**When does a functional correctly describe both the structure, and the energy of the transition state?**

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Table S1. Errors (in pm) in predicting transition state geometries.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | XYG3 | XYGJ-OS | xDH-PBE0 | B2PLYP | B2PLYP-D | B3LYP |
| **HTG9** | (1) HO…H…CH3 | R1(O…H) | 134.1 | 2.97 | 2.01 | 2.57 | 0.10 | -0.11 | 0.92 |
|  |  | R2(H…C) | 119.2 | -1.02 | -1.17 | -1.38 | -0.36 | -0.39 | -1.77 |
|  |  | R3(O…C) | 253.0 | 1.91 | 0.96 | 1.30 | -0.18 | -0.26 | -0.88 |
|  | (2) O…H1…H2 | R1(H1…H2) | 89.4 | 1.54 | 1.34 | 1.68 | 1.74 | 1.69 | -0.78 |
|  |  | R2(H1…O) | 121.5 | 0.03 | -0.96 | -0.87 | -1.32 | -1.39 | 0.74 |
|  |  | R3(H2…O) | 210.9 | 1.57 | 0.38 | 0.81 | 0.42 | 0.30 | -0.04 |
|  | (3) H1…H2…SH | R1(H1…H2) | 116.0 | -0.35 | -1.01 | 0.90 | -6.59 | -6.14 | -26.15 |
|  |  | R2(H1…S) | 142.6 | 1.24 | 0.64 | 0.29 | 1.97 | 1.75 | 4.64 |
|  |  | R3(H2…S) | 257.8 | 0.50 | -0.78 | 0.77 | -5.11 | -4.86 | -22.05 |
| **HATG9** | (4) H…O…NN | R1(H…O) | 143.1 | 2.14 | 1.70 | 3.13 | 2.70 | 2.64 | -4.06 |
|  |  | R2(O…N) | 122.6 | -0.35 | -0.09 | -0.41 | -0.34 | -0.37 | 0.48 |
|  |  | R3(H…N) | 218.7 | -1.08 | -0.66 | 0.49 | -2.00 | -2.17 | -8.96 |
|  | (5) H…Cl…H | R1,2(H…Cl) | 148.0 | 0.10 | 0.31 | 0.84 | 0.03 | 0.05 | -0.76 |
|  |  | R3(H…H) | 290.0 | 0.10 | 0.31 | 0.84 | 0.03 | 0.05 | -0.76 |
|  | (6) CH3…F…Cl | R1(C…F) | 204.7 | 0.73 | 0.62 | 1.67 | 0.05 | 0.10 | -1.52 |
|  |  | R2(F…Cl) | 176.7 | -7.91 | -7.54 | -4.70 | -8.82 | -8.86 | -31.43 |
|  |  | R3(C…Cl) | 381.4 | 1.89 | 1.11 | -0.03 | 1.08 | 1.30 | 4.61 |
| **NSG9** | (7) [Cl…CH3…Cl]- | R1,2(Cl…C) | 230.3 | -6.03 | -6.43 | -4.73 | -7.73 | -7.56 | -26.82 |
|  |  | R3(Cl…Cl) | 460.5 | -1.24 | -1.71 | -0.83 | -2.50 | -3.20 | -4.93 |
|  | (8) [F…CH3…Cl]- | R1(F…C) | 202.0 | -1.24 | -1.71 | -0.83 | -2.50 | -3.20 | -4.93 |
|  |  | R2(C…Cl) | 211.4 | -1.96 | -3.42 | -1.65 | -5.00 | -6.41 | -9.87 |
|  |  | R3(F…Cl) | 413.4 | -4.20 | -5.16 | -4.09 | -6.87 | -7.52 | -5.36 |
|  | (9) [HO…CH3…F]- | R1(O…C) | 198.8 | 1.39 | 1.73 | 1.44 | 1.96 | 1.44 | -4.20 |
|  |  | R2(C…F) | 175.8 | -2.80 | -3.44 | -2.65 | -4.91 | -6.08 | -9.56 |
|  |  | R3(O…F) | 374.5 | -3.07 | -3.18 | -3.56 | -3.99 | -4.40 | -5.92 |
| **UAG9** | (10) H…N1…N2 | R1(H…N1) | 143.9 | -0.20 | -0.39 | -0.29 | -0.22 | -0.65 | -1.02 |
|  |  | R2(N1…N2) | 112.7 | -3.31 | -3.61 | -3.89 | -4.24 | -5.09 | -6.97 |
|  |  | R3(H…N2) | 220.1 | 0.13 | -0.15 | 0.91 | -0.83 | -0.74 | -8.80 |
|  | (11) H…CH2=CH2 | R1(H…C1) | 192.5 | 0.46 | 0.51 | 0.15 | 0.91 | 0.91 | 1.71 |
|  |  | R2(C1…C2) | 135.1 | -0.86 | -1.20 | -0.72 | -5.44 | -2.54 | -8.47 |
|  |  | R3(H…C2) | 266.2 | -3.09 | -1.87 | 1.05 | -5.86 | -6.68 | -28.67 |
|  | (12) c-[H…C…N] | R1(H…C) | 118.8 | 1.23 | 0.95 | 0.76 | 1.40 | 1.43 | 1.85 |
|  |  | R2(H…N) | 137.8 | -0.02 | 0.93 | 3.13 | -2.77 | -3.20 | -21.13 |
|  |  | R3(C…N) | 119.4 | -0.02 | -0.52 | -0.29 | -0.23 | -0.19 | -0.63 |

a Internuclear distances involving atoms in breaking and making bonds at the transition state in the TSG36 set [9]. HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, where geometries were generally optimized at the BMC-CCSD [10] level.

c Deviation = Ref. – Calc. All values are in picometers. The 6-311+G(3df,2p) [56] basis sets are employed in the present work. QCISD [12] data are taken from Ref. 9, where the basis sets used were MG3 [13].

Table S1 (Continued). Errors (in pm) in predicting transition state geometries.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | B3LYP-D3 | B3PW91 | PBE0 | PBE0-D3 | O3LYP | X3LYP |
| **HTG9** | (1) HO…H…CH3 | R1(O…H) | 134.1 | 1.03 | -2.86 | -1.12 | -1.00 | -7.19 | 1.39 |
|  |  | R2(H…C) | 119.2 | -1.72 | 0.38 | 0.02 | 0.00 | 1.75 | -1.85 |
|  |  | R3(O…C) | 253.0 | -0.67 | -2.33 | -0.93 | -0.75 | -5.44 | -0.47 |
|  | (2) O…H1…H2 | R1(H1…H2) | 89.4 | -0.68 | 1.60 | 2.37 | 2.41 | -0.60 | -0.32 |
|  |  | R2(H1…O) | 121.5 | 0.35 | -2.24 | -3.24 | -3.56 | 1.19 | 0.36 |
|  |  | R3(H2…O) | 210.9 | -0.33 | -0.63 | -0.87 | -1.15 | 0.60 | 0.04 |
|  | (3) H1…H2…SH | R1(H1…H2) | 116.0 | -28.56 | -20.69 | -13.81 | -14.10 | -34.39 | -24.48 |
|  |  | R2(H1…S) | 142.6 | 5.04 | 4.06 | 3.07 | 3.17 | 5.52 | 4.51 |
|  |  | R3(H2…S) | 257.8 | -24.00 | -17.19 | -11.26 | -11.44 | -29.50 | -20.50 |
| **HATG9** | (4) H…O…NN | R1(H…O) | 143.1 | -4.15 | -2.14 | -1.10 | -1.13 | -3.22 | -3.85 |
|  |  | R2(O…N) | 122.6 | 0.51 | 1.16 | 1.45 | 1.46 | 1.11 | 0.58 |
|  |  | R3(H…N) | 218.7 | -8.69 | -6.69 | -5.14 | -5.07 | -8.59 | -8.55 |
|  | (5) H…Cl…H | R1,2(H…Cl) | 148.0 | -0.71 | 0.07 | 0.28 | 0.27 | 0.46 | -0.69 |
|  |  | R3(H…H) | 290.0 | -0.71 | 0.07 | 0.28 | 0.27 | 0.46 | -0.69 |
|  | (6) CH3…F…Cl | R1(C…F) | 204.7 | -1.41 | 0.14 | 0.56 | 0.54 | 0.91 | -1.38 |
|  |  | R2(F…Cl) | 176.7 | -36.07 | -18.78 | -13.35 | -13.36 | -21.09 | -28.09 |
|  |  | R3(C…Cl) | 381.4 | 6.01 | 3.35 | 3.32 | 3.54 | 1.70 | 4.38 |
| **NSG9** | (7) [Cl…CH3…Cl]- | R1,2(Cl…C) | 230.3 | -30.06 | -15.43 | -10.03 | -9.82 | -19.39 | -23.71 |
|  |  | R3(Cl…Cl) | 460.5 | -4.62 | -1.72 | -0.15 | 0.00 | -3.08 | -4.55 |
|  | (8) [F…CH3…Cl]- | R1(F…C) | 202.0 | -4.62 | -1.72 | -0.15 | 0.00 | -3.08 | -4.55 |
|  |  | R2(C…Cl) | 211.4 | -9.23 | -3.46 | -0.30 | 0.00 | -6.15 | -9.10 |
|  |  | R3(F…Cl) | 413.4 | -13.38 | -8.17 | -4.80 | -4.63 | -8.33 | -12.47 |
|  | (9) [HO…CH3…F]- | R1(O…C) | 198.8 | 4.22 | 4.08 | 3.84 | 3.83 | 1.71 | 3.93 |
|  |  | R2(C…F) | 175.8 | -9.16 | -4.10 | -0.96 | -0.80 | -6.62 | -8.54 |
|  |  | R3(O…F) | 374.5 | -6.17 | -3.60 | -1.51 | -1.55 | -5.45 | -5.15 |
| **UAG9** | (10) H…N1…N2 | R1(H…N1) | 143.9 | -0.82 | 0.78 | 1.83 | 1.88 | -0.02 | -0.69 |
|  |  | R2(N1…N2) | 112.7 | -7.03 | -2.87 | 0.28 | 0.28 | -5.51 | -5.87 |
|  |  | R3(H…N2) | 220.1 | -8.69 | -9.44 | -8.22 | -8.18 | -13.22 | -8.44 |
|  | (11) H…CH2=CH2 | R1(H…C1) | 192.5 | 1.70 | 1.82 | 1.90 | 1.90 | 1.57 | 1.78 |
|  |  | R2(C1…C2) | 135.1 | -8.34 | -8.87 | -7.33 | -7.29 | -13.17 | -8.01 |
|  |  | R3(H…C2) | 266.2 | -33.35 | -25.91 | -21.60 | -22.26 | -32.14 | -28.07 |
|  | (12) c-[H…C…N] | R1(H…C) | 118.8 | 2.00 | 1.94 | 1.93 | 1.97 | 1.63 | 1.92 |
|  |  | R2(H…N) | 137.8 | -23.49 | -19.79 | -16.77 | -16.86 | -23.93 | -20.70 |
|  |  | R3(C…N) | 119.4 | -0.67 | 0.06 | 0.52 | 0.51 | 0.19 | -0.49 |

