

Supporting Information

for

Direct estimate of the internal π -donation to the carbene centre within N-heterocyclic carbenes and related molecules

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Additional information

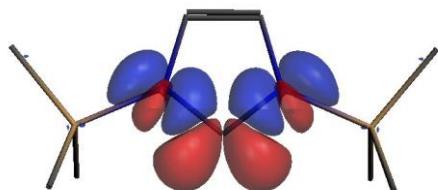
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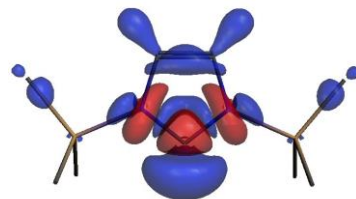
Table S2. Cartesian xyz coordinates (in Å) and electronic energies (in Hartree) of the calculated structures at BP86/def2-TZVPP.

Figure S1. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions on the carbenes **2–15**, associated energies ΔE in kcal/mol and eigenvalues v in a.u.

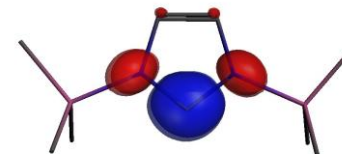
2



$$\Delta E_1 = -331.0; |v|_{\alpha} = 0.70; |v|_{\beta} = 0.67$$

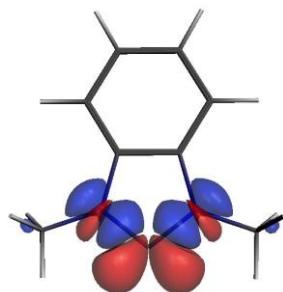


$$\Delta E_2 = -247.2; |v|_{\alpha} = 0.65; |v|_{\beta} = 0.37$$

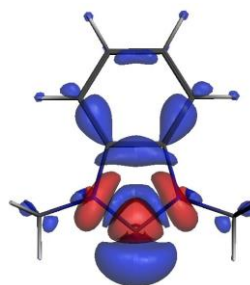


$$\Delta E_3 = -87.8; |v|_{\alpha} = 0.46; |v|_{\beta} = 0.46$$

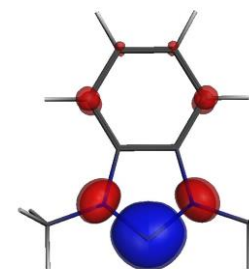
3



$$\Delta E_1 = -322.1; |v|_{\alpha} = 0.68; |v|_{\beta} = 0.64$$

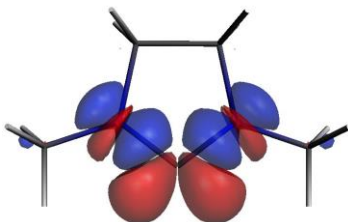


$$\Delta E_2 = -252.2; |v|_{\alpha} = 0.65; |v|_{\beta} = 0.36$$

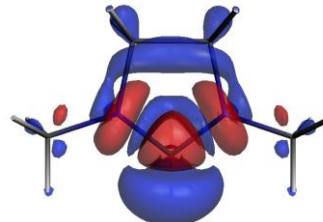


$$\Delta E_3 = -89.3; |v|_{\alpha} = 0.46; |v|_{\beta} = 0.46$$

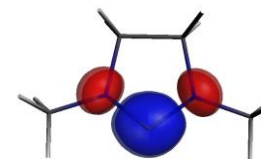
4



