Supplement for "Quantum Chemical Characterization of Low-Lying Excited States of an Arylperoxycarbonate: Mechanistic Implications for Photodissociation"

Seth Olsen, Dirk Schwarzer, Jürgen Troe and Sean C. Smith

Contents

Complete Reference 24:

MOLPRO, version 2008.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, , see http://www.molpro.net.

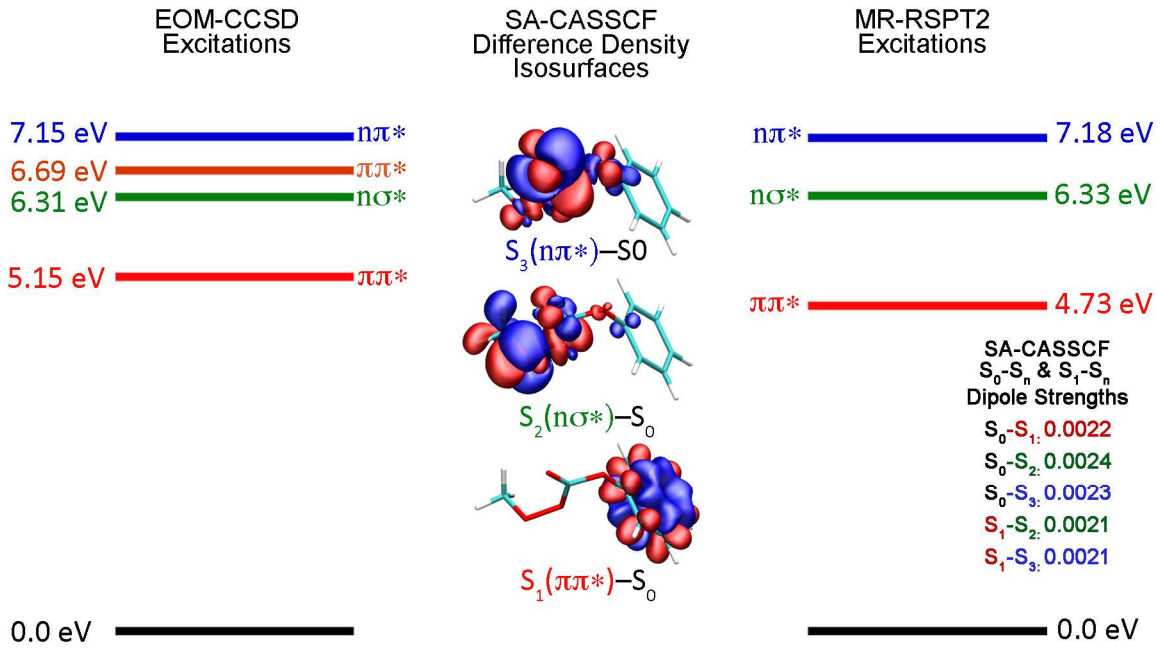


Figure S1. This figure presents results analogous to those shown in text figure 1, but using a correlation-consistent polarized double zeta valence (cc-pvdz) basis set as described by Dunning (T.H. Dunning Jr., J. Chem. Phys. v. 90, pp. 1007 (1989)). The molecular geometry was optimized using MP2 theory and the cc-pvdz basis set. Excitation energies are displayed as calculated using the EOM-CCSD (left) and MR-RSPT2 (right) methods with parameters (apart from the basis set) as described in the main text. The character of the states is identical to those obtained using the 6-31g* polarized split-valence basis set, and the excitations are nearly identical. The figure demonstrates that the results reported in the main text are robust with respect to changes in the basis set used. SA-CASSCF S_n–S_0 difference density isosurfaces (isovalue = ±0.001) are shown, and are visually indistinguishable from analogous surfaces calculated using the 6-31g* basis. When using a variational method, expansion of the basis set should provide a better approximation to the Born-Oppenheimer electronic energies for the molecule in isolation.

Data Provided for Reproduction of Text Figures 1 & 2.

Table S1a. Cartesian coordinates (Å), SA-CASSCF energies and dipoles, and MR-RSPT2 energies for the model at the MP2/6-31g* S_0 minimum

```
20
mpc.c1412s4rs2c.631d.mp2sp.out
C      -1.16967   5.76662   0.19926
C      -1.37124   6.16279  -1.12434
C      -0.72679   5.49226  -2.16889
C       0.12547   4.41958  -1.89125
C       0.33965   4.01345  -0.57176
C      -0.30539   4.70394   0.44999
C       0.70437   4.85449   2.61252
C       3.46981   5.98552   2.85241
O      -0.15627   4.23042   1.77102
O       1.36196   5.85445   1.92120
O       2.18277   6.60659   2.86525
O       0.85966   4.53845   3.76251
H      -2.03886   6.99346  -1.33887
H      -0.89089   5.80376  -3.19718
H       0.62197   3.89238  -2.70205
H       0.98866   3.17659  -0.32877
H      -1.66535   6.26760   1.02624
H       4.06096   6.62106   3.51531
H       3.41627   4.97140   3.25466
H       3.89226   5.99129   1.84448
 !MCSCF STATE 1.1 ENERGY             -607.075607050352 a.u.
 !MCSCF STATE 1.1 DIPOLE MOMENT        0.69197364     0.20754457    -1.16248681
a.u.
 !MCSCF STATE 2.1 ENERGY             -606.890590055974 a.u.
 !MCSCF STATE 2.1 DIPOLE MOMENT        0.69450387     0.19886752    -1.15582637
a.u.
 !MCSCF STATE 3.1 ENERGY             -606.827376020519 a.u.
 !MCSCF STATE 3.1 DIPOLE MOMENT        0.99435945     0.40238893    -0.91736042
a.u.
 !MCSCF STATE 4.1 ENERGY             -606.823413549051 a.u.
 !MCSCF STATE 4.1 DIPOLE MOMENT        0.77018056    -0.04697673    -0.41058434
a.u.
 S0->S1 Transition Dipole:    -0.020163     0.023906     0.015777 a.u.
 S0->S2 Transition Dipole:     0.042713     0.055290    -0.028361 a.u.
 S1->S2 Transition Dipole:    -0.002089     0.002809     0.001770 a.u.
 S0->S3 Transition Dipole:     0.008717    -0.001495    -0.017516 a.u.
 S1->S3 Transition Dipole:     0.001378     0.000538    -0.003450 a.u.
 S2->S3 Transition Dipole:     0.013856     0.025017    -0.030677 a.u.
!RSPT2 STATE 1.1 ENERGY:  -608.343456334563
!RSPT2 STATE 2.1 ENERGY:  -608.165369320797
!RSPT2 STATE 3.1 ENERGY:  -608.114419886199
!RSPT2 STATE 4.1 ENERGY:  -608.082526043898
```

