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Contributed Paper

Cyanuric Acid: Hydrothermal Crystal Growth and Alternative Crystallographic Description

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ABSTRACT

Single crystals of cyanuric acid in its keto form have been hydrothermally synthesized *via* the acid catalyzed hydrolysis of 1, 3, 5-triazine-2, 4, 6-triamine triacetic acid. The crystal structure has been solved and refined in a standard monoclinic *C*2/*c* which is better preferable than the commonly employed *C*2/*n* with b > > 90. The original cell in *C*2/*c* are a = 7.9070(13) Å, b = 6.7347(14) Å, c = 9.0788(15) Å, b = 90.794(14)°, V = 483.41(15) Å^3, R = 0.0473, R_w = 0.1288, S = 1.073, and the transformed *C*2/*n* cell are a = 7.907 Å, b = 6.7347 Å, c = 11.9564 Å, b =130.602°. Relationships between different crystallographic settings are discussed. The molecular motifs are assembled into two-dimensional layer in (1 0 -1) plane by the N-H···O type of hydrogen bonding interactions with graph sets $R^2_2(8)$ and $R^4_4(16)$. The molecule shows partial aromatic character, corresponding to the harmonic-oscillator model of aromaticity index of 0.89.

Keywords: cyanuric, hydrothermal, crystallography, crystal growth, hydrogen bond

1. INTRODUCTION

Cyanuric acid ($C_3H_3N_3O_3$) existing in either enol form (2,4,6-trihydroxy-1,3,5-triazine) or keto form (1,3,5-triazine-2,4,6-trione) has been exhaustively applied in both everyday life and industries since late 1950s [1, 2]. With the notable properties of biodegradability by soil bacteria and being non-toxic to human and aquatic animals, it is used for example as a chlorine-stabilizer against the sun for the outdoor swimming pools and large industrial water system [3]. Derivatives of the compound are also extensively applied, for instance, as dyestuffs, optical bleaches, surface active agents and pesticides [1, 4-6].

This organic compound was first identified over two centuries ago [1] and the crystal structure was reported for the first time in 1938 by Wiebenga and Moerman [7]. With 1,3,5-triazine or *s*-triazine ring as the core structure, the compound is aromatic and slightly acidic in nature [1]. The presence of both the N-H and C=O motifs in the molecular structure provides functionality as both hydrogen bonding donor and acceptor [8]. The re-investigations of the solid state structure for cyanuric acid were successively reported, all of which accounted mainly for the accuracy and precision of the previously proposed molecular models and intriguingly performed only in the monoclinic non-standard space group *C*2/*n* (No. 15) [9-12]. The non-standard choice of crystallographic setting was selected allegedly by virtue of simplicity in explaining the crystal packing [9]. However, the large deviation of β from 90° is undesirable for structure refinement [13].

In this work, the crystal structure of cyanuric acid has been solved and refined using an alternative monoclinic space group *C*2/*c* (Hall Symbol -*C* 2*yc*), which is the standard space group for *C*2/*n* (Hall Symbol -*C* 2*yac*), and yet has hitherto not appeared in detail. In this setting $\beta \approx 90°$, the analysis of hydrogen bonding interactions accounting for the molecular assembly is included. Relationship between the two crystal settings which have been modeled using the two different space groups is presented and discussed. An aromatic character of the compound in the solid state has been evaluated.

2. MATERIALS AND METHOD

2.1 Hydrothermal Crystal Growth and FT-IR Measurement

The 1,3,5-triazine-2,4,6-triamine triacetic acid (H_3TTTA) was synthesized following the report of W. Karuehanon *et al*. [14]. The other starting reagents were purchased commercially and used without further purification. A FT-IR spectrum of the ground crystals was collected as a KBr disc (BDH, 98.5%), using a Bruker Tensor 27 FT-IR spectrometer in the range of 4000-400 cm^{-1} with a resolution of 0.5 cm^{-1}.

