Supplementary Material

to the manuscript

The electronic structure of nitrilimine: absence of the carbenic form

by

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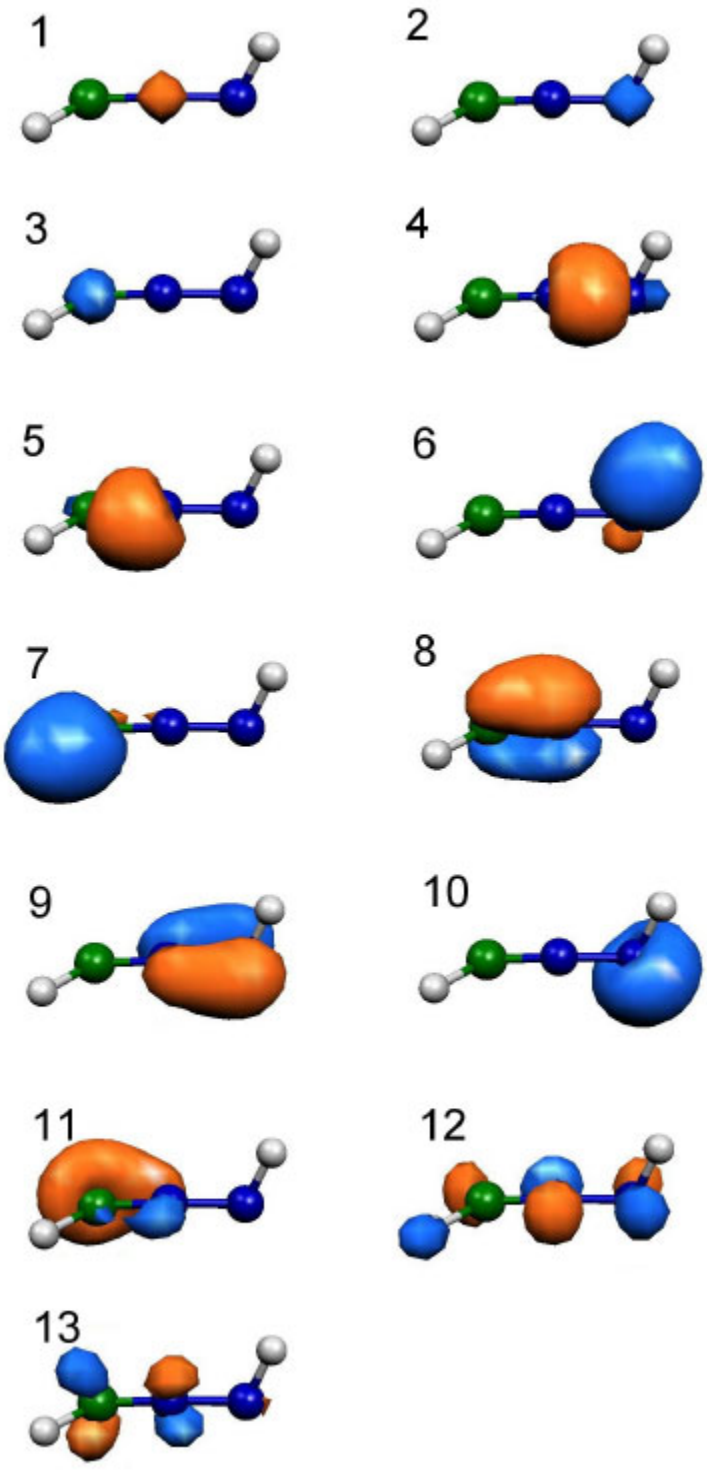
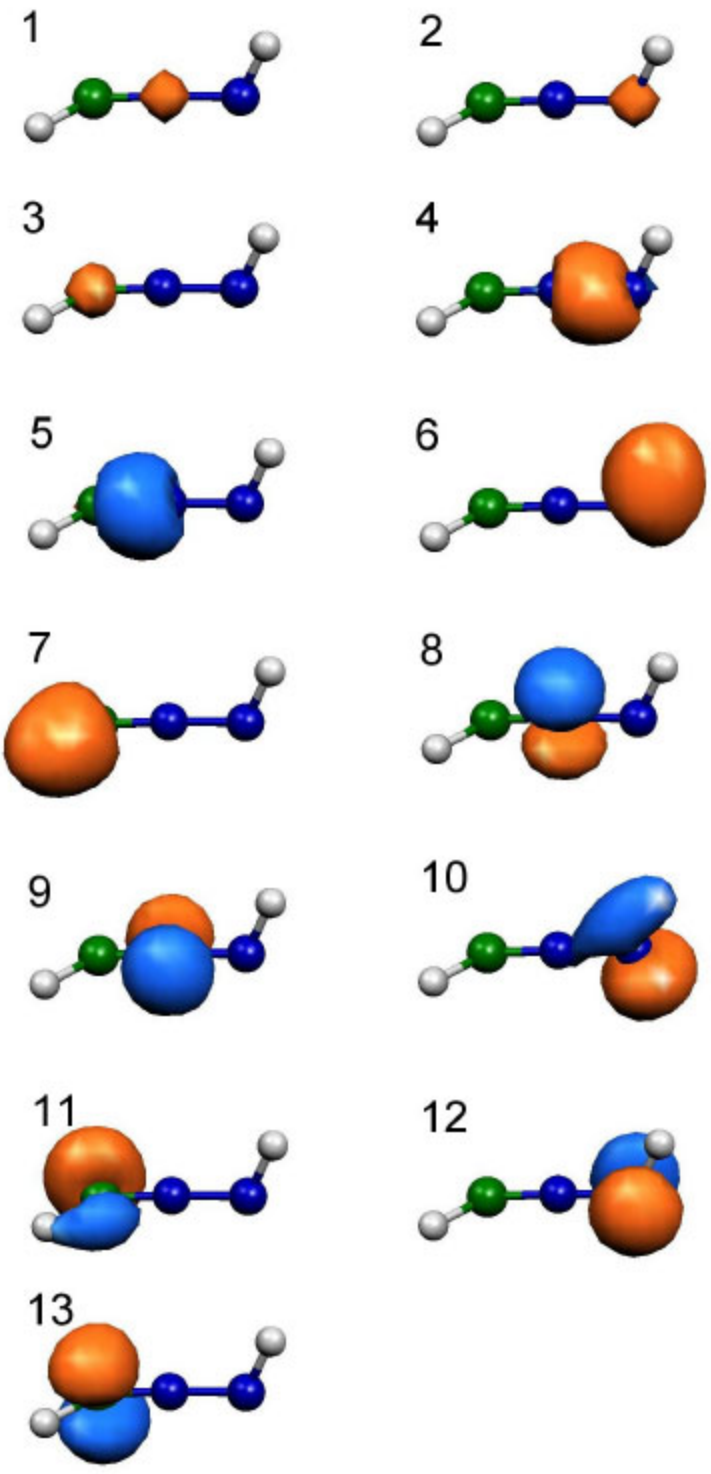


