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 **4b**[•+] calculated by the CASPT2 method

Figure S3: Active space of molecular orbitals of **4b**[•+] 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.
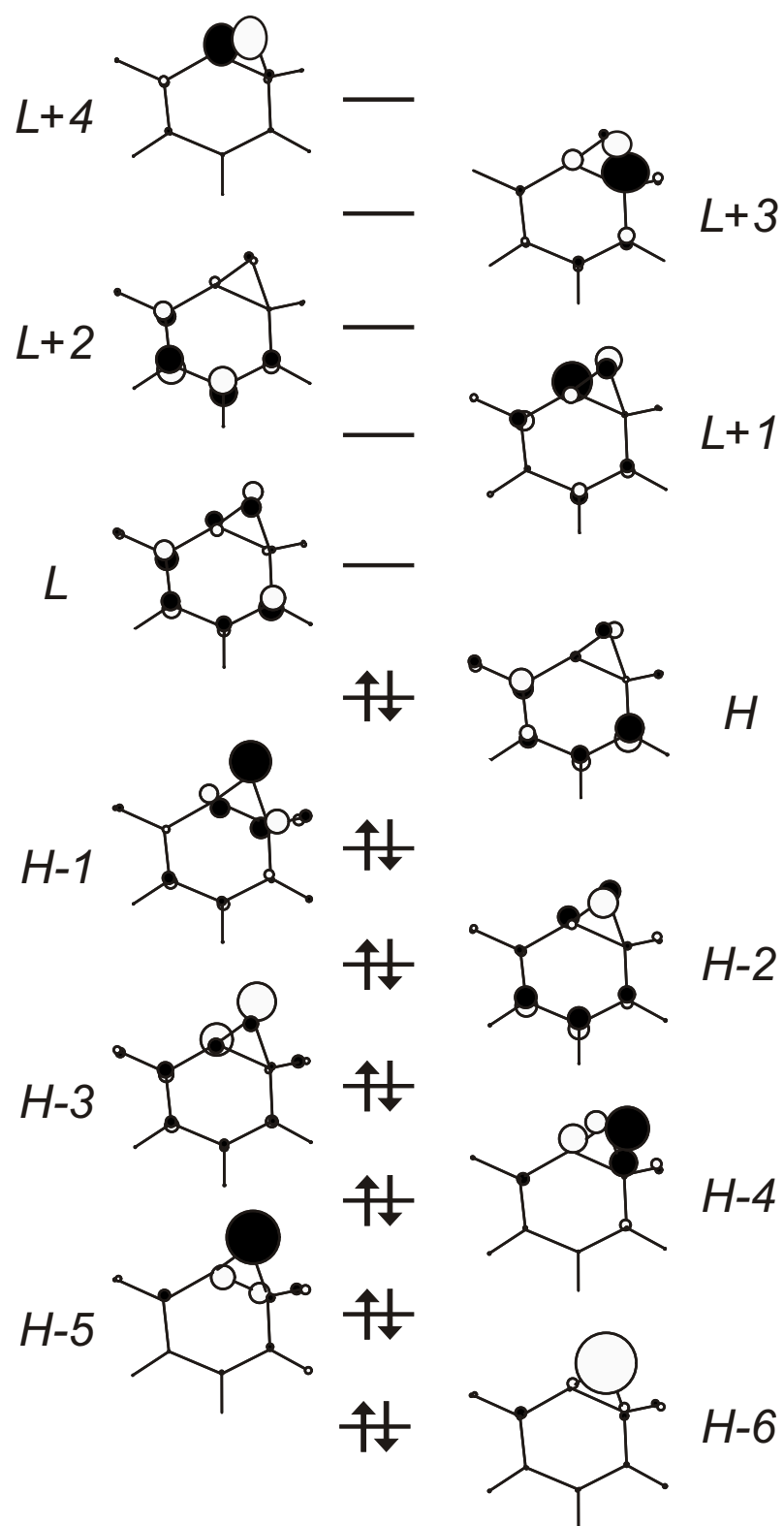
L+4

L+3

L+2

L+1

L

H

H-1

H-2

H-3

H-4

H-5

H-6

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.

