SUPPLEMENTARY MATERIAL

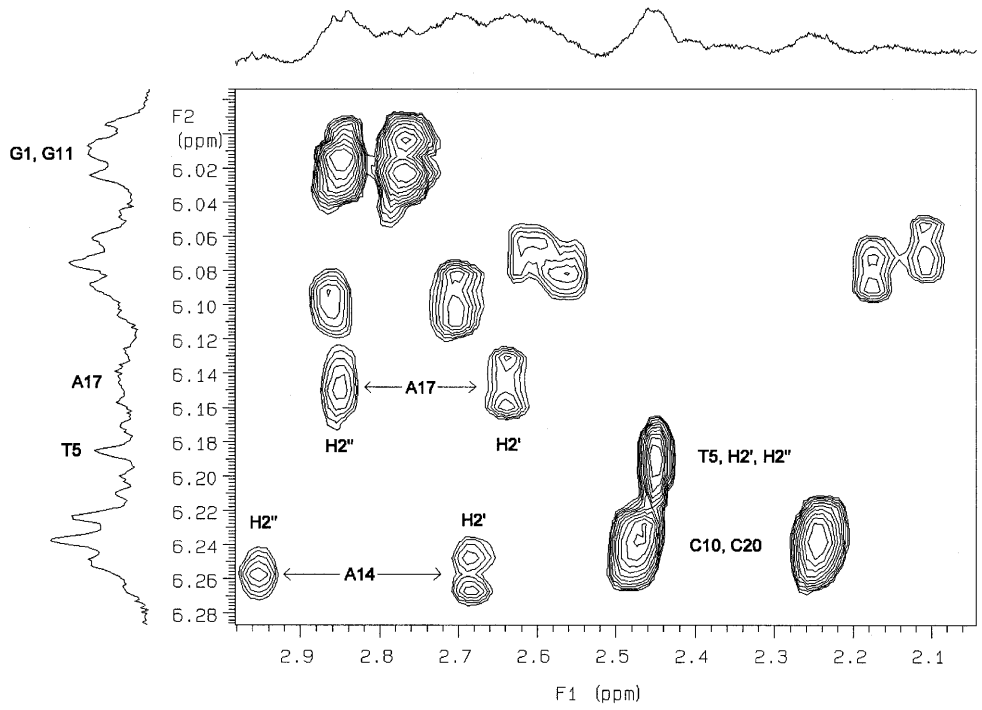

Figure S1. Expansion of TOCSY spectrum showing overlap of G1, G11 and C10, C20 resonances and coincidental degeneracy of T5 H2′ and H2″ protons at 2.45 p.p.m.

