Solution Structure of Duplex DNA Containing a β-Carba-Fapy-dG Lesion

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SUPPORTING INFORMATION

Proton chemical shifts (Table 1S) on the β-cFapy-dG•dC duplex measured at 25 ºC. One dimensional proton spectrum of the β-cFapy-dG•dC duplex recorded in 100% D_2O buffer at 25 ºC (Figure 1S), full 'finger print' region assignments on a 300 ms mixing time NOESY spectrum, recorded in 100% D_2O buffer at 25 °C for the damaged (Figure 2SA) and undamaged (Figure 2SB) strands of the duplex, and expanded contour plot of the aromatic proton region on a 300 ms mixing time NOESY spectrum recorded in 100% D2O buffer at 25 ºC (Figure 3S). Three-dimensional view of the twenty five *Z*- (Figure 4S) and *E*- (Figure 5S) β-cFapy-dG•dC duplex structures, and examples of water-mediated hydrogen bonds in the β-cFapy-dG•dC duplex (Figure 6S). UV_{260} melting curves for the β-cFapy-dG•dC and dG•dC duplexes (Figure 7S).

Table 1S. Proton chemical shifts on the β-cFapy-dG•dC duplex at 25 ˚C.									
	H6/H8	H1’	H2’’	H2’	H3’	H4’	Me/H5/H2	G(H1)/T (H3)	CN_4H
C1	7.59	5.74	2.39	1.98	4.66	4.03	5.85		
G2	7.93	5.95	2.76	2.64	4.94	4.33		12.81	
(*Z*)T3	7.23	5.71	2.47	2.11	4.85		1.48	13.50	
(*E*)T3	7.23	5.73	2.47	2.11	4.85		1.48	13.50	
(*Z*)A4	8.22	6.22	2.86	2.65	4.98	4.40	7.45		
(*E*)A4	8.22	6.21	2.86	2.64	4.97	4.40	7.42		
(*Z*)C5	7.35	5.90	2.37	2.10	4.80		5.29		8.28/6.64
(*E*)C5	7.27	5.89	2.30	2.00	4.76		5.20		8.22/6.76
(*Z*)F6	7.92	3.91	1.89	1.70	4.40	2.16		12.56	
(*E*)F6	7.21	3.83	1.90	1.72	4.41	2.17		12.63	
(*Z*)C7	7.50	5.91	2.53	2.14	4.87	4.23	5.65		8.59/6.90
(*E*)C7	7.54	5.86	2.50	2.13	4.85		5.69		8.39/6.76
(*Z*)A8	8.23	6.20	2.65	2.89	4.97	4.35	7.59		
(*E*)A8	8.26	6.20	2.64	2.90	4.97	4.35			
T9	7.08	5.72	2.32	1.94	4.82		1.37	13.57	
G10	7.81	5.88	2.55	2.65	4.92	4.32		12.74	
C11	7.38	6.13	2.13	2.16	4.44	4.01	5.33		8.15/6.62
G12	7.89	5.92	2.56	2.74	4.80	4.19		13.00	
C13	7.42	5.66	2.12	2.44	4.85	4.17	5.39		8.39/6.55
A14	8.30	6.24	2.66	2.92	4.99	4.39	7.68		
T15	7.04	5.68	1.98	2.37	4.81		1.43	13.55	
(*Z*)G16	7.68	5.91	2.52	2.71	4.86	4.33		12.59	
(*E*)G16	7.69	5.87	2.52	2.67	4.88	4.33		12.54	
(*Z*)C17	7.12	5.57	2.03	2.32	4.64	4.07	5.24		8.26/6.37
(*E*)C17	7.24	5.68	2.10	2.33	4.71		5.28		8.35/6.37
(*Z*)G18	7.53	5.84	2.65	2.47	4.75	4.24		12.54	
(*E*)G18	7.58	5.86	2.66	2.49	4.77	4.27		12.53	
(*Z*)T19	7.30	5.78	2.48	2.11	4.86		1.31	13.71	
(*E*)T19	7.30	5.79	2.48	2.11	4.86		1.31	13.71	
(*Z*)A20	8.23	6.17	2.81	2.63	4.98	4.37	7.52		
(*E*)A20	8.23	6.17	2.81	2.63	4.98	4.37	7.49		
C21	7.24	5.63	2.24	1.83	4.75		5.29		8.27/6.74
G22	7.84	6.09	2.32	2.54	4.61	4.12		13.01	
Chemical shifts are in ppm. Chemical shifts of the H6’/H6’’ protons of cFapy are 0.97/1.98 ppm and 0.96/2.07 ppm for the *Z* and *E* isomers, respectively.									

