Supporting Information: A computational journey across nitroxide radicals: from structure to spectroscopic properties and beyond

Vincenzo Barone,* Marco Fusè, Sandra Mónica Vieira Pinto, and Nicola Tasinato

Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy

E-mail: vincenzo.barone@sns.it

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1 Cartesian Coordinates

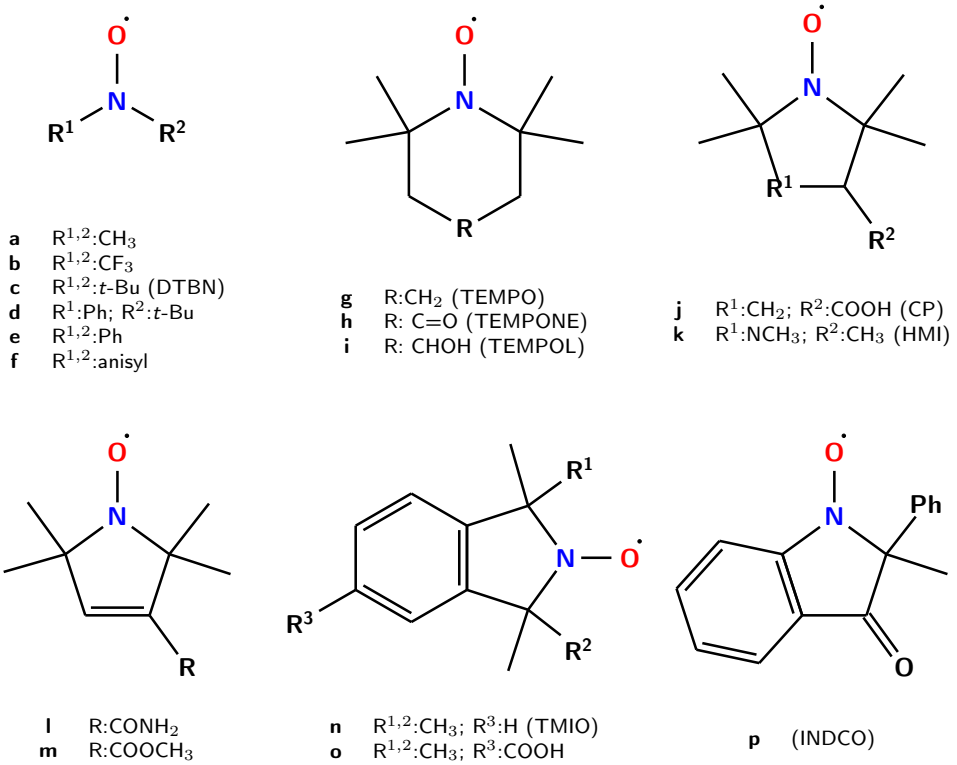

Figure S1: Molecular structures of the systems under investigation.

1.1 CCF12 Geometry

Here below the Cartesian coordinates of the dimethylnitroxide at the CCSD(T)-F12/CC-PVDZ-F12 level of theory are reported.

a-min-f12

```
  10
CCSD(T)-F12/CC-PVDZ-F12  ENERGY=-209.43744669
N          -0.1652567057       -0.0410695080        0.0000070584
O           0.0495014046       -1.3002380842       -0.0001787706
C           0.0403166370        0.6763798830       -1.2481398981
C           0.0403183822        0.6760979646        1.2483157350
H          -0.5040360628        1.6199617649       -1.2231184679
H          -0.5040343525        1.6196854736        1.2235081791
H          -0.3268452931        0.0488191718       -2.0553214283
H          -0.3268424194        0.0483549635        2.0553560203
H           1.1057957938        0.8783604365       -1.4008125401
H           1.1057977525        0.8780440313        1.4010325017
```

a-TS-f12

```
  10
CCSD(T)-F12/CC-PVTZ-F12  ENERGY=-209.46760885
N          -0.0000780709       -0.0420872872       -0.0000001760
O          -0.0001097767       -1.3184700435       -0.0000021383
C           0.0000052975        0.6864650274       -1.2519555359
C           0.0000053076        0.6864657482        1.2519558450
H          -0.8879137679        1.3204891671       -1.3246093784
H          -0.8879137226        1.3204906140        1.3246085141
H           0.0000538533       -0.0454683744       -2.0535345932
H           0.0000538291       -0.0454663814        2.0535367343
H           0.8879422478        1.3204796896       -1.3244875003
H           0.8879422075        1.3204811607        1.3244866017
```

