Corrigendum: Competition between hydrogen and halogen bonding in halogenated 1-methyluracil:water systems

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This article corrects:

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The counterpoise (CP)-corrected interaction energies of the I- and At-containing complexes consisting of halogenated 1-methyl-uracil and one water molecule (XmU-H_2O; X = I, At) should be 2.20 kJ mol^{-1} more negative than reported, see updated Table 3 below, and the scans for ImU-H_2O and AtU-H_2O reported in Figure 5 should be shifted down by 2.20 kJ mol^{-1}. Likewise, the interaction energies of the XmU-$(H_2O)_2$ complexes (X = I, At) should be 4.40 kJ mol^{-1} more negative than reported. Thus, the interaction energies of the halogen-bonded (X-bonded) ImU$(H_2O)_2$ and AtmU-$(H_2O)_2$ complexes (with the water dimer located between C5-X and C4=O4), reported in Table 4, should be -73.4 and -79.3 kJ mol^{-1}, respectively, and those of the "Above ring" complexes should be -88.2 and -87.3 kJ mol^{-1}, respectively.

The CP-corrected interaction energies of the XmU-$(H_2O)_n$ complexes (X = F, Cl, Br, I, At; n = 1, 2) were calculated by subtracting the energies of the optimised isolated fragments (XmU and water) from the CP-corrected dimer energy. We had used the 6-31+G(d) basis set for all atoms except I and At, for which the aug-cc-pVDZ-PP basis set was

used. Gaussian[1] uses by default 6 Cartesian d-functions in the 6-31+G(d) basis set. However, we had not realised that, when specifying basis sets via the "Gen" keyword (which is required when using different basis sets for different atoms), Gaussian uses by default 5 spherical harmonic d-functions for all atoms. Thus, 5 d-functions were used for the calculation of the CP-corrected dimer energy and isolated ImU and AtmU, whereas 6 d-functions were used for isolated H_2O. For consistency, spherical harmonic (5 d) basis functions should have been used for isolated H_2O (or, alternatively, 6 d-functions should have been used for all other calculations). Using 5 d-functions instead of 6 d-functions for the isolated water calculation makes the energy of the water molecule less negative by 2.20 kJ mol^{-1}, leading to the corrections listed above. These corrections make the increase in halogen-bond interaction energy from Cl or Br to At more linear, particularly for the system containing two water molecules. Note that, with this correction, the hydrogen-bond (H-bond) strength of the H-bonded XmU-H_2O systems increases going down the halogen-bond group, and does not peak at the BrmU-H_2O complex, as initially reported.

Table 3. Interaction energies (in kJ mol^{-1}) of minima and transition states (between H-bonded and X-bonded minima)						
Stationary point	X=H	X=F	X=Cl	X=Br	X=I	X=At
H-bonded	-35.8	-24.3	-24.4	-25.2	-25.4	-26.5
X-bonded	--	--	--	-12.2	-18.6	-25.5
Transition state	--	--	--	-11.7	-13.8	-15.7
Out-of-plane	--	-24.7	-24.5	-24.8	-24.6	-24.2
Second H-bonded	--	-25.2	-23.8	-24.7	-25.2	-24.5

We report two additional corrections: (i) The C5-X•••Ow angle for the H-bonded minimum (X=F) should be 117° instead of 81° and (ii) In Table 4 (first line) Table 6 (footnote) "C6=O6" should read "C4=O4".

References and Notes

[1]   M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; B. Mennucci; G. A. Petersson; H. Nakatsuji; M. Caricato; X. Li; H. P. Hratchian; A. F. Izmaylov; J. Bloino; G. Zheng; J. L. Sonnenberg; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; J. Montgomery, J. A.; J. E. Peralta; F. Ogliaro; M. Bearpark; J. J. Heyd; E. Brothers; K. N. Kudin; V. N. Staroverov; R. Kobayashi; J. Normand; K. Raghavachari; A. Rendell; J. C. Burant; S. S. Iyengar; J. Tomasi; M. Cossi; N. Rega; J. M. Millam; M. Klene; J. E. Knox; J. B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R. Cammi; C. Pomelli; J. W. Ochterski; R. L. Martin; K. Morokuma; V. G. Zakrzewski; G. A. Voth; P. Salvador; J. J. Dannenberg; S. Dapprich; A. D. Daniels; Ö. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; D. J. Fox, *Gaussian 09,* Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.