Electronic Supporting Information

A Molecular Electron Density Theory Study of the Mechanism, Chemo- and Stereoselectivity of the Epoxidation Reaction of R-Carvone with Peracetic Acid

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1. BET study of the epoxidation reaction of R-carvone\textsuperscript{8} with peracetic acid \textsuperscript{9}

The so-called Bonding Evolution Theory\textsuperscript{1} (BET) has proven to be a very useful methodological tool to achieve a better understanding of bonding changes in organic reactions. This approach allows characterising the bonding changes along the reaction path and, consequently, to establish the nature of the electronic rearrangement associated with a given molecular mechanism. Thus, in order to understand the C–O bond formation along in this epoxidation reaction, a BET study along the most favourable reaction path of the epoxidation reaction of R-carvone\textsuperscript{8} with peracetic acid \textsuperscript{9} was carried. The phases in which IRC of the molecular mechanism of the epoxidation reaction is divided is giving in Figure S1. A representation of the bonding changes taking place along reaction path by Lewis-like structures arising from the topological analysis of the ELF is shown in Scheme S1. The populations of the molecular regions directly involved in the reaction, among other relevant parameters, of the selected structures of the IRC, \textbf{S1}, defining the different topological phases are gathered in Table S1.

The topological analysis of Electron Localisation Function\textsuperscript{2} (ELF) at the first structure \textbf{S1} of the reaction path reveals that the O12–O13 single bond of the peracetic acid \textsuperscript{9} presents a very low electron population of 0.64 e [V(O12,O13)], which could suggest some labile character. Accordingly, the first relevant bonding change occurring along the reaction path is the rupture of the O12–O13 bond at a relatively early stage of the reaction, 35 % (\textit{Phase II}), with a moderate energy cost of 7.1 kcal\cdot mol\textsuperscript{-1}, leading to the formation of a hydroxyl pseudoradical and an acyloxy pseudoradical. Note that the total population associated with the two O12 and O13 oxygen centers is 4.98 [V(O12)] and 5.31 e [V(O13)], respectively, after the rupture of the O12–O13 bond. However, it should be mentioned that the electron density of the broken O12–O13 single bond is mostly gathered at the O13 oxygen, whose population increases by 0.50 e, while the O12 oxygen already has 4.86 e at the first structure \textbf{S1}. After that, the electron density at these two nuclei is redistributed, the total population belonging to the O13 oxygen remaining almost constant until the end of the reaction. It is interesting to emphasize that the bonding changes at the acyloxy system follow the expected behaviour associated with the formation of acetic acid \textsuperscript{11}; the population of the C10–O12 single bond, integrating 1.64 e at \textbf{S1}[V(C10,O12)], increases throughout the reaction path to 2.45 e,
while that of the C10–O11 single bond decreases from 2.43 e to 1.65 e [V(C10,O11)].

Simultaneously to the early rupture of the O12–O13 single bond, the depopulation of the C7–C8 double bond of R-carvone 8 [V(C7,C8)] also takes place since the beginning of the reaction, but more gradually. Thus, the population of the C7–C8 bonding region, 3.47 e, decreases by approximately 0.10 e progressively along the reaction path. For instance, at the TS, found almost at half of reaction path (45 % of reaction progress, Phase VI), the C7–C8 bonding region, integrating 3.96 e, could already be considered a half-double bond. Once the TS is achieved, the bonding changes related to the rupture and formation of the H–O and O–C single bonds take place. At exactly 50 % of reaction progress (Phase VIII), a non-bonding population of 0.17 e, coming from the depopulation of the C7–C8 bonding region of the ethylene framework, appears at the C8 carbon and subsequently disappears [V(C8)]. The analysis of the population changes of the other regions suggests that this non-bonding electron density is redistributed into the hydroxyl O13 oxygen, whose population increases by 0.15 e, by means of the GEDT taking place from the ethylene framework towards the acyloxy one. At 54 % of reaction progress (Phase XI), the O13–H14 single bond, which had even increased its population by 0.28 e [V(O13,H14)], breaks in an almost heterolytically fashion, approximately 75(O13):25(H14) relationship, releasing a hydrogen H14 free pseudoradical integrating 0.56 e and an anionic O13 oxygen integrating to 6.65 e. Subsequently, at 56 % of reaction progress (Phase XII), formation of the first C8–O13 single bond of the oxirane structure takes place with an initial population of 0.82 e [V(O8,C13)], by donation of some non-bonding electron density of the O13 oxygen anion, which decreases to 6.02 e, to the C8 carbon. Interestingly, after the C8–O13 single bond formation, the O13 oxygen should be still considered an anion. At 59 % of reaction progress (Phase XIV), similar to the formation pattern related to the first C8–O13 single bond, a small amount of non-bonding electron density of ca. 0.05 e is gathered at the C7 carbon [V(C7)]. Then, just before being redistributed in any other region, presumably at the O13 oxygen, which reaches 6.15 e, formation of the new O11–H14 single bond [V(O13,H14)], whose population had been progressively increasing from 5.32 e to 5.70 e, takes place by donation of 1.33 e of the non-bonding electron density of the O11 oxygen to the hydrogen H14 free pseudoradical. Formation of the C7–O13 single bond [V(C7,O13)] takes place later, at 65 % of reaction progress (Phase XVI), with an initial population of 0.74 e by donation of some non-bonding
electron density of the anionic O13 oxygen to the C7 carbon. At this stage, with 35 %
left to the end, all relevant bonding changes has practically occurred. At the last
structure S17 of the reaction path, the two new C7–O13 and C8–O13, single bonds
integrating 1.02 and 0.98 e, respectively, are markedly polarised towards the O13
oxygen, 5.33 e, due to the high strain of the three-membered oxiranering.