Hartree-Fock occupied MOs of HCNNH, localised after Pipek and Mezey, along with the two lowest virtual MOs (not localised).

Basis set: cc-pVTZ
Geometry: CASSCF(8|6)/cc-pVTZ



CASSCF(8|6) frozen (1-7, doubly occupied) and active (8-13, partially occupied) MOs of HCNNH, localised after Pipek and Mezey.

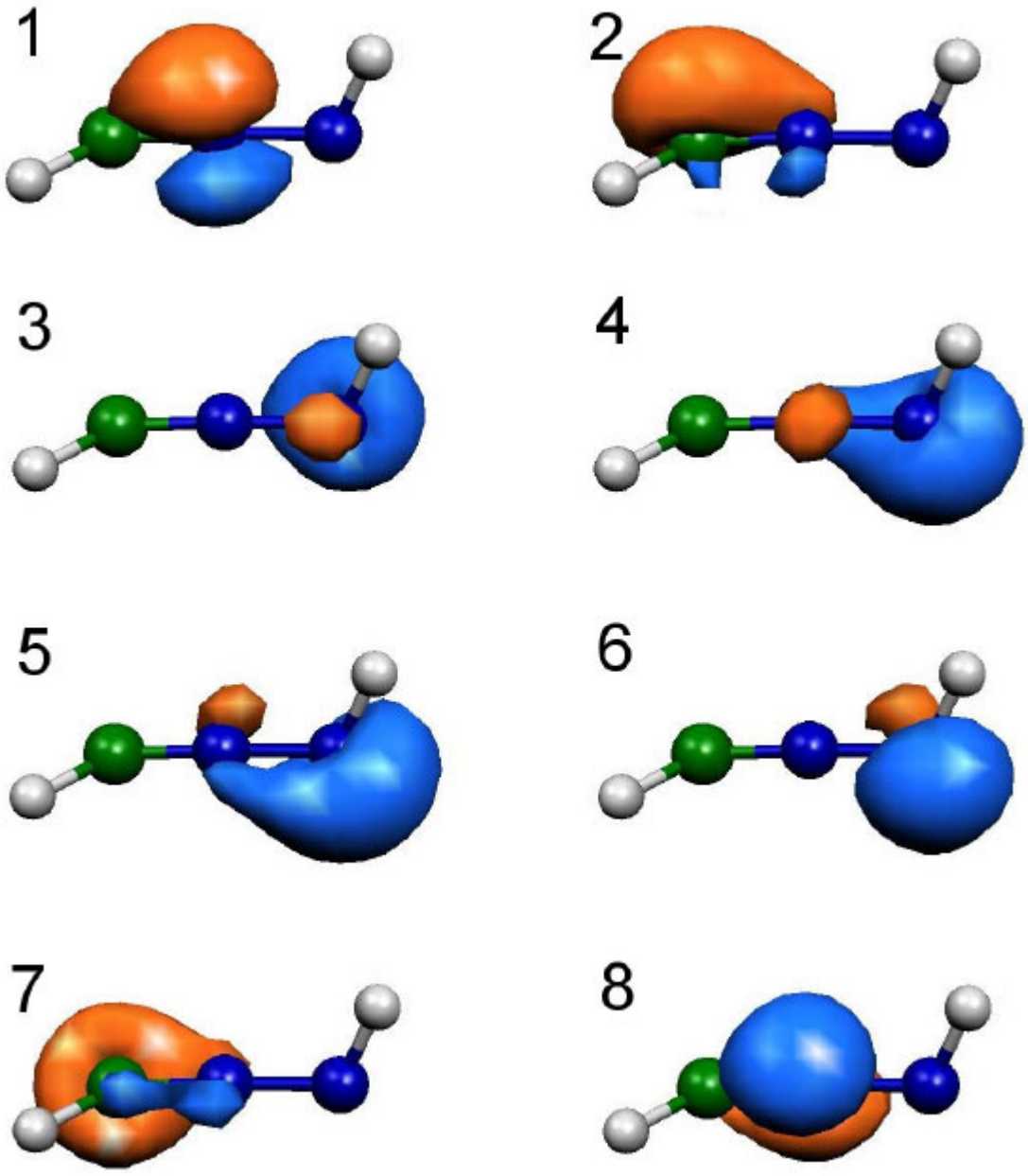
Basis set: cc-pVTZ
Geometry: CASSCF(8|6)/cc-pVTZ

Note the atomic nature of the localised π molecular orbitals (8-13).

SC(8) calculation using localised HF MOs as starting orbitals

HF energy	–147.8491272 hartree
SC(8) energy	–147.9332404 hartree
Correlation energy	84.1 millihartree

SC(8) ORBITALS



RUMER structures

```
    1 ==>  1- 2   3- 4   5- 6   7- 8
    2 ==>  2- 3   1- 4   5- 6   7- 8
    3 ==>  1- 2   4- 5   3- 6   7- 8
    4 ==>  2- 3   4- 5   1- 6   7- 8
    5 ==>  3- 4   2- 5   1- 6   7- 8
    6 ==>  1- 2   3- 4   6- 7   5- 8
    7 ==>  2- 3   1- 4   6- 7   5- 8
    8 ==>  1- 2   4- 5   6- 7   3- 8
    9 ==>  2- 3   4- 5   6- 7   1- 8
   10 ==>  3- 4   2- 5   6- 7   1- 8
