Supplementary Material (ESI) for PCCP

Supporting information for

Understanding the NMR Chemical Shifts for 6-Halopurines: Role of Structure, Solvent and Relativistic Effects.

by

Stanislav Standara, Kateřina Maliňáková, Radek Marek,
Jaromír Marek, Michal Hocek, Juha Vaara and Michal Straka

Figure S1. X-ray structure of α-glycine[1] with optimised positions of hydrogen atoms at the B3LYP/6-31G(d) level of theory (Gaussian03) used as a secondary reference structure for chemical shift calculations of $\delta(^{15}N)$. Color code: N blue, O red, C green, H white[2].

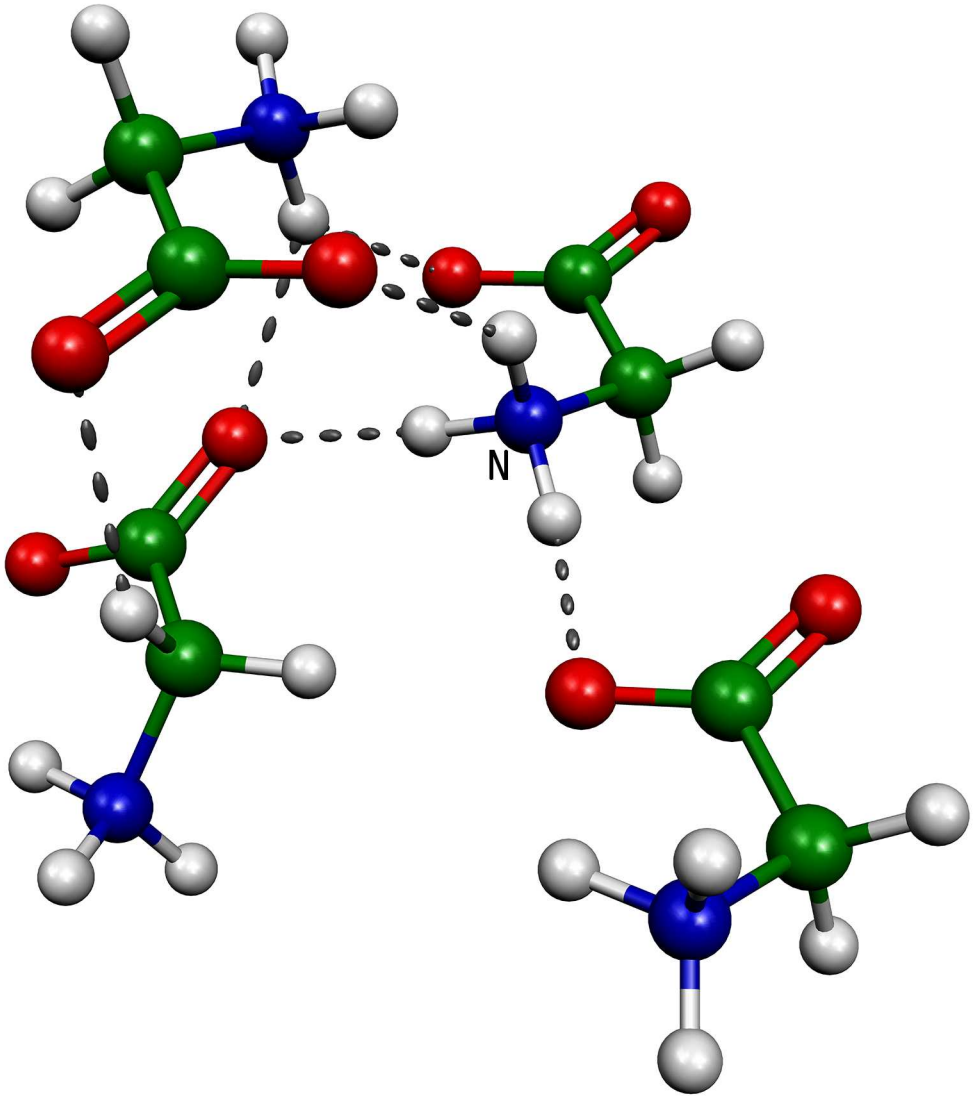


Figure S2. Basis-set convergence of the relativistic contribution to the chemical shifts (δ, ppm) N-1, C-6 and H-2 for structure **3c** at the BLYP/HIII(FIII) level. The data are shown as deviations from the results obtained with the contracted HIII basis set. U—uncontracted, UT1—uncontracted with one set of tight functions added, etc.