a Internuclear distances involving atoms in breaking and making bonds at the transition state in the TSG36 set [9]. HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, where geometries were generally optimized at the BMC-CCSD [10] level.

c Deviation = Ref. – Calc. All values are in picometers. The 6-311+G(3df,2p) [56] basis sets are employed in the present work. QCISD [12] data are taken from Ref. 9, where the basis sets used were MG3 [13].

Table S1 (Continued). Errors (in pm) in predicting transition state geometries.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | BHHLYP | M06-2X | M06 | TPSSh | BMK | B97-1 |
| **HTG9** | (1) HO…H…CH3 | R1(O…H) | 134.1 | 8.43 | -1.32 | 5.74 | 2.07 | 3.27 | -1.70 |
|  |  | R2(H…C) | 119.2 | -4.59 | 0.65 | -3.96 | -2.63 | -2.48 | -0.41 |
|  |  | R3(O…C) | 253.0 | 3.80 | -0.25 | 1.93 | -0.62 | 0.86 | -1.98 |
|  | (2) O…H1…H2 | R1(H1…H2) | 89.4 | -2.08 | -2.31 | -1.32 | -2.90 | -0.78 | -2.14 |
|  |  | R2(H1…O) | 121.5 | 4.31 | 3.25 | 2.13 | 2.80 | 1.21 | 2.98 |
|  |  | R3(H2…O) | 210.9 | 2.23 | 0.94 | 0.80 | -0.09 | 0.42 | 0.84 |
|  | (3) H1…H2…SH | R1(H1…H2) | 116.0 | -6.13 | -4.90 | -11.42 | -59.49 | -10.90 | -16.85 |
|  |  | R2(H1…S) | 142.6 | 2.43 | 1.37 | 2.38 | 7.51 | 1.33 | 2.92 |
|  |  | R3(H2…S) | 257.8 | -4.18 | -3.77 | -9.61 | -18.52 | -10.05 | -14.46 |
| **HATG9** | (4) H…O…NN | R1(H…O) | 143.1 | -0.17 | -1.14 | -0.27 | -1.92 | -3.26 | -4.17 |
|  |  | R2(O…N) | 122.6 | 1.58 | 1.00 | 1.43 | 0.06 | -0.03 | 0.37 |
|  |  | R3(H…N) | 218.7 | -3.83 | -1.99 | -5.26 | -8.21 | -7.55 | -9.65 |
|  | (5) H…Cl…H | R1,2(H…Cl) | 148.0 | 0.43 | 0.38 | -0.29 | -0.85 | -0.77 | -0.30 |
|  |  | R3(H…H) | 290.0 | 0.43 | 0.38 | -0.29 | -0.85 | -0.77 | -0.30 |
|  | (6) CH3…F…Cl | R1(C…F) | 204.7 | 0.85 | 4.10 | -0.58 | -1.70 | -1.54 | -0.59 |
|  |  | R2(F…Cl) | 176.7 | -6.26 | -1.66 | -14.36 | 8.64 | -9.20 | -27.12 |
|  |  | R3(C…Cl) | 381.4 | 1.85 | 0.38 | 2.38 | -40.38 | 1.41 | 4.51 |
| **NSG9** | (7) [Cl…CH3…Cl]- | R1,2(Cl…C) | 230.3 | -4.40 | -1.28 | -11.98 | 147.38 | -7.79 | -22.61 |
|  |  | R3(Cl…Cl) | 460.5 | -2.73 | 0.52 | -2.80 | -2.65 | -2.01 | -2.89 |
|  | (8) [F…CH3…Cl]- | R1(F…C) | 202.0 | -2.73 | 0.52 | -2.80 | -2.65 | -2.01 | -2.89 |
|  |  | R2(C…Cl) | 211.4 | -5.46 | 1.04 | -5.59 | -5.29 | -4.02 | -5.77 |
|  |  | R3(F…Cl) | 413.4 | -4.70 | -1.53 | -2.69 | -54.36 | -3.10 | -9.39 |
|  | (9) [HO…CH3…F]- | R1(O…C) | 198.8 | 1.35 | 2.03 | -1.20 | 24.72 | 1.75 | 2.98 |
|  |  | R2(C…F) | 175.8 | -3.35 | 0.50 | -3.89 | -20.39 | -1.35 | -6.41 |
|  |  | R3(O…F) | 374.5 | 0.11 | 2.53 | -3.90 | -5.17 | -0.40 | -4.54 |
| **UAG9** | (10) H…N1…N2 | R1(H…N1) | 143.9 | 0.27 | 2.62 | -0.18 | 0.50 | 0.64 | 0.01 |
|  |  | R2(N1…N2) | 112.7 | 0.35 | 5.10 | -4.11 | -4.70 | 0.20 | -4.57 |
|  |  | R3(H…N2) | 220.1 | -3.73 | -1.97 | -8.94 | -9.02 | -4.66 | -9.50 |
|  | (11) H…CH2=CH2 | R1(H…C1) | 192.5 | 2.78 | 1.87 | 1.82 | 1.30 | 1.46 | 1.46 |
|  |  | R2(C1…C2) | 135.1 | -1.35 | -1.13 | -8.41 | -8.82 | -3.87 | -8.80 |
|  |  | R3(H…C2) | 266.2 | -18.30 | -5.94 | -12.22 | -68.88 | -8.66 | -18.27 |
|  | (12) c-[H…C…N] | R1(H…C) | 118.8 | 2.45 | 1.62 | 1.94 | 1.97 | 1.17 | 1.26 |
|  |  | R2(H…N) | 137.8 | -11.25 | -2.84 | -8.62 | 4.80 | -5.47 | -13.42 |
|  |  | R3(C…N) | 119.4 | 1.54 | 1.19 | 1.03 | -0.41 | 0.15 | -0.30 |

a Internuclear distances involving atoms in breaking and making bonds at the transition state in the TSG36 set [9]. HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, where geometries were generally optimized at the BMC-CCSD [10] level.