   11 ==>  1- 2   5- 6   4- 7   3- 8
   12 ==>  2- 3   5- 6   4- 7   1- 8
   13 ==>  3- 4   5- 6   2- 7   1- 8
   14 ==>  4- 5   3- 6   2- 7   1- 8
```

OVERLAP matrix

	1	2	3	4	5	6	7	8
1	1.00000	0.54071	0.08510	0.15291	0.30365	0.15795	0.12010	-0.59366
2	0.54071	1.00000	-0.10065	-0.09508	0.01531	0.11213	0.66013	0.09538
3	0.08510	-0.10065	1.00000	0.73673	0.42598	-0.13536	-0.04297	-0.23098
4	0.15291	-0.09508	0.73673	1.00000	0.70735	0.40230	0.02590	-0.36292
5	0.30365	0.01531	0.42598	0.70735	1.00000	0.72926	0.10565	-0.06184
6	0.15795	0.11213	-0.13536	0.40230	0.72926	1.00000	0.16579	0.05405
7	0.12010	0.66013	-0.04297	0.02590	0.10565	0.16579	1.00000	0.48266
8	-0.59366	0.09538	-0.23098	-0.36292	-0.06184	0.05405	0.48266	1.00000

SPIN COUPLING COEFFICIENTS - RUMER BASIS

```
 1 ==>  0.266608
 2 ==>  0.018936
 3 ==> -0.024789
 4 ==> -0.023314
 5 ==>  0.008506
 6 ==>  0.023620
 7 ==> -0.025562
 8 ==> -0.024126
 9 ==>  0.044258
10 ==> -0.024582
11 ==>  0.002560
12 ==> -0.017285
13 ==> -0.057456
14 ==> -0.001669
```

