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THEORETICAL CALCULATION OF EQUILIBRIUM CONSTANT FOR KETO-ENOL TAUTOMERISM IN CYANURIC ACID

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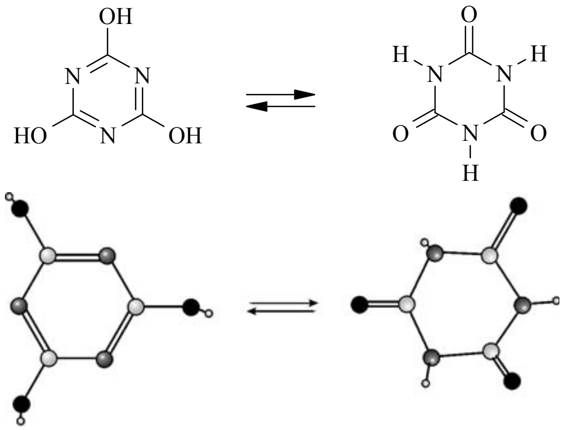
Cyanuric acid (1,3,5-triazine-2,4,6-triol) is the cyclic trimer of cyanic acid [1]. It is an organic compound with the chemical formula $C_3H_3N_3O_3$. Synonyms include 1,3,5-triazinetriol, *s*-triazinetriol, 1,3,5-triazine-2,4,6-(1H,3H,5H)trione, *s*-triazinetrione, tricarbimide, isocyanuric acid, and pseudocyanuric acid. This triazine derivative is a stable, white, odorless, and hygroscopic solid at room temperature. It is used as a stabilizer in recreational water treatment to minimize the decomposition of hypochlorous acid by light in outdoor swimming pools and hot tubs [2]. Chlorinated derivatives of cyanuric acid, such as trichloro-*s*-triazinetrione and sodium dichloro-*s*-triazinetrione, are used as algacides or microbiocides in swimming pool water and large scale water systems in industry [3]. The ring in its molecule has an aromatic character and the hydroxyl groups in the triol form of the molecule take on a phenolic character, becoming somewhat more acidic than hydroxyls in an alcohol. The hydrogen of any one of cyanuric acid hydroxyls can be neutralized to form a cyanurate salt [4].



1,3,5-Triazine-2,4,6-triol 1,3,5-Triazine-2,4,6(1H,3H,5H)-trione

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TABLE 1. Binding energies and corresponding equilibrium constants of cyanuric acid tautomers

	DFT/B3LYP/6–311++G(d,p)		HF/6–311++G(d,p)	
Compound	Triazinetriol	Triazinetrione	Triazinetriol	Triazinetrione
E, kJ·mol^{-1}	-1329235.3	-1329364.9	-1321997.0	-1322126.0
ΔE, kJ·mol^{-1}		-129.6		-129.0
K*		5×10^{22}		4×10^{22}

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* $K = \exp(-\Delta E/(RT))$; T = 298 K; R = 8.314 J·K^{-1}·mol^{-1}.

The two chemical structures shown in the Scheme are keto-enol tautomers of cyanuric acid. In this work we calculated the equilibrium constant for keto-enol tautomers according to the Scheme by HF and DFT methods assuming as a solvent.

The Gaussian program package [5] was used for the estimation of the binding energy and compound geometry. The geometries of isomers (Scheme) were completely optimized with the Gaussian 98 program [5], employing the B3LYP functional [6–8] within the scope of density functional theory (DFT) [9, 10] and at the Hartree–Fock (HF) [11] level with the polarized triple-zeta split valence 6–311++G(d,p) basis set and water as an appropriate solvent.

The energy difference of the isomers (ΔE) was estimated without a zero point vibrational energy correction. The energies and corresponding equilibrium constants are listed in Table 1.

While the values presented in Table 1 are probably too inaccurate for reliable prediction of relative stability of tautomers, the order of stabilization energies and calculated equilibrium constants ($\Delta E \approx -RT \ln K$) agree well with the fact that the keto form is more stable than its enol counterpart. According to given data the keto form is -129.6 and -129.0 kJ·mol^{-1} more stable than the enol form in the DFT and HF levels, respectively. On the other hand, the very great value of the calculated the equilibrium constant ($K = 4–5 \times 10^{22}$) is due to with the fact that the equilibrium goes mainly toward the more stable *s*-triazinetrione isomer.

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