## Supporting information

**Table S1.** Heats of formation by PM3, PDDG and PM6 methods as well as the experimental values (in kJ/mol).

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| **Alkane** | methane | $CH_4$ | −74.6 | −54.5 | −75.0 | −68.1 | −74.3 | −51.4 | −75.4 |
| | ethane | $C_2H_6$ | −84.0 | −76.0 | −94.2 | −78.8 | −84.4 | −66.1 | −89.8 |
| | propane | $C_3H_8$ | −103.8 | −99.0 | −114.7 | −101.1 | −105.3 | −87.6 | −110.9 |
| | butane | $C_4H_{10}$ | −125.7 | −121.8 | −135.0 | −123.1 | −125.9 | −108.8 | −131.7 |
| | iso-butane | $C_4H_{10}$ | −134.2 | −123.7 | −136.7 | −133.8 | −136.0 | −114.9 | −137.7 |
| | pentane | $C_5H_{12}$ | −146.9 | −144.5 | −155.3 | −145.0 | −146.6 | −129.5 | −152.0 |
| | neopentane | $C_5H_{12}$ | −168.0 | −150.1 | −160.3 | −174.9 | −174.6 | −146.2 | −168.4 |
| | isopentane | $C_5H_{12}$ | −153.6 | −144.2 | −155.0 | −154.0 | −155.0 | −132.2 | −154.7 |
| | hexane | $C_6H_{14}$ | −166.9 | −167.2 | −175.6 | −167.0 | −167.2 | −150.4 | −172.5 |
| | 2-methylpentane | $C_6H_{14}$ | −174.6 | −167.5 | −175.8 | −175.8 | −175.5 | −153.3 | −175.4 |
| | 3-methylpentane | $C_6H_{14}$ | −171.9 | −163.7 | −172.4 | −173.0 | −172.9 | −148.9 | −171.0 |
| | 2,2-dimethyltane | $C_6H_{14}$ | −185.9 | −166.3 | −174.8 | −190.8 | −189.6 | −158.7 | −180.7 |
| | 2,3-dimethyltane | $C_6H_{14}$ | −178.1 | −164.4 | −173.1 | −179.9 | −179.3 | −151.9 | −174.0 |
| | heptane | $C_7H_{16}$ | −187.6 | −189.9 | −195.8 | −189.0 | −187.9 | −171.3 | −193.0 |
| | 2-methylhexane | $C_7H_{16}$ | −194.5 | −190.2 | −196.1 | −197.8 | −196.1 | −174.2 | −195.9 |
| | 3-methylhexane | $C_7H_{16}$ | −191.3 | −187.0 | −193.2 | −194.7 | −193.2 | −170.1 | −191.8 |
| | 3-ethylpentane | $C_7H_{16}$ | −189.5 | −182.0 | −188.8 | −189.4 | −188.2 | −163.3 | −185.2 |
| | 2,2-dimethylpentane | $C_7H_{16}$ | −205.7 | −190.0 | −195.9 | −212.3 | −209.8 | −180.0 | −201.6 |
| | 2,3-dimethylpentane | $C_7H_{16}$ | −198.7 | −184.7 | −191.2 | −196.0 | −194.5 | −168.9 | −190.7 |
| | 2,4-dimethylpentane | $C_7H_{16}$ | −201.6 | −191.5 | −197.2 | −204.8 | −202.7 | −177.5 | −199.1 |
| | 3,3-dimethylpentane | $C_7H_{16}$ | −201.0 | −182.9 | −189.6 | −203.3 | −201.3 | −170.1 | −191.8 |
| | 2,2,3-trimethylbutane | $C_7H_{16}$ | −204.4 | −183.4 | −190.0 | −214.0 | −211.4 | −175.0 | −196.7 |
| | octane | $C_8H_{18}$ | −208.5 | −212.7 | −216.2 | −211.0 | −208.5 | −192.1 | −213.4 |
| | 2-methylheptane | $C_8H_{18}$ | −215.3 | −213.0 | −216.4 | −219.7 | −216.8 | −195.0 | −216.3 |
| | 2-methylheptane | $C_8H_{18}$ | −212.5 | −209.2 | −213.0 | −216.6 | −213.8 | −190.9 | −212.2 |
| | 2-methylheptane | $C_8H_{18}$ | −211.9 | −210.1 | −213.8 | −216.3 | −213.5 | −191.2 | −212.5 |
| | 2-ethylhexane | $C_8H_{18}$ | −210.7 | −205.3 | −209.6 | −210.8 | −208.4 | −184.4 | −205.9 |
| | 2,2-dimethylhexane | $C_8H_{18}$ | −224.5 | −212.7 | −216.2 | −234.3 | −230.4 | −200.8 | −222.0 |
| | 2,2-dimethylhexane | $C_8H_{18}$ | −213.8 | −208.1 | −212.1 | −217.7 | −214.9 | −190.0 | −211.4 |
| | 2,2-dimethylhexane | $C_8H_{18}$ | −219.2 | −210.4 | −214.1 | −223.8 | −220.6 | −194.4 | −215.7 |
| | 2,5-dimethylhexane | $C_8H_{18}$ | −222.5 | −212.0 | −215.5 | −227.9 | −224.4 | −197.9 | −219.1 |
| | 3,2-dimethylhexane | $C_8H_{18}$ | −219.9 | −203.7 | −208.1 | −224.3 | −221.1 | −191.6 | −212.9 |
| | 3,2-dimethylhexane | $C_8H_{18}$ | −212.8 | −205.5 | −209.7 | −211.3 | −208.8 | −185.4 | −206.9 |
| | nonane | $C_9H_{20}$ | −228.2 | −235.4 | −236.4 | −233.0 | −229.2 | −213.0 | −233.9 |
| | decane | $C_{10}H_{22}$ | −249.5 | −258.1 | −256.7 | −254.9 | −249.8 | −233.8 | −254.3 |
| | undecane | $C_{11}H_{24}$ | −270.8 | −280.8 | −276.9 | −276.9 | −270.5 | −254.7 | −274.8 |
| | dodecane | $C_{12}H_{26}$ | −289.4 | −303.5 | −297.2 | −298.9 | −291.2 | −275.6 | −295.3 |
| | hexadecane | $C_{16}H_{34}$ | −374.8 | −394.4 | −378.3 | −386.8 | −373.8 | −359.0 | −377.2 |
| | octadecane | $C_{18}H_{38}$ | −414.6 | −439.9 | −418.9 | −430.8 | −415.1 | −400.7 | −418.1 |
| | 5-butyldocosane | $C_{26}H_{54}$ | −587.6 | −618.3 | −578.1 | −606.7 | −580.4 | −562.5 | −576.8 |
| | dotriacontane | $C_{32}H_{66}$ | −697.2 | −758.0 | −702.8 | −738.6 | −704.3 | −692.6 | −704.4 |
| | MAD | | | 11.6 | 6.0 | 6.0 | 3.0 | 21.2 | 4.2 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | MSD | | | −2.7 | 0.0 | −3.4 | 0.0 | 21.2 | −0.1 |
| | RMSD | | | 15.6 | 7.0 | 9.6 | 5.3 | 21.9 | 4.9 |
| **Halogenated alkane** | 1-chloromethane | $CH_3Cl$ | −81.9 | −61.5 | −77.9 | −70.2 | −72.5 | −63.0 | −71.5 |
| | pentachloroethane | $C_2HCl_5$ | −142.0 | −139.9 | −156.8 | −139.1 | −141.6 | −141.2 | −148.5 |
| | 1,1-difluoroethane | $C_2H_4F_2$ | −497.0 | −468.1 | −487.1 | −480.6 | −484.5 | −489.7 | −492.2 |
| | 1,2-dichloroethane | $C_2H_4Cl_2$ | −127.7 | −111.1 | −127.8 | −131.2 | −133.7 | −129.6 | −137.1 |
| | 1,1,1-trichloroethane | $C_2H_3Cl_3$ | −144.4 | −133.7 | −150.5 | −156.1 | −158.7 | −154.1 | −161.3 |
| | iodoethane | $C_2H_5I$ | −8.1 | 8.6 | −7.4 | −3.4 | −5.3 | 5.3 | −4.1 |
| | hexachloroethane | $C_2Cl_6$ | −143.6 | −152.8 | −169.8 | −135.1 | −137.6 | −141.2 | −148.5 |
| | chloroethane | $C_2H_5Cl$ | −112.1 | −92.4 | −109.0 | −104.1 | −106.5 | −99.8 | −107.8 |
