Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Developing a computational model that accurately reproduces the structural features of a dinucleoside monophosphate unit within B-DNA

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# Electronic Supplementary Information (ESI)

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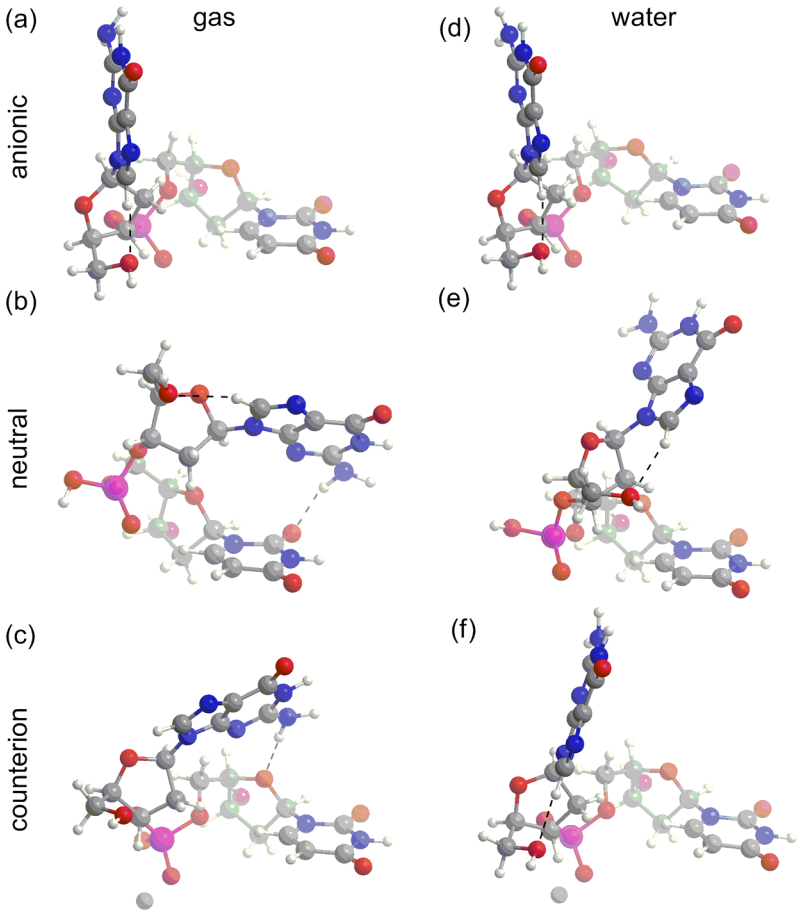


Figure ESI–1: B3LYP structures of the 5′–GU–3′ dinucleoside monophosphate sequence optimized in the gas phase (a–c) and water (d–f) using the anionic (a,d), neutral (b,e) and counterion (c,f) phosphate models.

