

# Supramolecular Organization of Organoammonium Squarates

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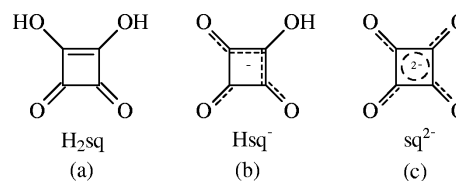
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Syntheses, thermal behavior, and IR data of three hydrogen squarates,  $\text{Hsq}^-$ , with 2-(acetyl-amino)-4-methylpyridinium,  $[(\text{C}_8\text{H}_{11}\text{N}_2\text{O})(\text{HC}_4\text{O}_4)]$  (**1**), 2-carboxamido-pyridinium,  $[(\text{C}_6\text{H}_7\text{N}_2\text{O})(\text{HC}_4\text{O}_4)]$  (**2**), and 2-methylpyridinium cations,  $[(\text{C}_6\text{H}_8\text{N})(\text{HC}_4\text{O}_4)(\text{H}_2\text{O})]$  (**3**), and one squarate,  $\text{sq}^{2-}$ , with 2-amino-4-methyl-pyrimidinium cations,  $[(\text{C}_6\text{H}_9\text{N}_2)_2(\text{C}_4\text{O}_4)]$  (**4**) are reported. The crystal structures of **1** and **4** have been studied. The compounds decompose in two thermal stages: (i) release of organic base, (ii) decomposition of squarate. Crystallographic analyses show that **1** and **4** have  $S_6$ ,  $R_2^{2(10)} R_2^{2(9)} R_2^{2(7)}$  rings. The hydrogen bonding motifs formed by the hydrogensquarate anions interact with the ammonium cations through  $\text{N-H}\cdots\text{O}$  hydrogen bonds and give rise to predominantly layered structures, which also exhibit three-dimensional connectivity.

**Key words:** Squaric Acid, Organic Amine, Thermal Decomposition

## Introduction

Hydrogen bonding is the most common concept of generating supramolecular organic systems by crystal-engineering and molecular recognition. Hydrogen-bonded systems generated from organic cations and anions are of special interest since they would be expected to show stronger hydrogen bonds than neutral molecules [1,2]. Squaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ ,  $\text{H}_2\text{sq}$ ), has been of interest because of its cyclic structure and possible aromaticity and used as a building block in crystal engineering due to the simplicity of the cyclic units [3,4]. It can be found in three forms (Scheme 1), (a) as uncharged  $\text{H}_2\text{sq}$ , (b) as  $\text{Hsq}^-$  monoanion and (c) as  $\text{sq}^{2-}$  dianion. There are reports of a few assorted organoammonium squarates in the literature [4–15]. Recently, we reported the crystal structures of dinicotinamidium squarate [16], picolinamidium squarate and di-*p*-toluidinium squarate dihydrate [17]. In the present paper, we describe the synthesis and characterization of four novel organoammonium squarates: 2-(acetyl-amino)-4-methylpyridinium hydrogensquarate (**1**), 2-carboxamido-pyridinium hydrogensquarate (**2**), 2-methylpyridinium



Scheme 1. Squaric acid and its anions.

hydrogensquarate monohydrate (**3**), and di(2-amino-4-methylpyrimidinium) squarate (**4**), and the crystal structures of **1** and **4**. Because squarates are stable up to 300 °C [18] and exhibit strong hydrogen bonding networks, the thermal behavior of the compounds was also studied.

## Results and Discussion

### IR spectra

The important IR absorption bands of the compounds are listed in Table 1. The infrared spectra of **1**–**3** show an intense band at 3510, 3508 and 3512  $\text{cm}^{-1}$ , respectively, due to the O–H stretching vibrations. In the IR spectra of **1** and **3**, the bands around 3388  $\text{cm}^{-1}$  are attributed to the N–H stretching vibrations involved

