



Formation and phase transition enthalpies for N-dimethylglycolurils

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Abstract Combining quantum chemical thermochemistry and experimental data from literature, a series of thermochemical parameters ($\Delta_{\text{solv}}\text{H}^0$; $\Delta_{\text{cr}}^{\text{g}}\text{H}^0$; $\Delta_{\text{cr}}^{\text{l}}\text{H}^0$; $\Delta_{\text{l}}^{\text{g}}\text{H}^0$; $\Delta_{\text{f}}^{\text{g}}\text{H}^0$; $\Delta_{\text{f}}^{\text{l}}\text{H}^0$; $\Delta_{\text{f}}^{\text{cr}}\text{H}^0$; C_v and C_p) were obtained for 2,4-dimethylglycoluril (2,4-DMGU), 2,6-dimethylglycoluril (2,6-DMGU) and 2,8-dimethylglycoluril (2,8-DMGU).

Keywords Computational thermochemistry, Formation enthalpies, 2,4-dimethylglycoluril, 2,6-dimethylglycoluril, 2,8-dimethylglycoluril.

Introduction

N-alkyl-substituted bicyclic bisureas of the octane series exhibit pronounced physiological or biological activity [1]. However, the available thermochemical data for such class of compounds is relatively scarce.

A series of thermochemical parameters (dissolution enthalpy, melting enthalpy, etc.), have been established for methylated glycolurils [2-7].

In the present work, by using computational thermochemistry and available experimental data [2-7], formation and phase transitions enthalpies, as well as heat capacities for 2,4-dimethylglycoluril (2,4-DMGU), 2,6-dimethylglycoluril (2,6-DMGU) and 2,8-dimethylglycoluril (2,8-DMGU) are calculated.

Methodology

All quantum thermochemical calculation were performed by using Spartan'16[8] at SE-PM6 and DFT/EDF2/6-31G* levels of theory. The computations were employed to calculate the total energy (in vacuum and water), the $\Delta_{\text{f}}^{\text{g}}\text{H}^0$ (by SE-PM6) and the C_v values. Experimental $\Delta_{\text{soln}}\text{H}^0$ and melting temperature values from literature [2-7] were also employed.

Results and Discussion

Using the calculated C_p values shown in Table 1, and experimental melting temperatures [2-7] the melting enthalpies ($\Delta_{\text{cr}}^{\text{l}}\text{H}^0$) for 2,4-DMGU; 2,6-DMGU and 2,8-DMGU were calculated. As can be verified in Table 1, all calculated $\Delta_{\text{cr}}^{\text{l}}\text{H}^0$ are above the experimental ones (obtained by DSC) [2-7]. However, must be emphasized that the experimental values were not standard ($T = 298.15$ K) ones, but the melting enthalpies at the respective melting temperatures. The standard values must be higher, of course.

The experimental [2-4] $\Delta_{\text{soln}}\text{H}^0$ values were plotted as function of the calculated $\Delta_{\text{cr}}^{\text{l}}\text{H}^0$ values. As can be verified (Figure 1), a linear relationship ($r = 0.997$) is obtained. Furthermore, the fact that $\Delta_{\text{cr}}^{\text{l}}\text{H}^0$ values are higher than $\Delta_{\text{soln}}\text{H}^0$ is in agreement with the fact that the solute-water interaction is weaker than the interaction between glycoluril's molecules in their own crystals [2].

It is known [9,10] that $\Delta_{\text{cr}}^{\text{g}}\text{H}^0 = \Delta_{\text{soln}}\text{H}^0 - \Delta_{\text{solv}}\text{H}^0$. Using experimental [2-4] $\Delta_{\text{soln}}\text{H}^0$ values and the quantum thermochemical $\Delta_{\text{solv}}\text{H}^0$ values calculated in the present work, the $\Delta_{\text{cr}}^{\text{g}}\text{H}^0$ shown in Table 1 were obtained.



Using appropriated thermochemical relations, the other thermochemical parameters shown in Table 1 were calculated.

Table 1: Thermochemical data for N-dimethylglycolurils. Experimental values are between ().

