

Hydrogen bonded complexes of cyanuric acid with pyridine and guanidinium carbonate

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Abstract. Hydrogen bonded complexes of cyanuric acid (CA) with pyridine, $[\text{C}_3\text{N}_3\text{H}_3\text{O}_3:\text{C}_5\text{H}_5\text{N}]$, **1**, and guanidinium carbonate $[\text{C}_3\text{H}_2\text{N}_3][\text{C}(\text{NH}_2)_3]$, **2**, have been prepared at room temperature and characterized by single-crystal X-ray diffraction. Structure of **1** shows pyridine molecules substituting the inter-tape hydrogen bond in CA by N–H...N and C–H...O hydrogen bonds. The structure reveals CA-pyridine hydrogen-bonded single helices held together by dimeric N–H...O hydrogen bonding between CA molecules. In **2**, the CA tapes, resembling a sine wave interact with the guanidinium cations through N–H...O and N–H...N hydrogen bonds forming guanidinium cyanurate sheets.

Keywords. Cyanuric acid-pyridine adduct; guanidinium cyanurate; single helices; crystal structure analysis.

1. Introduction

Cyanuric acid, CA, crystallizes as molecular tapes with dimeric N–H...O hydrogen bonding¹. Adjacent tapes are held together by N–H...O interactions forming CA molecular sheets perpendicular to the *a* axis as shown in figure 1. Cyanuric acid has been co-crystallized with several heterocyclic molecules such as bipyridyl^{2,3} to obtain interesting intermolecular hydrogen-bonded assemblies. With melamine, CA forms the well-known rosette structure giving rise to channels⁴. We have investigated the adducts of CA with pyridine and guanidinium carbonate and have obtained novel hydrogen-bonded structures. In this work we describe the interesting features of these adducts.

2. Experimental

Rod-shaped single crystals of the 1:1 complex of CA with pyridine were obtained from a solution of CA in pyridine at room temperature. The composition of this complex was $\text{C}_3\text{N}_3\text{H}_3\text{O}_3:\text{C}_5\text{H}_5\text{N}$, **1**. Good quality single crystals of the adduct of CA with guanidinium carbonate (GC) were obtained from an aqueous solution containing 1 mmol each of CA and GC. The composition of the adduct is $[\text{C}_3\text{H}_2\text{N}_3][\text{C}(\text{NH}_2)_3]$, **2**. Crystal data of **1** and **2** are listed in table 1.

High quality single crystals were chosen after careful examination under a polarizing microscope. X-ray diffraction intensities were measured at room temperature by ω scans using a Siemens three-circle diffractometer attached to a CCD area detector and a

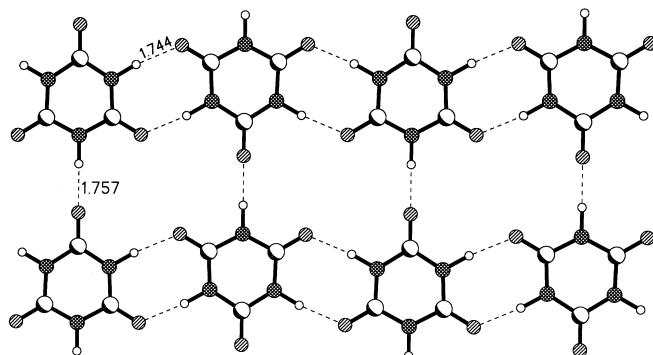


Figure 1. Structure of CA with tapes formed by N–H...O hydrogen bonds along the *c* axis and the inter-tape N–H...O hydrogen bonds along the *b* axis.

Table 1. Crystal data for **1** and **2**.