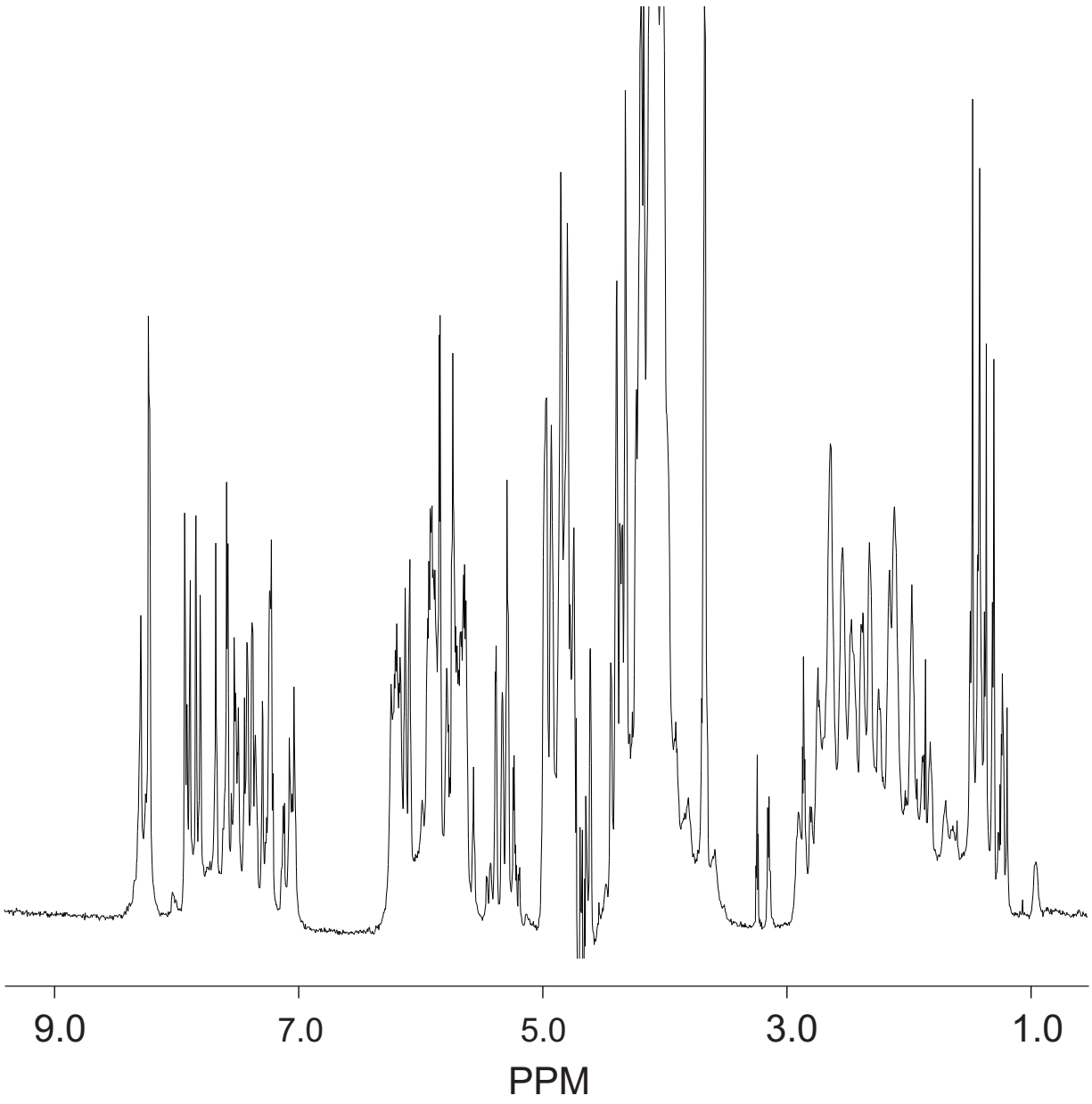


Figure 1S. One dimensional proton spectrum of the cFapy-dG·dC duplex recorded at 600 MHz in 100% D_2O buffer, at 25 °C.