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Table S1 (Continued). Errors (in pm) in predicting transition state geometries.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | B97-2 | B98 | CAM-B3LYP | ωB97X | ωB97X-D | HSE06 |
| **HTG9** | (1) HO…H…CH3 | R1(O…H) | 134.1 | -1.09 | -2.02 | 2.01 | 3.76 | 1.64 | 0.03 |
|  |  | R2(H…C) | 119.2 | -0.10 | -0.22 | -1.31 | -2.21 | -1.36 | -0.62 |
|  |  | R3(O…C) | 253.0 | -1.11 | -2.15 | 0.78 | 1.76 | 0.51 | -0.41 |
|  | (2) O…H1…H2 | R1(H1…H2) | 89.4 | -4.41 | -2.80 | 1.25 | -3.03 | -2.18 | 1.89 |
|  |  | R2(H1…O) | 121.5 | 5.86 | 3.87 | -1.55 | 4.53 | 3.41 | -2.62 |
|  |  | R3(H2…O) | 210.9 | 1.45 | 1.06 | -0.30 | 1.51 | 1.23 | -0.73 |
|  | (3) H1…H2…SH | R1(H1…H2) | 116.0 | -16.64 | -20.38 | -12.85 | -6.25 | -10.22 | -13.58 |
|  |  | R2(H1…S) | 142.6 | 3.64 | 3.57 | 3.19 | 1.94 | 2.40 | 3.03 |
|  |  | R3(H2…S) | 257.8 | -13.53 | -17.34 | -10.14 | -4.70 | -8.26 | -11.07 |
| **HATG9** | (4) H…O…NN | R1(H…O) | 143.1 | -2.18 | -4.42 | -2.27 | -1.52 | -2.08 | -1.07 |
|  |  | R2(O…N) | 122.6 | 1.44 | 0.56 | 0.94 | 0.98 | 1.10 | 1.41 |
|  |  | R3(H…N) | 218.7 | -7.17 | -9.66 | -4.89 | -3.09 | -4.70 | -5.28 |
|  | (5) H…Cl…H | R1,2(H…Cl) | 148.0 | 0.80 | -0.32 | -0.18 | 1.13 | 0.64 | 0.15 |
|  |  | R3(H…H) | 290.0 | 0.80 | -0.32 | -0.18 | 1.13 | 0.64 | 0.15 |
|  | (6) CH3…F…Cl | R1(C…F) | 204.7 | 1.64 | -0.64 | -0.37 | 2.27 | 1.28 | 0.30 |
|  |  | R2(F…Cl) | 176.7 | -19.09 | -23.85 | -10.33 | -6.16 | -9.59 | -15.73 |
|  |  | R3(C…Cl) | 381.4 | 3.80 | 3.89 | 2.24 | 1.69 | 2.22 | 3.67 |
| **NSG9** | (7) [Cl…CH3…Cl]- | R1,2(Cl…C) | 230.3 | -15.29 | -19.96 | -8.10 | -4.47 | -7.38 | -12.06 |
|  |  | R3(Cl…Cl) | 460.5 | -2.16 | -3.01 | -2.10 | -1.52 | -1.93 | -0.90 |
|  | (8) [F…CH3…Cl]- | R1(F…C) | 202.0 | -2.16 | -3.01 | -2.10 | -1.52 | -1.93 | -0.90 |
|  |  | R2(C…Cl) | 211.4 | -4.31 | -6.04 | -4.19 | -3.05 | -3.86 | -1.79 |
|  |  | R3(F…Cl) | 413.4 | -7.61 | -10.22 | -4.91 | -1.23 | -2.94 | -5.60 |
|  | (9) [HO…CH3…F]- | R1(O…C) | 198.8 | 3.14 | 3.51 | 1.77 | -0.30 | 0.18 | 3.67 |
|  |  | R2(C…F) | 175.8 | -4.47 | -6.71 | -3.14 | -1.53 | -2.76 | -1.92 |
|  |  | R3(O…F) | 374.5 | -3.21 | -4.27 | -1.66 | -0.84 | -1.92 | -2.06 |
| **UAG9** | (10) H…N1…N2 | R1(H…N1) | 143.9 | 0.29 | 0.08 | 0.74 | -0.11 | 0.09 | 1.29 |
|  |  | R2(N1…N2) | 112.7 | -2.96 | -4.23 | -0.96 | -0.99 | -1.87 | -0.81 |
|  |  | R3(H…N2) | 220.1 | -10.07 | -10.07 | -6.04 | -6.21 | -7.23 | -7.85 |
|  | (11) H…CH2=CH2 | R1(H…C1) | 192.5 | 1.93 | 1.67 | 2.09 | 1.85 | 1.97 | 1.91 |
|  |  | R2(C1…C2) | 135.1 | -9.12 | -9.14 | -4.95 | -4.59 | -6.00 | -7.07 |
|  |  | R3(H…C2) | 266.2 | -19.63 | -22.77 | -19.15 | -11.02 | -13.36 | -21.82 |
|  | (12) c-[H…C…N] | R1(H…C) | 118.8 | 1.68 | 1.51 | 2.20 | 1.57 | 1.68 | 1.95 |
|  |  | R2(H…N) | 137.8 | -13.80 | -16.47 | -12.35 | -5.43 | -7.22 | -17.01 |
|  |  | R3(C…N) | 119.4 | 0.68 | -0.35 | 0.20 | 1.08 | 0.53 | 0.47 |

a Internuclear distances involving atoms in breaking and making bonds at the transition state in the TSG36 set [9]. HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, where geometries were generally optimized at the BMC-CCSD [10] level.

c Deviation = Ref. – Calc. All values are in picometers. The 6-311+G(3df,2p) [56] basis sets are employed in the present work. QCISD [12] data are taken from Ref. 9, where the basis sets used were MG3 [13].

Table S1 (Continued). Errors (in pm) in predicting transition state geometries.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | LC-ωPBE | LC-PBE | TPSS | M06-L | B97-D | B97-D3 |
| **HTG9** | (1) HO…H…CH3 | R1(O…H) | 134.1 | 0.40 | -2.99 | -2.52 | 8.94 | -22.35 | -5.46 |
|  |  | R2(H…C) | 119.2 | 0.03 | 2.35 | -0.97 | -6.19 | 4.31 | 1.21 |
|  |  | R3(O…C) | 253.0 | 0.78 | 0.29 | -3.51 | 2.70 | -17.36 | -4.15 |
|  | (2) O…H1…H2 | R1(H1…H2) | 89.4 | 3.85 | 6.07 | -3.55 | -2.72 | -47.86 | -51.86 |
|  |  | R2(H1…O) | 121.5 | -5.17 | -11.02 | 2.67 | 3.64 | 19.99 | 20.55 |
|  |  | R3(H2…O) | 210.9 | -1.32 | -4.95 | -0.88 | 0.91 | -27.87 | -31.30 |
|  | (3) H1…H2…SH | R1(H1…H2) | 116.0 | -1.10 | 2.62 | -59.72 | -18.44 | -47.58 | -50.32 |
|  |  | R2(H1…S) | 142.6 | 0.91 | 0.07 | 7.13 | 4.11 | 5.94 | 6.28 |
|  |  | R3(H2…S) | 257.8 | -0.65 | 2.31 | -15.71 | -14.88 | -42.11 | -44.46 |
| **HATG9** | (4) H…O…NN | R1(H…O) | 143.1 | 0.95 | 2.07 | -3.19 | -0.11 | -8.55 | -8.87 |
|  |  | R2(O…N) | 122.6 | 1.30 | 2.34 | -0.61 | 0.61 | 0.56 | 0.77 |
|  |  | R3(H…N) | 218.7 | -0.06 | 2.25 | -10.35 | -8.37 | -14.90 | -13.82 |
|  | (5) H…Cl…H | R1,2(H…Cl) | 148.0 | 0.97 | 1.17 | -1.49 | 0.57 | -0.47 | -0.48 |
|  |  | R3(H…H) | 290.0 | 0.97 | 1.17 | -1.49 | 0.57 | -0.47 | -0.48 |
|  | (6) CH3…F…Cl | R1(C…F) | 204.7 | 1.94 | 2.34 | -2.98 | 1.14 | 2.59 | 2.57 |
|  |  | R2(F…Cl) | 176.7 | -1.07 | 3.44 | 7.07 | 5.40 | 2.27 | 2.32 |
|  |  | R3(C…Cl) | 381.4 | 1.02 | 3.44 | -41.70 | -44.50 | -45.13 | -46.16 |
| **NSG9** | (7) [Cl…CH3…Cl]- | R1,2(Cl…C) | 230.3 | -0.05 | 6.88 | 146.00 | 144.66 | 141.74 | 140.90 |
|  |  | R3(Cl…Cl) | 460.5 | 1.90 | 5.01 | -3.89 | -4.97 | -9.15 | -6.82 |
|  | (8) [F…CH3…Cl]- | R1(F…C) | 202.0 | 1.90 | 5.01 | -3.89 | -4.97 | -9.15 | -6.82 |
|  |  | R2(C…Cl) | 211.4 | 3.81 | 10.02 | -7.78 | -9.94 | -18.30 | -13.65 |
|  |  | R3(F…Cl) | 413.4 | 2.12 | 6.32 | -54.47 | -10.89 | -61.91 | -57.80 |
|  | (9) [HO…CH3…F]- | R1(O…C) | 198.8 | 0.88 | 3.17 | 22.75 | 3.59 | 22.14 | 22.58 |
|  |  | R2(C…F) | 175.8 | 3.00 | 9.49 | -20.94 | -7.30 | -29.26 | -25.78 |
|  |  | R3(O…F) | 374.5 | 0.83 | 4.96 | -8.54 | -7.19 | -12.25 | -12.20 |
| **UAG9** | (10) H…N1…N2 | R1(H…N1) | 143.9 | 2.40 | 5.32 | 0.20 | -2.16 | -3.86 | -1.74 |
|  |  | R2(N1…N2) | 112.7 | 3.18 | 10.23 | -8.38 | -9.41 | -16.18 | -14.00 |
|  |  | R3(H…N2) | 220.1 | -3.78 | -3.48 | -11.14 | -11.79 | -20.41 | -21.61 |
|  | (11) H…CH2=CH2 | R1(H…C1) | 192.5 | 2.02 | 2.69 | 0.86 | 1.23 | 1.31 | 1.39 |
|  |  | R2(C1…C2) | 135.1 | -2.46 | -1.59 | -11.69 | -11.96 | -20.43 | -20.80 |
|  |  | R3(H…C2) | 266.2 | -10.76 | -11.44 | -68.63 | -25.41 | -60.37 | -64.02 |
|  | (12) c-[H…C…N] | R1(H…C) | 118.8 | 2.08 | 2.97 | 1.58 | 2.01 | 1.41 | 1.62 |
|  |  | R2(H…N) | 137.8 | -5.77 | -6.30 | 5.08 | -18.76 | -45.09 | -46.31 |
|  |  | R3(C…N) | 119.4 | 1.46 | 1.93 | -1.33 | 1.26 | -1.43 | -1.57 |

a Internuclear distances involving atoms in breaking and making bonds at the transition state in the TSG36 set [9]. HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, where geometries were generally optimized at the BMC-CCSD [10] level.

c Deviation = Ref. – Calc. All values are in picometers. The 6-311+G(3df,2p) [56] basis sets are employed in the present work. QCISD [12] data are taken from Ref. 9, where the basis sets used were MG3 [13].