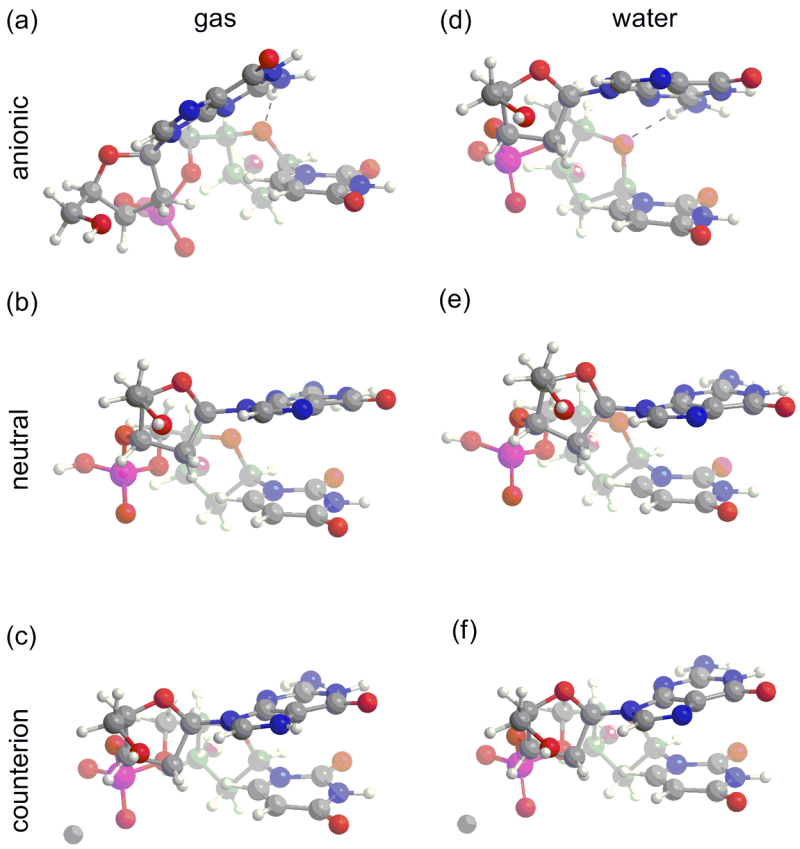


Figure ESI–2: MPWB1K structures of the 5′–GU–3′ dinucleoside monophosphate sequence optimized in the gas phase (a–c) and water (d–f) using the anionic (a,d), neutral (b,e) and counterion (c,f) phosphate models.

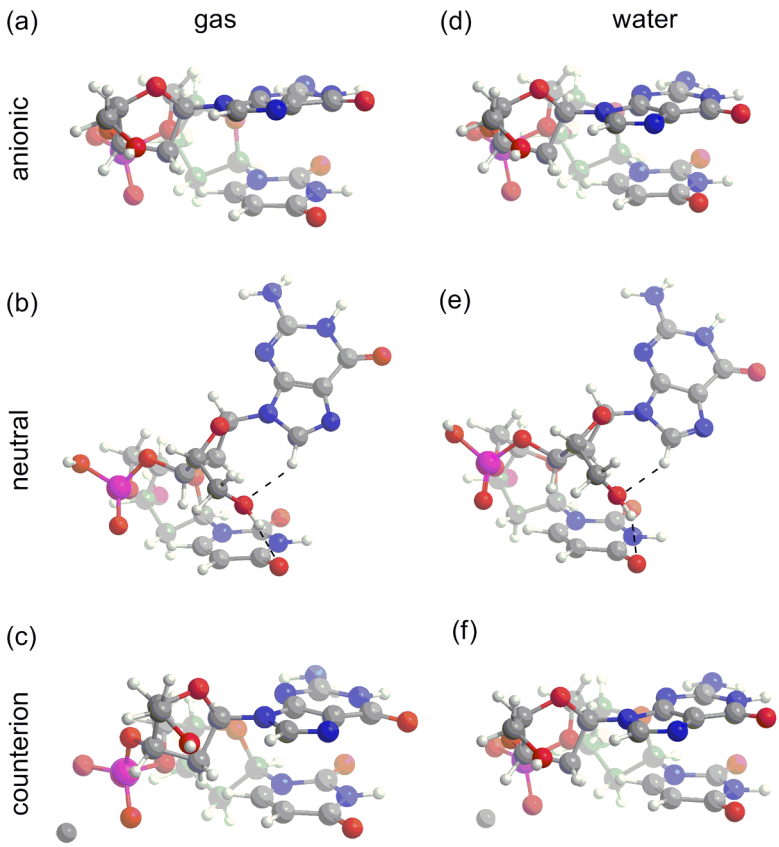


Figure ESI–3: M06-2X structures of the 5′–GU–3′ dinucleoside monophosphate sequence optimized in the gas phase (a–c) and water (d–f) using the anionic (a,d), neutral (b,e) and counterion (c,f) phosphate models.