References
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**Figure S1.** Phases in which the molecular mechanism of the most favourable reaction path associated with the monoepoxidation of R-carvone 8 with peracetic acid 9 is divided.
Scheme S1. Representation of the bonding changes taking place along the most favourable reaction path associated with the monoeoxidation of R-carvone 8 with peracetic acid 9 by Lewis-like structures arising from the topological analysis of the ELF.
**Table S1.** ELF valence basin populations, GEDT, relative energies, percentage of reaction progress and distances of the breaking and forming bonds, of the IRC structures S1 – S17 defining the sixteen topological phases along the most favourable reaction path associated with the monoepoxidation of R-carvone 8 with peracetic acid 9. Electron populations are given in average number of electrons, e, relative energies in kcal·mol\(^{-1}\) and distances in angstroms, Å.

| Structures | S1     | S2     | S3     | S4     | S5     | S6     | TS    | S7     | S8     | S9     | S10    | S11    | S12    | S13    | S14    | S15    | S16    | S17    |
|------------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Phases     | I      | II     | III    | IV     | V      | VI     | VII   | VIII   | IX     | X      | XI     | XII    | XIII   | XIV    | XV     | XVI    |
| d(O13-H14) | 0.984  | 0.985  | 0.987  | 0.990  | 0.991  | 0.998  | 1.002 | 1.018  | 1.026  | 1.043  | 1.049  | 1.081  | 1.155  | 1.193  | 1.466  | 1.531  | 1.728  | 1.805  |
| d(O12-O13) | 1.440  | 1.483  | 1.550  | 1.661  | 1.682  | 1.808  | 1.859 | 1.989  | 2.037  | 2.103  | 2.122  | 2.196  | 2.266  | 2.281  | 2.324  | 2.333  | 2.498  | 3.417  |
| d(O11-H14) | 1.936  | 1.793  | 1.761  | 1.729  | 1.723  | 1.692  | 1.680 | 1.645  | 1.631  | 1.607  | 1.599  | 1.556  | 1.464  | 1.421  | 1.135  | 1.072  | 0.986  | 0.982  |
| d(C8-O13)  | 3.195  | 2.439  | 2.335  | 2.210  | 2.188  | 2.051  | 1.992 | 1.839  | 1.779  | 1.697  | 1.674  | 1.586  | 1.516  | 1.504  | 1.472  | 1.466  | 1.419  | 1.438  |
| d(C7-O13)  | 3.350  | 2.554  | 2.472  | 2.372  | 2.355  | 2.250  | 2.207 | 2.099  | 2.059  | 2.003  | 1.987  | 1.921  | 1.853  | 1.837  | 1.786  | 1.775  | 1.549  | 1.449  |
| Reaction progress | 0 | 35 | 37 | 40 | 41 | 44 | 45 | 49 | 50 | 52 | 52 | 54 | 56 | 57 | 59 | 60 | 65 | 100 |
| ΔE         | 0.0    | 7.1    | 9.6    | 13.3   | 13.8   | 16.2   | 16.4  | 14.6   | 12.8   | 9.4    | 8.3    | 3.2    | -2.3   | -4.0   | -18.7  | -22.6  | -40.7  | -51.8  |
| GEDT       | 0.00   | 0.04   | 0.08   | 0.17   | 0.19   | 0.33   | 0.39  | 0.54   | 0.59   | 0.66   | 0.67   | 0.73   | 0.75   | 0.74   | 0.67   | 0.65   | 0.61   | 0.62   |
| V(C7,C8)   | 1.77   | 1.75   | 1.75   | 3.20   | 3.18   | 3.03   | 2.96  | 2.83   | 2.62   | 2.50   | 2.47   | 2.36   | 2.30   | 2.25   | 2.21   | 2.20   | 2.05   | 1.98   |
| V'(C7,C8)  | 1.70   | 1.64   | 1.58   |        |        |        |       |        |        |        |        |        |        |        |        |        |        |        |
| V(C10,O11) | 2.43   | 2.39   | 2.36   | 2.32   | 2.31   | 2.24   | 2.21  | 2.12   | 2.09   | 2.03   | 2.02   | 1.96   | 1.89   | 1.87   | 1.76   | 1.72   | 1.62   | 1.65   |
| V(O11)     | 2.55   | 2.52   | 2.52   | 2.51   | 2.50   | 2.48   | 2.41  | 2.36   | 2.27   | 2.24   | 2.04   | 1.69   | 1.56   | 4.37   | 4.35   | 4.35   | 4.30   |        |
| V(C10,O12) | 2.77   | 2.82   | 2.85   | 2.89   | 2.90   | 3.03   | 3.17  | 3.23   | 3.36   | 3.40   | 3.63   | 4.00   | 4.14   |        |        |        |        |        |
| V(O12)     | 1.64   | 1.70   | 1.73   | 1.80   | 1.82   | 1.94   | 1.99  | 2.06   | 2.09   | 2.12   | 2.13   | 2.18   | 2.24   | 2.25   | 2.35   | 2.37   | 2.45   | 2.45   |
| V'(O12)    | 2.41   | 2.42   | 2.47   | 2.53   | 2.62   | 5.24   | 5.25  | 4.84   | 4.12   | 3.47   | 3.36   | 3.04   | 2.87   | 2.83   | 2.73   | 2.65   | 2.65   | 2.61   |
| V''(O12)   | 2.40   | 2.43   | 2.46   | 2.52   | 2.61   |        | 0.48  | 1.22   | 1.90   | 2.03   | 2.39   | 2.57   | 2.60   | 2.65   | 2.71   | 2.65   | 2.69   |
| V(O13)     | 2.44   | 2.47   | 2.53   | 2.53   | 2.52   | 2.50   | 2.51  | 2.43   | 2.36   | 4.99   | 5.14   | 5.11   | 4.15   | 4.06   | 3.41   | 3.40   | 2.81   | 2.62   |
|                  | V'(O13) | 2.42 | 2.45 | 2.50 | 2.53 | 2.54 | 2.54 | 2.57 | 2.61 | V''(O13) | 0.06 |
|------------------|---------|------|------|------|------|------|------|------|------|----------|------|
| V(O12,O13)      | 0.64    |      |      |      |      |      |      |      |      |          |      |
| V(O13,H14)      | 1.73    | 1.75 | 1.75 | 1.77 | 1.77 | 1.81 | 1.82 | 1.89 | 1.91 | 1.99     | 2.01 |
| V(H14)          |         |      |      |      |      |      |      |      |      |          |      |
| V(O11,H14)      |         |      |      |      |      |      |      |      |      |          |      |
| V(C8)           | 0.17    | 0.15 |      |      |      |      |      |      |      |          |      |
| V(C8,O13)       |         |      |      |      |      |      |      |      |      |          |      |
| V(C7)           |         |      |      |      |      |      |      |      |      |          |      |
| V(C7,O13)       |         |      |      |      |      |      |      |      |      |          |      |

