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Supporting Information for *ChemBioChem* F444

Solution structure and stability of tryptophan-containing nucleopeptide duplexes

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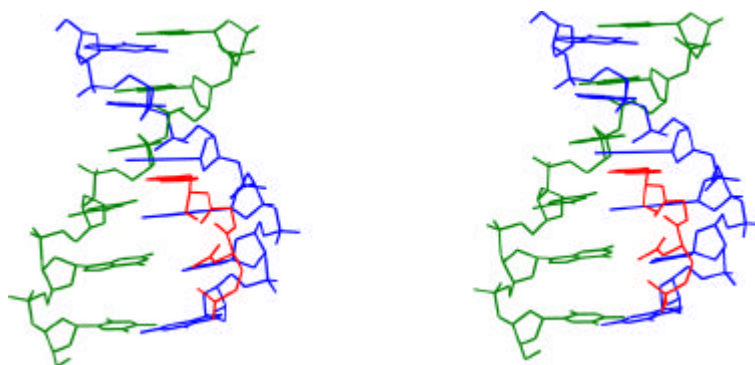


Figure S1: Stereoview of a model of [Ac-Lys-Trp-Lys-Hse(p³dGCATCG)-Ala]-[p⁵dCGTAGC] (compound **I**), with the tryptophan intercalated between the central AT base-pairs. Blue: oligonucleotide chain of the nucleopeptide. Red: peptide chain. Green: complementary oligonucleotide strand.

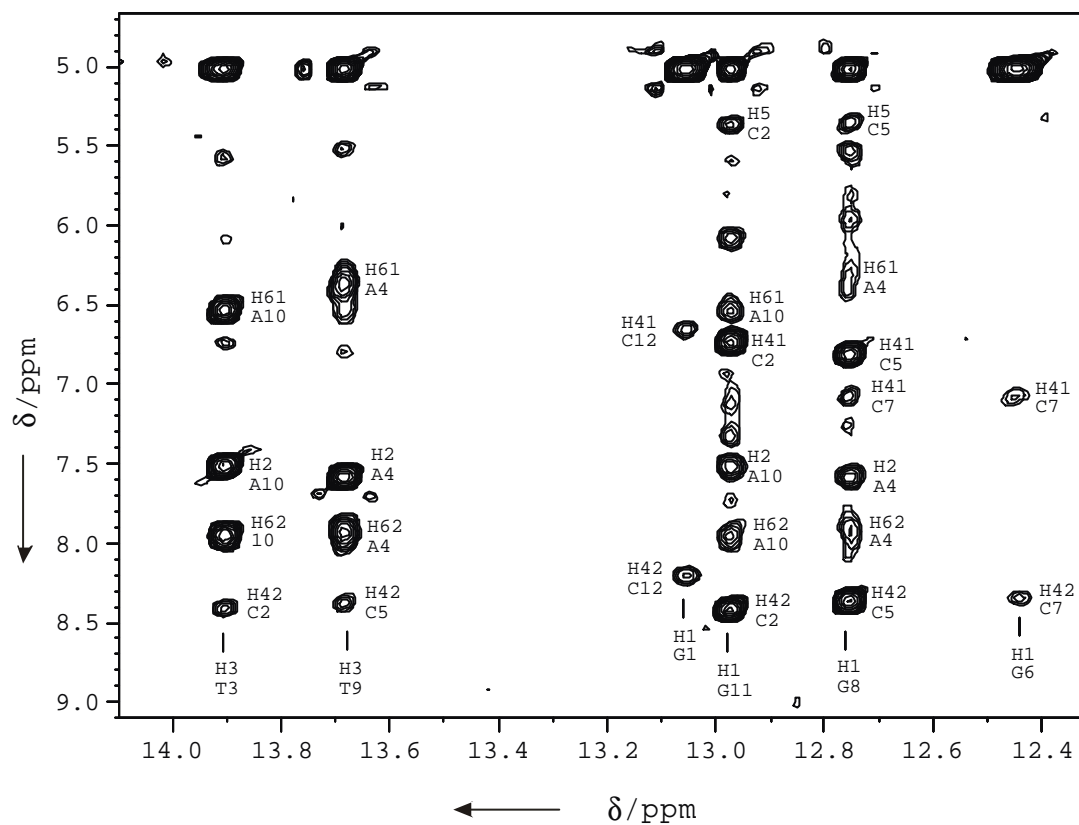


Figure S2. Imino region of the NOESY spectra of [Ac-Lys-Trp-Lys-Hse(^{p3}dGCATCG)-Ala]-[^{p5}dCGTAGC] in H₂O (100mM NaCl, T=5°C, pH=7, τ_m = 200 ms).