$$\Delta E_1 = -335.9; |v|_{\alpha} = 0.66; |v|_{\beta} = 0.66$$

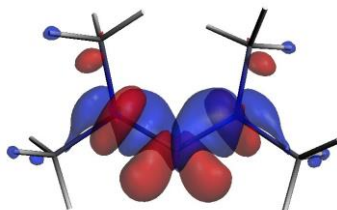


$$\Delta E_2 = -242.3; |v|_{\alpha} = 0.60; |v|_{\beta} = 0.37$$

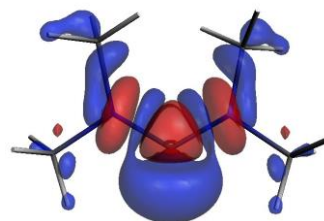


$$\Delta E_3 = -86.1; |v|_{\alpha} = 0.41; |v|_{\beta} = 0.41$$

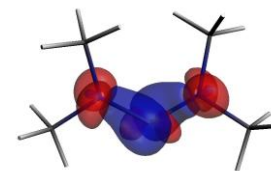
5



$$\Delta E_1 = -379.5; |v|_{\alpha} = 0.73; |v|_{\beta} = 0.69$$

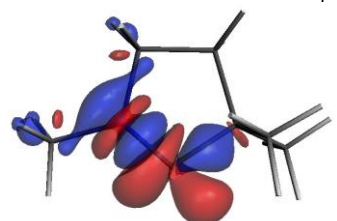


$$\Delta E_2 = -335.4; |v|_{\alpha} = 0.60; |v|_{\beta} = 0.37$$

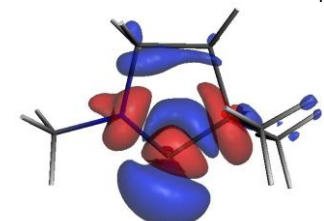


$$\Delta E_3 = -84.3; |v|_{\alpha} = 0.38; |v|_{\beta} = 0.42$$

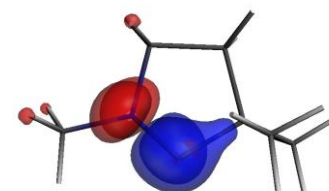
6



$$\Delta E_1 = -331.7; |v|_{\alpha} = 0.64; |v|_{\beta} = 0.70$$

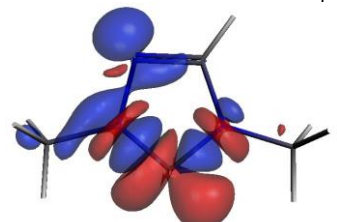


$$\Delta E_2 = -182.6; |v|_{\alpha} = 0.54; |v|_{\beta} = 0.41$$

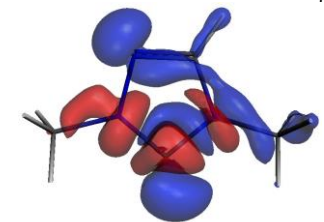


$$\Delta E_3 = -72.2; |v|_{\alpha} = 0.38; |v|_{\beta} = 0.38$$

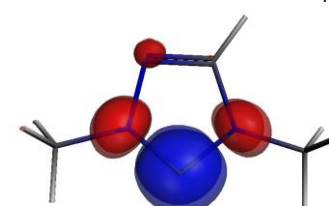
7



$$\Delta E_1 = -338.7; |v|_{\alpha} = 0.69; |v|_{\beta} = 0.63$$

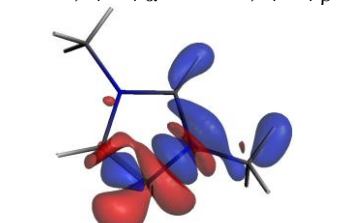


$$\Delta E_2 = -241.7; |v|_{\alpha} = 0.68; |v|_{\beta} = 0.36$$

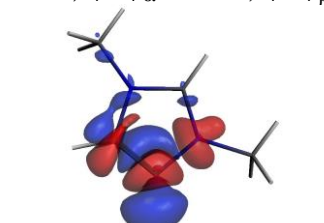


$$\Delta E_3 = -92.2; |v|_{\alpha} = 0.44; |v|_{\beta} = 0.44$$

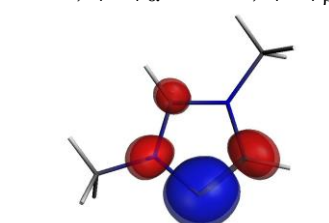
8



$$\Delta E_1 = -327.6; |v|_{\alpha} = 0.67; |v|_{\beta} = 0.67$$