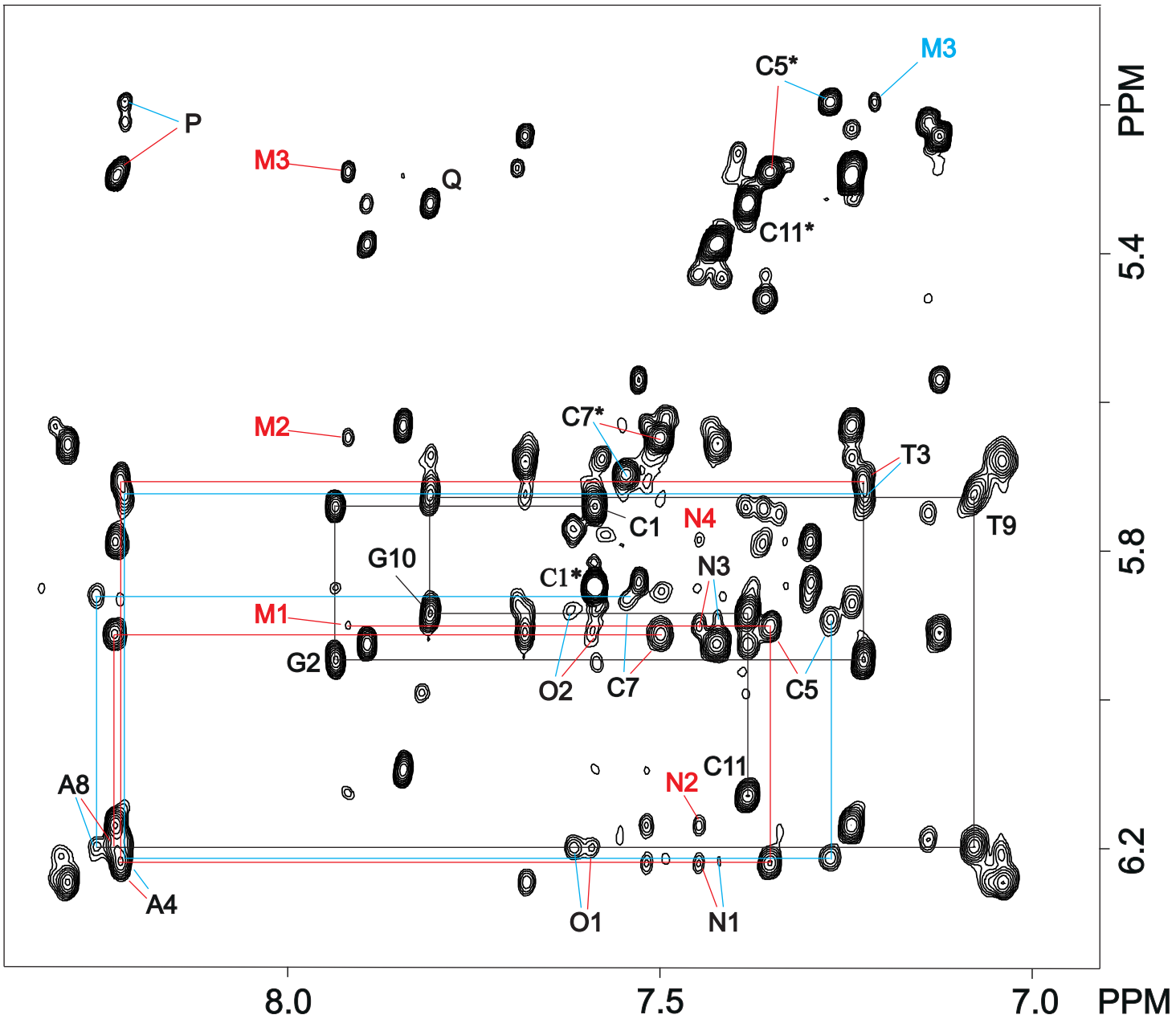


Figure 2SA. Expanded contour plot depicting NOE interactions in the base to H1' proton region of a 800 MHz NOESY spectrum (300 ms. mixing time) recorded in 100% D_2O buffer, at 25 °C. Lines connect inter residue and sequential base-H1' NOE peaks seen in the modified strand of the damaged duplex. Red and blue colors trace these connectivities on the *Z* and *E* isomeric duplexes, respectively. Numbered letters label the intra residue NOE, and asterisks indicate cytosine(H5-H6) peaks. Other labels are assigned as follows: M1, F6H8-C5H1'; M2, F6H8-C7H5; M3, F6H8-C5H5; N1, A4H2-A4H1'; N2, A4H2-A20-H1'; N3, A4H2-C5H1'; N4, A4H2-T19H1'; O1, A8H2-A8H1'; O2, A8H2-G16H1'; P, A4H8-C5H5; Q, G10H8-C11H5.

