

Supplementary Materials

DFT Studies of the Activity and Reactivity of Limonene in Comparison with Selected Monoterpenes

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Table S1. Energy of the HOMO and LUMO orbitals along with ΔE_{gap} levels for limonene and selected monoterpenes, structures optimized using different methods without the PCM model.

| | B3LYP/6-311+G(d) | | | B3PW91/6-311+G(d) | | | CAM-B3LYP/6-311+G(d)/ DEF2TZV | | | ω B97XD/6-311+G(d)/ DEF2TZV | | |
|----------|-----------------------------|-----------------------------|----------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------------|-----------------------------|----------------------------|---------------------------------------|-----------------------------|----------------------------|
| | E_{HOMO} , [eV] | E_{LUMO} , [eV] | E_{gap} , [eV] | E_{HOMO} , [eV] | E_{LUMO} , [eV] | E_{gap} , [eV] | E_{HOMO} , [eV] | E_{LUMO} , [eV] | E_{gap} , [eV] | E_{HOMO} , [eV] | E_{LUMO} , [eV] | E_{gap} , [eV] |
| limonene | -6.419 | -0.024 | 6.395 | -6.436 | 0.142 | 6.578 | -7.928 | 0.780 | 8.708 | -8.437 | 1.643 | 10.079 |
| cymene | -6.451 | -0.328 | 6.123 | -6.492 | -0.304 | 6.188 | -7.855 | 0.806 | 8.661 | -8.392 | 1.590 | 9.982 |
| pinene | -6.207 | 0.027 | 6.235 | -6.211 | 0.270 | 6.482 | -7.718 | 0.807 | 8.525 | -8.224 | 1.678 | 9.902 |
| thymol | -6.087 | -0.392 | 5.695 | -6.103 | -0.352 | 5.750 | -7.494 | 0.625 | 8.118 | -8.013 | 1.507 | 9.520 |
| menthol | -7.272 | -0.038 | 7.234 | -7.232 | 0.261 | 7.493 | -8.944 | 0.752 | 9.697 | -9.393 | 1.631 | 11.025 |

Table S2. The energies (with and without zero point correction), enthalpies, free energies (G), and bound dissociation enthalpy (BDE) values for the limonene molecules and its radicals were calculated using B3LYP and water as the PCM model.

| Molecules | | Electronic Energy | Sum of electronic and zero-point Energies | Sum of electronic and thermal Energies | Sum of electronic and thermal Enthalpies | Sum of electronic and thermal Free Energies | BDE [kcal/mol] |
|-----------|---------------------|----------------------|--|--|---|--|-------------------|
| | | [a.u.] | [a.u.] | [a.u.] | [a.u.] | [a.u.] | |
| | | ϵ_0 | $\epsilon_0 + \text{ZPE}$ | $\epsilon_0 + E_{\text{tot}}$ | $\epsilon_0 + H_{\text{corr}}$ | $\epsilon_0 + G_{\text{corr}}$ | |
| 6-31g(d) | Limonene | -390.723274 | -390.487083 | -390.476384 | -390.475440 | -390.522996 | – |
| | Limonene bond C3–H | -390.083064 | -389.860782 | -389.850005 | -389.849060 | -389.897609 | 80.61 |
| | Limonene bond C4–H | -390.081014 | -389.858711 | -389.847983 | -389.847039 | -389.895407 | 81.88 |
| | Limonene bond C6–H | -390.079414 | -389.857634 | -389.846560 | -389.845616 | -389.895805 | 82.77 |
| | Limonene bond C7–H | -390.074327 | -389.851753 | -389.841326 | -389.840382 | -389.888014 | 86.05 |
| | Limonene bond C10–H | -390.074069 | -389.851785 | -389.841332 | -389.840387 | -389.888063 | 86.05 |
| | Limonene bond C5–H | -390.055788 | -389.834694 | -389.823626 | -389.822682 | -389.871925 | 97.16 |
| | Limonene bond C2–H | -390.040630 | -389.817306 | -389.806558 | -389.805614 | -389.853932 | 107.87 |
| | H atom | -0.500281 | -0.500281 | -0.498865 | -0.497921 | -0.510936 | – |
| Def2SVP | Limonene | -390.442898 | -390.209224 | -390.198477 | -390.197533 | -390.245133 | – |
| | Limonene bond C3–H | -389.803888 | -389.583857 | -389.573045 | -389.572101 | -389.620704 | 79.85 |
| | Limonene bond C4–H | -389.801440 | -389.581636 | -389.570826 | -389.569882 | -389.618403 | 81.24 |
| | Limonene bond C6–H | -389.800006 | -389.580607 | -389.569415 | -389.568471 | -389.619925 | 82.12 |
| | Limonene bond C7–H | -389.795201 | -389.574792 | -389.564335 | -389.563391 | -389.611020 | 85.31 |
| | Limonene bond C10–H | -389.794682 | -389.574604 | -389.564095 | -389.56315 | -389.611017 | 85.46 |
| | Limonene bond C5–H | -389.776801 | -389.558078 | -389.546954 | -389.54601 | -389.595370 | 96.22 |
| | Limonene bond C2–H | -389.760030 | -389.539095 | -389.528307 | -389.527363 | -389.575713 | 107.92 |
| | H atom | -0.500549 | -0.50055 | -0.499134 | -0.498189 | -0.511204 | – |