| | bromoethane | $C_2H_5Br$ | −61.9 | −47.7 | −64.0 | −53.4 | −55.6 | −54.5 | −63.0 |
| | 1,1-diiodoethane | $C_2H_4I_2$ | 75.0 | 104.4 | 89.0 | 65.3 | 63.6 | 91.5 | 80.9 |
| | 2-bromo-2-chloro-1,1,1-trifluoroethane-trifluoroethane | $C_2HBrClF_3$ | −690.4 | −670.9 | −691.2 | −687.7 | −692.5 | −687.1 | −686.9 |
| | 1,2,2-trichloropropane | $C_3H_5Cl_3$ | −182.9 | −141.5 | −158.4 | −171.6 | −174.2 | −175.0 | −181.9 |
| | 1-chloro-2-methylbutane | $C_5H_{11}Cl$ | −179.9 | −159.4 | −176.4 | −178.4 | −181.0 | −166.3 | −173.3 |
| | 1-chloro-2-methylpropane | $C_4H_9Cl$ | −159.3 | −138.0 | −154.9 | −156.9 | −159.5 | −146.4 | −153.7 |
| | 2,2-dibromo-2-methylbutane | $C_5H_{10}Br_2$ | −137.6 | −130.1 | −147.0 | −140.9 | −143.5 | −131.3 | −138.8 |
| | 1-bromobutane | $C_4H_9Br$ | −107.1 | −92.6 | −109.3 | −96.8 | −99.1 | −96.5 | −104.5 |
| | 2-chloro-2-methylbutane | $C_5H_{11}Cl$ | −202.2 | −174.9 | −192.1 | −214.8 | −217.6 | −201.9 | −208.5 |
| | 2-chloro-2-methylbutane | $C_5H_{11}Cl$ | −185.1 | −166.4 | −183.5 | −195.4 | −198.2 | −183.1 | −189.9 |
| | 1-bromohexane | $C_6H_{13}Br$ | −148.5 | −138.1 | −154.9 | −140.7 | −143.2 | −138.2 | −145.6 |
| | 2-chlorohexane | $C_6H_{13}Cl$ | −204.3 | −191.4 | −208.6 | −212.2 | −215.0 | −202.9 | −209.5 |
| | 1-cholropentane | $C_5H_{11}Cl$ | −174.9 | −160.1 | −177.2 | −169.1 | −171.7 | −162.4 | −169.4 |
| | 1,2-dibromobutane | $C_4H_8Br_2$ | −91.6 | −79.5 | −96.0 | −77.3 | −79.6 | −84.2 | −92.4 |
| | MAD | | | 17.7 | 7.0 | 8.0 | 3.0 | 8.1 | 5.2 |
| | MSD | | | 16.8 | −0.2 | 2.6 | 0.0 | 7.1 | 0.0 |
| | RMSD | | | 19.6 | 10.0 | 8.8 | 8.3 | 9.7 | 6.3 |
| **Alkene** | ethene | $C_2H_4$ | 52.4 | 69.5 | 58.9 | 60.85 | 57.95 | 65.9 | 62.8 |
| | propene | $C_3H_6$ | 20.0 | 29.5 | 21.8 | 22.30 | 22.98 | 24.9 | 22.2 |
| | 1-butene | $C_4H_8$ | 0.1 | 5.8 | −0.1 | 2.02 | 4.59 | 5.3 | 2.8 |
| | trans-2-butene | $C_4H_8$ | −11.4 | −16.0 | −20.3 | −20.63 | −15.95 | −14.1 | −16.3 |
| | cis-2-butene | $C_4H_8$ | −7.1 | −10.5 | −15.2 | −17.55 | −13.15 | −10.1 | −12.3 |
| | isobutene | $C_4H_8$ | −16.9 | −14.1 | −18.6 | −20.78 | 109.29 | −20.8 | −22.9 |
| | 1,2-butadiene | $C_4H_6$ | 110.0 | 129.7 | 114.7 | 117.47 | −15.35 | 119.6 | 115.8 |
| | 1-pentene | $C_5H_{10}$ | −21.1 | −17.0 | −21.3 | −19.98 | −32.01 | −15.9 | −18.1 |
| | cis-2-pentene | $C_5H_{10}$ | −27.6 | −32.8 | −35.9 | −38.35 | −33.48 | −30.2 | −32.2 |
| | trans-2-pentene | $C_5H_{10}$ | −31.9 | −36.7 | −39.6 | −39.97 | −30.78 | −32.8 | −34.8 |
| | 2-methyl-1-butene | $C_5H_{10}$ | −35.2 | −33.1 | −36.2 | −36.99 | −21.77 | −36.3 | −38.2 |
| | 2-methyl-1-butene | $C_5H_{10}$ | −27.5 | −16.7 | −21.0 | −27.06 | −51.17 | −19.0 | −21.1 |
| | 2-methyl-2-butene | $C_5H_{10}$ | −41.7 | −51.2 | −53.0 | −59.48 | 76.68 | −48.9 | −50.7 |
| | 2-methyl-1,2-butadiene | $C_5H_8$ | 75.5 | 94.6 | 82.2 | 78.4 | 73.9 | −79.7 | −76.4 |
| | cis-1,2-pentadiene | $C_5H_8$ | 81.4 | 92.4 | 80.1 | 81.51 | −36.93 | 82.5 | 79.1 |
| | 1,2-pentadiene | $C_5H_8$ | 105.7 | 111.0 | 97.4 | 104.13 | 97.19 | 99.7 | 96.1 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | 1-hexene | $C_6H_{12}$ | −43.5 | −39.7 | −42.3 | −43.78 | −36.93 | −36.7 | −38.6 |
| | cis-2-hexene | $C_6H_{12}$ | −53.9 | −55.5 | −57.0 | −60.40 | −52.01 | −51.2 | −53.0 |
| | 2-methyl-1-pentene | $C_6H_{12}$ | −59.4 | −56.0 | −57.5 | −64.33 | −55.57 | −53.4 | −55.1 |
| | 2-methyl-1-pentene | $C_6H_{12}$ | −49.5 | −36.7 | −39.5 | −47.15 | −39.99 | −36.8 | −38.7 |
| | 2-methyl-cis-2-pentene | $C_6H_{12}$ | −62.3 | −65.1 | −65.9 | −78.67 | −68.58 | −63.4 | −65.0 |
| | 2-methyl-trans-2-pentene | $C_6H_{12}$ | −63.1 | −65.1 | −65.9 | −77.56 | −67.56 | −60.7 | −62.3 |
| | 2-ethyl-1-butene | $C_6H_{12}$ | −56.0 | −40.8 | −43.3 | −59.63 | −51.31 | −44.9 | −46.8 |
| | 2,2-dimethyl-1-butene | $C_6H_{12}$ | −62.4 | −52.9 | −54.5 | −69.68 | −60.42 | −56.9 | −58.5 |
| | 2,2-dimethyl-2-butene | $C_6H_{12}$ | −68.1 | −82.3 | −83.7 | −78.7 | −68.6 | −82.7 | −84.1 |
| | 2-methyl-1-pentene | $C_6H_{12}$ | −59.4 | −56.0 | −57.5 | −64.33 | −55.57 | −58.2 | −59.9 |
| | trans-2-hexene | $C_6H_{12}$ | −52.3 | −59.6 | −60.8 | −57.0 | −48.9 | −54.3 | −56.0 |
| | 1,5-hexadiene | $C_6H_{10}$ | 84.2 | −87.8 | −75.9 | 83.64 | 78.61 | −77.6 | −74.3 |
| | 1-heptene | $C_7H_{14}$ | −62.3 | −62.4 | −63.4 | −90.70 | −95.54 | −57.5 | −59.2 |
| | Cis-2-methyl-2-hexene | $C_7H_{14}$ | −79.4 | −95.2 | −93.8 | −89.16 | −74.86 | −87.1 | −88.5 |
| | 2,2-dimethyl-1-pentene | $C_7H_{14}$ | −83.8 | −77.7 | −77.5 | −90.7 | −79.5 | −83.2 | −84.6 |
| | 4,2-dimethyl-1-pentene | $C_7H_{14}$ | −81.6 | −62.8 | −63.8 | −85.61 | −76.78 | −68.7 | −70.2 |
| | 2,2-dimethyl-2-pentene | $C_7H_{14}$ | −88.7 | −98.5 | −96.9 | −101.90 | −91.56 | −95.8 | −97.0 |
| | 2-ethyl-2-methyl-1-butene | $C_7H_{14}$ | −79.5 | −70.2 | −70.7 | −85.61 | −74.86 | −72.2 | −73.7 |
| | 2,3,2-Trimethyl-1-butene | $C_7H_{14}$ | −85.5 | −68.7 | −69.2 | −101.9 | −89.6 | −77.0 | −78.4 |
| | 1-octene | $C_8H_{16}$ | −81.3 | −85.1 | −84.5 | −87.7 | −76.8 | −78.4 | −79.8 |
| | 2-ethyl-2-methyl-1-pentene | $C_8H_{16}$ | −100.3 | −88.0 | −87.1 | −104.0 | −91.6 | −94.3 | −95.5 |