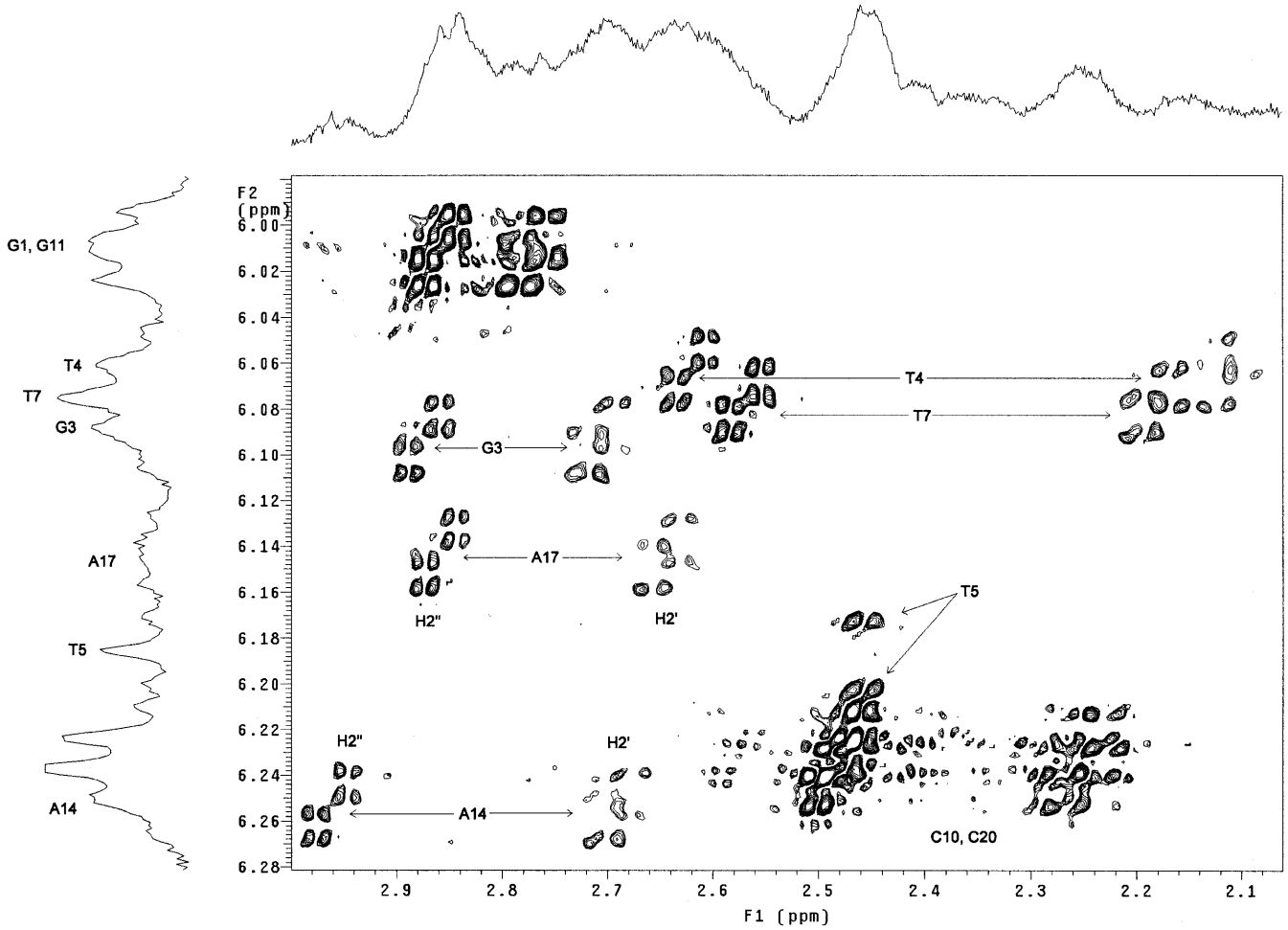

Figure S2. Expansion of E.COSY spectrum (as in Fig. S1) showing phase-sensitive patterns used for evaluation of vicinal H1′–H2′, H2″ protons. The degeneracy of the cross-peak for T5 prevents determination of ^{3}J(H1′, H2′/H2″) coupling constants. This coupling constant can, however, be estimated from the 1-D spectrum.

