## Chain length, temperature and solvent effects on the structural properties of α-aminoisobutyric acid homooligopeptides

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## Content

Table S1. Averaged intramolecular hydrogen bonds<sup>a</sup> (in Å) as issuing from MD simulations

solvent	H1	H2	Н3	H4	Н5	H6	H7	H8	H9
Ac-(Aib) <sub>10</sub> -NMe									
water	3.25	3.27	3.27	2.29	3.29	3.27	3.28	3.27	3.19
water	3.15	3.25	3.25	3.25	3.25	3.25	3.25	3.25	
Ac-(Aib) <sub>7</sub> -NMe									
water	3.27	3.26	3.24	3.27	3.20	3.28			
water	3.25	3.24	3.25	3.10	3.25				
Ac-(Aib) <sub>7</sub> -NMe									
DMSO	3.20	3.23	3.23	3.21	3.15	3.23			
DMSO	3.22	3.20	3.23	3.11	3.22				
Ac-(Aib) <sub>6</sub> -NMe									
water	3.26	3.27	3.27	3.27	3.27				
water	3.16	3.24	3.25	2.92					
Ac-(Aib) <sub>5</sub> -NMe									
water	3.35	3.39	3.37	3.31					
water	3.11	3.15	2.91						
	solvent Aib) <sub>10</sub> -NM water water Aib) <sub>7</sub> -NM water Aib) <sub>7</sub> -NM DMSO DMSO DMSO Aib) <sub>6</sub> -NM water water Aib) <sub>5</sub> -NM water water water	solvent         H1           Aib) <sub>10</sub> -NM $3.25$ water $3.25$ water $3.15$ Aib) <sub>7</sub> -NM $3.27$ water $3.27$ water $3.25$ Aib) <sub>7</sub> -NM $3.27$ water $3.25$ Aib) <sub>7</sub> -NM $3.25$ Aib) <sub>7</sub> -NM $3.20$ DMSO $3.20$ DMSO $3.20$ DMSO $3.22$ Aib) <sub>6</sub> -NM $3.26$ water $3.16$ Aib) <sub>5</sub> -NM $3.35$ water $3.35$ water $3.11$	solvent       H1       H2         Aib) <sub>10</sub> -NMe $3.25$ $3.27$ water $3.25$ $3.27$ water $3.15$ $3.25$ Aib) <sub>7</sub> -NMe $3.27$ $3.26$ water $3.27$ $3.26$ water $3.25$ $3.24$ Aib) <sub>7</sub> -NMe $3.25$ $3.24$ Aib) <sub>7</sub> -NMe $3.20$ $3.23$ DMSO $3.20$ $3.23$ DMSO $3.20$ $3.23$ DMSO $3.22$ $3.20$ Aib) <sub>6</sub> -NMe $3.26$ $3.27$ water $3.26$ $3.27$ water $3.16$ $3.24$ Aib) <sub>5</sub> -NMe $3.24$ water $3.35$ $3.39$ water $3.35$ $3.39$ water $3.11$ $3.15$	solventH1H2H3Aib)10-NMewater $3.25$ $3.27$ $3.27$ water $3.15$ $3.25$ $3.25$ Aib)7-NMewater $3.27$ $3.26$ $3.24$ water $3.25$ $3.24$ $3.25$ Aib)7-NMeMater $3.25$ $3.24$ $3.25$ Aib)7-NMeDMSO $3.20$ $3.23$ $3.23$ DMSO $3.22$ $3.20$ $3.23$ DMSO $3.22$ $3.20$ $3.23$ Aib)6-NMewater $3.26$ $3.27$ $3.27$ water $3.26$ $3.27$ $3.27$ water $3.26$ $3.27$ $3.23$ Aib)6-NMewater $3.26$ $3.27$ $3.27$ water $3.16$ $3.24$ $3.25$ Aib)5-NMewater $3.35$ $3.39$ $3.37$ water $3.11$ $3.15$ $2.91$	solventH1H2H3H4Aib)10-NMwater3.253.273.272.29water3.153.253.253.25Aib)7-NMwater3.273.263.243.27water3.253.243.253.10Aib)7-NMwater3.253.243.253.10Aib)7-NMDMSO3.203.233.21DMSO3.203.233.21DMSO3.223.203.233.11Aib)6-NMwater3.263.273.27water3.163.243.252.92Aib)5-NMwater3.353.393.373.31water3.113.152.91	solventH1H2H3H4H5Aib)10-NMwater3.253.273.272.293.29water3.153.253.253.253.25Aib)7-NMewater3.273.263.243.273.20water3.253.243.253.103.25Aib)7-NMewater3.253.243.253.103.25Aib)7-NMeDMSO3.203.233.233.213.15DMSO3.203.233.233.113.22Aib)6-NMewater3.263.273.273.27water3.163.243.252.92Aib)5-NMewater3.353.393.373.31water3.113.152.91I	