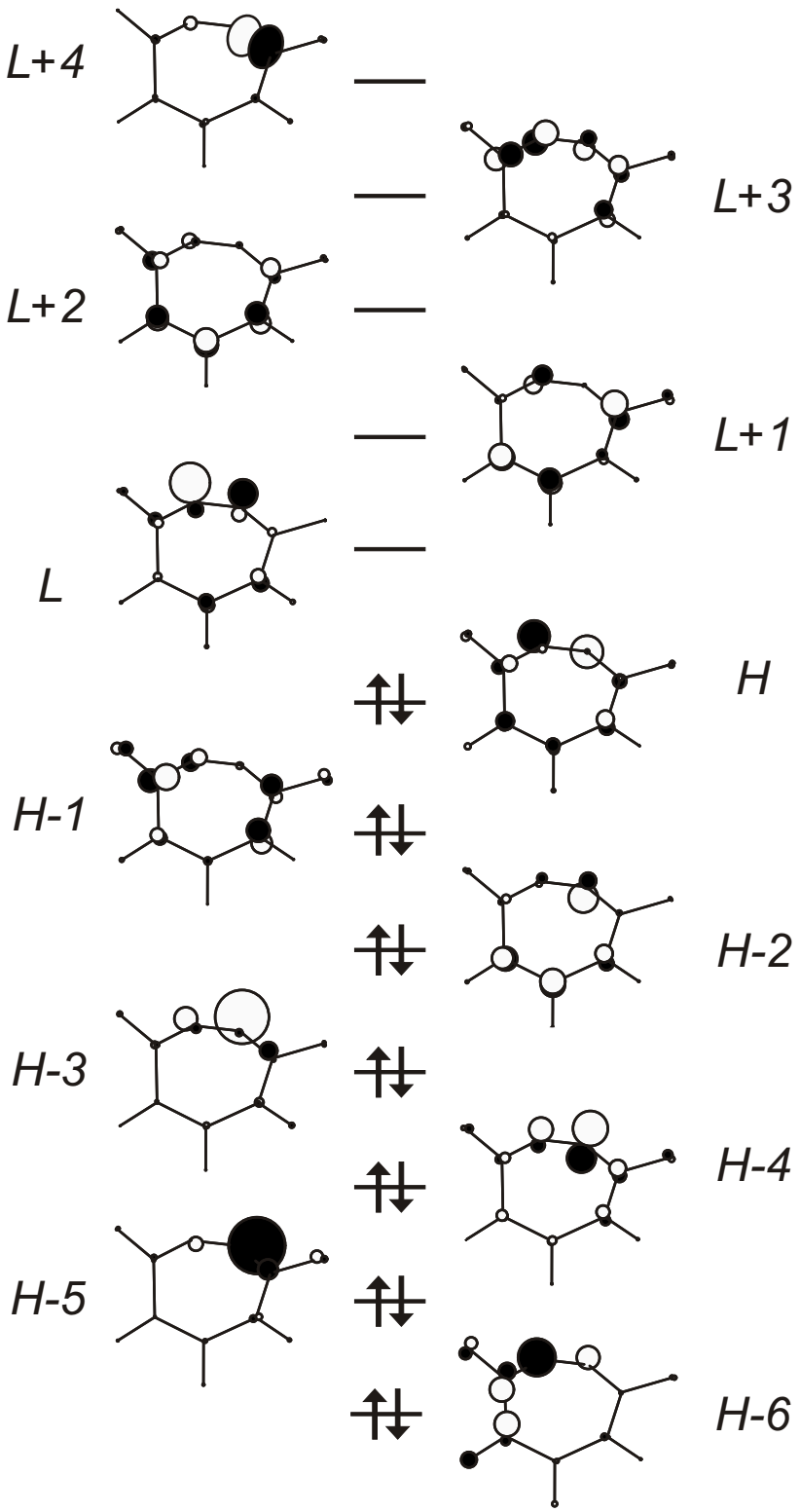

Figure S2

Table S3: Vertical excitation energies of difluoroketeneinime radical cation calculated by the CASPT2 method [a].