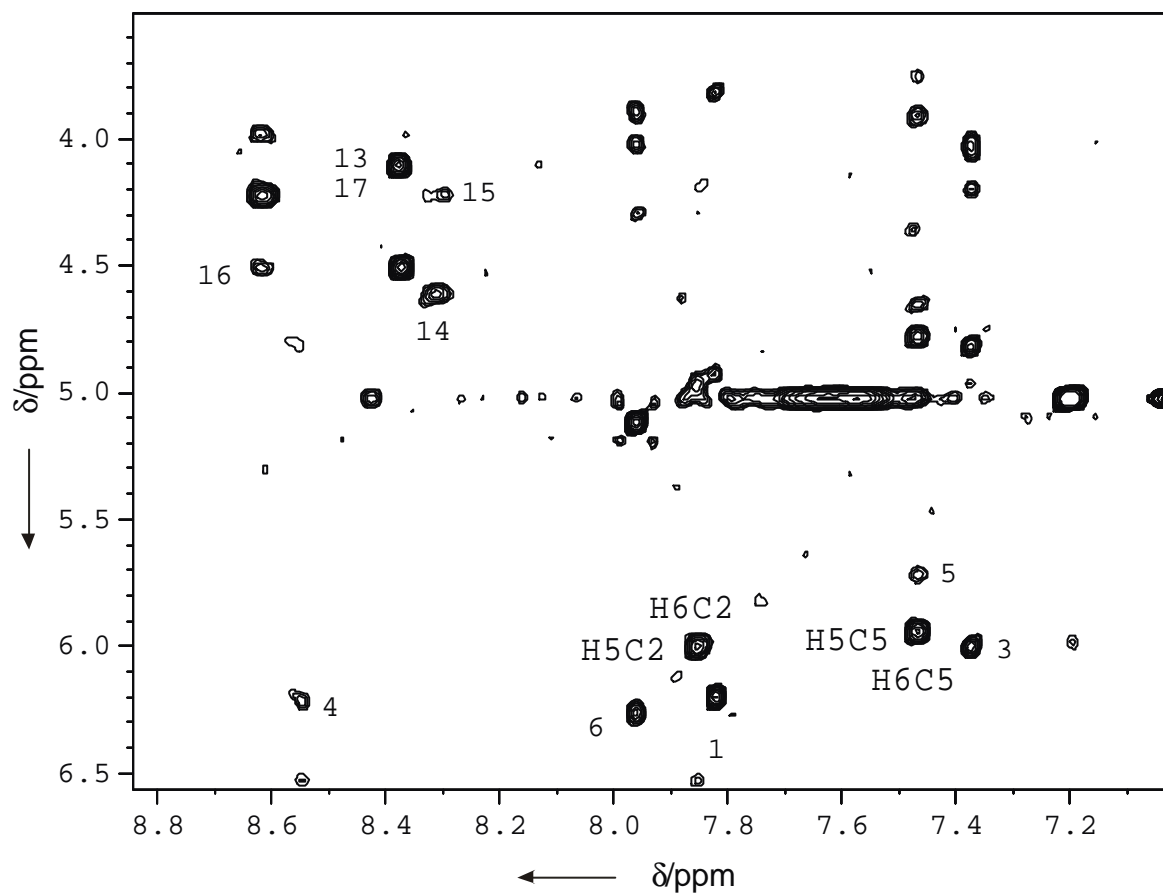


Figure S3. Fragment of the NOESY spectra of the single stranded form of [Ac-Lys-Trp-Lys-Hse(p^3 'dGCATCG)-Ala] in H₂O (100mM NaCl, T=5°C, pH=7, τ_m = 200 ms). Intra-residual H α -HN, and H1'-H6/H8 are labelled with the residue number.

