

Article

1,4-Diazabicyclo[2.2.2]octane (DABCO) 5-aminotetrazolates

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Abstract: The crystal structures of four salts of 1,4-diazabicyclo[2.2.2]octane (DABCO) and 5-aminotetrazole are described. Anhydrous 1:1 (*Pbca*, $R_{gt} = 0.041$) and 1:2 ($P\bar{1}$, $R_{gt} = 0.038$) salts form hydrogen-bonded layers of anions and cations. The monohydrate of the 1:1 compound ($P2_1/c$, $R_{gt} = 0.038$) shows infinite chains of DABCO cations and an undulated layer of anions and water molecules. The octahydrate of the 3:2 compound ($P2_1/c$, $R_{gt} = 0.042$) features DABCO triples and clusters of four tetrazolate ions in a network of water molecules.

Keywords: 5-aminotetrazolate; DABCO; hydrate; hydrogen bond

1. Introduction

The crystal structures of anhydrous 5-aminotetrazole [1] and its monohydrate [2] are known. Due to its amphiprotic nature [3–5], this nitrogen-rich heterocycle has served as cation [6–10] or as anion in energetic salts [11]. Organic salts containing 5-aminotetrazole as anion have been first described by Henry [12]. Crystal structures of several metal 5-aminotetrazolates have been reported [13]. This compound has also received much attention lately as ligand in coordination polymers [14–20].

1,4-Diazabicyclo[2.2.2]octane (DABCO) is a widely used complexing ligand, and numerous crystal structures of its salts and coordination compounds have been reported [21,22]. The two nitrogen atoms of this tertiary diamine show markedly different basicities [23], facilitating the formation of

monocations (DABCO–H⁺). Dicationic species (DABCO–H₂²⁺) are obtained only with strong acids, e.g., the dihydrochloride [24], dinitrate [25], and sulfate [26].

Continuing our interest in DABCO salts [21] and hydrates [22] we decided to explore combinations of DABCO and 5-aminotetrazole.

2. Results and Discussion

The DABCO molecules typically adopt a cage-like structure. The aminotetrazole molecules are planar (largest deviation 0.023 Å). The four new salts contain DABCO monocations in different arrangements. In all cases, association among the aminotetrazole molecules is observed. Hydrogen bond interactions between cations and anions are found only in the anhydrous salts, whereas the hydrates show preferred interactions between anions and water molecules. Crystal data and details of the structure refinement are summarized in Table 1. Hydrogen bond parameters are shown in Table 2.

Table 1. Crystal data and structure refinement details for compounds 1–4.