state	ΔE_{CASSCF} eV	ΔE_{CASPT2} eV	reference weight [b]	λ nm	*f* [c]	Major configurations [d]
1A’	0.00	0.00	0.76	–	–	86% ground config.
1A”	1.75	1.48	0.76	836	8.2×10^{-4}	78% 27a’→6a”
2A”	2.12	1.83	0.76	677	1.6×10^{-4}	77% 27a’→7a”
2A’	3.69	3.54	0.76	350	1.0×10^{-4}	43% 5a”→6a” +20% 4a”→6a” +12% 5a”→7a”
3A’	4.43	3.83	0.75	324	2.0×10^{-3}	51% 5a”→7a”
4A’	4.65	4.32	0.76	287	3.8×10^{-3}	22% 4a”→6a” +30% 5a”→6a”
5A’	4.84	4.38	0.75	283	8.4×10^{-3}	29% 5a”→6a” +15% 4a”→6a” +12% 4a”→7a”
3A”	5.19	4.68	0.76	265	3.8×10^{-4}	78% 26a’→6a”
4A”	5.53	4.75	0.75	261	5.5×10^{-5}	66% 26a’→7a”
5A”	6.07	5.07	0.75	245	2.9×10^{-4}	64% 5a”→27a’

[a] based on a CASSCF(13,12)/ANO-S wavefunction at the B3LYP/6-3G(d) geometry; to eliminate intruder states, a level shift of 0.2 h was applied in the CASPT2 calculations; [b] weight of the zero-order CASSCF in the CASPT2 wavefunction; [c] oscillator strength for electronic transition; [d] Electron excitations within the active space of orbitals depicted in Figure S3.

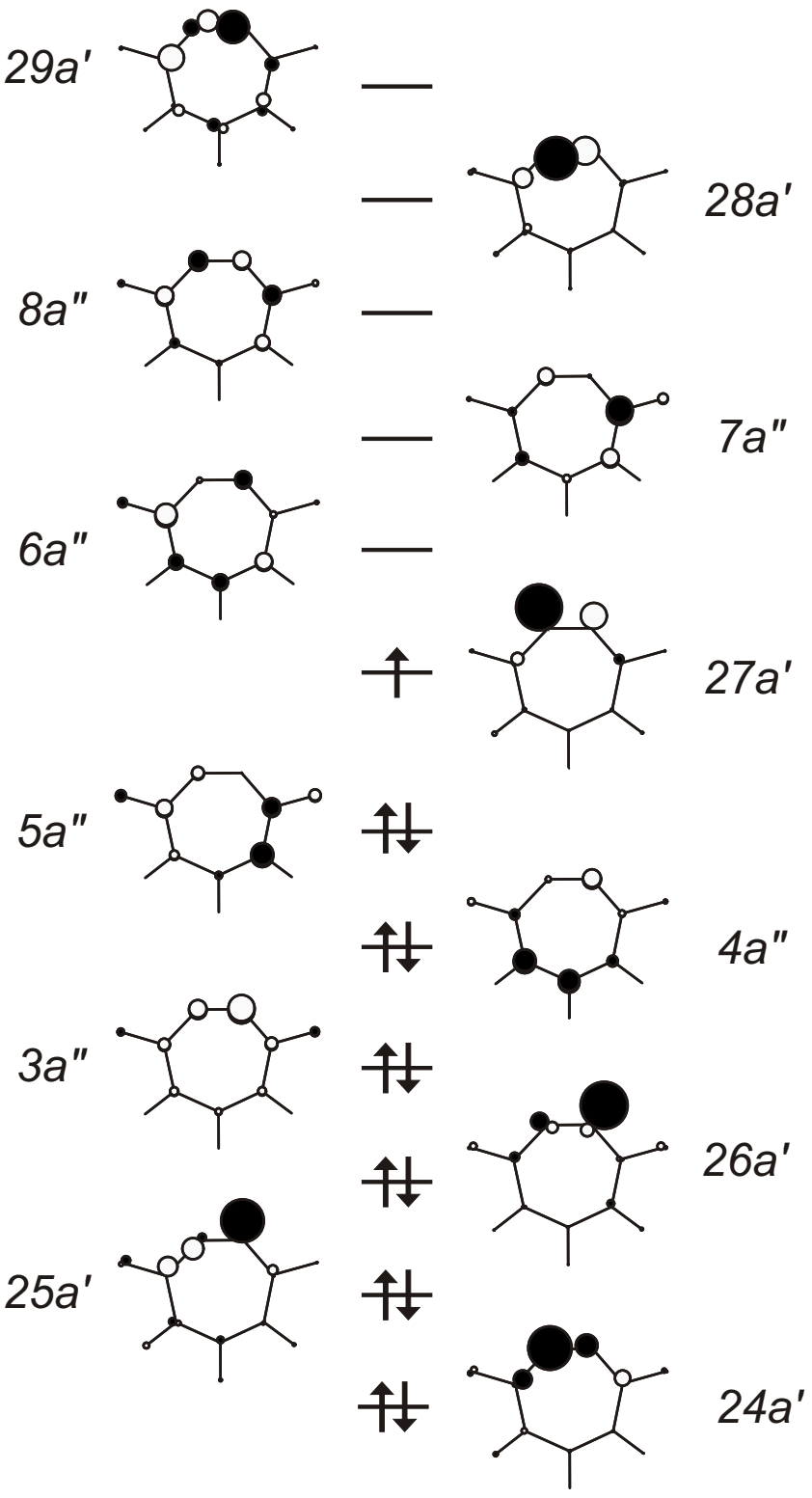

Figure S3

Experimental and Theoretical Study of 2,6-Difluorophenylnitrene, its Radical Cation, and of their Rearrangement Products in Argon Matrices.