In an attempt to synthesize new metal-organic frameworks using the H_3TTTA ligand by hydrothermal technique, single crystals of 1,3,5-triazine-2,4,6-trione (cyanuric acid) were generated *in situ*. In a typical reaction, the H_3TTTA ligand (0.556 mmol) was first dissolved in 10.00 cm^3 of HCl(aq) solution (151 mmol; Merck 37%) and then transferred to a 23 cm^3 Teflon lined autoclave. The pH of the reaction was measured using the universal pH paper (Merck KGaA, Germany) and indicated pH < 2. After the treatment under an autogenous pressure generated at 180°C for 48 h, colorless prismatic crystals of cyanuric acid were obtained.

2.2 Single Crystal Structure Determination

Full intensity data set for the yielded crystal was collected on a Bruker AXS smart Apex CCD diffractometer (X8 APEX II) at 293(2) *K* using Mo *K*a (*l* = 0.71073 Å) radiation. A single crystal was chosen under an optical microscope and mounted on to the end of a glass fiber. The collected data were processed by the APEX2 software [15], and analytically corrected for absorption using the Tompa method [16]. The structure was solved by direct methods and refined by the full matrix least squares on F^2 within SHELX-97 [17] *via* the WinGX program [18]. The anisotropic thermal parameters were applied for all non-hydrogen atoms. Hydrogen atoms were located in difference Fourier maps, as exemplified in Figure 1. Hydrogen atoms were placed at geometrically calculated positions with N-H bond lengths refined subject to weak restraints.

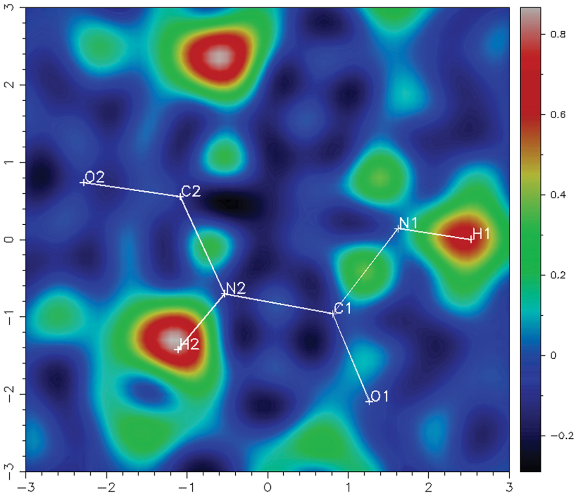
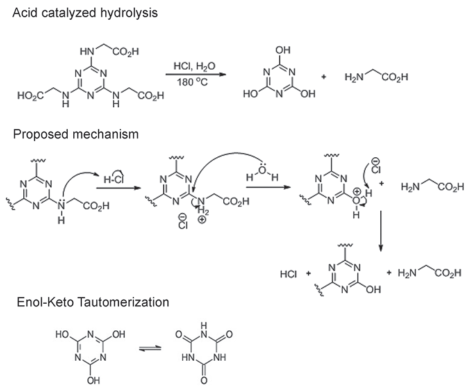


Figure 1. View of locations for hydrogen atoms in difference Fourier map.

3. RESULTS AND DISCUSSION

3.1 The *in situ* Hydrothermal Crystal Growth

Although the title compound is rather well known, the difference in the synthesis technique may be noted. Previous studies on the compound reported solely on crystals grown under ambient temperature and pressure using a conventional solution method [9], whereas low vapor pressure was involved for the hydrothermal condition. Without an addition of cyanuric acid in the reaction mixture, single crystals of the compound are presumably generated *in situ* from the hydrolysis reaction of the H_3TTTA ligand, particularly under highly acidic hydrothermal conditions. Scheme 1 depicts a plausible mechanism for the acid catalyzed hydrolysis of the H_3TTTA ligand [19-20]. The enol-keto tautomerization is included in Scheme 1. As revealed later by single crystal X-ray data, differences in the synthesis method and condition between the reported hydrothermal technique and the previously reported solution technique do not significantly impart effect on the yielded crystal structure. Both molecular structure and crystal packing of these reported structures are mostly alike.



