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ELECTRONIC SUPPLEMENTARY INFORMATION

Propensity for local folding induced by the urea fragment in short chain oligomers

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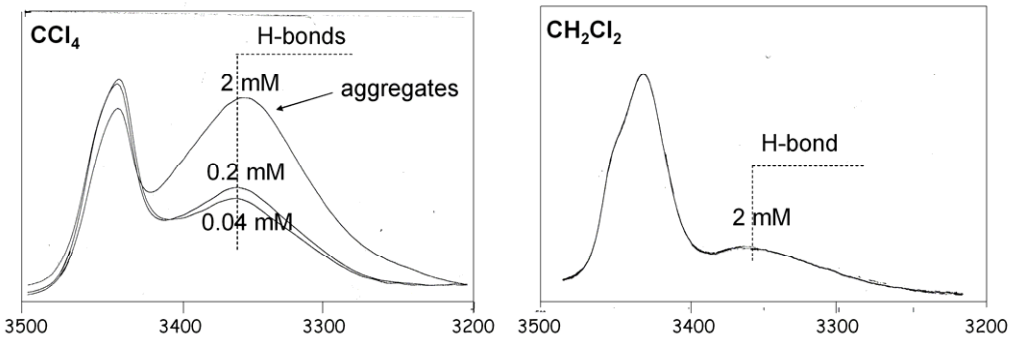

Figure S1. Influence of the concentration and the solvent on the N-H stretching absorption in compound V series. NH stretch region FT-IR data for compound **V.1b** in CCl_4 at 2, 0.2 and 0.04 mM(left) and in CH_2Cl_2 at 2 mM (right).

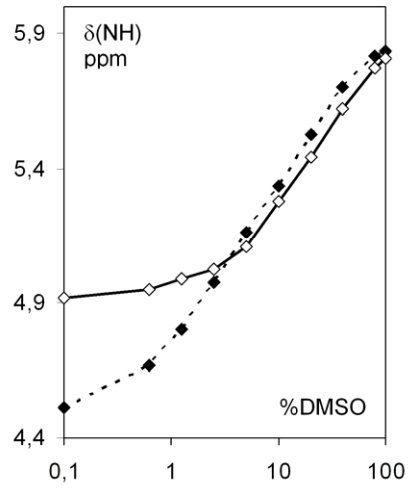

Figure S2. Influence of DMSO-d_6 content in $CDCl_3$/DMSO-d_6 mixtures on the N^2H proton resonances for **VI.1** (heavy line) and **V.1a** (broken line).

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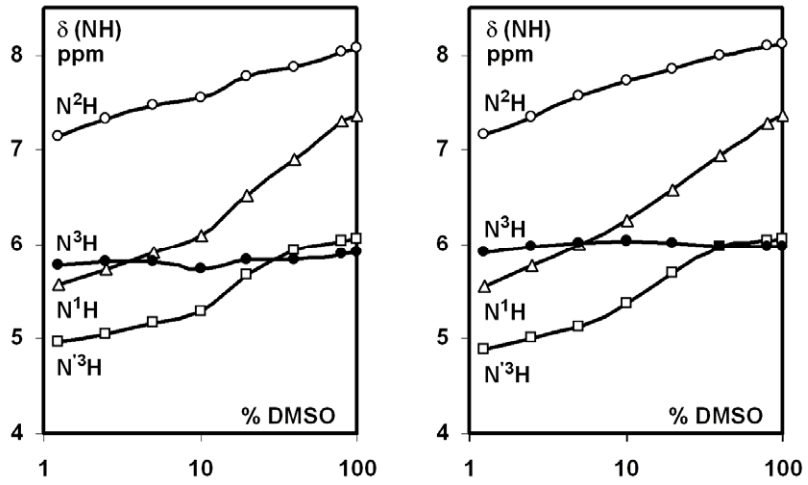

Figure S3. Influence of DMSO-d_6 content in $CDCl_3$/DMSO-d_6 mixtures on the NH proton resonances for **II.3** (left) and **II.4** (right).