Table S1b. Summary of CCSD and EOM-CCSD Results at MP2/6-31g* S_0 minimum

```
**** Ground State CCSD Results ****
 Reference energy:                   -606.94061205
 MP2 total energy:                   -608.65269370
 !CCSD STATE 1.1 ENERGY              -608.704844150344

**** Right EOM-CCSD State Results ****

 Results for state 2.1:  Excitation energy         0.19289007 au        5.249 eV
42334.48 cm-1

  Coefficient     Excitation
     0.68238     44.1 -> 45.1
     0.61519     43.1 -> 46.1
     0.12808     44.1 -> 46.1    38.1 -> 45.1
     0.12575     44.1 -> 45.1    38.1 -> 46.1
     0.11718     44.1 -> 58.1    43.1 -> 46.1
     0.11364     44.1 -> 46.1    43.1 -> 58.1

  Results for state 3.1:  Excitation energy         0.22754550 au        6.192
eV       49940.46 cm-1

  Coefficient     Excitation
     0.42222     40.1 -> 48.1
     0.41355     40.1 -> 47.1
    -0.36857     42.1 -> 47.1
    -0.33682     42.1 -> 48.1
    -0.20089     41.1 -> 47.1
    -0.19034     41.1 -> 48.1
    -0.12838     29.1 -> 48.1
    -0.12795     29.1 -> 47.1
    -0.11572     44.1 -> 47.1
    -0.11064     38.1 -> 47.1
    -0.10970     31.1 -> 47.1
    -0.10823     38.1 -> 48.1
    -0.10816     31.1 -> 48.1
     0.10358     40.1 -> 59.1
    -0.10168     44.1 -> 48.1

  Results for state 4.1:  Excitation energy         0.25440042 au        6.923
eV       55834.44 cm-1

  Coefficient     Excitation
    -0.74575     44.1 -> 46.1
     0.57710     43.1 -> 45.1

  Results for state 5.1:  Excitation energy         0.25940763 au        7.059
eV       56933.39 cm-1

  Coefficient     Excitation
    -0.45990     41.1 -> 47.1
    -0.41008     40.1 -> 47.1
     0.37635     41.1 -> 48.1
    -0.31748     42.1 -> 47.1
     0.25183     40.1 -> 48.1
     0.23306     42.1 -> 48.1
    -0.19557     44.1 -> 47.1
     0.13293     37.1 -> 47.1
     0.12604     44.1 -> 48.1

****Left EOM-CCSD State Results****

  Results for state 2.1:  Excitation energy         0.19289044 au        5.249
eV       42334.56 cm-1
```

```
  Coefficient     Excitation
     0.69423     44.1 -> 45.1
     0.62436     43.1 -> 46.1
     0.11067     44.1 -> 46.1    38.1 -> 45.1
     0.10924     44.1 -> 45.1    38.1 -> 46.1
     0.10216     44.1 -> 58.1    43.1 -> 46.1

  Contribution of reference determinant     -0.00014

  Results for state 3.1:  Excitation energy         0.22754549 au        6.192
eV       49940.46 cm-1

  Coefficient     Excitation
    -0.42415     40.1 -> 48.1
    -0.41608     40.1 -> 47.1
     0.37388     42.1 -> 47.1
     0.34112     42.1 -> 48.1
     0.20348     41.1 -> 47.1
     0.19325     41.1 -> 48.1
     0.12794     29.1 -> 48.1
     0.12794     29.1 -> 47.1
     0.11882     44.1 -> 47.1
     0.11132     38.1 -> 47.1
     0.11064     31.1 -> 47.1
     0.10880     38.1 -> 48.1
     0.10875     31.1 -> 48.1
    -0.10595     40.1 -> 59.1
     0.10467     44.1 -> 48.1

  Contribution of reference determinant     -0.00572

  Results for state 4.1:  Excitation energy         0.25440049 au        6.923
eV       55834.45 cm-1

  Coefficient     Excitation
     0.75363     44.1 -> 46.1
    -0.57467     43.1 -> 45.1

  Contribution of reference determinant      0.00384

  Results for state 5.1:  Excitation energy         0.25940749 au        7.059
eV       56933.36 cm-1

  Coefficient     Excitation
    -0.46437     41.1 -> 47.1
    -0.41295     40.1 -> 47.1
     0.37937     41.1 -> 48.1
    -0.31967     42.1 -> 47.1
     0.25344     40.1 -> 48.1
     0.23373     42.1 -> 48.1
    -0.19947     44.1 -> 47.1
     0.13314     37.1 -> 47.1
     0.12875     44.1 -> 48.1

  Contribution of reference determinant      0.00540
--------------------------------------------------------------------------------
                        Final Results for EOM-CCSD
                             (moments in a.u.)
--------------------------------------------------------------------------------

  State    Exc. Energy (eV)           X             Y             Z
   2.1          5.249

 Right transition moment          0.03927201    -0.05285317    -0.03551908
 Left  transition moment          0.04037328    -0.05495435    -0.03736848
 Dipole strength                  0.00581734
```

```
 Oscillator strength                0.00074807
 Dipole moment                      0.66722641     0.23639794    -1.23840499
Norm:     1.42643681

           <1.1|OPER|  2.1><  2.1|OPER|1.1>

-------------------------------------------------------------------------------


  State    Exc. Energy (eV)            X              Y              Z
   3.1          6.192

 Right transition moment          -0.09083825    -0.03525629    -0.08139607
 Left  transition moment          -0.09399054    -0.03731028    -0.08522215
 Dipole strength                   0.01679011
 Oscillator strength               0.00254701
 Dipole moment                     1.18738184     0.52393170    -1.04048374
Norm:     1.66342613

           <1.1|OPER|  3.1><  3.1|OPER|1.1>

-------------------------------------------------------------------------------


  State    Exc. Energy (eV)            X              Y              Z
   4.1          6.923

 Right transition moment           0.20712588    -0.02567116     0.40249483
 Left  transition moment           0.21398919    -0.02967115     0.41481350
 Dipole strength                   0.21204468
 Oscillator strength               0.03596285
 Dipole moment                     0.68434035     0.22767182    -1.13255400
Norm:     1.34269681

           <1.1|OPER|  4.1><  4.1|OPER|1.1>

-------------------------------------------------------------------------------

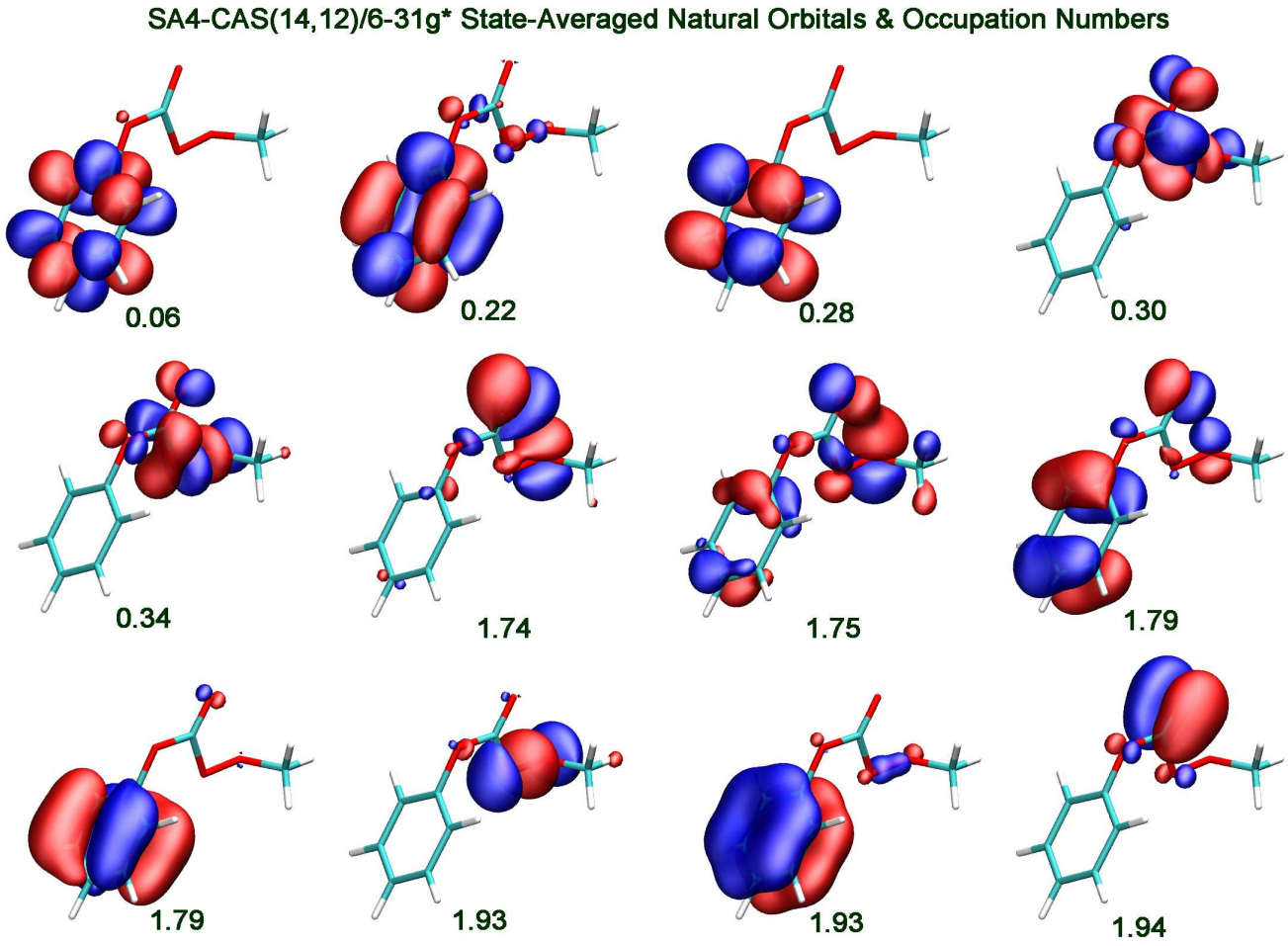

  State    Exc. Energy (eV)            X              Y              Z
   5.1          7.059

 Right transition moment           0.03783621    -0.04406481    -0.01782691
 Left  transition moment           0.04077413    -0.04789563    -0.01914320
 Dipole strength                   0.00399451
 Oscillator strength               0.00069080
 Dipole moment                     0.71382063     0.03960940    -0.63125227
Norm:     0.95372334

           <1.1|OPER|  5.1><  5.1|OPER|1.1>

-------------------------------------------------------------------------------
```