Table S1 (Continued). Errors (in pm) in predicting transition state geometries.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | HCTH407 | BLYP | PBE | QCISD | MP2 | HF |
| **HTG9** | (1) HO…H…CH3 | R1(O…H) | 134.1 | -19.15 | -131.17 | -112.39 | 5.65 | 1.22 | 11.99 |
|  |  | R2(H…C) | 119.2 | 4.67 | 9.66 | 9.42 | -3.55 | 0.96 | -9.38 |
|  |  | R3(O…C) | 253.0 | -14.23 | -58.42 | -38.40 | 2.18 | 2.42 | 2.44 |
|  | (2) O…H1…H2 | R1(H1…H2) | 89.4 | -11.96 | 1.01 | 9.49 | -1.76 | 3.86 | -5.96 |
|  |  | R2(H1…O) | 121.5 | 10.69 | -4.07 | -27.49 | 2.57 | -1.59 | 6.32 |
|  |  | R3(H2…O) | 210.9 | -1.28 | -3.06 | -18.00 | 0.81 | 2.26 | 0.36 |
|  | (3) H1…H2…SH | R1(H1…H2) | 116.0 | -37.86 | -63.09 | -35.66 | 1.05 | 11.36 | 10.94 |
|  |  | R2(H1…S) | 142.6 | 5.74 | 6.21 | 4.57 | -0.31 | -2.58 | -5.54 |
|  |  | R3(H2…S) | 257.8 | -32.56 | -57.53 | -31.71 | 0.47 | 8.30 | 4.95 |
| **HATG9** | (4) H…O…NN | R1(H…O) | 143.1 | -3.58 | -8.23 | -5.27 | 0.80 | 13.35 | -1.40 |
|  |  | R2(O…N) | 122.6 | 1.43 | -0.98 | 0.08 | -0.41 | -0.48 | 0.92 |
|  |  | R3(H…N) | 218.7 | -9.21 | -14.88 | -10.97 | -2.17 | 7.20 | -4.82 |
|  | (5) H…Cl…H | R1,2(H…Cl) | 148.0 | 1.01 | -1.99 | -1.08 | -0.58 | 1.79 | -1.67 |
|  |  | R3(H…H) | 290.0 | 1.01 | -1.99 | -1.08 | -0.58 | 1.79 | -1.67 |
|  | (6) CH3…F…Cl | R1(C…F) | 204.7 | 5.23 | -0.38 | -2.16 | -1.16 | 3.58 | -3.35 |
|  |  | R2(F…Cl) | 176.7 | 5.99 | 2.51 | 7.97 | -1.68 | 12.42 | -54.89 |
|  |  | R3(C…Cl) | 381.4 | -43.65 | -46.12 | -41.66 | -1.14 | 6.03 | -12.07 |
| **NSG9** | (7) [Cl…CH3…Cl]- | R1,2(Cl…C) | 230.3 | 144.88 | 140.33 | 147.36 | -2.82 | 18.45 | -66.96 |
|  |  | R3(Cl…Cl) | 460.5 | -5.10 | -8.56 | -3.05 | -1.75 | 2.54 | -7.65 |
|  | (8) [F…CH3…Cl]- | R1(F…C) | 202.0 | -5.10 | -8.56 | -3.05 | -1.75 | 2.54 | -7.65 |
|  |  | R2(C…Cl) | 211.4 | -10.20 | -17.12 | -6.16 | -3.51 | 5.08 | -15.29 |
|  |  | R3(F…Cl) | 413.4 | -11.31 | -57.70 | -52.58 | -2.96 | 3.46 | -7.34 |
|  | (9) [HO…CH3…F]- | R1(O…C) | 198.8 | 1.44 | 19.98 | 23.86 | 0.11 | 0.34 | -2.68 |
|  |  | R2(C…F) | 175.8 | -9.86 | -27.38 | -21.26 | -2.84 | 3.80 | -10.02 |
|  |  | R3(O…F) | 374.5 | -7.88 | -14.20 | -9.38 | 0.22 | 1.23 | 0.37 |
| **UAG9** | (10) H…N1…N2 | R1(H…N1) | 143.9 | -1.65 | -2.48 | 0.57 | -0.19 | 1.91 | -3.07 |
|  |  | R2(N1…N2) | 112.7 | -9.57 | -16.71 | -8.86 | -0.02 | 3.12 | -2.73 |
|  |  | R3(H…N2) | 220.1 | -16.34 | -13.46 | -14.43 | 0.84 | 8.31 | 5.20 |
|  | (11) H…CH2=CH2 | R1(H…C1) | 192.5 | 1.51 | 0.62 | 0.76 | 0.42 | 2.39 | 2.27 |
|  |  | R2(C1…C2) | 135.1 | -16.57 | -14.58 | -15.20 | 1.17 | 3.05 | 10.40 |
|  |  | R3(H…C2) | 266.2 | -35.05 | -47.55 | -31.76 | -5.55 | 8.21 | -4.10 |
|  | (12) c-[H…C…N] | R1(H…C) | 118.8 | 1.59 | 1.20 | 1.20 | 0.64 | 2.39 | -0.25 |
|  |  | R2(H…N) | 137.8 | -27.11 | -38.39 | -27.69 | -3.24 | 9.54 | -2.16 |
|  |  | R3(C…N) | 119.4 | 0.02 | -2.77 | -1.67 | 0.07 | 1.20 | 2.95 |

a Internuclear distances involving atoms in breaking and making bonds at the transition state in the TSG36 set [9]. HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, where geometries were generally optimized at the BMC-CCSD [10] level.

c Deviation = Ref. – Calc. All values are in picometers. The 6-311+G(3df,2p) [56] basis sets are employed in the present work. QCISD [12] data are taken from Ref. 9, where the basis sets used were MG3 [13].