| | trans-2,2-dimethyl-2-heptene | $C_8H_{16}$ | −89.3 | −99.7 | −98.0 | −124.9 | −110.5 | −100.4 | −101.5 |
| | cis-2,2-dimethyl-2-heptene | $C_8H_{16}$ | −107.7 | −98.9 | −97.2 | −115.7 | −102.2 | −95.7 | −96.9 |
| | MAD | | | 8.4 | 6.9 | 14.6 | 5.8 | 6.0 | 5.7 |
| | MSD | | | 2.3 | 0.1 | −6.4 | 0.0 | 2.1 | 0.5 |
| | RMSD | | | 10.0 | 8.4 | 11.2 | 7.1 | 7.1 | 6.8 |
| **Halogenated alkene** | 1-chloro-2,2-difluoroethene | $C_2HClF_2$ | −315.5 | −350.4 | −342.7 | −357.9 | −350.0 | −372.5 | −348.1 |
| | 2-chloroethene | $C_2H_3Cl$ | −21.0 | −4.7 | −14.0 | 27.5 | 31.0 | −30.4 | −22.6 |
| | trifluoroethene | $C_2HF_3$ | −490.5 | −508.0 | −492.5 | −513.1 | −503.5 | −522.8 | −491.1 |
| | trichloroethene | $C_2HCl_3$ | −9.0 | −9.8 | −19.0 | −6.6 | −2.7 | −21.2 | −13.8 |
| | 3,3,2-trifluoropropene | $C_3H_3F_3$ | −614.2 | −600.7 | −580.7 | −627.0 | −616.0 | −624.7 | −588.1 |
| | 2-iodopropene | $C_3H_5I$ | −91.5 | −113.5 | −98.3 | 108.0 | 110.6 | −96.2 | −97.9 |
| | 2-bromopropene | $C_3H_5Br$ | −45.2 | −56.0 | −43.7 | 51.0 | 54.2 | −41.8 | −46.2 |
| | 1,1-difluoroethene | $C_2H_2F_2$ | −335.0 | −333.0 | −326.2 | −346.0 | −338.3 | −355.9 | −332.3 |
| | trans-1,2-dichloroethene | $C_2H_2Cl_2$ | 5.0 | 14.8 | 4.5 | 0.6 | 4.4 | −5.7 | 1.0 |
| | fluoroethene | $C_2H_3F$ | −138.8 | −119.7 | −123.3 | −133.3 | −128.0 | −139.1 | −126.0 |
| | cis-1,2-dichloroethene | $C_2H_2Cl_2$ | 4.6 | 16.6 | 6.2 | 12.9 | 16.5 | 4.0 | 10.2 |
| | cis-1-bromopropene | $C_3H_5Br$ | 40.8 | 61.8 | 49.2 | 42.2 | 45.4 | 30.4 | 35.3 |
| | tetrafluoroethene | $C_2F_4$ | −658.9 | −703.3 | −678.2 | −699.5 | −687.7 | −707.3 | −666.7 |
| | bromoethene | $C_2H_3Br$ | 79.2 | 99.4 | 84.9 | 79.4 | 82.2 | 72.7 | 75.6 |
| | 1,1-dichloroethene | $C_2H_2Cl_2$ | 2.8 | 12.9 | 2.7 | 0.6 | 4.4 | −5.3 | 1.3 |
| | chloroethene | $C_2H_3Cl$ | 37.2 | 40.6 | 29.0 | 27.5 | 31.0 | 24.6 | 29.8 |
| | MAD | | | 16.1 | 9.8 | 14.6 | 12.9 | 15.5 | 7.7 |
| | MSD | | | 0.0 | 0.0 | −3.6 | 1.9 | 0.0 | 0.0 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | RMSD | 17.0 | | 19.6 | 13.5 | 21.1 | 18.9 | 22.3 | 11.7 |
| **Cycloalkane** | cyclopropane | $C_3H_6$ | 53.3 | 67.9 | 77.5 | −13.7 | −3.5 | 47.3 | 75.2 |
| | cyclobutane | $C_4H_8$ | 27.7 | −16.0 | −6.5 | 21.5 | 33.5 | −14.4 | 3.0 |
| | methylcyclopropane | $C_4H_8$ | 25.7 | 35.6 | 33.0 | −18.6 | −8.6 | 17.0 | 21.7 |
| | 1,1-dimethylcyclopropane | $C_5H_{10}$ | −8.2 | 3.1 | 12.6 | −87.4 | −80.8 | −16.3 | 0.7 |
| | cyclopetane | $C_5H_{10}$ | −76.4 | −100.1 | −90.6 | −115.3 | −110.1 | −84.0 | −78.5 |
| | cyclohexane | $C_6H_{12}$ | −123.4 | −130.0 | −120.5 | −118.5 | −113.5 | −114.7 | −114.4 |
| | methylcyclopentane | $C_6H_{12}$ | −106.2 | −125.4 | −115.9 | −67.2 | −59.7 | −112.3 | −111.6 |
| | ethylcyclobutane | $C_6H_{12}$ | −27.5 | −62.3 | −52.8 | 56.4 | 70.1 | −58.1 | −48.2 |
| | cycloheptane | $C_7H_{14}$ | −118.1 | −129.4 | −119.9 | −113.7 | −108.5 | −118.7 | −119.1 |
| | 1,1-dimethylcyclopetane | $C_7H_{14}$ | −138.2 | −150.7 | −141.2 | −156.7 | −153.6 | −140.3 | −144.4 |
| | ethylcyclopetane | $C_7H_{14}$ | −126.9 | −146.2 | −136.7 | −139.4 | −135.4 | −130.6 | −133.0 |
| | methylcyclohexane | $C_7H_{14}$ | −154.7 | −154.5 | −145.0 | −147.8 | −144.3 | −142.4 | −146.9 |
| | cis-1,2-dimethylcyclopetane | $C_7H_{14}$ | −135.8 | −149.2 | −139.7 | −148.0 | −144.5 | −139.7 | −143.7 |
| | cyclooctane | $C_8H_{16}$ | −124.4 | −119.3 | −109.8 | −92.5 | −86.3 | −112.0 | −111.3 |
| | ethylcyclohexane | $C_8H_{16}$ | −171.5 | −174.9 | −165.5 | −164.1 | −161.4 | −159.6 | −167.0 |
| | 1,1-dimethylcyclohexane | $C_8H_{16}$ | −180.9 | −174.3 | −164.9 | −183.7 | −182.0 | −167.0 | −175.7 |
| | cis-1,2-dimethycyclohexane | $C_8H_{16}$ | −172.1 | −168.9 | −159.5 | −172.2 | −169.9 | −158.8 | −166.1 |
| | trans-1,2-dimethylcyclohexane | $C_8H_{16}$ | −184.5 | −169.5 | −160.1 | −172.6 | −170.3 | −158.0 | −165.1 |
| | propylcyclopentane | $C_8H_{16}$ | −147.7 | −169.1 | −159.7 | −158.3 | −155.3 | −151.7 | −157.7 |
| | trans-1-ethyl-2-methylcyclopentane | $C_8H_{16}$ | −156.2 | −173.1 | −163.7 | −164.6 | −161.9 | −155.9 | −162.7 |
| | MAD | | | 15.1 | 13.1 | 12.9 | 12.2 | 11.0 | 9.6 |
| | MSD | | | −9.5 | 0.0 | −5.5 | 0.0 | −1.1 | 0.0 |
| | RMSD | | | 18.3 | 15.7 | 17.1 | 15.9 | 15.1 | 11.7 |
| **Cycloalkene** | cyclopropene | $C_3H_4$ | 277.1 | 285.1 | 273.3 | 262.2 | 270.5 | 255.3 | 268.9 |
| | cyclopentene | $C_5H_8$ | 34.0 | 12.4 | 31.4 | 18.3 | 33.5 | 21.7 | 36.3 |
| | cycloButene | $C_4H_6$ | 156.7 | 157.4 | 160.0 | 150.2 | 161.7 | 141.6 | 155.7 |
| | cyclohexene | $C_6H_{10}$ | −5.0 | −20.6 | 2.1 | −7.0 | 9.0 | −16.2 | −1.5 |
| | 1-methylcyclopentene | $C_6H_{10}$ | −3.8 | −29.7 | −5.9 | −22.1 | −5.7 | −22.6 | −7.8 |
| | 2-methylcyclopentene | $C_6H_{10}$ | 7.4 | −12.8 | 9.0 | −11.7 | 4.4 | −5.9 | 8.8 |
| | 2-methylcyclopentene | $C_6H_{10}$ | 14.6 | 11.2 | 10.5 | −10.1 | 6.0 | −4.3 | 10.3 |
| | 1-ethylcyclopentene | $C_7H_{12}$ | −19.8 | −48.9 | −23.0 | −41.0 | −24.0 | −38.8 | −24.0 |
| | 1,2-cyclopentadiene | $C_5H_6$ | 134.3 | 132.7 | 138.1 | 128.0 | 140.1 | 134.8 | 148.9 |
| | MAD | | | 16.5 | 3.5 | 14.3 | 5.5 | 14.6 | 4.8 |
| | MSD | | | −5.6 | −0.7 | −14.3 | 0.0 | −9.3 | 0.9 |