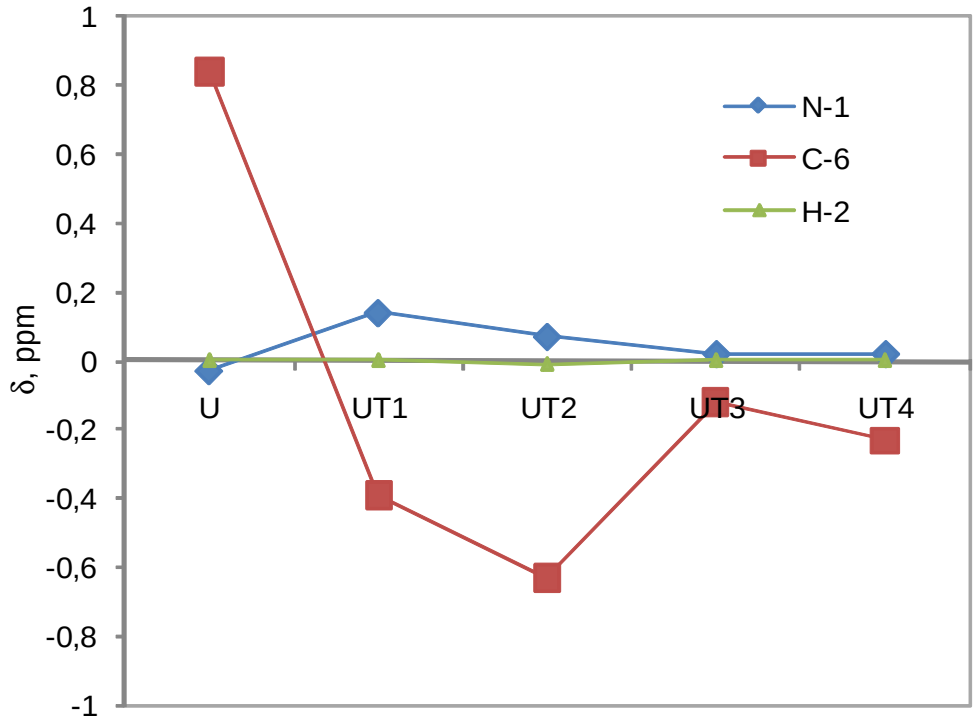
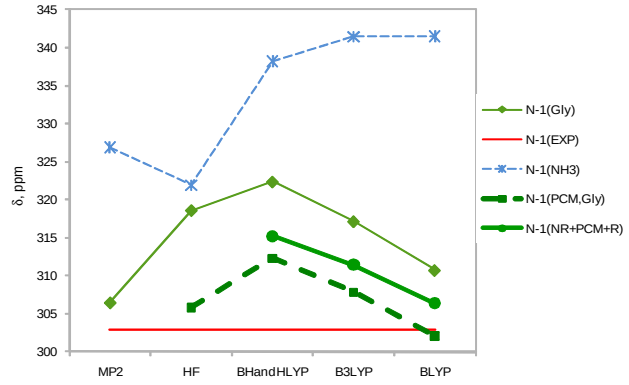


Table S1. Relativistic corrections to the chemical shifts (δ, ppm) for compound **4c** calculated at the BLYP/HIII(FIII) level using Breit-Pauli perturbation theory.[a]