1.2 B2 Geometry

b

```
10
Enegy:    -805.03575048
N                -0.006524        0.615139       -0.117025
O                -0.052767        1.878762       -0.032136
C                -1.268928       -0.110997       -0.014382
C                 1.280615       -0.086148       -0.008236
F                -2.134228        0.396584       -0.874637
F                -1.773100       -0.001488        1.211208
F                -1.065361       -1.395002       -0.285701
F                 1.290333       -0.870564        1.070367
F                 1.485688       -0.847361       -1.079704
F                 2.238521        0.807209        0.086065
```

c

```
28
Enegy:    -445.37671366
N                -0.003065       -0.489337       -0.187150
O                 0.033998       -1.768600       -0.081257
C                -1.354020        0.153614       -0.009090
C                 1.345514        0.157785       -0.009617
C                -2.403678       -0.937650       -0.225251
H                -2.311327       -1.732371        0.506729
H                -3.389151       -0.482497       -0.136654
H                -2.309534       -1.379407       -1.214415
C                -1.499941        0.703535        1.414584
H                -0.810080        1.518178        1.618927
H                -2.511962        1.084226        1.551758
H                -1.331583       -0.086731        2.143967
C                -1.594073        1.250033       -1.054175
H                -1.337503        0.891160       -2.049682
H                -2.652914        1.505111       -1.052214
H                -1.040779        2.160708       -0.857845
C                 1.363689        1.658324       -0.286507
H                 2.385249        2.005762       -0.138453
H                 1.084443        1.884814       -1.312251
H                 0.729989        2.225710        0.388791
C                 1.824978       -0.116443        1.421250
H                 1.769912       -1.181542        1.630640
H                 2.858825        0.209697        1.530444
H                 1.223150        0.417437        2.153915
C                 2.283728       -0.526618       -1.008400
H                 3.284530       -0.108451       -0.908980
H                 2.324004       -1.595316       -0.826803
H                 1.940230       -0.361195       -2.028847
```

d

```
26
Enegy:    -519.14908212
O                  -0.748000       -0.922176        1.774595
N                  -0.297771       -0.678538        0.599170
C                  -0.131808        0.685789        0.242165
C                   0.105023        1.598680        1.274458
C                   0.255292        2.946511        0.989315
C                   0.164297        3.407984       -0.321087
C                  -0.087951        2.502453       -1.343994
C                  -0.239282        1.147991       -1.071459
H                   0.161863        1.229017        2.285603
H                   0.446285        3.640090        1.795817
H                  -0.181724        2.847829       -2.363759
H                  -0.466519        0.473982       -1.878970
H                   0.280535        4.459357       -0.539961
C                   0.056552       -1.850438       -0.272046
C                  -1.124684       -2.167985       -1.195744
C                   1.341782       -1.569178       -1.053957
C                   0.302440       -3.044079        0.650912
H                  -2.023883       -2.330658       -0.604456
H                  -1.323354       -1.372154       -1.908773
H                  -0.913730       -3.077161       -1.757891
H                   2.145608       -1.286372       -0.375918
H                   1.639038       -2.480310       -1.570648
H                   1.234098       -0.786109       -1.796488
H                   0.594992       -3.895022        0.037812
H                   1.101208       -2.831697        1.358067
H                  -0.587810       -3.301422        1.214174
```

e

```
24
Enegy:    -592.92786581
N                -0.000000        0.000000        0.978789
O                -0.000000        0.000000        2.261650
C                -0.000000        1.249611        0.302168
C                 0.600682        2.339838        0.930101
C                -0.633795        1.404680       -0.931032
C                 0.584016        3.579978        0.308628
H                 1.061562        2.196072        1.894509
C                -0.644638        2.652634       -1.540460
H                -1.128866        0.566642       -1.396635
C                -0.033218        3.742174       -0.928679
H                 1.056053        4.422845        0.792652
H                -1.143660        2.773553       -2.491213
H                -0.044046        4.710146       -1.408079
C                -0.000000       -1.249611        0.302168
C                 0.633795       -1.404680       -0.931032
C                -0.600682       -2.339838        0.930101
C                 0.644638       -2.652634       -1.540460
H                 1.128866       -0.566642       -1.396635
C                -0.584016       -3.579978        0.308628
H                -1.061562       -2.196072        1.894509
C                 0.033218       -3.742174       -0.928679
H                 1.143660       -2.773553       -2.491213
H                -1.056053       -4.422845        0.792652
H                 0.044046       -4.710146       -1.408079
```