Table S2. SA4-CAS(14,12)/6-31g* State-averaged natural orbitals and occupation numbers for the model at the MP2/6-31g* S_0 minimum



Data for the Reproduction of Text Figures 3 & 4.

Table S3. Cartesian coordinates (Å), SA-CASSCF energies and dipoles, and MR-RSPT2 energies for the model at the SA4-CAS(14,12)/6-31g* S_0 minimum

```
   20
mpc.c1412s4rs2c.631d.s0sp.s0.out
C      -1.18162   5.77318   0.17097
C      -1.39825   6.15727  -1.15291
C      -0.76774   5.47457  -2.19605
C       0.08128   4.40259  -1.91476
C       0.30661   4.01324  -0.59272
C      -0.32393   4.70958   0.43134
C       0.68917   4.85015   2.58750
C       3.54162   6.01871   2.92016
O      -0.15451   4.27097   1.73633
O       1.45765   5.75467   1.94741
O       2.23270   6.53593   2.95221
O       0.75025   4.55532   3.72670
H      -2.05651   6.97947  -1.36589
H      -0.93972   5.77172  -3.21441
H       0.56338   3.87088  -2.71457
H       0.94924   3.18623  -0.35491
H      -1.66384   6.28136   0.98506
H       4.08793   6.63946   3.61698
H       3.55912   4.99033   3.25314
H       3.96650   6.11049   1.93016
 !MCSCF STATE 1.1 ENERGY             -607.081481531286 a.u.
 !MCSCF STATE 1.1 DIPOLE MOMENT         0.74533215     0.25888061    -1.15938825
a.u.
 !MCSCF STATE 2.1 ENERGY             -606.895831110985 a.u.
 !MCSCF STATE 2.1 DIPOLE MOMENT         0.74775804     0.25264397    -1.15328173
a.u.
 !MCSCF STATE 3.1 ENERGY             -606.856055399974 a.u.
 !MCSCF STATE 3.1 DIPOLE MOMENT         1.02929274     0.44910113    -0.93745106
a.u.
 !MCSCF STATE 4.1 ENERGY             -606.815374184137 a.u.
 !MCSCF STATE 4.1 DIPOLE MOMENT         0.75541530    -0.00721613    -0.38703963
a.u.
 S0->S1 Transition Dipole:    -0.026561     0.029472     0.014481 a.u.
 S0->S2 Transition Dipole:     0.030471     0.058144    -0.033708 a.u.
 S1->S2 Transition Dipole:    -0.001398     0.001608     0.000630 a.u.
 S0->S3 Transition Dipole:     0.015314    -0.002356    -0.013678 a.u.
 S1->S3 Transition Dipole:     0.001328     0.000726    -0.003839 a.u.
 S2->S3 Transition Dipole:     0.007685     0.008035    -0.011564 a.u.
!RSPT2 STATE 1.1 ENERGY:  -608.340682454552
!RSPT2 STATE 2.1 ENERGY:  -608.162048394342
!RSPT2 STATE 3.1 ENERGY:  -608.133151801890
!RSPT2 STATE 4.1 ENERGY:  -608.067867879888
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Table S4. SA4-CAS(14,12)/6-31g* State-averaged natural orbitals and occupation numbers for the model at the SA4-CAS(14,12)/6-31g* S_0 minimum

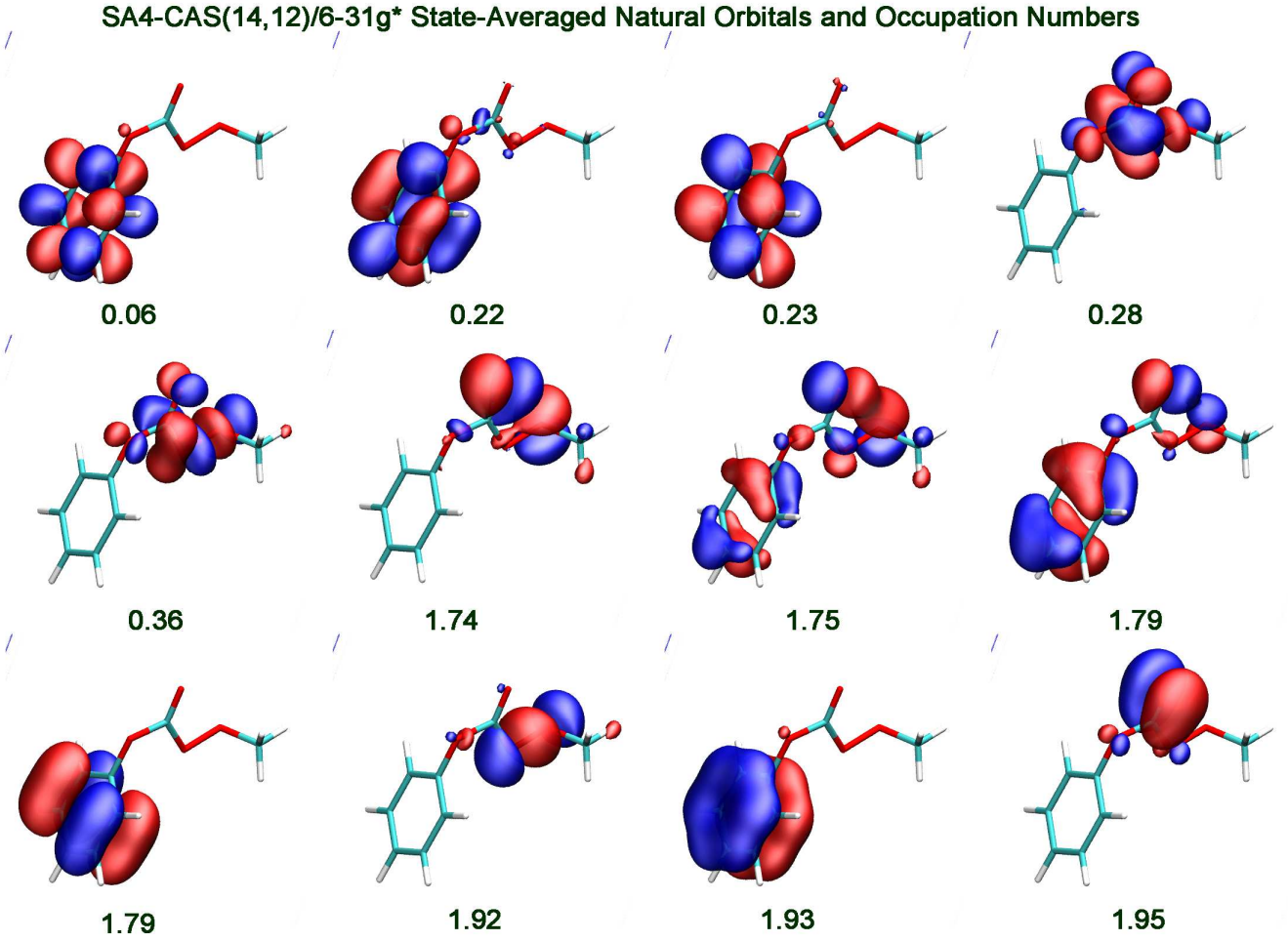

Table S5. Cartesian coordinates (Å), SA-CASSCF energies and dipoles, and MR-RSPT2 energies for the model at the SA4-CAS(14,12)/6-31g* S_1 optimized geometry

