- Supporting Information -

Designing a $\sigma^0\pi^2$ singlet ground state carbene from dicationic carbones

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Table of Contents

1. Computational methods

For all geometry optimizations, we utilized the B3LYP hybrid density functional[1, 2] as implemented in the Gaussian16 electronic structure[3] code together with the D3-dispersion correction[4] and a def2-TZVPP basis set.[5] For open-shell systems (triplets), we employed an unrestricted Kohn-Sham formalism. Vibrational frequencies were computed in order to correct the electronic energy for effects of the zero-point vibrational motion and to assure the correct nature of the stationary structure; minima exhibit zero imaginary vibrational modes and transition states exactly one. More reliable energies were secured by applying the G4MP2 composite energy method.[6] NEVPT2 and CASSCF computations were performed with the ORCA 5 program employing a (2,2) active space.[7] The natural orbital analysis including natural resonance theory was executed with the NBO 6 software.[8]

References

1. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
2. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Chem. Phys.*, 1994, **98**, 11623-11627.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2016*.
4. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
5. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
6. L. A. Curtiss, P. C. Redfern and K. Raghavachari, *J. Chem. Phys.*, 2007, **127**.
7. F. Neese, *Wiley Interdiscip. Rev.-Comput. Mol. Sci.*, 2022, **12**, e1606.
8. E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2013, **34**, 1429-1437.

2. Optimized geometries, energies, and selected orbitals

2.1 Singlet dication 5

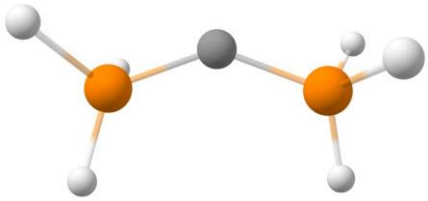
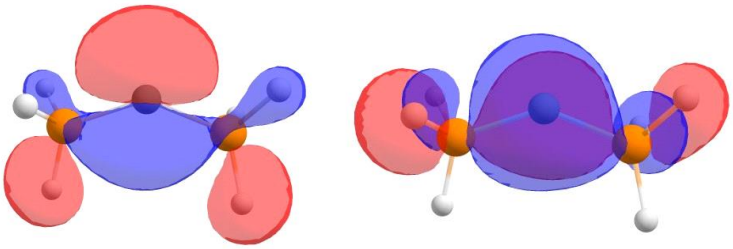


Figure S1. Optimized geometry of ^{1}**5** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.530898000
15	0.000000000	1.662608000	-0.078638000
15	0.000000000	-1.662608000	-0.078638000
1	-1.331400000	1.993925000	0.283707000
1	0.888777000	2.381920000	0.744513000
1	-0.888777000	-2.381920000	0.744513000
1	0.215633000	1.952340000	-1.441351000
1	-0.215633000	-1.952340000	-1.441351000
1	1.331400000	-1.993925000	0.283707000