|                  | V(O13) | 1.54 | 1.87 | 1.98 | 2.66 | 2.75 | 2.68 | 2.71 | V(O13) | 1.54 | 1.87 | 1.98 | 2.66 | 2.75 | 2.68 | 2.71 |
|------------------|--------|------|------|------|------|------|------|------|--------|------|------|------|------|------|------|------|
| V(O12,O13)      | 0.64   |      |      |      |      |      |      |      |        |      |      |      |      |      |      |      |
| V(O13,H14)      | 1.73   | 1.75 | 1.75 | 1.77 | 1.77 | 1.81 | 1.82 | 1.89 | 1.91   | 1.99 | 2.01 |      |      |      |      |      |
| V(H14)          | 0.56   | 0.45 | 0.43 |      |      |      |      |      |        |      |      |      |      |      |      |      |
| V(O11,H14)      | 1.73   | 1.76 | 1.81 | 1.82 |      |      |      |      |        |      |      |      |      |      |      |      |
| V(C8)           | 0.17   | 0.15 |      |      |      |      |      |      |        |      |      |      |      |      |      |      |
| V(C8,O13)       | 0.82   | 0.85 | 0.94 | 0.95 | 1.05 | 0.98 |      |      |        |      |      |      |      |      |      |      |
| V(C7)           | 0.03   | 0.05 |      |      |      |      |      |      |        |      |      |      |      |      |      |      |
| V(C7,O13)       | 0.74   | 1.02 |      |      |      |      |      |      |        |      |      |      |      |      |      |      |
Table S2. B3LYP/6-31G(d,p) enthalpies (H, in a.u.), entropies (S, in cal·mol$^{-1}$·K$^{-1}$) and Gibbs free energies (G, in a.u.), computed at 25 ºC and 1 atm in DCM, for the stationary points involved in the reaction of R-carvone 8 with peracetic acid 9.

|     | H       | S    | G       |
|-----|---------|------|---------|
| 8   | -464.599661 | 98.3 | -464.639325 |
| 9   | -304.238030  | 71.4 | -304.266847  |
| TS1 | -768.819029  | 133.3 | -768.872806  |
| TS2 | -768.818858  | 132.5 | -768.872317  |
| TS3 | -768.814118  | 132.5 | -768.867587  |
| TS4 | -768.814703  | 132.7 | -768.868232  |
| 10  | -539.816996  | 100.2 | -539.857433  |
| 13  | -539.817054  | 99.9  | -539.857356  |
| 14  | -539.810492  | 101.0 | -539.851234  |
| 15  | -539.810931  | 99.9  | -539.851217  |
| TS5 | -768.786988  | 128.8 | -768.838955  |
| IN1 | -768.827312  | 123.7 | -768.877234  |
| TS6 | -768.816568  | 125.6 | -768.867246  |
| 16  | -539.834406  | 102.2 | -539.875634  |
| TS7 | -768.786197  | 129.3 | -768.838369  |
| IN2 | -768.829953  | 128.9 | -768.881934  |
| TS8 | -768.807237  | 126.6 | -768.858307  |
| 17  | -539.832970  | 100.4 | -539.873480  |
| TS9 | -844.031328  | 134.5 | -844.085573  |
| TS10| -844.030072  | 134.9 | -844.084486  |
| 12  | -615.028861  | 102.9 | -615.070381  |
| 18  | -615.028554  | 102.6 | -615.069957  |
B3LYP/6-311G(d,p) computed total energies, single imaginary frequencies and cartesian coordinates, in DCM, of the stationary points involved in the reaction of R-carvone with peracetic acid.

|       |       |       |       |
|-------|-------|-------|-------|
|       |       |       |       |
| C     | 3.06026400 | 1.17061100 | 0.67174900 |
| H     | 4.13635000 | 1.16522600 | 0.49111200 |
| C     | 2.39459300 | -0.04044100 | 0.06205300 |
| C     | 3.10371400 | -0.95183000 | -0.60766300 |
| H     | 4.17423500 | -0.83567700 | -0.74055600 |
| H     | 2.65965000 | -1.83836000 | -1.04335000 |
| C     | 0.89419000 | -0.14029200 | 0.28821900 |
| C     | 0.11470000 | 0.92493700 | -0.51182300 |
| C     | 0.27441200 | -1.51374700 | 0.00371100 |
| H     | 0.72172000 | 0.07367300 | 1.35280800 |
| C     | -1.37921700 | 0.90066600 | -0.22813400 |
| H     | 0.24581400 | 0.73296400 | -1.58562400 |
| H     | 0.46851600 | 1.93884500 | -0.32070100 |
| C     | -1.21866100 | -1.50581100 | 0.16555900 |
| H     | 0.50689700 | -1.83301500 | -1.02186500 |
| H     | 0.70971600 | -2.27422100 | 0.65888000 |
| C     | -1.99670000 | -0.41158000 | 0.08653300 |
| H     | -1.68927200 | -2.46856800 | 0.35181800 |
| O     | -2.05016900 | 1.92026800 | -0.29679800 |
| H     | 2.65523800 | 2.10332000 | 0.26662800 |
| H     | 2.89308700 | 1.20003100 | 1.75432300 |
| C     | -3.48878900 | -0.43712600 | 0.27608500 |
| H     | -3.78753000 | 0.21630800 | 1.10063400 |
| H     | -4.00262500 | -0.06684300 | -0.61573000 |
| H     | -3.84045400 | -1.44815500 | 0.48827400 |