CHIRGWIN-COULSON occupation numbers

```
Chirgwin-Coulson occupation number for structure  1 is   1.40148
Chirgwin-Coulson occupation number for structure  2 is   0.04920
Chirgwin-Coulson occupation number for structure  3 is  -0.09314
Chirgwin-Coulson occupation number for structure  4 is  -0.04229
Chirgwin-Coulson occupation number for structure  5 is   0.02126
Chirgwin-Coulson occupation number for structure  6 is   0.06297
Chirgwin-Coulson occupation number for structure  7 is  -0.03847
Chirgwin-Coulson occupation number for structure  8 is  -0.04131
Chirgwin-Coulson occupation number for structure  9 is   0.07445
Chirgwin-Coulson occupation number for structure 10 is  -0.06141
Chirgwin-Coulson occupation number for structure 11 is   0.00588
Chirgwin-Coulson occupation number for structure 12 is  -0.04016
Chirgwin-Coulson occupation number for structure 13 is  -0.29247
Chirgwin-Coulson occupation number for structure 14 is  -0.00599
```

Expectation values of (s(i)+s(j))**2
Lower triangle uses SPIN function with Snorm=0.916976
Upper triangle uses FULL function with Snorm=1.000000

	1	2	3	4	5	6	7	8
1	0.00000	-0.32250	1.46904	1.51978	1.45762	1.55060	1.94992	1.37555
2	0.13496	0.00000	1.50809	1.49081	1.55260	1.44870	1.37463	1.94768
3	1.49150	1.51173	0.00000	-0.06970	1.63440	1.43998	1.40141	1.61678
4	1.50103	1.48245	0.05250	0.00000	1.43972	1.63486	1.59914	1.38539
5	1.47370	1.51435	1.23485	1.72474	0.00000	-0.07320	1.49431	1.49455
6	1.51974	1.47990	1.72605	1.23683	0.05137	0.00000	1.49981	1.49926
7	1.02282	1.85462	1.45569	1.53924	1.49267	1.49925	0.00000	-0.31921
8	1.85624	1.02199	1.52768	1.46320	1.50832	1.48685	0.13572	0.00000

SPIN COUPLING COEFFICIENTS - KOTANI BASIS

```
 1 ==>  -0.0009
 2 ==>  -0.1648
 3 ==>   0.0814
 4 ==>  -0.0180
 5 ==>   0.0863
 6 ==>  -0.0869
 7 ==>   0.0165
 8 ==>  -0.0211
 9 ==>   0.0019
10 ==> -0.0146
11 ==> -0.0058
12 ==> -0.1113
13 ==>  0.0028
14 ==>  0.8422
```