B3LYP-D3/def2-TZVPP:	-723.5914106
ZPVE:	35.86643
G4MP2(0K):	-722.569273

Selected orbitals



Natural resonance theory

76.4%

CASSCF results

```
-------------------------------------------
CAS-SCF STATES FOR BLOCK  1 MULT= 3 NROOTS= 1
-------------------------------------------

ROOT   0:  E=    -722.0811155682 Eh
      1.00000 [     0]: 11


-------------------------------------------
CAS-SCF STATES FOR BLOCK  2 MULT= 1 NROOTS= 3
-------------------------------------------

ROOT   0:  E=    -722.0417734872 Eh
      0.89269 [     0]: 20
      0.10731 [     2]: 02
ROOT   1:  E=    -722.0224359133 Eh  0.526 eV   4244.1 cm**-1
      1.00000 [     1]: 11
ROOT   2:  E=    -721.9469766245 Eh  2.580 eV  20805.5 cm**-1
      0.89269 [     2]: 02
      0.10731 [     0]: 20

-----------------------
 NEVPT2 TOTAL ENERGIES
-----------------------

STATE   ROOT MULT  Energy/a.u.   MRCI SOC BLOCK INPUT (cm**-1)
   0:    0    3  -722.481219    EDIAG[0] -158566299.280155
   1:    0    1  -722.452570    EDIAG[1] -158560011.473332
   2:    1    1  -722.432635    EDIAG[2] -158555636.157829
   3:    2    1  -722.363633    EDIAG[3] -158540492.076119
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2.2 Triplet dication 5

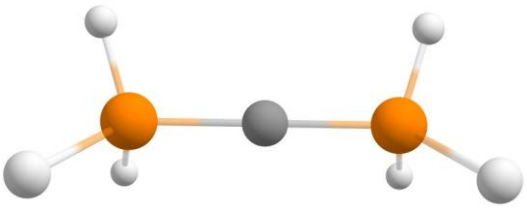
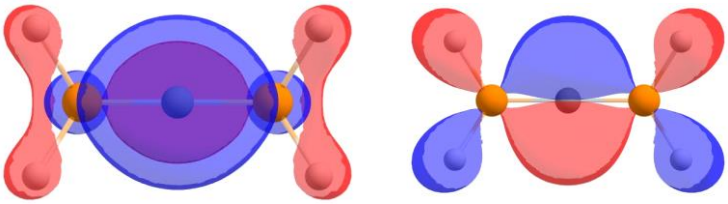


Figure S2. Optimized geometry of ^{3}**5** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.000000000
15	0.000000000	0.000000000	1.751352000
15	0.000000000	0.000000000	-1.751352000
1	0.000000000	1.331175000	2.208277000
1	-1.152831000	-0.665587000	2.208277000
1	0.000000000	1.331175000	-2.208277000
1	1.152831000	-0.665587000	2.208277000
1	1.152831000	-0.665587000	-2.208277000
1	-1.152831000	-0.665587000	-2.208277000

B3LYP-D3/def2-TZVPP:	-723.6320821
ZPVE:	36.52287
G4MP2(0K):	-722.606049

Selected orbitals (ROKS)



2.3 Singlet dication 6

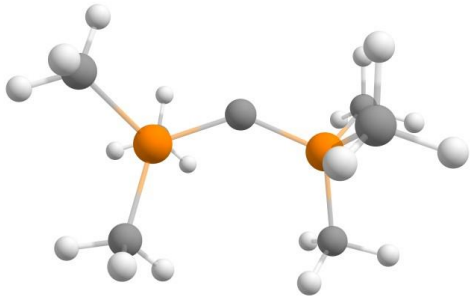
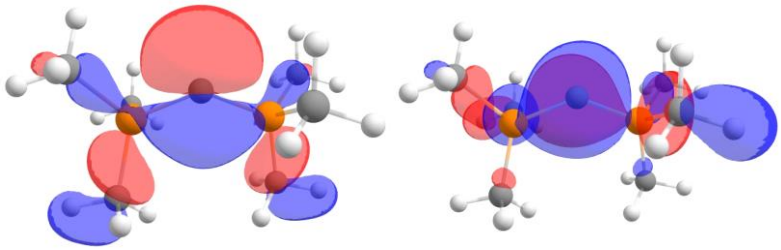


Figure S3. Optimized geometry of ^{1}**6** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.675275000
15	-1.115128000	1.191484000	0.040841000
6	-1.614968000	1.138023000	-1.690332000
1	-0.743701000	1.165743000	-2.343112000
1	-2.199081000	0.237967000	-1.884486000
1	-2.243987000	2.006518000	-1.897896000
6	-2.559958000	1.289272000	1.105041000
1	-3.147259000	2.159364000	0.803989000
1	-3.170882000	0.394124000	0.984790000
1	-2.246989000	1.386324000	2.143185000
6	0.000000000	2.614384000	0.327734000
1	0.911886000	2.541310000	-0.262082000
1	-0.574047000	3.479502000	-0.023796000
1	0.221575000	2.725390000	1.386311000
15	1.115128000	-1.191484000	0.040841000
6	1.614968000	-1.138023000	-1.690332000
1	0.743701000	-1.165743000	-2.343112000
1	2.199081000	-0.237967000	-1.884486000
1	2.243987000	-2.006518000	-1.897896000
6	0.000000000	-2.614384000	0.327734000
1	-0.221575000	-2.725390000	1.386311000
1	-0.911886000	-2.541310000	-0.262082000
1	0.574047000	-3.479502000	-0.023796000
6	2.559958000	-1.289272000	1.105041000
1	3.170882000	-0.394124000	0.984790000
1	2.246989000	-1.386324000	2.143185000
1	3.147259000	-2.159364000	0.803989000

B3LYP-D3/def2-TZVPP:	-959.7992534
ZPVE:	144.63428
G4MP2(0K):	-958.225479

Selected orbitals



HOMO LUMO

Natural resonance theory

61.4%

2.4 Triplet dication 6

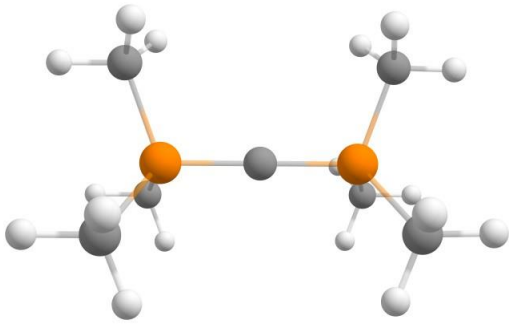
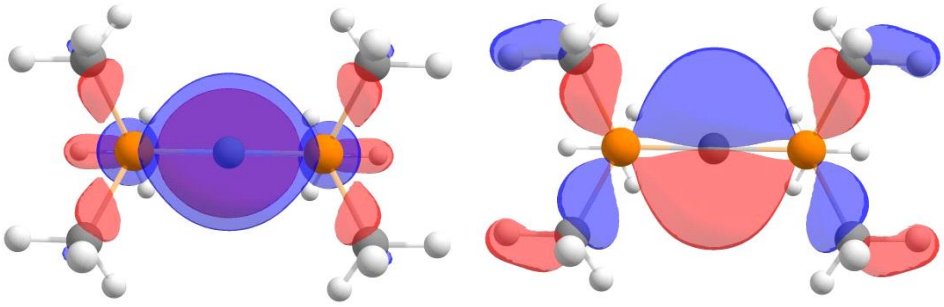


Figure S4. Optimized geometry of ^{3}**6** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.000000000
15	0.000000000	0.000000000	1.756395000
6	0.000000000	1.707911000	2.328485000
1	0.893084000	2.224850000	1.979601000
1	-0.893084000	2.224850000	1.979601000
1	0.000000000	1.691506000	3.420912000