Parameter/Compound	2,4-DMGU	2,6-DMGU	2,8-DMGU
Total energy/au (gas phase)	-603.776801	-603.778614	-603.777008
Total energy/au (in water)	-603.803244	-603.803312	-603.802135
$\Delta_{\text{soln}}H^0/\text{kJmol}^{-1}$	-69.42	64.84	-65.97
		$(-85 \pm 2)^3$	
$\Delta_{\text{soln}}H^0/\text{kJmol}^{-1}$ (in water)	$(20.78 \pm 0.07)^2$	$(13.88 \pm 0.06)^2$	$(9.73 \pm 0.04)^2$
$\Delta_f^g H^0/\text{kJmol}^{-1}$	-296.28	-296.36	-295.10
$\Delta_f^l H^0/\text{kJmol}^{-1}$	-343.73	-328.65	-319.45
$\Delta_f^{\text{cr}} H^0/\text{kJmol}^{-1}$	-386.48	375.08	-370.60
$\Delta_{\text{cr}}^g H^0/\text{kJmol}^{-1}$	90.20	78.72	75.70
		$(99 \pm 2)^3$	
$\Delta_l^g H^0/\text{kJmol}^{-1}$	47.45	32.29	24.35
$\Delta_{\text{cr}}^l H^0/\text{kJmol}^{-1}$	42.75	46.43	51.15
	$(32.2)^1$	$(24.4)^1$	$(43.1 \pm 0.5)^1$
$C_v/\text{JK}^{-1}\text{mol}^{-1}$	178.99	175.91	175.80
$C_p/\text{JK}^{-1}\text{mol}^{-1}$	187.30	184.22	184.11

¹At melting temperatures: 526.4 K, 550.2 K and 576.0 K, for 2,4-DMGU, 2,6-DMGU and 2,8-DMGU, respectively (Ref. 2-4); ²Experimental values(Ref. 2-4); ³Obtained by Knudsen's effusion mass-spectrometric method (Ref. 2,7).

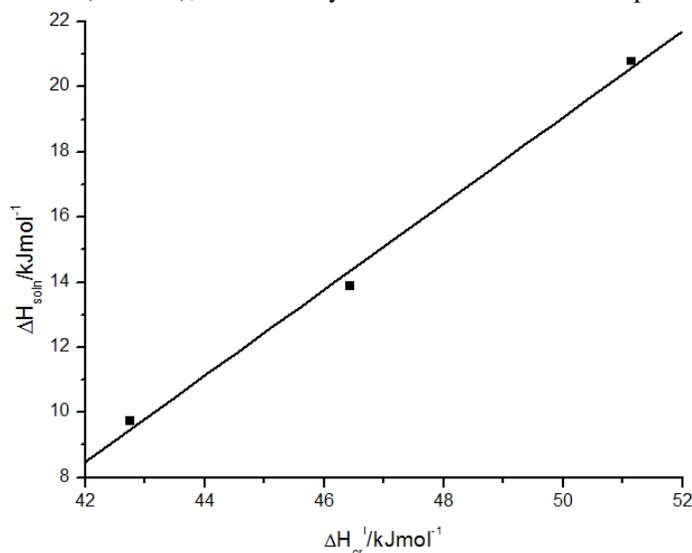


Figure 1: Experimental $\Delta_{\text{soln}}H^0$ values as function of calculated $\Delta_{\text{cr}}^l H^0$ enthalpies

It is worth noting that the $\Delta_{\text{cr}}^l H^0$ values increases from 2,4-DMGU to 2,8-DMGU, whereas the $\Delta_l^g H^0$ decreases in the same sequence. That is, in the solid state, the intermolecular interactions are stronger to 2,8-DMGU and weaker to 2,4-DMGU, with 2,6-DMGU exhibiting an intermediate value. On the other hand, in the liquid state, the sequence is inverted. Such facts are certainly related with the orientation of the molecules in the space, inside the unite cell, been licit to suppose that in the solid state the hydrogen bonds are stronger for 2,8-DMGU. On the other hand, if in the liquid state the weaker intermolecular interactions are observed exactly to this molecule, it is possible to suppose that the presence of two methyl groups on the sane side of the molecule provokes weaker interactions with the neighbour molecules, and then, the lower $\Delta_l^g H^0$ value.



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