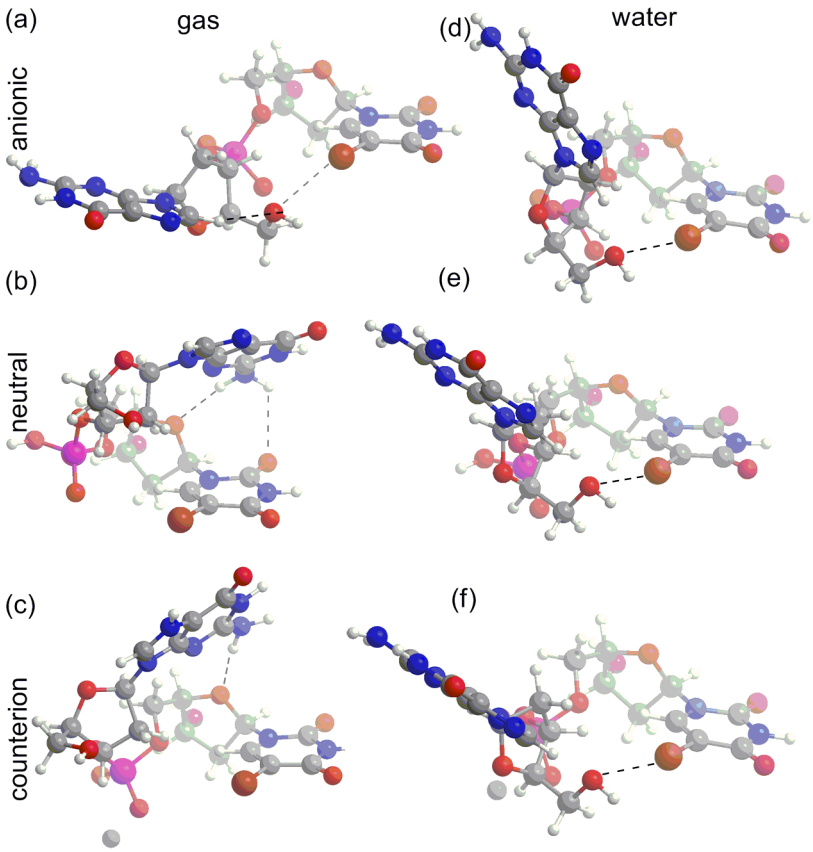


Figure ESI–4: B3LYP structures of the 5′–G$^{Br}$U–3′ dinucleoside monophosphate sequence optimized in the gas phase (a–c) and water (d–f) using the anionic (a,d), neutral (b,e) and counterion (c,f) phosphate models.