| | RMSD | | | 17.4 | 3.8 | 16.0 | 6.7 | 14.8 | 6.3 |
| **Alkanol** | carbinol | $CH_4O$ | −201.0 | −217.0 | −222.2 | −205.0 | −197.6 | −202.0 | −212.3 |
| | ethanol | $C_2H_6O$ | −234.8 | −237.9 | −241.7 | −230.5 | −224.5 | −229.3 | −238.1 |
| | 1-propanol | $C_3H_8O$ | −255.1 | −260.3 | −262.6 | −252.0.7.6 | −247.2 | −251.1 | −258.7 |
| | 1-butanol | $C_4H_{10}O$ | −274.9 | −282.8 | −283.5 | −273.7.8 | −270.1 | −271.2 | −277.7 |
| | 2-methyl-2-propanol | $C_4H_{10}O$ | −312.5 | −298.2 | −297.9 | −324.3.0 | −324.6 | −313.8 | −318.0 |
| | 2-methyl-1-propanol | $C_4H_{10}O$ | −283.8 | −277.1 | −278.2 | −280.0.5 | −276.8 | −268.9 | −275.6 |
| | 1-pentanol | $C_5H_{12}O$ | −294.6 | −305.5 | −304.7 | −295.7.7 | −293.4 | −292.3 | −297.7 |
| | 2-pentanol | $C_5H_{12}O$ | −311.0 | −309.2 | −308.1 | −313.4.6 | −312.1 | −309.7 | −314.1 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | 2-pentanol | $C_5H_{12}O$ | −314.9 | −308.9 | −307.9 | −312.3 | −311.0 | −306.5 | −311.1 |
| | 2-methyl-1-butanol | $C_5H_{12}O$ | −300.7 | −305.5 | −304.7 | −304.2.2 | −302.4 | −296.1 | −301.3 |
| | 2-methyl-2-butanol | $C_5H_{12}O$ | −329.3 | −313.8 | −312.4 | −337.6.0 | −337.7 | −326.6 | −330.1 |
| | 1-hexanol | $C_6H_{14}O$ | −315.9 | −328.2 | −325.9 | −317.6.4 | −316.6 | −313.0 | −317.2 |
| | 2-hexanol | $C_6H_{14}O$ | −333.5 | −331.9 | −329.3 | −335.2.2 | −335.2 | −330.4 | −333.7 |
| | 1-heptanol | $C_7H_{16}O$ | −336.5 | −351.0 | −347.1 | −339.6.3 | −339.8 | −333.9 | −337.0 |
| | 1-octanol | $C_8H_{18}O$ | −355.6 | −373.7 | −368.3 | −361.6.7 | −363.0 | −354.7 | −356.6 |
| | 2-ethyl-1-hexanol | $C_8H_{18}O$ | −365.3 | −365.6 | −360.7 | −359.9.8 | −360.9 | −358.3 | −360.0 |
| | 1-nonanol | $C_9H_{20}O$ | −376.5 | −396.4 | −389.4 | −383.5.6 | −386.2 | −375.6 | −376.4 |
| | 1-decanol | $C_{10}H_{22}O$ | −396.6 | −419.1 | −410.6 | −405.5.6 | −409.5 | −396.4 | −396.0 |
| | 1-dodecanol | $C_{12}H_{26}O$ | −436.6 | −464.6 | −453.0 | −449.5.2 | −455.9 | −438.1 | −435.5 |
| | 1-hexadecanol | $C_{16}H_{34}O$ | −517.0 | −555.5 | −537.8 | −537.4 | −548.9 | −521.5 | −514.3 |
| | ethylene glycol | $C_2H_6O_2$ | −392.2 | −398.3 | −391.2 | −380.2.6 | −382.7 | −399.8 | −399.3 |
| | 1,2-propanediol | $C_3H_8O_2$ | −408.0 | −358.8 | −354.4 | −371.9 | −373.9 | −385.7 | −385.9 |
| | 1,2-propanediol | $C_3H_8O_2$ | −429.8 | −419.9 | −411.3 | −400.7 | −404.4 | −427.3 | −425.2 |
| | 2,2-butanediol | $C_4H_{10}O_2$ | −482.3 | −448.6 | −438.1 | −456.8 | −463.7 | −476.3 | −471.6 |
| | 1,2-butanediol | $C_4H_{10}O_2$ | −428.7 | −444.1 | −433.9 | −424.6 | −429.6 | −433.7 | −431.3 |
| | 1,2-butanediol | $C_4H_{10}O_2$ | −433.2 | −448.2 | −465.1 | −442.6 | −448.6 | −469.1 | −431.3 |
| | 1,5−pentanediol | $C_5H_{10}O_2$ | −450.8 | −466.2 | −454.5 | −445.8 | −452.1 | −453.6 | −450.1 |
| | pentaerythritol | $C_5H_{10}O_4$ | −776.7 | −811.4 | −776.3 | −734.9 | −757.6 | −810.4 | −787.3 |
| | MAD | | | 15.8 | 12.4 | 9.9 | 9.8 | 6.9 | 4.3 |
| | MSD | | | −5.4 | −0.8 | 2.6 | 0.0 | 0.1 | 0.2 |
| | RMSD | | | 19.3 | 18.0 | 14.5 | 13.4 | 11.2 | 6.4 |
| **Carboxylic acid** | formic acid | $CH_2O_2$ | −378.7 | −394.9 | −398.5 | −389.9 | −388.2 | −367.3 | −374.9 |
| | acetic acid | $C_2H_4O_2$ | −432.2 | −426.6 | −429.8 | −432.4 | −430.9 | −423.0 | −433.3 |
| | propionic acid | $C_3H_6O_2$ | −455.7 | −441.0 | −444.0 | −448.6 | −447.2 | −435.3 | −446.2 |
| | butyric acid | $C_4H_8O_2$ | −457.9 | −467.6 | −470.2 | −471.0 | −469.7 | −461.5 | −473.7 |
| | pentanoic acid | $C_5H_{10}O_2$ | −492.0 | −490.2 | −492.5 | −488.4 | −487.2 | −482.0 | −495.2 |
| | hexanoic acid | $C_6H_{12}O_2$ | −511.9 | −512.8 | −514.8 | −510.4 | −509.3 | −502.8 | −517.1 |
| | heptylic acid | $C_7H_{14}O_2$ | −536.2 | −531.7 | −533.4 | −536.6 | −535.6 | −520.4 | −535.5 |
| | octanoic acid | $C_8H_{16}O_2$ | −554.3 | −554.4 | −555.8 | −558.6 | −557.7 | −541.2 | −557.4 |
| | 2,2-dimethylpropanoic acid | $C_5H_{10}O_2$ | −491.3 | −483.5 | −485.9 | −506.6 | −505.4 | −486.5 | −500.0 |
| | 2-methylbutanoic acid | $C_5H_{10}O_2$ | −510.0 | −488.7 | −491.0 | −499.7 | −498.6 | −488.7 | −502.3 |
| | 2-ethylhexoic acid | $C_8H_{16}O_2$ | −559.5 | −545.7 | −547.2 | −556.2 | −555.3 | −536.1 | −552.0 |
| | oxalic acid | $C_2H_2O_4$ | −731.8 | −738.2 | −737.0 | −746.6 | −746.7 | −679.1 | −702.0 |
| | butanedioic acid | $C_4H_6O_4$ | −823.0 | −810.2 | −807.9 | −810.6 | −810.9 | −804.5 | −833.6 |
| | dodecanoic acid | $C_{12}H_{24}O_2$ | −642.0 | −649.1 | −649.1 | −639.8 | −639.3 | −624.6 | −644.9 |
| | tetradecanoic acid | $C_{14}H_{28}O_2$ | −693.7 | −694.5 | −693.9 | −690.4 | −690.2 | −669.5 | −692.0 |
| | pentadecanoic acid | $C_{15}H_{30}O_2$ | −699.0 | −717.3 | −716.4 | −712.4 | −712.3 | −687.1 | −710.4 |
| | hexadecanoic acid | $C_{16}H_{32}O_2$ | −737.1 | −740.0 | −738.7 | −734.4 | −734.4 | −711.2 | −735.7 |
| | MAD | | | 8.2 | 8.1 | 6.1 | 6.3 | 17.2 | 7.3 |
| | MSD | | | 1.2 | 0.1 | −0.9 | 0.0 | 16.8 | 0.0 |
| | RMSD | | | 10.7 | 10.5 | 7.8 | 7.7 | 20.4 | 10.1 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| **Amino acid** | aminopentanoic acid | $C_5H_{11}NO_2$ | −460.0 | −445.3 | −458.6 | −465.2 | −456.7 | −446.2 | −462.5 |