solventH1H2H3H4H5H6Aib)10-NMwater3.253.273.272.293.293.27water3.153.253.253.253.253.25Aib)7-NMwater3.273.263.243.273.203.28water3.253.243.253.103.253.28water3.253.243.253.103.253.24Aib)7-NM3.253.243.253.103.253.23DMSO3.203.233.233.213.153.23DMSO3.223.203.233.113.221Aib)6-NM	solventH1H2H3H4H5H6H7Aib)10-NMwater $3.25$ $3.27$ $3.27$ $2.29$ $3.29$ $3.27$ $3.28$ water $3.15$ $3.25$ $3.25$ $3.25$ $3.25$ $3.25$ $3.25$ $3.25$ Aib)7-NMwater $3.27$ $3.26$ $3.24$ $3.27$ $3.20$ $3.28$ water $3.27$ $3.26$ $3.24$ $3.27$ $3.20$ $3.28$ Aib)7-NMwater $3.25$ $3.24$ $3.27$ $3.20$ $3.28$ Aib)7-NMDMSO $3.20$ $3.23$ $3.21$ $3.15$ $3.23$ DMSO $3.22$ $3.20$ $3.23$ $3.11$ $3.22$ $1$ DMSO $3.22$ $3.20$ $3.23$ $3.11$ $3.22$ $1$ water $3.26$ $3.27$ $3.27$ $3.27$ $3.27$ $1$ Aib)6-NMwater $3.16$ $3.24$ $3.25$ $2.92$ $1$ $1$ water $3.16$ $3.24$ $3.25$ $2.92$ $1$ $1$ Aib)5-NMwater $3.35$ $3.39$ $3.37$ $3.31$ $1$ $1$ $1$ water $3.35$ $3.39$ $3.37$ $3.31$ $1$ $1$ $1$	solventH1H2H3H4H5H6H7H8Aib)10-NMwater3.253.273.272.293.293.273.283.27water3.153.253.253.253.253.253.253.253.25Aib)7-NMwater3.273.263.243.273.203.28[]water3.253.243.253.103.25[][]Mater3.253.243.253.103.25[][]Mater3.203.233.213.153.23[][]DMSO3.203.233.233.113.22[][]DMSO3.223.273.273.27[][]Aib)6-NMwater3.263.273.273.27[][]water3.263.273.273.27[][]water3.263.273.273.27[][]Mater3.263.273.273.27[][]water3.163.243.252.92[][][]Mater3.353.393.373.31[][][]water3.113.152.91[][][][]

of Aib homopeptides.

<sup>a</sup> Distances are between the donor nitrogen and the acceptor oxygen (N...O)



**Figure S1.** Ramachandran plots of all residues (from base up) for the 1-100ns simulations at 300 K with four different initial configurations: (a) random coil, (b) right-handed  $\alpha$ -helix, (c) fully-extended conformation and (d) right-handed semi-extended conformation. Red and blue regions correspond to the highest and lowest population density, respectively.



**Figure S2.** Superposition of the initial  $3_{10}$  structure (blue) and the representative unfolded structure (grey) taken at 60 ns of the 400 K MD simulation in water.



**Figure S3.** Solvent accessible surface areas (SASA's) of the Aib heptapeptide as issuing from the MD simulation at room temperature (grey line, water; blue line, DMSO).



**Figure S4.** Radial distribution functions of the hydrogen and oxigen atoms of water around the selected CO (a) and NH (b) groups of the Aib heptapeptide as issuing from the 1-100ns MD simulation at 300 K (red curves), 350 K (blue curves) and 400 K (green curves).



**Figure S5.** Radial distribution function of the oxigen atom of DMSO around the selected NH group of the Aib heptapeptide as issuing from the 1-100ns MD simulation at 300 K.