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Supplementary Material

Density functional calculations of chemical shielding of backbone ^{15}N in helical residues of protein G

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Supplementary Table S1. Computed dipole moments (in Debye) for the various models in the vacuum calculation

Residue	Model A neutral	Model B neutral –CH_3	Model C neutral –CH_3
A26	10.47	21.67	31.26
E27	10.40	29.41	41.95
K28	11.28	29.55	39.49
A29	9.10	28.52	39.04
F30	9.73	29.40	39.32
K31	8.22	28.52	38.58
Q32	5.73	26.24	36.86
Y33	5.71	25.23	33.98

Supplementary Table S2. Characteristics of the calculated ^{15}N chemical shielding tensor for selected residues. The definitions of the Euler angles α, β, γ and A_1, A_2, A_3 are in (Cai et al. 2008). The principal values of the tensor are in ppm, the angles are in degrees.

"Model C neutral"									
Residue	σ_{11}	σ_{22}	σ_{33}	α	β	γ	A_1	A_2	A_3
A26	14.14	155.28	197.2	-4.42	15.06	-3.19	86.81	12.83	77.58
E27	21.57	162.81	191.13	-7.67	17.16	-2.74	87.26	15.65	74.61
K28	19.52	160.76	194.91	-7.63	17.19	-0.35	89.65	7.67	82.34
A29	19.64	161.51	196.08	-14.22	14.97	-3.48	86.52	12.38	78.14
F30	25.06	160.73	193.85	-9.48	19.04	0.51	89.49	15.48	74.53
K31	7.59	163.19	187.04	-8.93	18.10	-1.69	88.31	24.32	65.75
Q32	19.23	160.88	196.49	0.02	15.73	-1.71	88.29	18.67	71.41
Y33	13.61	160.89	188.36	-6.12	17.22	-1.80	88.20	11.95	78.19

Model C									
Residue	σ_{11}	σ_{22}	σ_{33}	α	β	γ	A_1	A_2	A_3
A26	8.60	158.04	193.56	-11.27	15.17	-2.55	87.45	17.03	73.17
E27	1.53	159.82	180.58	-17.78	16.26	-2.38	87.62	24.82	65.31
K28	26.40	160.47	198.37	-5.28	18.16	-0.42	89.58	5.53	84.49
A29	13.18	161.31	192.12	-17.44	15.04	-3.58	86.42	15.87	74.56
F30	23.32	160.14	191.58	-10.35	18.50	0.81	89.19	15.63	74.39
K31	15.74	163.45	190.33	-6.32	18.74	-1.38	88.62	20.2	69.85
Q32	14.80	159.47	193.82	-1.56	15.81	-2.29	87.71	22.35	67.78
Y33	22.96	159.13	192.26	-4.68	16.28	-1.29	88.71	9.06	81.03

Supplementary Table S3. The effect of the side chain charges on the chemical shielding of the amide nitrogens of interest in GB3. Shown are the distances (in Å) between the center of the side chain charge (Cγ of Asp, Cδ of Glu, ε-amine N of Lys) of all ionizable helical residues in GB3 (indicated in the left column for each row) and the amide nitrogens of the residues under examination (A26 to Y33, indicated on top of each column). Shown in blue for each amide is the distance to the charge (two for Q32) that was not included in the corresponding 8-residue long-chain fragment but would be necessary in order to neutralize the charge of its salt-bridge partner. The bottom row shows the change in ^{15}N chemical shielding (in ppm) caused by the inclusion of such charges into a dipeptide model calculation. The fragment used for K28 already was neutral. Point charges of -1 (for Asp and Glu) or 1 (for Lys) were placed at the coordinate of the charge center atom in the dipeptide model. Doing so allowed us to estimate the effect of these "side-chain counterions" on the chemical shielding of the amide nitrogen of interest. As discussed in the main text, no significant effect was observed except for E27, in which case K31 was finally included in the (extended) Model C calculation.

	A26	E27	K28	A29	F30	K31	Q32	Y33
D22	5.74	7.69	8.83	10.04	11.79	13.29	14.66	16.09
E24	7.45	7.95	7.70	9.79	11.85	12.28	13.35	15.51
E27	7.30	4.97	4.82	7.45	7.73	6.83	8.84	10.99
K28	7.44	7.72	6.18	7.77	10.24	10.45	10.80	13.07
K31	10.41	7.82	6.87	8.84	8.49	6.36	7.95	10.17
D36	14.91	13.90	12.15	10.14	9.40	8.81	6.46	4.88
Δσ, ppm	0.21	4.77	N/A	1.08	0.12	-0.89	1.96	0.20