Electronic Supplementary Material (ESI) for Faraday Discussions.

Stereochemistry-dependent Hydrogen Bonds Stabilise Stacked Conformations in Cyclic Dipeptides: (LD) *vs.* (LL) cyclo Tyrosine-Tyrosine.

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Table S1: Energetic parameters of all stable calculated conformers calculated for c-LL (left) and c-LD (right), including the isomerism due to the torsion of the tyrosine hydroxyls.

	Electronic Energy ΔE (kcal/mol)	**ZPE-corrected electronic Energy ΔE_{ZPE} (kcal/mol)**	**Gibbs Free Energy ΔG (kcal/mol)**	**Population (%)**		**Electronic Energy ΔE (kcal/mol)**	**ZPE-corrected electronic Energy ΔE_{ZPE} (kcal/mol)**	**Gibbs Free Energy ΔG (kcal/mol)**	**Population (%)**
c-$g^+_{LII}g^-_{LI}$	1.6	1.2	0.0	20	c-$g^+_{LI}g^-_{DI}$	0.0 (2.0)*	0.0 (1.5)*	0.0 (0.5)*	24
c-$g^+_{LII}g^-_{LII}$	1.8	1.3	0.1	16	c-$g^+_{LII}g^-_{DI}$	0.2	0.2	0.1	20
c-$g^+_{LI}g^-_{LII}$	1.7	1.3	0.3	13	c-$g^+_{LII}g^-_{DII}$	0.2	0.2	0.1	20
c-$g^+_{LI}g^-_{LI}$	1.8	1.3	0.3	12	c-$g^+_{LI}g^-_{DII}$	0.5	0.4	0.3	14
c-$g^+_{LI}g^+_{LI}$	0.6	0.3	0.2	15	c-$g^+_{LII}g^+_{DII}$	1.9	1.7	1.2	3
c-$g^+_{LI}g^+_{LII}$	0.0	0.0	0.6	7.0	c-$g^+_{LII}g^+_{DI}$	1.9	1.7	1.3	3
c-$g^+_{LII}g^+_{LI}$ (identical to c-$g^+_{LI}g^+_{LII}$)	0.0	0.0	0.6	7.0	c-$g^+_{LI}g^+_{DI}$	2.1	1.9	1.4	2
c-$g^+_{LII}g^+_{LII}$	1.2	0.9	0.7	6	c-$g^+_{LI}g^+_{DII}$	2.2	2.0	1.4	2
c-$g^-_{LI}g^-_{LI}$	5.1	4.4	1.8	1	c-$g^-_{LI}g^-_{DI}$	3.6	3.2	1.2	3
c-$g^-_{LII}g^-_{LI}$	5.3	4.5	1.9	1	c-$g^-_{LI}g^-_{DII}$	3.8	3.4	1.3	3
c-$g^-_{LI}g^-_{LII}$ (identical to c-$g^-_{LII}g^-_{LI}$)	5.3	4.5	1.9	1	c-$g^-_{LII}g^-_{DI}$	3.7	3.3	1.3	3
c-$g^-_{LII}g^-_{LII}$	5.4	4.5	1.9	1	c-$g^-_{LII}g^-_{DII}$	3.9	3.4	1.4	2
c-$g^+_{LI}t_{LII}$	5.7	5.0	3.6	0	c-$t_{LI}g^+_{DII}$	1.7	1.8	2.1	1
c-$g^+_{LII}t_{LI}$ (identical to c-$g^+_{LI}t_{LII}$)	5.7	5.0	3.7	0	c-$t_{LII}g^+_{DII}$	1.8	1.8	2.3	1
c-$g^+_{LII}t_{LII}$	5.7	5.0	3.7	0	c-$t_{LII}g^+_{DI}$	3.7	3.4	3.3	0
c-$g^+_{LI}t_{LI}$	6.0	5.2	3.7	0	c-$t_{LI}g^+_{DI}$	3.7	3.4	3.4	0

c-$t_{LII}g^{-}_{LI}$	9.2	8.0	5.2	0	c-$t_{LI}g^{-}_{DI}$	7.1	6.6	4.4	0
c-$t_{LI}g^{-}_{LI}$	9.4	8.2	5.2	0	c-$t_{LI}g^{-}_{DII}$	7.3	6.7	4.5	0
c-$t_{LII}g^{-}_{LII}$	9.3	8.0	5.2	0	c-$t_{LII}g^{-}_{DI}$	6.9	6.3	4.6	0
c-$t_{LI}g^{-}_{LII}$	9.6	8.3	5.3	0	c-$t_{LII}g^{-}_{DII}$	7.0	6.4	4.6	0
c-$t_{LII}t_{LII}$	12.2	10.8	7.5	0	c-$t_{LI}t_{DII}$	10.0	9.1	7.2	0
c-$t_{LI}t_{LII}$	12.4	11.0	7.6	0	c-$t_{LII}t_{DII}$	9.9	9.0	7.2	0
c-$t_{LII}t_{LI}$ (identical to c-$t_{LI}t_{LII}$)	12.4	11.0	7.8	0	c-$t_{LI}t_{DI}$	10.3	9.4	7.4	0
c-$t_{LI}t_{LI}$	12.6	11.1	7.9	0	c-$t_{LII}t_{DI}$	10.2	9.3	7.4	0

Figure S1: Simulated infrared spectra of *c*-$g^{+}_{LI}g^{+}_{LII}$ obtained by convoluting the mode-selected anharmonic frequencies by a Lorentzian line shape (FWHM 3 cm^{-1}). Only the ν(OH), ν(NH), ν(CO) and β(NH) have been included for the anharmonic calculations. The red and blue lines in the spectrum denote the overtones and combination bands of the ν(CO) stretches, respectively (see text).