| | glycine | $C_2H_5NO_2$ | −392.1 | −392.3 | −382.7 | −399.8 | −375.5 | −374.7 | −376.6 |
| | oxamic acid | $C_2H_3NO_3$ | −552.3 | −535.7 | −555.6 | −517.0 | −567.1 | −508.2 | −536.9 |
| | 2-aminobutyric acid | $C_4H_9NO_2$ | −441.0 | −436.4 | −435.8 | −442.3 | −434.0 | −426.8 | −439.2 |
| | 2-amino-2-methylbutyric acid | $C_5H_{11}NO_2$ | −455.1 | −452.2 | −454.8 | −481.0 | −450.8 | −456.0 | −474.3 |
| | 2-amino-2-methylpentanoic acid | $C_6H_{13}NO_2$ | −486.8 | −480.1 | −488.5 | −506.4 | −488.7 | −478.0 | −500.7 |
| | l-proline | $C_5H_9NO_2$ | −366.6 | −416.6 | −411.9 | −402.8 | −345.0 | −398.9 | −405.7 |
| | sarcosine | $C_3H_7NO_2$ | −367.3 | −403.3 | −396.0 | −396.0 | −345.9 | −377.4 | −379.9 |
| | l-alanine | $C_3H_7NO_2$ | −465.9 | −421.0 | −417.3 | −436.9 | −463.8 | −413.2 | −422.9 |
| | b-alanine | $C_3H_7NO_2$ | −424.0 | −414.8 | −409.8 | −422.1 | −413.7 | −404.5 | −412.5 |
| | MAD | | | 17.6 | 15.8 | 19.1 | 10.3 | 21.4 | 17.5 |
| | MSD | | | 1.3 | 0.0 | −5.9 | 7.0 | 12.7 | 0.0 |
| | RMSD | | | 25.4 | 23.6 | 23.2 | 12.7 | 26.5 | 21.7 |
| **Aldehyde** | acetaldehyde | $C_2H_4O$ | −166.2 | −185.1 | −164.8 | −180.3 | −163.0 | −159.6 | −167.6 |
| | glyoxal | $C_2H_2O_2$ | −212.0 | −269.3 | −242.7 | −259.4 | −238.8 | −191.6 | −201.0 |
| | trichloroacetaldehyde | $C_2HCl_3O$ | −196.6 | −217.3 | −194.6 | −213.8 | −195.1 | −197.5 | −207.1 |
| | propionaldehyde | $C_3H_6O$ | −185.6 | −205.9 | −184.1 | −201.1 | −183.0 | −177.4 | −186.2 |
| | isobutyraldehyde | $C_4H_8O$ | −215.7 | −229.3 | −205.7 | −259.4 | −238.8 | −198.7 | −208.4 |
| | butanal | $C_4H_8O$ | −204.8 | −229.1 | −205.5 | −230.9 | −211.5 | −198.1 | −207.7 |
| | pentanal | $C_5H_{10}O$ | −228.4 | −251.8 | −226.5 | −244.8 | −244.8 | −219.1 | −229.7 |
| | octanal | $C_8H_{16}O$ | −291.1 | −319.3 | −289.0 | −310.6 | −287.8 | −281.4 | −294.6 |
| | heptanal | $C_7H_{14}O$ | −263.8 | −296.6 | −268.0 | −288.7 | −266.8 | −260.6 | −272.9 |
| | 2-ethylhexylaldehyde | $C_8H_{16}O$ | −299.6 | −312.7 | −282.8 | −311.4 | −288.5 | −274.8 | −287.7 |
| | MAD | | | 25.3 | 7.1 | 20.1 | 6.0 | 10.7 | 6.0 |
| | MSD | | | −25.3 | 0.0 | −20.1 | 0.0 | 10.5 | 0.0 |
| | RMSD | | | 28.0 | 11.7 | 22.3 | 9.5 | 12.9 | 7.3 |
| **Ester** | methyl-cyclobutanecarboxylate | $C_6H_{10}O_2$ | −350.2 | −353.4 | −368.6 | −364.0 | −369.4 | −371.5 | −375.5 |
| | dimethyl sulfate | $C_2H_6O_4S$ | −687.0 | −719.9 | −739.1 | −700.3 | −708.5 | −690.4 | −704.3 |
| | s-ethyl thioacetate | $C_4H_8OS$ | −228.1 | −240.7 | −254.7 | −240.7 | −245.1 | −239.5 | −239.5 |
| | diethyl carbonate | $C_5H_{10}O_3$ | −637.9 | −599.3 | −617.2 | −610.6 | −618.1 | −610.6 | −622.1 |
| | methyl-2,2-dimethylpropanoate | $C_6H_{12}O_2$ | −491.2 | −449.5 | −465.8 | −481.7 | −488.1 | −469.4 | −476.5 |
| | butyl acetate | $C_5H_{10}O_2$ | −481.6 | −436.6 | −452.7 | −475.8 | −482.2 | −475.6 | −482.9 |
| | ethyl acetate | $C_4H_8O_2$ | −443.6 | −413.9 | −429.8 | −470.6 | −476.9 | −441.4 | −447.6 |
| | butyl acetate | $C_6H_{12}O_2$ | −485.3 | −460.5 | −476.9 | −432.0 | −437.9 | −481.7 | −489.2 |
| | methyl pentanoate | $C_6H_{12}O_2$ | −471.1 | −457.4 | −473.8 | −467.8 | −474.1 | −465.9 | −472.9 |
| | methyl methanoate | $C_2H_4O_2$ | −357.4 | −352.8 | −368.0 | −358.4 | −363.8 | −352.8 | −356.3 |
| | propyl formate | $C_4H_8O_2$ | −462.7 | −406.8 | −422.6 | −404.4 | −410.1 | −406.8 | −411.9 |
| | ethyl propanoate | $C_5H_{10}O_2$ | −463.4 | −432.3 | −448.4 | −444.9 | −451.0 | −457.4 | −464.1 |
| | propiolactone | $C_3H_4O_2$ | −282.9 | −260.5 | −274.7 | −274.2 | −278.9 | −275.4 | −276.5 |
| | diethyl oxalate | $C_6H_{10}O_4$ | −742.0 | −718.8 | −738.0 | −741.4 | −750.0 | −728.9 | −744.0 |
| | butyrolactone | $C_4H_{10}O_2$ | −366.5 | −382.8 | −398.3 | −391.2 | −396.8 | −381.3 | −385.6 |
| | MAD | | | 25.4 | 20.8 | 14.9 | 14.0 | 12.9 | 11.0 |
| | MSD | | | 15.9 | −0.2 | 6.2 | 0.0 | 6.5 | 0.2 |
| | RMSD | | | 29.3 | 24.5 | 20.2 | 19.2 | 18.6 | 16.9 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| **Aromatic compound** | 2-nitroaniline | $C_6H_6N_2O_2$ | 58.4 | 73.5 | 63.7 | 33.4 | 31.9 | 70.1 | 64.5 |
| | 2-methylaniline | $C_7H_9N$ | 55.3 | 63.4 | 53.6 | 50.7 | 49.1 | 53.2 | 47.9 |
| | aniline-2-carboxylic acid | $C_7H_7NO_2$ | −296.7 | −271.9 | −279.3 | −284.2 | −283.9 | −292.5 | −292.3 |
| | 2-nitroaniline | $C_6H_6N_2O_2$ | 58.8 | 72.9 | 63.1 | 56.9 | 55.3 | 51.7 | 46.4 |
| | 2-nitrotoluene | $C_7H_7NO_2$ | 31.0 | 19.2 | 9.7 | 8.5 | 7.1 | 31.4 | 26.4 |
| | benzene | $C_6H_6$ | 82.9 | 98.0 | 88.0 | 97.0 | 95.1 | 102.1 | 96.0 |
| | aniline | $C_6H_7N$ | 87.5 | 89.0 | 79.1 | 91.6 | 89.8 | 90.3 | 84.4 |
| | benzoxazole | $C_7H_5NO$ | 44.8 | 66.5 | 56.7 | 38.9 | 37.4 | 70.3 | 64.7 |
| | phenol | $C_6H_6O$ | −96.4 | −90.7 | −99.4 | −90.0 | −90.8 | −87.4 | −90.5 |
| | phenylhydrazine | $C_6H_8N_2$ | 202.9 | 199.2 | 188.5 | 200.7 | 198.2 | 176.0 | 168.7 |
| | benzylamine | $C_7H_9N$ | 94.4 | 91.7 | 81.7 | 87.4 | 85.6 | 99.6 | 93.6 |
| | phenylcarbinol | $C_7H_8O$ | −100.4 | −93.7 | −102.4 | −83.7 | −84.5 | −88.2 | −91.2 |
| | cyanobenzene | $C_7H_5N$ | 215.7 | 244.4 | 233.4 | 234.7 | 232.0 | 232.3 | 224.1 |