Scheme 1. Schematic illustration of an acid catalyzed hydrolysis of the H_3TTTA ligand, and the enol-keto tautomerization of cyanuric acid.

3.2 Crystal Structure and Hydrogen Bonding Analysis

The structure of cyanuric acid reported here has been solved and refined in the standard monoclinic space group *C*2/*c* (Hall Symbol -*C* 2*yc*) using unique axis *b* and cell choice 1 [21], where the unit cell origin is located in an inversion center on the glide plane *c*. The refined cell parameters are summarized in Table 1, in comparison to the data retrieved from the references of the previous works [9-12]. The previously reported solid state structures will be hereafter cited using the Cambridge Structural Database (CSD) entry codes, namely CYURAC03 [9], CYURAC04 [11], CYURAC05 [12], CYURAC10 [9] and CYURAC12 [10]. In order to compare the present structure to the former data, the refined cell parameters have also been transformed into the non-standard *C*2/*n* (Hall Symbol -*C* 2*yac*) by MERCURY [22], using the unique axis -*b* and cell origin located in an inversion center on the glide plane *n*. The cell parameters in *C*2/*n* are a = 7.907 Å, b = 6.7347 Å, c = 11.9564 Å, b = 130.602°. The transformed cell shows an excellent agreement with those of CYURAC10, with deviation only in the third decimal digit except for the value of b where the deviation is approximately 0.07°. The unit cell volume of the reported structure (483.411(15) Å^3) is slightly larger than that of CYURAC10 (482.078 Å^3). Details on the relationship between the two cells will be discussed later in detail.

Table 1. Summary of crystallographic details for the reported cyanuric acid, compared to the data retrieved from the previous works.

	this work	CYURAC03 [9]	CYURAC04 [11]	CYURAC05 [12]	CYURAC10 [9]	CYURAC12 [10]
Empirical formula	$C_3H_3N_3O_3$	$C_3H_3N_3O_3$	$C_3H_3N_3O_3$	$C_3H_3N_3O_3$	$C_3H_3N_3O_3$	$C_3H_3N_3O_3$
Formula weight	129.08	129.08	129.08	129.08	129.08	129.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*n*	*C*2/*n*	*C*2/*n*	*C*2/*n*	*C*2/*n*
Unit cell dimensions	a = 7.9070(13) Å b = 6.7347(14) Å c = 9.0788(15) Å b = 90.794(14)°	a = 7.749(1) Å b = 6.736(3) Å c = 11.912(4) Å b = 130.69(2)°	a = 7.749(1) Å b = 6.736(3) Å c = 11.912(4) Å b = 130.69(2)°	a = 7.749(1) Å b = 6.736(3) Å c = 11.912(4) Å b = 130.69(2)°	a = 7.900(3) Å b = 6.732(3) Å c = 11.951(6) Å b = 130.67(2)°	a = 7.749(1) Å b = 6.736(3) Å c = 11.912(4) Å b = 130.69(2)°
Volume	483.41(15) Å^3	471.459 Å^3	471.459 Å^3	471.459 Å^3	482.078 Å^3	471.459 Å^3
Z	4	4	4	4	4	4
Temperature	293(2) *K*	100 *K*	100 *K*	100 *K*	296 *K*	100 *K*
Density (calculated)	1.774 g cm^{-3}	N/A	N/A	N/A	N/A	N/A
Absorption coefficient	0.159 mm^{-1}	N/A	N/A	N/A	N/A	N/A
Theta range for data collection	3.95-34.25°	5-37°	5-37°	N/A	5-37°	N/A
Wavelength (Mo $K\alpha$)	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	1.067 Å
Reflection collected	691	N/A	N/A	N/A	N/A	1345
Unique reflections	577 (R_{int} = 0.0445)	N/A	N/A	N/A	N/A	N/A
R, Rw[I>2s(I)]	0.0473, 0.1288	N/A	N/A	N/A	N/A	N/A
R, Rw (all data)	0.0537, 0.1336	N/A	N/A	N/A	N/A	N/A
Goodness of fit	1.073	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*

