

Solvent effects on NMR shieldings of stacked DNA base pairs

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Table 1: NMR magnetic shieldings of atoms belonging to the witness pair calculated at B97-D/6-311++G level of theory. Chemical shifts^a are given between parenthesis and all values are in ppm**

	Guanine									Cytosine					
	N ₁	N ₂	N ₃	N ₇	C ₆	C ₂	H ₁	H ₂	H' ₂	N ₄	N ₃	C ₄	C ₂	H ₄	H' ₄
VAC															
F1	109.35 (147.54)	184.89 (71.91)	87.32 (169.48)	5.52 (251.28)	31.39 (151.11)	32.29 (150.21)	18.51 (13.19)	22.23 (9.47)	27.37 (4.33)	160.39 (96.41)	52.29 (204.51)	21.49 (161.01)	27.93 (154.57)	21.50 (10.2)	27.80 (3.9)
F3	108.53 (148.27)	175.93 (80.87)	86.07 (170.73)	5.03 (251.77)	30.93 (151.57)	31.16 (151.34)	18.02 (13.68)	22.16 (9.54)	27.24 (4.46)	164.48 (92.32)	51.22 (205.58)	21.21 (161.29)	28.53 (153.97)	22.15 (9.55)	28.25 (3.45)
F5	108.51 (148.29)	174.16 (82.64)	81.80 (175.00)	6.12 (250.68)	30.82 (151.68)	31.44 (151.06)	18.21 (13.49)	22.68 (9.02)	27.27 (4.43)	165.81 (90.99)	51.83 (204.97)	21.55 (160.95)	28.63 (153.87)	22.1 (9.60)	28.42 (3.28)
ES															
F1	109.53 (147.27)	179.80 (77.00)	92.45 (164.35)	21.53 (235.27)	32.40 (150.10)	31.84 (150.66)	18.35 (13.35)	22.31 (9.39)	26.41 (5.29)	151.06 (105.74)	58.44 (198.36)	21.71 (160.79)	28.99 (153.51)	22.09 (9.61)	24.39 (7.31)
F3	109.09 (147.71)	171.10 (85.70)	90.53 (166.27)	21.14 (235.66)	32.67 (149.83)	27.13 (155.37)	18.12 (13.58)	22.89 (8.81)	26.36 (5.34)	154.31 (102.49)	59.24 (197.56)	21.52 (160.98)	29.70 (152.80)	22.50 (9.20)	24.92 (6.78)
F5	109.52 (147.28)	168.66 (88.14)	90.21 (166.59)	21.92 (234.88)	32.21 (150.29)	27.97 (154.53)	18.29 (13.41)	22.74 (8.96)	26.12 (5.58)	156.71 (100.09)	58.49 (198.31)	20.59 (161.91)	29.20 (153.30)	22.60 (9.10)	25.07 (6.63)
IS															
F1	108.54 (148.26)	181.48 (75.32)			30.70 (151.80)	31.46 (151.04)	18.01 (13.69)	21.95 (9.60)		163.82 (92.98)	59.42 (197.38)	20.71 (161.79)	27.04 (155.46)	22.19 (9.51)	27.23 (4.47)
F3	109.13 (147.67)	176.89 (79.91)			30.54 (151.96)	31.33 (151.17)	17.88 (13.82)	22.16 (9.54)		165.87 (90.93)	54.11 (202.69)	20.80 (161.70)	27.96 (154.54)	22.51 (9.19)	27.82 (3.88)
F5	108.76 (148.04)	175.29 (81.51)			30.50 (152.00)	31.54 (150.96)	18.02 (13.68)	22.66 (9.04)		166.56 (90.24)	54.35 (202.45)	21.18 (161.32)	28.05 (154.65)	22.50 (9.20)	27.93 (3.77)
ES + IS															
F1	108.29 (148.51)	178.09 (78.71)			31.90 (150.60)	31.08 (151.42)	18.19 (13.51)	22.10 (9.60)		156.13 (100.67)	60.41 (196.39)	21.03 (161.47)	28.52 (153.98)	22.47 (9.23)	24.20 (7.5)
F3	109.50 (147.30)	172.68 (84.12)			32.58 (149.92)	27.38 (155.38)	18.12 (13.58)	22.95 (8.75)		155.86 (100.94)	58.83 (197.97)	21.29 (161.21)	29.54 (152.96)	22.58 (9.12)	24.82 (6.88)
F5	110.09 (146.71)	170.37 (86.43)			32.42 (150.08)	29.12 (153.38)	18.34 (13.36)	22.76 (8.94)		156.77 (100.03)	57.82 (198.98)	20.14 (162.36)	28.99 (153.51)	22.51 (9.19)	24.83 (6.87)
exp ^b	(147.4)	(76.1)	167	238	(161.4)	(156.7)	(12-13.6)	(8-9)	(5-6)	(98.2)	(196.3)	(167.8)	(158.8)	(8.1-8.8)	(6-7)

