Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information for

Interpretation of Substituent Effects on ^{13}C and ^{15}N NMR Chemical Shifts in 6-Substituted Purines

by

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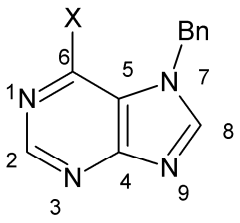

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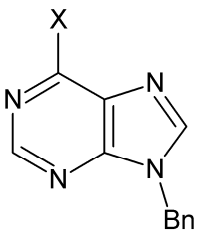

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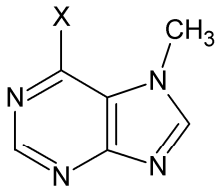
a: X = NH_2 **b:** X = $NH(CH_3)$ **c:** X = $N(CH_3)_2$

d: X = OCH_3 **e:** X = CH_3 **f:** X = CCH **g:** X = CN



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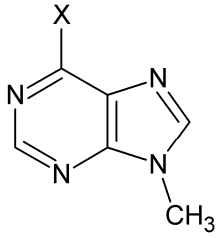

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Table S1a. ^{1}H NMR chemical shifts (ppm) for compounds **1** and **2** in DMF-d_7 or $CDCl_3$ at 303K

	1a DMF-d_7	**2a** DMF-d_7	**1d** DMF-d_7	**2d** DMF-d_7	**1f** $CDCl_3$	**2f** $CDCl_3$
H-2	8.24	8.22	8.55	8.56*	9.11	8.99
H-8	8.55	8.29	8.73	8.56*	8.22	8.11
H_2C	5.90	5.47	5.68	5.58	5.74	5.46
H_3C	-	-	4.12	4.15	-	-
HCC	-	-	-	-	3.64	3.71
H_{ortho}	7.27	7.40	7.29-7.41	7.42	7.37	7.28-7.42
H_{meta}	7.34	7.36	7.29-7.41	7.37	7.17-7.25	7.28-7.42
H_{para}	7.28	7.30	7.29-7.41	7.31	7.33-7.43	7.28-7.42
H_2N	6.84	7.23	-	-	-	-

* H-8 slightly shifted to higher value

Table S1b. ^{13}C NMR chemical shifts (ppm) for compounds **1** and **2** in DMF-d_7 or $CDCl_3$ at 303K

	1a DMF-d_7	**2a** DMF-d_7	**1d** DMF-d_7	**2d** DMF-d_7	**1f** $CDCl_3$	**2f** $CDCl_3$
C-2	153.22	153.51	152.22	152.43	153.55	152.96
C-4	161.51	150.67	162.75	153.13	161.68	152.01
C-5	112.00	119.90	113.39	121.80	125.39	135.06
C-6	152.47	157.12	157.79	161.49	133.16	140.95
C-8	147.07	141.53	147.67	144.29	149.29	145.67
CH_3	-	-	54.20	54.30	-	-
C_{CH}	-	-	-	-	78.42	78.21
$_{C}$CH	-	-	-	-	86.24	86.27
CH_2	50.10	47.01	50.98	47.51	50.15	47.72
$C_{quart.}$	138.32	138.15	138.05	137.72	135.01	134.94
C_{ortho}	127.44	128.34	128.26	128.44	127.51	128.13
C_{meta}	129.39	129.31	129.43	129.42	129.58	129.46
C_{para}	128.43	128.39	128.66	128.60	129.08	129.01

Table S1c. ^{15}N NMR chemical shifts (ppm) for compounds **1** and **2** in DMF-d_7 or $CDCl_3$ at 303K

	1a DMF-d_7	**2a** DMF-d_7	**1d** DMF-d_7	**2d** DMF-d_7	**1f** $CDCl_3$	**2f** $CDCl_3$
N-1	239.8	237.0	240.6	239.9	283.1	280.5
N-3	247.9	226.7	261.1	240.5	274.9	252.0
N-7	154.4	241.3	157.3	241.5	154.5	241.7
N-9	247.4	163.6	248.9	165.1	246.8	163.4
NH_2	77.6	77.5	-	-	-	-

Table S1d. ^{1}H-^{13}C coupling constants (Hz) for compounds **1** and **2** in DMF-d_7 or $CDCl_3$ at 303K

	1a DMF-d_7	**2a** DMF-d_7	**1d** DMF-d_7	**2d** DMF-d_7	**1f** $CDCl_3$	**2f** $CDCl_3$
C2-H2	197.5	198.5	203.5	204.5	206.0	206.0
C8-H8	209.5	211.0	211.0	212.5	209.0	209.5
C4-H2	11.7	12.0	12.0	12.6*	10.8	11.2
C4-H8	12.5	4.7	13.0	5.0*	13.0	5.2
C5-H8	3.9	11.1	4.1	11.7	4.5	11.3
C6-H2	11.7	11.3	11.6	11.3	12.1	11.5