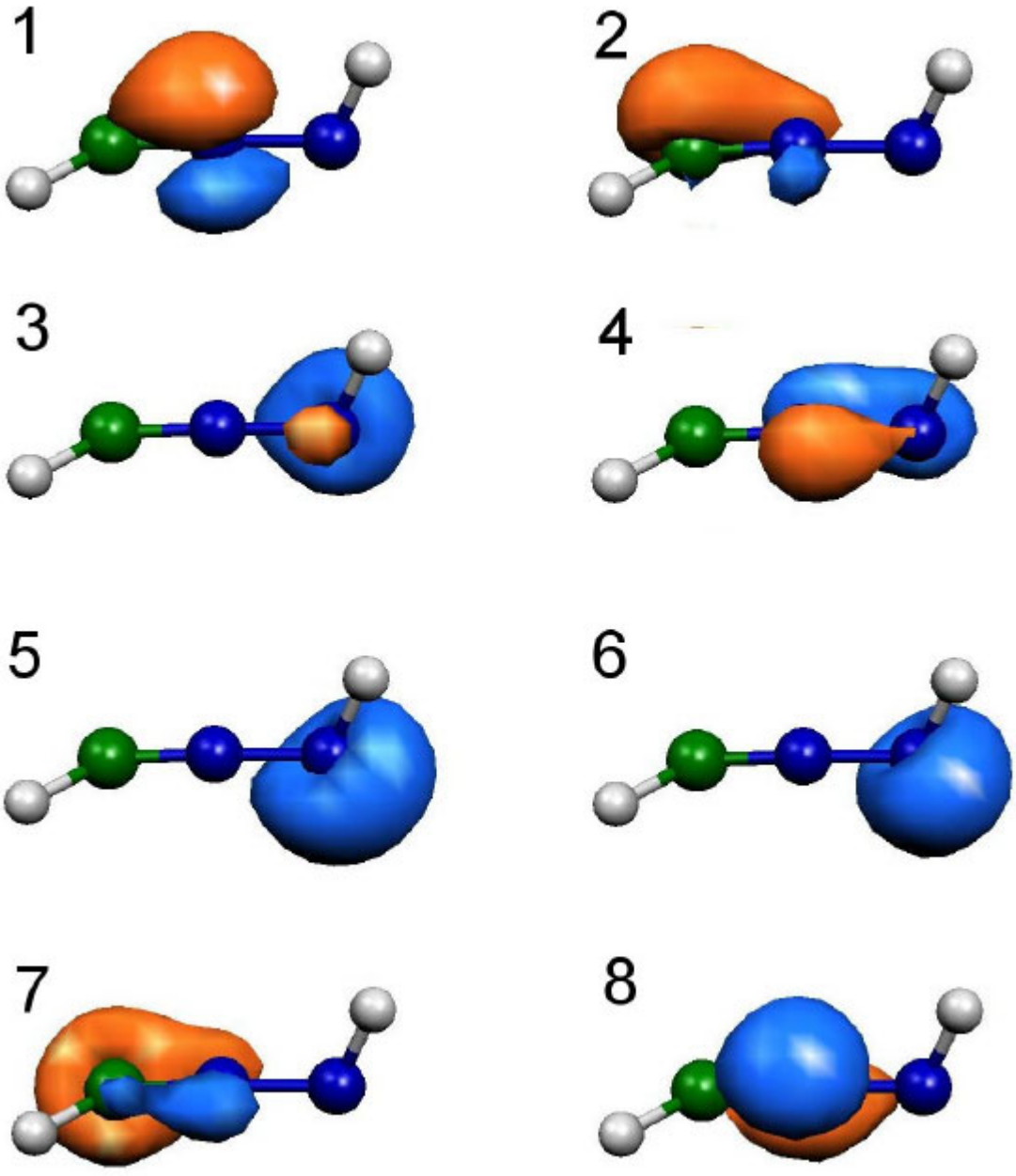
KOTANI Populations, i .e,
OCCUPATION NUMBERS THAT NORMALIZE THE TOTAL SPIN FUNCTIONS

```
 1 ==>  0.0000
 2 ==>  0.0352
 3 ==>  0.0086
 4 ==>  0.0004
 5 ==>  0.0096
 6 ==>  0.0098
 7 ==>  0.0004
 8 ==>  0.0006
 9 ==>   0.0000
10 ==>  0.0003
11 ==>  0.0000
12 ==>  0.0161
13 ==>  0.0000
14 ==>  0.9191
```

SC(8) calculation using localised HF MOs as starting orbitals under the following constraint: SC orbitals 5 and 6 (see figure below) are not allowed to mix with the ninth orbital of the localised HF guess (see first figure of this Supplementary Material)

HF energy	–147.8491272
SC(8) energy	–147.9308781
Correlation energy	81.8 millihartrees

ORBITALS



RUMER structures

```
    1 ==>  1- 2   3- 4   5- 6   7- 8
    2 ==>  2- 3   1- 4   5- 6   7- 8
    3 ==>  1- 2   4- 5   3- 6   7- 8
    4 ==>  2- 3   4- 5   1- 6   7- 8
    5 ==>  3- 4   2- 5   1- 6   7- 8
    6 ==>  1- 2   3- 4   6- 7   5- 8
    7 ==>  2- 3   1- 4   6- 7   5- 8
    8 ==>  1- 2   4- 5   6- 7   3- 8
    9 ==>  2- 3   4- 5   6- 7   1- 8
   10 ==>  3- 4   2- 5   6- 7   1- 8
   11 ==>  1- 2   5- 6   4- 7   3- 8
   12 ==>  2- 3   5- 6   4- 7   1- 8
   13 ==>  3- 4   5- 6   2- 7   1- 8
   14 ==>  4- 5   3- 6   2- 7   1- 8
```

OVERLAP matrix

	1	2	3	4	5	6	7	8
1	1.00000	0.48898	0.07535	-0.08247	0.20664	0.16638	0.15163	-0.55474
2	0.48898	1.00000	-0.36222	-0.32480	-0.28511	-0.17387	0.73918	0.24271
3	0.07535	-0.36222	1.00000	0.76515	0.68445	0.62198	-0.29895	-0.36132
4	-0.08247	-0.32480	0.76515	1.00000	0.34159	0.42809	-0.24734	-0.48875
5	0.20664	-0.28511	0.68445	0.34159	1.00000	0.89738	-0.19794	-0.25961
6	0.16638	-0.17387	0.62198	0.42809	0.89738	1.00000	-0.11567	-0.23668
7	0.15163	0.73918	-0.29895	-0.24734	-0.19794	-0.11567	1.00000	0.53910
8	-0.55474	0.24271	-0.36132	-0.48875	-0.25961	-0.23668	0.53910	1.00000