|       |       |       |       |
|-------|-------|-------|-------|
| O     | 1.85523800 | -0.24063600 | 0.00006500 |
| H     | 1.64698800 | 0.72057800 | 0.00026300 |
| O     | -0.12325600 | 1.34306200 | -0.00001600 |
| C     | -0.42074000 | 0.17070900 | -0.00014100 |
| O     | 0.52745500 | -0.79939900 | -0.00009000 |
| C     | -1.79574300 | -0.42156400 | 0.00007800 |
| H     | -2.32833900 | -0.06479600 | -0.88336800 |
| H     | -1.76744900 | -1.50944000 | -0.00029600 |
| H     | -2.32780300 | -0.06542700 | 0.88410800 |
**10**

E(RB3LYP) = -540.047007 A.U.

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -2.98886100 | -1.11353000 | -0.81231800 |
| H    | -4.04435900  | -0.93780000  | -0.59902700  |
| C    | -2.13800200  | -0.02432900  | -0.19075500  |
| C    | -2.77531000  | 1.27115400   | 0.09434300   |
| H    | -3.82279000  | 1.40513000   | -0.16392100  |
| H    | -2.19300700  | 2.18475900   | 0.14291400   |
| O    | -2.52549000  | 0.33016100   | 1.15696400   |
| C    | -0.62795600  | -0.15618400  | -0.40854200  |
| C    | 0.17803500   | 1.07381900   | 0.02744300   |
| C    | -0.08206400  | -1.40423200  | 0.31202700   |
| H    | -0.47405700  | -0.29707100  | -1.48597700  |
| C    | 1.68040200   | 0.90140000   | -0.12390700  |
| H    | -0.01937300  | 1.27762500   | 1.08844100   |
| H    | -0.09663700  | 1.96868400   | -0.53267300  |
| C    | 1.41555400   | -1.48878900  | 0.29111300   |
| H    | -0.42498800  | -1.39857600  | 1.35654400   |
| H    | -0.48974900  | -2.31757400  | 0.12970300   |
| C    | 2.24597900   | -0.45556200  | 0.06821300   |
| H    | 1.84268400   | -2.47185000  | 0.47647600   |
| O    | 2.39910500   | 1.86359100   | -0.35311800  |
| H    | -2.85341800  | -1.13346200  | -1.89749600  |
| H    | -2.72500000  | -2.09806700  | -0.41919500  |
| C    | 3.74387200   | -0.58702500  | 0.02539900   |
| H    | 4.13598900   | -0.25711500  | -0.94078800  |
| H    | 4.21391400   | 0.04556500   | 0.78382100   |
| H    | 4.05197600   | -1.62059900  | 0.19172100   |

**11**

E(RB3LYP) = -229.162261 A.U.

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -0.09106600 | 0.12454700 | -0.00001100 |
| O    | -0.63302700 | 1.20378600 | -0.00010000 |
| O    | -0.78547600 | -1.03564400 | 0.00004200 |
| H    | -1.72822500 | -0.80848300 | 0.00000600 |
| C    | 1.39290500  | -0.11879400 | 0.00005000 |
| H    | 1.67204600  | -0.70123400 | 0.88073300 |
| H    | 1.67207800  | -0.70160700 | -0.88037400 |
| H    | 1.92108600  | 0.83166700  | -0.00013100 |

**12**

E(RB3LYP) = -615.26384 A.U.

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 2.16696900 | -0.25513000 | 0.01756200 |
| C    | 1.32522300 | -1.43780500 | 0.29777700 |
| C    | 3.64859300 | -0.24728600 | 0.28139900 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -0.152133 | -1.323753 | 0.592947  |
| H       | 1.834278  | -2.297886 | 0.727836  |
| C       | 1.483112  | 1.098524  | -0.056623 |
| H       | 4.163173  | 0.358050  | -0.466918 |
| H       | 3.862520  | 0.179320  | 1.264663  |
| H       | 4.039937  | -1.264994 | 0.247093  |
| C       | -0.781137 | -0.148357 | -0.170808 |
| H       | -0.274183 | -1.204061 | 1.675299  |
| H       | -0.648023 | -2.260455 | 0.318087  |
| C       | -0.023458 | 1.155137  | 0.124787  |
| O       | 2.142230  | 2.107748  | -0.201491 |
| H       | -0.672893 | -0.356091 | -1.238112 |
| H       | -0.160395 | 1.439518  | 1.177427  |
| H       | -0.408243 | 1.983509  | -0.473699 |
| O       | 1.726831  | -1.144895 | -1.048602 |
| C       | -2.754003 | 0.271956  | 1.496490  |
| H       | -3.838692 | 0.388567  | 1.504634  |
| C       | -2.278505 | -0.010374 | 0.087742  |
| C       | -3.201103 | -0.650846 | -0.861908 |
| H       | -4.198208 | -0.931424 | -0.532531 |
| H       | -2.803023 | -1.227732 | -1.692834 |
| O       | -2.955461 | 0.766177  | -0.928575 |
| H       | -2.492638 | -0.544023 | 2.175120  |
| H       | -2.313763 | 1.193063  | 1.887065  |

