

3-Acetoxy-2-(acetylamino)pyridinium-1-squarate

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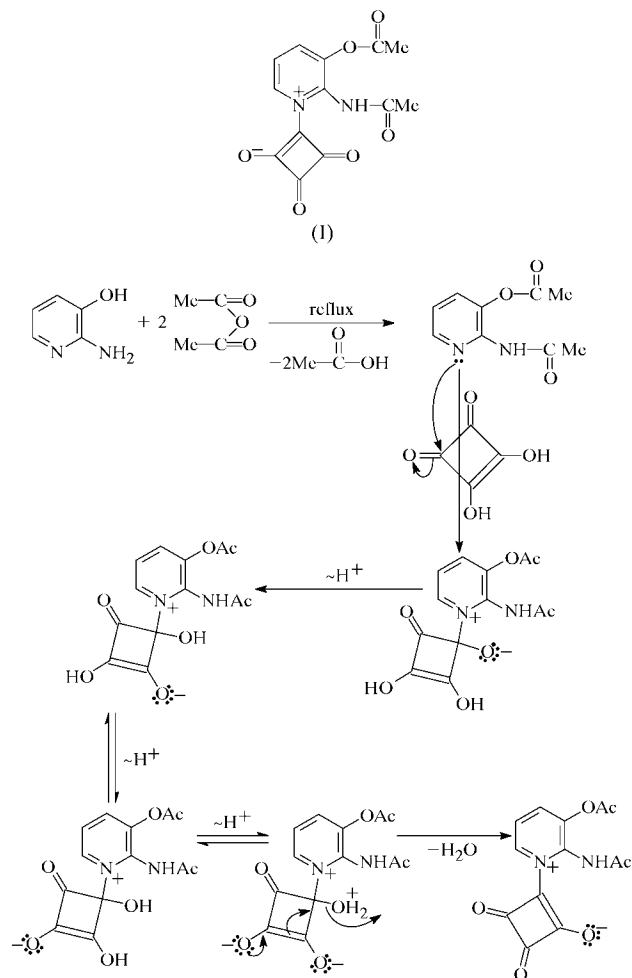
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The title compound, alternatively known as 3-acetoxy-2-(acetylamino)pyridinium betaine of squaric acid, C₁₃H₁₀N₂O₆, has been synthesized. The bond distances within the squarate ring indicate two possible resonance structures. The mean planes of the pyridinium and squarate systems are inclined at an angle of 24.0 (2)° with respect to one another due to a strong intramolecular hydrogen-bonding interaction between the amide NH group and a squarate O atom. In the extended structure, there are additional weak π - π and π -ring interactions, which also stabilize the crystal structure.

Comment

Over the past decade, extensive studies have been made of the synthesis of non-linear optical (NLO) materials based on organic compounds, because of their potential application in various fields, such as telecommunications, optical data storage and optical information processing (Chemla & Zyss, 1987; Prasad & Williams, 1991). Because of their notable chemical flexibility, which allows for molecular engineering of the non-linear optical response, and their fast electronic response, organic materials are particularly interesting candidates for the elaboration of optimized NLO materials. Their non-linearity is based on the presence of molecular units containing a strongly delocalized π -electron system, with donor and acceptor groups located at opposite ends of the molecule (Nalwa *et al.*, 1997; Wolff & Wortmann, 1999). Among such materials, the substituted betaines play an important role because of their dipolar structure (Schmidt *et al.*, 1984; Kolev *et al.*, 2004). The conversion of the N atom of 3-acetoxy-2-(acetylamino)pyridine into the corresponding pyridinium betaine provides a way of enhancing the charge-transfer transition at the molecular level, a requisite for a design of efficient second- and third-order non-linear optical materials. As part of our ongoing research on squaric acid (H₂SQ; Uçar *et al.*, 2004), the title compound, (I), has been synthesized and its crystal structure (Fig. 1) is reported. The

reaction mechanism for the title compound is shown in the scheme below.



The C—C distances in the squarate ring systems of (I) reflect partial double-bond character for C1—C2 [1.437 (5) Å] and C1—C4 [1.411 (5) Å], and single-bond character for C2—C3 [1.515 (6) Å] and C3—C4 [1.519 (6) Å]. These lengths represent average values for the two possible resonance structures. The bond distances of the semicarbonyl bonds are

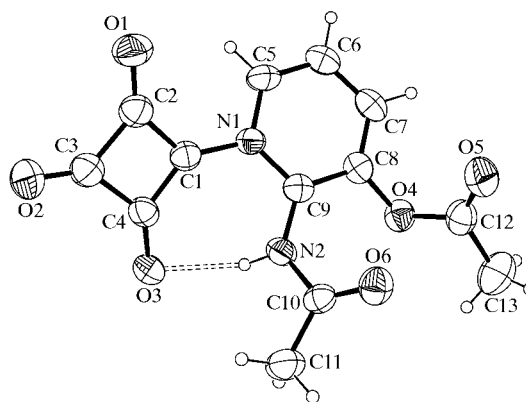


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

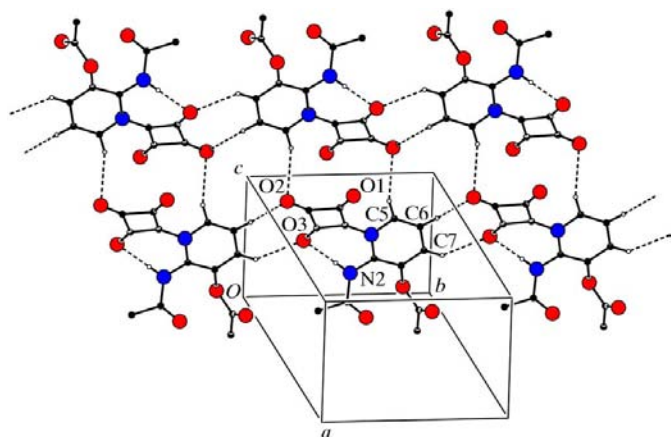


Figure 2
A view of a double chain of molecules extending along [010] and linked by C—H...O hydrogen bonds (dashed lines).