	1	2
Formula	C ₃ N ₃ H ₃ O ₃ :C ₅ H ₅ N	[C ₃ H ₂ N ₃ O ₃][C(NH ₂) ₃]
Molecular weight	208.18	47.04
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> −1
<i>a</i> (Å)	10.8152(4)	3.7745 (5)
<i>b</i> (Å)	11.9889(10)	9.8488 (14)
<i>c</i> (Å)	7.4529(2)	10.499 (2)
a	90	87.924 (3)
b	94.282(2)	83.217 (2)
g	90	79.235 (2)
Cell volume (Å ³)	963.66(4)	380.69 (9)
<i>Z</i>	4	8
<i>F</i> (000)	432	196
<i>d</i> _{calc} (mg/m ³)	1.435	1.642
<i>I</i> (Å) (Mo- <i>K</i> _α)	0.7103	0.7103
<i>m</i> (mm ^{−1})	0.113	0.140
Crystal size (mm)	0.12 × 0.2 × 0.12	0.14 × 0.18 × 0.12
Diffractometer	Siemens, Smart CCD	Siemens, Smart CCD
<i>T</i> (K)	293 (2)	293 (2)
q range (deg)	1.89–23.31	2–24
<i>h</i>	−10 ≤ <i>h</i> ≤ 12	−4 ≤ <i>h</i> ≤ 4
<i>k</i>	−9 ≤ <i>k</i> ≤ 13	−6 ≤ <i>k</i> ≤ 10
<i>l</i>	−8 ≤ <i>l</i> ≤ 8	−11 ≤ <i>l</i> ≤ 11
Total reflections	3866	1596
Non-zero reflections	1383 [<i>R</i> (int) = 0.0365]	1075 [<i>R</i> (int) = 0.0719]
<i>R</i> [<i>I</i> > 2σ]	<i>R</i> 1 = 0.0354, <i>wR</i> 2 = 0.0777	<i>R</i> 1 = 0.0376, <i>wR</i> 2 = 0.0984
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0549, <i>wR</i> 2 = 0.0864	<i>R</i> 1 = 0.0412, <i>wR</i> 2 = 0.1045
GOF on <i>F</i> ²	0.048(3)	1.102
max. <i>e</i> (Å ^{−3})	0.167	0.156

graphite monochromator for the MoK α radiation (40 kV, 40 mA). A hemisphere of reciprocal space was collected using SMART⁵ software with 2 θ setting of the detector at 28°. The crystal-to-detector distance was 5 cm. Data reduction was performed using the SAINT program and the orientation matrix along with the detector and cell parameters were refined for every 40 frames on all measured reflections. The crystal structures were solved by direct methods SHELXTL program⁶ and refined by full matrix least squares on F^2 . All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by the difference Fourier method and were refined isotropically.

The atomic coordinates of **1** and **2** are listed in table 2. Selected bond lengths and angles for both are given in table 3. Details of the hydrogen bonds in **1** and **2** given in table 4 were computed using PLATON and the plots of arrangement of molecules were generated using XP.

3. Results and discussion

3.1 Cyanuric acid–pyridine adduct, **1**

The 1:1 complex of CA with pyridine, C₃N₃O₃H₃:C₅H₅N, **1**, crystallizes in a monoclinic ($P2_1/c$) space group (table 1). The asymmetric unit of **1** (figure 2a) consists of one molecule each of CA and pyridine as expected. The structure of **1** shown in figure 3a reveals that the molecular tapes formed by dimeric N–H...O hydrogen bonds in CA are retained. The pyridine molecules replace the intertape N–H...O hydrogen bond in CA by a strong N–H...N (H...N, 1.75 Å) bond in addition to C–H...O (H...O, 2.55 Å) interaction. The H...O distance of 2.55 Å suggests that the C–H...O bond is moderately strong⁷.

In **1**, cyanuric acid is able to accommodate a foreign molecule such as pyridine without making any significant compromise in its original H-bonding features. The cell parameter along the direction of the CA tapes in both CA and **1** show a difference of only 0.05 Å. The increase along the c axis in **1** roughly corresponds to the size of the pyridine molecule with the H-bonding distances. The structure also shows single helices of hydrogen bonded CA and pyridine held by the dimeric N–H...O hydrogen bonds between the CA molecules (figure 4). The distance between the adjacent helices is about 5.99 Å. The helicity of chains here is induced by the pyridine molecules, which tilt from the plane of the CA tapes. All the CA molecules in a particular chain are in the same plane.

3.2 Guanidinium cyanurate, **2**

Guanidinium cyanurate, **2**, crystallizes in a triclinic ($P\bar{1}$) space group (table 1). The asymmetric unit of **2** is shown in figure 2b. The asymmetric unit consists of cyanurate monoanion and the guanidinium cation. The structure of **2** contains CA tapes and the guanidinium cations held between the adjacent tapes by N–H...N and N–H...O hydrogen bonds as shown in figure 3b. The CA tapes resemble a sine-wave unlike the linear tapes present in both CA and **1**. The axis parameter along the direction of the tapes is shorter (10.4987 Å) in comparison to that in CA (11.912 Å) due to the sine-wave like structure of the tapes adopted by CA molecules. The effect of the negative charge on N(11) manifests itself in the distances of the neighbouring bonds. Thus, the C–N bond distances of C(11)–N(11) and C(12)–N(11) are shorter than the other C–N distances observed in the

fragment. The carbonyl groups adjacent to N(11) show an increase in the bond length. The N(12)–C(12) and N(13)–C(13) bonds also show an increase in their lengths. The above variations in the bond distances result from the delocalization of the negative charge on N(11) to the adjacent carbonyls. The increase in the bond lengths of