6	-1.479095000	-0.853956000	2.328485000
1	-1.464887000	-0.845753000	3.420912000
1	-2.373318000	-0.338992000	1.979601000
1	-1.480235000	-1.885858000	1.979601000
6	1.479095000	-0.853956000	2.328485000
1	2.373318000	-0.338992000	1.979601000
1	1.464887000	-0.845753000	3.420912000
1	1.480235000	-1.885858000	1.979601000
15	0.000000000	0.000000000	-1.756395000
6	0.000000000	1.707911000	-2.328485000
1	-0.893084000	2.224850000	-1.979601000
1	0.893084000	2.224850000	-1.979601000
1	0.000000000	1.691506000	-3.420912000
6	-1.479095000	-0.853956000	-2.328485000
1	-1.480235000	-1.885858000	-1.979601000
1	-2.373318000	-0.338992000	-1.979601000
1	-1.464887000	-0.845753000	-3.420912000
6	1.479095000	-0.853956000	-2.328485000
1	2.373318000	-0.338992000	-1.979601000
1	1.480235000	-1.885858000	-1.979601000
1	1.464887000	-0.845753000	-3.420912000

B3LYP-D3/def2-TZVPP:	-959.8333022
ZPVE:	145.14166
G4MP2(0K):	-958.262911

Selected orbitals (ROKS)



SOMO1 SOMO2

2.5 Singlet dication 7

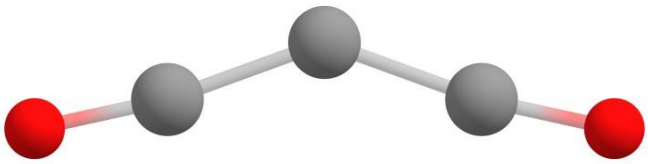
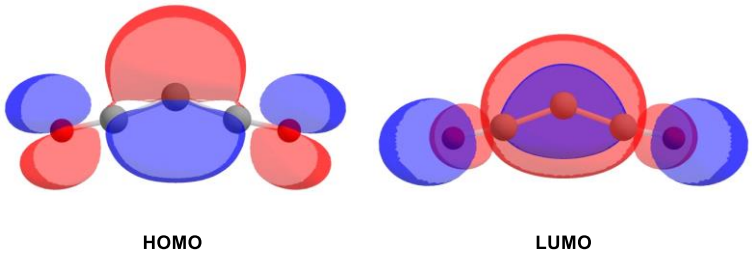


Figure S5. Optimized geometry of ^{1}**7** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

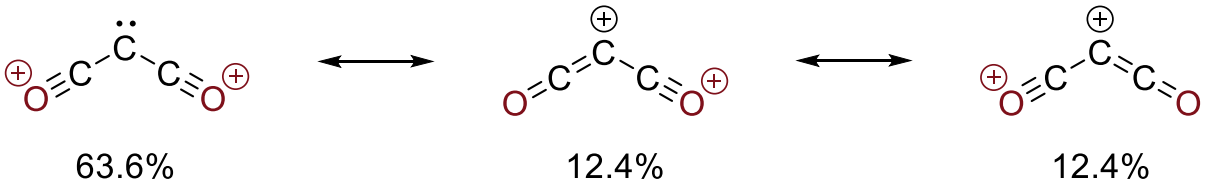
6	0.000000000	0.000000000	0.498145000
6	0.000000000	1.296342000	0.030024000
8	0.000000000	2.392742000	-0.209322000
6	0.000000000	-1.296342000	0.030024000
8	0.000000000	-2.392742000	-0.209322000

B3LYP-D3/def2-TZVPP:	-263.7419526
ZPVE:	11.76049
G4MP2(0K):	-263.345817

Selected orbitals



Natural resonance theory



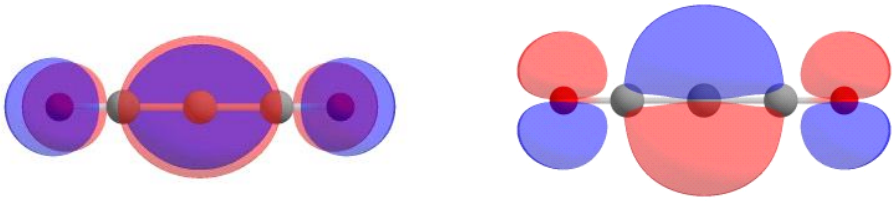
2.6 Triplet dication 7

Figure S6. Optimized geometry of ^{3}**7** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.000000000
6	0.000000000	0.000000000	1.356771000
8	0.000000000	0.000000000	2.479026000
6	0.000000000	0.000000000	-1.356771000
8	0.000000000	0.000000000	-2.479026000

B3LYP-D3/def2-TZVPP:	-263.7849443
ZPVE:	11.7795
G4MP2(0K):	-263.381361

Selected orbitals (UKS)



2.7 Singlet dication 8

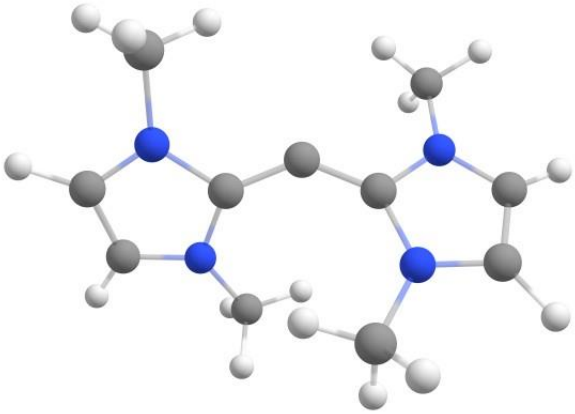
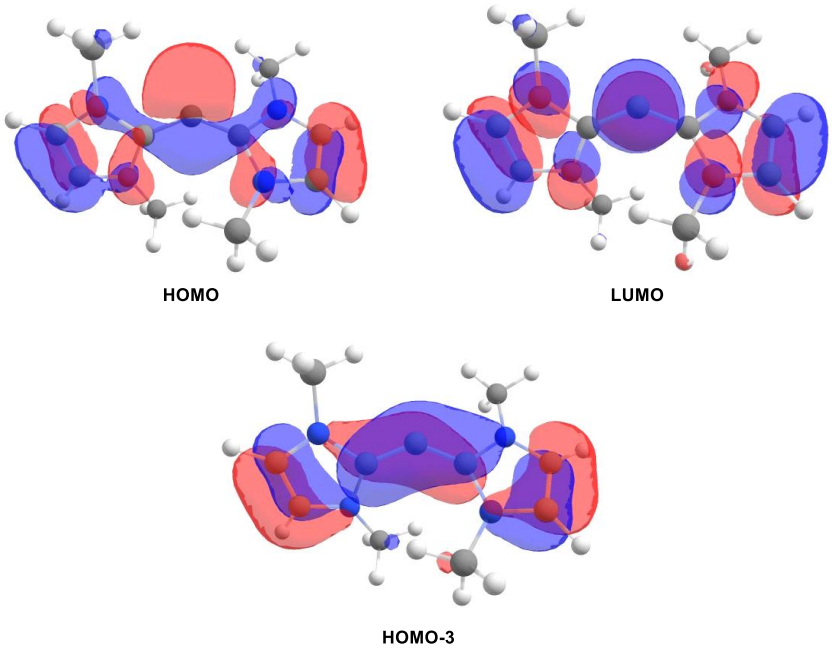


Figure S7. Optimized geometry of ^{1}**8** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

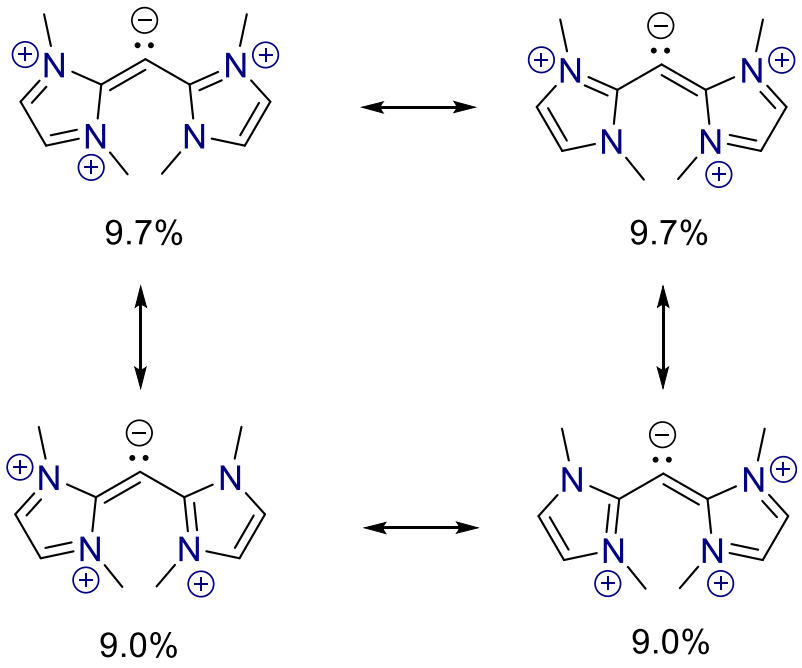
6	0.000000000	0.000000000	0.719110000
6	0.000000000	1.266070000	0.203414000
6	0.000000000	-1.266070000	0.203414000
7	-0.454364000	2.364983000	0.922313000
7	0.545467000	1.807998000	-0.960705000
7	-0.545467000	-1.807998000	-0.960705000
7	0.454364000	-2.364983000	0.922313000
6	-0.240833000	3.491075000	0.230053000
6	0.436878000	3.146818000	-0.930126000
6	-0.436878000	-3.146818000	-0.930126000
6	0.240833000	-3.491075000	0.230053000
1	-0.556505000	4.461775000	0.573917000
1	0.853763000	3.784887000	-1.691733000
1	-0.853763000	-3.784887000	-1.691733000
1	0.556505000	-4.461775000	0.573917000
6	-1.282088000	-1.078953000	-1.999268000
1	-1.440796000	-0.056038000	-1.678930000
1	-0.715280000	-1.099287000	-2.927594000
1	-2.247846000	-1.554371000	-2.152810000
6	1.122632000	-2.282251000	2.225368000
1	0.948764000	-3.211029000	2.760740000
1	2.190624000	-2.127998000	2.085642000
1	0.701198000	-1.438695000	2.765538000
6	1.282088000	1.078953000	-1.999268000
1	1.440796000	0.056038000	-1.678930000
1	0.715280000	1.099287000	-2.927594000
1	2.247846000	1.554371000	-2.152810000
6	-1.122632000	2.282251000	2.225368000
1	-0.948764000	3.211029000	2.760740000
1	-2.190624000	2.127998000	2.085642000
1	-0.701198000	1.438695000	2.765538000

B3LYP-D3/def2-TZVPP:	-647.430387
ZPVE:	165.82089
G4MP2(0K):	-646.153037

Selected orbitals



Natural resonance theory



2.8 Triplet dication 8

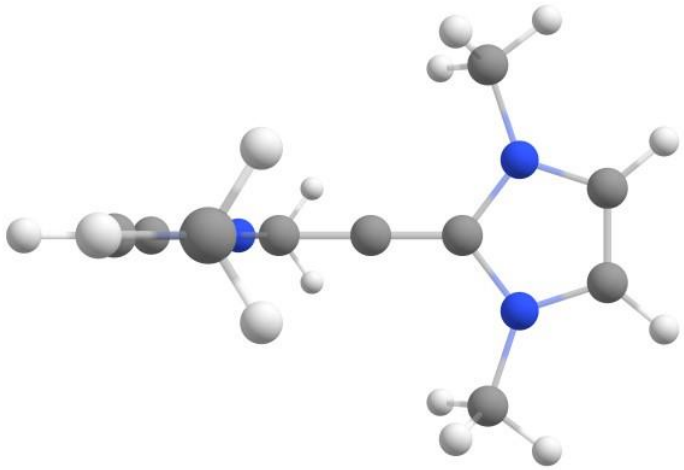
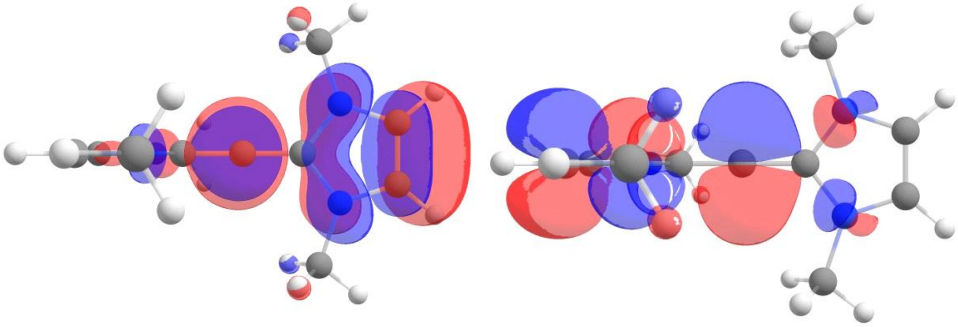