L+4

L+3

L+2

L+1

L

H

H-1

H-2

H-3

H-4

H-5

H-6

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.
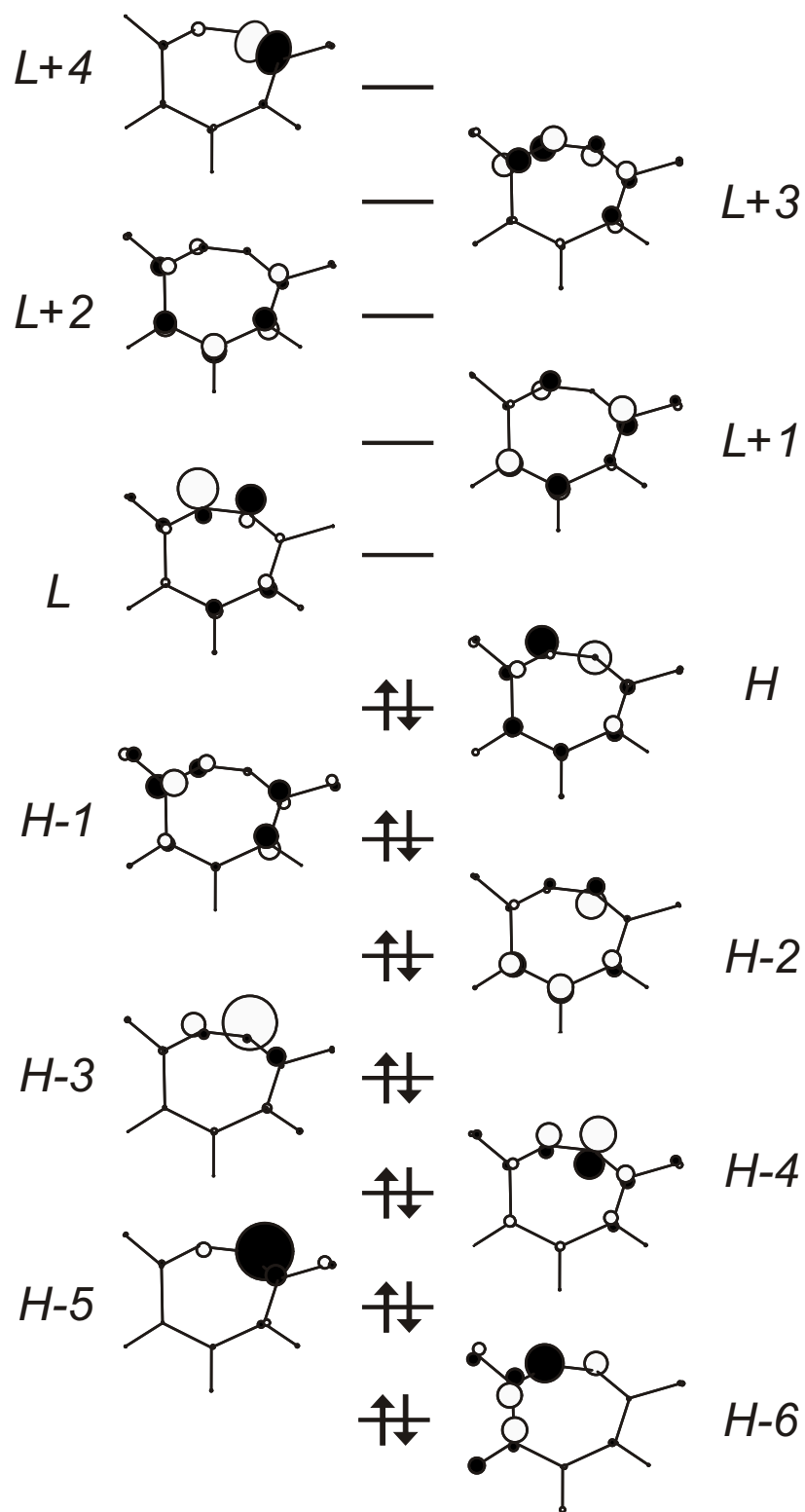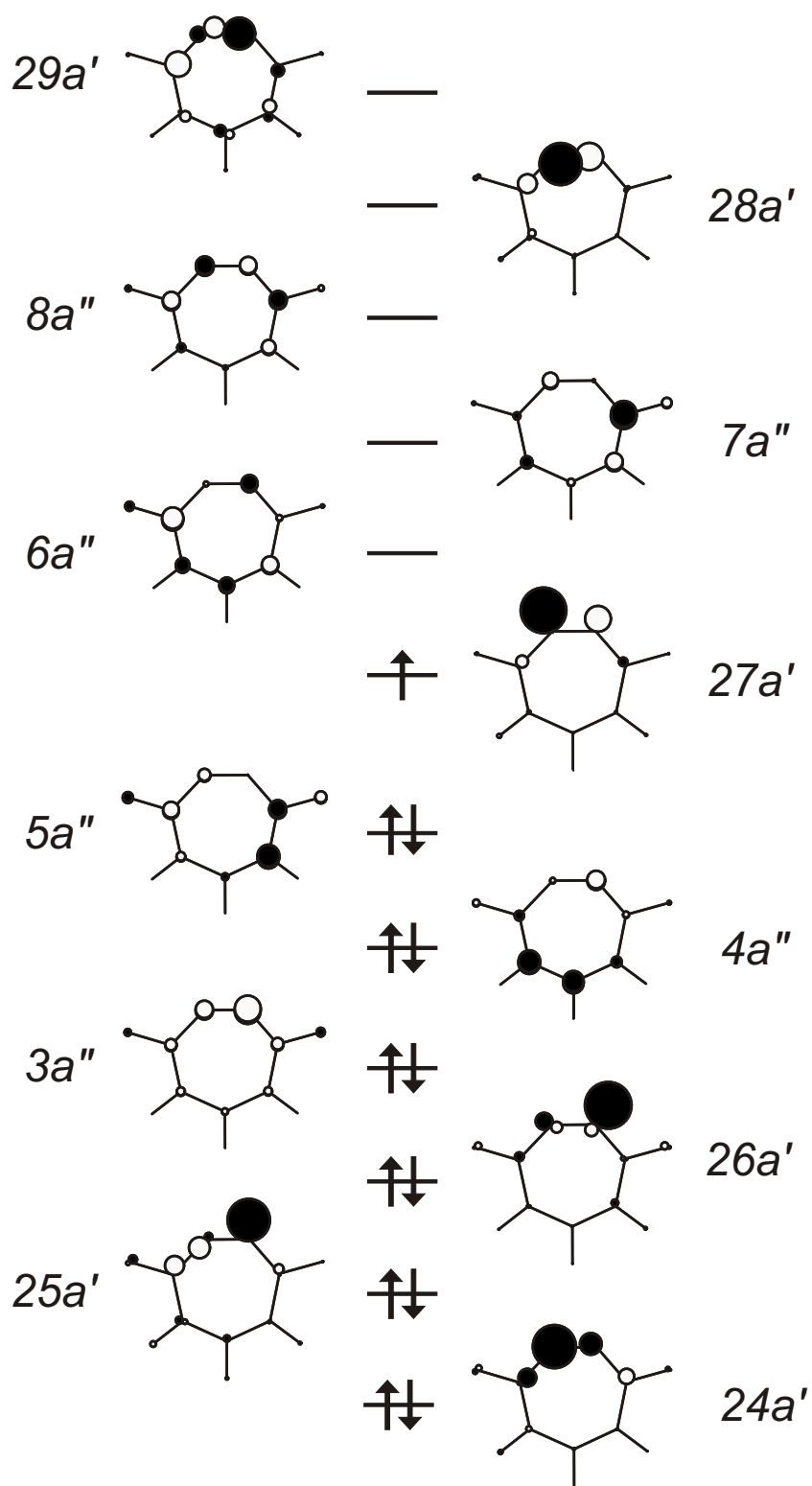
Figure S3

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
```

```
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*
```

- 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
```

#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
```

#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

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```