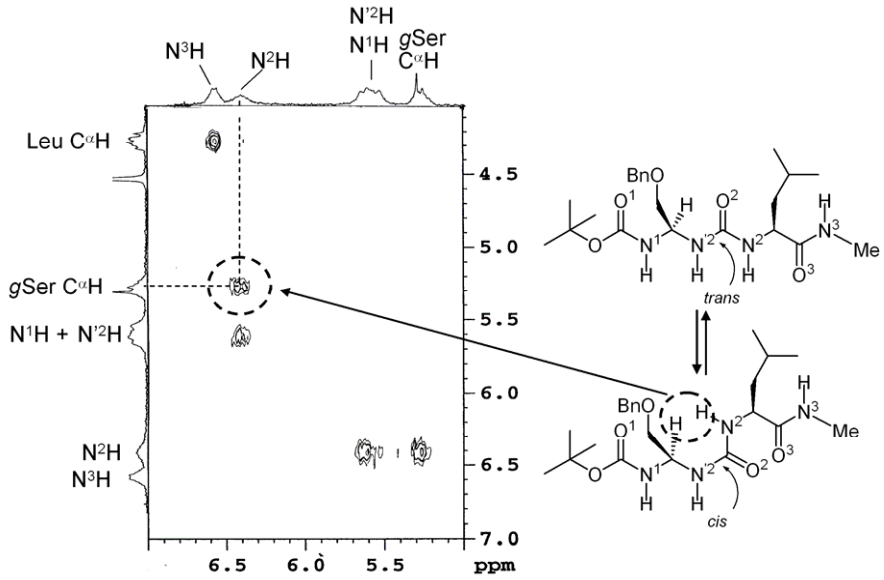

Figure S4. NOESY correlations demonstrating the *cis,trans* conformation of the *N,N'*-disubstituted urea fragment for **III.1** in $CDCl_3$.

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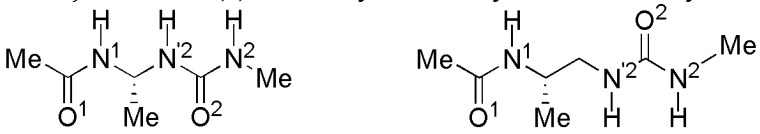

I.M **V.M**

Figure S5: formulae of model compounds **I.M** and **V.M** used for DFT calculations.

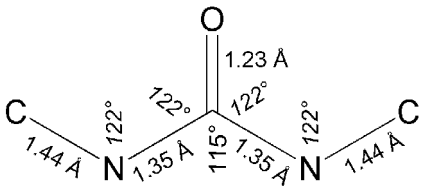

Figure S6. Average dimensions of the *N,N'*-disubstituted urea fragment.

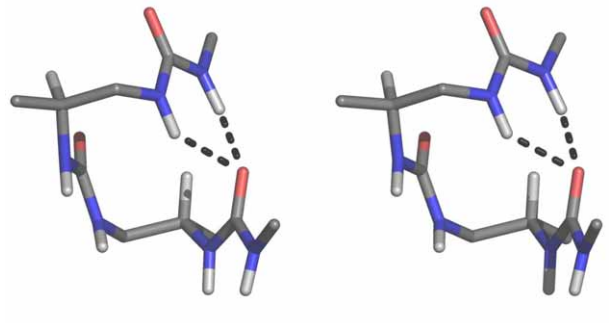

Figure S7. Urea-urea H-bond stabilizing the helical structure in oligoureas of the H-(NH-CHR-CH_2-NH)$_n$-CO-NH_2 type (stereoview), and also populated in tetraurea **VIII**.

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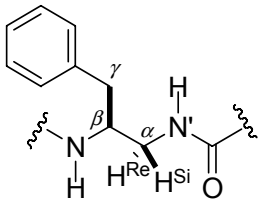

Figure S8. Nomenclature used for the description of residues in compounds **VI-VIII**

Table S1. Calculated energetics, backbone torsion angles and hydrogen bond parameters for urea-peptide derivatives containing a *gem*-diamino residue.