SPIN COUPLING COEFFICIENTS - RUMER BASIS

```
 1 ==>  0.304270
 2 ==>  0.006478
 3 ==>  0.034649
 4 ==> -0.019721
 5 ==> -0.008664
 6 ==>  0.021476
 7 ==> -0.024611
 8 ==> -0.014210
 9 ==>  0.039724
10 ==> -0.014976
11 ==>  0.009477
12 ==> -0.010409
13 ==> -0.067764
14 ==> -0.017884
```

CHIRGWIN-COULSON occupation numbers

```
 Chirgwin-Coulson occupation number for structure   1 is    1.26696
 Chirgwin-Coulson occupation number for structure   2 is    0.01371
 Chirgwin-Coulson occupation number for structure   3 is    0.07080
 Chirgwin-Coulson occupation number for structure   4 is   -0.02073
 Chirgwin-Coulson occupation number for structure   5 is   -0.01823
 Chirgwin-Coulson occupation number for structure   6 is    0.04476
 Chirgwin-Coulson occupation number for structure   7 is   -0.02589
 Chirgwin-Coulson occupation number for structure   8 is   -0.01325
 Chirgwin-Coulson occupation number for structure   9 is    0.04011
 Chirgwin-Coulson occupation number for structure  10 is   -0.03209
 Chirgwin-Coulson occupation number for structure  11 is    0.01795
 Chirgwin-Coulson occupation number for structure  12 is   -0.02103
 Chirgwin-Coulson occupation number for structure  13 is   -0.28602
 Chirgwin-Coulson occupation number for structure  14 is   -0.03706
```

Expectation values of (s(i)+s(j))**2
Lower triangle uses SPIN function with Snorm=0.916976
Upper triangle uses FULL function with Snorm=1.000000

	1	2	3	4	5	6	7	8
1	0.00000	-0.34117	1.47921	1.51993	1.46080	1.53976	2.02596	1.31551
2	0.12518	0.00000	1.49926	1.50366	1.53246	1.46775	1.31389	2.02415
3	1.44273	1.56572	0.00000	-0.00478	1.53963	1.46187	1.46785	1.55697
4	1.55568	1.42805	0.01622	0.00000	1.46282	1.53809	1.53404	1.44625
5	1.41077	1.58503	1.59846	1.39451	0.00000	-0.00161	1.49787	1.50804
6	1.57877	1.40450	1.39751	1.59934	0.01755	0.00000	1.50273	1.49140
7	1.04381	1.84219	1.53969	1.45680	1.53302	1.46447	0.00000	-0.34233
8	1.84306	1.04934	1.43967	1.54941	1.46065	1.53785	0.12002	0.00000

SPIN COUPLING COEFFICIENTS - KOTANI BASIS

1 ==>	0.0343
2 ==>	-0.1608
3 ==>	0.1168
4 ==>	0.0104
5 ==>	0.1264
6 ==>	-0.0429
7 ==>	-0.0219
8 ==>	0.0276
9 ==>	0.0134
10 ==>	-0.0392
11 ==>	0.0273
12 ==>	0.0555
13 ==>	-0.0326
14 ==>	-0.9662