^a TMS was used as the reference for Hydrogen and Carbon atoms ($\sigma(\text{H})=31.7$ ppm and $\sigma(\text{C})=182.5$ ppm). For Nitrogen atom, the reference was NH_3 ($\sigma(\text{N})=256.8$ ppm) Both references were calculated at the same level of theory used for shieldings. ^b Experimental values of chemical shifts were taken from Ref.¹ for Hydrogen atoms, and from Ref.² for Carbon and Nitrogen atoms.

References

- (1) Wijmenga, S. S.; van Buuren, B. N. M. *Prog. Nucl. Magn. Reson. Spectrosc.* **1998**, *32*, 287–387.
- (2) Abramov, G.; Goldbourn, A. Nucleotide-type chemical shift assignment of the encapsulated 40 kbp dsDNA in intact bacteriophage T7 by MAS solid-state NMR. *Journal of biomolecular NMR* **2014**, *59*, 219–230.

Table 2: Calculated magnetic shieldings (in ppm) at PBE0/6-311++G level of theory.**

	Guanine									Cytosine					
	N ₁	N ₂	N ₃	N ₇	C ₆	C ₂	H ₁	H ₂	H ₂ '	N ₄	N ₃	C ₄	C ₂	H ₄	H ₄ '
VAC															
F1	110.62	188.81	88.29	-4.13	28.32	29.15	18.14	22.01	27.07	163.38	52.9	17.72	25.03	21.34	27.58
F3	110.23	179.88	87.09	-4.56	27.92	28.18	17.63	21.99	26.92	167.48	51.78	17.56	25.47	21.92	28.03
F5	110.32	178.03	82.79	-3.43	28.01	28.07	18.01	22.55	27.02	168.91	53.12	17.47	25.84	21.95	28.27
ES															
F1	110.79	184.15	93.44	14.73	29.18	28.45	18.02	22.14	26.21	153.88	58.96	18.36	25.84	21.9	24.27
F3	111.05	175.42	91.5	14.25	29.54	22.78	17.82	22.58	26.14	156.93	59.9	17.61	27.04	22.3	24.81
F5	111.1	172.74	91.22	15.01	29.35	24.53	17.98	22.56	25.81	159.57	59.16	16.35	26.16	22.44	25.01

Table 3: Calculated chemical shifts (in ppm) at PBE0/6-311++G level of theory. Experimental values are also included.**

	Guanine									Cytosine					
	N ₁	N ₂	N ₃	N ₇	C ₆	C ₂	H ₁	H ₂	H ₂ '	N ₄	N ₃	C ₄	C ₂	H ₄	H ₄ '
VAC															
F1	146.18	67.99	168.51	260.93	154.18	153.35	13.56	9.69	4.63	93.42	203.9	164.78	157.47	10.36	4.12
F3	146.57	76.92	169.71	261.36	154.58	154.32	14.07	9.71	4.78	89.32	205.02	164.94	157.03	9.78	3.67
F5	146.48	78.77	174.01	260.23	154.49	154.03	13.69	9.15	4.68	87.89	203.68	165.03	156.66	9.75	3.43
ES															
F1	146.01	72.65	163.36	242.07	153.32	154.05	13.68	9.56	5.49	102.92	197.84	164.14	156.66	10.51	7.43
F3	145.75	81.38	165.3	242.55	152.96	159.72	13.88	9.12	5.56	99.87	196.9	164.89	155.46	9.4	6.89
F5	145.7	84.06	165.58	241.79	153.15	157.97	13.72	9.14	5.89	97.23	197.64	166.15	156.34	9.26	6.69
EXP	147.4	76.1	167	238	161.4	156.7	12-13.6	8-9	5-6	98.2	196.3	167.8	158.8	8.1-8.8	6.7-7