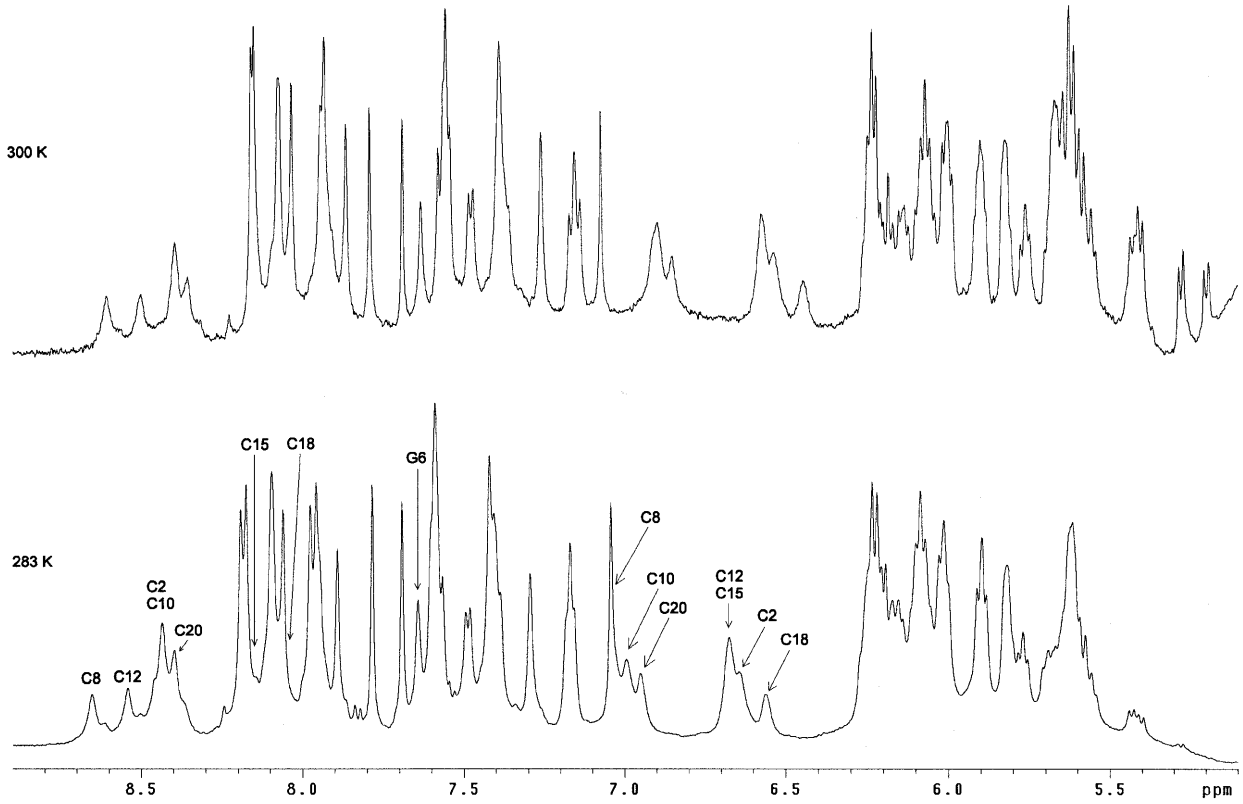

Figure S3. Expansions of 1-D spectra of the nicked decamer in K^+ buffer at 10 and 27°C, pH 7.0 (sample 3) showing a negligible shift of the aromatic resonances and ~0.2 p.p.m. shifts of H^F protons of cytidines to higher frequencies.