	u-I	*u'-I*	*C6A-I*	*C6A'-I*	*C6B-I*	*C6B'-I*	*C6C-I*	*C6D-I*	*C6D'-I*	*C8-I*	*C8'-I*
						I.M					
ΔE [a]			4.0	0.8	4.2	0.9	5.8	5.3	1.9	5.7	0.0
$\Delta_r G°$ [a]			3.1	0.3	3.6	0.1	5.6	4.6	1.3	5.8	0.0
ϕ [b]			-55.5	53.3	-177.2	-75.0	55.6	-177.0	-81.4	75.4	-84.6
ψ [b]			170.9	74.8	57.7	-55.1	71.2	56.9	-53.6	-100.3	108.1
r_{hb}(H•••O) [c]			2.099	2.326	2.206	2.486	2.385	2.188	2.402	1.878	1.948
θ(N-H•••O) [b]			129.6	116.6	122.9	106.4	116.6	123.5	110.0	168.8	167.5
						I.3a					
ΔE [a]	4.4	4.2	3.9	3.8	4.4	3.3	5.3	5.3	3.4	6.6	0.0
$\Delta_r G°$ [a]	3.3	2.8	3.5	2.6	3.8	2.5	5.0	4.9	3.5	7.6	0.0
ϕ [b]	-161.5	-83.4	-52.6	52.8	-173.4	-93.3	53.9	-173.7	-102.4	70.0	-78.6
ψ [b]	112.8	154.7	168.3	75.4	60.5	-52.4	132.4	56.9	-57.2	-108.6	112.3
r_{hb}(H•••O) [c]	-		2.004	2.438	2.079	2.269	2.390	2.036	2.134	1.898	1.998
θ(N-H•••O) [b]	-		133.7	112.8	126.9	116.2	115.3	128.8	120.7	166.5	164.8

[a] in kcal/mol
[b] in degrees
[c] in Å

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Table S2. Calculated energetics, backbone torsion angles and hydrogen bond parameters for urea-peptide derivatives having two sp^3 carbons in the main chain.

	u-V	*C7A-V*	*C7B-V*	*C7C-V*	*C7D-V*	*//-V*	*C9-V*
				V.M			
ΔE [a]	0.3	-1.9	-3.0	1.6	-2.2	-2.7	0.0
$\Delta_r G°$ [a]	2.5	-4.2	-4.4	-0.5	-3.4	-3.5	0.0
ϕ [b]	-79.1	-74.9	-158.2	-90.1	-158.2	-86.9	-97.3
ν [b]	170.9	78.4	-71.8	60.7	-71.6	48.8	46.9
ψ [b]	107.5	116.3	82.0	167.3	82.6	-102.2	87.8
r_{hb}(H•••O) [c]	-	1.954	1.976	2.144	1.968	2.310	1.965
θ(N-H•••O) [b]	-	148.9	150.5	143.0	150.7	128.5	164.2
				V.2a			
ΔE [a]	-1.7	-1.5	-3.3	1.2	-2.4	-2.0	0.0
$\Delta_r G°$ [a]	-2.7	-3.4	-3.3	-0.5	-2.2	-1.9	0.0
ϕ [b]	-77.6	-80.1	-160.6	-89.2	-160.8	-84.8	-94.3
ν [b]	169.6	75.0	-62.5	60.5	-61.8	41.7	46.7
ψ [b]	104.4	125.6	84.5	172.2	85.2	-105.3	89.1
r_{hb}(H•••O) [c]	-	2.030	2.048	2.189	2.020	2.279	1.993
θ(N-H•••O) [b]	-	150.1	148.4	141.5	149.1	132.2	161.9

[a] in kcal/mol
[b] in degrees
[c] in Å

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Table S3. Crystal data and structure refinement