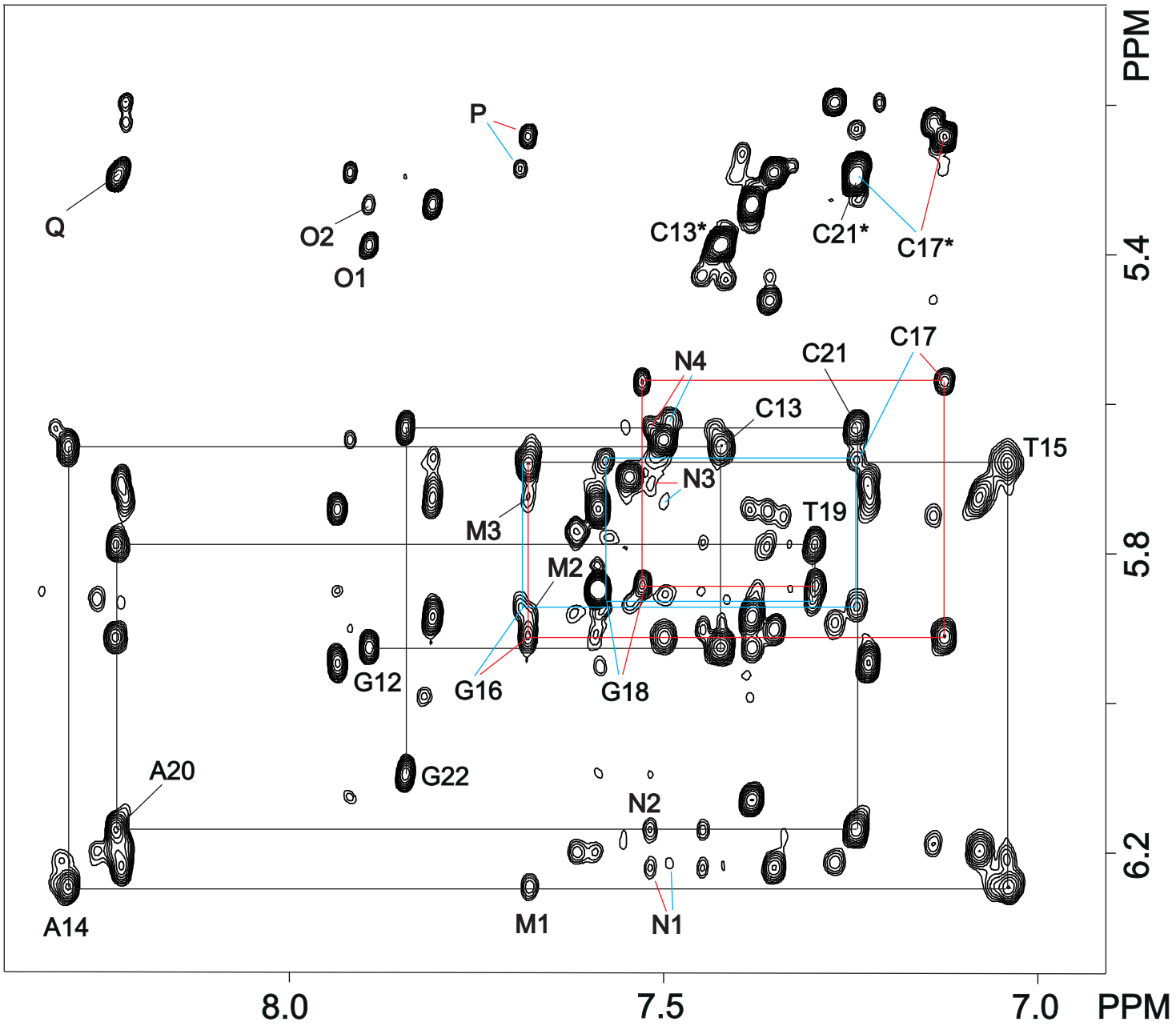


Figure 2SB. Expanded contour plot depicting NOE interactions in the base to H1' proton region of an 800 MHz NOESY spectrum (300 ms. mixing time) recorded in 100% D_2O buffer, at 25 °C. Lines connect inter residue and sequential base-H1' NOE peaks seen in the unmodified strand of the damaged duplex. Red and blue colors trace these connectivities in the *Z* and *E* isomeric duplexes, respectively. Numbered letters label the intra residue NOE, and asterisks indicate cytosine(H5-H6) peaks. Other labels are assigned as follows: M1, A14H2-A14H1'; M2, A14H2-G10H1'; A3, A14H2-T9H1'; N1, A20H2-A4H1'; N2, A20H2-A20-H1'; N3, A20H2-T3H1'; N4, A20H2-C21H1'; O1, G12H8-C13H5; O2, G12H8-C11H5; P, G16H8-C17H5; Q, A20H8-C21H5.