Table S3. The energies (with and without zero point correction), enthalpies, free energies (G), and bound dissociation enthalpy (BDE) values for the cymene molecules and its radicals were calculated using B3LYP and water as the PCM model.

| Molecules | | Electronic Energy | Sum of electronic and zero-point Energies | Sum of electronic and thermal Energies | Sum of electronic and thermal Enthalpies | Sum of electronic and thermal Free Energies | BDE [kcal/mol] |
|-----------|-------------------|-------------------|---|--|--|---|----------------|
| | | [a.u.] | [a.u.] | [a.u.] | [a.u.] | [a.u.] | |
| | | ϵ_0 | $\epsilon_0 + \text{ZPE}$ | $\epsilon_0 + E_{tot}$ | $\epsilon_0 + H_{corr}$ | $\epsilon_0 + G_{corr}$ | |
| 6-31g(d) | Cymene | -389.555152 | -389.341949 | -389.331436 | -389.330491 | -389.378865 | – |
| | Cymene bond C8–H | -388.910371 | -388.711413 | -388.700480 | -388.699536 | -388.749801 | 83.48 |
| | Cymene bond C7–H | -388.903557 | -388.703594 | -388.693642 | -388.692698 | -388.739302 | 87.77 |
| | Cymene bond C9–H | -388.881739 | -388.683809 | -388.672956 | -388.672012 | -388.721604 | 100.75 |
| | Cymene bond C10–H | -388.881739 | -388.683818 | -388.672965 | -388.672021 | -388.721530 | 100.75 |
| | Cymene bond C2–H | -388.867216 | -388.666970 | -388.656483 | -388.655539 | -388.704164 | 111.09 |
| | Cymene bond C6–H | -388.867103 | -388.666823 | -388.656324 | -388.655380 | -388.704203 | 111.19 |
| | Cymene bond C3–H | -388.866994 | -388.666771 | -388.656256 | -388.655312 | -388.704222 | 111.23 |
| | Cymene bond C5–H | -388.866989 | -388.666775 | -388.666775 | -388.655310 | -388.704228 | 111.23 |
| Def2SVP | Cymene | -389.275316 | -389.063989 | -389.053455 | -389.052511 | -389.101032 | – |
| | Cymene bond C8–H | -388.631996 | -388.434799 | -388.424782 | -388.423838 | -388.470953 | 81.88 |
| | Cymene bond C7–H | -388.624933 | -388.426488 | -388.416528 | -388.415584 | -388.462345 | 87.06 |
| | Cymene bond C9–H | -388.603421 | -388.407084 | -388.396206 | -388.395262 | -388.445269 | 99.81 |
| | Cymene bond C10–H | -388.601681 | -388.405119 | -388.394211 | -388.393267 | -388.443655 | 101.06 |
| | Cymene bond C2–H | -388.587080 | -388.388728 | -388.378208 | -388.377263 | -388.426110 | 111.11 |
| | Cymene bond C6–H | -388.586948 | -388.388562 | -388.378030 | -388.377086 | -388.426118 | 111.22 |
| | Cymene bond C3–H | -388.587821 | -388.388531 | -388.377978 | -388.377978 | -388.426325 | 110.66 |
| | Cymene bond C5–H | -388.586875 | -388.388562 | -388.377975 | -388.377031 | -388.426890 | 111.25 |

Table S4. The energies (with and without zero point correction), enthalpies, free energies (G), and bound dissociation enthalpy (BDE) values for the pinene molecules and its radicals were calculated using B3LYP and water as the PCM model.