* Signal overlap

Table S1e. ^{1}H-^{15}N coupling constants (Hz) of compounds **1** and **2** in DMF-d_7 or $CDCl_3$ at 303K

	1a DMF-d_7	**2a** DMF-d_7	**1d** DMF-d_7	**2d** DMF-d_7	**1f** $CDCl_3$	**2f** $CDCl_3$
N1-H2	16.0	15.8	16.1	15.8	15.7	15.6
N3-H2	14.8	15.5	14.9	15.4	14.7	15.4
N7-H8	7.8	11.9	7.8	12.1	7.8	11.7
N9-H8	11.8	8.1	12.0	8.1	11.8	8.1
$^{1}J(NH_2)$	88.0	90.0	-	-	-	-

Table S2. Calculated natural atomic charges* for compounds **3a**, **3d-g**.

	3a	**3d**	**3e**	**3f**	**3g**
N-1	-0.54	-0.52	-0.49	-0.45	-0.42
N-3	-0.51	-0.49	-0.47	-0.45	-0.43
C-6	+0.36	+0.50	+0.23	0.11	+0.06
X1 (subst.)	-0.74	-0.45	-0.65	-0.06	+0.29

*Gaussian03; BLYP/HIII//B3LYP/6-31G(d), GIAO, IEF-PCM(solvent DMSO)

Table S3. Selected interatomic distances (Å), bond angles (°), and dihedral angles (°) for fully optimized structures (B3LYP/6-31G(d); PCM) of compounds **1a**, **1c** and **2a**, **2c**.

	1 (7Bn-)		**2 (9Bn-)**	
	a (-NH_2)	**c (-NMe_2)**	**a (-NH_2)**	**c (-NMe_2)**
C6-N(subst.)	1.368	1.387	1.348	1.358
N1-C6	1.345	1.344	1.352	1.358
N1-C2	1.346	1.346	1.344	1.337
N1-H(subst.)	2.436	2.583	2.517	2.263
N1-C6-N(subst.)	117.5	118.7	118.8	117.7
N1-C6-N-$C_a(H_a)$	12.6	-12.7	6.8	0.5
C5-C6-N-$C_b(H_b)$	-29.7	-55.7	-7.5	-1.7
$C_a(H_a)$-C6-N-$C_b(H_b)$	140.4	139.6	166.4	178.0
N1-C6-N- $C_b(H_b)$	153.0	126.9	173.3	178.5

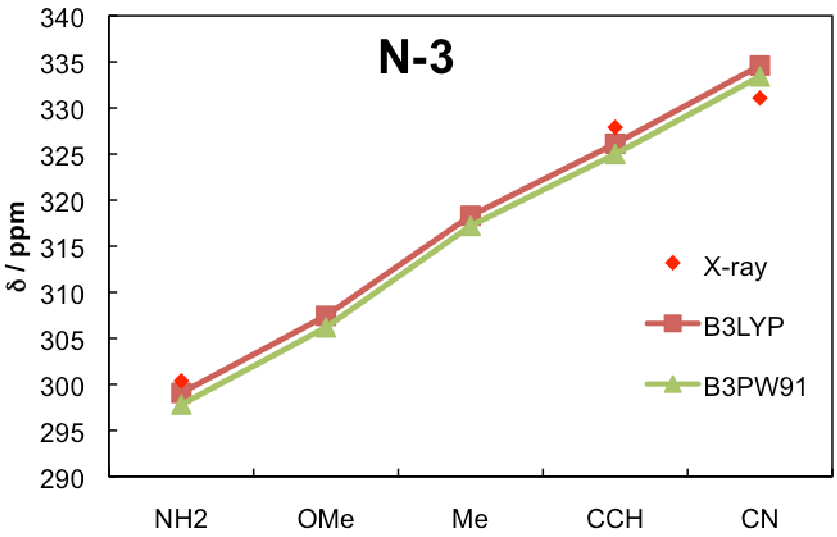

Figure S1. ^{15}N NMR chemical shift of atom N-3 (referenced to NH_3) calculated using BLYP/HIII for optimized geometries of compounds **3** (B3LYP/6-31G(d) and B3PW91/6-31G(d)) and for X-ray geometries of compounds **1** with B3LYP/6-31G(d) optimized proton positions.