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Supporting Information, Part 2

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Neutral systems

#n b3lyp/6-311+g(3d,2p)

- STRUCTURE 1b -

0,3

7	0.000000	0.000000	-2.158529
6	0.000000	0.000000	-0.840209
6	0.000000	0.000000	1.993055
6	-1.207787	0.000000	-0.068346
6	1.207787	0.000000	-0.068346
6	1.217875	0.000000	1.304655
6	-1.217875	0.000000	1.304655
9	-2.363307	0.000000	-0.742736
9	2.363307	0.000000	-0.742736
1	2.163240	0.000000	1.826566
1	-2.163240	0.000000	1.826566
1	0.000000	0.000000	3.073049

E(UB+HF-LYP) = -484.927516183
Zero-point correction= 0.074925 (Hartree/Particle)
Thermal correction to Energy= 0.081800
Thermal correction to Enthalpy= 0.082744
Thermal correction to Gibbs Free Energy= 0.043166

#N B3LYP/6-31G*

- STRUCTURE 1b -

0,3

7	0.000000	0.000000	-2.165935
6	0.000000	0.000000	-0.838326
6	0.000000	0.000000	2.001912
6	-1.211078	0.000000	-0.068636
6	1.211078	0.000000	-0.068636
6	1.220191	0.000000	1.310480
6	-1.220191	0.000000	1.310480
9	-2.364183	0.000000	-0.748518
9	2.364183	0.000000	-0.748518
1	2.171068	0.000000	1.832143
1	-2.171068	0.000000	1.832143
1	0.000000	0.000000	3.086941

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 E(UB+HF-LYP) =  -484.766419476
 Zero-point correction=                           0.075208 (Hartree/Particle)
 Thermal correction to Energy=                    0.082135
 Thermal correction to Enthalpy=                  0.083079
 Thermal correction to Gibbs Free Energy=         0.043419

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#N  B3LYP/6-31G*

- STRUCTURE 3b -

0,1
  6        -1.511467   -0.953073    0.373700
  6        -1.608513    0.493379    0.288891
  6        -0.509743    1.275286    0.102261
  1        -2.576022    0.969649    0.418648
  6         0.701138    0.519196    0.112100
  9        -0.552620    2.602191   -0.054047
  7         1.574480   -0.093520    0.826141
  6         0.835547   -0.901354   -0.187966
  9         1.568906   -1.347383   -1.253058
  1        -0.383193   -2.745960    0.052056
  6        -0.370088   -1.662698    0.129186
  1        -2.429969   -1.486741    0.601213

 E(RB+HF-LYP) =  -484.737462732
 Zero-point correction=                           0.076232 (Hartree/Particle)
 Thermal correction to Energy=                    0.082936
 Thermal correction to Enthalpy=                  0.083880
 Thermal correction to Gibbs Free Energy=         0.045044

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#N  B3LYP/6-31G*

- STRUCTURE 4b -

0,1
  7        -1.205441    0.755393   -0.586009
  6        -1.342016    0.088045    0.615871
  6        -0.330660   -0.144073    1.511624
  6         1.067967    0.155740    1.338702
  6         1.771816    0.234847    0.166555
  6         1.093356   -0.106789   -1.061916
  6        -0.140193    0.366641   -1.166617
  9        -2.599279   -0.174014    0.972588
  1        -0.654227   -0.450066    2.502257
  1         1.615464    0.340099    2.261871
  1         2.816419    0.542464    0.166204
  9         1.703592   -0.857843   -2.000764

  E(RB+HF-LYP) =  -484.745623809
 Zero-point correction=                           0.076325 (Hartree/Particle)
 Thermal correction to Energy=                    0.083174
 Thermal correction to Enthalpy=                  0.084118
 Thermal correction to Gibbs Free Energy=         0.044927

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#N  B3LYP/6-31G*
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- STRUCTURE TS 1b <-> 3b   -