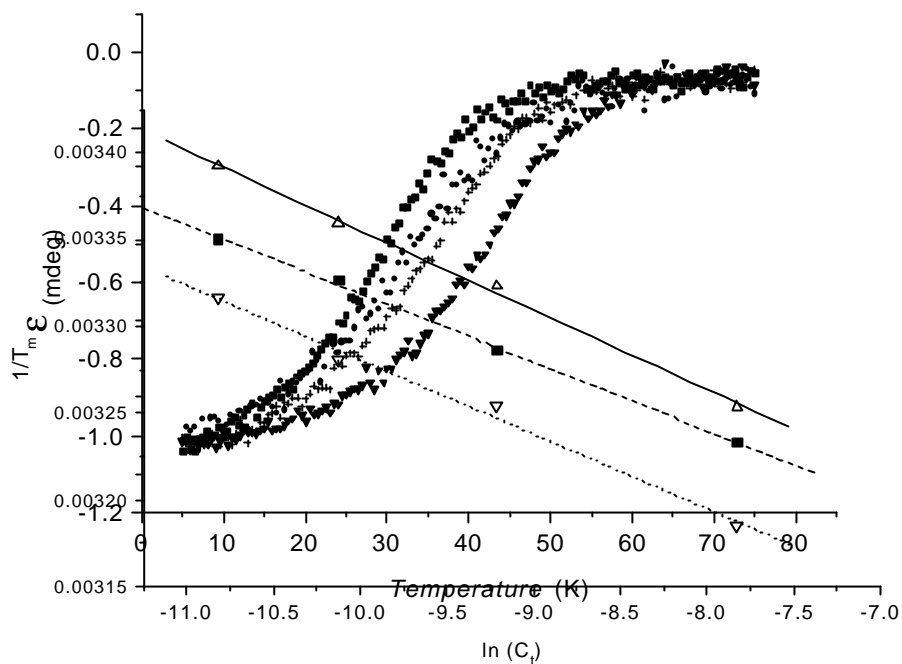


Figure S4: Top: CD melting curves of [Ac-Ala-Trp-Ala-HSE(p^{3'}GCATGC)-Ala]₂ at different concentrations (20 μ M, 40 μ M, 100 μ M, and 400 μ M). Bottom: Plot of $1/T_m$ versus $\ln C$ for the melting transition of [Ac-Ala-Trp-Ala-HSE(p^{3'}GCATGC)-Ala]₂ (up triangle), [Ac-Lys-Trp-Lys-HSE(p^{3'}GCATCG)-Ala]₂ (black square), and d(GCATCG)₂ (down triangle).

Table S1. $^1\text{H-NMR}$ assignments of [Ac-Lys-Trp-Lys-Hse(p^3 dGCATCG)-Ala-OH]-
[p^5 dCGTAGC] (100mM NaCl, T=5°C, pH=7).