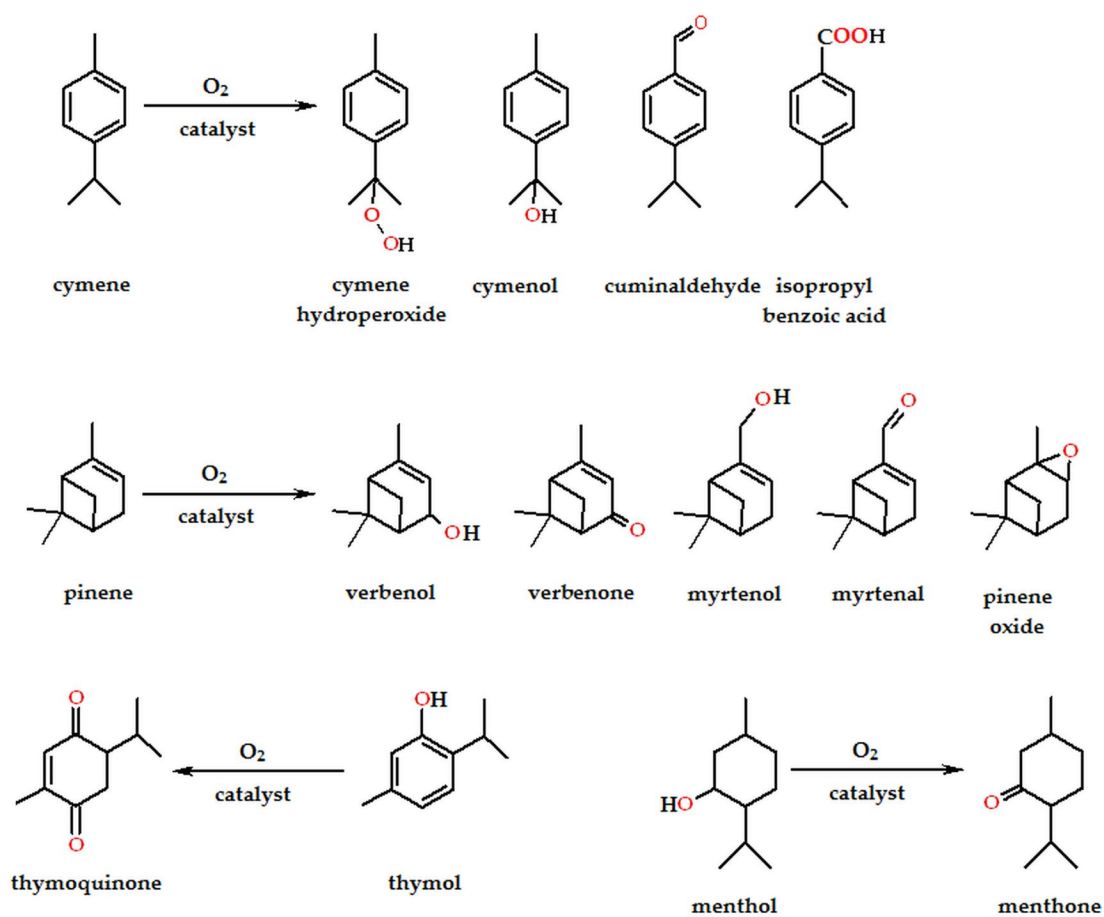
| Molecules | | Electronic Energy | Sum of electronic and zero-point Energies | Sum of electronic and thermal Energies | Sum of electronic and thermal Enthalpies | Sum of electronic and thermal Free Energies | BDE [kcal/mol] |
|-----------|-------------------|-------------------|---|--|--|---|----------------|
| | | [a.u.] | [a.u.] | [a.u.] | [a.u.] | [a.u.] | |
| | | ϵ_0 | $\epsilon_0 + \text{ZPE}$ | $\epsilon_0 + E_{tot}$ | $\epsilon_0 + H_{corr}$ | $\epsilon_0 + G_{corr}$ | |
| 6-31g(d) | Pinene | -390.708843 | -390.471941 | -390.462154 | -390.461210 | -390.505616 | – |
| | Pinene bond C8–H | -390.079188 | -389.856260 | -389.845401 | -389.845401 | -389.893485 | 73.98 |
| | Pinene bond C5–H | -390.065830 | -389.844644 | -389.833299 | -389.832355 | -389.882267 | 82.16 |
| | Pinene bond C10–H | -390.064658 | -389.841275 | -389.831792 | -389.830848 | -389.875179 | 83.11 |
| | Pinene bond C7–H | -390.056664 | -389.835537 | -389.824540 | -389.823596 | -389.872224 | 87.66 |
| | Pinene bond C6–H | -390.035119 | -389.811436 | -389.801625 | -389.800681 | -389.800681 | 102.04 |
| | Pinene bond C9–H | -390.033759 | -389.811450 | -389.801417 | -389.800473 | -389.845898 | 102.17 |
| | Pinene bond C2–H | -390.032536 | -389.808942 | -389.799074 | -389.798130 | -389.843390 | 103.64 |
| | Pinene bond C4–H | -390.023077 | -389.798840 | -389.789024 | -389.788079 | -389.833281 | 109.95 |
| Def2SVP | Pinene | -390.428322 | -390.193871 | -390.184076 | -390.183132 | -390.227508 | – |
| | Pinene bond C8–H | -389.798736 | -389.579128 | -389.568160 | -389.567216 | -389.617346 | 73.87 |
| | Pinene bond C5–H | -389.787027 | -389.568127 | -389.556749 | -389.555805 | -389.605826 | 81.04 |
| | Pinene bond C10–H | -389.785459 | -389.564175 | -389.554702 | -389.553757 | -389.598022 | 82.32 |
| | Pinene bond C7–H | -389.777872 | -389.559032 | -389.548007 | -389.547063 | -389.595758 | 86.52 |
| | Pinene bond C6–H | -389.754627 | -389.533279 | -389.523462 | -389.522518 | -389.567580 | 101.92 |
| | Pinene bond C9–H | -389.754602 | -389.534857 | -389.524639 | -389.523695 | -389.569475 | 101.18 |
| | Pinene bond C2–H | -389.752097 | -389.530830 | -389.520950 | -389.520006 | -389.565246 | 103.50 |
| | Pinene bond C4–H | -389.742248 | -389.520352 | -389.510525 | -389.509581 | -389.554772 | 110.04 |