Assignment	1	2	3	4	Squaric acid <sup>b</sup>
$\nu$ OH	3510 m	3508 m	3512 m	—	3462 s
$\nu$ NH <sub>2</sub>	—	3388 m; 3282 m	—	3324 m; 3180 m	—
$\nu$ NH	3385 m	3161 m	3392 m	3159 m	—
$\nu$ CH	2888 w	2897 w	2838 w	2931 w	—
$\nu$ CH <sub>3</sub>	2781 m	—	2569 m	2780 w	—
$\nu$ CN	1645 s	1643 s	1674 s	1633 s	—
$\nu$ CO	1688 s; 1813 m	1712 s; 1812 m	1805 m	1689 s; 1805 w	1822 w
$\nu$ CO+ $\nu$ CC	1579 s	1601 s	1552 s	1533 s	1530, 1516 vs
$\delta$ NH	1492 m	1402 m	1436 m	1471 m	—
$\delta$ NH+ $\nu$ CC+ $\nu$ CO	1407 m	1351 m	1394 m	1321 m	—
$\nu$ CC	1097 w	1047 w	1051 w	1077 w	1643 m

Table 1. Selected IR spectral data<sup>a</sup>.

<sup>a</sup> w = weak; m = medium; s = strong; vs = very strong; <sup>b</sup> reference [24].

in hydrogen bonds. However, this peak appears around 3160 cm<sup>-1</sup> in the IR spectra of **2** and **4** (Table 1). In the IR spectra of **2** and **4**, the  $\nu$ NH<sub>2</sub> stretching vibration appears as two split bands at 3388; 3282 and 3324; 3180 cm<sup>-1</sup>, respectively. The peaks in the 2569–3091 cm<sup>-1</sup> range are due to  $\nu$ CH<sub>3</sub> and  $\nu$ CH stretching. The carbonyl stretching modes in **1** and **2** are observed at 1688 and 1712 cm<sup>-1</sup>, respectively. C=N stretching vibrations appear at 1645, 1643, 1674, and 1633 cm<sup>-1</sup> for **1–4**, respectively. A very strong absorption centered in the range of 1601–1533 cm<sup>-1</sup> is assigned to a combination of squarate C–O and C–C stretching vibrations. This type of absorption is characteristic of salts of C<sub>n</sub>O<sub>n</sub><sup>2-</sup> ions. It was found at 1500 cm<sup>-1</sup> in the IR spectrum of K<sub>2</sub>C<sub>4</sub>O<sub>4</sub> [19], and at 1822 and 1643 cm<sup>-1</sup> in the IR spectrum of squaric acid [20].

### Thermal analyses

Compound **1** is stable in air up to 198 °C and thermal decomposition starts with the release of 2-(acetyl-amino)-4-methylpyridine in two stages, corresponding to an endothermic and then several exothermic peaks (DTA<sub>max</sub> = 227, 256, 341 °C; found 57.97, calcd. 56.83%). The third (exothermic) stage, in the temperature range of 350–590 °C, is related to the decomposition of squarate (DTG<sub>max</sub> = 519 °C; found 42.03, calcd. 43.17%).

Compound **2** is thermally stable up to about 185 °C. The thermal decomposition proceeds in three stages. The first stage is related to the release of pyridine-2-carboxamide giving an endothermic effect (DTG<sub>max</sub> = 207 °C) in the temperature range of 185–218 °C. In the second and third stages, in the 219–535 °C temperature range, an endothermic and four exothermic decomposition processes are observed.

The thermal decomposition pathway of **3** consists of four stages. The first stage is related to the dehydration with one water molecule being released in

Table 2. Crystal data of **1** and **4**.

	1	4
Empirical formula	C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> OC <sub>4</sub> HO <sub>4</sub>	(C <sub>5</sub> H <sub>8</sub> N <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> O <sub>4</sub>
Formula mass	264.24	332.32
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	8.8320(7)	9.5017(9)
<i>b</i> (Å)	17.2954(11)	7.4745(6)
<i>c</i> (Å)	8.3069(6)	11.8189(13)
$\beta$ (°)	104.515(6)	111.488(8)
<i>V</i> (Å <sup>3</sup> )	1228.40(15)	781.04(13)
<i>Z</i>	4	4
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.515	1.415
$\mu$ (mm <sup>-1</sup> )	0.12	0.11
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (obsd data: 2 $\sigma$ ( <i>I</i> ))	0.0413/0.1078	0.0533/0.1428
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0557/0.1151	0.0630/0.1519
Goodness of fit	1.024	1.049

an endothermic effect (DTG<sub>max</sub> = 51 °C; found 7.40; calcd. 7.99%). In the second and third stages, 2-picolinamide is released and squaric acid is also decomposed (DTG<sub>max</sub> = 211, 282 °C) in successive endothermic and exothermic processes. In the last stage, the remaining organic residue is burnt (DTG<sub>max</sub> = 473 °C).