| Residue | H4' | H1' | H6/H8 | H2' | H2'' | H3' | H5' | H2/H5 /M | NH ₂ (2) | NH ₂ (1) | NH |
|---------|------|------|-------|------|------|------|------|-------------|---------------------|---------------------|-------|
| 1GUA | 4.30 | 6.01 | 8.01 | 2.71 | 2.80 | 4.87 | 3.76 | | | | 13.06 |
| 2CYT | 4.27 | 6.09 | 7.57 | 2.53 | 2.17 | 4.86 | | 5.36 | 8.41 | 6.74 | |
| 3THY | 4.16 | 5.59 | 7.49 | 2.22 | 2.48 | 4.91 | | 1.70 | | | 13.91 |
| 4ADE | 4.46 | 6.22 | 8.38 | 2.76 | 2.87 | 5.07 | 4.18 | 7.58 | 7.92 | 6.36 | |
| 5CYT | 4.10 | 5.54 | 7.24 | 1.65 | 2.11 | 4.79 | 4.26 | 5.35 | 8.36 | 6.81 | |
| 6GUA | 4.33 | 5.91 | 7.93 | 2.76 | 2.56 | 5.04 | 4.10 | | | | 12.46 |
| 7CYT | 4.14 | 5.79 | 7.73 | 2.13 | 2.49 | 4.78 | 3.78 | 5.97 | 8.34 | 7.09 | |
| 8GUA | 4.19 | 6.00 | 8.05 | 2.73 | 2.81 | 4.86 | | | | | 12.76 |
| 9THY | 4.19 | 5.51 | 7.34 | 2.16 | 2.41 | 4.89 | | 1.55 | | | 13.69 |
| 10ADE | 4.44 | 6.09 | 8.25 | 2.78 | 2.94 | 5.08 | 4.16 | 7.51 | 7.95 | 6.53 | |
| 11GUA | 4.38 | 5.80 | 7.72 | 2.48 | 2.66 | 4.98 | | | | | 12.98 |
| 12CYT | 4.05 | 6.08 | 7.34 | 2.18 | 2.18 | 4.47 | 4.27 | 5.22 | 8.21 | 6.65 | |

| | HN | HA | HB/2/3 | | Others |
|--------------------|------|------|-----------|-----|--|
| 13LYS ⁺ | 8.24 | 3.96 | 1.49 | | HG 1.16, HD 1.50, HE 2.82 |
| 14TRP | 7.87 | 4.40 | 2.75/2.80 | HD1 | 6.73, HE3 6.95, HE1 9.77, HZ3 6.72, HZ2 7.06 HH2 6.86 |
| 15LYS | 7.99 | 4.14 | 1.55/1.67 | | HG 1.18, HD 1.55, HE 2.89 |
| 16HSE | 8.49 | 4.54 | 2.01/2.26 | | HG2 3.97, HG3 4.12 |
| 17ALA | 8.38 | 4.09 | 1.36 | | |

⁺Acetyl terminal group = 1.82 ppm

Table S2. $^1\text{H-NMR}$ assignments of $^5\text{d}(\text{GCTACG})\cdot^5\text{d}(\text{CGTAGC})$ (100mM NaCl, T=5°C, pH=7).

| Residue | H4' | H1' | H6/H8 | H2' | H2'' | H3' | H5' | H2/H5 /M | NH ₂ (2) | NH ₂ (1) | NH |
|---------|------|------|-------|------|------|------|------|-------------|---------------------|---------------------|-------|
| 1GUA | 4.31 | 6.03 | 8.03 | 2.73 | 2.81 | 4.88 | 3.78 | | | | 13.04 |
| 2CYT | 4.28 | 6.10 | 7.59 | 2.56 | 2.19 | 4.87 | | 5.38 | 8.41 | 6.76 | |
| 3THY | 4.21 | 5.62 | 7.51 | 2.26 | 2.53 | 4.94 | 4.12 | 1.73 | | | 13.93 |
| 4ADE | 4.49 | 6.11 | 8.42 | 2.80 | 2.92 | 5.09 | | 7.60 | 7.95 | 6.41 | |
| 5CYT | 4.19 | 5.63 | 7.35 | 1.88 | 2.31 | 4.83 | | 5.42 | 8.41 | 6.89 | |
| 6GUA | 4.21 | 6.16 | 7.95 | 2.65 | 2.39 | 4.70 | | | | | 12.88 |
| 7CYT | 4.11 | 5.76 | 7.70 | 2.12 | 2.48 | 4.76 | 3.76 | 5.94 | 8.21 | 7.13 | |
| 8GUA | | 6.01 | 8.06 | 2.73 | 2.83 | 4.89 | | | | | 12.88 |
| 9THY | 4.22 | 5.55 | 7.37 | 2.19 | 2.45 | 4.92 | | 1.57 | | | 13.73 |
| 10ADE | 4.47 | 6.12 | 8.27 | 2.80 | 2.95 | 5.09 | 4.05 | 7.49 | 7.95 | 6.53 | |
| 11GUA | 4.40 | 5.81 | 7.75 | 2.51 | 2.68 | 5.00 | | | | | 12.98 |
| 12CYT | 4.07 | 6.11 | 7.39 | 2.20 | 2.20 | 4.50 | | 5.31 | 8.21 | 6.67 | |