Table S2. Errors (in kcal/mol) in predicting transition state energies.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | XYG3 | XYGJ-OS | xDH-PBE0 | B2PLYP | B2PLYP-D | B3LYP |
| **HTE9** | (1) HO…H…CH3 | V≠f | 134.1 | -0.21 | 0.05 | -1.45 | 2.11 | 0.84 | 4.40 |
|  |  | V≠r | 119.2 | 0.85 | 1.23 | 0.13 | 2.59 | -12.17 | 5.74 |
|  |  | ΔE | 253.0 | -1.06 | -1.18 | -1.59 | -0.48 | -0.53 | -1.34 |
|  | (2) O…H1…H2 | V≠f | 89.4 | 0.41 | 0.48 | -1.18 | 2.57 | 17.07 | 6.68 |
|  |  | V≠r | 121.5 | -0.81 | 0.31 | -1.50 | 2.91 | -0.95 | 6.94 |
|  |  | ΔE | 210.9 | 1.22 | 0.17 | 0.32 | -0.34 | -0.34 | -0.25 |
|  | (3) H1…H2…SH | V≠f | 116.0 | -0.47 | -0.55 | -1.25 | 1.18 | -4.82 | 3.86 |
|  |  | V≠r | 142.6 | -0.90 | -0.29 | -1.19 | 0.30 | -27.96 | 1.40 |
|  |  | ΔE | 257.8 | 0.43 | -0.26 | -0.07 | 0.88 | 0.76 | 2.46 |
| **HATE9** | (4) H…O…NN | V≠f | 143.1 | -2.54 | -2.92 | -5.07 | 0.88 | 1.05 | 6.40 |
|  |  | V≠r | 122.6 | 0.99 | 1.40 | 0.61 | 6.28 | 6.48 | 10.33 |
|  |  | ΔE | 218.7 | -3.53 | -4.32 | -5.68 | -5.40 | -5.43 | -3.92 |
|  | (5) H…Cl…H | V≠f | 148.0 | -0.60 | -0.64 | -2.01 | 1.66 | 1.69 | 5.34 |
|  |  | V≠r | 290.0 | -0.60 | -0.64 | -2.01 | 1.66 | 1.69 | 5.34 |
|  |  | ΔE | 290.0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|  | (6) CH3…F…Cl | V≠f | 204.7 | 1.08 | 0.15 | -1.35 | 4.55 | 5.22 | 8.82 |
|  |  | V≠r | 176.7 | -2.02 | -2.11 | -3.16 | 3.24 | 3.85 | 9.06 |
|  |  | ΔE | 381.4 | 3.10 | 2.26 | 1.81 | 1.31 | 1.38 | -0.24 |
| **NSE9** | (7) [Cl…CH3…Cl]- | V≠f | 230.3 | 1.44 | 1.16 | -0.39 | 2.37 | 3.16 | 3.52 |
|  |  | V≠r | 460.5 | 1.43 | 1.19 | -0.05 | 2.83 | 2.91 | 4.48 |
|  |  | ΔE | 460.5 | 0.01 | -0.03 | -0.34 | -0.46 | 0.25 | -0.95 |
|  | (8) [F…CH3…Cl]- | V≠f | 202.0 | 2.69 | 2.71 | 0.78 | 2.92 | 3.52 | 3.86 |
|  |  | V≠r | 211.4 | 0.76 | -0.04 | -0.16 | 1.22 | 1.87 | 2.07 |
|  |  | ΔE | 413.4 | 1.94 | 2.75 | 0.95 | 1.70 | 1.66 | 1.79 |
|  | (9) [HO…CH3…F]- | V≠f | 198.8 | 2.46 | 2.07 | 0.85 | 2.77 | 3.59 | 3.25 |
|  |  | V≠r | 175.8 | 2.29 | 2.22 | 0.89 | 2.70 | 3.28 | 2.95 |
|  |  | ΔE | 374.5 | 0.17 | -0.16 | -0.04 | 0.08 | 0.31 | 0.30 |
| **UAE9** | (10) H…N1…N2 | V≠f | 143.9 | -0.64 | -0.83 | -2.29 | 1.88 | 1.96 | 7.00 |
|  |  | V≠r | 112.7 | -0.66 | -0.54 | -0.92 | 0.25 | 0.31 | -0.10 |
|  |  | ΔE | 220.1 | 0.02 | -0.29 | -1.37 | 1.63 | 1.65 | 7.10 |
|  | (11) H…CH2=CH2 | V≠f | 192.5 | -0.86 | -1.21 | -2.02 | -0.32 | 0.18 | 1.82 |
|  |  | V≠r | 135.1 | -1.97 | -1.22 | -2.37 | -0.62 | -0.40 | -0.02 |
|  |  | ΔE | 266.2 | 1.12 | 0.01 | 0.36 | 0.30 | 0.58 | 1.84 |
|  | (12) c-[H…C…N] | V≠f | 118.8 | -1.64 | -1.40 | -1.22 | -0.95 | -1.04 | 0.46 |
|  |  | V≠r | 137.8 | -0.61 | -0.76 | 0.08 | -0.67 | -0.72 | -0.69 |
|  |  | ΔE | 119.4 | -1.03 | -0.64 | -1.30 | -0.29 | -0.31 | 1.15 |

a Forward V≠f and backward V≠r reaction barriers in the TSG36 set [9]. ΔE = V≠f – V≠r HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, which are generally the W1 [11] values calculated at the optimized geometries at the QCISD/MG3 [12,13] level.

c Deviation = Ref. – Calc. The G3Large [55] basis sets are generally used in the present work. The xDH-PBE0 data are taken from Ref. 53.

Table S2 (Continued). Errors (in kcal/mol) in predicting transition state energies.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | B3LYP-D3 | B3PW91 | PBE0 | PBE0-D3 | O3LYP | X3LYP |
| **HTG9** | (1) HO…H…CH3 | V≠f | 134.1 | 5.27  | 4.53  | 4.66  | 5.20  | 4.22  | 4.55  |
|  |  | V≠r | 119.2 | 6.63  | 5.16  | 5.71  | 6.26  | 4.47  | 5.99  |
|  |  | ΔE | 253.0 | -1.36  | -0.64  | -1.05  | -1.06  | -0.25  | -1.44  |
|  | (2) O…H1…H2 | V≠f | 89.4 | 6.89  | 4.86  | 3.64  | 3.76  | 7.75  | 6.57  |
|  |  | V≠r | 121.5 | 7.15  | 6.73  | 7.26  | 7.37  | 5.89  | 7.19  |
|  |  | ΔE | 210.9 | -0.25  | -1.86  | -3.61  | -3.61  | 1.86  | -0.62  |
|  | (3) H1…H2…SH | V≠f | 116.0 | 4.26  | 2.77  | 2.21  | 2.44  | 3.91  | 3.86  |
|  |  | V≠r | 142.6 | 1.83  | 3.11  | 4.88  | 5.12  | 1.11  | 1.94  |
|  |  | ΔE | 257.8 | 2.43  | -0.35  | -2.66  | -2.68  | 2.80  | 1.92  |
| **HATG9** | (4) H…O…NN | V≠f | 143.1 | 6.75  | 4.42  | 3.78  | 3.98  | 5.54  | 6.48  |
|  |  | V≠r | 122.6 | 10.82  | 13.88  | 14.31  | 14.58  | 16.43  | 10.25  |
|  |  | ΔE | 218.7 | -4.07  | -9.46  | -10.53  | -10.61  | -10.89  | -3.77  |
|  | (5) H…Cl…H | V≠f | 148.0 | 5.41  | 4.75  | 4.36  | 4.41  | 6.12  | 5.38  |
|  |  | V≠r | 290.0 | 5.41  | 4.75  | 4.36  | 4.41  | 6.12  | 5.38  |
|  |  | ΔE | 290.0 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
|  | (6) CH3…F…Cl | V≠f | 204.7 | 10.12  | 6.63  | 6.42  | 7.21  | 6.87  | 8.92  |
|  |  | V≠r | 176.7 | 9.91  | 7.50  | 6.49  | 7.03  | 8.01  | 8.82  |
|  |  | ΔE | 381.4 | 0.21  | -0.87  | -0.07  | 0.18  | -1.13  | 0.10  |
| **NSG9** | (7) [Cl…CH3…Cl]- | V≠f | 230.3 | 5.10  | 2.04  | 2.10  | 2.99  | -0.42  | 3.72  |
|  |  | V≠r | 460.5 | 4.52  | 3.44  | 2.45  | 2.46  | 2.38  | 4.29  |
|  |  | ΔE | 460.5 | 0.58  | -1.40  | -0.35  | 0.53  | -2.80  | -0.57  |
|  | (8) [F…CH3…Cl]- | V≠f | 202.0 | 5.12  | 2.30  | 2.78  | 3.49  | 0.39  | 4.23  |
|  |  | V≠r | 211.4 | 3.44  | 0.99  | 0.96  | 1.73  | -0.57  | 2.16  |
|  |  | ΔE | 413.4 | 1.69  | 1.30  | 1.82  | 1.76  | 0.96  | 2.07  |
|  | (9) [HO…CH3…F]- | V≠f | 198.8 | 4.49  | 2.06  | 2.43  | 3.14  | 0.33  | 3.55  |
|  |  | V≠r | 175.8 | 4.03  | 1.04  | 1.14  | 1.76  | -0.40  | 3.21  |
|  |  | ΔE | 374.5 | 0.46  | 1.02  | 1.29  | 1.39  | 0.74  | 0.33  |
| **UAG9** | (10) H…N1…N2 | V≠f | 143.9 | 7.11  | 6.47  | 5.93  | 6.00  | 7.72  | 6.99  |
|  |  | V≠r | 112.7 | -0.02  | -0.62  | -0.93  | -0.89  | -0.58  | -0.20  |
|  |  | ΔE | 220.1 | 7.13  | 7.09  | 6.87  | 6.88  | 8.29  | 7.18  |
|  | (11) H…CH2=CH2 | V≠f | 192.5 | 2.48  | 1.02  | 0.93  | 1.32  | 1.34  | 1.94  |
|  |  | V≠r | 135.1 | 0.38  | -2.00  | -2.42  | -2.18  | -1.38  | -0.05  |
|  |  | ΔE | 266.2 | 2.10  | 3.02  | 3.36  | 3.51  | 2.72  | 1.98  |
|  | (12) c-[H…C…N] | V≠f | 118.8 | 0.37  | 1.05  | 1.40  | 1.35  | 1.37  | 0.50  |
|  |  | V≠r | 137.8 | -0.76  | -0.02  | 0.06  | 0.02  | 0.49  | -0.79  |
|  |  | ΔE | 119.4 | 1.13  | 1.07  | 1.34  | 1.33  | 0.88  | 1.29  |

a Forward V≠f and backward V≠r reaction barriers in the TSG36 set [9]. ΔE = V≠f – V≠r HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, which are generally the W1 [11] values calculated at the optimized geometries at the QCISD/MG3 [12,13] level.

c Deviation = Ref. – Calc. The G3Large [55] basis sets are generally used in the present work. The xDH-PBE0 data are taken from Ref. 53.