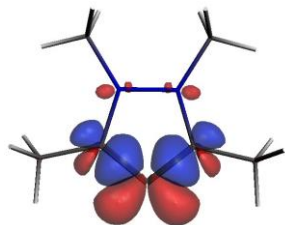


$$\Delta E_2 = -170.8; |v|_{\alpha} = 0.48; |v|_{\beta} = 0.37$$

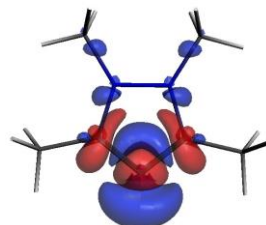


$$\Delta E_3 = -101.3; |v|_{\alpha} = 0.47; |v|_{\beta} = 0.47$$

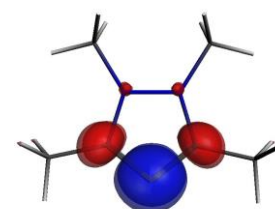
9



$$\Delta E_1 = -285.9; |v|_{\alpha} = 0.55; |v|_{\beta} = 0.68$$

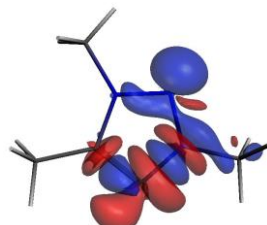


$$\Delta E_2 = -178.5; |v|_{\alpha} = 0.46; |v|_{\beta} = 0.42$$

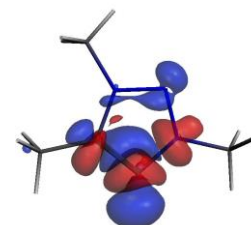


$$\Delta E_3 = -109.9; |v|_{\alpha} = 0.45; |v|_{\beta} = 0.45$$

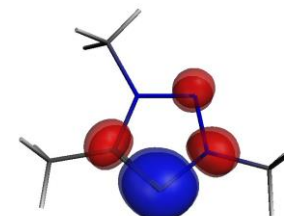
10



$$\Delta E_1 = -335.8; |v|_{\alpha} = 0.69; |v|_{\beta} = 0.67$$

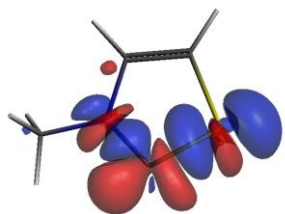


$$\Delta E_2 = -186.6; |v|_{\alpha} = 0.52; |v|_{\beta} = 0.38$$

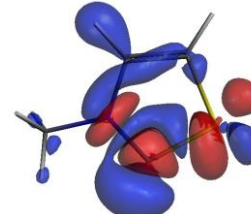


$$\Delta E_3 = -100.6; |v|_{\alpha} = 0.46; |v|_{\beta} = 0.46$$

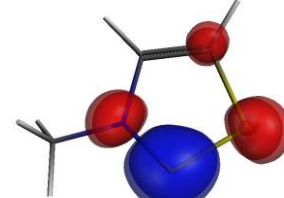
11



$$\Delta E_1 = -256.9; |v|_{\alpha} = 0.67; |v|_{\beta} = 0.67$$

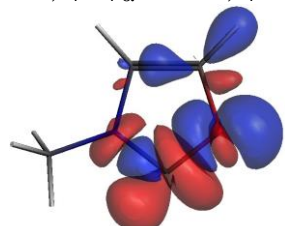


$$\Delta E_2 = -219.0; |v|_{\alpha} = 0.62; |v|_{\beta} = 0.39$$

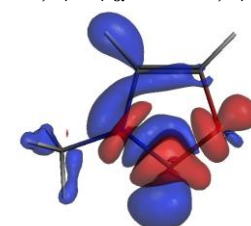


$$\Delta E_3 = -90.0; |v|_{\alpha} = 0.47; |v|_{\beta} = 0.47$$

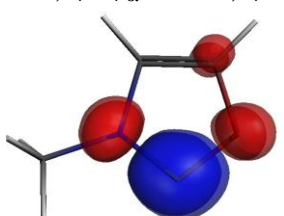
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$$\Delta E_1 = -361.0; |v|_{\alpha} = 0.83; |v|_{\beta} = 0.61$$