Table S3. Melting temperatures for some protons of [Ac-Lys-Trp-Lys-Hse(p^{3'}dGCATCG)-Ala-OH]-[p^{5'}dCGTAGC] (**I**), and the control duplex (**II**).

| Residue | Proton | T _m (°C) |
|------------------|--------|----------------------|
| W14 (I) | HZ2 | 44 |
| W14 (I) | HE3 | 44 |
| W14 (I) | HH2 | 45 |
| W14 (I) | HD1 | 42 |
| W14 (I) | HZ3 | 45 |
| T3 (I) | Met | 46 |
| T9 (I) | Met | 48 |
| T3 (II) | Met | 37 |
| T9 (II) | Met | 44 |

Table S4. Relaxation times.

| Residue | Proton | T ₁ (s) | T ₂ (ms) | τ _c (ns) |
|---------|----------|--------------------|---------------------|---------------------|
| A4 | H8 | 2.16 | 52.42 | 1.97 |
| A10 | H8 | 2.10 | 45.73 | 2.07 |
| G8 | H8 | 1.93 | 71.35 | 1.59 |
| G1 | H8 | 1.98 | 51.04 | 1.91 |
| G6 | H8 | 2.25 | 83.56 | 1.59 |
| C7, G11 | H6, H8 | 1.96 | 78.63 | 1.53 |
| C2, A4 | H6, H2 | 3.06 | 51.08 | 2.37 |
| A10 | H2 | 3.69 | 59.18 | 2.42 |
| T3 | H6 | 2.22 | 59.18 | 1.88 |
| T9, C12 | H6 | 2.01 | 31.03 | 2.47 |
| C5 | H6 | 2.19 | 49.08 | 2.05 |
| W14 | HZ2 | 3.33 | 99.83 | 1.77 |
| W14 | HE3 | 2.27 | 79.36 | 1.64 |
| W14 | HH2 | 2.84 | 86.35 | 1.76 |
| W14 | HD1, HZ3 | 2.44 | 132.68 | 1.31 |

Table S5. List of peptide-DNA distance constraints.

| Constraint | | | | UPPER | LOWER |
|------------|-----|------|------------|-------|-------|
| 6 | GUA | H2'' | 14 TRP HZ3 | 3.69 | 3.19 |
| 6 | GUA | H1' | 14 TRP HE3 | 4.28 | 3.78 |
| 6 | GUA | H2'' | 14 TRP HE3 | 4.25 | 3.75 |
| 6 | GUA | H2' | 16 HSE HA | 4.16 | 3.62 |
| 6 | GUA | H2'' | 16 HSE HA | 3.67 | 3.17 |
| 6 | GUA | H1' | 16 HSE HG2 | 3.58 | 3.08 |
| 6 | GUA | H1' | 16 HSE HG3 | 4.00 | 1.80 |
| 6 | GUA | H2' | 16 HSE HG2 | 4.00 | 2.57 |
| 6 | GUA | H2'' | 16 HSE HG2 | 4.00 | 2.50 |
| 6 | GUA | H1' | 14 TRP HZ3 | 3.50 | 2.50 |
| 6 | GUA | H1' | 14 TRP HH2 | 5.00 | 4.00 |
| 6 | GUA | H8 | 14 TRP HZ3 | 5.50 | 4.00 |
| 6 | GUA | H8 | 14 TRP HE3 | 5.00 | 4.00 |
| 6 | GUA | H1' | 16 HSE HA | 5.00 | 4.16 |
| 7 | CYT | H1' | 14 TRP HD1 | 5.00 | 1.80 |
| 7 | CYT | H1' | 14 TRP HE1 | 5.00 | 1.80 |
| 6 | GUA | H1' | 14 TRP HE1 | 5.50 | 1.80 |
| 6 | GUA | H8 | 16 HSE HA | 4.51 | 3.76 |