Figure S8. Optimized geometry of ^{3}**8** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.000000000
6	0.000000000	0.000000000	1.342055000
6	0.000000000	0.000000000	-1.342055000
7	0.000000000	-1.105565000	2.179135000
7	0.000000000	1.105565000	2.179135000
7	-1.105565000	0.000000000	-2.179135000
7	1.105565000	0.000000000	-2.179135000
6	0.000000000	-0.690375000	3.465580000
6	0.000000000	0.690375000	3.465580000
6	-0.690375000	0.000000000	-3.465580000
6	0.690375000	0.000000000	-3.465580000
1	0.000000000	-1.374941000	4.296612000
1	0.000000000	1.374941000	4.296612000
1	-1.374941000	0.000000000	-4.296612000
1	1.374941000	0.000000000	-4.296612000
6	-2.494125000	0.000000000	-1.714948000
1	-2.682179000	0.891322000	-1.120022000
1	-3.149577000	0.000000000	-2.580169000
1	-2.682179000	-0.891322000	-1.120022000
6	2.494125000	0.000000000	-1.714948000
1	3.149577000	0.000000000	-2.580169000
1	2.682179000	0.891322000	-1.120022000
1	2.682179000	-0.891322000	-1.120022000
6	0.000000000	2.494125000	1.714948000
1	-0.891322000	2.682179000	1.120022000
1	0.000000000	3.149577000	2.580169000
1	0.891322000	2.682179000	1.120022000
6	0.000000000	-2.494125000	1.714948000
1	0.000000000	-3.149577000	2.580169000
1	-0.891322000	-2.682179000	1.120022000
1	0.891322000	-2.682179000	1.120022000

B3LYP-D3/def2-TZVPP:	-647.4355484
ZPVE:	164.53957
G4MP2(0K):	-646.158661

Selected orbitals (ROKS)



SOMO1 SOMO2

2.9 Singlet dication 9

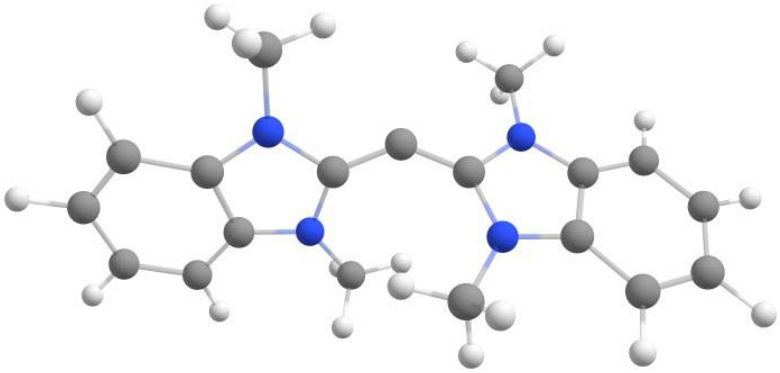


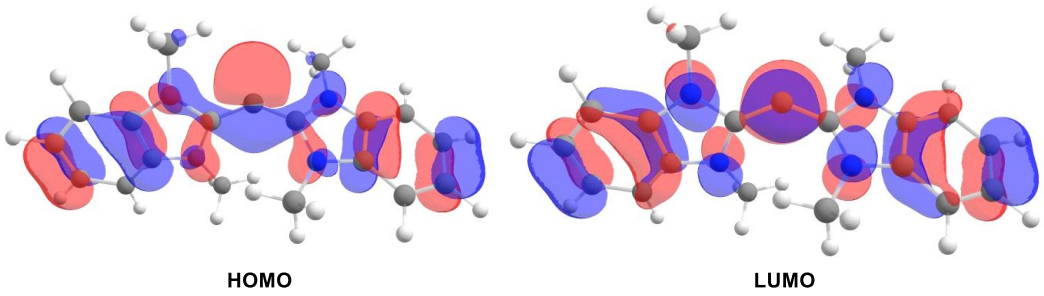
Figure S9. Optimized geometry of **^{1}9** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	1.009089000
6	0.107888000	1.259199000	0.495028000
6	-0.107888000	-1.259199000	0.495028000
7	-0.311498000	2.385727000	1.186690000
7	0.739135000	1.722699000	-0.655921000
7	-0.739135000	-1.722699000	-0.655921000
7	0.311498000	-2.385727000	1.186690000
6	0.000000000	3.503640000	0.485419000
6	0.732268000	3.084100000	-0.660658000
6	-0.732268000	-3.084100000	-0.660658000
6	0.000000000	-3.503640000	0.485419000
6	-1.466837000	-0.917346000	-1.632321000
1	-1.377184000	0.132116000	-1.379731000
1	-1.056264000	-1.092627000	-2.625168000
1	-2.519825000	-1.194183000	-1.623476000
6	1.025570000	-2.354677000	2.460362000
1	0.676367000	-3.179726000	3.075807000
1	2.098235000	-2.445467000	2.296718000
1	0.810827000	-1.404962000	2.942700000
6	1.466837000	0.917346000	-1.632321000
1	1.377184000	-0.132116000	-1.379731000
1	1.056264000	1.092627000	-2.625168000
1	2.519825000	1.194183000	-1.623476000
6	-1.025570000	2.354677000	2.460362000
1	-0.676367000	3.179726000	3.075807000
1	-2.098235000	2.445467000	2.296718000
1	-0.810827000	1.404962000	2.942700000
6	-0.249955000	4.858693000	0.737253000
1	-0.819937000	5.182892000	1.595008000
6	0.286962000	5.756044000	-0.155522000
1	0.137439000	6.815049000	0.001453000
6	1.285414000	4.007290000	-1.552838000
1	1.854429000	3.697562000	-2.416726000

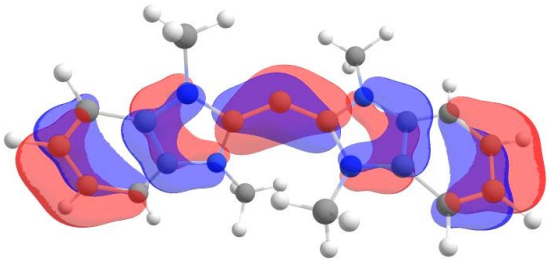
6	1.043982000	5.336262000	-1.285679000
1	1.433031000	6.090385000	-1.955492000
6	0.249955000	-4.858693000	0.737253000
1	0.819937000	-5.182892000	1.595008000
6	-0.286962000	-5.756044000	-0.155522000
1	-0.137439000	-6.815049000	0.001453000
6	-1.285414000	-4.007290000	-1.552838000
1	-1.854429000	-3.697562000	-2.416726000
6	-1.043982000	-5.336262000	-1.285679000
1	-1.433031000	-6.090385000	-1.955492000

B3LYP-D3/def2-TZVPP: -954.8684627
ZPVE: 224.58955
G4MP2(0K): ---

Selected orbitals



HOMO LUMO



HOMO-4

2.10 Triplet dication 9

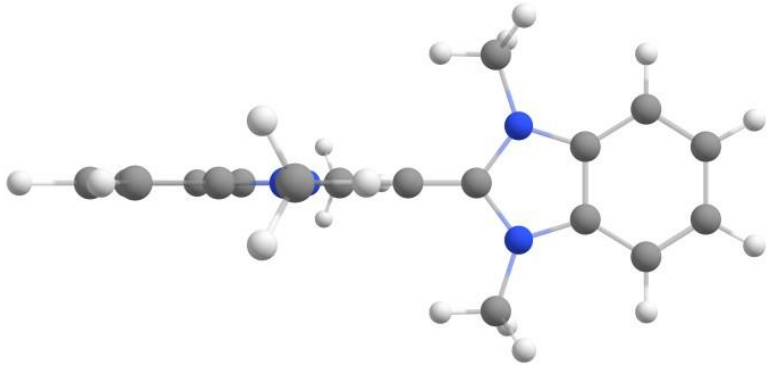


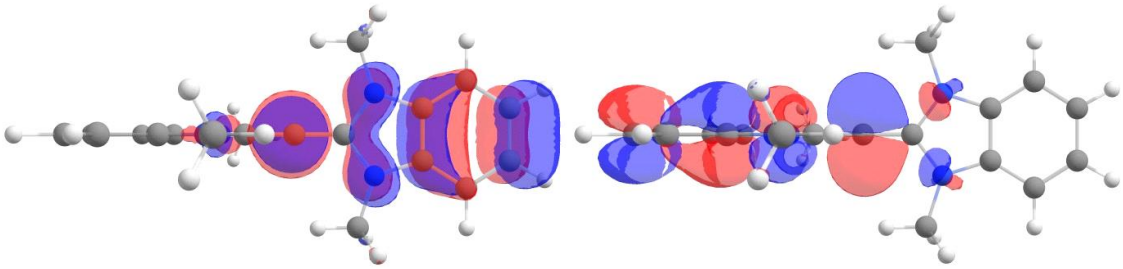
Figure S10. Optimized geometry of ^{3}**9** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.000000000