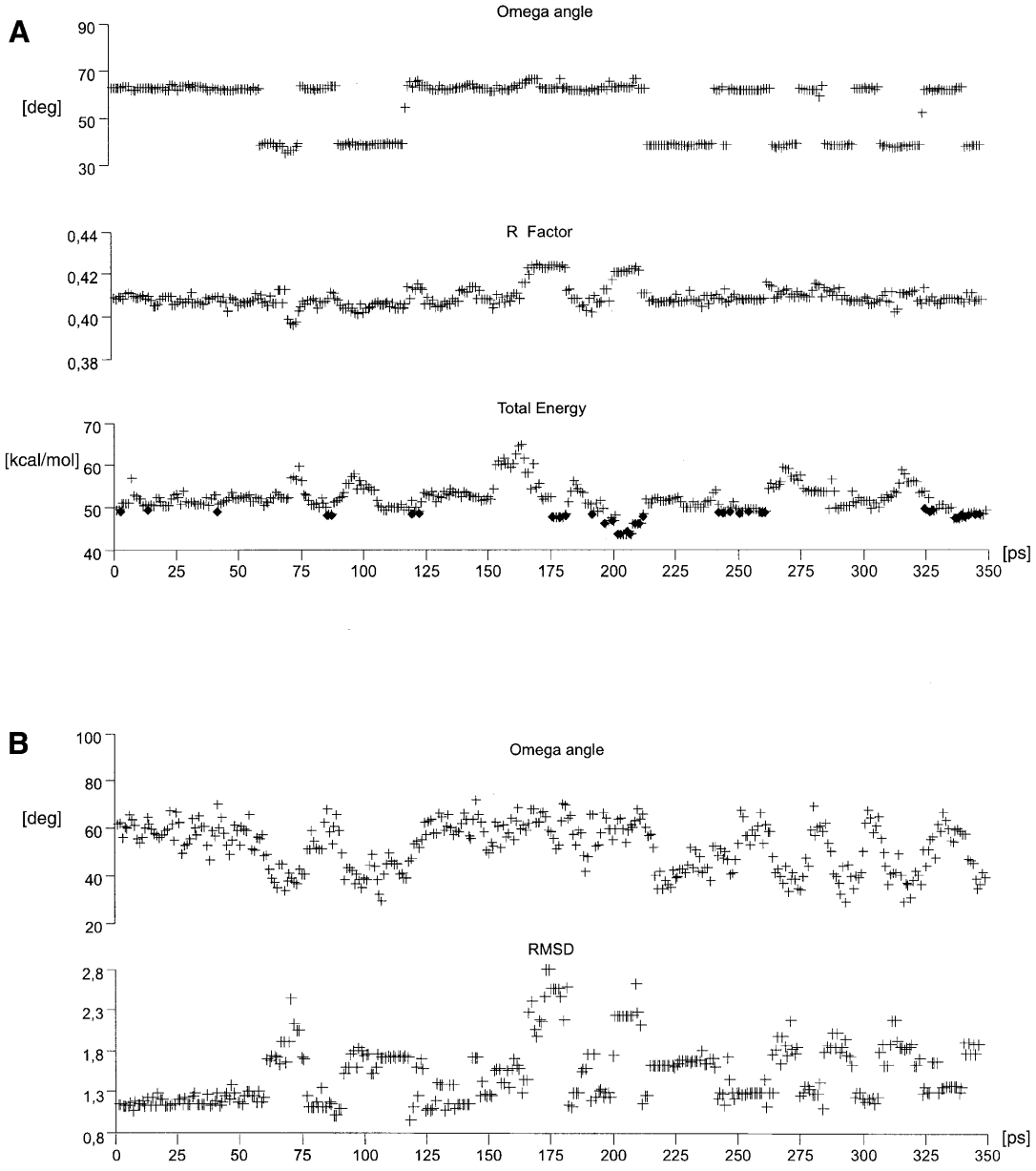

Figure S4. The Ω angle, R-factor, r.m.s.d. and E_{tot} parameters during the MD trajectory. (**A**) After EM, the conformations marked with closed diamonds were used for discussion of structural features, and (**B**) the original MD run.

Table S1. 1-H and 31-P chemical shifts δ (p.p.m. of decamer tethered with PEG_6)[a]

	H1′	H2′	H2″	H3′	H4′	H6/8	H2/5/Me	NH	NH_2		^{31}P
									H^B	H^F	
G1	6.01	2.76	2.85	4.96	4.34	8.07		13.23			+0.10
C2	5.68	2.14	2.46	4.86	4.22	7.39	5.40		8.44	6.64	–1.50
G3	6.09	2.69	2.85	5.02	4.44	7.94		12.96			–0.83
T4	6.06	2.10	2.62	4.88	4.27	7.26	1.45	14.0			–1.27
T5	6.19	2.44	2.44	4.68	4.04	7.39	1.67	13.34			–1.36
G6	5.83	2.64	2.64	4.66	4.18	7.63		12.51			
T7	6.07	2.17	2.56	4.87	4.32	7.56	1.16	13.83			–1.46
C8	5.76	2.05	2.42	4.87	4.13	7.47	5.64		8.65	7.03	
G9	5.91	2.61	2.69	5.00	4.35	7.93		13.13			–1.09
C10	6.24	2.23	2.46	4.85	4.20	7.58	5.61		8.43	6.99	–0.92(–0.59)[b]
G11	6.00	2.76	2.85	4.96	4.34	8.08		13.29			+0.10
C12	5.67	2.01	2.39	4.85	4.18	7.37	5.43		8.54	6.68	–1.57
G13	5.66	2.72	2.82	5.04	4.39	7.92		12.91			–0.95
A14	6.25	2.67	2.95	5.03	4.49	8.15	7.79				–1.19
C15	5.56	1.91	2.35	4.76	4.13	7.15	5.28		8.18	6.68	
A16	5.83	2.58	2.81	5.01	4.34	8.03	7.07				–1.33
A17	6.14	2.64	2.85	5.04	4.46	8.16	7.69				–1.28
C18	5.62	1.84	2.28	4.80	4.13	7.17	5.19		8.08	6.56	
G19	5.89	2.61	2.69	4.99	4.35	7.86		13.04			–1.17
C20	6.22	2.24	2.48	4.85	4.20	7.54	5.58		8.40	6.95	–0.92(–0.59)[b]