For **4**, the first stage is related to the endothermic removal of the 2-amino-4-methyl-pyrimidine molecule in the temperature range of 137–215 °C (DTG<sub>max</sub> = 200 °C, found 31.75, calcd. 32.84%). In the following two stages, pyrolysis of the compound takes place (DTG<sub>max</sub> = 240, 273 °C). In the last stage, a strongly exothermic mass loss occurs due to the abrupt burning of the organic residue (DTG<sub>max</sub> = 562 °C).

Based on the initial DTG<sub>max</sub> temperatures of the anhydrous compounds, the thermal stability sequence is **1** (227 °C) > **3** (211 °C) > **2** (207 °C) > **4** (200 °C).

### Crystal structures

Crystal data of **1** are listed in Table 2. The asymmetric unit of **1** contains a 2-(acetyl-amino)-4-methylpyridinium cation and one Hsq<sup>-</sup> anion (Fig. 1). Each

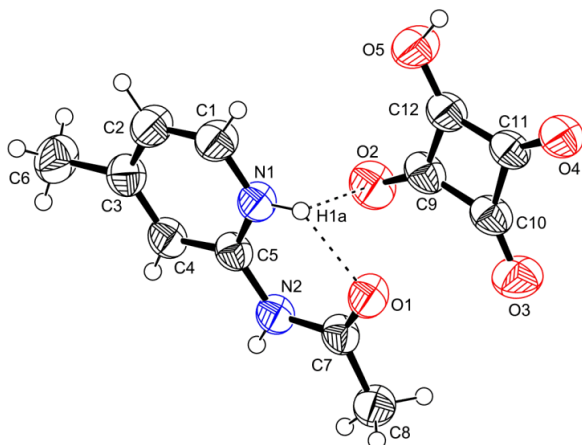


Fig. 1. A view of the ion pair of **1** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

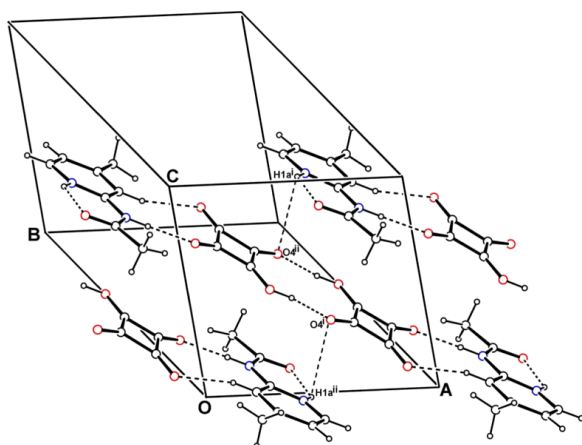


Fig. 2. Head-to-head  $R_2^2(10)$  HSQ and  $R_2^2(9)$  2-AAMP-HSQ hydrogen bonded forms. Stacking of the HSQ-pyridine layers in **1** in an ABBA fashion through N-H...O hydrogen bonding to form a 2D plane. Symmetry codes: (i)  $-x, y + 1/2, -z + 1/2$ ; (ii)  $x, -y + 1/2, z + 1/2$ .

squaric acid molecule has donated one H atom to the pyridine N atom of a 2-(N-acetylamino)-4-methylpyridine molecule, forming the 2-(acetylamino)-4-methylpyridinium hydrogensquarate salt. The  $\text{Hsq}^-$  ion has one C-O bond [ $\text{C12-O5} = 1.307(2) \text{ \AA}$ ] which is shorter than a normal single C-O bond ( $1.426 \text{ \AA}$  in methanol,  $1.36 \text{ \AA}$  in acetic acid [8]), and one intermediate C-O bond [ $\text{C11-O4} = 1.2578(19) \text{ \AA}$ ] that is slightly longer than a normal C=O bond, while two C-O bonds [ $\text{C9-O2} = 1.239(2) \text{ \AA}$ ;  $\text{C10-O3} = 1.218(2) \text{ \AA}$ ] are typical C=O double bonds ( $1.21 \text{ \AA}$  in acetaldehyde and acetone [8]). These bond lengths indicate a degree of

Table 3. Hydrogen bonding geometry for **1** ( $\text{\AA}, ^\circ$ ).