0,1
 6   -1.659246   0.191721   -0.522478
 6   -1.685325   0.216649   0.854069
 6   -0.499928   0.191727   1.673306
 6   0.710978   -0.044018   1.105277
 6   0.756784   -0.266105   -0.344960
 6   -0.377444   0.191269   -1.125837
 9   1.835648   -0.107591   1.816321
 7   1.147263   -1.200094   -1.113492
 9   -0.249330   0.620675   -2.375987
 1   -0.580149   0.301907   2.749701
 1   -2.560448   0.301872   -1.117704
 1   -2.642027   0.291672   1.363182

 E(RB+HF-LYP) = -484.711176481
 Zero-point correction=   0.075026 (Hartree/Particle)
 Thermal correction to Energy=   0.081554
 Thermal correction to Enthalpy=   0.082498
 Thermal correction to Gibbs Free Energy=   0.043983

#N B3LYP/6-31G*

- STRUCTURE TS 3b <-> 4b -

0,1
  6   -1.557424   0.183686   -0.492767
  6   -1.566818   0.004446   0.895626
  6   -0.411440   -0.050572   1.691781
  6   0.863209   -0.057447   1.118859
  6   0.870376   -0.468297   -0.183466
  6   -0.413227   -0.011760   -1.279150
  9   1.963937   0.353313   1.775769
  7   0.463393   -1.145811   -1.175298
  9   -0.242384   0.737758   -2.384505
  1   -0.496593   -0.058348   2.775591
  1   -2.423769   0.623450   -0.980434
  1   -2.525429   0.035589   1.405258

 E(RB+HF-LYP) = -484.726787630
 Zero-point correction=   0.074635 (Hartree/Particle)
 Thermal correction to Energy=   0.081114
 Thermal correction to Enthalpy=   0.082058
 Thermal correction to Gibbs Free Energy=   0.043663

Radical Cations

#n b3lyp/6-311++g**

- STRUCTURE 2b+ -

1,2
  7   0.000000   0.000000   -2.108289
  6   0.000000   0.000000   -0.840896
  6   0.000000   0.000000   1.954114

```
  6        -1.264476    0.000000   -0.063778
  6         1.264476    0.000000   -0.063778
  6         1.248841    0.000000    1.299133
  6        -1.248841    0.000000    1.299133
  9        -2.366587    0.000000   -0.749909
  9         2.366587    0.000000   -0.749909
  1         2.177597    0.000000    1.856497
  1        -2.177597    0.000000    1.856497
  1         0.000000    0.000000    3.039819

 E(UB+HF-LYP) =  -484.596116444
 Zero-point correction=                           0.075944 (Hartree/Particle)
 Thermal correction to Energy=                    0.083040
 Thermal correction to Enthalpy=                  0.083984
 Thermal correction to Gibbs Free Energy=         0.044132

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#n b3lyp/6-31g*

- STRUCTURE 2b+ -

1,2
  7         0.000000    0.000000   -2.112962
  6         0.000000    0.000000   -0.839992
  6         0.000000    0.000000    1.960351
  6        -1.265862    0.000000   -0.063760
  6         1.265862    0.000000   -0.063760
  6         1.250628    0.000000    1.303626
  6        -1.250628    0.000000    1.303626
  9        -2.367856    0.000000   -0.754411
  9         2.367856    0.000000   -0.754411
  1         2.181395    0.000000    1.860975
  1        -2.181395    0.000000    1.860975
  1         0.000000    0.000000    3.047624

 E(UB+HF-LYP) =  -484.466717281
 Zero-point correction=                           0.076605 (Hartree/Particle)
 Thermal correction to Energy=                    0.083689
 Thermal correction to Enthalpy=                  0.084633
 Thermal correction to Gibbs Free Energy=         0.044827

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#n b3lyp/6-31g*

- STRUCTURE 4b+ -

1,2
  7         1.136670    0.846180    0.000000
  6         1.486661   -0.433087    0.000000
  6         0.641861   -1.552913    0.000000
  6        -0.745554   -1.537082    0.000000
  6        -1.646774   -0.453360    0.000000
  6        -1.318804    0.890760    0.000000
  6         0.000000    1.385339    0.000000
  9         2.767284   -0.659767    0.000000
  1         1.142667   -2.515885    0.000000
  1        -1.215113   -2.516074    0.000000
  1        -2.708898   -0.685477    0.000000
  9        -2.287250    1.770461    0.000000
```

E(UB+HF-LYP) = -484.592568598
 Zero-point correction=   0.076948 (Hartree/Particle)
 Thermal correction to Energy=   0.083995
 Thermal correction to Enthalpy=   0.084939
 Thermal correction to Gibbs Free Energy=   0.043798