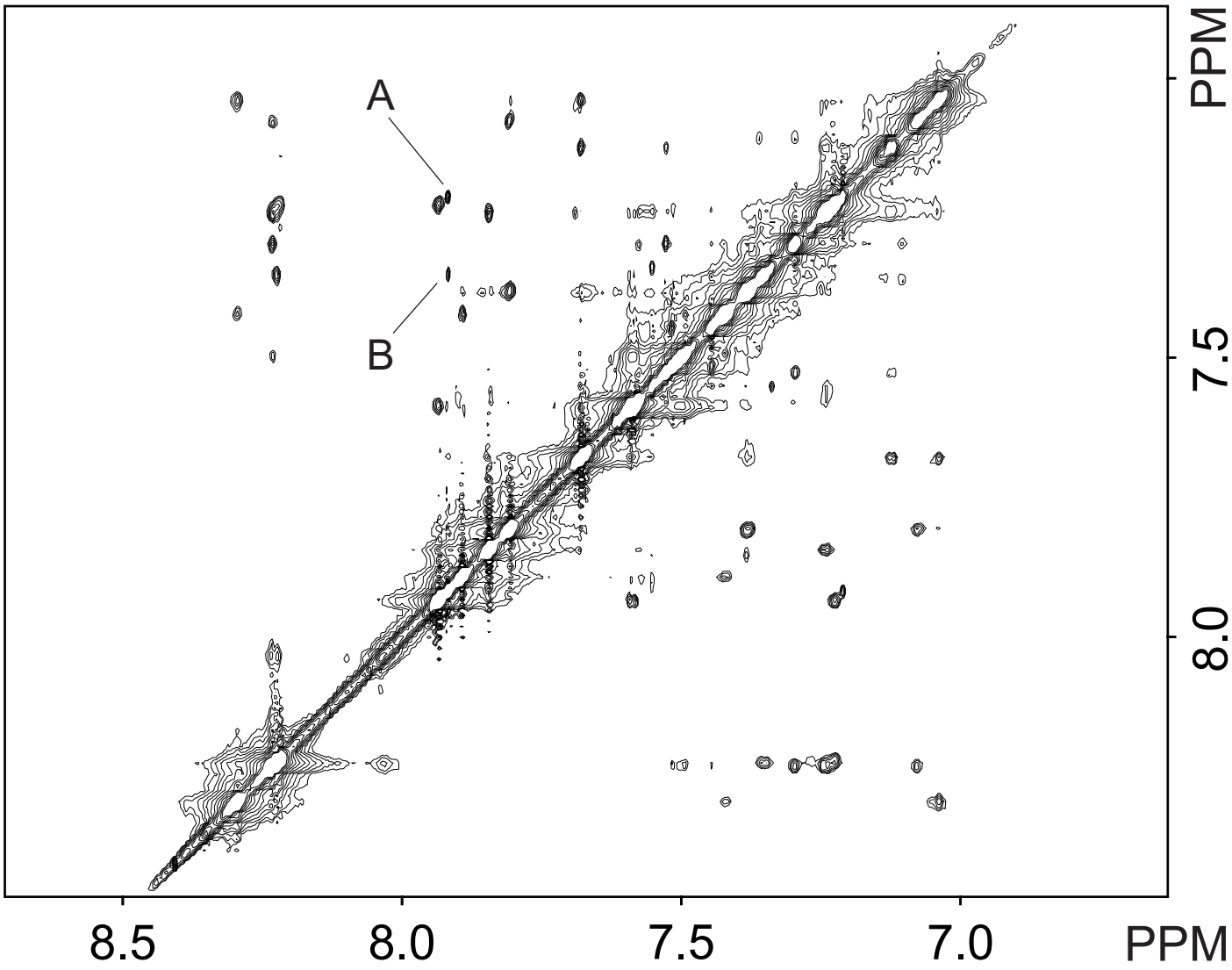


Figure 3S. Expanded contour plot showing the aromatic proton region of an 800 MHZ NOESY spectrum (300 ms. mixing time) recorded in 100% D_2O buffer at 25 °C. Labeled peaks are assigned as follows:
A, *Z*-F6(HCO)-*E*-F6(HCO) exchange cross-peaks; B, *Z*-F6(HCO)-C5(H6).