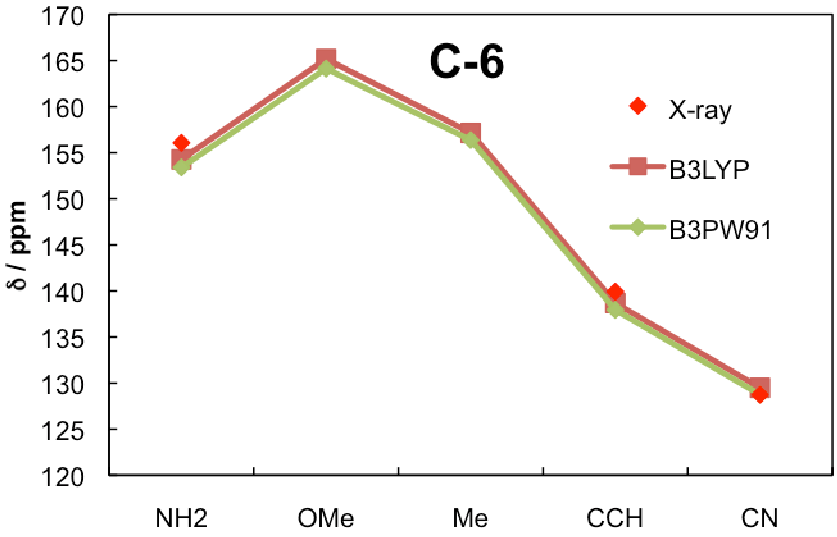

Figure S2. ^{13}C NMR chemical shift of atom C-6 (referenced to TMS) calculated using BLYP/HIII for optimized geometries of compounds **3** (B3LYP/6-31G(d) and B3PW91/6-31G(d)) and for X-ray geometries of compounds **1** with B3LYP/6-31G(d) optimized proton positions.

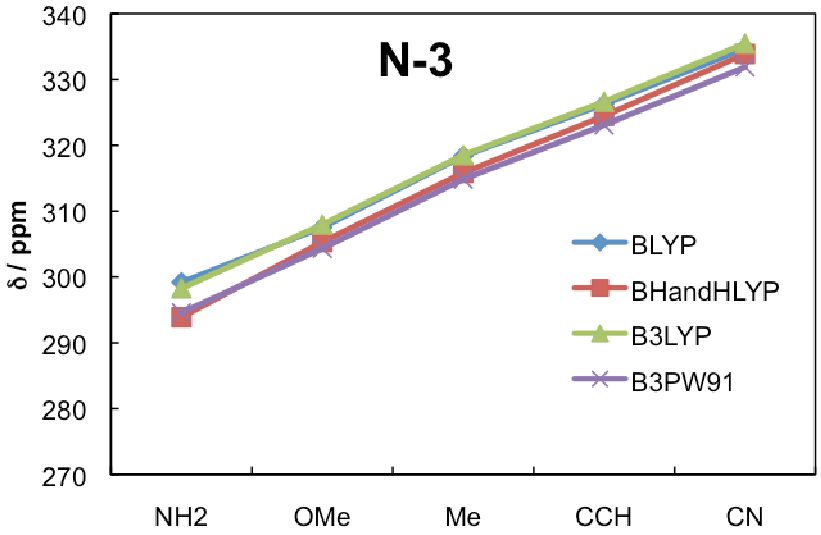

Figure S3. ^{15}N NMR chemical shift of atom N-3 (referenced to NH_3) calculated by using various functionals (BLYP/HIII, B3LYP/HIII, BHandHLYP/HIII, and B3PW91/HIII) for the B3LYP/6-31G(d) optimized geometries of compounds **3**.

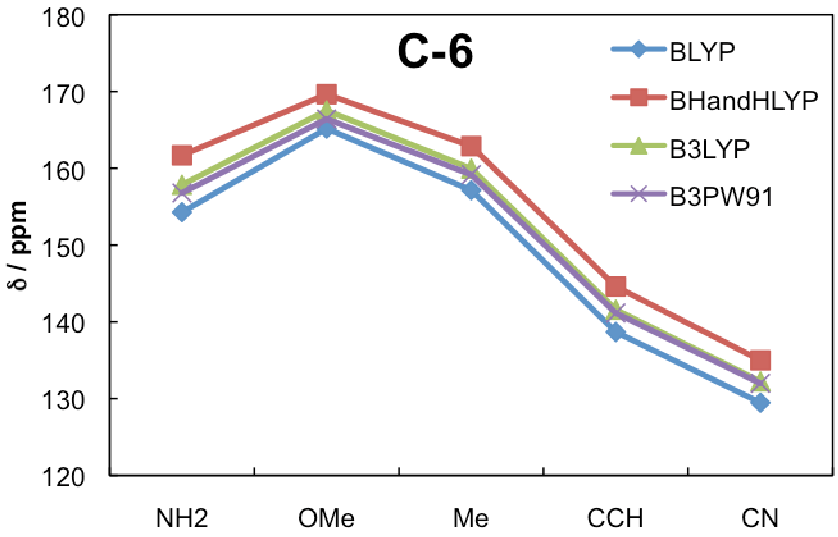

Figure S4. ^{13}C NMR chemical shift of atom C-6 (referenced to TMS) calculated by using various functionals (BLYP/HIII, B3LYP/HIII, BHandHLYP/HIII, and B3PW91/HIII) for the B3LYP/6-31G(d) optimized geometries of compounds **3**.