Table S2 (Continued). Errors (in kcal/mol) in predicting transition state energies.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | BHHLYP | M06-2X | M06 | TPSSh | BMK | B97-1 |
| **HTG9** | (1) HO…H…CH3 | V≠f | 134.1 | -3.30  | 1.29  | 2.25  | 5.12  | 1.20  | 5.69  |
|  |  | V≠r | 119.2 | 1.19  | 2.14  | 2.00  | 7.96  | 2.76  | 7.48  |
|  |  | ΔE | 253.0 | -4.48  | -0.85  | 0.25  | -2.84  | -1.56  | -1.78  |
|  | (2) O…H1…H2 | V≠f | 89.4 | 3.28  | 1.08  | 2.17  | 10.93  | 0.63  | 2.86  |
|  |  | V≠r | 121.5 | -0.77  | 1.41  | 3.74  | 6.18  | 2.62  | 6.82  |
|  |  | ΔE | 210.9 | 4.05  | -0.32  | -1.58  | 4.75  | -1.99  | -3.96  |
|  | (3) H1…H2…SH | V≠f | 116.0 | 1.27  | -1.00  | -0.53  | 7.04  | -0.04  | 0.04  |
|  |  | V≠r | 142.6 | -1.59  | -0.85  | 0.76  | 3.74  | 0.66  | 2.59  |
|  |  | ΔE | 257.8 | 2.85  | -0.15  | -1.29  | 3.30  | -0.70  | -2.55  |
| **HATG9** | (4) H…O…NN | V≠f | 143.1 | 2.13  | 0.62  | 0.06  | 8.34  | 1.27  | 1.86  |
|  |  | V≠r | 122.6 | -8.08  | 1.36  | 11.91  | 16.96  | 1.22  | 10.67  |
|  |  | ΔE | 218.7 | 10.21  | -0.75  | -11.85  | -8.62  | 0.05  | -8.81  |
|  | (5) H…Cl…H | V≠f | 148.0 | 1.16  | -0.12  | 0.47  | 9.00  | 0.92  | 1.51  |
|  |  | V≠r | 290.0 | 1.16  | -0.12  | 0.47  | 9.00  | 0.92  | 1.51  |
|  |  | ΔE | 290.0 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
|  | (6) CH3…F…Cl | V≠f | 204.7 | 1.57  | 2.59  | 8.17  | 9.76  | 4.32  | 9.32  |
|  |  | V≠r | 176.7 | -3.45  | 0.54  | 5.81  | 12.36  | 1.71  | 8.96  |
|  |  | ΔE | 381.4 | 5.02  | 2.06  | 2.36  | -2.60  | 2.61  | 0.36  |
| **NSG9** | (7) [Cl…CH3…Cl]- | V≠f | 230.3 | -0.11  | 0.84  | 2.56  | 6.06  | -0.30  | 3.94  |
|  |  | V≠r | 460.5 | 0.66  | -0.02  | 2.08  | 6.42  | 0.13  | 3.86  |
|  |  | ΔE | 460.5 | -0.77  | 0.86  | 0.48  | -0.36  | -0.43  | 0.08  |
|  | (8) [F…CH3…Cl]- | V≠f | 202.0 | 1.37  | 2.19  | 2.41  | 6.65  | 0.76  | 4.24  |
|  |  | V≠r | 211.4 | -3.92  | -3.42  | 2.77  | 3.89  | -2.32  | 2.45  |
|  |  | ΔE | 413.4 | 5.29  | 5.61  | -0.36  | 2.76  | 3.08  | 1.80  |
|  | (9) [HO…CH3…F]- | V≠f | 198.8 | -1.22  | 0.15  | 2.01  | 5.89  | -0.75  | 3.41  |
|  |  | V≠r | 175.8 | -2.61  | -0.08  | -0.25  | 6.33  | -2.31  | 2.75  |
|  |  | ΔE | 374.5 | 1.38  | 0.23  | 2.26  | -0.44  | 1.56  | 0.66  |
| **UAG9** | (10) H…N1…N2 | V≠f | 143.9 | 3.40  | 0.72  | 3.50  | 10.35  | 1.79  | 3.24  |
|  |  | V≠r | 112.7 | -2.86  | -0.49  | -0.76  | 1.29  | -2.51  | -1.70  |
|  |  | ΔE | 220.1 | 6.26  | 1.21  | 4.26  | 9.06  | 4.30  | 4.94  |
|  | (11) H…CH2=CH2 | V≠f | 192.5 | 1.14  | -1.20  | -0.98  | 5.53  | -1.28  | -1.63  |
|  |  | V≠r | 135.1 | -3.69  | -1.82  | -3.48  | 0.31  | -2.81  | -1.46  |
|  |  | ΔE | 266.2 | 4.82  | 0.62  | 2.50  | 5.22  | 1.52  | -0.17  |
|  | (12) c-[H…C…N] | V≠f | 118.8 | -0.13  | 1.99  | 1.23  | 0.38  | 2.01  | 1.76  |
|  |  | V≠r | 137.8 | -2.85  | -0.23  | -1.48  | 0.10  | -1.94  | -0.11  |
|  |  | ΔE | 119.4 | 2.73  | 2.22  | 2.70  | 0.28  | 3.95  | 1.87  |

a Forward V≠f and backward V≠r reaction barriers in the TSG36 set [9]. ΔE = V≠f – V≠r HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, which are generally the W1 [11] values calculated at the optimized geometries at the QCISD/MG3 [12,13] level.

c Deviation = Ref. – Calc. The G3Large [55] basis sets are generally used in the present work. The xDH-PBE0 data are taken from Ref. 53.

Table S2 (Continued). Errors (in kcal/mol) in predicting transition state energies.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | B97-2 | B98 | CAM-B3LYP | ωB97X | ωB97X-D | HSE06 |
| **HTG9** | (1) HO…H…CH3 | V≠f | 134.1 | 4.36  | 5.24  | 3.40  | 2.43  | 3.25  | 4.67  |
|  |  | V≠r | 119.2 | 6.01  | 6.63  | 4.33  | 4.24  | 4.49  | 5.78  |
|  |  | ΔE | 253.0 | -1.66  | -1.39  | -0.94  | -1.81  | -1.24  | -1.11  |
|  | (2) O…H1…H2 | V≠f | 89.4 | 2.47  | 3.96  | 5.06  | 0.93  | 1.93  | 3.73  |
|  |  | V≠r | 121.5 | 4.92  | 6.12  | 6.58  | 3.25  | 3.72  | 7.13  |
|  |  | ΔE | 210.9 | -2.44  | -2.16  | -1.53  | -2.32  | -1.78  | -3.41  |
|  | (3) H1…H2…SH | V≠f | 116.0 | -1.16  | 0.96  | 2.68  | -2.32  | -0.85  | 2.31  |
|  |  | V≠r | 142.6 | 1.31  | 1.73  | 1.40  | -0.24  | 0.69  | 4.78  |
|  |  | ΔE | 257.8 | -2.47  | -0.77  | 1.27  | -2.08  | -1.54  | -2.47  |
| **HATG9** | (4) H…O…NN | V≠f | 143.1 | -0.49  | 2.79  | 5.02  | -1.38  | 0.36  | 3.92  |
|  |  | V≠r | 122.6 | 10.98  | 9.17  | 6.42  | 2.58  | 5.39  | 14.23  |
|  |  | ΔE | 218.7 | -11.47  | -6.38  | -1.41  | -3.96  | -5.03  | -10.31  |
|  | (5) H…Cl…H | V≠f | 148.0 | -0.37  | 2.38  | 3.40  | -3.00  | -0.49  | 4.36  |
|  |  | V≠r | 290.0 | -0.37  | 2.38  | 3.40  | -3.00  | -0.49  | 4.36  |
|  |  | ΔE | 290.0 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
|  | (6) CH3…F…Cl | V≠f | 204.7 | 7.31  | 8.61  | 4.65  | 3.31  | 4.47  | 7.17  |
|  |  | V≠r | 176.7 | 6.12  | 8.07  | 3.16  | 1.56  | 3.50  | 7.45  |
|  |  | ΔE | 381.4 | 1.19  | 0.54  | 1.48  | 1.75  | 0.97  | -0.28  |
| **NSG9** | (7) [Cl…CH3…Cl]- | V≠f | 230.3 | 1.34  | 3.84  | 0.27  | -1.62  | -0.68  | 2.80  |
|  |  | V≠r | 460.5 | 2.58  | 4.04  | 0.94  | -2.23  | -0.52  | 2.97  |
|  |  | ΔE | 460.5 | -1.24  | -0.20  | -0.67  | 0.61  | -0.16  | -0.17  |
|  | (8) [F…CH3…Cl]- | V≠f | 202.0 | 1.73  | 4.14  | 1.90  | 0.42  | 0.92  | 3.32  |
|  |  | V≠r | 211.4 | -0.10  | 1.68  | -0.33  | -0.21  | -0.77  | 1.68  |
|  |  | ΔE | 413.4 | 1.83  | 2.46  | 2.23  | 0.63  | 1.68  | 1.64  |
|  | (9) [HO…CH3…F]- | V≠f | 198.8 | 1.14  | 2.87  | 1.71  | 1.14  | 0.82  | 3.01  |
|  |  | V≠r | 175.8 | 0.24  | 2.32  | 0.71  | -0.43  | -0.69  | 1.80  |
|  |  | ΔE | 374.5 | 0.90  | 0.56  | 1.00  | 1.57  | 1.52  | 1.21  |
| **UAG9** | (10) H…N1…N2 | V≠f | 143.9 | 2.22  | 4.13  | 5.56  | 0.51  | 2.18  | 5.94  |
|  |  | V≠r | 112.7 | -2.15  | -1.86  | -1.10  | -3.59  | -2.70  | -0.77  |
|  |  | ΔE | 220.1 | 4.37  | 5.99  | 6.65  | 4.11  | 4.88  | 6.70  |
|  | (11) H…CH2=CH2 | V≠f | 192.5 | -2.66  | -0.83  | 1.46  | -2.42  | -1.36  | 1.06  |
|  |  | V≠r | 135.1 | -2.44  | -1.91  | -1.72  | -5.29  | -3.69  | -2.16  |
|  |  | ΔE | 266.2 | -0.23  | 1.08  | 3.18  | 2.87  | 2.33  | 3.22  |
|  | (12) c-[H…C…N] | V≠f | 118.8 | 0.96  | 1.66  | 0.77  | 1.48  | 1.37  | 1.14  |
|  |  | V≠r | 137.8 | -0.30  | -0.49  | -1.17  | -0.66  | -0.78  | -0.12  |
|  |  | ΔE | 119.4 | 1.26  | 2.15  | 1.95  | 2.14  | 2.15  | 1.26  |

a Forward V≠f and backward V≠r reaction barriers in the TSG36 set [9]. ΔE = V≠f – V≠r HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, which are generally the W1 [11] values calculated at the optimized geometries at the QCISD/MG3 [12,13] level.

c Deviation = Ref. – Calc. The G3Large [55] basis sets are generally used in the present work. The xDH-PBE0 data are taken from Ref. 53.