6	0.000000000	0.000000000	1.339430000
6	0.000000000	0.000000000	-1.339430000
7	0.000000000	-1.114802000	2.165114000
7	0.000000000	1.114802000	2.165114000
7	-1.114802000	0.000000000	-2.165114000
7	1.114802000	0.000000000	-2.165114000
6	0.000000000	-0.710510000	3.469002000
6	0.000000000	0.710510000	3.469002000
6	-0.710510000	0.000000000	-3.469002000
6	0.710510000	0.000000000	-3.469002000
6	-2.504199000	0.000000000	-1.718149000
1	-2.530021000	0.000000000	-0.632963000
1	-3.009403000	0.889425000	-2.090884000
1	-3.009403000	-0.889425000	-2.090884000
6	2.504199000	0.000000000	-1.718149000
1	3.009403000	-0.889425000	-2.090884000
1	3.009403000	0.889425000	-2.090884000
1	2.530021000	0.000000000	-0.632963000
6	0.000000000	2.504199000	1.718149000
1	0.000000000	2.530021000	0.632963000
1	-0.889425000	3.009403000	2.090884000
1	0.889425000	3.009403000	2.090884000
6	0.000000000	-2.504199000	1.718149000
1	0.889425000	-3.009403000	2.090884000
1	-0.889425000	-3.009403000	2.090884000
1	0.000000000	-2.530021000	0.632963000
6	0.000000000	-1.441070000	4.657927000
1	0.000000000	-2.520908000	4.664112000
6	0.000000000	-0.710164000	5.827556000
1	0.000000000	-1.228320000	6.776217000
6	0.000000000	1.441070000	4.657927000
1	0.000000000	2.520908000	4.664112000
6	0.000000000	0.710164000	5.827556000

1	0.000000000	1.228320000	6.776217000
6	1.441070000	0.000000000	-4.657927000
1	2.520908000	0.000000000	-4.664112000
6	0.710164000	0.000000000	-5.827556000
1	1.228320000	0.000000000	-6.776217000
6	-1.441070000	0.000000000	-4.657927000
1	-2.520908000	0.000000000	-4.664112000
6	-0.710164000	0.000000000	-5.827556000
1	-1.228320000	0.000000000	-6.776217000

B3LYP-D3/def2-TZVPP: -954.8745939
ZPVE: 223.17079
G4MP2(0K): ---

Selected orbitals (ROKS)



SOMO1 SOMO2

2.11 Singlet dication 10

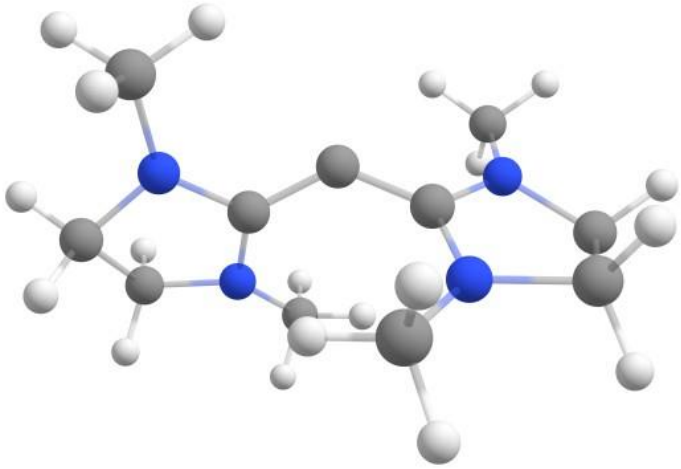


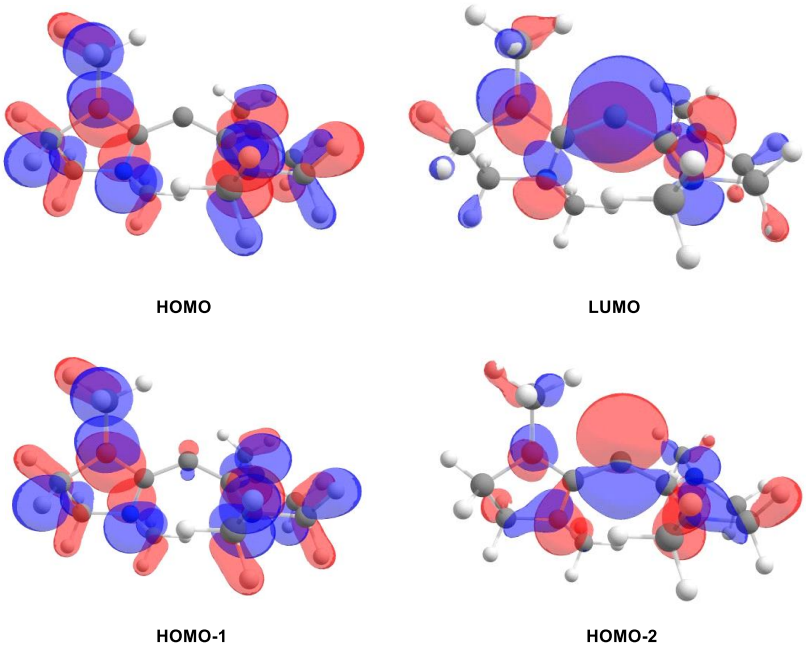
Figure S11. Optimized geometry of ^{1}**10** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.831569000
6	0.000000000	1.276817000	0.242299000
6	0.000000000	-1.276817000	0.242299000
7	-0.788224000	2.253515000	0.715673000
7	0.821290000	1.719963000	-0.728880000
7	-0.821290000	-1.719963000	-0.728880000
7	0.788224000	-2.253515000	0.715673000
6	-0.627593000	3.451020000	-0.127072000
6	0.739040000	3.196849000	-0.769744000
6	-0.739040000	-3.196849000	-0.769744000
6	0.627593000	-3.451020000	-0.127072000
1	-0.662235000	4.345213000	0.492515000
1	0.806021000	3.543457000	-1.798630000
1	-1.563969000	-3.625658000	-0.195225000
1	1.438696000	-3.501022000	-0.858265000
1	-1.438696000	3.501022000	-0.858265000
1	1.563969000	3.625658000	-0.195225000
1	-0.806021000	-3.543457000	-1.798630000
1	0.662235000	-4.345213000	0.492515000
6	1.837860000	-2.121571000	1.714696000
1	2.812510000	-1.982857000	1.242520000
1	1.620744000	-1.265867000	2.353679000
1	1.863028000	-3.031115000	2.311035000
6	-1.955531000	-1.019690000	-1.314286000
1	-2.873454000	-1.236391000	-0.763756000
1	-1.776901000	0.052805000	-1.318863000
1	-2.075128000	-1.353636000	-2.342621000
6	1.955531000	1.019690000	-1.314286000
1	2.075128000	1.353636000	-2.342621000
1	2.873454000	1.236391000	-0.763756000
1	1.776901000	-0.052805000	-1.318863000

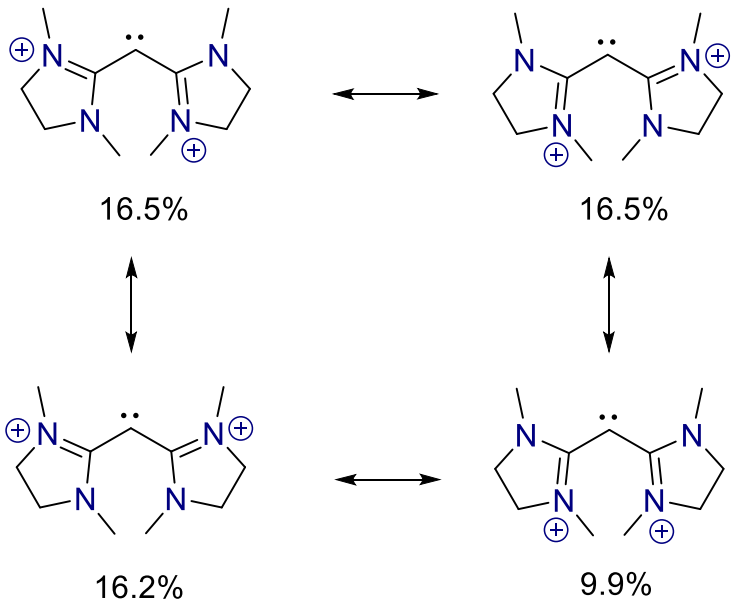
6	-1.837860000	2.121571000	1.714696000
1	-1.620744000	1.265867000	2.353679000
1	-1.863028000	3.031115000	2.311035000
1	-2.812510000	1.982857000	1.242520000

B3LYP-D3/def2-TZVPP: -649.8000057
ZPVE: 193.39445
G4MP2(0K): -648.4777

Selected orbitals



Natural resonance theory



2.12 Triplet dication 10

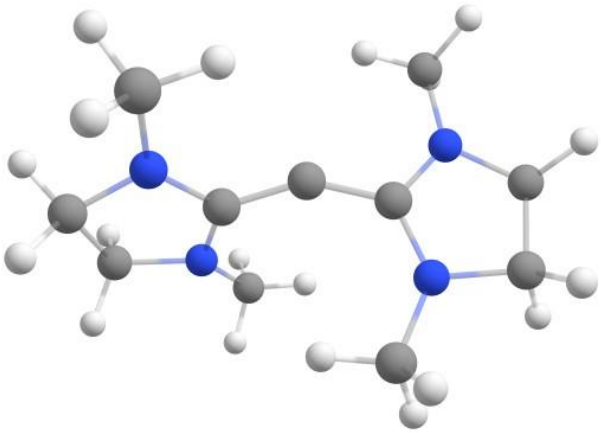


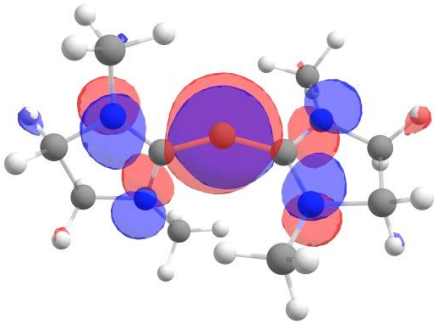
