Supporting Information for:

Exocyclic Delocalization at the Expense of Aromaticity in 3,5-bis(π-Donor) Substituted Pyrazolium Ions and Corresponding Cyclic Bent Allenes

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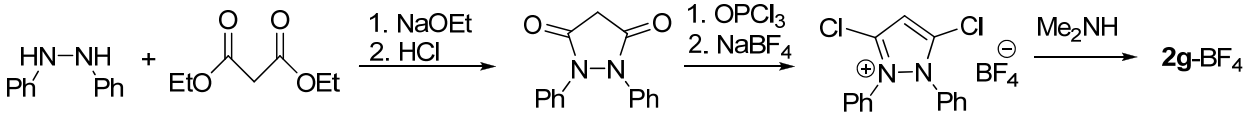
Contents:

1. Experimental Procedures:

Preparation of compound **2g**-BF_4 was prepared by modified literature procedures according to the Scheme outlined below:



1,2-diphenyl-3,5-pyrazolidinedione[1]

700 mL of absolute Ethanol was added to a 2L, 2 neck flask charged with N_2. Sodium (32 g, 1.39 mol) was added over a 3 hour period with periodic cooling to avoid reflux. Once all the sodium had been consumed (additional absolute Ethanol can be added as needed) diethyl malonate (Aldrich, 200 g, 1.25 mol) was added at which point a large amount of colorless precipitate formed. 100 mL of absolute Ethanol was added and the solid was broken up with a spatula under N_2. Stirring was continued until all solid had dissolved. Hydrazobenzene (TCI, 230 g, 1.25 mol) was added in one portion to the flask under a flow of N_2. A distillation head was attached and the mixture heated in a high temperature oil bath so that the ethanol was removed by distillation under a gentle flow of N_2. The oil bath was gradually heated to a temperature of 190°C and left overnight. The next day, 700 mL of H_2O was added to the solid mass, followed by 300 mL of diethylether (once cool enough). A slight precipitate may be observed and should be filtered off, then the layers separated and the aqueous layer washed with 2 x 200 mL ether. The dione was precipitated from the aqueous layer as an light yellow solid by addition of 1 L of 2N HCl and collected via filtration. The solid was washed with water (3 x 300 mL), and MeOH (3 x 300 mL). Drying afforded 247 g (77 % yield) of a colorless to light yellow solid. Mp. 183 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.55 (s, 2H), 7.17–7.33 (m, 10H); ^{13}C NMR

($CDCl_3$, 75 MHz): δ 36.9 (CH_2), 122.7 ($C_{Ar}H$), 126.9 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 135.5 (C_{Ar}), 166.8 (C).

1,2-diphenyl-3,5-dichloropyrazolium[2] tetrafluoroborate

A 35 mL toluene suspension of the dione (20.7 g, 82.0 mmol) is treated with phosphorus oxychloride (51 g, 330 mmol) and refluxed for at least 3 hours. The reaction mixture is cooled to room temperature and excess H_2O (! HCl produced) is slowly added. After separating the layers, an H_2O solution of sodium tetrafluoroborate (18 g, 164 mmol) is added to the aqueous fraction and the resulting solid was isolated via filtration and washed with H_2O (4 x 250mL) followed by 95% ethanol (2 x 75 mL) and diethyl ether (2 x 250 mL). Drying afforded 26.0 g (84% yield) of a colorless solid. Mp. 229 °C; ^1H NMR (CD_3CN, 300 MHz): δ 7.43 (s,1H), 7.47–7.61 (m, 10H); ^{13}C NMR (CD_3CN, 75 MHz): δ 109.8 (CH), 130.3 ($C_{Ar}H$), 131.3 ($C_{Ar}H$), 131.4 (C), 134.2 ($C_{Ar}H$), 141.4 (C_{Ar}).

(1) Gilbert, A. M.; Failli, A.; Shumsky, J.; Yang, Y.; Severin, A.; Singh, G.; Hu, W.; Keeney, D.; Petersen, P. J.; Katz, A. H. *J Med Chem* **2006**, *49*, 6027-6036.