	I.1b	**I.3c**	**I.4b**	**II.1'a**	**II.2**	**V.1a**	**V.1c**	**VI.2**
formula	$C_{14}H_{29}N_3O_3$	$C_{17}H_{27}N_3O_4$	$C_{13}H_{25}N_3O_3$	$C_{17}H_{32}N_4O_3$	$C_{26}H_{40}N_4O_6$	$C_{16}H_{25}N_3O_3$	$C_{17}H_{27}N_3O_3$	$C_{19}H_{24}N_4O_2$
Mr	287.4	337.42	271.36	340.47	504.62	307.39	321.42	340.42
Wavelength λ (Å)	1.5406	0.71073	0.71073	0.71073	0.71073	0.71073	1.5406	1.5406
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	triclinic
space group	*P*2(1)/*c*	*P*2(1)	*P*2(1)/*c*	*P*2(1)	*P*2(1)2(1)2(1)	*C*2	*P*2(1)2(1)2(1)	*P*1
a (Å)	12.169(6)	10.1826(8)	9.4284(2)	10.1850(12)	9.3903(7)	20.565(5)	5.241(1)	4.675(2)
b (Å)	9.397(3)	9.5473(7)	15.8240(3)	9.4470(7)	16.069(1)	5.223(1)	17.883(3)	9.497(2)
c (Å)	16.467(2)	10.2926(11)	21.0020(5)	10.571(2)	19.446(2)	17.230(4)	19.356(2)	10.809(3)
α••deg•	90	90	90	90	90	90	90	76.78(2)
β••deg•	103.86(3)	103.133(3)	98.536(1)	103.216(4)	90	105.921(8)	90	81.59(3)
γ••deg•	90	90	90	90	90	90	90	77.55(2)
Z / *Z'*	4 / 1	2 / 1	8 / 2	2 / 1	4 / 1	4 / 1	4 / 1	1 / 1
volume (Å^3)	1828(1)	974.4(2)	3098.7(1)	990.2(2)	2934.3(4)	1779.7(7)	1814.1(5)	453.8(3)
D_{calc} (g cm^{-3})	1.044	1.15	1.163	1.142	1.142	1.147	1.177	1.246
μ (mm^{-1})	0.593	0.082	0.083	0.079	0.081	0.08	0.656	0.666
2θ scan range •deg•	7.48-129.88	5.08-46.38	4.36-51.0	7.66-50.04	5.02-41.32	4.12-46.46	6.72-139.66	8.44-139.58
range *h*	0 to 14	-11 to 11	-11 to 11	-12 to 12	-9 to 9	-22 to 22	0 to 6	-5 to 5
range *k*	0 to 11	-9 to 9	-19 to 19	-11 to 11	-15 to 15	-5 to 5	0 to 21	-11 to 11
range *l*	-19 to 18	-11 to 11	-25 to 25	-12 to 12	-19 to 19	-18 to 18	0 to 23	-13 to 13
reflns collected	3249	4334	11307	15160	7886	4290	2026	3348
unique reflns	3097	1461	5770	1857	1660	1410	2026	1723
R_{int}	0.09	0.042	0.044	0.043	0.079	0.096	0	0.0518
R1, wR2 [*I* >	0.0656, 0.1825	0.0642, 0.1654	0.0517, 0.128	0.045, 0.1102	0.0441, 0.0809	0.0856, 0.2327	0.0503, 0.1307	0.0461, 0.1039

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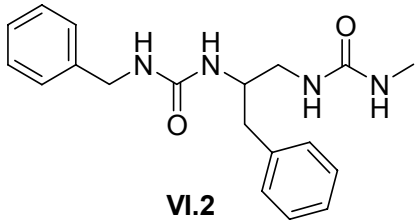

VI.2

Table S4. ^{1}H-NMR Chemical Shifts (in ppm) of **VI.2** in DMSO-d_6 at 298K (400 MHz)

N*H*Bn	NH	N'H	N*H*Me	$^{\alpha}$CH	$\Delta\delta$($^{\delta}$CH)	$^{\beta}$CH	CH_2Ph (Bn)	$^{\gamma}$CH	CH_3
6.38	6.00	5.90	5.85	3.07, 2.96	0.11	3.79	4.17	2.72, 2.62	2.54

Table S5. ^{1}H-NMR Chemical Shifts (in ppm) of **VI.2** in $CDCl_3$/DMSO-d_6 (70:30) at 298K (400 MHz)

N*H*Bn	NH	N'H	N*H*Me	$^{\alpha}$CH	$\Delta\delta$($^{\alpha}$CH)	$^{\beta}$CH	CH_2Ph (Bn)	$^{\gamma}$CH	CH_3
6.22	5.81	5.83	5.70	3.16, 2.96	0.20	3.92	4.27	2.77 (d)	2.66

Table S6. Evolution of the NH resonance (ppm) for **VI.2** in DMSO-d_6 and $CDCl_3$/DMSO-d_6 (70:30) at 298K

$\Delta\delta$ (N*H*Bn)	$\Delta\delta$ (NH)	$\Delta\delta$ (NH')	$\Delta\delta$ (N*H*Me)
0.16	0.19	0.07	0.15

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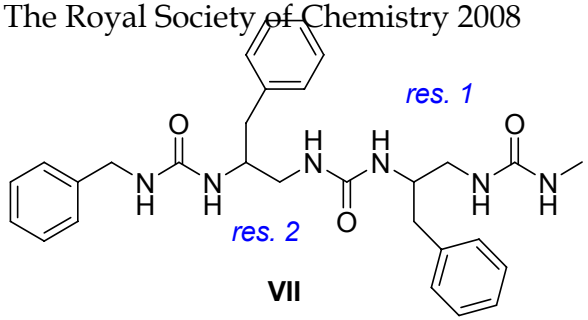