Figure S12. Optimized geometry of ^{3}**10** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.540806000
6	0.332614000	1.319014000	0.170369000
6	-0.332614000	-1.319014000	0.170369000
7	0.000000000	2.366785000	0.922594000
7	1.027046000	1.661817000	-0.918923000
7	-1.027046000	-1.661817000	-0.918923000
7	0.000000000	-2.366785000	0.922594000
6	0.443232000	3.616296000	0.274942000
6	1.323119000	3.111468000	-0.883555000
6	-1.323119000	-3.111468000	-0.883555000
6	-0.443232000	-3.616296000	0.274942000
1	0.983125000	4.235210000	0.989112000
1	1.075701000	3.566985000	-1.839967000
1	-2.389191000	-3.249857000	-0.695254000
1	0.435195000	-4.166790000	-0.066617000
1	-0.435195000	4.166790000	-0.066617000
1	2.389191000	3.249857000	-0.695254000
1	-1.075701000	-3.566985000	-1.839967000
1	-0.983125000	-4.235210000	0.989112000
6	0.847009000	-2.382676000	2.106750000
1	1.773738000	-2.916186000	1.890493000
1	1.078985000	-1.367074000	2.418381000
1	0.325053000	-2.893869000	2.914971000
6	-1.737020000	-0.783927000	-1.838626000
1	-2.806830000	-0.796468000	-1.622384000
1	-1.367441000	0.234535000	-1.758847000
1	-1.579893000	-1.134486000	-2.857281000
6	1.737020000	0.783927000	-1.838626000
1	1.579893000	1.134486000	-2.857281000
1	2.806830000	0.796468000	-1.622384000
1	1.367441000	-0.234535000	-1.758847000
6	-0.847009000	2.382676000	2.106750000

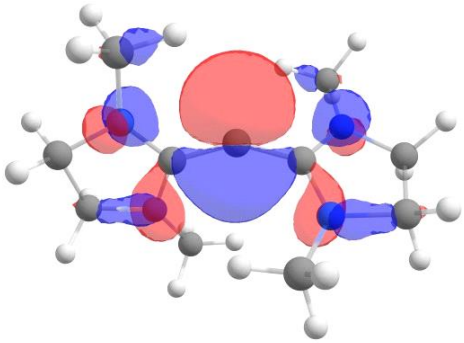
1	-1.078985000	1.367074000	2.418381000
1	-0.325053000	2.893869000	2.914971000
1	-1.773738000	2.916186000	1.890493000

B3LYP-D3/def2-TZVPP:	-649.8203097
ZPVE:	193.60823
G4MP2(0K):	-648.503829

Selected orbitals (ROKS)



SOMO1



SOMO2

2.13 Singlet dication 11

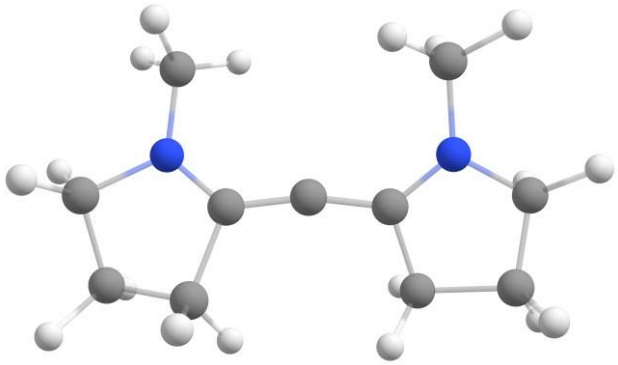


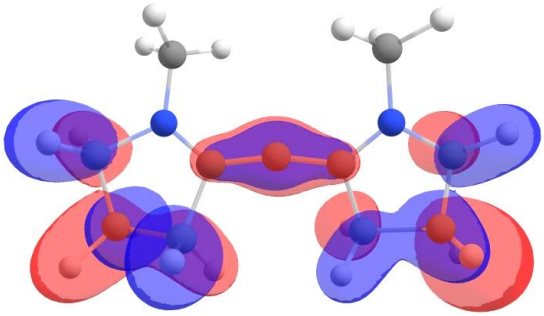
Figure S13. Optimized geometry of ^{1}**11** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.021372000	0.000001000
6	1.328719000	-0.133125000	-0.046279000
6	-1.328719000	-0.133125000	0.046279000
7	2.320676000	0.707060000	0.094429000
6	1.845460000	-1.564447000	-0.362031000
6	-1.845461000	-1.564447000	0.362030000
7	-2.320675000	0.707060000	-0.094430000
6	3.639464000	0.051817000	-0.109112000
6	3.313161000	-1.421568000	0.101351000
6	-3.313162000	-1.421567000	-0.101351000
6	-3.639464000	0.051818000	0.109112000
1	4.348454000	0.457564000	0.610181000
1	3.951568000	-2.085310000	-0.479990000
1	1.295932000	-2.345575000	0.156600000
1	-1.295934000	-2.345576000	-0.156601000
1	-3.398807000	-1.687855000	-1.152898000
1	-3.992316000	0.281861000	1.116328000
1	3.992316000	0.281860000	-1.116328000
1	3.398805000	-1.687855000	1.152898000
1	-3.951570000	-2.085309000	0.479991000
1	-4.348453000	0.457566000	-0.610182000
1	1.740957000	-1.706689000	-1.439501000
1	-1.740957000	-1.706691000	1.439501000
6	2.190807000	2.155031000	0.254640000
1	2.995429000	2.507202000	0.895730000
1	2.266352000	2.649201000	-0.714953000
1	1.233549000	2.389814000	0.718549000
6	-2.190806000	2.155031000	-0.254640000
1	-2.266351000	2.649200000	0.714953000
1	-1.233547000	2.389814000	-0.718549000
1	-2.995427000	2.507202000	-0.895730000

B3LYP-D3/def2-TZVPP: -539.0461529
ZPVE: 172.68867

G4MP2(0K): -537.903667

Selected orbitals



HOMO-2

2.14 Triplet dication 11

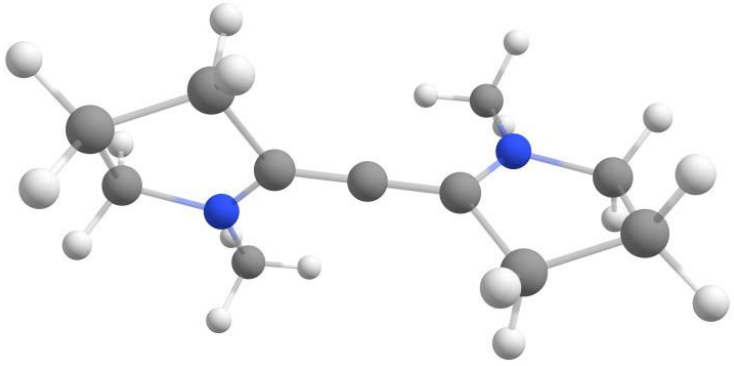


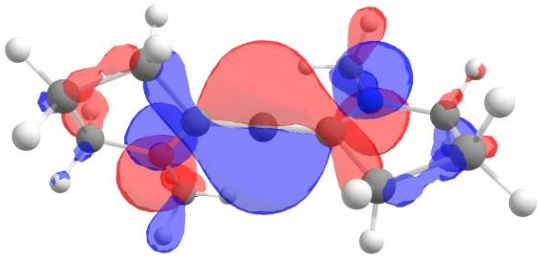
Figure S14. Optimized geometry of ^{3}**11** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.084815000
6	0.000000000	1.343496000	-0.131165000
6	0.000000000	-1.343496000	-0.131165000
7	0.746303000	2.215114000	0.546573000
6	-0.887101000	2.066164000	-1.129643000
6	0.887101000	-2.066164000	-1.129643000
7	-0.746303000	-2.215114000	0.546573000
6	0.502884000	3.608195000	0.113605000