(2) Kira, M. A.; Osman, A. I.; Shoeb, H. A.; Mansy, F.; Ghaleb, H. A. *U. A. R. J. Chem.* **1970**, *13*, 513-&.

2. Complete Reference 18:

Gaussian 03, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.;

Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

3. Cartesian coordinates (in Å) and total energies (in hartrees) of all the stationary points discussed in the text. The level of theory is given in parentheses. All compounds had zero imaginary frequencies, except **2c'** which was found to be a transition state with i=1.

allenes 1a-g (BP86/def2-TZVPP).

1a: E= -226.1959661

C	0.155000000	0.753000000	1.214000000
C	0.050000000	-0.645000000	1.161000000
N	-0.057000000	-1.112000000	-0.127000000
N	-0.027000000	-0.032000000	-0.947000000
C	0.101000000	1.079000000	-0.149000000
H	0.040000000	-1.391000000	1.956000000
H	0.144000000	2.044000000	-0.654000000
H	-0.087000000	-0.167000000	-1.956000000
H	-0.155000000	-2.044000000	-0.529000000

1b: E= -376.7482115

N	-1.573412000	-1.173210000	0.211950000
C	-1.124765000	0.139890000	0.056668000
C	0.250123000	0.312602000	0.006999000
C	0.625609000	-1.021553000	0.047645000
N	-0.414395000	-1.952997000	0.026892000
O	-2.104260000	1.062741000	-0.029063000
O	1.860899000	-1.558724000	0.110260000
H	-2.376921000	-1.490817000	-0.334585000
H	-0.362361000	-2.768443000	0.641338000
H	-1.632673000	1.910395000	-0.146650000
H	2.462150000	-0.788783000	0.130895000

1c: E= -336.9904953

C	0.033000000	1.063000000	0.356000000
C	-0.033000000	-1.063000000	0.356000000
N	-0.052000000	0.709000000	-1.011000000
N	0.052000000	-0.709000000	-1.011000000
C	0.000000000	0.000000000	1.255000000
H	-0.651000000	-1.127000000	-1.628000000
H	0.651000000	1.127000000	-1.628000000
N	-0.206000000	-2.400000000	0.635000000
H	0.257000000	-3.073000000	0.030000000

N	0.206000000	2.400000000	0.635000000
H	-0.257000000	3.073000000	0.030000000
H	-0.115000000	-2.599000000	1.628000000
H	0.115000000	2.599000000	1.628000000

1d: E= -688.485950

C	-0.818000000	-0.695000000	2.627000000
C	0.817000000	0.697000000	2.627000000
N	-0.537000000	-0.427000000	1.292000000
N	0.537000000	0.427000000	1.292000000
C	-0.002000000	0.002000000	3.517000000
H	1.588000000	1.446000000	2.800000000
H	-1.590000000	-1.444000000	2.801000000
C	0.981000000	1.140000000	0.143000000
C	2.362000000	1.293000000	-0.046000000
C	0.075000000	1.745000000	-0.740000000
C	2.831000000	2.057000000	-1.115000000
C	0.558000000	2.488000000	-1.816000000
C	1.934000000	2.651000000	-2.007000000
H	3.054000000	0.806000000	0.640000000
H	-0.996000000	1.639000000	-0.577000000
H	3.906000000	2.176000000	-1.258000000
H	-0.148000000	2.954000000	-2.503000000
H	2.304000000	3.239000000	-2.846000000
C	-0.981000000	-1.140000000	0.143000000
C	-0.075000000	-1.747000000	-0.738000000
C	-2.362000000	-1.291000000	-0.047000000
C	-0.558000000	-2.491000000	-1.814000000
C	-2.831000000	-2.056000000	-1.116000000
C	-1.934000000	-2.652000000	-2.006000000
H	0.997000000	-1.642000000	-0.574000000
H	-3.054000000	-0.804000000	0.638000000
H	0.149000000	-2.957000000	-2.500000000
H	-3.905000000	-2.174000000	-1.260000000
H	-2.303000000	-3.240000000	-2.845000000