There are six non-hydrogen atoms in the asymmetric unit of the reported crystal, as shown in Figure 2, of which three atoms (C2, N1 and O2) are located on a special Wyckoff position 4*e* (a two-fold rotation axis) and the other three (C1, N2 and O1) occupied a general position 8*f*. The molecule is completed by the rotation about the two-fold axis, and is absolutely planar coinciding with the (1 0 -1) plane. The difference in orientations of the established layers reported here to the previously reported (1 0 1) by Wiebenga [23], should be noted. The C-N bond distances are distributed in a narrow range of 1.3672(16)-1.3695(11) Å, which are rather short in comparison to those of the previously reported CYURAC10, as listed in Table 2. The C-O bond distances, the C-N-C and N-C-N bond angles however show better agreement with the reported figures for the CYURAC10 structure [9]. Based on the refined bond distances, an aromatic character of the *s*-triazine core of the reported cyanuric has been evaluated using the harmonic-oscillator model of aromaticity (HOMA) index [24]. The optimal bond length R_{optimal}(C-N) and the empirical constant a of 1.334 Å and 93.52 were used [25], giving the HOMA index of 0.89. In comparison to the two extremes of HOMA index, *i.e.* HOMA < 0 for the non-aromatic cyclohexane (-4.34) and HOMA = 1 for the fully aromatic benzene [25], the calculated value of 0.89 suggests the partial aromatic character. The calculated value is as expected slightly less than 0.977 for the triazine [26], but larger than the theoretical value of 0.7373 for cyanuric acid in the gas phase [26].

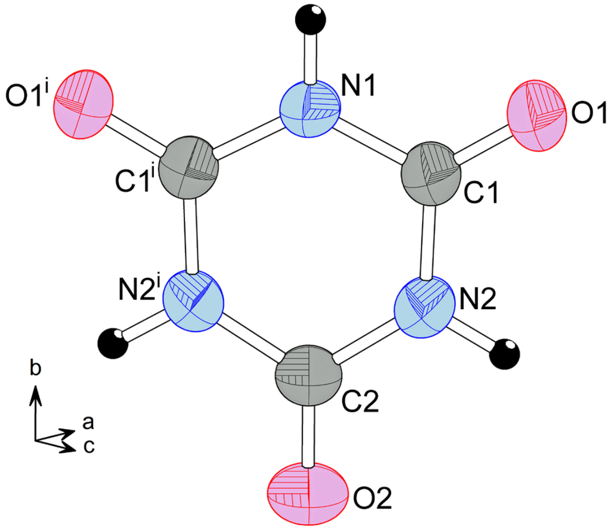


Figure 2. Molecular structure of cyanuric acid, shown with thermal ellipsoids of 70% probability. The molecule is completed by symmetry operation (i) -*x*, *y*, 0.5-*z*.

Table 2. Average bond lengths and angles in the reported cyanuric acid, compared to the data retrieved from CYURAC10 [9].

Compound	C-N (Å)	C-O (Å)	N-C-N (°)	C-N-C (°)
this work	1.368(1)	1.218(1)	115.2(1)	124.8(1)
CYURAC10	1.374(1)	1.213(1)	115.39	124.60

Standard deviation is not available.

The molecular motifs of the cyanuric acid are packed in the solid state by the strong hydrogen bonding interactions of N-H×××O type, orientating in three different directions, including the [0 1 0] direction, and the [1 0 1] and [-1 0 -1] which are related by the rotation about the two-fold axis. Figure 3a shows the hydrogen-bonding network in the crystal packing of cyanuric acid, illustrating two different types of hydrogen bonding ring patterns, *i.e.* R_2^2 (8) and R_4^4(16). The smaller ring can be identified as the synthon for an establishment of the hydrogen bonding molecular tape, running in the [1 0 1] direction. These tape are condensed by the other hydrogen bonding interactions in the [0 1 0] direction to form the larger hydrogen bonding ring and therefore the two-dimensional hydrogen bonding layer parallel to the (1 0 -1) plane. These layers are stacked with the inter-layer distance of *ca.* 3 Å, and related to each other by the *c* axial glide operation, as shown in Figure 3b. The hydrogen bonding geometries of the structure reported in this article compared with the data available of the previously reported structures are listed in Table 3. Accuracy of the reported values for this work for the hydrogen bonding geometries in comparable degree to the neutron diffraction data is noted.