Table S2 (Continued). Errors (in kcal/mol) in predicting transition state energies.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | LC-ωPBE | LC-PBE | TPSS | M06-L | B97-D | B97-D3 |
| **HTG9** | (1) HO…H…CH3 | V≠f | 134.1 | 1.03  | 4.04  | 7.59  | 3.61  | 9.45  | 9.83  |
|  |  | V≠r | 119.2 | 0.96  | 1.78  | 9.85  | 7.22  | 9.04  | 9.59  |
|  |  | ΔE | 253.0 | 0.08  | 2.26  | -2.26  | -3.61  | 0.41  | 0.24  |
|  | (2) O…H1…H2 | V≠f | 89.4 | 0.12  | -0.66  | 12.32  | 3.78  | 9.00  | 9.60  |
|  |  | V≠r | 121.5 | 4.69  | 8.65  | 8.35  | 7.17  | 6.93  | 7.65  |
|  |  | ΔE | 210.9 | -4.57  | -9.30  | 3.97  | -3.39  | 2.07  | 1.95  |
|  | (3) H1…H2…SH | V≠f | 116.0 | -0.58  | -0.20  | 7.86  | -0.47  | 3.17  | 4.10  |
|  |  | V≠r | 142.6 | 0.95  | 5.51  | 4.46  | 4.43  | -0.54  | 0.78  |
|  |  | ΔE | 257.8 | -1.53  | -5.71  | 3.41  | -4.90  | 3.72  | 3.32  |
| **HATG9** | (4) H…O…NN | V≠f | 143.1 | -0.34  | 0.29  | 9.77  | -0.98  | 4.76  | 5.66  |
|  |  | V≠r | 122.6 | 5.24  | 11.02  | 22.92  | 16.64  | 18.87  | 20.55  |
|  |  | ΔE | 218.7 | -5.59  | -10.73  | -13.15  | -17.62  | -14.10  | -14.89  |
|  | (5) H…Cl…H | V≠f | 148.0 | -0.68  | 0.17  | 10.28  | -0.02  | 3.94  | 4.59  |
|  |  | V≠r | 290.0 | -0.68  | 0.17  | 10.28  | -0.02  | 3.94  | 4.59  |
|  |  | ΔE | 290.0 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
|  | (6) CH3…F…Cl | V≠f | 204.7 | -2.05  | -2.68  | 12.60  | 12.21  | 13.90  | 13.96  |
|  |  | V≠r | 176.7 | -3.19  | -5.62  | 17.10  | 12.20  | 15.92  | 15.95  |
|  |  | ΔE | 381.4 | 1.14  | 2.94  | -4.49  | 0.02  | -2.01  | -1.99  |
| **NSG9** | (7) [Cl…CH3…Cl]- | V≠f | 230.3 | -5.41  | -6.12  | 8.06  | 4.04  | 7.14  | 7.85  |
|  |  | V≠r | 460.5 | -4.03  | -5.41  | 8.22  | 3.43  | 6.85  | 7.38  |
|  |  | ΔE | 460.5 | -1.38  | -0.71  | -0.16  | 0.60  | 0.29  | 0.47  |
|  | (8) [F…CH3…Cl]- | V≠f | 202.0 | -3.38  | -3.39  | 8.50  | 5.17  | 6.40  | 6.29  |
|  |  | V≠r | 211.4 | -2.76  | -4.19  | 6.62  | 2.38  | 5.49  | 6.80  |
|  |  | ΔE | 413.4 | -0.62  | 0.80  | 1.89  | 2.80  | 0.91  | -0.51  |
|  | (9) [HO…CH3…F]- | V≠f | 198.8 | -1.29  | -1.67  | 8.17  | 4.11  | 6.18  | 6.43  |
|  |  | V≠r | 175.8 | -4.32  | -5.43  | 9.19  | 3.44  | 6.57  | 6.48  |
|  |  | ΔE | 374.5 | 3.03  | 3.76  | -1.02  | 0.67  | -0.38  | -0.05  |
| **UAG9** | (10) H…N1…N2 | V≠f | 143.9 | 2.08  | 2.84  | 11.53  | 4.10  | 6.85  | 7.75  |
|  |  | V≠r | 112.7 | -2.36  | -2.76  | 2.36  | -0.23  | -0.47  | -0.29  |
|  |  | ΔE | 220.1 | 4.45  | 5.60  | 9.17  | 4.33  | 7.33  | 8.04  |
|  | (11) H…CH2=CH2 | V≠f | 192.5 | -0.52  | 0.22  | 5.87  | -1.83  | 1.00  | 1.54  |
|  |  | V≠r | 135.1 | -5.85  | -5.91  | 1.84  | -3.87  | -0.44  | -0.15  |
|  |  | ΔE | 266.2 | 5.33  | 6.13  | 4.03  | 2.04  | 1.43  | 1.69  |
|  | (12) c-[H…C…N] | V≠f | 118.8 | 0.82  | 1.25  | 0.49  | 0.24  | 1.10  | 1.31  |
|  |  | V≠r | 137.8 | -0.83  | -1.37  | 0.76  | -0.53  | 0.53  | 0.49  |
|  |  | ΔE | 119.4 | 1.65  | 2.62  | -0.27  | 0.77  | 0.57  | 0.82  |

a Forward V≠f and backward V≠r reaction barriers in the TSG36 set [9]. ΔE = V≠f – V≠r HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, which are generally the W1 [11] values calculated at the optimized geometries at the QCISD/MG3 [12,13] level.

c Deviation = Ref. – Calc. The G3Large [55] basis sets are generally used in the present work. The xDH-PBE0 data are taken from Ref. 53.