1e: E= -917.666285

N	-0.410000000	-0.214000000	-0.646000000
C	-0.673000000	0.117000000	-1.988000000
C	0.247000000	0.962000000	-2.583000000
C	1.137000000	1.113000000	-1.534000000
N	0.826000000	0.389000000	-0.369000000
O	-1.767000000	-0.469000000	-2.495000000
O	2.238000000	1.871000000	-1.434000000
C	-0.748000000	-1.440000000	0.003000000
C	1.127000000	0.774000000	0.973000000
C	-1.999000000	-0.194000000	-3.894000000
C	2.520000000	2.676000000	-2.600000000
H	3.419000000	3.245000000	-2.344000000
H	2.693000000	2.033000000	-3.472000000
H	1.676000000	3.342000000	-2.815000000
H	-2.898000000	-0.763000000	-4.151000000
H	-2.153000000	0.880000000	-4.050000000
H	-1.139000000	-0.517000000	-4.492000000

C	2.471000000	0.878000000	1.360000000
C	2.786000000	1.275000000	2.659000000
C	1.775000000	1.547000000	3.585000000
C	0.438000000	1.426000000	3.198000000
C	0.108000000	1.048000000	1.896000000
H	3.255000000	0.653000000	0.641000000
H	3.833000000	1.361000000	2.951000000
H	2.027000000	1.846000000	4.602000000
H	-0.359000000	1.634000000	3.911000000
H	-0.934000000	0.966000000	1.592000000
C	-2.101000000	-1.768000000	0.164000000
C	-2.453000000	-2.972000000	0.774000000
C	-1.467000000	-3.843000000	1.248000000
C	-0.120000000	-3.503000000	1.098000000
C	0.246000000	-2.311000000	0.472000000
H	-2.865000000	-1.082000000	-0.194000000
H	-3.507000000	-3.223000000	0.890000000
H	-1.747000000	-4.777000000	1.733000000
H	0.657000000	-4.175000000	1.463000000
H	1.296000000	-2.053000000	0.345000000

1f: E= -1458.616393

O	2.330000000	0.237000000	0.537000000
O	-2.070000000	-0.648000000	-1.091000000
N	0.167000000	0.741000000	1.159000000
N	-1.116000000	0.565000000	0.623000000
C	0.393000000	-0.579000000	-0.784000000
C	1.020000000	0.086000000	0.254000000
C	-0.921000000	-0.266000000	-0.493000000
C	0.458000000	1.930000000	1.897000000
C	1.473000000	1.895000000	2.862000000
H	2.013000000	0.967000000	3.042000000
C	1.788000000	3.052000000	3.576000000
H	2.584000000	3.019000000	4.321000000
C	1.083000000	4.237000000	3.353000000
H	1.325000000	5.135000000	3.921000000
C	0.061000000	4.262000000	2.399000000
H	-0.496000000	5.181000000	2.217000000
C	-0.251000000	3.117000000	1.665000000
H	-1.038000000	3.140000000	0.913000000
C	-2.244000000	0.564000000	1.501000000
C	-2.112000000	0.195000000	2.848000000
H	-1.137000000	-0.093000000	3.238000000
C	-3.234000000	0.200000000	3.677000000
H	-3.125000000	-0.084000000	4.724000000
C	-4.488000000	0.555000000	3.174000000
H	-5.362000000	0.553000000	3.825000000
C	-4.613000000	0.917000000	1.830000000
H	-5.586000000	1.201000000	1.427000000
C	-3.496000000	0.936000000	0.994000000
H	-3.588000000	1.229000000	-0.050000000
C	3.263000000	-0.282000000	-0.393000000
C	3.650000000	-1.622000000	-0.281000000
C	4.660000000	-2.068000000	-1.144000000
H	4.980000000	-3.109000000	-1.086000000