$$\Delta E_2 = -235.7; |v|_{\alpha} = 0.64; |v|_{\beta} = 0.34$$



$$\Delta E_3 = -82.4; |v|_{\alpha} = 0.44; |v|_{\beta} = 0.44$$

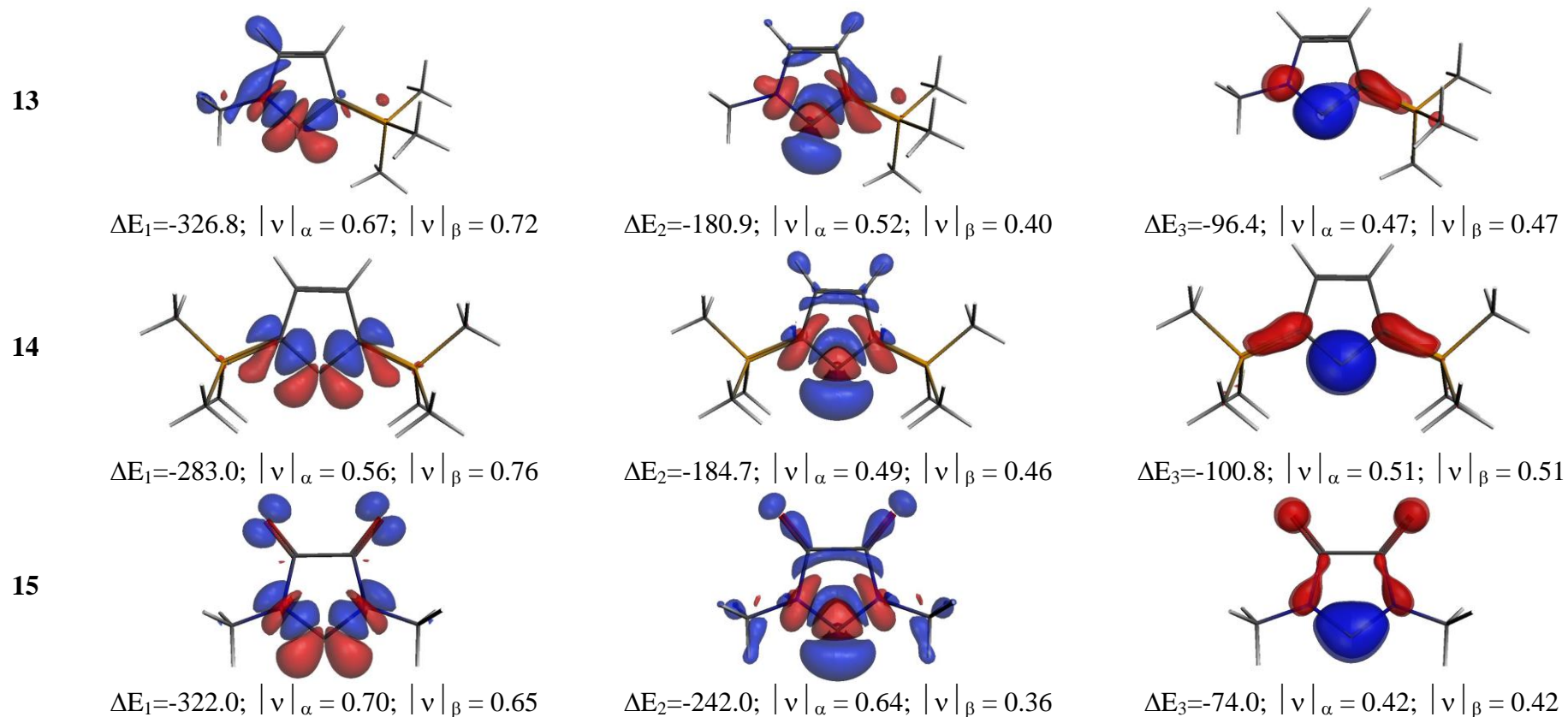


Figure S1. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions on the carbenes **2-15**, associated energies ΔE in kcal/mol and eigenvalues v in a.u. The color-code is red \rightarrow blue for the charge flow.

Table S1. Vertical singlet-triplet energy gap and single-triplet gap [in kcal/mol] at BP86/def2-TZVPP.

	$\Delta E_{(S-T)}^{\text{vert}}$	$\Delta E_{(S-T)}$
1	99.1	91.6
2	89.7	77.5
3	82.8	78.4
4	90.9	72.9
5	77.0	42.2
6	63.5	49.3
7	99.1	83.3
8	86.5	59.6
9	83.8	40.7
10	83.3	60.0
11	75.6	66.2
12	90.9	83.3
13	85.1	61.4
14	74.6	54.1
15	70.9	27.5

Table S2. Cartesian xyz coordinates (in Å) and electronic energies (in Hartree) of the calculated structures at BP86/def2-TZVPP.