Table S5. The energies (with and without zero point correction), enthalpies, free energies (G), and bound dissociation enthalpy (BDE) values for the thymol molecules and its radicals were calculated using B3LYP and water as the PCM model.

| Molecules | | Electronic Energy | Sum of electronic and zero-point Energies | Sum of electronic and thermal Energies | Sum of electronic and thermal Enthalpies | Sum of electronic and thermal Free Energies | BDE [kcal/mol] |
|-----------|-------------------|-------------------|---|--|--|---|----------------|
| | | [a.u.] | [a.u.] | [a.u.] | [a.u.] | [a.u.] | |
| | | ϵ_0 | $\epsilon_0 + \text{ZPE}$ | $\epsilon_0 + E_{tot}$ | $\epsilon_0 + H_{corr}$ | $\epsilon_0 + G_{corr}$ | |
| 6-31g(d) | Thymol | -464.776596 | -464.559153 | -464.547553 | -464.546609 | -464.597260 | – |
| | Thymol bond O–H | -464.143389 | -463.938570 | -463.927308 | -463.926364 | -463.976194 | 76.76 |
| | Thymol bond C7–H | -464.127874 | -463.924706 | -463.912660 | -463.911716 | -463.964917 | 85.95 |
| | Thymol bond C10–H | -464.124821 | -463.920626 | -463.909603 | -463.908659 | -463.957230 | 87.87 |
| | Thymol bond C9–H | -464.103276 | -463.901672 | -463.890244 | -463.889300 | -463.940314 | 100.02 |
| | Thymol bond C8–H | -464.102683 | -463.900181 | -463.888245 | -463.887301 | -463.887301 | 101.27 |
| | Thymol bond C2–H | -464.089812 | -463.885584 | -463.873891 | -463.872946 | -463.924230 | 110.28 |
| | Thymol bond C3–H | -464.086981 | -463.882450 | -463.870837 | -463.869893 | -463.921101 | 112.20 |
| | Thymol bond C5–H | -464.086987 | -463.882211 | -463.870657 | -463.869713 | -463.920262 | 112.31 |
| Def2SVP | Thymol | -464.446307 | -464.230377 | -464.218875 | -464.217930 | -464.267764 | – |
| | Thymol bond O–H | -463.806235 | -463.603106 | -463.591876 | -463.590932 | -463.640595 | 80.83 |
| | Thymol bond C7–H | -463.798723 | -463.596914 | -463.585924 | -463.584980 | -463.634279 | 84.56 |
| | Thymol bond C10–H | -463.795752 | -463.592817 | -463.581838 | -463.580894 | -463.629384 | 87.13 |
| | Thymol bond C9–H | -463.774592 | -463.573671 | -463.561814 | -463.560870 | -463.612099 | 99.69 |
| | Thymol bond C8–H | -463.773767 | -463.572579 | -463.560709 | -463.559765 | -463.611098 | 100.39 |
| | Thymol bond C2–H | -463.759118 | -463.556407 | -463.544787 | -463.543842 | -463.594885 | 110.38 |
| | Thymol bond C3–H | -463.756372 | -463.553505 | -463.541904 | -463.540960 | -463.592329 | 112.19 |
| | Thymol bond C5–H | -463.756234 | -463.553025 | -463.541494 | -463.540549 | -463.591022 | 112.44 |