Compound	1	2	3	4
CCDC no.	855698	855697	855700	855699
Chemical formula	C ₆ H ₁₃ N ₂ ·CH ₂ N ₅	C ₆ H ₁₄ N ₂ ·(CH ₂ N ₅) ₂	C ₆ H ₁₃ N ₂ ·CH ₂ N ₅ ·H ₂ O	(C ₆ H ₁₃ N ₂) ₂ ·C ₆ H ₁₂ N ₂ ·(CH ₂ N ₅) ₂ ·(H ₂ O) ₈
<i>M_r</i>	197.26	282.34	215.28	650.82
Crystal size/mm ³	0.40 × 0.40 × 0.38	0.36 × 0.36 × 0.28	0.36 × 0.24 × 0.08	0.2 × 0.1 × 0.05
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	5.9696(1)	8.7982(6)	8.8064(3)	12.6856(3)
<i>b</i> /Å	16.7493(4)	8.8927(7)	11.1285(3)	8.8200(2)
<i>c</i> /Å	19.0799(4)	9.7756(5)	10.5456(3)	31.3885(8)
α /°	90	67.827(6)	90	90
β /°	90	86.181(5)	102.894(3)	99.390(2)
γ /°	90	71.794(7)	90	90
<i>V</i> /Å ³	1907.73(7)	671.68(9)	1007.43(5)	3464.91(14)
<i>Z</i>	8	2	4	4
<i>D_x</i> /g cm ^{−3}	1.37	1.40	1.42	1.25
μ /mm ^{−1}	0.10	0.10	0.10	0.10
<i>F</i> (000)/e	848	300	464	1416
Diffractionmeter	Gemini-R Ultra	Gemini-R Ultra	Gemini-R Ultra	Nonius KappaCCD
Data collection method	ω scans	ω scans	ω scans	φ and ω scans
Temperature/K	173(2)	173(2)	173(2)	233(2)
$\theta_{\max}$ /°	25.4	25.3	25.4	23.1
<i>h</i> , <i>k</i> , <i>l</i> range	−6 ≤ <i>h</i> ≤ 7 −20 ≤ <i>k</i> ≤ 17 −22 ≤ <i>l</i> ≤ 19	−10 ≤ <i>h</i> ≤ 10 −10 ≤ <i>k</i> ≤ 10 −11 ≤ <i>l</i> ≤ 11	−8 ≤ <i>h</i> ≤ 10 −10 ≤ <i>k</i> ≤ 13 −12 ≤ <i>l</i> ≤ 12	−13 ≤ <i>h</i> ≤ 13 −9 ≤ <i>k</i> ≤ 9 −34 ≤ <i>l</i> ≤ 34
Absorption correction	multi-scan	multi-scan	multi-scan	none
Measured reflections	10377	5025	7322	15576
Independent reflections (<i>R</i> _{int})	1743 (0.028)	2445 (0.025)	1850 (0.033)	4769 (0.042)
Observed reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	1534	1986	1492	3567
Restraints/parameters	4/136	8/199	6/152	22/486
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.041, 0.108	0.038, 0.098	0.038, 0.083	0.042, 0.099
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.049, 0.112	0.049, 0.102	0.056, 0.089	0.064, 0.108
Goodness of fit	1.06	1.09	1.03	1.03
$\Delta\rho_{\max/\min}$ /e Å ^{−3}	0.23, −0.20	0.27, −0.28	0.19, −0.17	0.18, −0.18

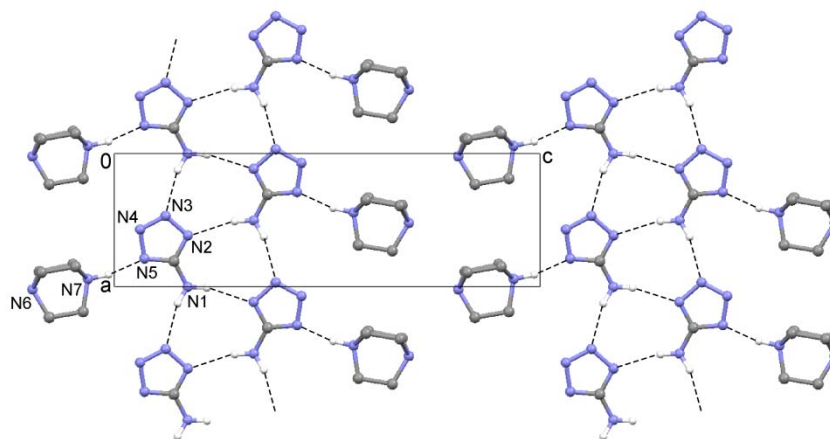
Table 2. Hydrogen bond parameters (Å, °).