C	5.252000000	-1.205000000	-2.068000000
H	6.037000000	-1.571000000	-2.729000000
C	4.839000000	0.125000000	-2.144000000
H	5.300000000	0.801000000	-2.866000000
C	3.833000000	0.617000000	-1.302000000
C	-1.975000000	-1.590000000	-2.144000000
C	-2.233000000	-2.930000000	-1.833000000
C	-2.253000000	-3.842000000	-2.897000000
H	-2.448000000	-4.895000000	-2.686000000
C	-2.028000000	-3.420000000	-4.207000000
H	-2.049000000	-4.143000000	-5.023000000
C	-1.779000000	-2.074000000	-4.475000000
H	-1.600000000	-1.744000000	-5.499000000
C	-1.748000000	-1.125000000	-3.444000000
C	2.988000000	-2.546000000	0.703000000
H	3.013000000	-2.138000000	1.724000000
H	3.483000000	-3.524000000	0.711000000
H	1.931000000	-2.692000000	0.434000000
C	3.367000000	2.047000000	-1.377000000
H	2.310000000	2.102000000	-1.677000000
H	3.958000000	2.608000000	-2.110000000
H	3.450000000	2.551000000	-0.404000000
C	-2.463000000	-3.368000000	-0.411000000
H	-2.697000000	-4.438000000	-0.369000000
H	-3.289000000	-2.814000000	0.055000000
H	-1.570000000	-3.189000000	0.205000000
C	-1.459000000	0.326000000	-3.715000000
H	-2.232000000	0.981000000	-3.289000000
H	-1.401000000	0.516000000	-4.793000000
H	-0.499000000	0.612000000	-3.258000000

1g: E= -956.548499

C	-1.566000000	1.681000000	0.881000000
C	-0.603000000	1.809000000	-0.113000000
N	0.149000000	0.621000000	-0.391000000
N	-0.390000000	-0.362000000	0.527000000
C	-1.407000000	0.349000000	1.244000000
N	-0.288000000	2.935000000	-0.818000000
N	-2.125000000	-0.345000000	2.176000000
C	-0.720000000	-1.599000000	-0.150000000
C	1.596000000	0.659000000	-0.343000000
C	-1.681000000	-1.592000000	2.775000000
C	0.439000000	2.926000000	-2.076000000
C	-3.280000000	0.289000000	2.791000000
C	-0.899000000	4.199000000	-0.438000000
H	-4.147000000	-0.391000000	2.760000000
H	-3.076000000	0.541000000	3.845000000
H	-3.493000000	1.211000000	2.240000000
H	-2.295000000	-2.450000000	2.454000000
H	-0.638000000	-1.790000000	2.511000000
H	-1.753000000	-1.514000000	3.872000000
H	-0.129000000	4.982000000	-0.353000000
H	-1.638000000	4.521000000	-1.192000000
H	-1.410000000	4.053000000	0.520000000
H	1.448000000	3.359000000	-1.977000000

H	0.534000000	1.903000000	-2.452000000
H	-0.115000000	3.520000000	-2.820000000
C	2.330000000	-0.048000000	-1.301000000
C	3.727000000	-0.030000000	-1.264000000
C	4.393000000	0.703000000	-0.278000000
C	3.658000000	1.415000000	0.675000000
C	2.262000000	1.392000000	0.648000000
H	1.796000000	-0.606000000	-2.071000000
H	4.295000000	-0.584000000	-2.012000000
H	5.483000000	0.723000000	-0.254000000
H	4.174000000	1.989000000	1.446000000
H	1.678000000	1.936000000	1.391000000
C	0.192000000	-2.660000000	-0.118000000
C	-0.107000000	-3.857000000	-0.774000000
C	-1.320000000	-4.003000000	-1.452000000
C	-2.234000000	-2.944000000	-1.477000000
C	-1.936000000	-1.742000000	-0.832000000
H	1.129000000	-2.535000000	0.424000000
H	0.608000000	-4.681000000	-0.748000000
H	-1.555000000	-4.940000000	-1.957000000
H	-3.182000000	-3.053000000	-2.004000000
H	-2.637000000	-0.907000000	-0.852000000

allenes 1a-c (MP2/def2-TZVPP).