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1A...O1	0.90 (2)	1.95 (2)	2.632 (2)	131 (2)
N1-H1A...O1 <sup>i</sup>	0.90 (2)	2.11 (2)	2.836 (2)	137 (2)
N2-H3...O2 <sup>ii</sup>	0.90 (2)	1.86 (2)	2.753 (2)	175.8 (19)
O5-H5...O4 <sup>iii</sup>	0.91 (3)	1.62 (3)	2.491 (2)	160 (3)

Symmetry codes: <sup>i</sup>  $1-x, 1-y, 1-z$ ; <sup>ii</sup>  $-x, 1-y, 1-z$ ; <sup>iii</sup>  $1-x, 1-y, -z$ .

delocalization in the  $\text{Hsq}^-$  ion as observed in previous studies [2, 4, 17].

Pairs of the crystallographically unique  $\text{Hsq}^-$  unit interact to give self-complimentary O-H...O bonds (Table 3) and form a head-to-head cyclic  $R_2^2(10)$  dimer [21] (Fig. 2). This  $R_2^2(10)$  hydrogen-bonded dimer is similar to that commonly found in carboxylic acids [22–24]. Such a dimeric unit has been found in a few other hydrogensquarates [4] and can be regarded as an expanded acetate moiety [25]. The dimers are further connected to the two ends of the pyridine rings through N-H...O (Table 3) hydrogen-bonding to form  $R_2^2(9)$  and S6 rings [21]. Such layers are stacked one above the other in the ABBA fashion and interact through C-H... $\pi$  and N-H...O bonds to form a 3D network. For the C6-H6...Cg contact (Cg = pyridine ring), the distance between atom H6 and the aromatic ring centroid is  $3.212 \text{ \AA}$  [symmetry code  $(x, 1/2 - y, -1/2 + z)$ ], with a C-H...Cg angle of  $126.6^\circ$ . In compound **1**, the ions have rings A (N1/C1/C2/C3/C4/C5), B (H1A/N1/C5/N2/C7/O1), C (H4/C4/C5/N2/H3/O3/C10/C11/O4), D (C9/C10/C11/C12), and E (O4/C11/C12/O5/H5/O4'/C11'/C12'/O5'/H5') and the dihedral angles between rings A/B, A/C, A/D, A/E, C/D, C/E, D/E are  $1.6(1)^\circ$ ,  $33.4(1)^\circ$ ,  $8.5(1)^\circ$ ,  $7.9(1)^\circ$ ,  $36.4(1)^\circ$ ,  $36.7(1)^\circ$ ,  $0.9(1)^\circ$ , respectively.

A summary of crystallographic data and refinement results for **4** are given in Table 2. Each squaric acid molecule donates one H atom to each of the pyrimidine N atoms of the 2-amino-4-methylpyrimidine molecules, forming the 2-(N-acetylamino)-4-methylpyridinium squarate salt, which has two 2-amino-4-methylpyrimidinium cations and one squarate dianion (Fig. 3). The  $\text{sq}^{2-}$  ion has two C-O bonds [ $\text{C6-O1} = 1.261(2) \text{ \AA}$ ;  $\text{C7-O2} = 1.240(2) \text{ \AA}$ ] that are approximately equal and slightly longer than a normal C=O bond [26]. As for **1**, these lengths indicate a degree of delocalization in the  $\text{sq}^{2-}$  ion. The C1-N1 bond length [ $1.315(2) \text{ \AA}$ ] in the pyrimidinium ring is approximately equal to the length of a previously reported C=N double bond [27–31]. The formal positive charge residing on the  $\text{N1}^+\text{H}$  group does not appear to affect the