Compound	D–H...A	H...A	D...A	D–H...A	Symmetry operation (A)
1	N7–H...N5	1.77(2)	2.698(2)	168(1)	$-1/2+x, 1/2-y, -z$
	N1–H...N2	2.24(1)	3.102(2)	166(1)	$1/2+x, y, 1/2-z$
	N1–H...N3	2.24(2)	3.105(2)	164(1)	$1+x, y, z$
2	N10–H...N12	1.86(2)	2.752(2)	165(2)	–
	N11–H...N5	1.68(2)	2.636(2)	167(2)	$-1+x, y, z$
	N1–H...N7	2.17(2)	3.059(2)	172(1)	$x, -1+y, z$
	N1–H...N8	2.29(1)	3.125(2)	159(1)	$2-x, -y, 2-z$
	N6–H...N2	2.14(2)	3.003(2)	175(2)	$x, 1+y, z$
	N6–H...N3	2.08(2)	2.970(2)	172(2)	$1-x, 1-y, 1-z$
3	N1–H...N2	2.27(2)	3.152(2)	169(1)	$1-x, -y, -z$
	N1–H...N4	2.20(2)	3.061(2)	161(1)	$x, 1/2-y, -1/2+z$
	N7–H...N6	1.85(2)	2.763(2)	174(2)	$x, 3/2-y, -1/2+z$
	O1–H...N3	2.17(2)	3.001(2)	159(2)	$1-x, 1/2+y, 1/2-z$
	O1–H...N5	2.05(2)	2.938(2)	174(2)	–
4	N3–H...N2	1.73(2)	2.707(2)	176(2)	–
	N5–H...N1	1.72(2)	2.687(2)	175(2)	–
	N11–H...N10	2.17(2)	3.074(2)	173(2)	$1-x, 1-y, 1-z$
	N11–H...N15	2.22(2)	3.078(3)	164(2)	–
	N16–H...N7	2.16(2)	3.048(3)	164(2)	–
	N16–H...N12	2.22(2)	3.101(2)	178(2)	$-x, 1-y, 1-z$
	O1–H...N4	1.98(3)	2.811(2)	165(3)	–
	O1–H...O2	1.92(5)	2.788(3)	177(5)	–
	O2–H...N6	1.90(2)	2.760(2)	173(2)	$1+x, 3/2-y, 1/2+z$
	O2–H...O8	1.87(4)	2.749(3)	169(5)	$2-x, -1/2+y, 3/2-z$
	O3–H...O2	1.95(3)	2.788(3)	166(4)	–
	O3–H...O4	1.93(2)	2.759(3)	170(3)	–
	O4–H...N9	1.98(3)	2.843(3)	180(2)	$1-x, 1-y, 1-z$
	O4–H...O5	1.88(2)	2.761(3)	178(2)	–
	O5–H...N14	1.97(2)	2.828(2)	175(3)	–
	O5–H...O1	1.98(2)	2.841(3)	169(3)	$1-x, -1/2+y, 3/2-z$
	O6–H...O1	1.96(3)	2.800(3)	169(3)	–
	O6–H...O3	1.89(4)	2.715(4)	167(4)	$x, 1+y, z$
	O7–H...N13	1.99(3)	2.847(3)	176(3)	$1-x, 1/2+y, 3/2-z$
	O7–H...O6	1.88(4)	2.748(3)	166(4)	–
	O8–H...N8	1.97(2)	2.822(2)	174(2)	$1+x, 3/2-y, 1/2+z$
	O8–H...O7	1.94(3)	2.764(3)	164(5)	–

2.1. 1-Aza-4-azoniabicyclo[2.2.2]octane 5-aminotetrazolate (1)

In this most primitive salt of DABCO and aminotetrazole, the aminotetrazolate anions form ribbons parallel to the (0 1 0) plane, assembled from nine-membered rings and propagating in the direction of the crystallographic *a* axis. The DABCO cations are attached to the edges of the ribbons by hydrogen bonds (Figure 1).

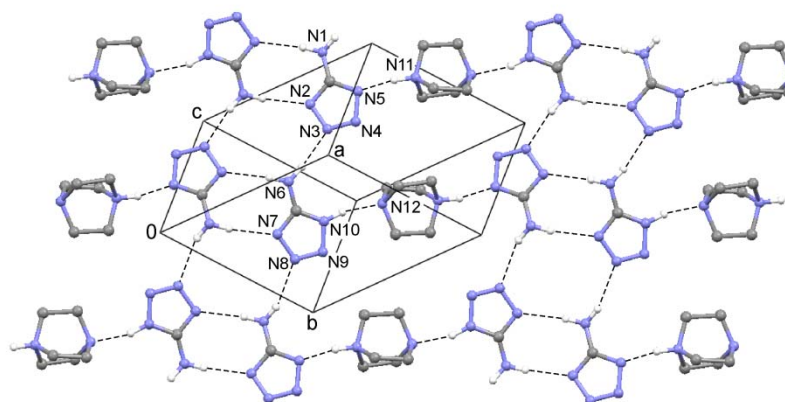
Figure 1. Hydrogen-bonded layer of ions parallel to the (0 1 0) plane in compound 1.