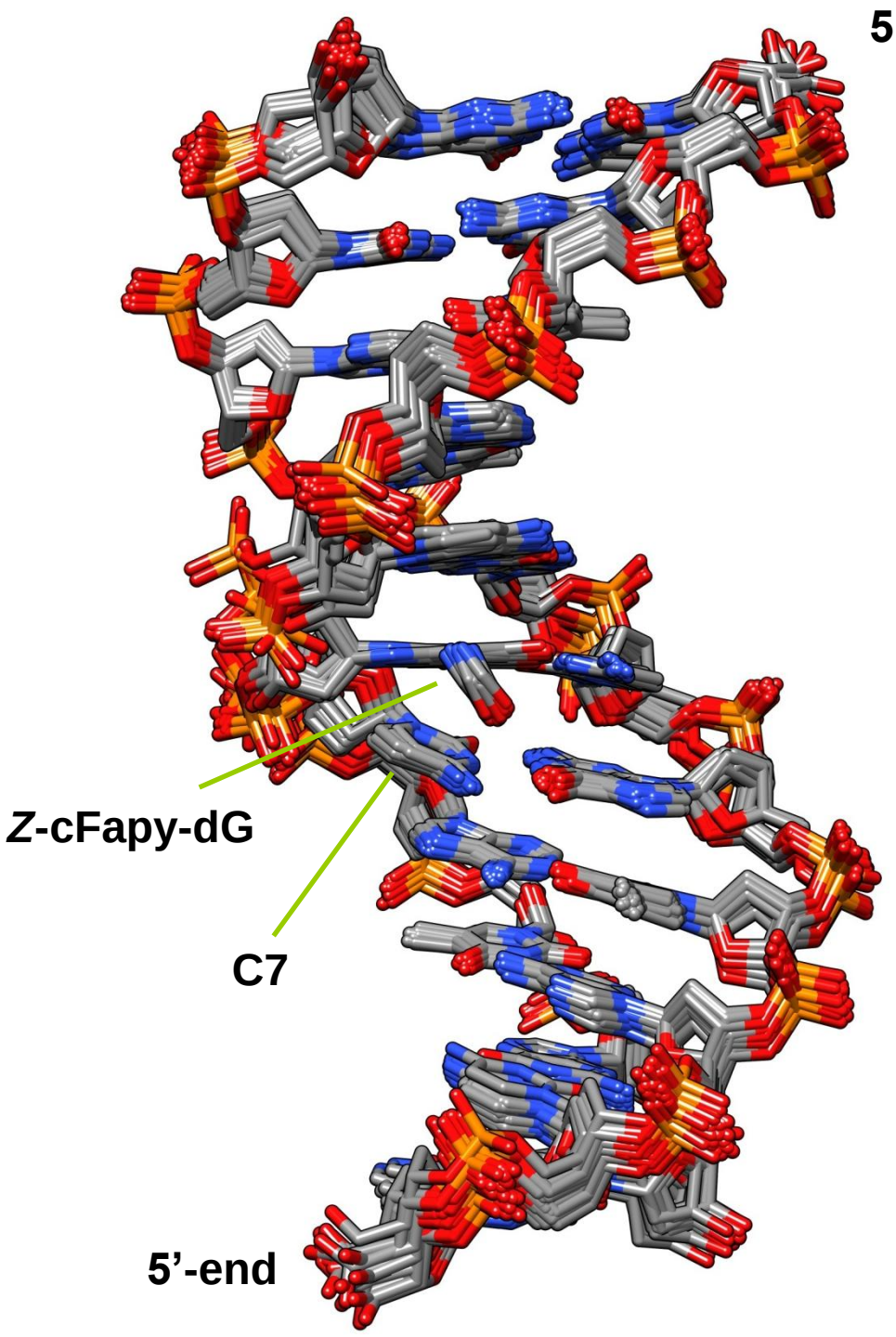


Figure 4S: Superposition of the final 25 structures of the *Z*-cFapy-dG•dC duplex seen with the major groove prominent.