f

```
32
Enegy:   -821.89861748
O                -0.000001        2.832909       -0.000001
N                -0.000001        1.547215       -0.000005
C                 1.246127        0.871140        0.039924
C                 2.325062        1.499172        0.669162
C                 3.561961        0.887643        0.694556
C                 3.749907       -0.357873        0.087018
C                 2.679319       -0.978794       -0.554856
C                 1.432655       -0.360378       -0.578519
O                 5.004311       -0.876689        0.170804
C                 5.240909       -2.133006       -0.445831
C                -1.246127        0.871139       -0.039931
C                -2.325069        1.499176       -0.669154
C                -1.432650       -0.360385        0.578503
C                -3.561967        0.887647       -0.694542
C                -2.679314       -0.978800        0.554845
C                -3.749907       -0.357873       -0.087015
O                -5.004312       -0.876689       -0.170793
C                -5.240904       -2.133012        0.445833
H                -2.171509        2.466148       -1.121619
H                -4.403244        1.357397       -1.182446
H                -0.615429       -0.835645        1.098934
H                -2.799650       -1.928956        1.049613
H                -5.060595       -2.085502        1.520837
H                -6.285209       -2.361896        0.264074
H                -4.615783       -2.912328        0.006992
H                 2.171499        2.466140        1.121634
H                 4.403232        1.357388        1.182471
H                 2.799658       -1.928945       -1.049631
H                 0.615439       -0.835634       -1.098961
H                 4.615782       -2.912327       -0.007003
H                 5.060610       -2.085486       -1.520836
H                 6.285212       -2.361892       -0.264063
```

g

29
Enegy: -483.47268394

N	0.203718	-0.715521	-0.000000
O	0.063008	-1.989504	-0.000000
C	0.017709	-0.040268	1.320439
C	0.487681	1.415451	1.237575
C	-0.014961	2.143633	0.000000
C	0.487681	1.415451	-1.237575
C	0.017709	-0.040268	-1.320439
C	-1.458434	-0.131601	1.728859
H	-1.793536	-1.163874	1.657562
H	-1.572783	0.201645	2.759950
H	-2.099171	0.484953	1.103245
C	0.870582	-0.793926	2.339386
H	0.808493	-0.287579	3.302134
H	0.526381	-1.817041	2.453174
H	1.912574	-0.814182	2.024226
H	0.170628	1.921478	2.150388
H	1.580238	1.429945	1.230632
H	-1.104106	2.203037	0.000000
H	0.349797	3.171048	0.000000
H	0.170628	1.921478	-2.150388
H	1.580238	1.429945	-1.230632
C	-1.458434	-0.131601	-1.728859
H	-1.572783	0.201645	-2.759950
H	-1.793536	-1.163874	-1.657562
H	-2.099171	0.484953	-1.103245
C	0.870582	-0.793926	-2.339386
H	0.526381	-1.817041	-2.453174
H	0.808493	-0.287579	-3.302134
H	1.912574	-0.814182	-2.024226