VII

Table S7. ^{1}H-NMR Chemical Shifts (in ppm) of **VII** in DMSO-d_6 at 298K (500 MHz)

Residue	N*H*Bn	NH	N'H	N*H*Me	$^{\alpha}$CH	Δδ ($^{\alpha}$CH)	$^{\beta}$CH	CH_2Ph (Bn)	$^{\gamma}$CH	CH_3
1	-	5.94	5.92	5.86	3.13, 2.85	0.28	3.82	-	3.74	2.49
2	6.41	5.94	6.01	-	3.10, 2.86	0.24	3.88	4.28, 4.20	3.81	-

Table S8. ^{1}H-NMR Chemical Shifts (in ppm) of **VII** $CDCl_3$/DMSO-d_6 (70:30) at 298K (500 MHz)

Residue	N*H*Bn	NH	N'H	N*H*Me	$^{\alpha}$CH	Δδ ($^{\alpha}$CH)	$^{\beta}$CH	CH_2Ph (Bn)	$^{\gamma}$CH	CH_3
1	-	5.83	5.80	5.73	3.30, 2.90	0.40	4.00	-	2.74	2.58
2	6.28	5.81	5.88	-	3.30, 2.86	0.44	3.92	4.31, 4.22	2.73	-

Table S9. Evolution of the NH resonance (ppm) for **VI.2** in DMSO-d_6 and $CDCl_3$/DMSO-*d6* (70:30) at 298K

Residue	Δδ (N*H*Bn)	Δδ (NH)	Δδ (NH')	Δδ (N*H*Me)
1	-	0.11	0.12	0.13
2	0.13	0.13	0.13	-

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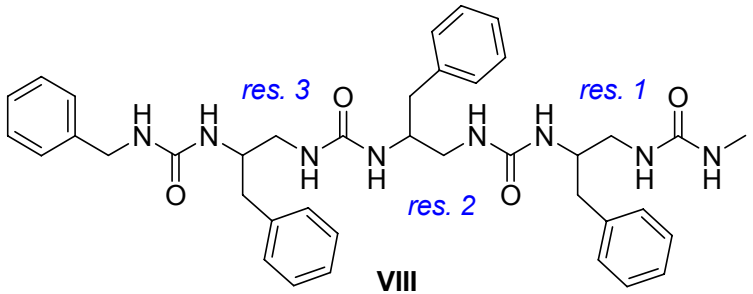

VIII

Table S10. ^{1}H-NMR Chemical Shifts (in ppm) of **VIII** in DMSO-d_6 at 298K (500 MHz)

Residue	N*H*Bn	NH	N'H	N*H*Me	$^{\alpha}$CH	Δδ($^{\alpha}$CH)	$^{\beta}$CH	CH_2Ph (Bn)	$^{\gamma}$CH	CH_3
1	-	5.93	6.02	5.96	3.27, 2.73	0.54	3.71	-	2.55, 2.43	2.55
2	-	5.93	5.84	-	3.24, 2.47	0.77	3.81	-	2.64, 2.55	-
3	6.47	6.02	6.13	-	3.20, 2.73	0.47	3.95	4.22, 4.11	2.68, 2.55	-

Table S11. ^{1}H-NMR Chemical Shifts (in ppm) of **VIII** $CDCl_3$/DMSO-*d6* (70:30) at 298K (400 MHz)

Residue	N*H*Bn	NH	N'H	N*H*Me	$^{\alpha}$CH	Δδ($^{\alpha}$CH)	$^{\beta}$CH	CH_2Ph (Bn)	$^{\gamma}$CH	CH_3
1	-	5.91	6.07	6.01	3.59, 2.71	0.88	3.89	-	2.55, 2.48	2.70
2	-	5.68	5.77	-	3.53, 2.24	1.29	4.06	-	2.67, 2.60	-
3	6.37	5.85	6.19	-	3.46, 2.56	0.90	4.18	4.31, 4.16	2.72, 2.56	-

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Table S12. Evolution of the NH resonance (ppm) for **VIII** in DMSO-*d6* and $CDCl_3$/DMSO-d_6 (70:30) at 298K

Residue	Δδ (N*H*Bn)	Δδ (NH)	Δδ (NH')	Δδ (N*H*Me)
1	-	0.02	−0.05	−0.05
2	-	0.25	0.07	-
3	0.10	0.17	−0.06	-