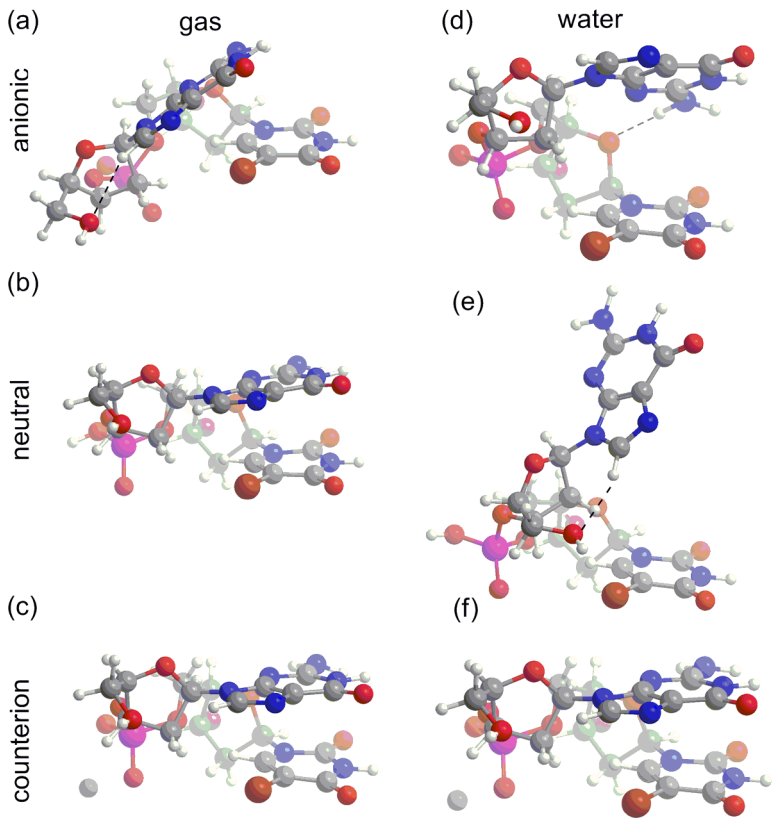


Figure ESI–5: MPWB1K structures of the 5′–G$^{Br}$U–3′ dinucleoside monophosphate sequence optimized in the gas phase (a–c) and water (d–f) using the anionic (a,d), neutral (b,e) and counterion (c,f) phosphate models.

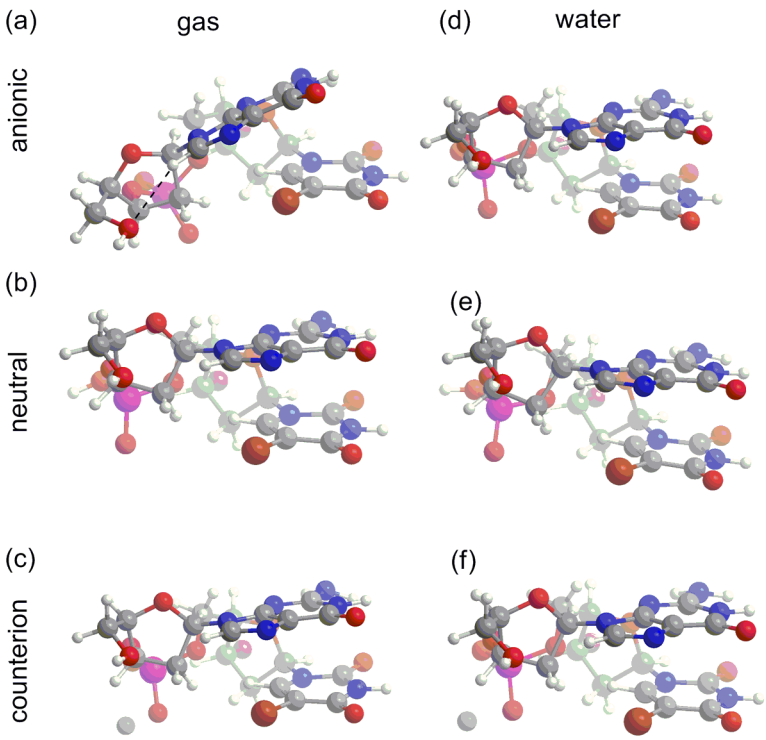


Figure ESI–6: M06-2X structures of the 5′–G$^{Br}$U–3′ dinucleoside monophosphate sequence optimized in the gas phase (a–c) and water (d–f) using the anionic (a,d), neutral (b,e) and counterion (c,f) phosphate models.

Table ESI–1: Backbone torsion angles (˚) and pseudorotation phase angles (P, ˚) of the 5′–GT–3′sequence calculated in the gas-phase and water, as well as the average value (Exp.) and standard deviation (SD) obtained from experiment.