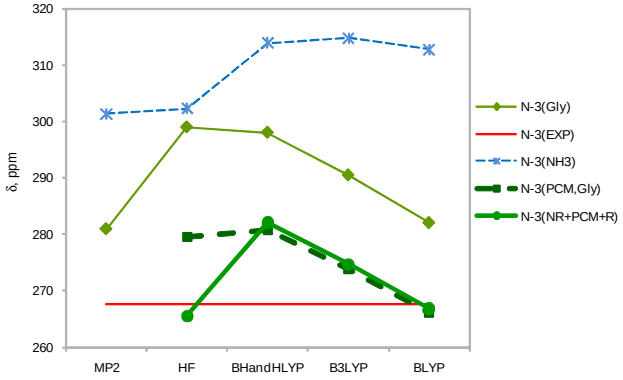
Term type	Term	N-1	N-3	C-2	C-4	C-5	C-6
FO	con	0.00	0.00	0.00	0.00	0.00	0.00
	dip	0.00	0.00	0.00	0.00	0.00	0.00
	d-ke	0.09	-0.14	0.10	0.00	0.13	0.12
	p-OZ	0.06	-012	0.07	0.00	0.09	0.08
SOS	p-ke/OZ	-0.52	-0.13	-0.26	-0.12	-0.32	-0.33
	p/OZ-KE	-0.19	0.44	-0.17	0.01	-0.23	-0.22
	d/mv	-0.05	-0.12	-0.03	-0.06	-0.08	-0.22
	d/Dar	0.06	0.17	0.02	0.06	0.08	0.20
SOT	FC/SZ-KE	0.01	0.00	0.05	0.03	0.04	0.05
	SD/SZ-KE	0.00	0.00	0.00	0.00	0.00	0.00
	FC-II(1)	-0.04	0.14	-0.04	0.00	-0.03	-0.04
	SD-II(1)	0.00	0.00	0.00	0.00	0.00	0.00
TOS	p/mv	-0.59	-1.63	-0.77	-1.19	-0.36	7.65
	p/Dar	0.40	1.78	1.06	0.94	0.14	-4.31
TOT(1el.SO)	FC-I(1)	5.41	-0.61	-2.14	-0.45	0.44	-56.77
	SD-I(1)	0.52	1.28	0.75	0.48	-0.03	0.19
TOT(2el.SO)	FC-I(2)	0.03	0.07	0.03	0.01	-0.19	1.85
	SD-I(2)	-0.08	0.01	-0.05	-0.06	-0.02	-0.06
Total		5.14	1.14	-1.40	-0.37	-0.33	-51.80

[a] See footnotes in Table 8 of the main paper.

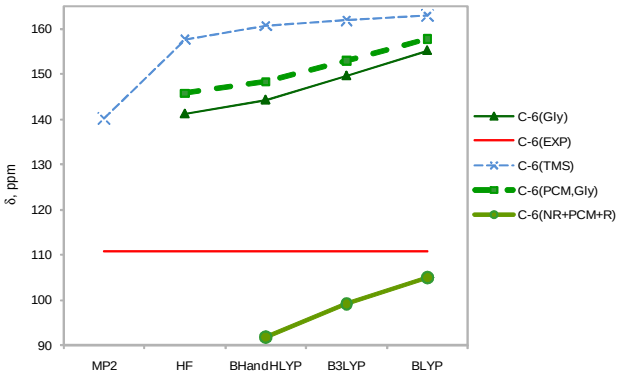
Figure S3. Solvent effect as well as relativistic contributions to the chemical shifts (δ, ppm) for (a) N-1, (b) N-3, (c) C-6 and (d) C-2, C-4, C-5 of compound **3c** at different levels of theory, and comparison with the experimental values. (NH3) and (TMS) denote chemical shifts referenced to NH_3 or TMS, (Gly) calculated chemical shifts referenced to α–glycine secondary standard, (PCM, Gly) calculated chemical shifts with PCM_{DMSO} and referenced to α–glycine, (NR+PCM+R) total chemical shifts with PCM_{DMSO} and referenced to α–glycine, with the relativistic contribution included, (EXP) experimental values (represented by horisontal lines in the panels). The HF(BPPT) data for N-1, C-6 were not calculated, and the MP2 data for C-4 and C-6 were not computationally accessible.



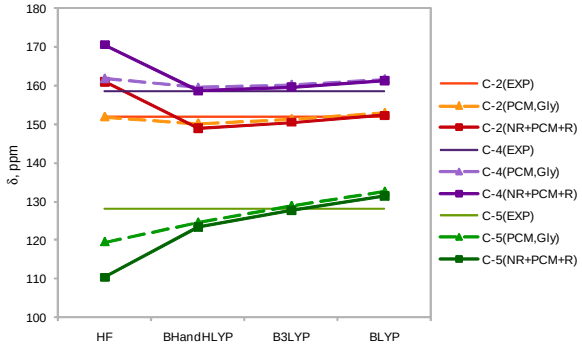
(a)



(b)



(c)



(d)

Table S2a. Solvent effect to the chemical shifts (δ, ppm) in explicit (+2DMSO, +3DMSO – number of the included solvent molecules, see Figure S4) and implicit (PCM) solvent models of compound **3a** at BLYP/HIII//B3LYP/6-31G(d),aug-cc-pVTZ(Cl) level.