1

E = -304.9123197

C	-0.00002000000	0.98676900000	-0.00001100000
N	1.06546200000	0.12000400000	-0.00005300000
N	-1.06546000000	0.12001100000	0.00005100000
C	0.68155200000	-1.21844700000	-0.00003100000
C	-0.68155200000	-1.21845400000	0.00003100000
C	2.44772900000	0.57482200000	0.00002500000
H	1.38617800000	-2.04330700000	-0.00006400000
H	-1.38618600000	-2.04330500000	0.00006300000
C	-2.44772800000	0.57482100000	-0.00002000000
H	2.97738500000	0.21799000000	0.89546200000
H	2.97775200000	0.21708400000	-0.89482600000
H	2.43181200000	1.66965200000	-0.00050700000
H	-2.97737400000	0.21802700000	-0.89547600000
H	-2.97775600000	0.21703800000	0.89481300000
H	-2.43182900000	1.66965000000	0.00058500000

2

E = -1043.8187311

C	0.00001200000	-0.38247100000	-0.00003300000
C	-0.67993800000	1.81387500000	0.00001400000
C	0.67994300000	1.81387900000	0.00003200000
N	-1.08451800000	0.47106500000	-0.00003400000
N	1.08453500000	0.47107500000	0.00000400000
H	-1.37688400000	2.64479700000	-0.00001800000
H	1.37688000000	2.64480900000	0.00004600000
Si	-2.73866300000	-0.23502100000	0.00001900000
Si	2.73867800000	-0.23501900000	-0.00000400000
C	-2.92978600000	-1.27268600000	-1.55112000000
H	-3.91787500000	-1.75598900000	-1.58747500000
H	-2.81665100000	-0.66044000000	-2.45760200000
H	-2.15832600000	-2.05486400000	-1.57270900000
C	-2.92962100000	-1.27284000000	1.55106700000
H	-3.91797500000	-1.75553500000	1.58797200000
H	-2.15857800000	-2.05544600000	1.57208400000
H	-2.81551600000	-0.66077700000	2.45755600000
C	-3.94160000000	1.21486700000	0.00008500000
H	-3.82219600000	1.84866500000	-0.89093200000
H	-4.97693700000	0.84179200000	0.00028800000
H	-3.82192500000	1.84884100000	0.89094300000
C	2.92958300000	-1.27311100000	1.55086700000
H	2.15862600000	-2.05580600000	1.57166900000
H	3.91798700000	-1.75570700000	1.58776900000
H	2.81533300000	-0.66123000000	2.45746000000
C	2.92978300000	-1.27244900000	-1.55130400000
H	2.15820700000	-2.05451200000	-1.57300600000
H	2.81673600000	-0.66006500000	-2.45770300000
H	3.91780100000	-1.75588800000	-1.58771100000
C	3.94160800000	1.21487100000	0.00038700000
H	4.97695300000	0.84182000000	0.00007300000
H	3.82191800000	1.84911700000	-0.89027300000
H	3.82218800000	1.84839200000	0.89160200000

3

E= -458.6160457

C	0.000000000000	0.000000000000	2.026913000000
C	0.000000000000	0.703268000000	-2.559152000000
C	0.000000000000	1.431684000000	-1.364398000000
C	0.000000000000	-0.703268000000	-2.559152000000
H	0.000000000000	2.522127000000	-1.369609000000
H	0.000000000000	-1.236881000000	-3.510446000000
C	0.000000000000	0.705470000000	-0.171217000000
C	0.000000000000	-1.431684000000	-1.364398000000
H	0.000000000000	-2.522127000000	-1.369609000000
C	0.000000000000	-0.705470000000	-0.171217000000
H	0.000000000000	1.236881000000	-3.510446000000
N	0.000000000000	-1.078214000000	1.173600000000
N	0.000000000000	1.078214000000	1.173600000000
C	0.000000000000	-2.454103000000	1.640761000000
H	0.000000000000	-2.428794000000	2.735079000000
H	-0.894670000000	-2.987652000000	1.286536000000
H	0.894670000000	-2.987652000000	1.286536000000
C	0.000000000000	2.454103000000	1.640761000000
H	-0.894670000000	2.987652000000	1.286536000000
H	0.000000000000	2.428794000000	2.735079000000
H	0.894670000000	2.987652000000	1.286536000000

4

E= -306.1130532

C	-0.000018000000	-1.023178000000	-0.000001000000
N	-1.076249000000	-0.210399000000	-0.038830000000
N	1.076226000000	-0.210411000000	0.038969000000
C	-0.767690000000	1.240147000000	0.033444000000
C	0.767762000000	1.240136000000	-0.033474000000
C	-2.447312000000	-0.663991000000	-0.001924000000
H	-1.236736000000	1.785980000000	-0.800182000000
H	1.153171000000	1.669485000000	-0.974471000000
C	2.447281000000	-0.664022000000	0.001871000000
H	-2.954444000000	-0.343313000000	0.925867000000
H	-3.022100000000	-0.268222000000	-0.856841000000
H	-2.444562000000	-1.758455000000	-0.046457000000
H	2.954358000000	-0.342935000000	-0.925812000000
H	3.022144000000	-0.268620000000	0.856914000000
H	2.444552000000	-1.758504000000	0.045952000000
H	1.236671000000	1.786035000000	0.800180000000
H	-1.153035000000	1.669660000000	0.974380000000