Table S6. The energies (with and without zero point correction), enthalpies, free energies (G), and bound dissociation enthalpy (BDE) values for the menthol molecules and its radicals were calculated using B3LYP and water as the PCM model.

| Molecules | | Electronic Energy | Sum of electronic and zero-point Energies | Sum of electronic and thermal Energies | Sum of electronic and thermal Enthalpies | Sum of electronic and thermal Free Energies | BDE [kcal/mol] |
|-----------|--------------------|-------------------|---|--|--|---|----------------|
| | | [a.u.] | [a.u.] | [a.u.] | [a.u.] | [a.u.] | |
| | | ϵ_0 | $\epsilon_0 + \text{ZPE}$ | $\epsilon_0 + E_{tot}$ | $\epsilon_0 + H_{corr}$ | $\epsilon_0 + G_{corr}$ | |
| 6-31g(d) | Menthol | -468.398657 | -468.109603 | -468.097407 | -468.096463 | -468.146508 | – |
| | Menthol bond C6–H | -467.741171 | -467.465332 | -467.452765 | -467.452765 | -467.503732 | 91.48 |
| | Menthol bond C4–H | -467.737287 | -467.462931 | -467.450209 | -467.449265 | -467.501841 | 93.67 |
| | Menthol bond C1–H | -467.736156 | -467.461144 | -467.448672 | -467.447728 | -467.499759 | 94.64 |
| | Menthol bond O–H | -467.734646 | -467.459417 | -467.447360 | -467.446416 | -467.446416 | 95.46 |
| | Menthol bond C2–H | -467.732684 | -467.458864 | -467.446221 | -467.445277 | -467.497167 | 96.18 |
| | Menthol bond C3–H | -467.731106 | -467.456837 | -467.444297 | -467.443353 | -467.494840 | 97.38 |
| | Menthol bond C5–H | -467.730480 | -467.455994 | -467.443530 | -467.442586 | -467.494084 | 97.86 |
| | Menthol bond C8–H | -467.728494 | -467.454422 | -467.442182 | -467.441238 | -467.491958 | 98.71 |
| | Menthol bond C10–H | -467.726818 | -467.453073 | -467.440548 | -467.439604 | -467.490944 | 99.74 |
| | Menthol bond C9–H | -467.725786 | -467.451985 | -467.439359 | -467.438415 | -467.490087 | 100.48 |
| Def2SVP | Menthol | -468.064812 | -467.778318 | -467.766109 | -467.765164 | -467.815239 | – |
| | Menthol bond C6–H | -467.409890 | -467.137290 | -467.124904 | -467.123960 | -467.175183 | 89.74 |
| | Menthol bond C4–H | -467.404233 | -467.132427 | -467.119683 | -467.118739 | -467.171407 | 93.02 |
| | Menthol bond C1–H | -467.403011 | -467.130489 | -467.118025 | -467.11708 | -467.168926 | 94.06 |
| | Menthol bond O–H | -467.394396 | -467.121912 | -467.109829 | -467.108885 | -467.159674 | 99.20 |
| | Menthol bond C2–H | -467.399940 | -467.128458 | -467.115860 | -467.114915 | -467.166685 | 95.42 |
| | Menthol bond C3–H | -467.398295 | -467.126447 | -467.113891 | -467.112947 | -467.164486 | 96.65 |
| | Menthol bond C5–H | -467.397400 | -467.125294 | -467.112832 | -467.111888 | -467.163345 | 97.32 |
| | Menthol bond C8–H | -467.393982 | -467.122686 | -467.109984 | -467.109040 | -467.160725 | 99.11 |
| | Menthol bond C10–H | -467.394365 | -467.122858 | -467.110359 | -467.109415 | -467.160694 | 98.87 |
| | Menthol bond C9–H | -467.393240 | -467.121687 | -467.109065 | -467.108121 | -467.159792 | 99.68 |



Scheme S1. Possible oxidation products of selected monoterpenes.