```
20
mpc.c1412s4rs2c.631d.s1sp.s0.out
C      -1.21069   5.79110   0.19573
C      -1.43084   6.18669  -1.16538
C      -0.77361   5.48547  -2.23185
C       0.10271   4.38453  -1.94652
C       0.33286   3.98597  -0.58858
C      -0.31987   4.70621   0.45748
C       0.69212   4.85033   2.60545
C       3.54819   6.01606   2.92148
O      -0.15490   4.26864   1.75661
O       1.46051   5.74934   1.95739
O       2.23994   6.53511   2.95516
O       0.75427   4.56163   3.74572
H      -2.08942   7.00438  -1.38320
H      -0.94188   5.78305  -3.24872
H       0.58563   3.85850  -2.74655
H       0.96925   3.15841  -0.34536
H      -1.69781   6.28934   1.01029
H       4.09762   6.64014   3.61284
H       3.56559   4.98957   3.26025
H       3.96968   6.10166   1.92950
 !MCSCF STATE 1.1 ENERGY             -607.073473561754 a.u.
 !MCSCF STATE 1.1 DIPOLE MOMENT         0.75346032     0.25246023    -1.13822452
a.u.
 !MCSCF STATE 2.1 ENERGY             -606.903748959866 a.u.
 !MCSCF STATE 2.1 DIPOLE MOMENT         0.75525698     0.24685575    -1.13489244
a.u.
 !MCSCF STATE 3.1 ENERGY             -606.848011338108 a.u.
 !MCSCF STATE 3.1 DIPOLE MOMENT         1.03910157     0.44310092    -0.91737596
a.u.
 !MCSCF STATE 4.1 ENERGY             -606.807351972419 a.u.
 !MCSCF STATE 4.1 DIPOLE MOMENT         0.76383119    -0.00944655    -0.36732013
a.u.
 S0->S1 Transition Dipole:    -0.030485     0.033519     0.016221 a.u.
 S0->S2 Transition Dipole:     0.031128     0.057686    -0.032950 a.u.
 S1->S2 Transition Dipole:    -0.001581     0.001812     0.000680 a.u.
 S0->S3 Transition Dipole:     0.016621    -0.003807    -0.013725 a.u.
 S1->S3 Transition Dipole:     0.001218     0.000947    -0.004552 a.u.
 S2->S3 Transition Dipole:     0.007278     0.007635    -0.011605 a.u.
!RSPT2 STATE 1.1 ENERGY:  -608.333094794880
!RSPT2 STATE 2.1 ENERGY:  -608.168563415257
!RSPT2 STATE 3.1 ENERGY:  -608.125644132928
!RSPT2 STATE 4.1 ENERGY:  -608.060406797066
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Table S6. SA4-CAS(14,12)/6-31g* State-averaged natural orbitals and occupation numbers for the model at the SA4-CAS(14,12)/6-31g* S_1 optimized geometry