5

E= -307.2971988

C	0.000019000000	-0.814852000000	-0.000004000000
N	-1.170947000000	-0.139636000000	-0.006927000000
N	1.170967000000	-0.139647000000	0.006875000000
C	1.470671000000	1.273594000000	-0.301421000000
H	1.652343000000	1.882896000000	0.600165000000
H	2.384805000000	1.308315000000	-0.913811000000
H	0.661291000000	1.722865000000	-0.883464000000
C	2.378275000000	-0.945177000000	0.186188000000
H	2.070544000000	-1.985908000000	0.326253000000
H	3.039837000000	-0.865584000000	-0.694851000000
H	2.947052000000	-0.610711000000	1.070676000000
C	-2.378241000000	-0.945194000000	-0.186173000000
H	-2.947238000000	-0.610517000000	-1.070442000000
H	-2.070505000000	-1.985875000000	-0.326565000000
H	-3.039628000000	-0.865875000000	0.695030000000

C	-1.470718000000	1.273532000000	0.301435000000
H	-2.384660000000	1.308179000000	0.914136000000
H	-0.661238000000	1.722973000000	0.883195000000
H	-1.652783000000	1.882794000000	-0.600108000000

6

E= -329.3730921

C	-0.227423000000	-1.024142000000	-0.111393000000
N	-1.268922000000	-0.229454000000	-0.062664000000
C	-1.023724000000	1.248888000000	0.043436000000
C	0.468795000000	1.341806000000	-0.268363000000
C	0.998105000000	-0.113880000000	-0.024036000000
H	-1.669754000000	1.790152000000	-0.664000000000
H	-1.286891000000	1.584592000000	1.060350000000
H	0.983389000000	2.090892000000	0.349247000000
H	0.618671000000	1.621349000000	-1.321723000000
C	-2.652869000000	-0.692860000000	-0.040339000000
H	-3.212820000000	-0.266075000000	-0.886936000000
H	-2.646241000000	-1.785074000000	-0.106625000000
H	-3.145834000000	-0.377629000000	0.892722000000
C	2.064059000000	-0.524740000000	-1.049370000000
H	2.396996000000	-1.555841000000	-0.866913000000
H	1.667466000000	-0.477320000000	-2.074314000000
H	2.939952000000	0.140776000000	-0.989599000000
C	1.560128000000	-0.272146000000	1.407343000000
H	0.835293000000	0.055687000000	2.168022000000
H	1.805563000000	-1.323492000000	1.611013000000
H	2.474240000000	0.330605000000	1.523732000000

7

E= -320.9616574

C	-0.002624000000	-1.004149000000	-0.000018000000
N	1.057836000000	-0.118874000000	0.000010000000
N	-1.041946000000	-0.135115000000	-0.000019000000
C	0.596852000000	1.180467000000	0.000051000000
N	-0.711673000000	1.214605000000	0.000047000000
C	2.456731000000	-0.526311000000	-0.000065000000
H	1.229353000000	2.063154000000	0.000078000000
C	-2.448872000000	-0.497194000000	0.000008000000
H	2.972130000000	-0.152912000000	-0.895861000000
H	2.972408000000	-0.152211000000	0.895276000000
H	2.477984000000	-1.620573000000	0.000351000000
H	-2.943422000000	-0.094771000000	0.894026000000
H	-2.943597000000	-0.094112000000	-0.893612000000
H	-2.506904000000	-1.589759000000	-0.000376000000

8

E=-304.8849308

C	-0.028675000000	-0.848518000000	0.000018000000
N	1.068662000000	-0.071926000000	0.000043000000
N	-1.096827000000	-0.021738000000	-0.000033000000
C	0.634828000000	1.260930000000	0.000021000000
C	-0.751322000000	1.345926000000	-0.000004000000
C	2.446613000000	-0.548793000000	-0.000042000000
H	1.378743000000	2.052635000000	0.000035000000
C	-2.479267000000	-0.486423000000	0.000005000000
H	2.971515000000	-0.185722000000	-0.894005000000
H	2.971867000000	-0.184868000000	0.893363000000
H	2.462147000000	-1.644656000000	0.000488000000
H	-2.992227000000	-0.101706000000	0.890139000000