O1—C2 = 1.224 (4) Å and O3—C4 = 1.242 (4) Å, and these bond lengths indicate that the negative charge is located partially on atoms O1 and O3. A strong donor effect is observed for the acetoxy group. Conjugation between this group and the positively charged strong acceptor atom N1 results in a shortening of C3—O2 [1.202 (5) Å].

The pyridinium and squarate planes are essentially planar (r.m.s. deviations = 0.0195 and 0.0070 Å, respectively), and the largest deviations from these mean planes are 0.030 (3) Å for atom C8 and 0.012 (4) Å for atom C2. The dihedral angle between the mean planes of the pyridinium and squarate ring systems is 24.0 (2)°, whereas this angle is 5.3 (2)° in the related 4-methoxypyridinium-3-squarate compound (Kolev *et al.*, 2004). This is apparently due to a strong intramolecular hydrogen-bonding interaction between atom H2 on the amide N atom and squarate atom O3 (Table 2), and the steric hindrance of the substituted groups.

The most striking feature of this structure is the occurrence of C—H...O interactions. Indeed, pyridine atoms C5, C6 and C7 form intermolecular hydrogen bonds with atoms O2 and O3 of symmetry-related squarate rings. These C—H...O hydrogen bonds build a double chain of molecules extending along [010], as shown in Fig. 2. Although, two symmetry-related pyridine rings of neighbouring molecules are oriented in such a way that the perpendicular distance between them is 3.06 Å, the centroid-to-centroid distance of 4.82 Å is too long to be considered a π - π interaction. Indeed, the angle between the ring normal of the pyridine plane and the centroid vector is 50.6%, indicating that the two rings are too slipped with respect to each other to allow a π - π interaction (Janiak, 2000).

Experimental

The title compound was prepared according to the method of Schmidt *et al.* (1984). Squaric acid (1 g, 8.7 mmol) was dissolved in acetic anhydride (50 ml) by continuous stirring and heating under reflux. A solution of 2-amino-3-hydroxypyridine (0.957 g, 8.7 mmol) dissolved in acetic anhydride (10 ml) was then added. After a few minutes, the solution turned dark yellow. A yellow precipitate was obtained from this dark-yellow solution after heating for 60 min and

evaporating half the solvent. The product was filtered off after cooling and was recrystallized from methanol (yield 85%).

Crystal data

$C_{13}H_{10}N_2O_6$	$Z = 2$
$M_r = 290.23$	$D_x = 1.486 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.8959 (16) \text{ \AA}$	Cell parameters from 5022 reflections
$b = 8.9014 (16) \text{ \AA}$	$\theta = 2.5\text{--}26.0^\circ$
$c = 8.9288 (16) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\alpha = 88.895 (15)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 87.795 (15)^\circ$	Plate, yellow
$\gamma = 66.667 (14)^\circ$	$0.28 \times 0.20 \times 0.08 \text{ mm}$
$V = 648.7 (2) \text{ \AA}^3$	

Data collection

Stoe IPDS-2 diffractometer	1366 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.087$
Absorption correction: integration, (<i>X-RED32</i> ; Stoe & Cie, 2002)	$\theta_{\text{max}} = 25.8^\circ$
$T_{\text{min}} = 0.970$, $T_{\text{max}} = 0.992$	$h = -10 \rightarrow 10$
8629 measured reflections	$k = -10 \rightarrow 10$
2477 independent reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 0.2421P]$
$R[F^2 > 2\sigma(F^2)] = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.154$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
2475 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
193 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.027 (5)

Table 1

Selected geometric parameters (Å, °).

C1—C4	1.411 (5)	C3—O2	1.202 (5)
C1—N1	1.422 (5)	C3—C4	1.519 (6)
C1—C2	1.437 (5)	C4—O3	1.242 (4)
C2—O1	1.224 (4)	C10—O6	1.212 (5)
C2—C3	1.515 (6)		
C1—C2—C3	87.8 (3)	C5—C6—C7	120.2 (4)
O2—C3—C2	136.2 (4)		
C2—C1—N1—C5	−23.5 (6)		

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N2—H2...O3	0.86	1.96	2.733 (4)	149
C5—H5...O2 ⁱ	0.93	2.60	3.449 (6)	151
C6—H6...O2 ⁱⁱ	0.93	2.45	3.343 (5)	161
C7—H7...O3 ⁱⁱ	0.93	2.48	3.222 (4)	137

Symmetry codes: (i) $-x, 1 - y, 2 - z$; (ii) $x, 1 + y, z$.

All H atoms were located from difference maps and then treated as riding atoms, with pyridine C—H distances of 0.93 Å and an N—H distance of 0.86 Å. $U_{\text{eq}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C,N})$ and $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1073). Services for accessing these data are described at the back of the journal.

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