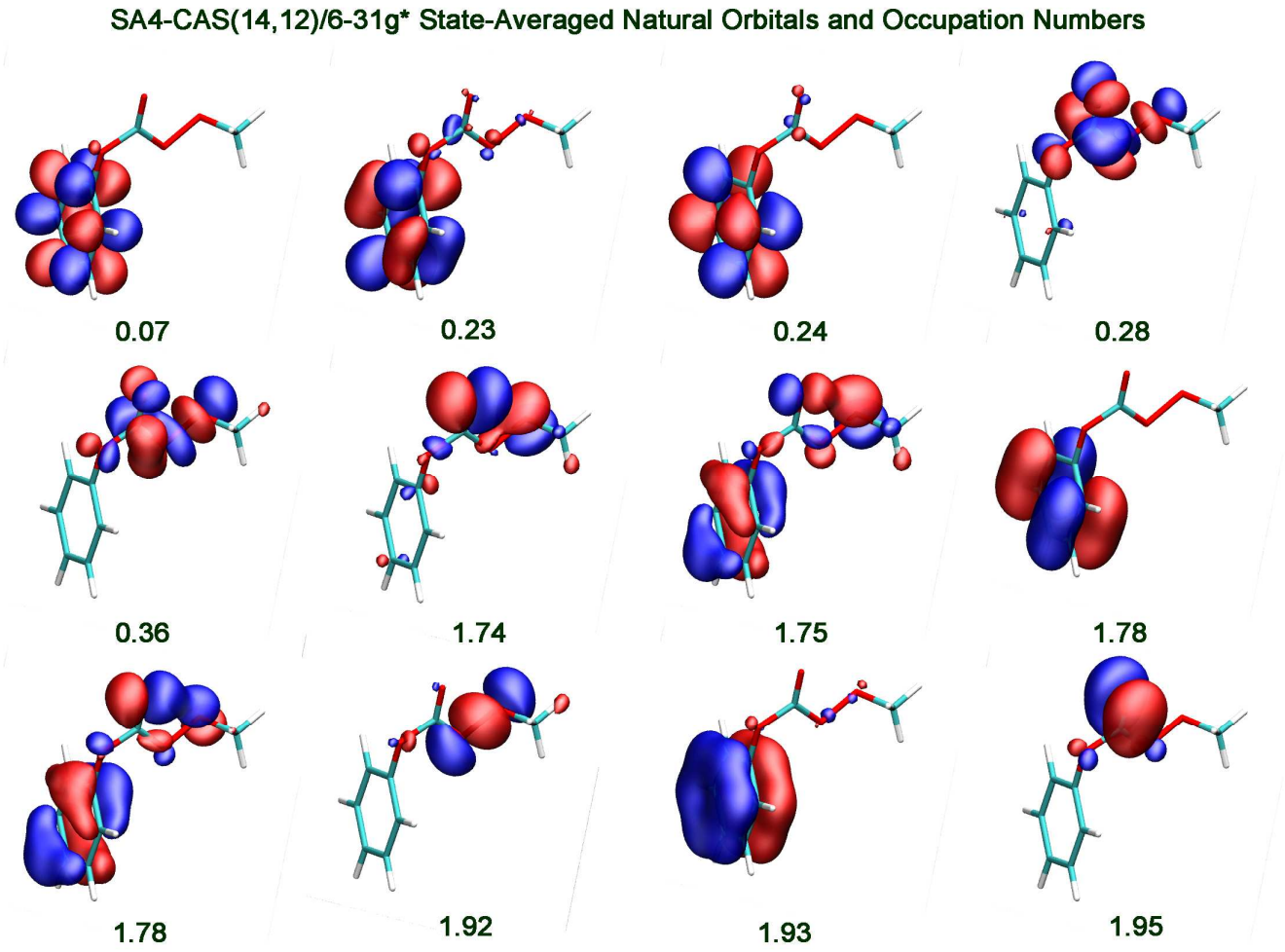

Table S7. Cartesian coordinates (Å), SA-CASSCF energies and dipoles, and MR-RSPT2 energies for the model at the SA4-CAS(14,12)/6-31g* S_2 optimized geometry

```
20
mpc.c1412s4rs2c.631d.s2sp.s0.out
C      -1.15688   5.89322   0.09737
C      -1.34123   6.29675  -1.22759
C      -0.88605   5.49543  -2.27733
C      -0.25218   4.28120  -2.00417
C      -0.07256   3.86533  -0.68450
C      -0.51968   4.68454   0.34890
C       0.77260   4.28302   2.29795
C       3.79124   6.46571   3.32440
O      -0.40146   4.26910   1.66705
O       1.82186   4.77194   1.63282
O       2.56636   7.00160   2.94413
O       0.87868   3.85815   3.41024
H      -1.83448   7.22930  -1.43408
H      -1.02572   5.81055  -3.29574
H       0.09754   3.66113  -2.81020
H       0.40287   2.92931  -0.45884
H      -1.50162   6.49313   0.92029
H       4.26932   7.20792   3.96493
H       3.66375   5.54148   3.87565
H       4.42697   6.30730   2.46045
 !MCSCF STATE 1.1 ENERGY             -607.049230356405 a.u.
 !MCSCF STATE 1.1 DIPOLE MOMENT         0.39565233     0.26242566    -1.30928728
a.u.
 !MCSCF STATE 2.1 ENERGY             -607.045401833176 a.u.
 !MCSCF STATE 2.1 DIPOLE MOMENT         0.38364450     0.20691138    -1.32251130
a.u.