2.2. 1-Aza-4-azoniabicyclo[2.2.2]octane 5-aminotetrazole 5-aminotetrazolate (2)

Since aminotetrazole is not sufficiently strong an acid to create DABCO dications, the additional molecule of aminotetrazole in this 1:2 salt is incorporated in neutral form. The aminotetrazole molecules again form ribbons, this time assembled from eight- and ten-membered rings. The ribbons are linked by hydrogen-bonded DABCO monocations into layers parallel to the (−1 1 2) plane (Figure 2).

Figure 2. Hydrogen-bonded layer of ions parallel to the (−1 1 2) plane in compound 2.



2.3. 1-Aza-4-azoniabicyclo[2.2.2]octane 5-aminotetrazolate Hydrate (3)

It is interesting to observe the differences in the structures of the anhydrous salt **1** and the hydrate **3**. The aminotetrazole anions obviously prefer coordination with water molecules if there is a choice. The resulting network and the chains of hydrogen-bonded DABCO monocations are shown in Figure 3. In this aesthetically appealing structure, the DABCO- H^+ rods are gently caressed by a wave of anions and water molecules (Figure 4).

Figure 3. (a) Hydrogen-bond network of anions and water molecules in the hydrate of the 1:1 salt. (b) Chain of hydrogen-bonded DABCO mono-cations in compound **3**. Symmetry operations i: $x, 3/2-y, -1/2+z$; ii: $x, 3/2-y, 1/2+z$.

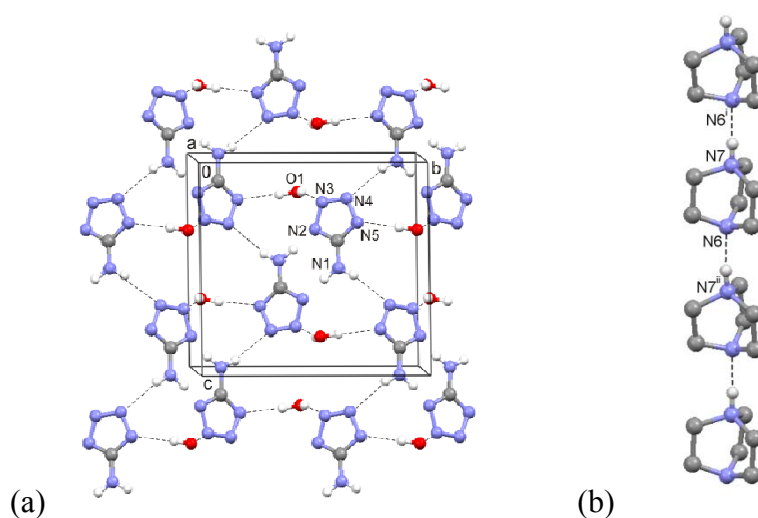
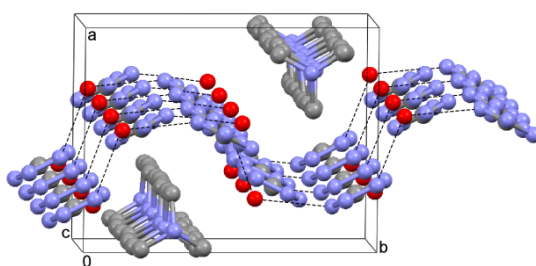


Figure 4. Packing diagram of the hydrate **3**. Hydrogen atoms omitted for clarity.



2.4. Bis(1-aza-4-azoniabicyclo[2.2.2]octane) 1,4-diazabicyclo[2.2.2]octane bis(5-aminotetrazolate) Octahydrate (4)

Small crystals of the octahydrate **4** were identified as a byproduct in **3**. Although a slightly lower data/parameter ratio (9.81) than desirable was obtained due to weak reflections at higher angles, the structure is still considered satisfactory. A linear array of three DABCO units [27] is observed, involving two monocations and a neutral molecule. These DABCO triples are cross-linked by two water molecules (Figure 5) into infinite zig-zag chains. Clusters of four tetrazolate ions are engulfed in a cloud of water molecules including cyclic water decamers (Figure 6).