1a: E = -225.656240

C	0.000000000	0.000000000	1.364980000
C	0.000000000	1.077559000	0.470174000
N	0.000000000	0.667846000	-0.835912000
N	0.000000000	-0.667846000	-0.835912000
C	0.000000000	-1.077559000	0.470174000
H	0.000000000	2.143554000	0.640487000
H	0.000000000	-2.143554000	0.640487000
H	0.000000000	-1.178500000	-1.705090000
H	0.000000000	1.178500000	-1.705090000

1b: E = -375.939873

N	-0.092693000	0.691249000	-1.115564000
C	0.000000000	1.040760000	0.218086000
C	0.000000000	0.000000000	1.127784000
C	0.000000000	-1.040760000	0.218086000
N	0.092693000	-0.691249000	-1.115564000
O	0.089544000	2.359663000	0.437881000
O	-0.089544000	-2.359663000	0.437881000
H	0.479671000	1.191863000	-1.783904000
H	-0.479671000	-1.191863000	-1.783904000
H	0.165534000	2.440769000	1.397939000
H	-0.165534000	-2.440769000	1.397939000

1c: E = -336.211425

C	0.063827000	-1.051421000	0.228423000
C	-0.063827000	1.051421000	0.228423000

N	0.124110000	-0.693524000	-1.123776000
N	-0.124110000	0.693524000	-1.123776000
C	0.000000000	0.000000000	1.132600000
H	0.529809000	1.184240000	-1.723536000
H	-0.529809000	-1.184240000	-1.723536000
N	0.000000000	2.394223000	0.493052000
H	-0.539099000	2.999112000	-0.105066000
N	0.000000000	-2.394223000	0.493052000
H	0.539099000	-2.999112000	-0.105066000
H	-0.108943000	2.587782000	1.475332000
H	0.108943000	-2.587782000	1.475332000

cations 2a-g (BP86/def2-TZVPP).

2a: E= -226.6502089

C	-1.115000000	0.000000000	0.112000000
C	1.115000000	0.000000000	0.112000000
C	0.000000000	0.000000000	0.949000000
H	-2.178000000	0.000000000	0.332000000
H	2.178000000	0.000000000	0.332000000
H	0.000000000	0.000000000	2.033000000
N	-0.676000000	0.000000000	-1.163000000
N	0.676000000	0.000000000	-1.163000000
H	1.206000000	0.000000000	-2.033000000
H	-1.206000000	0.000000000	-2.033000000

2a': E= -226.6391185

C	-0.644000000	1.079000000	-0.213000000
C	0.746000000	1.070000000	-0.284000000
N	1.191000000	-0.206000000	-0.173000000
N	0.089000000	-1.020000000	0.062000000
C	-1.021000000	-0.247000000	-0.018000000
H	0.179000000	-1.940000000	-0.381000000
H	2.008000000	-0.481000000	0.381000000
H	-1.298000000	1.940000000	-0.293000000
H	-2.008000000	-0.704000000	0.008000000
H	1.455000000	1.892000000	-0.344000000

2b: E= -377.1802542

C	-0.604000000	-0.709000000	-0.042000000
C	-0.232000000	0.634000000	-0.177000000
C	1.168000000	0.622000000	-0.186000000
N	1.611000000	-0.664000000	-0.120000000
N	0.513000000	-1.478000000	0.084000000
O	2.087000000	1.572000000	-0.221000000
O	-1.768000000	-1.337000000	-0.036000000
H	0.570000000	-2.462000000	-0.179000000
H	2.514000000	-0.944000000	0.260000000
H	-0.886000000	1.495000000	-0.257000000
H	-2.514000000	-0.718000000	-0.138000000

H	1.688000000	2.462000000	-0.260000000

2c: E= -337.4516794

C	-1.118000000	0.047000000	0.029000000
C	1.118000000	0.047000000	-0.029000000
N	-0.699000000	-1.269000000	0.092000000
N	0.699000000	-1.269000000	-0.092000000
C	0.000000000	0.888000000	0.000000000
H	1.181000000	-1.971000000	0.473000000
H	-1.181000000	-1.971000000	-0.473000000
H	0.000000000	1.971000000	0.000000000
N	2.424000000	0.351000000	0.038000000
H	3.139000000	-0.336000000	-0.176000000
N	-2.424000000	0.351000000	-0.038000000
H	-3.139000000	-0.336000000	0.176000000
H	2.713000000	1.322000000	0.052000000
H	-2.713000000	1.322000000	-0.052000000