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of **2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

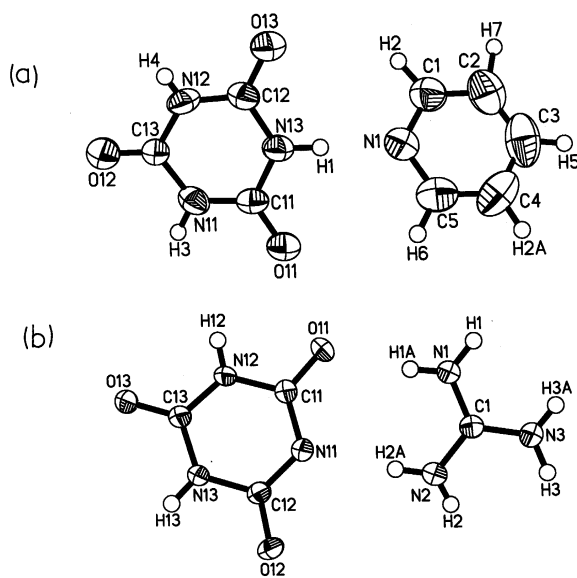
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
1				
N(13)	0.4693(2)	0.4616(1)	0.2161(2)	0.041(1)
N(12)	0.4632(2)	0.2698(1)	0.2315(2)	0.042(1)
N(11)	0.6238(2)	0.3660(1)	0.3839(2)	0.041(1)
O(13)	0.3132(1)	0.3653(1)	0.0665(2)	0.061(1)
O(12)	0.6191(1)	0.1771(1)	0.3889(2)	0.051(1)
O(11)	0.6220(1)	0.5547(1)	0.3798(2)	0.049(1)
C(13)	0.4079(2)	0.3655(2)	0.1641(3)	0.041(1)
C(12)	0.5719(2)	0.2656(2)	0.3370(3)	0.039(1)
C(11)	0.5747(2)	0.4664(2)	0.3289(3)	0.039(1)
N(1)	0.8477(2)	0.3703(2)	0.5823(2)	0.052(1)
C(1)	0.9299(2)	0.2911(2)	0.5545(3)	0.062(1)
C(3)	1.0885(3)	0.3842(3)	0.7239(4)	0.085(1)
C(4)	1.0054(3)	0.4667(3)	0.7550(4)	0.080(1)
C(5)	0.8861(2)	0.4567(2)	0.6811(4)	0.064(1)
C(2)	1.0496(2)	0.2951(3)	0.6220(4)	0.080(1)
H(13)	0.4388(19)	0.5244(19)	0.1837(29)	0.052(7)
H(12)	0.4319(19)	0.2066(19)	0.1998(28)	0.051(6)
H(5)	0.8262(23)	0.5128(21)	0.6967(33)	0.078(8)
H(3)	1.1665(32)	0.3918(25)	0.7740(43)	0.115(11)
H(1)	0.9006(22)	0.2275(20)	0.4796(34)	0.074(8)
H(11)	0.6998(23)	0.3664(18)	0.4563(32)	0.071(7)
H(4)	1.0249(27)	0.5255(26)	0.8289(43)	0.105(11)
H(2)	1.1068(29)	0.2323(25)	0.5972(43)	0.111(10)
2				
N(13)	0.0635(4)	0.4576(2)	0.3216(2)	0.033(1)
N(12)	0.2084(4)	0.3744(2)	0.1191(2)	0.035(1)
O(13)	−0.1664(4)	0.5816(1)	0.1524(1)	0.044(1)
N(11)	0.4450(4)	0.2394(2)	0.2904(1)	0.037(1)
O(12)	0.2826(4)	0.3326(2)	0.4883(1)	0.049(1)
N(3)	1.2808(5)	−0.2266(2)	0.3070(2)	0.040(1)
O(11)	0.5778(4)	0.1695(2)	0.0836(1)	0.050(1)
N(2)	0.8662(5)	−0.0340(2)	0.3704(2)	0.042(1)
C(13)	0.0225(5)	0.4780(2)	0.1951(2)	0.031(1)
N(1)	1.0551(6)	−0.0696(2)	0.1582(2)	0.053(1)
C(12)	0.4181(5)	0.2556(2)	0.1642(2)	0.033(1)
C(1)	1.0687(5)	−0.1105(2)	0.2773(2)	0.032(1)
H(13)	−0.0394(68)	0.5200(27)	0.3744(26)	0.049(6)
H(12)	0.1969(53)	0.3794(20)	0.0414(25)	0.032(6)
H(3A)	1.4238(66)	−0.2704(25)	0.2487(25)	0.044(6)
H(3)	1.3155(67)	−0.2469(26)	0.3886(28)	0.055(7)
H(2A)	0.7439(68)	0.0499(30)	0.3511(24)	0.051(7)
H(1)	1.1976(73)	−0.1179(28)	0.091(28)	0.066(8)
H(2)	0.8639(89)	−0.0693(34)	0.4399(34)	0.084(11)