 !MCSCF STATE 3.1 ENERGY             -607.044062007338 a.u.
 !MCSCF STATE 3.1 DIPOLE MOMENT         0.34626086     0.14319170    -1.02070142
a.u.
 !MCSCF STATE 4.1 ENERGY             -607.039636300783 a.u.
 !MCSCF STATE 4.1 DIPOLE MOMENT         0.33490336     0.08831379    -1.04132728
a.u.
 S0->S1 Transition Dipole:    -0.012626    -0.005326     0.020831 a.u.
 S0->S2 Transition Dipole:    -0.013580    -0.008827     0.042722 a.u.
 S1->S2 Transition Dipole:     0.007300     0.012740    -0.057934 a.u.
 S0->S3 Transition Dipole:    -0.000816    -0.002346     0.002973 a.u.
 S1->S3 Transition Dipole:     0.006859     0.003658    -0.024429 a.u.
 S2->S3 Transition Dipole:     0.016492     0.010000    -0.033160 a.u.
!RSPT2 STATE 1.1 ENERGY:  -608.275951010187
!RSPT2 STATE 2.1 ENERGY:  -608.272238416429
!RSPT2 STATE 3.1 ENERGY:  -608.267112886486
!RSPT2 STATE 4.1 ENERGY:  -608.260999812383
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Table S8. SA4-CAS(14,12)/6-31g* State-averaged natural orbitals and occupation numbers for the model at the SA4-CAS(14,12)/6-31g* S_2 optimized geometry

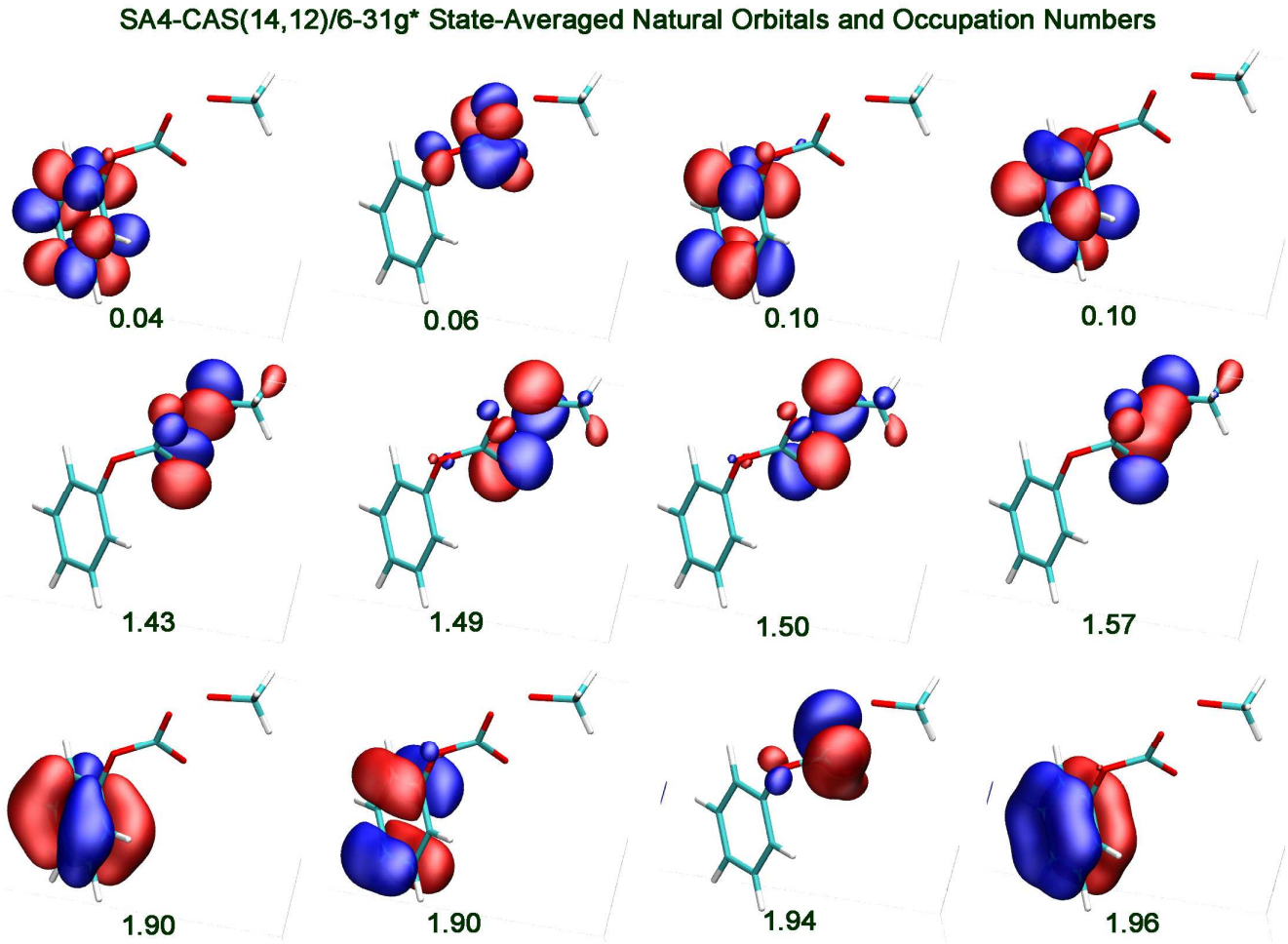

Table S9. Cartesian coordinates (Å), SA-CASSCF energies and dipoles, and MR-RSPT2 energies for the model at the SA4-CAS(14,12)/6-31g* S_1S_2 MECI