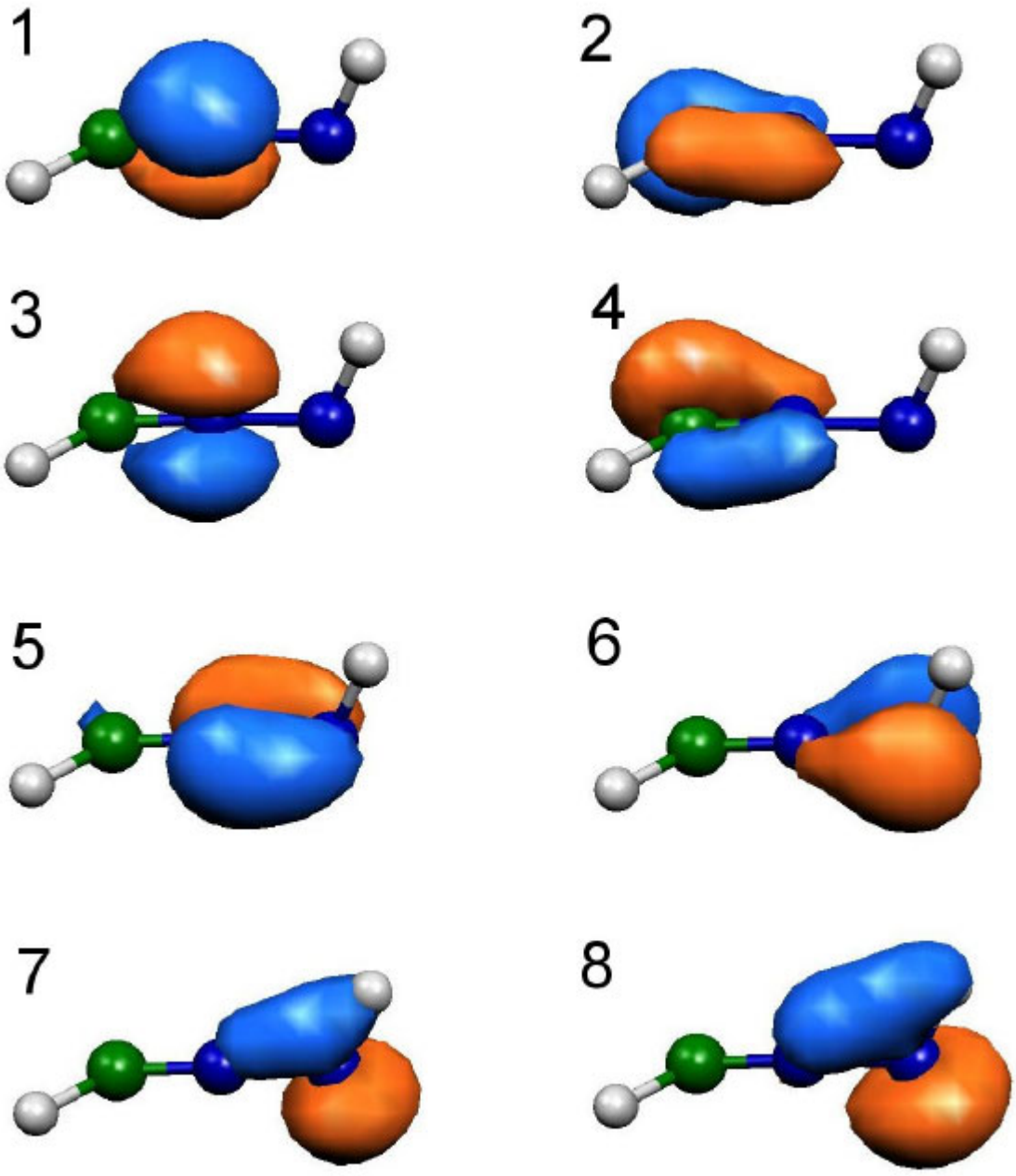
KOTANI populations, i. e.,
OCCUPATION NUMBER THAT NORMALIZE THE TOTAL SPIN FUNCTIONS

1 ==>	0.0012
2 ==>	0.0259
3 ==>	0.0136
4 ==>	0.0001
5 ==>	0.0160
6 ==>	0.0018
7 ==>	0.0005
8 ==>	0.0008
9 ==>	0.0002
10 ==>	0.0015
11 ==>	0.0007
12 ==>	0.0031
13 ==>	0.0011
14 ==>	0.9336

SC(8) calculation using localised CASSCF MOs as starting orbitals under the following constraint: SC orbitals 7 and 8 (see figure below) are not allowed to mix with the twelfth orbital of the localised CASSCF guess (see second figure of this Supplementary Material)

HF energy	–147.8491272
SC(8) energy	–147.9398337

ORBITALS



RUMER structures

```
    1 ==>  1- 2   3- 4   5- 6   7- 8
    2 ==>  2- 3   1- 4   5- 6   7- 8
    3 ==>  1- 2   4- 5   3- 6   7- 8
    4 ==>  2- 3   4- 5   1- 6   7- 8
    5 ==>  3- 4   2- 5   1- 6   7- 8
    6 ==>  1- 2   3- 4   6- 7   5- 8
    7 ==>  2- 3   1- 4   6- 7   5- 8
    8 ==>  1- 2   4- 5   6- 7   3- 8
    9 ==>  2- 3   4- 5   6- 7   1- 8
   10 ==>  3- 4   2- 5   6- 7   1- 8
   11 ==>  1- 2   5- 6   4- 7   3- 8
   12 ==>  2- 3   5- 6   4- 7   1- 8
   13 ==>  3- 4   5- 6   2- 7   1- 8
   14 ==>  4- 5   3- 6   2- 7   1- 8
```