h

```
28
Enegy:    -557.48595647
N                  0.000000      -0.000000      -1.035245
O                  0.000000      -0.000000      -2.314394
C                 -0.809371       1.032704      -0.334346
C                 -1.165270       0.531319       1.068538
C                 -0.000000       0.000000       1.870396
C                  1.165270      -0.531319       1.068538
C                  0.809371      -1.032704      -0.334346
C                  0.000000       2.334254      -0.273205
H                  0.306090       2.618521      -1.277680
H                 -0.609973       3.134281       0.145048
H                  0.891603       2.232980       0.343084
C                 -2.093764       1.262163      -1.127473
H                 -2.720605       1.975472      -0.593976
H                 -1.872649       1.652015      -2.115640
H                 -2.645250       0.330865      -1.243621
H                 -1.888566      -0.284314       0.988300
H                 -1.647916       1.321468       1.641041
O                 -0.000000       0.000000       3.083857
H                  1.647916      -1.321468       1.641041
H                  1.888566       0.284314       0.988300
C                 -0.000000      -2.334254      -0.273205
H                 -0.306090      -2.618521      -1.277680
H                  0.609973      -3.134281       0.145048
H                 -0.891603      -2.232980       0.343084
C                  2.093764      -1.262163      -1.127473
H                  2.720605      -1.975472      -0.593976
H                  1.872649      -1.652015      -2.115640
H                  2.645250      -0.330865      -1.243621
```

i

```
30
Enegy:   -558.67900583
C                -0.211615        1.806288        0.000000
C                 0.349220        1.123398        1.234515
C                 0.015232       -0.368896        1.319216
C                -1.446196       -0.595469        1.729503
C                 0.933914       -1.037734        2.340282
H                -1.299289        1.754209        0.000000
H                 1.021881        3.324689        0.000000
H                 1.437005        1.243442        1.222048
H                -0.020043        1.615952        2.133867
H                -1.591553       -0.264492        2.757149
H                -1.680135       -1.655869        1.668602
H                -2.144294       -0.049644        1.099788
H                 1.973669       -0.961406        2.026511
H                 0.685511       -2.088350        2.452893
H                 0.822978       -0.539442        3.302568
N                 0.265133       -1.024742       -0.000000
O                 0.066055        3.205850        0.000000
O                 0.246300       -2.305775       -0.000000
C                 0.349220        1.123398       -1.234515
C                 0.015232       -0.368896       -1.319216
H                 1.437005        1.243442       -1.222048
H                -0.020043        1.615952       -2.133867
C                -1.446196       -0.595469       -1.729503
C                 0.933914       -1.037734       -2.340282
H                -1.591553       -0.264492       -2.757149
H                -1.680135       -1.655869       -1.668602
H                -2.144294       -0.049644       -1.099788
H                 1.973669       -0.961406       -2.026511
H                 0.685511       -2.088350       -2.452893
H                 0.822978       -0.539442       -3.302568
```

j

```
29
Enegy:    -632.71898619
N                  1.275100        0.564405       -0.027376
O                  2.202555        1.429266        0.063969
C                  1.530220       -0.891897        0.082998
C                  0.104818       -1.438963        0.219346
C                 -0.772433       -0.423322       -0.520277
C                 -0.145668        0.954155       -0.181657
C                  2.225885       -1.367903       -1.194084
H                  3.144311       -0.803714       -1.343095
H                  2.473742       -2.425942       -1.115836
H                  1.591973       -1.226330       -2.068552
C                  2.399094       -1.169946        1.302180
H                  2.559915       -2.242290        1.407025
H                  3.363188       -0.678279        1.195951
H                  1.922699       -0.799200        2.208264
H                 -0.179649       -1.485762        1.267823
C                 -2.250485       -0.454521       -0.235839
O                 -3.087474        0.055582       -0.942644
C                 -0.641861        1.545117        1.140245
H                 -0.002110        2.382825        1.409094
H                 -1.663834        1.908198        1.038223
H                 -0.610718        0.814107        1.945976
C                 -0.291509        1.964074       -1.309620
H                 -1.343794        2.193192       -1.465768
H                  0.243558        2.877051       -1.059783
H                  0.120050        1.567476       -2.236296
H                  0.011074       -2.440245       -0.195858
H                 -0.682013       -0.561924       -1.597121
O                 -2.568461       -1.093143        0.914813
H                 -3.531417       -1.028490        1.004241
```