```
20
mpc.c1412s4rs2c.631d.s1s2sp.s0.out
C      -1.14820   5.80151   0.19107
C      -1.37835   6.20873  -1.16125
C      -0.78354   5.47909  -2.24030
C       0.04043   4.33796  -1.97569
C       0.28383   3.92951  -0.62674
C      -0.30335   4.67966   0.43297
C       0.69892   4.81969   2.58823
C       3.54655   6.07691   2.96582
O      -0.12721   4.22458   1.72439
O       1.41314   5.77903   1.96804
O       2.23324   6.56685   3.07359
O       0.78107   4.48941   3.71636
H      -2.00036   7.05883  -1.36338
H      -0.96074   5.78549  -3.25327
H       0.47558   3.78779  -2.78729
H       0.88292   3.07020  -0.39800
H      -1.59071   6.32410   1.01620
H       4.11532   6.66765   3.67225
H       3.59050   5.03257   3.24245
H       3.93028   6.22658   1.96628
 !MCSCF STATE 1.1 ENERGY             -607.072396102004 a.u.
 !MCSCF STATE 1.1 DIPOLE MOMENT         0.74284314     0.29943560    -1.15408546
a.u.
 !MCSCF STATE 2.1 ENERGY             -606.901328153492 a.u.
 !MCSCF STATE 2.1 DIPOLE MOMENT         0.78445414     0.32036608    -1.11838957
a.u.
 !MCSCF STATE 3.1 ENERGY             -606.901201309383 a.u.
 !MCSCF STATE 3.1 DIPOLE MOMENT         0.91600784     0.40012757    -1.01692109
a.u.
 !MCSCF STATE 4.1 ENERGY             -606.807458859638 a.u.
 !MCSCF STATE 4.1 DIPOLE MOMENT         0.75894241     0.00948893    -0.39788071
a.u.
 S0->S1 Transition Dipole:    -0.013455     0.054103     0.003570 a.u.
 S0->S2 Transition Dipole:     0.031156     0.032151    -0.037528 a.u.
 S1->S2 Transition Dipole:     0.083375     0.053897     0.066255 a.u.
 S0->S3 Transition Dipole:     0.014610     0.000296    -0.019220 a.u.
 S1->S3 Transition Dipole:     0.005119     0.002927    -0.007291 a.u.
 S2->S3 Transition Dipole:     0.006972     0.007158    -0.004842 a.u.
!RSPT2 STATE 1.1 ENERGY:  -608.329997317319
!RSPT2 STATE 4.1 ENERGY:  -608.059405767564
```

Table S10. SA4-CAS(14,12)/6-31g* State-averaged natural orbitals and occupation numbers for the model at the SA4-CAS(14,12)/6-31g* S_1/S_2 MECI

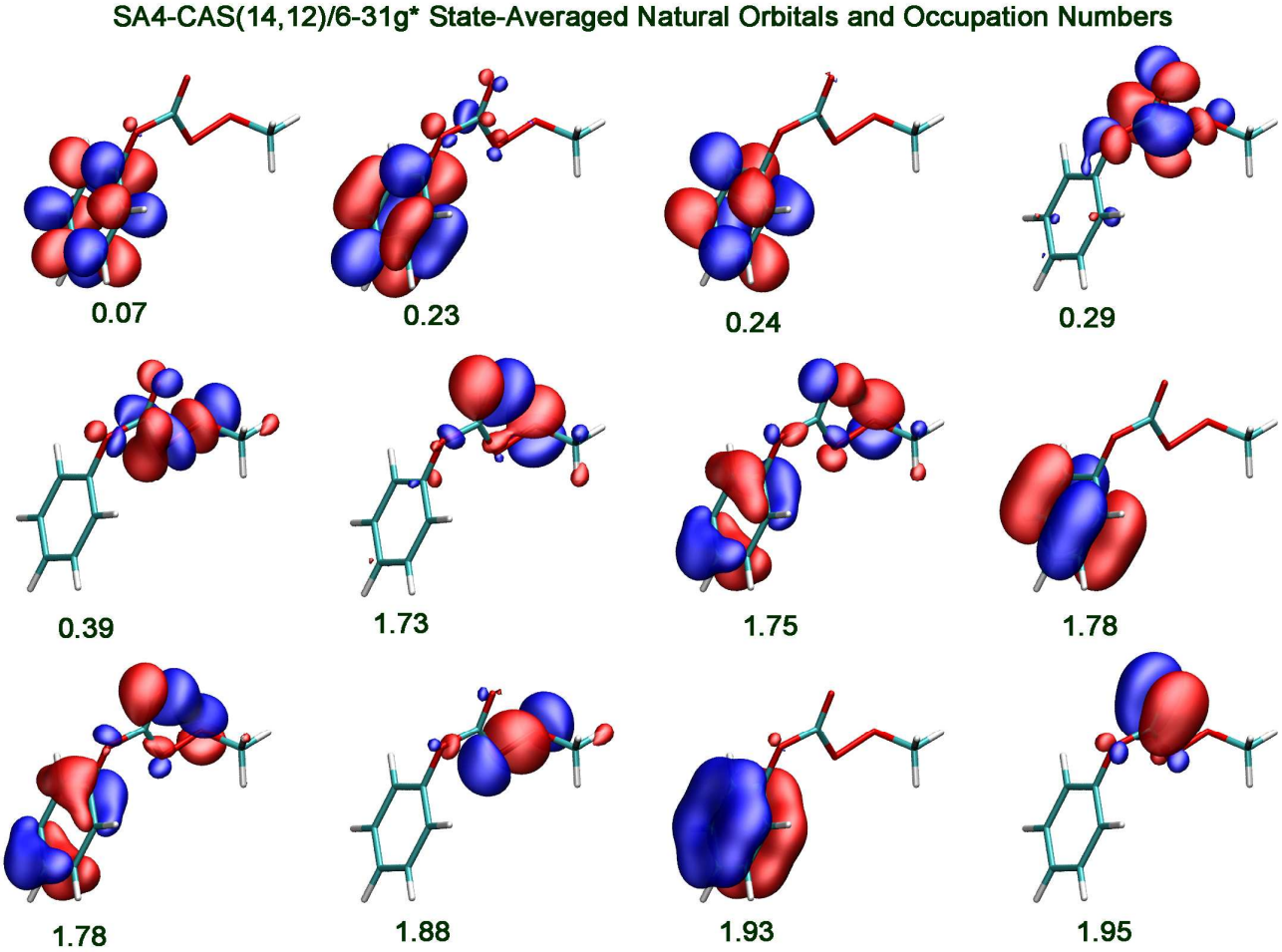

Table S11. Cartesian coordinates (Å), SA-CASSCF energies and dipoles, and MR-RSPT2 energies for the model at the SA4-CAS(14,12)/6-31g* S_2/S_3 MECI