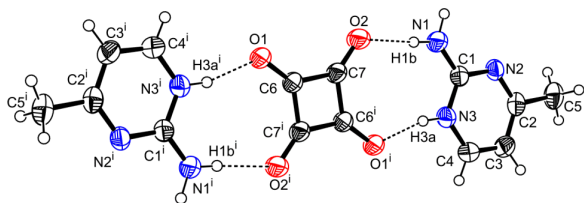


Fig. 3. A view of the ion pair of **4** with the atomic numbering scheme and two  $R_2^2(9)$  hydrogen-bonded rings.

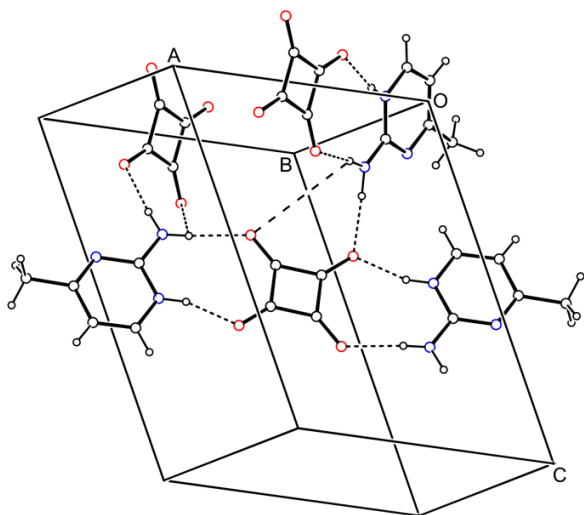


Fig. 4. Interionic hydrogen bonds between 2-amino-4-methylpyrimidinium and squarate ions in **4**.

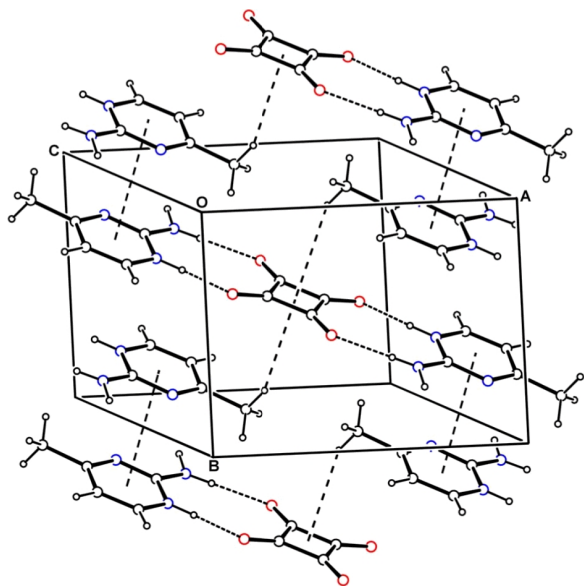


Fig. 5.  $C-H\cdots\pi$  and  $\pi\cdots\pi$  interactions between 2-amino-4-methylpyrimidinium squarate planes in **4**.

Table 4. Hydrogen-bonding geometry for **4** (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
N3–H3A...O1 <sup>i</sup>	0.86(3)	1.79(3)	2.628(2)	163(2)
N1–H1A...O1 <sup>ii</sup>	0.94(3)	1.92(3)	2.863(2)	175(2)
N1–H1B...O2 <sup>iii</sup>	0.84(3)	1.95(3)	2.785(2)	176(2)

Symmetry codes: <sup>i</sup>  $2-x, 1-y, 1-z$ ; <sup>ii</sup>  $2-x, y-1, 2-z$ ; <sup>iii</sup>  $1+x, y, z$ .