k

```
31
Enegy:    -538.08261683
N                  8.063114       8.927242       7.235577
C                  7.220309      10.137056       7.308630
N                  7.928800      11.010567       6.361109
C                  9.346560      10.642029       6.397262
C                  9.298311       9.106076       6.449182
O                  7.691495       7.807710       7.709805
C                  9.110562       8.443589       5.083475
C                 10.476647       8.495102       7.192216
H                  8.315311       8.929925       4.522925
H                  8.844220       7.399205       5.234076
H                 10.029601       8.484822       4.500858
H                 11.398200       8.660858       6.635283
H                 10.328074       7.423942       7.306799
H                 10.582588       8.934388       8.182699
C                  5.813047       9.824848       6.822672
C                  7.202109      10.620028       8.764002
H                  5.846570       9.456714       5.800579
H                  5.195690      10.721357       6.854534
H                  5.362186       9.068386       7.460722
H                  8.195725      10.917052       9.095539
H                  6.860647       9.803808       9.396919
H                  6.524132      11.462460       8.888863
C                 10.132434      11.222544       5.235113
H                  9.642428      11.008061       4.288015
H                 11.137322      10.802279       5.213148
H                 10.235541      12.301231       5.332287
C                  7.667147      12.429413       6.512378
H                  8.117429      12.861766       7.416596
H                  6.593975      12.603719       6.547690
H                  8.055530      12.965985       5.650492
H                  9.814462      10.988578       7.334265
```

l

```
28
Enegy:    -611.62488161
O                -2.786272        1.039016       -0.197765
O                 2.536018        1.120380        0.529481
N                -1.680721        0.414981       -0.151131
C                -0.376095        1.110077        0.008478
C                 0.546275       -0.086235        0.064283
C                -0.127387       -1.241390        0.070103
C                -1.612539       -1.057419       -0.010377
C                -0.388730        1.925090        1.304271
C                -0.126258        2.011064       -1.198934
C                -2.231422       -1.722228       -1.240644
C                -2.335083       -1.498871        1.265529
C                 2.020703        0.080127        0.144613
H                 0.311535       -2.225819        0.152625
H                -1.204193        2.644254        1.257445
H                -0.543849        1.278081        2.166053
H                 0.557374        2.444118        1.423504
H                -0.107439        1.429342       -2.119387
H                -0.926931        2.744344       -1.269397
H                 0.823715        2.527473       -1.084155
H                -3.273729       -1.421281       -1.324962
H                -1.708382       -1.421822       -2.146486
H                -2.185804       -2.806861       -1.149877
H                -1.887725       -1.038480        2.143963
H                -3.379481       -1.199162        1.207983
H                -2.284175       -2.581594        1.373889
N                 2.764933       -1.010643       -0.210453
H                 2.366371       -1.742193       -0.769116
H                 3.762097       -0.883568       -0.241359
```

m

30
Enegy: -670.77665600

O	2.812328	1.054963	0.000001
O	-2.571713	1.130138	-0.000000
N	1.706945	0.429142	-0.000001
O	-2.624411	-1.124481	0.000000
C	0.392456	1.121366	-0.000000
C	-0.523737	-0.079626	-0.000000
C	0.146192	-1.236598	-0.000000
C	1.631230	-1.049315	-0.000000
C	0.268076	1.979709	-1.259314
C	0.268078	1.979708	1.259314
C	2.299490	-1.605634	1.259667
C	2.299491	-1.605636	-1.259666
C	-1.990229	0.065539	-0.000000
C	-4.059375	-1.045833	-0.000000
H	-0.313383	-2.213138	0.000000
H	1.075545	2.708935	-1.272606
H	0.341110	1.364533	-2.154806
H	-0.687523	2.497395	-1.262657
H	0.341112	1.364531	2.154806
H	1.075546	2.708934	1.272606
H	-0.687522	2.497394	1.262659
H	3.344809	-1.303748	1.273224
H	1.814429	-1.223928	2.155844
H	2.246196	-2.693453	1.267884
H	1.814429	-1.223932	-2.155844
H	3.344809	-1.303749	-1.273223
H	2.246196	-2.693455	-1.267881
H	-4.409709	-0.522224	-0.885324
H	-4.404631	-2.072914	-0.000001
H	-4.409709	-0.522225	0.885324