	Gas phase	+2DMSO[a]		+3DMSO[a]		PCM[c]	Exp.
	δ	δ	Δ[b]	δ	Δ[b]		
N-1	286.40	287.58	1.18	284.85	-1.55	277.96	276.6
N-3	287.13	276.18	-10.95	281.83	-5.30	270.59	271.5
N-7	145.62	147.08	1.46	146.54	0.91	154.65	156.4
N-9	265.30	255.18	-10.12	255.58	-9.72	248.16	247.6
C-2	153.53	158.24	4.71	159.73	6.20	153.53	151.77
C-4	165.26	164.34	-0.92	164.82	-0.44	164.79	161.68
C-5	123.93	123.94	0.01	123.36	-0.58	124.90	122.00
C-6	151.86	152.19	0.33	151.42	-0.44	153.43	142.19
C-8	145.32	152.43	7.10	152.94	7.62	149.95	151.31

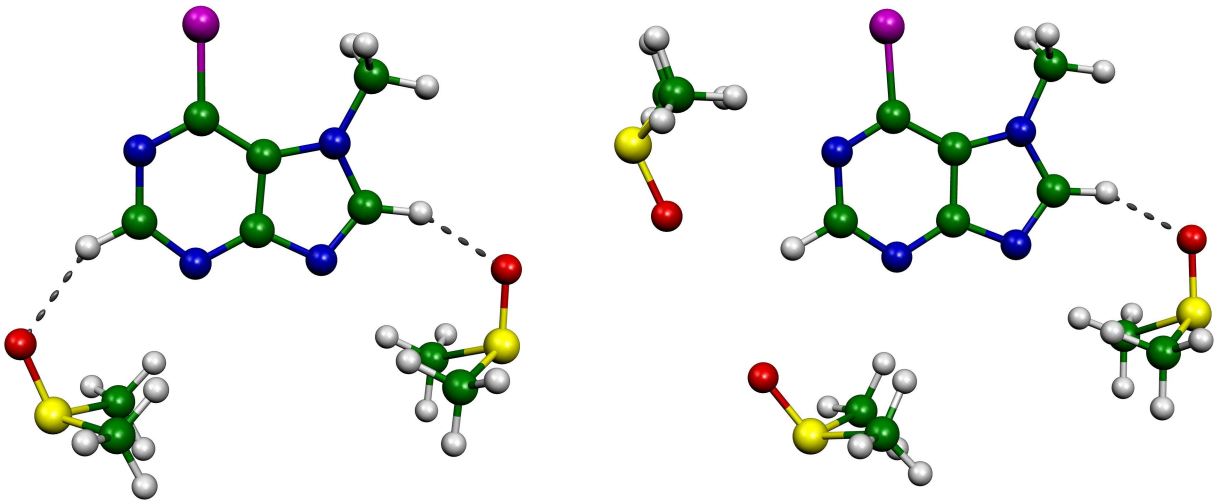
[a] C_s symmetry imposed
[b] Δ = DMSO - gas phase
[c] PCM values from the main paper

Table S2b. Solvent effect to the chemical shifts (δ, ppm) in explicit (+2DMSO, +3DMSO – number of the included solvent molecules, see Figure S4) and implicit (PCM) solvent models of compound **3a** at BLYP/HIII (PCM)// B3LYP/6-31G(d),aug-cc-pVTZ(Cl) level.

	Gas phase	+2DMSO[a] + PCM		+3DMSO[a] + PCM		PCM[c]	Exp.
	δ	δ	Δ[b]	δ	Δ[b]		
N-1	286.40	276.64	-9.76	281.27	-5.13	277.96	276.6
N-3	287.13	274.43	-12.70	277.35	-9.78	270.59	271.5
N-7	145.62	154.78	9.16	154.39	8.77	154.65	156.4
N-9	265.30	250.76	-14.54	250.90	-14.40	248.16	247.6
C-2	153.53	155.54	2.01	155.29	1.76	153.53	151.77
C-4	165.26	164.48	-0.78	164.49	-0.77	164.79	161.68
C-5	123.93	125.43	1.50	125.07	1.14	124.90	122.00
C-6	151.86	152.35	0.49	152.91	1.05	153.43	142.19
C-8	145.32	154.24	8.92	154.38	9.06	149.95	151.31

[a] C_s symmetry imposed
[b] Δ=DMSO-gas phase
[c] PCM values from the main paper

Figure S4. Explicit solvent models (a - +2DMSO, b - +3DMSO) of compound **3a** optimised at B3LYP/6-31G(d),aug-cc-pVTZ(Cl) level.



(a) (b)

[1] A. Dawson, D. R. Allan, S. A. Belmonte, S. J. Clark, W. I. F. David, P. A. McGregor, S. Parsons, C. R. Pulham, L. Sawyer, *Cryst.Growth Des.*, 2005, **5**, 1415.

[2] MOLEKEL 4.0, P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss National Supercomputing Centre CSCS, Manno (Switzerland), 2000.