Table 3. Bond lengths and angles in **1** and **2**.

<i>Bond lengths, 1</i>			
N(13)–C(11)	1.367(2)	N(13)–C(13)	1.370(2)
N(13)–H(13)	0.85(2)	N(12)–C(12)	1.365(2)
N(12)–C(13)	1.371(2)	N(12)–H(12)	0.86(2)
N(11)–C(12)	1.363(2)	N(11)–C(11)	1.365(2)
N(11)–H(11)	0.95(2)	O(12)–C(12)	1.228(2)
O(13)–C(13)	1.211(2)	O(11)–C(11)	1.223(2)
N(1)–C(5)	1.320(3)	N(1)–C(1)	1.327(3)
C(1)–C(2)	1.355(4)	C(3)–C(2)	1.359(4)
C(3)–C(2)	1.359(4)	C(3)–C(4)	1.368(5)
C(3)–H(3)	0.90(3)	C(4)–C(5)	1.369(4)
C(4)–H(4)	0.91(3)	C(5)–H(5)	0.95(3)
C(2)–H(2)	1.00(3)		
<i>Bond angles, 1</i>			
C(11)–N(13)–C(13)	125.0(2)	C(11)–N(13)–H(13)	115(2)
C(13)–N(13)–H(13)	120(2)	C(12)–N(12)–H(12)	115.6(14)
C(12)–N(12)–C(13)	125.1(2)	C(13)–N(12)–H(12)	119.1(14)
C(12)–N(11)–C(11)	123.9(2)	C(12)–N(11)–H(11)	118.2(14)
C(11)–N(11)–H(11)	117.8(14)	O(13)–C(13)–N(13)	122.7(14)
O(13)–C(13)–N(12)	123.0(2)	N(13)–C(13)–N(12)	114.3(2)
O(12)–C(12)–N(11)	121.9(2)	O(12)–C(12)–N(12)	122.2(2)
N(11)–C(12)–N(12)	115.8(2)	O(11)–C(11)–N(13)	122.5(2)
N(11)–C(11)–N(13)	115.8(2)	C(5)–N(1)–C(1)	117.5(2)
N(1)–C(1)–C(2)	123.3(3)	N(1)–C(1)–H(1)	116.9(14)
C(2)–C(1)–H(1)	119.8(14)	C(2)–C(3)–C(4)	118.9(3)
C(2)–C(3)–H(3)	124(2)	C(4)–C(3)–H(3)	118(2)
C(3)–C(4)–C(5)	118.7(3)	C(3)–C(4)–H(4)	122(2)
C(5)–C(4)–H(4)	119(2)	N(1)–C(5)–H(5)	116(2)
C(4)–C(5)–H(5)	116(2)	C(1)–C(2)–C(3)	118.9(3)
C(1)–C(2)–H(2)	119(2)	C(3)–C(2)–H(2)	122(2)
<i>Bond lengths, 2</i>			
N(13)–C(13)	1.358(2)	N(3)–C(1)	1.318(3)
N(13)–C(12)	1.389(2)	N(3)–H(3A)	0.840(3)
N(13)–H(13)	0.850(3)	N(3)–H(3)	0.890(3)
N(12)–C(13)	1.353(2)	O(11)–C(11)	1.240(2)
N(12)–C(11)	1.387(2)	N(2)–C(1)	1.336(3)
N(12)–H(12)	0.820(3)	N(2)–H(2A)	0.890(3)
O(13)–C(13)	1.233(2)	N(2)–H(2)	0.800(4)
N(11)–C(11)	1.342(2)	N(1)–C(1)	1.303(3)
N(11)–C(12)	1.345(2)	N(1)–H(1A)	0.840(3)
O(12)–C(12)	1.242(2)	N(1)–H(1)	0.870(3)
<i>Bond angles, 2</i>			
C(13)–N(13)–C(12)	123.6(2)	O(13)–C(13)–N(13)	123.4(2)
C(13)–N(13)–H(13)	119(2)	N(12)–C(13)–N(13)	114.1(2)
C(12)–N(13)–H(13)	117(2)	C(1)–N(1)–H(1A)	118(2)
C(13)–N(12)–C(11)	123.9(2)	C(1)–N(1)–H(1)	119(2)
C(13)–N(12)–H(12)	119.7(14)	H(1A)–N(1)–H(1)	123(3)
C(11)–N(12)–H(12)	116.3(14)	O(12)–C(12)–N(11)	122.8(2)
C(11)–N(11)–C(12)	119.1(2)	O(12)–C(12)–N(13)	117.6(2)
C(1)–N(3)–H(3A)	119(2)	N(11)–C(12)–N(13)	119.7(2)
C(1)–N(3)–H(3)	120(2)	O(11)–C(11)–N(11)	123.1(2)
H(3A)–N(3)–H(3)	119(2)	O(11)–C(11)–N(12)	117.3(2)
C(1)–N(2)–H(2A)	119(2)	N(11)–C(11)–N(12)	119.6(2)
C(1)–N(2)–H(2)	114(2)	N(1)–C(1)–N(3)	121.0(2)
H(2A)–N(2)–H(2)	126(3)	N(1)–C(1)–N(2)	119.4(2)
O(13)–C(13)–N(12)	122.5(2)	N(3)–C(1)–N(2)	119.6(2)