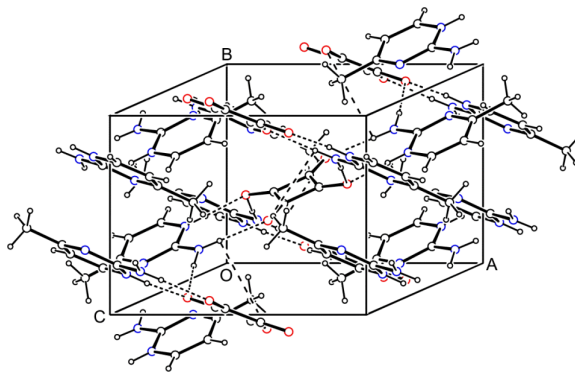


Fig. 6. The packing diagram for **4**.

resonance structure of the pyridine ring. This was also observed in the crystal structure of picolinamide [17].

The components of the asymmetric unit interact between themselves through a pair of self-complementary  $N-H\cdots O$  bonds (Table 4) to form a  $R_2^2(9)$  ring [21] (Fig. 3). The asymmetric units are linked by  $N-H\cdots O$  hydrogen bonded  $R_2^2(7)$  rings (Fig. 4) and  $C-H\cdots\pi$  and  $\pi\cdots\pi$  interactions (Fig. 5) to generate a three-dimensional network (Fig. 6). For the  $C5-H5A\cdots Cg1$  contact ( $Cg1 = sq$  ring), the distance between atom H5A and the sq ring centroid is 2.935 Å [symmetry codes;  $(1-x, 1/2+y, 1/2-z)$  and  $(x, 1/2-y, 1/2+z)$ ], with a  $C-H\cdots Cg$  angle of 136.9°. Compound **4** also undergoes  $\pi\cdots\pi$  interactions between pyrimidinium rings [symmetry code;  $-x, 2-y, 1-z$ ] with a perpendicular distance from  $Cg2$  to  $Cg2$  of 3.286 Å (Fig. 4).

## Experimental Section

### Materials and measurements

All chemicals used were analytical grade. The IR spectra were recorded in the 4000–400  $\text{cm}^{-1}$  region with a Mattson 1000 FT-IR spectrometer using KBr pellets. A TG8110 thermal analyzer was used to record simultaneous TG, DTG and DTA curves in static air atmosphere at a heating rate of 10  $\text{K min}^{-1}$  in the 20–700 °C temperature range using platinum crucibles. Highly sintered  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference and the DTG sensitivity was 0.05  $\text{mg s}^{-1}$ .

*Crystallographic analyses*

Data collections were performed on a STOE IPDS II image plate detector using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Intensity data were collected in the  $\theta$  range 3.45–26.00° at 296 K. Data collections: Stoe X-AREA [32]. Cell refinement: Stoe X-AREA [32]. Data reduction: Stoe X-RED [32]. The structures were solved by direct methods using SIR97 [33], and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on  $F^2$  using SHELXL-97 [34]. Molecular drawings were obtained using ORTEP-III [35].

*Synthesis of compounds*

Squaric acid and the organic amines were dissolved in water/methanol (20 ml) mixtures in the molar ratio 1 : 1 for **2** and **3** and 1 : 2 for **4**. The solutions were heated to 50 °C in a temperature-controlled bath and stirred for 1 h at 50 °C. The reaction mixtures were then slowly cooled to r. t. The crystals were filtered and washed with 10 ml of water and methanol and dried in air. – C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>5</sub> (**2**) (236.18): calcd. C 50.85, H 3.41, N 11.86; found C 50.62, H 3.11, N 11.55. C<sub>10</sub>H<sub>11</sub>NO<sub>5</sub> (**3**) (225.20): calcd. C 53.33, H 4.92, N 6.22; found C 53.42, H 4.75, N 6.26. C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub> (**4**) (330.34):

calcd. C 58.17, H 5.49, N 16.96; found C 58.47, H 5.07, N 16.82.

Squaric acid and 2-amino-4-methyl-pyrimidine were dissolved in acetic anhydride (20 ml) in the molar ratio 1 : 1 for **1** and heated under reflux for 1 h. The mixture was slowly cooled to r. t. The precipitate was filtered off, washed with methanol and dried in air. – C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub> (**1**) (264.24): calcd. C 54.55, H 4.58, N 10.60; found C 54.50, H 4.41, N 10.51.

*Supplementary material*

Crystallographic data for the structures have been deposited at the CCDC as supplementary data, CCDC No. 293755 and 293756. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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