| Gas | Anionic | | | Neutral | | | Counterion | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ∠[a] | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K[d] | M06-2X | Exp.[b] | SD[b] |
| χ5′ | 232.0 | 201.3 | 210.3 | 195.3 | 237.9 | 244.9 | 200.7 | 236.7 | 236.8 | 258 | 14 |
| δ5′ | 145.4 | 147.5 | 148.1 | 143.4 | 147.0 | 146.1 | 143.9 | 146.8 | 147.2 | 128 | 13 |
| ε | 201.8 | 167.5 | 161.9 | 193.7 | 197.6 | 224.1 | 182.2 | 160.1 | 170.6 | 184 | 11 |
| ζ | 277.6 | 278.3 | 279.0 | 261.7 | 173.9 | 275.7 | 278.8 | 272.7 | 264.9 | 265 | 10 |
| α | 261.0 | 268.6 | 271.3 | 314.8 | 23.2 | 310.4 | 295.4 | 285.5 | 295.1 | 298 | 15 |
| β | 260.0 | 247.5 | 250.5 | 185.8 | 84.5 | 152.6 | 229.3 | 221.6 | 197.2 | 176 | 9 |
| γ | 64.6 | 59.8 | 56.1 | 55.3 | 51.3 | 56.8 | 51.9 | 49.7 | 54.5 | 48 | 11 |
| χ3′ | 251.3 | 273.7 | 277.9 | 262.4 | 250.6 | 268.5 | 240.3 | 255.0 | 257.9 | 241 | 8 |
| δ3′ | 145.4 | 153.7 | 155.4 | 148.3 | 126.8 | 151.9 | 145.7 | 148.1 | 149.8 | 128 | 13 |
| P5′ | 172.2 | 164.8 | 165.7 | 160.8 | 173.5 | 174.3 | 158.7 | 165.7 | 165.9 | 144–190[c] | |
| P3′ | 171.1 | 189.5 | 199.5 | 171.9 | 127.3 | 170.7 | 166.6 | 164.3 | 171.2 | 144–190[c] | |

| Water | Anionic | | | Neutral | | | Counterion | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ∠[a] | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K[d] | M06-2X | Exp.[b] | SD[b] |
| χ5′ | 237.3 | 210.4 | 227.2 | 238.1 | 241.2 | 241.3 | 236.8 | 234.5 | 230.0 | 258 | 14 |
| δ5′ | 147.0 | 150.1 | 149.8 | 146.2 | 147.2 | 145.7 | 147.2 | 150.8 | 149.8 | 128 | 13 |
| ε | 203.3 | 162.8 | 158.0 | 220.7 | 187.1 | 217.4 | 203.8 | 172.0 | 155.8 | 184 | 11 |
| ζ | 279.5 | 277.0 | 276.8 | 264.4 | 218.0 | 280.2 | 281.0 | 266.7 | 277.2 | 265 | 10 |
| α | 284.3 | 271.5 | 274.6 | 315.5 | 323.8 | 304.1 | 281.3 | 284.4 | 274.4 | 298 | 15 |
| β | 242.3 | 244.3 | 240.7 | 157.0 | 150.3 | 159.2 | 237.8 | 209.7 | 236.8 | 176 | 9 |
| γ | 59.8 | 60.5 | 48.0 | 58.2 | 60.3 | 57.4 | 54.7 | 50.6 | 50.2 | 48 | 11 |
| χ3′ | 242.6 | 273.0 | 265.0 | 246.8 | 249.0 | 273.8 | 233.7 | 248.6 | 263.8 | 241 | 8 |
| δ3′ | 146.8 | 155.1 | 154.0 | 143.7 | 147.0 | 154.5 | 147.1 | 146.6 | 152.5 | 128 | 13 |
| P5′ | 177.8 | 170.1 | 170.6 | 177.6 | 176.8 | 174.8 | 178.4 | 170.8 | 172.6 | 144–190[c] | |
| P3′ | 170.1 | 184.1 | 178.7 | 159.1 | 158.3 | 179.9 | 167.1 | 157.7 | 172.8 | 144–190[c] | |

[a]See Figure 2 for definitions of backbone torsion angles. [b]See Ref. 113. [c]See Ref. 72. [d]Due to SCF convergence issues, structures were obtained using M06-2X-optmized structures as input rather than the standard HyperChem-generated structures.