2c’: E= -337.4454836

C	1.128000000	0.000000000	0.121000000
C	-1.128000000	0.000000000	0.121000000
N	0.692000000	0.000000000	-1.170000000
N	-0.692000000	0.000000000	-1.170000000
C	0.000000000	0.000000000	0.957000000
H	-1.209000000	0.000000000	-2.040000000
H	1.209000000	0.000000000	-2.040000000
H	0.000000000	0.000000000	2.040000000
N	-2.437000000	0.000000000	0.441000000
H	-3.171000000	0.000000000	-0.256000000
N	2.437000000	0.000000000	0.441000000
H	3.171000000	0.000000000	-0.256000000
H	-2.717000000	0.000000000	1.413000000
H	2.717000000	0.000000000	1.413000000

2d: E= -688.9593021

C	-1.752000000	1.021000000	2.001000000
C	-1.427000000	-1.166000000	2.173000000
C	-2.098000000	-0.096000000	2.754000000
H	-2.024000000	2.065000000	2.105000000
H	-1.420000000	-2.222000000	2.417000000
H	-2.754000000	-0.125000000	3.615000000
N	-0.910000000	0.644000000	1.012000000
N	-0.711000000	-0.717000000	1.117000000
C	0.101000000	-1.488000000	0.209000000
C	1.211000000	-2.164000000	0.723000000
C	-0.265000000	-1.586000000	-1.136000000
C	1.970000000	-2.959000000	-0.137000000
C	0.512000000	-2.374000000	-1.985000000
C	1.625000000	-3.060000000	-1.487000000
H	1.476000000	-2.067000000	1.776000000
H	-1.147000000	-1.067000000	-1.510000000
H	2.836000000	-3.495000000	0.250000000
H	0.238000000	-2.463000000	-3.035000000

H	2.222000000	-3.679000000	-2.155000000
C	-0.278000000	1.480000000	0.024000000
C	1.112000000	1.625000000	0.024000000
C	-1.091000000	2.169000000	-0.880000000
C	1.696000000	2.476000000	-0.915000000
C	-0.492000000	3.026000000	-1.805000000
C	0.897000000	3.175000000	-1.825000000
H	1.725000000	1.095000000	0.752000000
H	-2.172000000	2.034000000	-0.861000000
H	2.778000000	2.602000000	-0.925000000
H	-1.113000000	3.572000000	-2.513000000
H	1.361000000	3.842000000	-2.550000000

2e: E= -918.125003

N	-0.177000000	-0.449000000	-1.012000000
C	-0.338000000	-0.280000000	-2.355000000
C	0.132000000	0.983000000	-2.736000000
C	0.572000000	1.583000000	-1.550000000
N	0.363000000	0.740000000	-0.499000000
O	-0.911000000	-1.259000000	-3.034000000
O	1.153000000	2.744000000	-1.302000000
C	-0.744000000	-1.469000000	-0.174000000
C	0.886000000	0.842000000	0.835000000
H	0.152000000	1.403000000	-3.731000000
C	-1.105000000	-1.039000000	-4.455000000
C	1.399000000	3.606000000	-2.442000000
H	1.888000000	4.491000000	-2.031000000
H	2.062000000	3.106000000	-3.159000000
H	0.449000000	3.886000000	-2.917000000
H	-1.596000000	-1.944000000	-4.820000000
H	-1.752000000	-0.167000000	-4.618000000
H	-0.137000000	-0.907000000	-4.954000000
C	1.909000000	-0.018000000	1.247000000
C	2.415000000	0.107000000	2.541000000
C	1.915000000	1.091000000	3.400000000
C	0.901000000	1.951000000	2.971000000
C	0.372000000	1.824000000	1.686000000
H	2.306000000	-0.769000000	0.565000000
H	3.210000000	-0.559000000	2.874000000
H	2.320000000	1.188000000	4.407000000
H	0.512000000	2.717000000	3.640000000
H	-0.426000000	2.481000000	1.342000000
C	-1.793000000	-1.150000000	0.694000000
C	-2.341000000	-2.157000000	1.488000000
C	-1.856000000	-3.466000000	1.399000000
C	-0.814000000	-3.772000000	0.519000000
C	-0.244000000	-2.770000000	-0.267000000
H	-2.177000000	-0.132000000	0.743000000
H	-3.156000000	-1.921000000	2.171000000
H	-2.293000000	-4.249000000	2.017000000
H	-0.437000000	-4.791000000	0.449000000
H	0.575000000	-2.994000000	-0.950000000