6	-0.218279000	3.452698000	-1.225679000
6	0.218279000	-3.452698000	-1.225679000
6	-0.502884000	-3.608195000	0.113605000
1	1.453128000	4.138888000	0.068652000
1	-0.942933000	4.244405000	-1.394869000
1	-0.948168000	1.538622000	-2.078851000
1	0.948168000	-1.538622000	-2.078851000
1	-0.500026000	-3.469879000	-2.043389000
1	0.110448000	-4.081656000	0.887760000
1	-0.110448000	4.081656000	0.887760000
1	0.500026000	3.469879000	-2.043389000
1	0.942933000	-4.244405000	-1.394869000
1	-1.453128000	-4.138888000	0.068652000
1	-1.896306000	2.118176000	-0.713163000
1	1.896306000	-2.118176000	-0.713163000
6	1.678886000	1.923824000	1.624819000
1	2.676748000	2.243853000	1.320349000
1	1.388059000	2.501168000	2.504086000
1	1.680561000	0.863291000	1.857335000
6	-1.678886000	-1.923824000	1.624819000
1	-1.388059000	-2.501168000	2.504086000
1	-1.680561000	-0.863291000	1.857335000
1	-2.676748000	-2.243853000	1.320349000

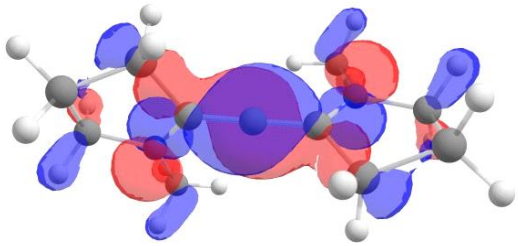
B3LYP-D3/def2-TZVPP: -539.0575207
ZPVE: 172.18286

G4MP2(0K): -537.920976

Selected orbitals (ROKS)



SOMO1



SOMO2

2.15 Singlet dication 12

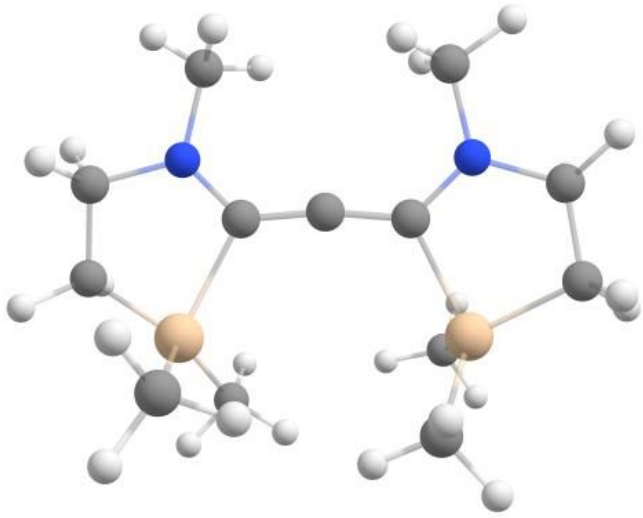


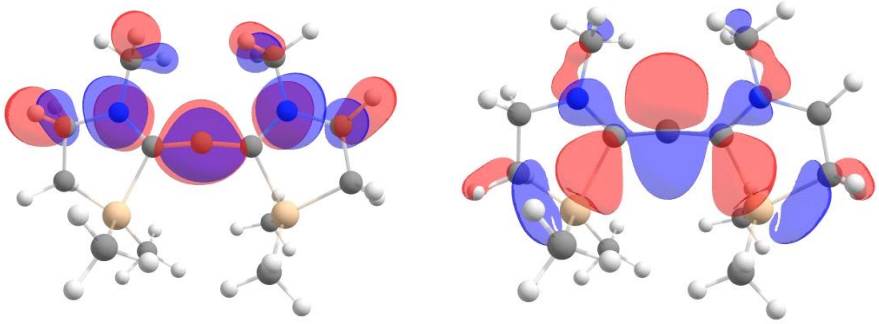
Figure S15. Optimized geometry of ^{1}**12** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.771718000
6	-0.092276000	1.309881000	0.667259000
6	0.092276000	-1.309881000	0.667259000
7	-0.104677000	2.242196000	1.593135000
14	-0.352683000	2.215506000	-1.159933000
14	0.352683000	-2.215506000	-1.159933000
7	0.104677000	-2.242196000	1.593135000
6	-0.313131000	3.662149000	1.203843000
6	0.000000000	3.836148000	-0.273768000
6	0.000000000	-3.836148000	-0.273768000
6	0.313131000	-3.662149000	1.203843000
1	0.331990000	4.267167000	1.839214000
1	-0.591551000	4.644282000	-0.706310000
1	-1.052483000	-4.084913000	-0.418207000
1	1.347026000	-3.921251000	1.441330000
1	-1.347026000	3.921251000	1.441330000
1	1.052483000	4.084913000	-0.418207000
1	0.591551000	-4.644282000	-0.706310000
1	-0.331990000	-4.267167000	1.839214000
6	-0.082303000	1.904618000	3.021684000
1	0.113678000	2.802530000	3.599637000
1	-1.045244000	1.490356000	3.325124000
1	0.709523000	1.180075000	3.210396000
6	0.082303000	-1.904618000	3.021684000
1	1.045244000	-1.490356000	3.325124000
1	-0.709523000	-1.180075000	3.210396000
1	-0.113678000	-2.802530000	3.599637000
6	0.954326000	1.726132000	-2.375711000
1	0.778363000	0.766059000	-2.854928000

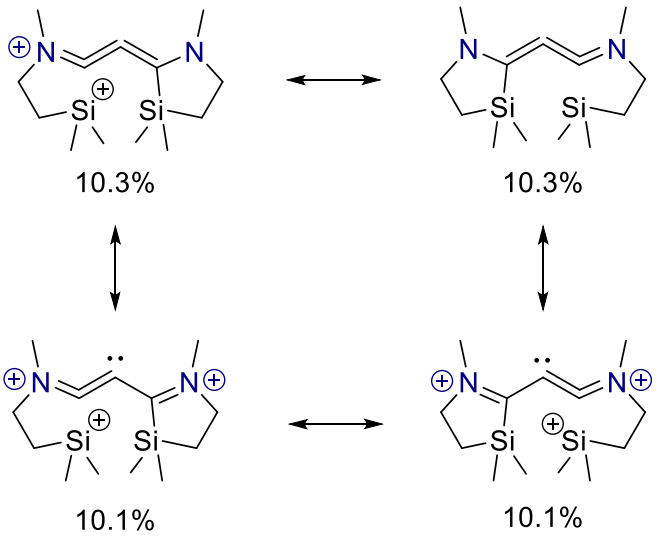
1	0.960107000	2.480623000	-3.168730000
1	1.947257000	1.727788000	-1.925205000
6	-2.116669000	1.908269000	-1.631387000
1	-2.806477000	2.206144000	-0.840999000
1	-2.349311000	2.509429000	-2.515258000
1	-2.310370000	0.867179000	-1.885621000
6	-0.954326000	-1.726132000	-2.375711000
1	-0.778363000	-0.766059000	-2.854928000
1	-0.960107000	-2.480623000	-3.168730000
1	-1.947257000	-1.727788000	-1.925205000
6	2.116669000	-1.908269000	-1.631387000
1	2.806477000	-2.206144000	-0.840999000
1	2.349311000	-2.509429000	-2.515258000
1	2.310370000	-0.867179000	-1.885621000

B3LYP-D3/def2-TZVPP: -1199.3057965
ZPVE: 230.34931
G4MP2(0K): -1197.068858

Selected orbitals



Natural resonance theory



2.16 Triplet dication 12

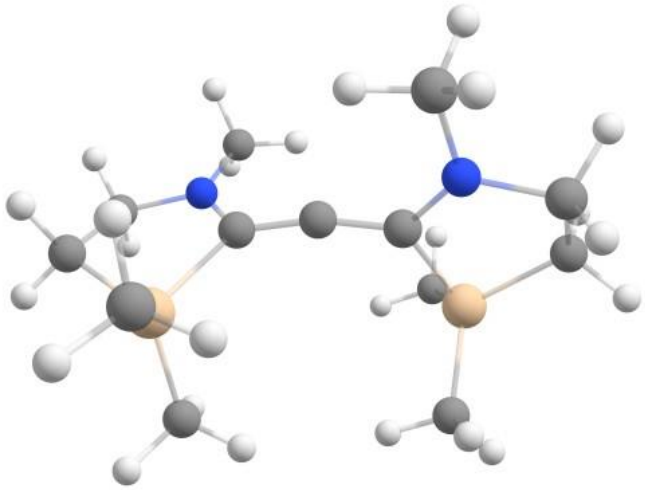


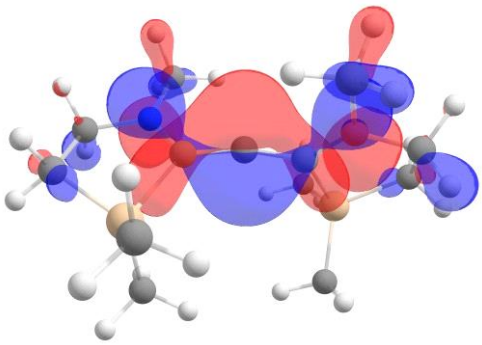
Figure S16. Optimized geometry of ^{3}**12** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	0.000000000	0.000000000	0.609481000
6	0.000000000	1.332078000	0.457322000
6	0.000000000	-1.332078000	0.457322000
7	0.763663000	2.190380000	1.142387000
14	-1.165597000	2.314081000	-0.805353000
14	1.165597000	-2.314081000	-0.805353000
7	-0.763663000	-2.190380000	1.142387000
6	0.629500000	3.636668000	0.831018000