Table ESI–2: Backbone torsion angles (˚) and pseudorotation phase angles (P, ˚) of the 5′–GU–3′ sequence calculated in the gas-phase and water, as well as the average value (Exp.) and standard deviation (SD) obtained from experiment.

| Gas | Anionic | | | Neutral | | | Counterion | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ∠[a] | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K[d] | M06-2X | Exp.[b] | SD[b] |
| χ5′ | 232.2 | 209.1 | 217.3 | 241.5 | 236.8 | 58.4 | 201.3 | 237.0 | 239.0 | 258 | 14 |
| δ5′ | 146.0 | 149.6 | 147.7 | 147.3 | 149.0 | 144.0 | 144.2 | 147.8 | 149.3 | 128 | 13 |
| ε | 206.9 | 165.8 | 157.2 | 195.2 | 173.0 | 223.2 | 182.1 | 168.4 | 170.1 | 184 | 11 |
| ζ | 280.1 | 274.7 | 278.1 | 181.6 | 253.2 | 275.9 | 278.9 | 266.0 | 265.5 | 265 | 10 |
| α | 250.1 | 264.8 | 265.9 | 27.4 | 304.0 | 309.8 | 294.8 | 291.3 | 291.2 | 298 | 15 |
| β | 264.2 | 254.3 | 253.0 | 88.1 | 190.7 | 154.8 | 230.2 | 206.5 | 199.5 | 176 | 9 |
| γ | 64.2 | 54.2 | 53.7 | 51.2 | 53.5 | 57.2 | 51.3 | 51.8 | 52.5 | 48 | 11 |
| χ3′ | 252.4 | 232.6 | 277.4 | 246.5 | 250.6 | 269.8 | 237.4 | 247.6 | 254.8 | 241 | 8 |
| δ3′ | 146.6 | 151.8 | 155.6 | 119.1 | 147.7 | 152.3 | 146.0 | 149.2 | 149.7 | 128 | 13 |
| P5′ | 172.7 | 164.5 | 164.4 | 180.2 | 168.6 | 173.1 | 159.1 | 169.0 | 169.2 | 140–190[c] | |
| P3′ | 170.8 | 170.3 | 196.6 | 121.2 | 165.4 | 172.7 | 166.5 | 168.0 | 172.5 | 144–190[c] | |

| Water | Anionic | | | Neutral | | | Counterion | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ∠[a] | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | Exp.[b] | SD[b] |
| χ5′ | 239.6 | 216.3 | 226.7 | 237.8 | 250.7 | 242.8 | 237.2 | 237.1 | 229.6 | 258 | 14 |
| δ5′ | 147.7 | 150.8 | 149.9 | 212.8 | 149.9 | 145.9 | 146.7 | 151.3 | 149.6 | 128 | 13 |
| ε | 206.8 | 161.3 | 154.8 | 219.2 | 171.4 | 216.5 | 199.3 | 171.7 | 155.8 | 184 | 11 |
| ζ | 284.0 | 277.2 | 277.6 | 263.3 | 249.9 | 280.0 | 278.3 | 265.0 | 277.1 | 265 | 10 |
| α | 276.9 | 269.0 | 267.1 | 315.0 | 179.7 | 304.2 | 284.4 | 287.2 | 272.0 | 298 | 15 |
| β | 243.4 | 245.6 | 246.5 | 162.1 | 181.4 | 160.0 | 238.0 | 205.6 | 236.2 | 176 | 9 |
| γ | 55.2 | 57.7 | 52.8 | 58.0 | 55.1 | 57.2 | 54.0 | 53.3 | 51.7 | 48 | 11 |
| χ3′ | 234.9 | 273.7 | 274.2 | 243.2 | 246.6 | 275.6 | 233.7 | 245.7 | 259.8 | 241 | 8 |
| δ3′ | 148.3 | 155.4 | 155.8 | 144.3 | 147.6 | 154.9 | 146.8 | 149.5 | 152.5 | 128 | 13 |
| P5′ | 178.7 | 171.9 | 171.7 | 178.0 | 180.0 | 174.0 | 178.1 | 173.5 | 172.8 | 144–190[c] | |
| P3′ | 170.2 | 187.9 | 189.2 | 160.0 | 160.1 | 180.7 | 166.9 | 167.9 | 176.8 | 144–190[c] | |

[a]See Figure 2 for definitions of backbone torsion angles. [b]See Ref. 113. [c]See Ref. 72. [d]Due to SCF convergence issues, structures were obtained using M06-2X-optmized structures as input rather than the standard HyperChem-generated structures.