| | anisole | $C_7H_8O$ | −67.9 | −61.2 | −70.1 | −75.6 | −76.5 | −69.6 | −72.9 |
| | benzaldehyde | $C_7H_6O$ | −36.7 | −44.8 | −53.8 | −39.7 | −40.7 | −11.2 | −15.5 |
| | benzoic acid | $C_7H_6O_2$ | −249 | −276.8 | −284.2 | −278.8 | −278.4 | −269.2 | −269.3 |
| | benzamide | $C_7H_7NO$ | −100.9 | −67.7 | −76.5 | −83.2 | −84.0 | −76.2 | −79.4 |
| | benzenethiol | $C_6H_6O$ | 113.0 | 115.6 | 105.5 | 122.0 | 120.0 | 101.6 | 95.5 |
| | toluene | $C_7H_8$ | 50.5 | 58.8 | 49.1 | 56.0 | 54.3 | 60.4 | 55.0 |
| | resorcinol | $C_6H_6O_2$ | −274.7 | −281.4 | −288.7 | −297.3 | −296.9 | −284.3 | −284.2 |
| | catechol | $C_6H_6O_2$ | −267.5 | −272.0 | −279.4 | −283.3 | −283.0 | −259.4 | −259.7 |
| | hexafluorobenzene | $C_6F_6$ | −995.4 | −959.0 | −961.6 | −957.3 | −953.0 | −991.2 | −979.8 |
| | hexachlorobenzene | $C_6Cl_6$ | −35.5 | −38.4 | −47.5 | 2.8 | 1.5 | −41.0 | −44.8 |
| | (chloromethyl)benzene | $C_7H_7Cl$ | 18.9 | 47.6 | 37.9 | 41.3 | 39.8 | 39.9 | 34.8 |
| | nitrobenzene | $C_6H_5NO_2$ | 68.5 | 60.5 | 50.8 | 52.4 | 50.8 | 78.7 | 73.0 |
| | iodobenzene | $C_6H_5I$ | 164.9 | 187.0 | 176.4 | 167.2 | 164.9 | 168.3 | 161.2 |
| | cluorobenzene | $C_6H_5F$ | −115.9 | −84.7 | −93.4 | −93.8 | −94.6 | −100.9 | −103.7 |
| | chlorobenzene | $C_6H_5Cl$ | 52.0 | 69.6 | 59.8 | 62.4 | 60.7 | 58.1 | 52.7 |
| | chloropentafluorobenzene | $C_6ClF_5$ | −809.3 | −804.0 | −807.7 | −802.9 | −799.5 | −850.8 | −841.6 |
| | 1,2,2-benzenetriol | $C_6H_6O_3$ | −434.2 | −455.2 | −461.3 | −472.4 | −471.0 | −439.2 | −436.6 |
| | 1,2,2-benzenetriol | $C_6H_6O_3$ | −444 | −458.8 | −464.9 | −476.8 | −475.3 | −444.7 | −442.0 |
| | 1,3,5−benzenetriol | $C_6H_6O_3$ | −452.9 | −471.6 | −477.6 | −495.0 | −493.5 | −484.3 | −481.0 |
| | 2-fluorotoluene | $C_7H_7F$ | −147.1 | −124.0 | −132.5 | −134.8 | −135.3 | −140.6 | −142.8 |
| | (nitromethyl)benzene | $C_7H_{10}N$ | 30.7 | 47.9 | 38.2 | 42.4 | 40.8 | 48.3 | 43.1 |
| | 1,2,2-trichlorobenzene | $C_6H_3Cl_3$ | 3.8 | 23.7 | 14.2 | 29.3 | 27.8 | 8.6 | 4.0 |
| | 1,2,2-trichlorobenzene | $C_6H_3Cl_3$ | −8.1 | 19.9 | 10.4 | 13.4 | 12.1 | −4.5 | −8.9 |
| | 1,3,5−trichlorobenzene | $C_6H_3Cl_3$ | −13.4 | 16.4 | 7.0 | −3.1 | −4.4 | −18.3 | −22.5 |
| | 2-methylaniline | $C_7H_9N$ | 56.4 | 55.0 | 45.3 | 41.3 | 39.7 | 57.7 | 52.3 |
| | 2-hydroxybenzoic acid | $C_7H_6O_3$ | −494.8 | −473.5 | −479.5 | −471.6 | −470.2 | −451.3 | −448.5 |
| | aniline-2-carboxylic acid | $C_7H_7NO_2$ | −296 | −280.9 | −288.3 | −276.1 | −275.8 | −300.6 | −300.2 |
| | 2-nitroaniline | $C_6H_6N_2O_2$ | 63.8 | 71.7 | 61.9 | 41.0 | 39.5 | 47.0 | 41.8 |
| | 2-methylaniline | $C_7H_9N$ | 54.6 | 50.0 | 40.3 | 36.1 | 34.6 | 45.7 | 40.5 |
| | Aniline-2-carboxylic acid | $C_7H_7NO_2$ | −283.6 | −270.3 | −277.7 | −289.0 | −288.6 | −276.8 | −276.8 |
| | MAD | | | 15.0 | 13.1 | 16.5 | 16.4 | 12.0 | 11.3 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | MSD | | | 8.7 | 0.0 | 0.7 | 0 | 2.8 | 0.0 |
| | RMSD | | | 18.0 | 15.6 | 19.7 | 19.6 | 15.9 | 15.1 |
| **Ketone** | Propanone | $C_3H_6O$ | −217.1 | −223.2 | −214.0 | −304.1 | −291.5 | −227.5 | −218.3 |
| | 1,2-propanedione | $C_3H_4O_2$ | −271.0 | −309.8 | −306.2 | −251.2 | −242.6 | −260.8 | −257.8 |
| | 2-butanone | $C_4H_8O$ | −238.5 | −242.3 | −234.3 | −291.5 | −279.9 | −240.7 | −234.0 |
| | 2-hexanone | $C_6H_{12}O$ | −278.9 | −287.7 | −282.7 | −293.1 | −281.4 | −283.4 | −284.7 |
| | 2-methyl-2-pentanone | $C_6H_{12}O$ | −286.0 | −280.7 | −275.2 | −273.0 | −262.8 | −274.1 | −273.7 |
| | 2-pentanone | $C_5H_{10}O$ | −258.8 | −263.5 | −256.9 | −282.9 | −271.9 | −263.0 | −260.5 |
| | 2-hexanone | $C_6H_{12}O$ | −277.6 | −282.4 | −277.0 | −276.3 | −265.8 | −275.3 | −275.1 |
| | 2-methyl-2-butanone | $C_5H_{10}O$ | −262.6 | −261.7 | −255.0 | −268.1 | −258.3 | −260.6 | −257.6 |
| | 2-pentanone | $C_5H_{10}O$ | −257.9 | −260.6 | −253.8 | −243.0 | −235.0 | −254.3 | −250.1 |
| | cyclohexanone | $C_6H_{10}O$ | −226.1 | −251.9 | −244.5 | −226.0 | −219.3 | −249.7 | −244.6 |
| | cyclopentanone | $C_5H_8O$ | −192.1 | −231.0 | −222.3 | −169.8 | −167.3 | −225.1 | −215.4 |
| | bromoacetone | $C_3H_5BrO$ | −181.0 | −180.7 | −168.7 | −311.6 | −298.5 | −197.4 | −182.5 |
| | 2-heptanone | $C_7H_{14}O$ | −297.1 | −303.2 | −299.2 | −311.5 | −298.4 | −295.7 | −299.3 |
| | 2-heptanone | $C_7H_{14}O$ | −298.3 | −303.7 | −299.7 | −324.9 | −310.8 | −298.1 | −302.2 |
| | 2,2-dimethyl-2-pentanone | $C_7H_{14}O$ | −313.6 | −300.0 | −295.8 | −318.2 | −304.6 | −296.5 | −300.3 |
| | 2,4dimethyl-2-pentanone | $C_7H_{14}O$ | −313.3 | −300.7 | −296.5 | −357.9 | −341.4 | −293.3 | −296.5 |
| | 2-nonanone | $C_9H_{18}O$ | −340.7 | −354.2 | −353.5 | −348.4 | −332.6 | −345.9 | −359.0 |
| | 2,2,2-trimethyl-2-pentanone | $C_8H_{16}O$ | −338.3 | −322.0 | −319.2 | −355.3 | −339.0 | −316.9 | −324.5 |
| | 5-nonanone | $C_9H_{18}O$ | −344.9 | −348.7 | −347.6 | −371.1 | −353.5 | −338.9 | −350.7 |
| | 2,6-dimethyl-2-heptanone | $C_9H_{18}O$ | −357.6 | −350.4 | −349.4 | −201.8 | −196.8 | −350.9 | −364.9 |
| | MSD | | | 11.2 | 10.7 | 14.1 | 7.1 | 10.1 | 8.9 |
| | MSD | | | −5.4 | 0.0 | −11.4 | 0.0 | 0.2 | 0.0 |
| | RMSD | | | 15.4 | 14.3 | 15.8 | 10.3 | 13.4 | 11.1 |
