

Acid dissociation constants of melamine derivatives from DFT calculations

Yun Hee Jang,[†] Sungu Hwang,[‡] Seo Bong Chang,[§] Jamin Ku,[†] and Doo Soo Chung^{*,§}

[†]Department of Materials Science and Technology, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea, [‡]Department of Nanomedical Engineering, Pusan National University, Miryang 627-706, Korea, and

[§]Department of Chemistry, Seoul National University, Seoul 151-747, Korea

*To whom correspondence should be sent (Phone +82-2-880-8130, Fax +82-2-872-3231, E-mail dschung@snu.ac.kr).

Supporting Information

1. Dependence on the atomic radii used in the solvation energy calculations

Starting from the original set taken from our previous studies (1.46, 1.41, 1.88, and 1.08 Å for O, N, C, and H, respectively), the atomic radii used in the solvation energy calculations were systematically varied. Figure S1 shows the effect of each radius on the calculated pK_a values of melamine, ammeline, and cyanuric acid (black, blue, and magenta dots in Figure S1, along with the horizontal lines indicating their experimental pK_a values). For instance, Figure S1(a) shows the variation of the pK_a values of ammeline (blue) and cyanuric acid (magenta) when the O radius was varied between 1.46 Å and 1.88 Å while the N, C, and H radii are fixed at the original parameters (1.41, 1.88, and 1.08 Å, respectively). This shows that changing the O radius to 1.76 Å was the most straightforward choice in order to reproduce the experimental pK_a values with our calculation. However, we do not exclude a possibility that variations of multiple radii can lead to other optimum sets of radii, which was not attempted in the current study.

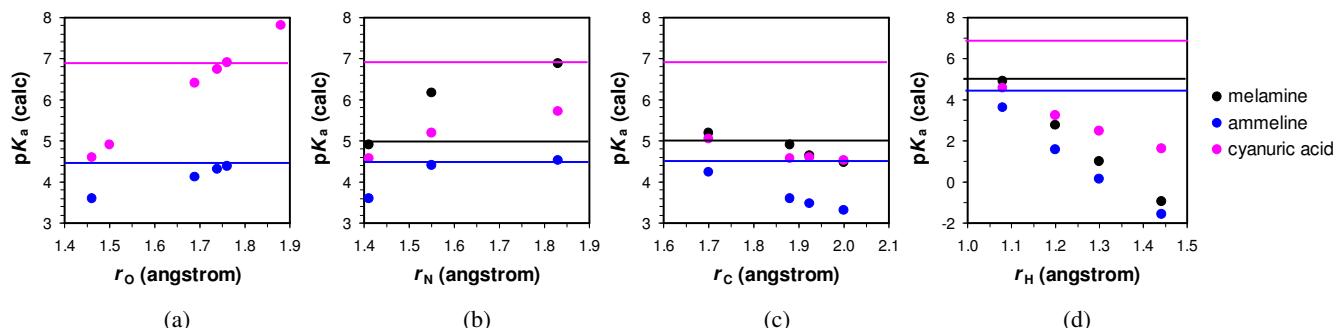


Figure S1. The dependence of the calculated pK_a values of melamine derivatives (melamine: black, ammeline: blue, and cyanuric acid: magenta) on each of the atomic radii (O, N, C, and H) employed in the solvation energy calculations. The colored horizontal lines indicates the experimental pK_a values of the corresponding compounds.

2. Dependence on the solvation model

We also calculated the pK_a values of the melamine derivatives using a different implicit solvation model, the Polarizable Continuum Model (PCM) as implemented in the *Gaussian03* software, at the same level of theory otherwise (Table S1). The calculated pK_a values show a severe dependence on the solvation models [Compare (c) and (d)] and the parameters [Compare (d) and (e)] employed in the calculation.

Table S1. The pK_a values of melamine derivatives calculated with various solvation models and parameters.

	melamine $pK_{a1}(\text{H}_2\text{A}^+ \rightarrow \text{HA})$	Ammeline $pK_{a1}(\text{H}_2\text{A}^+ \rightarrow \text{HA})$	ammelide $pK_{a1}(\text{H}_2\text{A}^+ \rightarrow \text{HA})$	ammelide $pK_{a2}(\text{HA} \rightarrow \text{A}^-)$	cyanuric acid $pK_{a2}(\text{HA} \rightarrow \text{A}^-)$
(a) Experiments ^a	5.0–5.1	4.44–4.5	1.8	6.9	6.9
(b) PB (this work) ^b	4.9	4.4	1.3	7.2	6.9
(c) PB (Bondi radii) ^c	4.3	3.5	−0.5	6.2	5.0
(d) PCM (Bondi radii) ^c	5.8	1.8	1.5	8.3	7.3
(e) PCM (UA0 = United-atom UFF) ^d	6.6	0.2	1.3	11.1	10.0

^aSee the text (Section 3.2) for the references.

^bOptimized in this work (O 1.76 Å, N 1.41 Å, C 1.88 Å, and H 1.08 Å).

^cBondi radii (O 1.52 Å, N 1.55 Å, C 1.70 Å, and H 1.20 Å).

^dUFF with a united-atom (that is, no explicit H) approach (O 1.75 Å, N 1.83 Å, C 1.925 Å, NH 1.93 Å, and NH₂ 2.03 Å).