n

```
30
Enegy:   -596.54866389
N                  -0.000000       -0.000000        1.512228
O                  -0.000000       -0.000000        2.783023
C                   0.000000        1.256226        0.720947
C                   0.000000        0.696814       -0.676118
C                  -0.000000       -0.696814       -0.676118
C                  -0.000000       -1.256226        0.720947
C                  -1.258929        2.061606        1.045343
H                  -1.273853        2.302431        2.106425
H                  -1.269467        2.988167        0.472934
H                  -2.154136        1.493077        0.801023
C                   1.258929        2.061606        1.045343
H                   1.269467        2.988167        0.472934
H                   1.273853        2.302431        2.106425
H                   2.154136        1.493077        0.801023
C                   0.000000        1.402304       -1.872511
H                   0.000000        2.484041       -1.876985
C                   0.000000        0.697195       -3.073348
H                   0.000000        1.233578       -4.011502
C                  -0.000000       -0.697195       -3.073348
H                  -0.000000       -1.233578       -4.011502
C                  -0.000000       -1.402304       -1.872511
H                  -0.000000       -2.484041       -1.876985
C                   1.258929       -2.061606        1.045343
H                   1.273853       -2.302431        2.106425
H                   1.269467       -2.988167        0.472934
H                   2.154136       -1.493077        0.801023
C                  -1.258929       -2.061606        1.045343
H                  -1.269467       -2.988167        0.472934
H                  -1.273853       -2.302431        2.106425
H                  -2.154136       -1.493077        0.801023
```

o

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33
Enegy:    -785.08776864
C                  -2.253211       -0.267680        0.000001
C                  -1.853455       -1.607894        0.000001
H                  -2.615260       -2.372921        0.000001
C                  -0.505296       -1.938567        0.000001
H                  -0.201600       -2.976343        0.000001
C                   0.440251       -0.919456        0.000001
C                   0.043271        0.417194        0.000001
C                  -1.300839        0.754756        0.000002
H                  -1.619853        1.786263        0.000002
C                   1.937598       -1.057022       -0.000000
C                   2.475408       -1.737822       -1.259650
H                   3.560819       -1.663856       -1.275109
H                   2.193063       -2.789581       -1.268574
H                   2.078164       -1.263817       -2.155074
C                   2.475410       -1.737823        1.259648
H                   2.078167       -1.263819        2.155073
H                   3.560821       -1.663857        1.275105
H                   2.193065       -2.789583        1.268571
C                   1.222359        1.352285        0.000001
C                   1.301700        2.216098       -1.259312
H                   0.488133        2.940067       -1.269616
H                   2.249395        2.750437       -1.274023
H                   1.230753        1.601639       -2.154713
C                   1.301701        2.216097        1.259314
H                   0.488134        2.940066        1.269619
H                   2.249397        2.750436        1.274024
H                   1.230755        1.601639        2.154715
C                  -3.706603        0.020123        0.000000
O                  -3.982142        1.348752       -0.000002
H                  -4.947479        1.421012       -0.000004
O                  -4.580606       -0.816844       -0.000001
N                   2.338184        0.372642        0.000000
O                   3.556057        0.733341       -0.000002
```

p

30
Enegy: -783.61897073

C	3.000248	-0.858326	0.112410
C	1.626258	-0.700087	-0.082651
C	1.040802	0.550896	-0.241604
C	1.892658	1.645618	-0.210154
C	3.275310	1.504244	-0.020596
C	3.839638	0.247319	0.147857
C	3.288565	-2.287379	0.292641
C	1.956705	-3.050796	0.066369
H	-0.024352	0.648282	-0.381298
H	1.479121	2.636521	-0.334150
H	3.900612	2.384522	-0.003145
H	4.900671	0.116766	0.304019
N	0.988771	-1.934575	-0.071299
O	4.342495	-2.811316	0.580400
O	-0.269525	-2.096305	-0.126528
C	1.589501	-3.903767	1.276039
H	0.622383	-4.371145	1.110587
H	2.344692	-4.671313	1.418812
H	1.540731	-3.290987	2.175027
C	2.053643	-3.857210	-1.220684
C	2.992175	-4.890306	-1.295902
C	1.250970	-3.586146	-2.328298
C	3.118431	-5.641839	-2.457225
H	3.639487	-5.090825	-0.455410
C	1.380811	-4.342953	-3.489565
H	0.511022	-2.802422	-2.286109
C	2.311585	-5.372232	-3.558806
H	3.850754	-6.435388	-2.501523
H	0.747947	-4.125303	-4.338156
H	2.409250	-5.958426	-4.461313