Table S2 (Continued). Errors (in kcal/mol) in predicting transition state energies.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  | Deviation d) |  |  |
| Subset a,b) | Transition State a) | Distance b) | Ref c) | HCTH407 | BLYP | PBE | QCISD | MP2 | HF |
| **HTG9** | (1) HO…H…CH3 | V≠f | 134.1 | 7.80  | 9.09  | 11.94  | -2.59  | -1.84  | -19.82  |
|  |  | V≠r | 119.2 | 6.37  | 9.12  | 10.78  | -1.14  | -5.55  | -9.04  |
|  |  | ΔE | 253.0 | 1.43  | -0.03  | 1.17  | -1.45  | 3.71  | -10.79  |
|  | (2) O…H1…H2 | V≠f | 89.4 | 7.24  | 9.24  | 7.03  | -0.45  | -7.22  | -6.59  |
|  |  | V≠r | 121.5 | 7.29  | 11.77  | 14.56  | -3.26  | -3.61  | -19.55  |
|  |  | ΔE | 210.9 | -0.05  | -2.53  | -7.53  | 2.81  | -3.62  | 12.96  |
|  | (3) H1…H2…SH | V≠f | 116.0 | 2.04  | 5.50  | 4.50  | -1.48  | -3.80  | -8.54  |
|  |  | V≠r | 142.6 | 1.39  | 2.93  | 7.82  | -3.64  | -0.08  | -9.86  |
|  |  | ΔE | 257.8 | 0.64  | 2.57  | -3.32  | 2.16  | -3.72  | 1.32  |
| **HATG9** | (4) H…O…NN | V≠f | 143.1 | 2.76  | 9.26  | 7.75  | -1.54  | -18.99  | -10.07  |
|  |  | V≠r | 122.6 | 24.18  | 21.52  | 30.70  | -6.58  | -5.33  | -40.59  |
|  |  | ΔE | 218.7 | -21.42  | -12.26  | -22.95  | 5.04  | -13.67  | 30.52  |
|  | (5) H…Cl…H | V≠f | 148.0 | 3.61  | 7.97  | 8.12  | -2.96  | -6.04  | -13.68  |
|  |  | V≠r | 290.0 | 3.61  | 7.97  | 8.12  | -2.96  | -6.04  | -13.68  |
|  |  | ΔE | 290.0 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
|  | (6) CH3…F…Cl | V≠f | 204.7 | 10.63  | 14.20  | 13.67  | -1.29  | -11.98  | -8.10  |
|  |  | V≠r | 176.7 | 12.98  | 18.26  | 18.34  | -5.46  | -15.14  | -19.10  |
|  |  | ΔE | 381.4 | -2.35  | -4.06  | -4.67  | 4.17  | 3.17  | 11.00  |
| **NSG9** | (7) [Cl…CH3…Cl]- | V≠f | 230.3 | 1.65  | 6.87  | 6.72  | -2.32  | -1.04  | -4.79  |
|  |  | V≠r | 460.5 | 2.92  | 7.95  | 6.57  | -2.12  | -1.27  | -2.87  |
|  |  | ΔE | 460.5 | -1.27  | -1.07  | 0.15  | -0.21  | 0.23  | -1.93  |
|  | (8) [F…CH3…Cl]- | V≠f | 202.0 | 2.41  | 6.69  | 6.87  | -0.93  | -0.63  | -1.91  |
|  |  | V≠r | 211.4 | 2.18  | 7.21  | 7.99  | -3.19  | -1.56  | -13.56  |
|  |  | ΔE | 413.4 | 0.23  | -0.52  | -1.11  | 2.26  | 0.92  | 11.65  |
|  | (9) [HO…CH3…F]- | V≠f | 198.8 | 2.66  | 7.17  | 8.02  | -1.63  | 0.00  | -9.40  |
|  |  | V≠r | 175.8 | 2.35  | 8.00  | 7.92  | -2.18  | -0.25  | -10.84  |
|  |  | ΔE | 374.5 | 0.31  | -0.84  | 0.09  | 0.55  | 0.25  | 1.44  |
| **UAG9** | (10) H…N1…N2 | V≠f | 143.9 | 5.98  | 9.24  | 9.27  | -1.28  | -13.95  | -8.40  |
|  |  | V≠r | 112.7 | -0.61  | 2.30  | 1.66  | -0.97  | 2.79  | -2.92  |
|  |  | ΔE | 220.1 | 6.59  | 6.94  | 7.61  | -0.31  | -16.73  | -5.48  |
|  | (11) H…CH2=CH2 | V≠f | 192.5 | -0.65  | 2.35  | 1.77  | -1.19  | -8.06  | -2.43  |
|  |  | V≠r | 135.1 | -1.35  | 3.60  | 1.50  | -2.29  | -4.07  | -2.43  |
|  |  | ΔE | 266.2 | 0.69  | -1.25  | 0.27  | 1.10  | -3.99  | 0.00  |
|  | (12) c-[H…C…N] | V≠f | 118.8 | 0.87  | 1.12  | 2.19  | 0.26  | -5.04  | 0.29  |
|  |  | V≠r | 137.8 | 0.76  | 0.99  | 2.11  | -0.38  | -2.32  | -4.96  |
|  |  | ΔE | 119.4 | 0.11  | 0.12  | 0.09  | 0.64  | -2.72  | 5.26  |

a Forward V≠f and backward V≠r reaction barriers in the TSG36 set [9]. ΔE = V≠f – V≠r HT: hydrogen transfer; HAT: heavy atom transfer; NS: nucleophilic substitution of anion; UA: unimolecular and association. Each subset contains 9 geometric data.

b Reference data are taken from Ref. 9, which are generally the W1 [11] values calculated at the optimized geometries at the QCISD/MG3 [12,13] level.

c Deviation = Ref. – Calc. The G3Large [55] basis sets are generally used in the present work. The xDH-PBE0 data are taken from Ref. 53.

Table S3: Statistics on the calculation errors1 for geometries (pm) and energies (kcal/mol) of the transition states.

|  |  |  |  |
| --- | --- | --- | --- |
| Method | Geometry errors |  | Energy errors |
| MAX | MSE | MAD | RMSD |  | MAX | MSE | MAD | RMSD |
| XYG3 | 7.9 | -0.6 | 1.6 | 2.3 |  | 3.5 | 0.1 | 1.2 | 1.5 |
| XYGJ-OS | 7.5 | -0.9 | 1.7 | 2.3 |  | 4.3 | -0.1 | 1.1 | 1.5 |
| xDH-PBE0 | 4.7 | -0.2 | 1.5 | 2.0 |  | 5.7 | -0.9 | 1.3 | 1.6 |
| B2PLYP | 8.8 | -1.8 | 2.5 | 3.1 |  | 6.3 | 1.2 | 1.7 | 2.0 |
| B2PLYP-D | 8.9 | -2.0 | 2.6 | 3.2 |  | 28.0 | 0.3 | 3.3 | 6.4 |
| B3LYP | 31.4 | -6.4 | 7.3 | 9.8 |  | 10.3 | 3.1 | 3.5 | 3.3 |
| B3LYP-D3 | 36.1 | -6.8 | 8.0 | 11.2 |  | 10.8 | 3.5 | 3.9 | 3.5 |
| B3PW91 | 25.9 | -4.4 | 5.6 | 7.7 |  | 13.9 | 2.4 | 3.3 | 3.9 |
| PBE0 | 21.6 | -2.8 | 4.1 | 6.1 |  | 14.3 | 2.3 | 3.5 | 4.0 |
| PBE0-D3 | 22.3 | -2.8 | 4.1 | 6.2 |  | 14.6 | 2.5 | 3.7 | 4.1 |
| O3LYP | 34.4 | -6.4 | 7.5 | 10.4 |  | 16.4 | 2.5 | 3.5 | 4.5 |
| X3LYP | 28.1 | -5.9 | 7.0 | 9.3 |  | 10.2 | 3.1 | 3.6 | 3.3 |
| BHHLYP | 18.3 | -1.4 | 3.5 | 4.8 |  | 10.2 | 0.6 | 2.8 | 3.6 |
| M06-2X | 5.9 | -0.1 | 2.0 | 2.5 |  | 5.6 | 0.5 | 1.1 | 1.5 |
| M06 | 14.4 | -2.9 | 4.1 | 5.0 |  | 11.9 | 1.3 | 2.5 | 3.6 |
| TPSSh | 147.4 | -3.3 | 14.5 | 32.1 |  | 16.9 | 4.7 | 5.5 | 5.0 |
| BMK | 10.9 | -2.2 | 3.1 | 3.7 |  | 4.3 | 0.6 | 1.6 | 1.9 |
| B97-1 | 27.1 | -4.8 | 5.8 | 7.5 |  | 10.7 | 2.0 | 3.2 | 3.9 |
| B97-2 | 19.6 | -3.7 | 5.3 | 6.8 |  | 11.5 | 0.9 | 2.6 | 3.7 |
| B98 | 23.9 | -5.1 | 6.2 | 7.9 |  | 9.2 | 2.2 | 3.1 | 3.3 |
| CAM-B3LYP | 19.2 | -2.7 | 3.7 | 5.1 |  | 6.7 | 2.0 | 2.5 | 2.4 |
| wB97X | 11.0 | -1.3 | 2.8 | 3.3 |  | 5.2 | 0.0 | 2.0 | 2.4 |
| wB97XD | 13.4 | -2.2 | 3.3 | 4.1 |  | 5.4 | 0.7 | 1.9 | 2.4 |
| HSE06 | 21.8 | -3.1 | 4.3 | 6.2 |  | 14.2 | 2.4 | 3.6 | 4.0 |
| LC-ωPBE | 10.8 | 0.1 | 2.1 | 2.9 |  | 5.8 | -0.6 | 2.3 | 3.0 |
| LC-PBE | 11.4 | 1.7 | 4.3 | 5.0 |  | 11.0 | -0.3 | 3.7 | 4.8 |
| TPSS | 146 | -4.3 | 15.1 | 31.9 |  | 22.9 | 5.7 | 6.9 | 6.5 |
| M06-L | 144.7 | -1.1 | 11.2 | 27.0 |  | 17.6 | 1.9 | 4.0 | 5.6 |
| B97-D | 141.7 | -10.5 | 21.8 | 33.6 |  | 18.8 | 4.0 | 5.0 | 5.7 |
| B97-D3 | 140.9 | -9.7 | 20.9 | 33.7 |  | 20.5 | 4.4 | 5.4 | 6.0 |
| HCTH407 | 144.9 | -4.0 | 14.3 | 28.7 |  | 24.2 | 2.6 | 4.2 | 6.4 |
| BLYP | 140.3 | -13.3 | 23.5 | 39.1 |  | 21.5 | 4.9 | 6.2 | 6.4 |
| PBE | 147.4 | -8.8 | 20.2 | 35.8 |  | 30.7 | 4.9 | 7.1 | 8.5 |
| QCISD | 5.7 | -0.6 | 1.5 | 2.1 |  | 6.6 | -1.0 | 2.0 | 2.4 |
| MP2 | 18.4 | 4.1 | 4.5 | 4.6 |  | 19.0 | -4.4 | 5.0 | 5.7 |
| HF | 67.0 | -4.9 | 8.4 | 15.2 |  | 40.6 | -5.2 | 9.3 | 11.6 |

1 MAX: maximum absolute error, MSE: mean signed error, MAD: mean absolute deviation, and RMSD: root mean square deviation.