| **Heterocyclic compound** | 1-methylpyrrole | $C_4H_5N$ | 103.1 | 108.0 | 110.6 | 105.6 | 118.7 | 104.9 | 101.9 |
| | 2-nitrofuran | $C_4H_3NO_3$ | −28.8 | −43.7 | −41.1 | −86.3 | −68.7 | −17.1 | −15.5 |
| | 2,2-dimethylpyridine | $C_7H_9N$ | 67.1 | 51.1 | 53.7 | 39.9 | 54.5 | 63.3 | 61.9 |
| | 2,2-dihydrothiophene | $C_4H_6S$ | 90.7 | 55.9 | 58.5 | 48.5 | 63.0 | 48.6 | 47.7 |
| | 2,5-dihydrothiophene | $C_4H_6S$ | 86.9 | 61.9 | 64.5 | 50.7 | 65.1 | 47.5 | 46.7 |
| | 2-methylpyridine | $C_6H_7N$ | 99.2 | 88.3 | 90.9 | 81.5 | 95.2 | 97.6 | 94.9 |
| | 2-methylpyrrole | $C_5H_7N$ | 74.0 | 70.9 | 73.5 | 65.0 | 79.0 | 65.5 | 64.0 |
| | 2-methylthiophene | $C_5H_6S$ | 83.5 | 96.8 | 99.4 | 81.2 | 94.9 | 79.8 | 77.8 |
| | 2-methyl-2-oxazoline | $C_4H_7NO$ | −130.5 | −134.5 | −131.9 | −143.5 | −124.6 | −136.7 | −130.6 |
| | 2-methylpyridine | $C_6H_7N$ | 106.4 | 86.9 | 89.5 | 79.6 | 93.4 | 102.7 | 99.8 |
| | 2-methylpyrrole | $C_4H_5N$ | 70.2 | 74.0 | 76.6 | 67.9 | 81.9 | 69.8 | 68.1 |
| | 2-methylthiophene | $C_6H_7N$ | 82.5 | 87.9 | 90.5 | 78.5 | 92.2 | 86.3 | 84.0 |
| | 2-methylpyridine | $C_6H_7N$ | 103.8 | 86.6 | 89.2 | 78.3 | 92.1 | 97.0 | 94.3 |
| | oxazole | $C_3H_3NO$ | −15.5 | −6.3 | −3.7 | −42.5 | −26.0 | −6.5 | −5.3 |
| | furan | $C_4H_4O$ | −34.8 | −17.0 | −14.4 | −50.5 | −33.8 | −34.0 | −31.8 |
| | furancarbinol | $C_4H_4O_2$ | −211.8 | −216.4 | −213.9 | −225.5 | −204.7 | −230.6 | −221.0 |
| | furfural | $C_5H_4O_2$ | −151.0 | −153.9 | −151.3 | −180.3 | −160.6 | −127.0 | −121.3 |
| | 2-furancarboxylic acid | $C_5H_4O_3$ | −390.0 | −383.1 | −380.6 | −417.0 | −391.8 | −375.7 | −360.7 |
| | imidazole | $C_3H_4N_2$ | 132.9 | 130.9 | 133.5 | 117.0 | 129.8 | 142.5 | 138.1 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | pyrimidine | $C_4H_4N_2$ | 195.7 | 158.7 | 161.4 | 148.1 | 160.2 | 189.1 | 183.0 |
| | uracil | $C_4H_4N_2O_2$ | −302.9 | −283.3 | −280.8 | −295.2 | −272.8 | −315.4 | −302.6 |
| | piperidine | $C_5H_{11}N$ | −47.1 | −78.7 | −76.1 | −58.0 | −41.1 | −67.3 | −63.8 |
| | pyrrole | $C_4H_4O$ | 108.2 | 108.1 | 110.7 | 103.0 | 116.2 | 108.1 | 105.0 |
| | thiophene | $C_4H_4S$ | 114.9 | 128.3 | 130.9 | 116.8 | 129.6 | 128.5 | 124.6 |
| | adenine | $C_5H_5N_5$ | 205.7 | 234.2 | 236.9 | 209.8 | 220.5 | 283.7 | 274.0 |
| | isoxazole | $C_3H_3NO$ | 78.6 | 146.5 | 149.2 | 108.5 | 121.6 | 98.1 | 95.4 |
| | 2,5-dimethylpyrrole | $C_6H_9N$ | 39.8 | 28.6 | 31.2 | 27.0 | 42.0 | 23.6 | 23.7 |
| | 2-methylpyridine | $C_6H_7N$ | 106.4 | 87.1 | 89.7 | 79.4 | 93.2 | 102.7 | 99.8 |
| | 2-methylthiazole | $C_4H_5NS$ | 111.8 | 128.4 | 131.0 | 147.2 | 159.4 | 124.2 | 120.5 |
| | Pyrazine | $C_4H_4O_2$ | 196.1 | 164.4 | 167.1 | 154.6 | 166.6 | 199.2 | 192.7 |
| | MAD | | | 16.4 | 16.1 | 20.6 | 15.6 | 13.2 | 13.1 |
| | MSD | | | −2.6 | 0.0 | −15.2 | 0.0 | 0.24 | 0.0 |
| | RMSD | | | 21.6 | 21.4 | 25.4 | 20.1 | 20.6 | 19.8 |
| **Nitrile** | 2,2-dimethylpropanenitrile | $C_5H_9N$ | −2.3 | 32.4 | 12.7 | −0.4 | −9.9 | 12.0 | 1.0 |
| | 2-methylpropanenitrile | $C_4H_5N$ | 23.4 | 55.9 | 36.1 | 37.3 | 28.2 | 42.1 | 32.8 |
| | malononitrile | $C_3H_2N_2$ | 265.5 | 269.4 | 248.3 | 254.6 | 247.7 | 250.7 | 253.7 |
| | acrylonitrile | $C_3H_3N$ | 180.6 | 209.7 | 188.9 | 194.3 | 186.8 | 192.7 | 192.3 |
| | butanedinitrile | $C_4H_4N_2$ | 209.7 | 239.5 | 218.6 | 223.3 | 216.2 | 213.2 | 214.0 |
| | butyronitrile | $C_4H_9N$ | 33.6 | 54.7 | 34.9 | 44.6 | 35.5 | 45.3 | 36.2 |
| | trans-2-butenenitrile | $C_4H_7N$ | 134.3 | 165.2 | 144.7 | 151.0 | 143.1 | 146.4 | 143.3 |
| | trans-2-butenedinitrile | $C_4H_2N_2$ | 340.2 | 359.5 | 337.8 | 340.0 | 334.1 | 334.1 | 342.0 |
| | cyclopropanecarbonitrile | $C_4H_5N$ | 182.8 | 218.1 | 197.3 | 194.8 | 187.3 | 180.8 | 179.7 |
| | cyclopentanecarbonitrile | $C_4H_9N$ | 44.1 | 54.4 | 34.6 | 53.0 | 44.0 | 45.0 | 35.9 |
| | adiponitrile | $C_6H_8N_2$ | 149.5 | 189.3 | 168.7 | 173.2 | 165.5 | 163.4 | 161.3 |
| | acetonitrile | $C_2H_3N$ | 74.0 | 97.3 | 77.2 | 85.2 | 76.5 | 85.9 | 79.2 |
| | Heptanenitrile | $C_7H_{13}N$ | −31.0 | −13.2 | −32.6 | −21.0 | −30.7 | −16.8 | −29.5 |
| | pentanenitrile | $C_5H_9N$ | 10.5 | 32.1 | 12.4 | 22.9 | 13.6 | 24.7 | 14.4 |
| | trans-2-pentenenitrile | $C_5H_7N$ | 125.7 | 140.2 | 119.9 | 128.3 | 120.1 | 124.7 | 120.3 |
| | 1-cyclohexenecarbonitrile | $C_7H_9N$ | 101.6 | 122.8 | 102.6 | 125.6 | 117.4 | 105.8 | 100.3 |
| | propanenitrile | $C_3H_5N$ | 51.7 | 77.5 | 57.6 | 66.4 | 57.6 | 67.2 | 59.4 |
| | cyclobutanecarbonitrile | $C_5H_7N$ | 147.4 | 135.2 | 114.9 | 124.5 | 116.3 | 115.3 | 110.3 |
| | octanenitrile | $C_8H_{15}N$ | −50.5 | −35.9 | −55.1 | −42.9 | −52.9 | −37.7 | −51.6 |
| | decanenitrile | $C_{10}H_{19}N$ | −91.5 | −81.4 | −100.4 | −86.9 | −97.3 | −79.3 | −95.7 |
| | MAD | | | 22.4 | 9.2 | 11.8 | 7.6 | 11.4 | 7.2 |
| | MSD | | | 21.2 | 1.0 | 8.4 | 0.0 | 5.8 | 0.0 |
| | RMSD | | | 24.3 | 12.0 | 13.5 | 10.5 | 13.4 | 10.6 |
| **Ether** | dimethyl ether | $C_2H_6O$ | −184.1 | −202.3 | −187.6 | −192.6 | −198.8 | −191.3 | −191.7 |
| | ethyl methyl ether | $C_3H_8O$ | −216.4 | −221.7 | −214.0 | −216.5 | −220.9 | −218.1 | −218.4 |
| | methyl propyl ether | $C_4H_{10}O$ | −238.1 | −244.0 | −244.2 | −237.8 | −240.6 | −239.5 | −239.7 |