```
20
mpc.c1412s4rs2c.631d.s2s3sp.s0.out
C      -1.15657   5.73257   0.14250
C      -1.45753   6.14329  -1.18054
C      -0.90273   5.44096  -2.28030
C      -0.05249   4.32791  -2.04623
C       0.24676   3.90438  -0.72985
C      -0.26978   4.65778   0.35180
C       0.60738   5.07062   2.53427
C       3.63929   6.05365   3.12546
O       0.07130   4.25509   1.63337
O       1.58672   5.84439   1.97255
O       2.31984   6.56587   3.15885
O       0.66158   4.64352   3.72913
H      -2.09716   6.99036  -1.33839
H      -1.11626   5.75562  -3.28322
H       0.39943   3.81956  -2.87663
H       0.90147   3.07738  -0.53832
H      -1.56784   6.25888   0.98293
H       4.20791   6.63803   3.83741
H       3.63132   5.01121   3.42536
H       4.04668   6.15506   2.13157
 !MCSCF STATE 1.1 ENERGY             -607.047932223071 a.u.
 !MCSCF STATE 1.1 DIPOLE MOMENT         0.61507912     0.31887000    -1.16544263
a.u.
 !MCSCF STATE 2.1 ENERGY             -606.883625231215 a.u.
 !MCSCF STATE 2.1 DIPOLE MOMENT         0.72122232    -0.04464495    -0.50635171
a.u.
 !MCSCF STATE 3.1 ENERGY             -606.871414469249 a.u.
 !MCSCF STATE 3.1 DIPOLE MOMENT         0.68183696     0.36975096    -1.08747322
a.u.
 !MCSCF STATE 4.1 ENERGY             -606.871302846873 a.u.
 !MCSCF STATE 4.1 DIPOLE MOMENT         0.73272744     0.40059067    -1.03455283
a.u.
 S0->S1 Transition Dipole:     0.082943     0.069315     0.023182 a.u.
 S0->S2 Transition Dipole:    -0.016685     0.067834     0.002457 a.u.
 S1->S2 Transition Dipole:     0.002330     0.004685    -0.000983 a.u.
 S0->S3 Transition Dipole:     0.038400     0.012633    -0.051331 a.u.
 S1->S3 Transition Dipole:     0.004369     0.007865    -0.011106 a.u.
 S2->S3 Transition Dipole:     0.089843     0.057126     0.094725 a.u.
!RSPT2 STATE 1.1 ENERGY:  -608.306849130631
!RSPT2 STATE 2.1 ENERGY:  -608.132210403757
```

Table S12. SA4-CAS(14,12)/6-31g* State-averaged natural orbitals and occupation numbers for the model at the SA4-CAS(14,12)/6-31g* S_2/S_3 MECI