# Cooperativity between OH···O and CH···O Hydrogen Bonds Involving Dimethyl Sulfoxide-$H_2O$-$H_2O$ Complex

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Table R1 Interaction energies of two hydrogen bonds calculated at the MP2/6-311++G(d,p) level.

| Interactions | $\Delta E$ (kJ·mol$^{-1}$) | *BSSE* (kJ·mol$^{-1}$) | *ZPVE* (kJ·mol$^{-1}$) | $\Delta E_{corr}$ (kJ·mol$^{-1}$) |
|---|---|---|---|---|
| $\Delta E_{C(1)–H(1)\cdots O(2)}$ (A) | -22.60 | 8.82 | 5.92 | -7.86 |
| $\Delta E_{C(1)–H(1)\cdots O(2)}$ (B) | -26.90 | 9.48 | 4.98 | -12.44 |
| $\Delta E_{O(2)–H(2)\cdots O(3)}$ (B) | -29.75 | 7.48 | 8.95 | -13.32 |
| $\Delta E_{O(2)–H(2)\cdots O(3)}$ (C) | -25.43 | 6.80 | 9.91 | -8.72 |

Note: The $\Delta E_{C(1)–H(1)\cdots O(2)}$ is sum of two C(1)–H(1)···O(2) hydrogen bonds in structures A and B.

Table R2. Cartesian coordinates of MP2/6-311++G(d,p) optimized geometry of complex A in gas phase.

No of imaginary frequencies = 0

| Atoms | X | Y | Z |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | 0.00000000 |
| S | 1.80408242 | 0.00000000 | 0.00000000 |
| O | 2.25312555 | 1.44250485 | 0.00000000 |
| C | 1.99080446 | -0.61972552 | -1.68397997 |
| H | -0.31935903 | 0.40831391 | 0.96033630 |
| H | -0.35529391 | -1.02598052 | -0.11137920 |
| H | -0.35094831 | 0.64681874 | -0.80809391 |
| H | 1.49502107 | 0.07217952 | -2.36956091 |
| H | 3.06052333 | -0.64382325 | -1.89863570 |
| H | 1.57117538 | -1.62567888 | -1.74093939 |
| O | 0.95623477 | -3.20606537 | 0.17754465 |
| H | 0.72280221 | -4.13536952 | 0.24357567 |
| H | 1.59427712 | -3.08028042 | 0.88554916 |

Table R3. Cartesian coordinates of MP2/6-311++G(d,p) optimized geometry of complex B in gas phase.

No of imaginary frequencies = 0

| Atoms | X | Y | Z |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | 0.00000000 |
| S | 1.80368883 | 0.00000000 | 0.00000000 |
| O | 2.25011483 | 1.44491376 | 0.00000000 |
| C | 1.99370246 | -0.61598182 | -1.68456363 |
| H | -0.31844069 | 0.40838622 | 0.96067372 |
| H | -0.35056676 | -1.02749726 | -0.11199852 |
| H | -0.35009034 | 0.64772841 | -0.80789336 |
| H | 1.49725490 | 0.07696567 | -2.36879358 |
| H | 3.06394392 | -0.63664807 | -1.89724626 |
| H | 1.57512926 | -1.62246755 | -1.73910063 |
| O | 0.81848416 | -3.22355310 | 0.01273037 |
| H | 0.50842374 | -4.13972142 | -0.01922164 |
| H | 1.43872242 | -3.22134792 | 0.74598389 |
| O | -0.09377321 | -5.95776572 | -0.06713867 |
| H | 0.11932203 | -6.52080565 | -0.81566983 |
| H | -1.00760141 | -6.17262714 | 0.13651550 |

Table R4. Cartesian coordinates of MP2/6-311++G(d,p) optimized geometry of complex C in gas phase.

No of imaginary frequencies = 0

| | | | |
|---|---|---|---|
| O | 1.53037500 | 0.00015700 | -0.11886700 |
| H | 0.57090500 | -0.00023700 | -0.01268500 |
| H | 1.85577000 | -0.00098400 | 0.78262600 |
| O | -1.37638900 | -0.00012000 | 0.09418700 |
| H | -1.82954900 | -0.75647600 | -0.28709000 |
| H | -1.82901500 | 0.75740000 | -0.28541100 |

Table R5. Cartesian coordinates of PCM/B3LYP/6-311++G(d,p) optimized geometry of complex A in heptane solvent.

No of imaginary frequencies = 0

| Atoms | X | Y | Z |
|---|---|---|---|
| C | 0.08561700 | -1.36857800 | 0.60073300 |
| S | 0.73178600 | 0.00001300 | -0.42540500 |
| O | 2.24847600 | -0.00025600 | -0.26926700 |
| C | 0.08578700 | 1.36894600 | 0.60041600 |
| H | 0.43313600 | -2.29441100 | 0.14249300 |
| H | -1.00400700 | -1.31792600 | 0.58853300 |
| H | 0.48742100 | -1.27603100 | 1.61116700 |
| H | 0.48756400 | 1.27665700 | 1.61088400 |
| H | 0.43328500 | 2.29466800 | 0.14194000 |
| H | -1.00383600 | 1.31825400 | 0.58820600 |
| O | -2.95213000 | -0.00056300 | -0.23712800 |
| H | -3.83344700 | 0.00300300 | 0.15833000 |
| H | -3.10787900 | -0.00008500 | -1.19080100 |

Table R6. Cartesian coordinates of PCM/B3LYP/6-311++G(d,p) optimized geometry of complex B in heptane solvent.

No of imaginary frequencies = 0

| Atoms | X | Y | Z |
|---|---|---|---|
| C | 0.88709800 | -1.36736700 | 0.49053000 |
| S | 1.73190300 | -0.00015600 | -0.38033800 |
| O | 3.18481100 | 0.00081700 | 0.08580900 |
| C | 0.88606200 | 1.36781200 | 0.48832800 |
| H | 1.31048100 | -2.29460800 | 0.10457700 |
| H | -0.17890600 | -1.30257800 | 0.26626600 |
| H | 1.08553500 | -1.28085900 | 1.56033600 |
| H | 1.08464500 | 1.28319700 | 1.55826100 |
| H | 1.30866900 | 2.29476900 | 0.10085400 |
| H | -0.17991000 | 1.30179600 | 0.26427000 |
| O | -1.98649800 | -0.00207800 | -0.70441100 |
| H | -2.90378000 | -0.00176900 | -0.37751200 |
| H | -2.06309900 | -0.00176500 | -1.66635400 |
| O | -4.67112300 | 0.00134100 | 0.24069600 |
| H | -5.01094400 | 0.77050500 | 0.71694200 |
| H | -5.01962100 | -0.76951000 | 0.70786600 |

Table R7. Cartesian coordinates of PCM/B3LYP/6-311++G(d,p) optimized geometry of complex C in heptane solvent.

No of imaginary frequencies = 0

| Atoms | X | Y | Z |
|---|---|---|---|
| O | -1.50658400 | 0.00073800 | -0.11891400 |
| H | -0.53940100 | 0.00046600 | -0.01996700 |
| H | -1.85073400 | -0.00502400 | 0.78159500 |
| O | 1.35561400 | -0.00045000 | 0.09549800 |
| H | 1.79939500 | 0.76992800 | -0.28349000 |
| H | 1.79850500 | -0.76767400 | -0.29081300 |