H	-2.992528000000	-0.100738000000	-0.889528000000
H	-2.512087000000	-1.584185000000	-0.000576000000
H	-0.023335000000	-1.933838000000	0.000023000000

9

E=-383.5049069

C	0.000000000000	1.687091000000	0.000001000000
C	-1.089701000000	0.802531000000	0.031315000000
C	1.089701000000	0.802531000000	-0.031315000000
N	-0.685939000000	-0.521545000000	0.034914000000
N	0.685939000000	-0.521545000000	-0.034913000000
C	-2.552667000000	1.126598000000	0.055827000000
C	2.552667000000	1.126598000000	-0.055828000000
H	-3.075043000000	0.798754000000	-0.858622000000
H	-3.076605000000	0.680136000000	0.917221000000
H	-2.644006000000	2.216084000000	0.124438000000
H	3.075047000000	0.798746000000	0.858616000000
H	3.076603000000	0.680145000000	-0.917228000000
H	2.644005000000	2.216085000000	-0.124429000000
C	1.445258000000	-1.749267000000	0.120350000000
H	1.313997000000	-2.191696000000	1.121578000000
H	1.171967000000	-2.495362000000	-0.640928000000
H	2.502387000000	-1.497544000000	-0.011247000000
C	-1.445258000000	-1.749267000000	-0.120350000000
H	-1.313996000000	-2.191695000000	-1.121578000000
H	-1.171967000000	-2.495362000000	0.640928000000
H	-2.502387000000	-1.497544000000	0.011246000000

10

E=-360.2530547

C	-0.584167000000	1.293713000000	0.000192000000
C	0.710663000000	0.741827000000	-0.000187000000
N	-1.327257000000	0.135024000000	0.000449000000
N	0.604040000000	-0.631439000000	-0.000172000000
N	-0.662044000000	-1.039072000000	0.000191000000
C	2.034240000000	1.432054000000	-0.000063000000
C	-2.784511000000	0.061750000000	-0.000246000000
H	2.636664000000	1.190016000000	0.890719000000
H	2.640725000000	1.182887000000	-0.886071000000
H	1.855573000000	2.513181000000	-0.004659000000
H	-3.139069000000	-0.458671000000	-0.899580000000
H	-3.138945000000	-0.474056000000	0.889987000000
H	-3.149738000000	1.091999000000	0.008274000000
C	1.660823000000	-1.634472000000	-0.000020000000
H	2.287676000000	-1.521367000000	0.894437000000
H	1.193607000000	-2.623636000000	-0.000244000000
H	2.288044000000	-1.521175000000	-0.894195000000

11

E=-608.4542923

C	-0.087560000000	-1.163656000000	0.000080000000
N	-0.901659000000	-0.076941000000	0.000070000000
S	1.511666000000	-0.524981000000	-0.000026000000
C	1.030316000000	1.151400000000	-0.000033000000
C	-0.325750000000	1.198736000000	0.000056000000
H	1.717463000000	1.992136000000	-0.000077000000
H	-0.960230000000	2.082729000000	0.000084000000
C	-2.361326000000	-0.234667000000	-0.000066000000
H	-2.796229000000	0.230409000000	0.895653000000
H	-2.795986000000	0.229530000000	-0.896364000000

H -2.574143000000 -1.307402000000 0.000412000000

12

E=-285.4502811

C -0.090966000000 -1.193126000000 -0.000024000000
O -1.399614000000 -0.764127000000 -0.000004000000
N 0.617230000000 -0.032391000000 -0.000013000000
C -0.209051000000 1.100013000000 -0.000045000000
C -1.467577000000 0.616569000000 0.000044000000
H -2.446337000000 1.080411000000 0.000087000000
H 0.167850000000 2.115833000000 -0.000074000000
C 2.073444000000 0.001360000000 0.000027000000
H 2.423182000000 -1.036263000000 -0.000204000000
H 2.448240000000 0.515231000000 0.895974000000
H 2.448262000000 0.515646000000 -0.895671000000