13

\[ E(\text{RB3LYP}) = -540.047106 \text{ A.U.} \]

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -2.753905 | 1.378811  | -0.731187 |
| H       | -3.816874 | 1.409260  | -0.487121 |
| C       | -2.126785 | 0.110183  | -0.189699 |
| C       | -3.003313 | -1.051219 | 0.032242  |
| H       | -2.611375 | -2.062484 | 0.013584  |
| H       | -4.059072 | -0.962171 | -0.211244 |
| O       | -2.563891 | -0.245081 | 1.142741  |
| C       | -0.623994 | -0.046758 | -0.434115 |
| C       | 0.172228  | 0.995436  | 0.372488  |
| C       | -0.076242 | -1.446647 | -0.124462 |
| H       | -0.455646 | 0.148097  | -1.500920 |
| C       | 1.674094  | 0.897042  | 0.167598  |
| H       | -0.020786 | 0.836782  | 1.442101  |
| H       | -0.120652 | 2.020168  | 0.141298  |
| C       | 1.422983  | -1.508464 | -0.161757 |
| H       | -0.419408 | -1.764990 | 0.869965  |
| H       | -0.473613 | -2.180300 | -0.832041 |
| C       | 2.247708  | -0.451908 | -0.057642 |
| H       | 1.856404  | -2.498749 | -0.282553 |
| O       | 2.384811  | 1.889676  | 0.231557  |
| H       | -2.284363 | 2.269150  | -0.306944 |
### 14

**E(RB3LYP) = -540.039899 A.U.**

| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| C    | -1.09332300 | -1.45565400 | 0.03331200 |
| C    | -1.91660000 | -0.22829700 | 0.02575600 |
| O    | -1.49672600 | -0.85347500 | 1.27251500 |
| C    | 0.38587300  | -1.43568100 | -0.27266400 |
| C    | -1.20457500 | 1.08726500  | -0.21915600 |
| C    | 0.30879500  | 1.07814000  | -0.35986000 |
| H    | 0.49376900  | 1.11484500  | -1.44298400 |
| C    | 1.04577500  | -0.14472500 | 0.22952100  |
| H    | 0.90361900  | -0.11391600 | 1.31521800  |
| H    | 0.50582300  | -1.54524500 | -1.35634000 |
| H    | 0.86236700  | -2.30531300 | 0.18983700  |
| O    | -1.61609200 | -2.38310000 | -0.19142600 |
| C    | -1.84203500 | 2.11205500  | -0.35568700 |
| C    | 2.54377500  | -0.05158700 | -0.02270000 |
| C    | 3.19147100  | -0.80767800 | -0.91159600 |
| C    | 3.27673400  | 0.96331600  | 0.82176000  |
| H    | 3.15719200  | 0.73644600  | 1.88708600  |
| H    | 4.34323700  | 0.97790100  | 0.59129300  |
| H    | 4.28531400  | 1.97469500  | 0.67149200  |
| H    | 2.69497300  | -1.55309200 | -1.52079600 |
| C    | 4.26134100  | -0.70210900 | -1.05761500 |
| C    | 0.67910400  | 2.02120300  | 0.04607900  |
| C    | -3.39655600 | -0.85639700 | -0.24502200 |
| H    | -3.80604800 | -1.23262300 | 0.01846000  |
| H    | -3.90386700 | 0.51255900  | 0.34044200  |
| H    | -3.59886000 | -0.06309900 | -1.30148100 |

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**E(RB3LYP) = -540.040556 A.U.**

| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| C    | 1.06361500 | -1.39444100 | -0.37346100 |
| C    | 1.91132600 | -0.21710700 | -0.04285800 |
| O    | 1.59927900 | -1.23186000 | 0.94530400 |
| C    | -0.44615000 | -1.32922800 | -0.49419800 |
| C    | 1.18304100 | 1.07980100  | 0.22116400 |
| C    | -0.26383700 | 0.94770200  | 0.64022900 |
| H    | -0.74665400 | -1.78170300 | -1.44278700 |
| H    | -0.85825700 | -1.95966600 | 0.30023100 |
| H    | 1.55385100  | -2.18327200 | -0.94041800 |
O  1.73518100  2.14992400  0.05752400
H  -0.30794300  0.46308500  1.61986800
C  -1.02760700  0.10190100  -0.41306400
H  -0.85457300  0.57558900  -1.38541100
C  -2.53007600  0.10364800  -0.18189400
C  -3.04100900  0.35737200  1.17116300
H  -2.70759200  0.35737200  1.95791600
C  -4.13175000  -0.34997400  1.18635400
H  -2.67815700  -1.32240900  1.44689800
C  -3.36111800  0.47934800  -1.15657900
H  -0.68737800  1.94974000  0.72117100
H  -4.43730300  0.47665200  -1.01804500
H  -2.99250200  0.80192000  -2.12495600
C  3.35032300  -0.12441100  -0.47150200
H  3.94086100  0.39558000  0.28619400
H  3.76489000  -1.12263000  -0.61864200
H  3.43589300  0.43583300  -1.40498300

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E(RB3LYP) = -540.064281 A.U.