2f: E= -1459.084218

O	2.000000000	1.238000000	0.684000000
O	-2.322000000	-0.777000000	-0.050000000
N	1.047000000	-0.294000000	-0.750000000
N	-0.191000000	-0.935000000	-0.913000000
C	-0.394000000	0.565000000	0.771000000
H	-0.807000000	1.157000000	1.576000000
C	-1.057000000	-0.381000000	-0.013000000
C	0.918000000	0.581000000	0.292000000
C	1.864000000	2.103000000	1.820000000
C	2.151000000	1.564000000	3.079000000
C	2.078000000	2.447000000	4.166000000
H	2.295000000	2.069000000	5.166000000
C	1.747000000	3.789000000	3.982000000
H	1.700000000	4.459000000	4.840000000
C	1.490000000	4.282000000	2.702000000
H	1.248000000	5.336000000	2.561000000
C	1.549000000	3.445000000	1.579000000
C	-3.235000000	-0.136000000	0.853000000
C	-3.440000000	-0.735000000	2.100000000
C	-4.388000000	-0.127000000	2.935000000
H	-4.580000000	-0.561000000	3.917000000
C	-5.088000000	1.007000000	2.522000000
H	-5.824000000	1.461000000	3.185000000
C	-4.861000000	1.554000000	1.259000000
H	-5.423000000	2.430000000	0.933000000
C	-3.924000000	0.987000000	0.383000000
C	-0.512000000	-1.688000000	-2.094000000
C	-1.021000000	-2.981000000	-1.949000000
H	-1.148000000	-3.409000000	-0.956000000
C	-1.367000000	-3.705000000	-3.090000000
H	-1.772000000	-4.711000000	-2.987000000
C	-1.183000000	-3.148000000	-4.358000000
H	-1.446000000	-3.721000000	-5.247000000
C	-0.662000000	-1.858000000	-4.490000000
H	-0.522000000	-1.422000000	-5.478000000
C	-0.332000000	-1.114000000	-3.357000000
H	0.058000000	-0.102000000	-3.451000000
C	2.260000000	-0.821000000	-1.311000000
C	2.610000000	-2.156000000	-1.085000000
H	1.963000000	-2.802000000	-0.493000000
C	3.799000000	-2.645000000	-1.628000000
H	4.078000000	-3.684000000	-1.462000000
C	4.633000000	-1.802000000	-2.369000000
H	5.563000000	-2.187000000	-2.784000000
C	4.276000000	-0.467000000	-2.578000000
H	4.925000000	0.190000000	-3.156000000
C	3.079000000	0.029000000	-2.059000000
H	2.784000000	1.063000000	-2.226000000
C	2.538000000	0.120000000	3.256000000
H	1.727000000	-0.563000000	2.961000000
C	1.311000000	3.970000000	0.188000000
H	0.465000000	3.469000000	-0.305000000
C	-2.703000000	-1.981000000	2.517000000
H	-1.614000000	-1.831000000	2.538000000
C	-3.690000000	1.545000000	-0.996000000
H	-3.854000000	0.782000000	-1.770000000
H	-4.370000000	2.381000000	-1.191000000

H	-2.662000000	1.916000000	-1.120000000
H	-3.015000000	-2.294000000	3.519000000
H	-2.903000000	-2.813000000	1.826000000
H	2.194000000	3.822000000	-0.451000000
H	1.091000000	5.043000000	0.216000000
H	2.780000000	-0.086000000	4.305000000
H	3.415000000	-0.138000000	2.646000000