OVERLAP matrix

```
        1         2         3         4         5         6         7         8
  1  1.00000 -0.46510 -0.68171  0.08053  0.28182 -0.14858  0.25636  0.37828
  2 -0.46510  1.00000 -0.09504 -0.72725 -0.29146  0.34641 -0.02307  0.00365
  3 -0.68171 -0.09504  1.00000  0.47953  0.28665 -0.15686 -0.26104 -0.38540
  4  0.08053 -0.72725  0.47953  1.00000  0.28805 -0.34389 -0.04748 -0.02768
  5  0.28182 -0.29146  0.28665  0.28805  1.00000 -0.73644 -0.00209 -0.00666
  6 -0.14858  0.34641 -0.15686 -0.34389 -0.73644  1.00000 -0.00238 -0.00031
  7  0.25636 -0.02307 -0.26104 -0.04748 -0.00209 -0.00238  1.00000  0.86343
  8  0.37828  0.00365 -0.38540 -0.02768 -0.00666 -0.00031  0.86343  1.00000
```

SPIN COUPLING COEFFICIENTS - RUMER BASIS

```
 1 ==>  0.214066
 2 ==>  0.083763
 3 ==> -0.013442
 4 ==>  0.009843
 5 ==> -0.004586
 6 ==> -0.019074
 7 ==> -0.004099
 8 ==>  0.008085
 9 ==> -0.019766
10 ==>  0.008189
11 ==> -0.51300
12 ==>  0.008691
13 ==> -0.014807
14 ==>  0.193159
```

CHIRGWIN-COULSON occupation numbers

```
 Chirgwin-Coulson occupation number for structure   1 is    1.15227
 Chirgwin-Coulson occupation number for structure   2 is   -0.04555
 Chirgwin-Coulson occupation number for structure   3 is   -0.03346
 Chirgwin-Coulson occupation number for structure   4 is   -0.00467
 Chirgwin-Coulson occupation number for structure   5 is   -0.01138
 Chirgwin-Coulson occupation number for structure   6 is   -0.05085
 Chirgwin-Coulson occupation number for structure   7 is    0.00111
 Chirgwin-Coulson occupation number for structure   8 is    0.01017
 Chirgwin-Coulson occupation number for structure   9 is    0.00420
 Chirgwin-Coulson occupation number for structure  10 is    0.01025
 Chirgwin-Coulson occupation number for structure  11 is   -0.01408
 Chirgwin-Coulson occupation number for structure  12 is   -0.00194
 Chirgwin-Coulson occupation number for structure  13 is   -0.04058
 Chirgwin-Coulson occupation number for structure  14 is    0.02451
```

Expectation values of (s(i)+s(j))**2

Lower triangle uses SPIN function with Snorm=0.916976
Upper triangle uses FULL function with Snorm=1.000000

	1	2	3	4	5	6	7	8
1	0.00000	-0.55706	1.35736	2.19940	1.43933	1.56066	1.51261	1.48770
2	0.18302	0.00000	2.19949	1.35736	1.56148	1.43841	1.49139	1.50893
3	1.90547	0.91718	0.00000	-0.55738	1.44435	1.55597	1.50961	1.49060
4	0.91729	1.90547	0.18302	0.00000	1.55520	1.44499	1.48774	1.51269
5	1.49671	1.50065	1.50002	1.49682	0.00000	0.00061	1.44063	1.55840
6	1.50170	1.49528	1.49842	1.49909	0.01258	0.00000	1.55785	1.44152
7	1.48565	1.50901	1.48771	1.51183	1.38246	1.61061	0.00000	0.00016
8	1.51016	1.48939	1.50818	1.48647	1.61076	1.38232	0.01273	0.00000

SPIN COUPLING COEFFICIENTS - KOTANI BASIS

```
 1 ==>   -0.0432
 2 ==>   -0.0007
 3 ==>    0.0029
 4 ==>   -0.0022
 5 ==>    0.0041
 6 ==>   -0.0058
 7 ==>    0.0070
 8 ==>    0.0227
 9 ==>   -0.0622
10 ==>   -0.0014
11 ==>    0.0011
12 ==>    0.0008
13 ==>    0.2984
14 ==>   -0.9511
```

KOTANI populations, i. e.,
OCCUPATION NUMBER THAT NORMALIZE THE TOTAL SPIN FUNCTIONS

```
 1 ==>   0.0019
 2 ==>   0.0000
 3 ==>   0.0000
 4 ==>   0.0000
 5 ==>   0.0000
 6 ==>   0.0000
 7 ==>   0.0000
 8 ==>   0.0005
 9 ==>   0.0039
10 ==>   0.0000
11 ==>   0.0000
12 ==>   0.0000
13 ==>   0.0891
14 ==>   0.9046
```