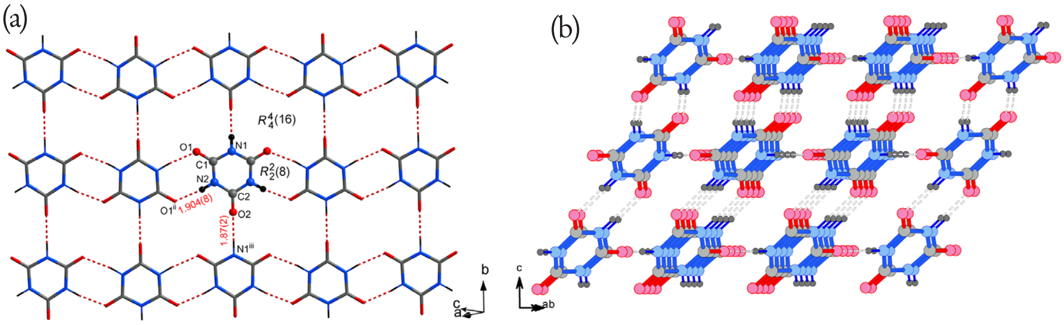


Figure 3. Views of (a) hydrogen bonding interactions about the cyanuric molecule and the hydrogen bonding R_2^2 (8) and R_4^4(16) motifs in the two-dimensional (1 0 -1) layer, and (b) the packing of the two-dimensional layers. Symmetry operations: (i) -*x*, *y*, 0.5-*z* (ii) 0.5-*x*, 0.5-*y*, 1-*z* (iii) *x*, -1+*y*, *z*.

Table 3. Details of the hydrogen bonding interactions in the reported cyanuric acid, compared to the data retrieved from the previous works.

Compound	N-H (Å)	H---O (Å)	N---O (Å)	N - H---O (°)	Note	Ref.
this work	0.925(8)	1.875(2)	2.7880(6)	180	N2^{iii}---O2^{i}	-
	0.91(2)	1.904(8)	2.8210(12)	170.9(7)	N1^{ii}---O1^{i}	
CYURAC03	0.90	*N/A*	2.778(3)	N/A		[9]
	0.90	*N/A*	2.812(3)	*N/A*		
CYURAC10	0.89	*N/A*	2.778(3)	N/A		[9]
	0.90	*N/A*	2.798(3)	*N/A*		
CYURAC12	1.0264(15)	1.757(2)	2.784(2)	180	Neutron data	[10]
	1.0365(11)	1.774(1)	2.805(1)	172.44(10)	at 100 *K*at	

Symmetry operations: (i) 0.5+*x*,0.5+*y*,-1+*z*; (ii) 0.5+*x*,1.5+*y*,-1+*z*; (iii) 1-*x*,0.5+*y*,-0.5-*z*

Standard deviation is not available.

Regarding the relationship of the reported *C*2/*c* and the transformed *C*2/*n* cells, as shown in Figure 4a, it is apparent that the orientation of the hydrogen bonding layers is altered after the transformation, *i.e.* from (1 0 -1) to (1 0 0), corresponding to *a*′ = *a*-*c* when *a*′ and *a* are the *a* axes of the transformed and original cells respectively. While the unit cell *b* and *c* axes reserve their directions with the extension of *ca.* 2.88 Å for *c*, axis *a* is slanted by *ca.* 39.81° to the original direction. As the transformed unit cell is overlaid with the previously reported CYURAC10, as shown in Figure 4b, the molecular planes of the two cells differ by *ca.* 0.59 Å measured between the centroids of two corresponding molecular motifs.