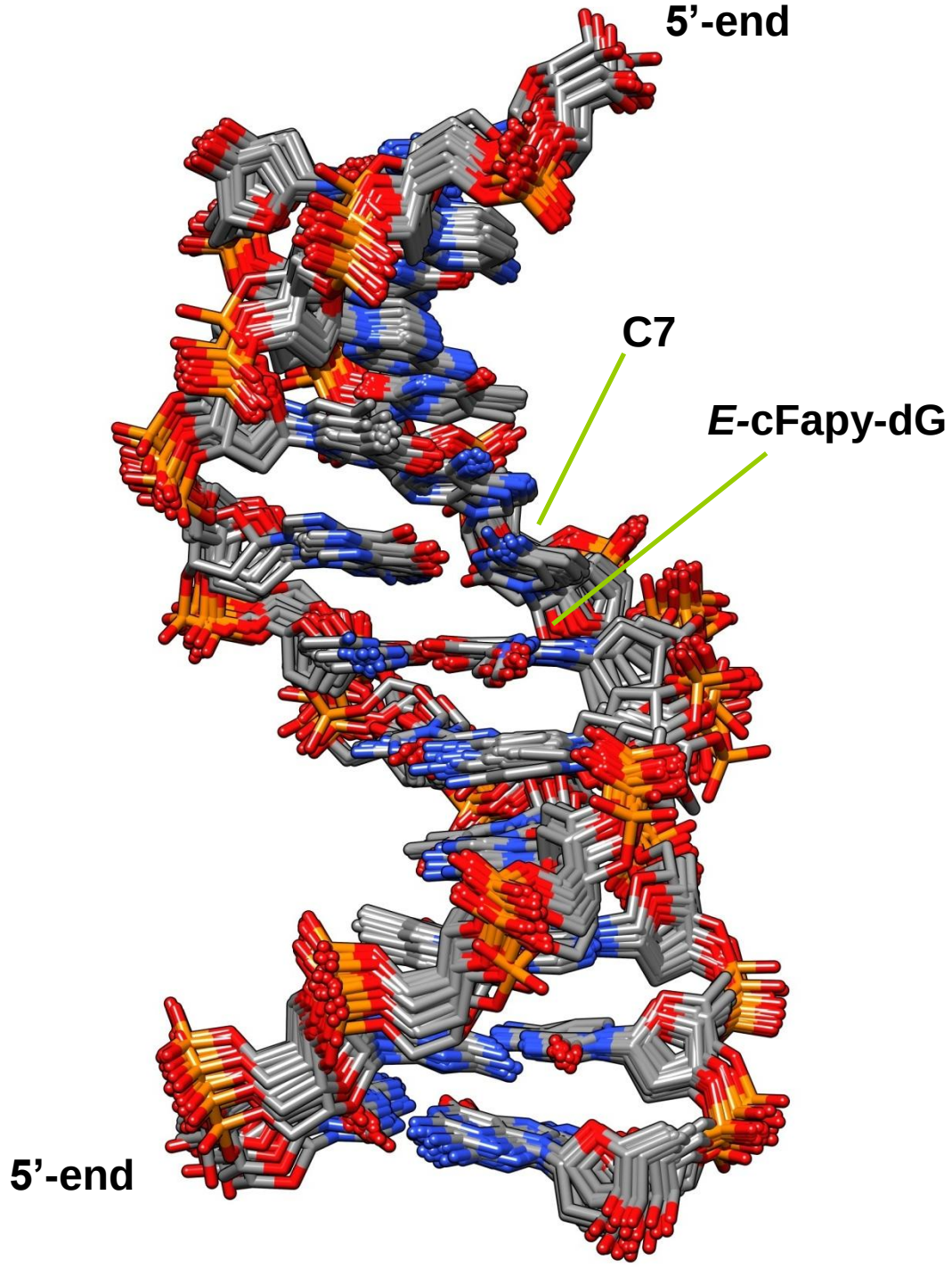
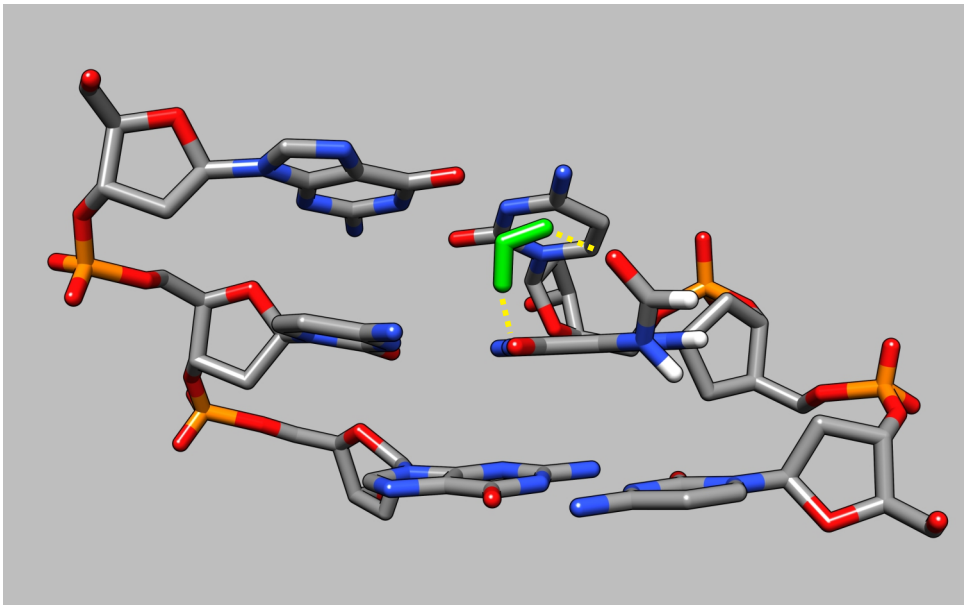
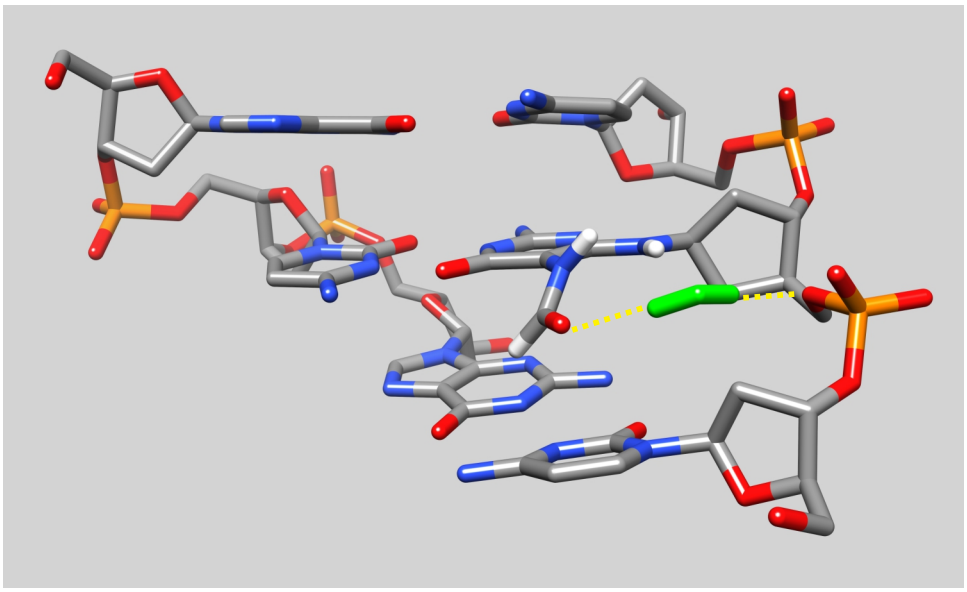