C  1.12928500  -1.60787900  -0.07805000
C  2.08826900  -0.68046000  -0.08615200
O  1.94198900  0.70376400  -0.25492200
C  0.90681500  1.49738300  0.15223100
C  -0.36727200  -1.52270200  -0.17721600
C  -0.32033900  0.84358100  0.72612700
H  -0.70108800  -2.13746400  -1.02137400
H  -0.77800900  -2.00920300  0.71611600
H  1.50353000  -2.62016300  0.04174800
O  1.02615700  2.68318800  -0.01587000
H  -0.06057200  0.29927100  1.63975000
C  -0.97163000  -0.11630000  -0.30975000
H  -0.74101200  0.26196400  -1.31041000
C  -2.48874300  -0.13407300  -0.18799300
C  -3.08983000  -0.51259300  1.14382300
H  -2.73887600  0.14796100  1.94351400
H  -4.17862700  -0.45150000  1.11036500
H  -2.81988900  -1.53209500  1.43664300
C  -3.25203800  0.18283600  -1.23578700
H  -0.99472200  1.65611500  0.99240800
H  -4.33513900  0.17402000  -1.17181600
H  -2.81945300  0.46114600  -2.19123100
C  3.55305100  -0.98381000  0.02408500
H  3.98034900  -0.49030800  0.90241400
H  3.72663700  -2.05663600  0.10264800
H  4.08629600  -0.60366500  -0.85234500
E(RB3LYP) = -540.063502 A.U.

C     -1.05239300   -1.46195300   -0.47289000
C     -1.97597300   -0.57031800   -0.08403800
O     -0.42559400    1.26439500    0.44476100
C      0.38145900   -1.13614000   -0.80877600
C     -1.64725500    0.88804900   -0.01427900
C      0.36836100    0.34913800    1.24253600
H      0.87561200   -2.01478000   -1.22568000
H      0.39846700   -0.36984100   -1.58896100
H     -1.36400800   -2.49667600   -0.58738000
O     -2.41739700    1.74821100   -0.37609800
H      1.00256700    0.99343300    1.85005800
C      1.20773800   -0.63063500    0.40592200
H      1.40165700   -1.48533600    1.06231400
C      2.55640400   -0.06787300   -0.83606600
H      2.02693900    2.00527400   -0.33883000
H      3.59819900    1.53357000   -1.01251300
H      2.09493700    1.05557900   -1.80950100
C      3.68421100   -0.68504900    0.34396400
H     -0.29698900   -0.20253400    1.90708000
H      4.65764300   -0.30055600    0.05751400
H      3.67165600   -1.59471500    0.93565900
C     -3.42023400   -0.92045300    0.16065400
H     -3.72901100   -0.64469300    1.17394200
H     -4.06765900   -0.37294300   -0.52881600
H     -3.58769500   -1.99007600    0.02749900

E(RB3LYP) = -615.263728 A.U.

C      2.18154100   -0.18320700   -0.08073700
C      1.37292700   -1.39365700   -0.38889900
C      3.59137200   -0.01876700   -0.57887400
C     -0.14315100   -1.39822700   -0.43050700
H      1.86845400   -2.15057600   -0.99322100
C      1.41144000    1.07601100    0.24460100
H      3.60465000    0.55559300   -1.50763500
H      4.19450100    0.51915500    0.15594200
H      4.04306400   -0.99501700   -0.76026900
C     -0.77394600    0.00152300   -0.29658300
H     -0.48125300   -2.05513700    0.37732600
H     -0.47090900   -1.85673100   -1.36733300
C     -0.00745500    0.87120900    0.72762600
O      1.90963600    2.17162500    0.08096000
H     -0.68389100    0.50253900   -1.26690200
H  0.01920800  0.37757400  1.70361000
H  -0.47603900  1.85006500  0.83593300
O  1.96599900 -1.22635300  1.34244300
C  -2.72065100 -0.58814900  1.41408000
H  -3.80816400 -0.53999900  0.00167900
C  -2.26939300 -0.05164800  0.90398200
H  -2.26227900 -0.05164800 -1.39233000
H  -1.72985900 -0.10524400 -2.15321700
H  -2.30086600 -0.00177100  2.16113900
H  -2.41477600 -1.62791800  1.48217000
H  -2.30086600  0.00177100  2.16113900

IN1

E(RB3LYP) = -769.123941 A.U.

C  -1.11339700  2.25005500  -0.13976900
C  0.12809200  1.76550700  -0.02441400
O  1.33254200 -0.22448900  -0.86958800
O  4.57098700 -0.59985200  0.27324300
C  3.45507000 -0.89215800  -0.06424400
O  3.64856000 -2.97794900  0.15749600
C  -2.37956900  1.44051600  -0.16089100
C  0.34123100  0.26140400  0.09960900
C  -0.88411700 -0.56004600  -0.30197800
H  -3.14095700  1.93675000  0.45010700
H  -2.77804100  1.43260100  -1.18411300
H  -1.23501800  3.32724800  -0.22823900
O  0.72520600  -0.12492500  1.39285000
H  -0.96580400 -0.54492000  -1.39203200
C  -2.15892300  0.00407000  0.34660500
H  -1.97166000  0.06179100  1.42335900
C  -3.36919000 -0.89233600  0.14475200
C  -3.76293100 -1.25613100 -1.26655800
H  -2.97106100 -1.82156500 -1.76872300
H  -4.66757900 -1.86627300 -1.27436500
H  -3.94958300 -0.36749000 -1.87784000
C  -4.03927500 -1.33890500  1.19674400
H  -0.70873500 -1.59149000  0.01086700
H  -4.93290300 -1.97147200  1.07706400
H  -3.77279400 -1.08554200  2.21235500
H  1.27938400  0.56265800  1.77993300
C  1.32771400  2.68266600  0.00421200
H  1.00019400  3.72345200  0.00873000
IN2

\[ E(\text{RB3LYP}) = -769.126466 \text{ A.U.} \]

TS1

\[ E(\text{RB3LYP}) = -769.112953 \text{ A.U.} \]