Table ESI–3: Backbone torsion angles (˚) and pseudorotation phase angles (P, ˚) of the 5′–G$^{Br}$U–3′sequence calculated in the gas-phase and water, as well as the average value (Exp.) and standard deviation (SD) obtained from experiment.

| Gas | Anionic | | | Neutral | | | Counterion | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ∠[a] | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | Exp.[b] | SD[b] |
| χ5′ | 230.5 | 212.1 | 210.7 | 196.8 | 233.6 | 231.2 | 206.8 | 229.2 | 228.5 | 258 | 14 |
| δ5′ | 144.5 | 150.7 | 150.6 | 144.2 | 149.2 | 149.6 | 145.3 | 146.4 | 147.0 | 128 | 13 |
| ε | 278.0 | 165.8 | 162.4 | 195.1 | 160.8 | 158.2 | 179.8 | 160.3 | 154.3 | 184 | 11 |
| ζ | 286.7 | 275.7 | 278.0 | 265.0 | 266.1 | 269.2 | 276.9 | 273.1 | 278.1 | 265 | 10 |
| α | 251.1 | 268.9 | 267.0 | 308.6 | 293.8 | 292.2 | 293.4 | 283.7 | 280.0 | 298 | 15 |
| β | 260.9 | 253.4 | 256.7 | 188.1 | 221.2 | 226.5 | 230.1 | 230.6 | 239.0 | 176 | 9 |
| γ | 57.6 | 52.4 | 52.1 | 52.1 | 45.3 | 44.4 | 51.8 | 47.1 | 47.0 | 48 | 11 |
| χ3′ | 238.8 | 233.0 | 240.6 | 261.3 | 256.5 | 258.6 | 238.6 | 257.7 | 260.4 | 241 | 8 |
| δ3′ | 148.5 | 152.5 | 154.7 | 148.3 | 150.6 | 151.7 | 147.1 | 151.1 | 153.1 | 128 | 13 |
| P5′ | 169.5 | 166.6 | 167.8 | 162.3 | 167.4 | 168.4 | 160.9 | 162.9 | 165.9 | 144–190[c] | |
| P3′ | 177.3 | 170.3 | 173.9 | 172.7 | 168.3 | 171.7 | 172.2 | 171.9 | 175.3 | 144–190[c] | |

| Water | Anionic | | | Neutral | | | Counterion | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ∠[a] | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K | M06-2X | B3LYP | MPWB1K[d] | M06-2X | Exp.[b] | SD[b] |
| χ5′ | 238.0 | 202.1 | 227.3 | 237.5 | 236.7 | 232.9 | 237.5 | 229.8 | 227.7 | 258 | 14 |
| δ5′ | 145.6 | 151.7 | 150.2 | 147.0 | 146.1 | 151.8 | 149.0 | 149.5 | 150.1 | 128 | 13 |
| ε | 219.0 | 166.2 | 202.8 | 276.1 | 215.3 | 161.1 | 275.6 | 162.5 | 157.2 | 184 | 11 |
| ζ | 298.4 | 279.6 | 276.6 | 270.8 | 273.0 | 265.7 | 286.8 | 271.8 | 276.6 | 265 | 10 |
| α | 253.4 | 268.6 | 276.4 | 301.6 | 304.5 | 295.1 | 277.6 | 280.4 | 277.6 | 298 | 15 |
| β | 249.5 | 245.4 | 242.3 | 192.5 | 176.2 | 217.4 | 222.2 | 227.3 | 238.1 | 176 | 9 |
| γ | 58.0 | 60.2 | 47.2 | 50.7 | 55.7 | 47.3 | 53.1 | 50.2 | 48.0 | 48 | 11 |
| χ3′ | 238.7 | 272.7 | 260.3 | 225.6 | 237.1 | 253.1 | 231.9 | 252.4 | 258.5 | 241 | 8 |
| δ3′ | 149.5 | 154.9 | 153.8 | 146.9 | 147.7 | 150.4 | 148.3 | 149.9 | 152.7 | 128 | 13 |
| P5′ | 176.6 | 172.2 | 170.4 | 176.0 | 170.9 | 172.2 | 178.5 | 170.0 | 171.3 | 144–190[c] | |
| P3′ | 174.4 | 180.6 | 176.7 | 167.3 | 157.8 | 167.0 | 173.0 | 166.2 | 173.5 | 144–190[c] | |