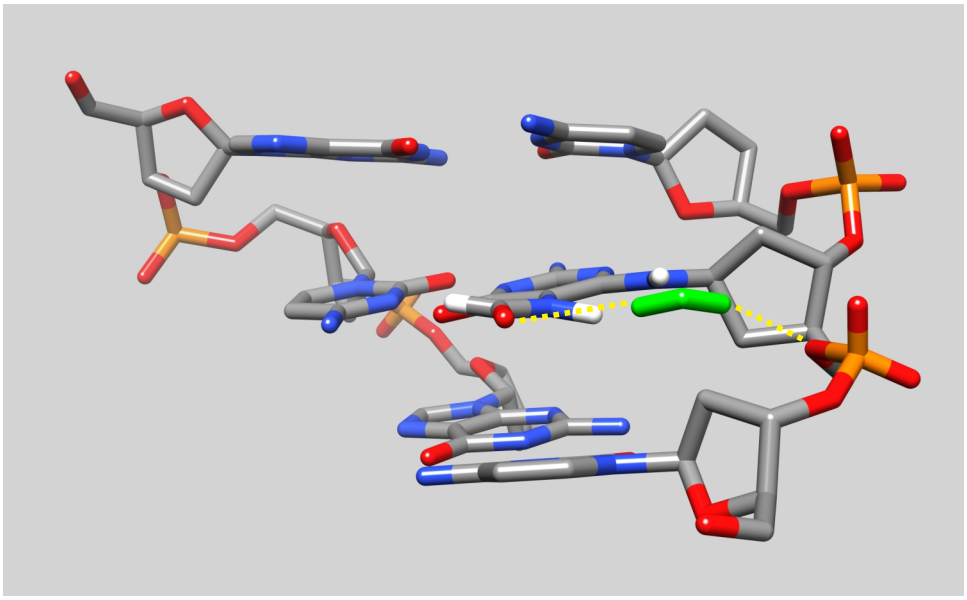
Figure 5S: Superposition of the final 25 structures of the *E*-cFapy-dG•dC duplex seen with the major groove prominent.



Z-cFapy-dG



E-cFapy-dG
(major form)



E-cFapy-dG
(minor form)

Figure 6S: Examples of water-mediated hydrogen bonds in the β-cFapy-dG•dC duplex. Water molecules are colored green.

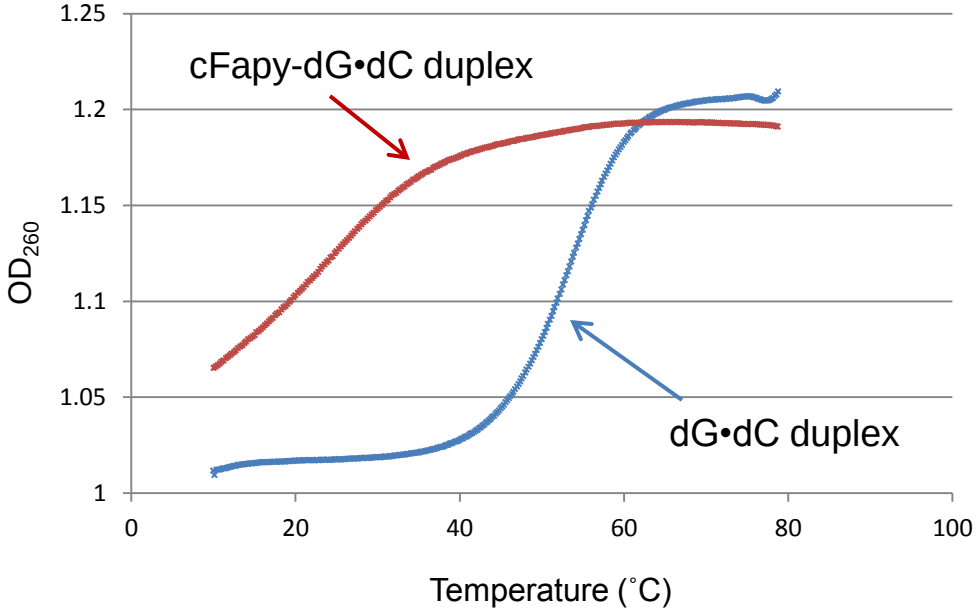


Figure 7S: UV melting profiles of the cFapy-dG•dC and dG•dC duplexes.