1 imaginary frequencies -428.6421 cm\(^{-1}\)
|        | X         | Y         | Z         |
|--------|-----------|-----------|-----------|
| C      | 0.79137000| 2.13106300| -1.02581400|
| H      | 1.64669500| 2.79233000| -1.09022100|
| H      | 0.32308200| 1.85829600| -1.06184000|
| O      | 1.67050100| 0.29744500| -0.70675100|
| H      | 2.40576200| 0.67588500| -0.16018400|
| O      | 3.98488400| 0.12012800| 0.43389400|
| C      | 3.76954500| -0.95319100| -0.13589600|
| O      | 2.69398300| -1.20888300| -0.81600600|
| C      | 4.76276700| -2.09899000| -0.09145900|
| H      | 4.41734800| -2.60051000| -0.66044300|
| H      | 5.71625300| -1.74866700| -0.49180000|
| H      | 4.91884700| -2.38349200| 0.95121900|
| C      | -1.06837400| 1.07591200| 0.33181600|
| C      | -1.70159600| 0.62215800| -0.98803900|
| C      | -0.91410800| -0.13933400| 1.27419800|
| H      | -1.77387000| 1.76343600| 0.82286600|
| C      | -3.01089100| -0.12581700| -0.78905500|
| H      | -1.01842400| -0.06158500| 1.50816200|
| H      | -1.90421500| 1.45784400| -1.65991400|
| C      | -2.15472000| -0.98041800| 1.33202900|
| H      | -0.06958100| -0.75142600| 0.93385100|
| H      | -0.66501600| 0.18618600| 2.28761700|
| C      | -3.14196400| -0.97495700| 0.41976300|
| H      | -2.23957900| -1.64302800| 2.19032800|
| O      | -3.89958100| -0.06405400| -1.62523100|
| H      | 0.07785300| 3.01485500| 1.98135600|
| H      | 1.11786100| 1.60836200| 2.13389800|
| C      | -4.38596500| -1.81231600| 0.53763000|
| H      | -5.27957200| -1.18193800| 0.54526200|
| H      | -4.48695600| -2.48520400| -0.31871300|
| H      | -4.37247200| -2.40823200| 1.45161100|

**TS2**

E(RB3LYP) = -769.112834 A.U.
1 imaginary frequencies -427.1433 cm⁻¹
H  -4.26834400  -2.95354900  -0.89681000
H  -4.56221700  -2.68896000   0.84120500
C   1.09658800   1.19065800   0.14262800
C   1.11329300  -0.15093100   0.90560400
C   1.57180000   0.96065300  -1.29716900
H   1.83489400   1.84431200   0.63228800
C   2.45778000  -0.85716800   0.83455400
H   0.35995300  -0.81442300   0.46436300
H   0.86625200  -0.03523400   1.96101300
C   2.83450900   0.15057600  -1.35749000
H   0.79253800   0.44040200  -1.86986000
H  -0.91394000  1.30624400   2.22880200
C   3.27573000  -0.66966900  -0.38810000
H   3.41835700   0.24294000  -0.27017600
O   2.82518100   1.58853100   1.74196500
H   4.55964100  -1.44787000  -0.47944400
H   5.22884000  -1.19207000   0.34681500
H   4.37094600  -2.52265700  -0.40580900
H   5.07449200  -1.24624600  -1.42014200

TS3

E(RB3LYP) = -769.107698 A.U.
1 imaginary frequencies -442.2501 cm\(^{-1}\)

C  -0.11803700   0.82623800   1.38745800
C   0.04535000   1.77554800   0.39866800
O   1.15169300  -0.11543100   0.12323300
H   1.98677300   0.33210100   0.43387500
O   3.69223200   0.01057700   0.47606100
C   3.46992200  -1.05236200  -0.11298700
O   2.28418000  -1.45205900   0.45170000
C   4.58635000  -2.00012900  -0.50657100
H   4.20474300  -2.90732400  -0.97099500
H   5.25070100  -1.48226900  -1.20162500
H   5.16108600  -2.25200800   0.38672500
C  -1.26451800  -0.13478000   1.44436400
C  -0.90026500   1.78666500  -0.76050300
C  -2.09883600   0.85877700  -0.70347900
H  -2.89864500   1.41599800  -0.19558800
C  -1.83927300  -0.45844300   0.06016600
H  -1.06023100  -0.99931400  -0.48772400
H  -2.02859400   0.32762000   2.08445600
H  -0.94600000  -1.04651800   1.95467300
H   0.49771000   0.90059700   2.27849400
O  -0.73613400   2.56913200  -1.67922700
C  -3.07225700  -1.34968800   0.07002000
C  -3.81771100  -1.57135200   1.15460400
TS4

E(RB3LYP) = -769.108316 A.U.
1 imaginary frequencies-434.4057  cm-1

C    -0.20004200   0.70560900  -1.36470500
C     0.02404700   1.65861500  -0.38971100
O     1.20930800  -0.10236800  -0.09802900
H     2.00822400   0.32111900  -0.52153800
O     3.70486400   0.05562100  -0.67140200
C     3.57694500  -0.94493900   0.04459800
O     2.44220100  -1.34236600   0.52417900
C     4.76371800  -1.80696000   0.42997400
H     5.24095600  -2.17061100  -0.48230800
H     4.46895600  -2.64859500   1.05378500
H     5.48574200  -1.18576800   0.96396900
C    -1.30524000  -0.30481700  -2.31071500
O    -0.85127400  -1.28902500  -1.17095600
H     0.36053400   0.77924900  -2.29150700
O    -0.67731800   2.49052300   1.70426000
H    -1.01911600  -0.42735700   1.42106800
C    -2.36326200  -0.00264400  -0.24303700
H    -2.93055300   0.87101100  -0.58235600
C    -3.35762300  -1.13863500  -0.06893700
C    -2.86249500  -2.43396400   0.52607300
H    -2.50719400  -2.29163800  1.55183200
H    -3.65741300  -3.18094000   0.54686300
H    -2.02350300  -2.84898900  -0.04144700
C    -4.63079000  -0.97844100  -0.43644900
H    -2.37689300   0.61841400   1.86359700
H    -5.35723000  -1.77726200  -0.32993300
H    -4.98846500  -0.04327100  -0.85488600
C     0.94823900   2.82175500  -0.57028000
H     1.59715500   2.94352700   0.29857200
H     1.55632000   2.71831800  -1.46948900
### TS5