13

E=-709.496093

C -1.131388000000 -0.822136000000 -0.054880000000
N -2.342798000000 -0.168569000000 0.008116000000
C -2.236732000000 1.224482000000 0.026751000000
C -0.902956000000 1.548873000000 -0.019069000000
C -0.217692000000 0.278391000000 -0.084637000000
H -3.112522000000 1.869484000000 0.054769000000
H -0.493012000000 2.556838000000 -0.022248000000
P 1.465377000000 -0.091236000000 -0.012899000000
C 1.765556000000 -1.669564000000 -0.847674000000
H 0.912165000000 -2.305929000000 -0.562896000000
H 1.735401000000 -1.520094000000 -1.934148000000
H 2.724538000000 -2.114291000000 -0.551603000000
C 2.496361000000 1.202340000000 -0.777482000000
H 3.562306000000 0.947731000000 -0.709212000000
H 2.211128000000 1.314367000000 -1.831019000000
H 2.324442000000 2.157759000000 -0.264109000000
C 2.127435000000 -0.278072000000 1.682680000000
H 1.945105000000 0.648163000000 2.243540000000
H 1.575975000000 -1.092574000000 2.170583000000
H 3.203342000000 -0.503333000000 1.683187000000
C -3.622553000000 -0.861192000000 0.031856000000
H -4.223305000000 -0.621412000000 -0.859919000000
H -3.411782000000 -1.935786000000 0.046367000000
H -4.203038000000 -0.591127000000 0.928118000000

14

E=-1114.0756502

C -0.000019000000 -0.401995000000 -0.144441000000
C -1.098673000000 0.516880000000 -0.100076000000
C -0.692522000000 1.906289000000 -0.002725000000
C 0.692585000000 1.906258000000 -0.002774000000
C 1.098681000000 0.516836000000 -0.100179000000
H -1.330322000000 2.791582000000 0.022210000000
H 1.330423000000 2.791526000000 0.022098000000
P 2.672941000000 -0.179576000000 -0.005421000000
P -2.672932000000 -0.179531000000 -0.005391000000
C 2.803289000000 -1.595547000000 -1.133363000000
H 1.856057000000 -2.141476000000 -1.000525000000
H 2.852946000000 -1.232331000000 -2.167770000000
H 3.670805000000 -2.231795000000 -0.911375000000
C 4.008439000000 1.001421000000 -0.398281000000
H 4.995457000000 0.527636000000 -0.313962000000

H	3.868948000000	1.379618000000	-1.418881000000
H	3.956702000000	1.848118000000	0.298925000000
C	3.107093000000	-0.847033000000	1.644508000000
H	3.078166000000	-0.030556000000	2.378206000000
H	2.333686000000	-1.580027000000	1.910358000000
H	4.098038000000	-1.323300000000	1.657427000000
C	-2.803477000000	-1.595307000000	-1.133561000000
H	-3.671304000000	-2.231238000000	-0.911858000000
H	-2.852744000000	-1.231940000000	-2.167932000000
H	-1.856517000000	-2.141654000000	-1.000596000000
C	-4.008458000000	1.001513000000	-0.398010000000
H	-3.956320000000	1.848424000000	0.298904000000
H	-3.869388000000	1.379373000000	-1.418792000000
H	-4.995486000000	0.527851000000	-0.313112000000
C	-3.106942000000	-0.847340000000	1.644429000000
H	-4.098051000000	-1.323258000000	1.657464000000
H	-2.333713000000	-1.580685000000	1.909842000000
H	-3.077502000000	-0.031112000000	2.378382000000

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E=-454.2397744

C	0.000000000000	1.419870000000	-0.000004000000
N	-1.098447000000	0.586421000000	-0.000004000000
N	1.098448000000	0.586421000000	0.000002000000
C	-0.778690000000	-0.775505000000	-0.000017000000
C	0.778689000000	-0.775505000000	0.000019000000
C	-2.472165000000	1.077088000000	-0.000026000000
C	2.472165000000	1.077087000000	0.000025000000
H	-3.004237000000	0.720222000000	-0.891916000000
H	-3.004474000000	0.719553000000	0.891452000000
H	-2.429020000000	2.170758000000	0.000377000000
H	3.004221000000	0.720271000000	0.891946000000
H	3.004491000000	0.719501000000	-0.891422000000
H	2.429022000000	2.170756000000	-0.000437000000
O	1.531584000000	-1.723072000000	0.000030000000
O	-1.531585000000	-1.723073000000	-0.000025000000