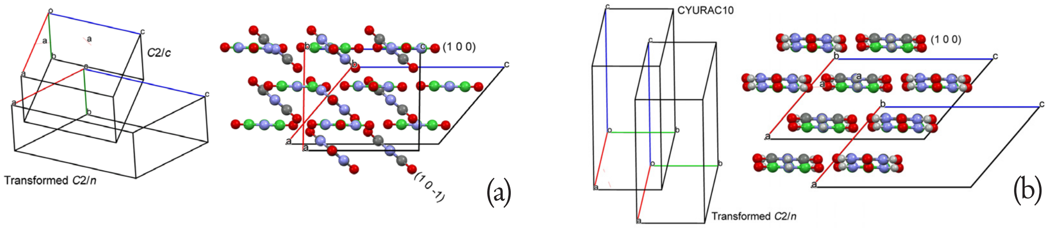


Figure 4. Relative orientations of the molecular packing and the unit cells for the reported *C*2/*c* cell compared to (a) the transformed *C*2/*n*, and (b) the previously reported CYURAC10 [9].

The FT-IR spectrum of the reported crystal, as shown in Figure 5, displays characteristic vibrations for the cyanuric molecule, which agree well with the formerly reported spectra [27, 28]. The profile of the absorption from single crystal sample is yet better refined. The most intense band at 1722 cm^{-1} is an indicative for the carbonyl n(C=O). The medium absorptions at 1540 and 1460 cm^{-1} are characteristic for the n_{sym}(C=N) and $_{sym}$(C-N), whereas those at 1055, 767 and 535 cm^{-1} are the characteristic breathing type of vibration of the 1,3,5-triazine ring. The two features at 3034 and 2800 cm^{-1} correspond to the n(N-H) and d(N-H) vibrations, respectively. The broadening effect exhibited by the n(C=O) and n(N-H) corresponds well with the involvement of both motifs in hydrogen bonding formation.

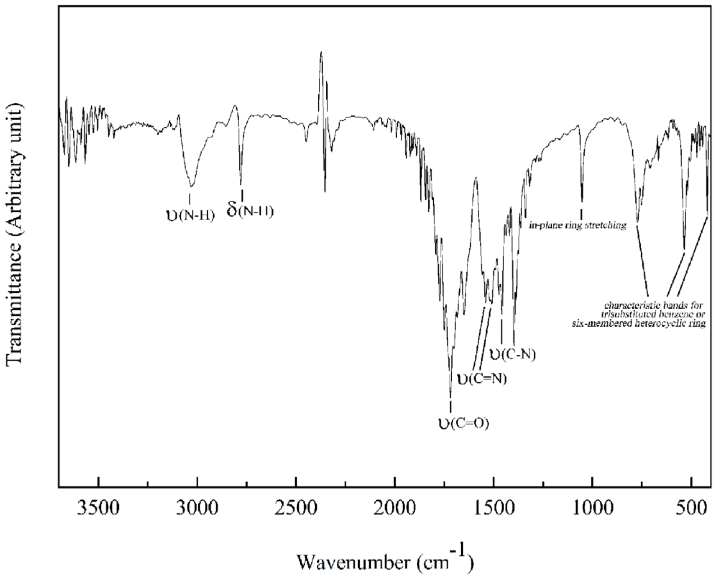


Figure 5. The FT-IR spectrum of cyanuric acid.

4. CONCLUSIONS

In summary, single crystals of cyanuric acid in its keto form have been *in situ* hydrothermally synthesized and growth *via* the acid catalyzed hydrolysis of the H_3TTTA organic molecule. The crystal structure has been solved and refined in a standard monoclinic space group *C*2/*c* rather than the commonly employed *C*2/*n*. Detailed analysis of the crystal structure and hydrogen bonding network is described, indicating the correction for the orientation of the two-dimensional hydrogen bonding layer from the previously reported (1 0 1) to (1 0 -1). Relationships between different crystallographic settings are presented and discussed. The aromaticity of the molecule is evaluated.

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