$$E(RB3LYP) = -769.080196 \text{ TS5 A.U.}$$

1 imaginary frequencies -220.8243 cm⁻¹

| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | 0.17906600 | 1.31034500 | -0.63838200 |
| O    | -1.81544300 | 0.31460800 | -1.24253100 |
| O    | -2.94116200 | -0.09191800 | -0.46641300 |
| H    | -1.29038000 | 1.82099200 | -1.58664000 |
| C    | 0.33099600  | 0.81765300  | 1.70019700  |
| C    | -0.27734300 | 1.52113000  | 0.71427500  |
| O    | -1.99184500 | -2.14985000 | -0.29164800 |
| C    | -2.89629800 | -1.37859000 | -0.07115800 |
| C    | -4.14954700 | -1.72171800 | 0.70252100  |
| H    | -4.83023700 | -0.87597900 | 0.78461000  |
| H    | -3.86606100 | -2.06321200 | 1.70024200  |
| H    | -4.65449100 | -2.54924500 | 0.19960100  |
| C    | 1.43571100  | -0.16476300 | 1.47911600  |
| C    | 1.36519300  | 0.45833800  | -0.94527500 |
| H    | 2.05635600  | -0.23863300 | 2.37548900  |
| H    | 0.98739200  | -1.15771300 | 1.32972400  |
| H    | -0.01432300 | 0.95841200  | 2.72044800  |
| O    | -0.29289900 | 2.00513500  | -1.64424400 |
| C    | 0.94010400  | -0.48980700 | -1.30005300 |
| C    | 2.29382700  | 0.22756600  | 0.25945200  |
| H    | 2.76321500  | 1.18804600  | 0.49677900  |
| C    | 3.40868400  | -0.75844200 | -0.04131200 |
| C    | 3.03467700  | -2.17672400 | -0.39436400 |
| H    | 2.39826700  | -2.21823400 | -1.28417100 |
| H    | 3.92507100  | -2.77580400 | -0.59048800 |
| H    | 2.47430300  | -2.65884600 | 0.41308500  |
| C    | 4.68249000  | -0.36229900 | 0.01110700  |
| H    | 1.89287100  | 0.89823300  | -1.79511700 |
| H    | 5.49839900  | -1.04580700 | -0.19891200 |
| H    | 4.95075000  | 0.65801800  | 0.26493400  |
| C    | -1.38769300 | 2.50424700  | 0.97512400  |
| H    | -1.49358500 | 2.68379600  | 2.04543100  |
| H    | -1.18920900 | 3.45996500  | 0.48324300  |
| H    | -2.33623500 | 2.12154100  | 0.59268800  |

### TS6

$$E(RB3LYP) = -769.109979 \text{ A.U.}$$

1 imaginary frequencies -327.6452 cm⁻¹

| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | -1.20291100 | 1.97155800 | -1.02627900 |
| C    | -0.05851800 | 2.03325400 | -0.30940200 |
| O    | 0.89353900  | 0.41674100  | -0.67101300 |
TS7

E(RB3LYP) = -769.079460 A.U.
1 imaginary frequencies -267.9882 cm⁻¹
H  -3.16233100  0.57669100  -1.74610300
H  -1.66296300 -0.27717400  -2.02761000
H  -1.58007600  2.35875200  -2.23309600
O   0.25433900  1.78208000  1.76543700
H  -0.14421900 -0.78438200   0.11673100
C  -2.23311700 -0.16839900   0.08138600
H  -2.86830000  0.49899200   0.67347100
C  -2.86236500  1.54896600   0.12832200
C  -2.14102400 -2.68964500  -0.54671300
H  -1.15744100 -2.86399500  -0.09874600
H  -2.71486300 -3.61388000  -0.46527700
H  -1.97128800 -2.49065400  -1.60975800
C  -4.02635300 -1.73113600   0.75652300
H  -0.82050000 -0.51696000   1.72265300
H  -4.50207100 -2.70530500   0.79833300
H  -4.54123300 -0.91250500   1.24850400
H   0.99665400  1.11796700   1.98341100
C   0.15389200  3.47089000  -0.46109800
H  -0.09947700  4.01041600  -1.37418800
H  -0.12552600  4.08703900   0.39680400
H   1.23698600  3.33142300  -0.42174300

**TS8**

E(RB3LYP) = -769.100177  TS8  A.U.
1 imaginary frequencies -383.2685 cm⁻¹
H  4.98260500  -1.52865300   1.31550600
H  4.72578200   0.21687600   1.22110300
C  3.75489600  -1.88858400  -0.95307700
H  0.84480200  -1.66131200   0.33344700
H  4.61128700  -2.53789800  -0.80566200
H  3.18324500  -2.02809300  -1.86416700
H  -1.49896400 -0.87743200  -1.15253800
C  -1.29154300  2.58764800  -0.32467800
H  -1.81761600  2.34842300  -1.25395900
H  -1.99137100  2.40613100   0.49357700
H  -1.02035800  3.64438900  -0.33910600

TS9

E(RB3LYP) = -844.330531 A.U.
1 imaginary frequencies -445.4464 cm⁻¹
E(RB3LYP) = -844.32928 A.U.
1 imaginary frequencies -442.6929 cm⁻¹

TS10