Table 4. Hydrogen bond distances (Å) and angles (°) in **1** and **2**^a.

D	H	A	D–H	H...A	D...A	D–H...A
1						
N(11)	H(11)	N(1)	0.966	1.776	2.738	174
N(12)	H(12)	O(11)	0.878	1.967	2.839	171
N(13)	H(13)	O(12)	0.843	2.004	2.846	175
C(2)	H(2)	O(13)	0.995	2.551	3.486	156
2						
N1	H1	O11	0.871	2.035	2.859	157
N1	H1A	O11	0.844	1.993	2.831	172
N2	H2A	N11	0.891	2.111	2.999	174
N3	H3	O12	0.891	2.142	2.908	143
N3	H3A	O13	0.840	2.106	2.916	161
N12	H12	O13	0.820	2.070	2.886	172
N13	H13	O12	0.848	2.091	2.939	177

^a D – donor; H – acceptor**Figure 2.** ORTEP plots of **1** (a) and **2** (b) showing 50% thermal ellipsoids.

the above mentioned C–N distances can be attributed to the suppression of the resonance effect involving N(12) and N(13) lone pairs due to the dominating influence of the negatively charged participant. The greater availability of the lone pairs on N(12) and N(13) towards resonance involving the third carbonyl reflect in the decrease in bond lengths of the N(12)–C(13) and N(13)–C(13) bonds and increase in the C(13)–O(13) bond length. It is to be noted that these changes in bond lengths are of lower magnitude when compared to that involving the N(11) anion. There is about 16.4% increase in the