Figure 5. Packing diagram of the octahydrate **4**. Uninteresting hydrogen atoms omitted for clarity. Symmetry operation i: $1+x, 3/2-y, 1/2+z$.

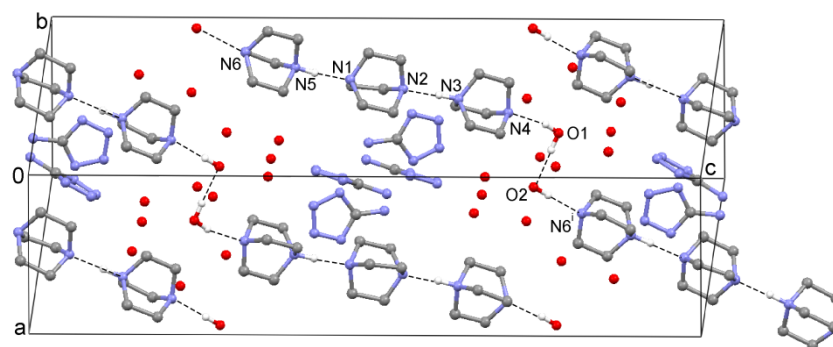
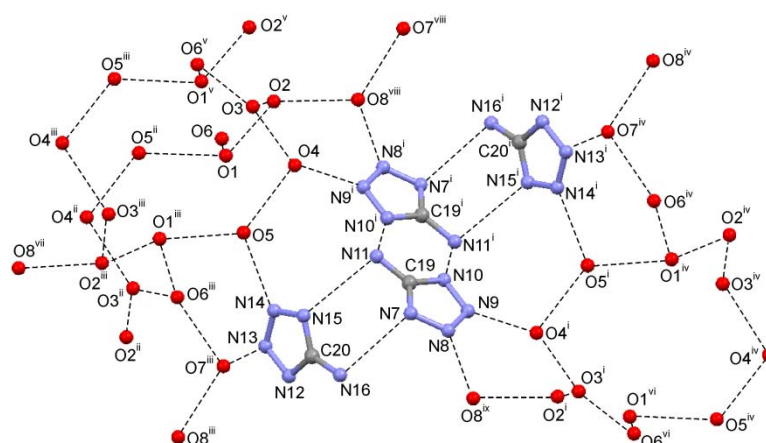


Figure 6. Cluster of four aminotetrazolate ions and network of water molecules in the octahydrate **4**. Hydrogen atoms omitted for clarity. Symmetry codes i: $1-x, 1-y, 1-z$; ii: $1-x, 1/2+y, 3/2-z$; iii: $1-x, -1/2+y, 3/2-z$; iv: $x, 3/2-y, -1/2+z$; v: $x, -1+y, z$; vi: $1-x, 2-y, 1-z$; vii: $-1+x, -1+y, z$; viii: $2-x, -1/2+y, 3/2-z$; ix: $-1+x, 3/2-y, -1/2+z$.



3. Experimental Section

3.1. Synthesis of DABCO 5-Aminotetrazolates

DABCO (0.56 g, 5 mmol) and the appropriate amount of 5-aminotetrazole were dissolved in MeOH (3 mL). For the hydrate, the required amount of H₂O was added. The solution was slowly refrigerated to $-20\text{ }^{\circ}\text{C}$. After 3 days the supernatant was discarded, and the crystals were collected.

3.2. Crystal Structure Determination

Intensity data were recorded with Oxford Diffraction Gemini-R Ultra and Nonius KappaCCD diffractometers using Mo K α radiation. Experimental details are summarized in Table 1. Structure solution and refinement was performed with the programs SIR2002 (direct methods) [28] and SHELXL-97 [29]. CCDC reference numbers: 855697-855700. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

4. Conclusions

Assembly of simple but versatile building blocks offers a treasure trove of opportunities and rich rewards for the curious investigator. The structures described herein are impressive examples of this successful concept.

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