| | diethyl ether | $C_4H_{10}O$ | −252.1 | −240.6 | −239.7 | −240.0 | −242.7 | −244.5 | −244.7 |
| | ethyl propyl ether | $C_5H_{12}O$ | −272 | −262.9 | −270.0 | −261.4 | −262.4 | −266.1 | −266.2 |
| | butyl methyl ether | $C_5H_{12}O$ | −258.1 | −266.5 | −274.9 | −259.5 | −260.7 | −259.7 | −259.9 |
| | dipropyl ether | $C_6H_{14}O$ | −293.0 | −285.1 | −300.3 | −282.7 | −282.2 | −287.6 | −287.7 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | ethyl tert-butyl ether | $C_6H_{14}O$ | −313.9 | −291.3 | −308.7 | −323.8 | −320.2 | −320.8 | −320.7 |
| | diisopropyl ether | $C_6H_{14}O$ | −319.2 | −293.2 | −311.3 | −326.1 | −322.3 | −322.0 | −322.0 |
| | tert-Butyl isopropyl ether | $C_7H_{16}O$ | −358.1 | −312.9 | −338.1 | −363.8 | −357.3 | −353.8 | −353.6 |
| | di-butyl ether | $C_8H_{18}O$ | −332.8 | −330.2 | −361.7 | −326.2 | −322.4 | −328.1 | −328.0 |
| | di-sec-butyl ether | $C_8H_{18}O$ | −360.6 | −328.3 | −359.0 | −354.4 | −348.5 | −354.3 | −354.1 |
| | tert-butyl isobutyl ether | $C_8H_{18}O$ | −369.0 | −331.6 | −363.4 | −373.7 | −366.4 | −363.6 | −363.4 |
| | di-tert-butyl ether | $C_8H_{18}O$ | −362.0 | −326.7 | −356.9 | −392.7 | −384.0 | −379.5 | −379.2 |
| | MAD | | | 19.1 | 8.9 | 8.1 | 8.0 | 5.6 | 5.7 |
| | MSD | | | 13.7 | 0.0 | −1.6 | 0.0 | 0.0 | 0.0 |
| | RMSD | | | 23.4 | 11.8 | 10.9 | 9.8 | 6.8 | 6.8 |
| **Amine** | methylamine | $CH_5N$ | −22.5 | −21.7 | −17.8 | −30.1 | −27.0 | −10.1 | −19.9 |
| | dimethylamine | $C_2H_7N$ | −18.8 | −33.1 | −29.3 | −25.8 | −22.6 | −12.9 | −22.8 |
| | ethylamine | $C_2H_7N$ | −47.5 | −40.8 | −37.0 | −29.1 | −26.0 | −35.1 | −45.2 |
| | propylamine | $C_3H_9N$ | −70.1 | −69.1 | −65.4 | −74.7 | −72.3 | −56.2 | −66.6 |
| | isopropylamine | $C_3H_9N$ | −83.7 | −72.5 | −68.9 | −86.2 | −84.0 | −64.6 | −75.1 |
| | trimethylamine | $C_3H_9N$ | −23.6 | −45.6 | −41.9 | −31.8 | −28.7 | −18.6 | −28.5 |
| | diethylamine | $C_4H_{11}N$ | −72.2 | −82.1 | −78.5 | −69.7 | −67.2 | −67.3 | −77.8 |
| | butylamine | $C_4H_{11}N$ | −91.9 | −91.7 | −88.2 | −90.1 | −88.0 | −76.6 | −87.2 |
| | sec-butylamine | $C_4H_{11}N$ | −104.6 | −97.2 | −93.6 | −106.4 | −104.5 | −92.9 | −103.7 |
| | tert-butylamine | $C_4H_{11}N$ | −121 | −105.5 | −102.0 | −134.4 | −132.9 | −109.0 | −120.0 |
| | isobutylamine | $C_4H_{11}N$ | −98.7 | −87.1 | −83.5 | −89.0 | −86.8 | −89.6 | −100.3 |
| | dipropylamine | $C_6H_{15}N$ | −116 | −124.2 | −120.8 | −112.9 | −111.1 | −102.0 | −112.9 |
| | diisopropylamine | $C_6H_{15}N$ | −143.8 | −133.9 | −130.5 | −138.4 | −137.0 | −135.2 | −146.5 |
| | triethylamine | $C_6H_{15}N$ | −92.7 | −111.4 | −107.9 | −96.7 | −94.6 | −79.0 | −89.6 |
| | cyclohexylamine | $C_6H_{13}N$ | −104 | −103.1 | −99.5 | −99.9 | −97.9 | −93.0 | −103.8 |
| | cyclopentylamine | $C_5H_{11}N$ | −47.1 | −74.5 | −70.8 | −70.5 | −68.1 | −61.9 | −72.4 |
| | 1,2-ethanediamine | $C_2H_8N_2$ | −18.0 | −15.3 | −11.4 | −25.0 | −21.8 | −2.4 | −12.2 |
| | 2-methyl-1,2-propanediamine | $C_4H_{12}N_2$ | −90.3 | −68.2 | −64.5 | −97.9 | −95.9 | −71.4 | −81.9 |
| | MAD | | | 10.6 | 11.8 | 7.3 | 6.7 | 12.1 | 4.9 |
| | MSD | | | −0.6 | 3.1 | −2.3 | 0.0 | 10.5 | 0.0 |
| | RMSD | | | 13.2 | 13.6 | 9.3 | 9.0 | 12.8 | 7.3 |
| **Nitro-compound** | 2,2-dinitrotoluene | $C_7H_6N_2O_4$ | 33.2 | 8.0 | 8.2 | 22.4 | 30.0 | 26.0 | 5.1 |
| | 1-nitronaphthalene | $C_{10}H_7NO_2$ | 111.2 | 147.7 | 151.8 | 144.9 | 100.5 | 154.5 | 119.5 |
| | 1,1-dnitropropane | $C_3H_6N_2O_2$ | −100.7 | −92.2 | −94.7 | −99.1 | −91.0 | −81.3 | −90.3 |
| | 2,2-dinitrophenol | $C_6H_4N_2O_5$ | −128.1 | −168.3 | −172.9 | −166.4 | −115.8 | −141.0 | −143.4 |
| | paranitrotoluene | $C_7H_7NO_2$ | 31.0 | 19.2 | 19.8 | 8.8 | 28.0 | 31.4 | 10.0 |
| | nitrobenzene | $C_6H_5NO_2$ | 68.5 | 60.5 | 62.2 | 61.9 | 61.9 | 78.7 | 52.1 |
| | methylnitrate | $CH_3NO_3$ | −122.0 | −126.3 | −129.7 | −146.4 | −110.3 | −126.1 | −130.2 |
| | 1-nitro propane | $C_3H_7NO_2$ | −124.3 | −112.2 | −115.3 | −118.8 | −112.3 | −111.6 | −117.2 |
| | 2-nitro propane | $C_3H_7NO_2$ | −138.9 | −113.8 | −116.9 | −127.4 | −125.5 | −120.0 | −124.8 |
| | ethyl nitrate | $C_2H_5NO_3$ | −154.1 | −152.3 | −156.4 | −169.4 | −139.3 | −182.7 | −180.6 |
| | tetranitromethane | $CN_4O_8$ | 82.4 | 26.4 | 27.1 | −132.1 | −130.1 | 142.0 | 108.4 |
| | nitroethane | $C_2H_5NO_2$ | −103.8 | −89.7 | −92.2 | −152.9 | −148.6 | −90.4 | −98.4 |
| | 1-nitrobutane | $C_4H_9NO_2$ | −143.9 | −134.8 | −138.4 | −163.0 | −160.1 | −132.1 | −135.5 |

**Table S1.** Continue.

| Species | Name | Formula | Expt. | PM3 | | PDDG | | PM6 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Calib.[a] | Calc. | Calib.[a] | Calc. | Calib.[a] |
| | 2-nitroisobutane | $C_4H_9NO_2$ | −177.1 | −135.3 | −138.9 | 44.7 | 74.5 | −150.3 | −151.7 |
| | 1-nitropentane | $C_5H_{11}NO_2$ | −164.4 | −157.4 | −161.7 | −90.4 | −93.8 | −152.9 | −154.0 |
| | MAD | | | 20.1 | 19.2 | 17.2 | 10.8 | 18.7 | 15.4 |
| | MSD | | | −0.7 | −1.1 | −3.5 | 6.6 | 11.7 | 0.0 |
| | RMSD | | | 25.7 | 25.6 | 20.5 | 11.5 | 24.0 | 17.2 |

[a] Calibrated values by substituting the HOFs from PM3 or PM6 into the corresponding fit equation.