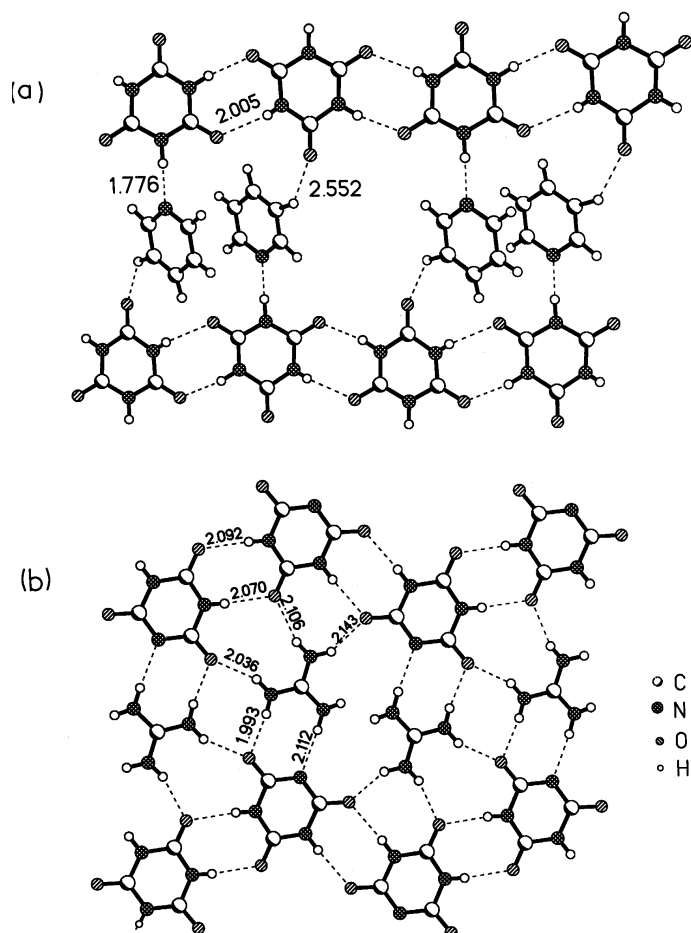


Figure 3. (a) Structure of the 1:1 CA-pyridine adduct showing the CA tapes along the *b* axis and N-H...N and C-H...O hydrogen bonds between CA and pyridine molecules. (b) Structure of guanidinium cyanurate showing the wave-like pattern adopted by CA tapes and the guanidinium cations holding the tapes by N-H...O and N-H...N hydrogen bonds.

double bond character of the C(11)–N(11) and C(12)–N(11) bonds and about 7.5% of the C(13)–N(12) and C(12)–N(13) bonds. Four of the six hydrogens in the guanidinium fragment participate in N–H...O hydrogen bonding with the carbonyl oxygens of CA with distances of 2.036 Å, 2.106 Å, 2.143 Å, and 1.993 Å. The last is a particularly strong hydrogen bond, considering that the N–H...N bond angle is 172°. Of the two remaining hydrogens, H(2) bonds to anionic N(11) and the other remains free. The bonding distance of N(2)–H(2)...N(11) (H...N, 2.11 Å) is comparable with the other N–H...O distances in the structure. The hydrogen, H(2A) of the guanidinium ion, which does not participate in hydrogen bonding, has the shortest N–H distance of all the N–H bonds.

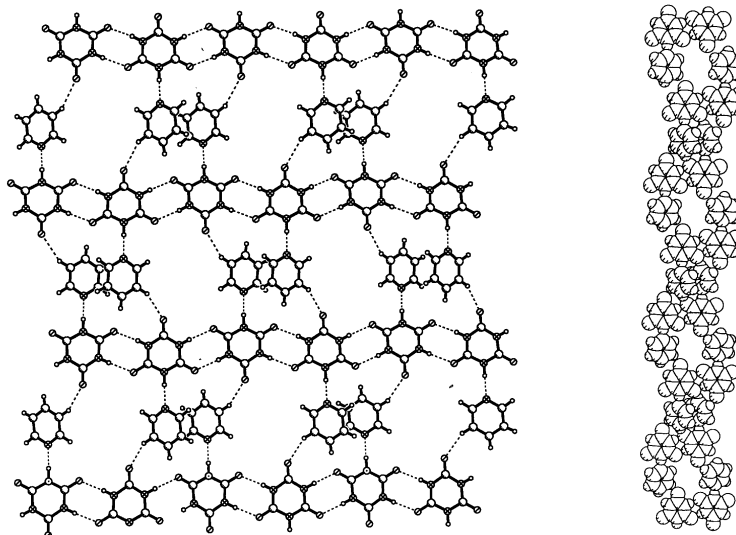


Figure 4. Helical hydrogen-bonded chains of CA and pyridine molecules held by dimeric N–H...O hydrogen bonds between the CA molecules.

4. Conclusions

Crystal structures of the 1:1 cyanuric acid-pyridine complex, **1**, and guanidinium cyanurate, **2**, illustrate how cyanuric acid accommodates the pyridine and the guanidinium cations without compromising the dimeric hydrogen-bonded tape present in its parent structure. The only difference is that in **2** the CA tapes are curved, unlike the linear tapes in the original structure of CA and in **1**. In **1**, the N–H...N hydrogen bonds formed by the pyridine molecules take the role of the single intermolecular N–H...O bond in CA, holding the tapes together. A novel feature in **1** is the formation of a beautiful helical structure of the hydrogen bonded CA-pyridine chains.

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