[a]See Figure 2 for definitions of backbone torsion angles. [b]See Ref. 113. [c]See Ref. 72. [d]Due to SCF convergence issues, structures were obtained using M06-2X-optmized structures as input rather than the standard HyperChem-generated structures.

Table ESI–4: Comparison of the 6-31G(d,p) and 6-31+G(d,p) backbone torsion angles (˚), pseudorotation phase angles (P, ˚) and the angle between nucleobase planes (φ, ˚) for the 5′–GT–3′ sequence calculated in the gas-phase and water with M06-2X for the anionic and counterion phosphate models, as well as the average value (Exp.) and standard deviation (SD) obtained from experiment.

| | Anionic | | | | Counterion | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 6-31+G(d,p) | | 6-31G(d,p) | | 6-31+G(d,p) | | 6-31G(d,p) | | Exp.[b] | SD[b] |
| ∠[a] | Gas | Water | Gas | Water | Gas | Water | Gas | Water | | |
| χ5′ | 201.7 | 233.9 | 210.7 | 227.3 | 238.3 | 260.5 | 228.5 | 227.7 | 258 | 14 |
| δ5′ | 146.1 | 149.5 | 150.6 | 150.2 | 146.7 | 147.5 | 147.0 | 150.1 | 128 | 13 |
| ε | 167.2 | 162.6 | 162.4 | 202.8 | 154.4 | 160.3 | 154.3 | 157.2 | 184 | 11 |
| ζ | 279.4 | 272.6 | 278.0 | 276.6 | 276.7 | 268.3 | 278.1 | 276.6 | 265 | 10 |
| α | 272.1 | 283.5 | 267.0 | 276.4 | 283.1 | 300.1 | 280.0 | 277.6 | 298 | 15 |
| β | 249.4 | 223.5 | 256.7 | 242.3 | 230.7 | 188.3 | 239.0 | 238.1 | 176 | 9 |
| γ | 56.2 | 49.1 | 52.1 | 47.2 | 46.7 | 55.8 | 47.0 | 48.0 | 48 | 11 |
| χ3′ | 279.1 | 254.3 | 240.6 | 260.3 | 257.9 | 251.5 | 260.4 | 258.5 | 241 | 8 |
| δ3′ | 154.2 | 149.4 | 154.7 | 153.8 | 150.2 | 146.0 | 153.1 | 152.7 | 128 | 13 |
| P5′ | 163.1 | 173.2 | 167.8 | 170.4 | 168.4 | 189.3 | 165.9 | 171.3 | 144–190[c] | |
| P3′ | 198.5 | 168.9 | 173.9 | 176.7 | 170.9 | 160.9 | 175.3 | 173.5 | 144–190[c] | |
| φ | 32.1 | 6.1 | 28.8 | 4.9 | 11.6 | 6.8 | 12.9 | 4.7 | – | |

[a]See Figure 2 for definitions of backbone torsion angles. [b]See Ref. 113. [c]See Ref. 72.