[a]Data were acquired on a sample in H_2O/D_2O (9:1), potassium buffer pH 7.0 (sample 3) with TSP-d_4 as internal standard. The δ values for non-exchangeable protons were taken from spectra at 27°C and for exchangeable protons at 10°C. The ^{31}P atoms are assigned to the 5′-end of each base. Their chemical shifts were acquired on sample 2. Unassigned signals (δ = –0.92; –1.32; –1.48 p.p.m.) are all correlated to three H4′ protons having identical chemical shift, 4.13 p.p.m.
[b]Linker side, 3′-end.

Table S2. Vicinal coupling constants ^3J(H,H) (Hz), $^3J(^{13}C,^{31}P)$ (Hz) and ^1H T_1 (s) relaxation times for PEG_6 tethered decamer[a]

	G1	C2	G3	T4	T5	G6	T7	C8	G9	C10
^3J(H1′,H2′)	9.84	9.40	9.44	8.60	7.50[b]	[c]	8.40	8.58	9.00	8.00
^3J(H1′,H2″)	5.60	5.50	5.80	6.00	7.50[b]	[c]	6.20	6.00	6.20	6.45
^3J(H3′,H2′)	6.10	6.85	5.60	7.20			6.55	7.20	5.80	7.00
^3J(H3′,H2″)	3.30	2.15	2.10	2.30			2.50	2.65	2.30	3.71
$^3J(^{13}C,^{31}P)$[f]	10.70; 9.20	9.30; 11.0	8.30; 10.20	11.40; 11.00	10.80	11.30	12.80; 12.30	10.90; 9.20	11.10; 9.80	
T_1 (H6/H8)	1.25	1.31	1.45	1.59	1.43	1.14	1.33	1.27	1.28	1.29
	C20	G19	C18	A17	A16	C15	A14	G13	C12	G11
^3J(H1′,H2′)	8.00[d]	9.00	8.40	9.35	9.70	8.10	9.12	9.90	9.10	9.84[e]
^3J(H1′,H2″)	6.45[d]	6.20	6.20	5.70	5.60	6.30	5.80	5.60	5.80	5.60[e]
^3J(H3′,H2′)	7.00	5.80	7.70	5.90	5.60	7.80	6.00	5.60	7.50	6.10
^3J(H3′,H2″)	3.81	2.30	2.60	2.10	2.16	2.43	2.10	2.00	2.60	3.30
$^3J(^{13}C,^{31}P)$[f]		11.10; 9.80	11.70; 11.10	11.60; 12.20	9.20; 11.50	11.30; 11.40	10.60; 11.50	9.90; 10.10	11.50; 10.40	10.70; 9.20
T_1 (H6/H8)	1.28	1.52	1.58	1.61	1.55	1.66	1.69	1.11	1.28	1.25

[a]Coupling constant data were acquired in D_2O at 27°C (sample 2). The relaxation times were acquired in D_2O solution (sample 1) at 27°C.
[b]From a 1-D spectrum.
[c]Not determined due to coincidence of H2′ and H2″ chemical shifts and lack of cross-peak.
[d]Taken as for G10, assumed to be equal due to nearly complete overlap of the signals.
[e]Taken as for G1, assumed to be equal due to complete overlap of the signals.
[f]The ^3J(C,P) values are given for carbon C-4′. The coupling constants are not assigned to 5′ and 3′ side P atoms. At the nick, one of the coupling constants is missing.