6	-0.668353000	3.910298000	0.075589000
6	0.668353000	-3.910298000	0.075589000
6	-0.629500000	-3.636668000	0.831018000
1	1.514603000	3.904868000	0.245734000
1	-1.459089000	4.192226000	0.772417000
1	0.537360000	-4.740679000	-0.617291000
1	-0.702543000	-4.174075000	1.777317000
1	0.702543000	4.174075000	1.777317000
1	-0.537360000	4.740679000	-0.617291000
1	1.459089000	-4.192226000	0.772417000
1	-1.514603000	-3.904868000	0.245734000
6	1.760010000	1.814618000	2.142354000
1	2.710636000	2.284014000	1.887558000
1	1.442903000	2.190288000	3.116628000
1	1.876174000	0.736263000	2.178827000
6	-1.760010000	-1.814618000	2.142354000
1	-1.442903000	-2.190288000	3.116628000
1	-1.876174000	-0.736263000	2.178827000
1	-2.710636000	-2.284014000	1.887558000
6	-0.473372000	2.079845000	-2.511999000
1	-0.637005000	1.063952000	-2.874220000
1	-0.986411000	2.753144000	-3.203376000

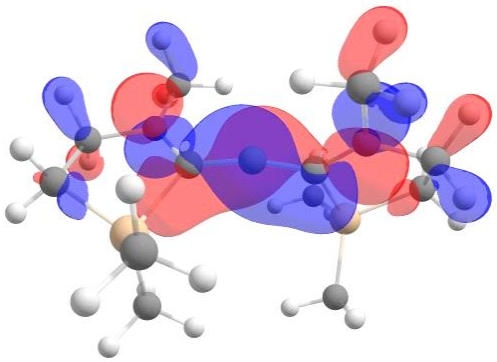
1	0.592643000	2.303693000	-2.566165000
6	-2.926236000	1.775850000	-0.591331000
1	-3.256523000	1.847919000	0.445350000
1	-3.578204000	2.417485000	-1.189161000
1	-3.079019000	0.753568000	-0.941525000
6	0.473372000	-2.079845000	-2.511999000
1	0.637005000	-1.063952000	-2.874220000
1	0.986411000	-2.753144000	-3.203376000
1	-0.592643000	-2.303693000	-2.566165000
6	2.926236000	-1.775850000	-0.591331000
1	3.256523000	-1.847919000	0.445350000
1	3.578204000	-2.417485000	-1.189161000
1	3.079019000	-0.753568000	-0.941525000

B3LYP-D3/def2-TZVPP: -1199.288705
ZPVE: 229.23014
G4MP2(0K): -1197.059739

Selected orbitals (ROKS)



SOMO1



SOMO2

2.16 TS-H_2

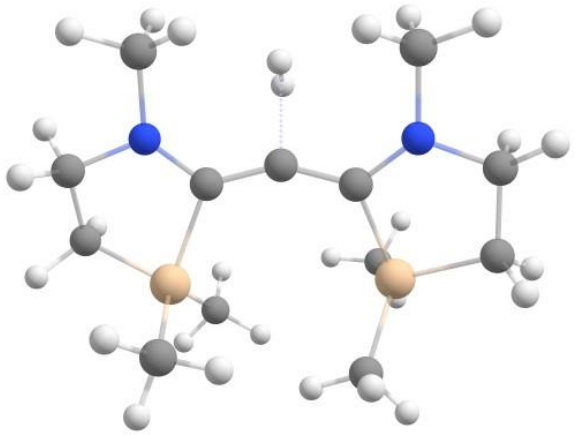


Figure S16. Optimized geometry of **TS-H_2** (in Å) at the B3LYP-D3/def2-TZVPP level of theory. The electronic energy is given in units of E_h and the ZPVE in kcal mol^{-1}.

6	-0.005334000	0.996423000	-0.282119000
6	-1.331252000	0.694152000	-0.133503000
6	1.309836000	0.713121000	-0.018876000
7	-2.357947000	1.519112000	-0.105498000
14	-2.075283000	-1.178289000	0.095067000
14	2.114899000	-1.150060000	-0.082777000
7	2.302214000	1.566581000	0.139563000
6	-3.749589000	0.968203000	-0.045582000
6	-3.748160000	-0.504791000	-0.402172000
6	3.740725000	-0.422070000	0.487474000
6	3.712043000	1.063303000	0.186198000
1	-4.350867000	1.566317000	-0.729260000
1	-4.556430000	-1.028169000	0.109050000
1	3.847116000	-0.594714000	1.559146000
1	4.160174000	1.299830000	-0.780978000
1	-4.118837000	1.152135000	0.965326000
1	-3.892506000	-0.645270000	-1.474316000
1	4.585746000	-0.901899000	-0.006181000
1	4.231421000	1.651234000	0.940074000
6	-2.308762000	2.987258000	-0.033881000
1	-3.219586000	3.325439000	0.453493000
1	-1.465184000	3.321070000	0.568986000
1	-2.265312000	3.434273000	-1.026279000
6	2.194401000	3.032231000	0.175008000
1	2.194039000	3.460558000	-0.827151000
1	1.301616000	3.339977000	0.717881000
1	3.058932000	3.417971000	0.707386000
6	-1.449077000	-2.416736000	-1.133757000
1	-0.488748000	-2.869179000	-0.910340000
1	-2.186641000	-3.225653000	-1.149494000
1	-1.421410000	-1.996269000	-2.139621000
6	-1.934941000	-1.557212000	1.907761000

1	-2.537292000	-0.858785000	2.490791000
1	-2.325268000	-2.561086000	2.093817000
1	-0.917353000	-1.524607000	2.288757000
6	1.479533000	-2.366247000	1.164134000
1	0.534697000	-2.846782000	0.935056000
1	2.236257000	-3.156879000	1.207941000
1	1.428546000	-1.926483000	2.160394000
6	2.058884000	-1.628701000	-1.875741000
1	2.610542000	-0.912814000	-2.487065000
1	2.539377000	-2.602878000	-1.998058000
1	1.049684000	-1.707684000	-2.274216000
1	-0.021981000	2.757168000	-0.577200000
1	0.014944000	2.276605000	-1.198132000

B3LYP-D3/def2-TZVPP: -1200.4572775
ZPVE: 240.70425