2g: E= -957.029823

C	-1.381000000	-0.641000000	1.198000000
C	0.839000000	-0.768000000	1.571000000
N	-0.752000000	-0.093000000	0.087000000
N	0.670000000	-0.118000000	0.356000000
C	-0.415000000	-1.080000000	2.114000000
H	-0.602000000	-1.567000000	3.060000000
N	2.052000000	-1.056000000	2.078000000
N	-2.720000000	-0.681000000	1.328000000
C	-3.303000000	-1.093000000	2.605000000
H	-3.381000000	-2.189000000	2.683000000
H	-2.704000000	-0.711000000	3.439000000
H	-4.308000000	-0.665000000	2.684000000
C	-3.642000000	-0.585000000	0.194000000
H	-4.144000000	0.392000000	0.159000000
H	-3.108000000	-0.744000000	-0.747000000
H	-4.403000000	-1.370000000	0.296000000
C	2.148000000	-1.910000000	3.262000000
H	1.393000000	-2.702000000	3.223000000
H	3.136000000	-2.384000000	3.271000000
H	2.027000000	-1.334000000	4.192000000
C	3.278000000	-0.361000000	1.677000000
H	3.839000000	-0.095000000	2.582000000
H	3.912000000	-0.992000000	1.038000000
H	3.036000000	0.560000000	1.139000000
C	1.498000000	-0.380000000	-0.804000000
C	2.065000000	0.697000000	-1.489000000
C	1.701000000	-1.695000000	-1.239000000
C	2.850000000	0.455000000	-2.619000000
C	2.492000000	-1.929000000	-2.365000000
C	3.065000000	-0.855000000	-3.054000000
H	1.892000000	1.713000000	-1.134000000
H	1.241000000	-2.526000000	-0.702000000
H	3.295000000	1.291000000	-3.157000000
H	2.659000000	-2.950000000	-2.706000000
H	3.682000000	-1.041000000	-3.933000000
C	-1.220000000	1.108000000	-0.575000000
C	-1.484000000	2.264000000	0.170000000
C	-1.377000000	1.098000000	-1.963000000
C	-1.924000000	3.414000000	-0.486000000
C	-1.810000000	2.257000000	-2.612000000
C	-2.086000000	3.411000000	-1.875000000
H	-1.345000000	2.260000000	1.251000000
H	-1.164000000	0.188000000	-2.523000000
H	-2.136000000	4.316000000	0.088000000
H	-1.936000000	2.255000000	-3.695000000
H	-2.429000000	4.312000000	-2.384000000

4. Orbital occupations from the output of the CASSCF/def2-TZVPP calculation for 1a (including the π-framework (5 orbitals) and the lone pair orbital at the central carbon atom in the active space).

Final one electron symbolic density matrix:

	1	2	3	4	5	6
1	***0.197323D+01***					
2	-0.146012D-11	***0.197651D+01***				
3	0.272560D-14	0.193808D-12	***0.196479D+01***			
4	-0.338849D-06	0.947491D-12	-0.427714D-16	***0.199994D+01***		
5	-0.116637D-15	0.108268D-11	0.368604D-03	-0.433355D-16	***0.580027D-01***	
6	-0.400385D-12	0.683639D-15	0.805755D-11	0.131030D-11	0.765253D-11	***0.275228D-01***

MCSCF converged.

5. Stability analysis of the BP86 wavefunction for 1a

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Stability analysis using <AA,BB:AA,BB> singles matrix:

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Eigenvectors of the stability matrix:

Eigenvector 1: Triplet-A Eigenvalue= 0.0798196
18 -> 19 0.70575
Eigenvector 2: Singlet-A Eigenvalue= 0.0899944
18 -> 19 0.70632
Eigenvector 3: Triplet-A Eigenvalue= 0.1087000
18 -> 20 0.70444
Eigenvector 4: Triplet-A Eigenvalue= 0.1173997
17 -> 19 0.70050
Eigenvector 5: Triplet-A Eigenvalue= 0.1376423
16 -> 19 0.67316
17 -> 22 0.18840
Eigenvector 6: Triplet-A Eigenvalue= 0.1387724
18 -> 22 0.69637

The wavefunction is stable under the perturbations considered.

Similar outputs were obtained for **1b** and **1c** at the BP86/def2-TZVPP level and also at the MP2/def2-TZVPP for allene **1a**.