

Linear hydrogen-bonded molecular tapes in the cocrystals of squaric acid with 4,4'-dipyridylacetylene and 1,2-bis(4-pyridyl)ethylene

Md. Badruz Zaman,^{a†} Masaaki Tomura^{a*} and Yoshiro Yamashita^b

^aInstitute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and

^bDepartment of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Correspondence e-mail: tomura@ims.ac.jp

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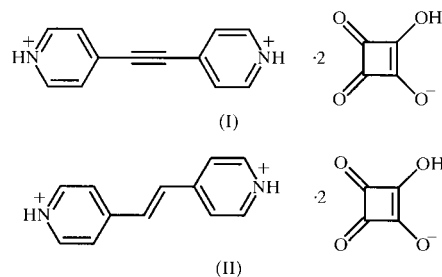
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The title compounds, 4,4'-(ethyne-1,2-diyl)dipyridinium bis(squarate), $C_{12}H_{10}N_2^{2+} \cdot 2C_4HO_4^-$, and 4,4'-(ethene-1,2-diyl)dipyridinium bis(squarate), $C_{12}H_{12}N_2^{2+} \cdot 2C_4HO_4^-$, are isomorphous and crystallize in space group $P\bar{1}$. The cocrystals contain linear hydrogen-bonded molecular tape structures along the [120] direction. The squarate monoanions form a ten-membered dimer linked by two intermolecular O—H...O hydrogen bonds. Each component molecule forms a segregated stack along the *c* axis. The bond lengths of the squarate monoanion indicate delocalization of the enolate anion.

Comment

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) is a very strong dibasic acid and has been studied for potential application to xerographic photoreceptors, organic solar cells and optical recording (Seitz & Imming, 1992; Liebeskind *et al.*, 1993). From the viewpoint of crystal engineering, squaric acid is also a useful tool for constructing crystalline architectures, because of its rigid and flat four-membered ring framework, and its proton donating and accepting capabilities for hydrogen bonding (Braga *et al.*, 1999; Reetz *et al.*, 1994). We have recently shown that the simple combination of chloranilic acid and various dipyridyl-type ligands can create a variety of supramolecular architectures involving an infinite one-dimensional molecular tape structure (Zaman *et al.*, 1999, 2000). In the course of our crystal-engineering studies on the combination of squaric acid and dipyridyl-type ligands, we have obtained cocrystals of 4,4'-dipyridylacetylene–squaric acid (1/2), (I), and 1,2-bis(4-pyridyl)ethylene–squaric acid (1/2), (II), where a rare ten-membered hydrogen-bonded

dimer of a squarate monoanion is formed. We report here the structures of the resulting hydrogen-bonded molecular tapes.



Cocrystals (I) and (II) are isomorphous and crystallize in space group $P\bar{1}$, with one molecule of squaric acid and half a molecule of the dipyridyl-type ligand in the asymmetric unit. The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively, and selected geometric parameters are listed in Tables 1 and 2, respectively. The coordinates in (I) can be related to those in (II) by the transformation $(1 - x, \frac{1}{2} - y, \frac{1}{2} - z)$ subject to a permutation of the O labels; O1–O4 in (I) correspond to O2–O4 and O1, respectively, in (II). The molar ratio of the dipyridinium dication and the monoanion of squaric acid is 1:2 in both (I) and (II). The bond lengths in the squarate monoanion display delocalization of the enolate anion. Thus, the average bond lengths in the four-membered squarate frameworks are 1.421 (5) Å (C1–C4, C3–C4) and 1.494 (5) Å (C1–C2, C2–C3) for (I), and 1.429 (2) Å (C1–C2, C1–C4) and 1.495 (2) Å (C2–C3, C3–C4) for (II). The bond lengths of O1–C1 [1.255 (4) Å] and O3–C3 [1.240 (4) Å] in (I), and O2–C2 [1.245 (2) Å] and O4–C4 [1.244 (2) Å] in (II), are intermediate between a double and single bond. Such bond-length distribution has been found in cobalt and nickel squarate octahydrates (Brach *et al.*, 1987)

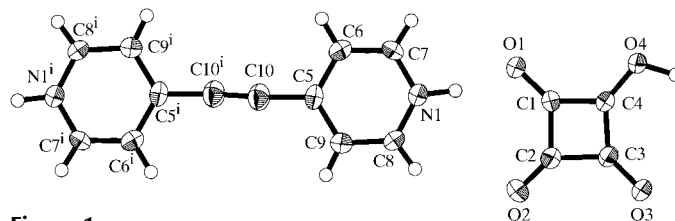


Figure 1

The molecular structure of (I) 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 [symmetry code: (i) $1 - x, 2 - y, 3 - z$].

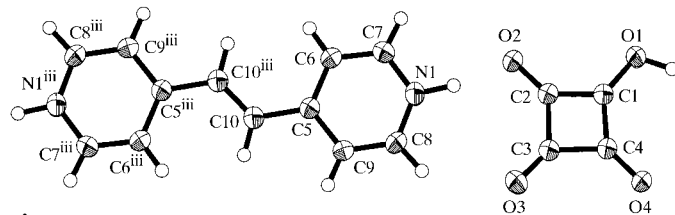


Figure 2

The molecular structure of (II) 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 [symmetry code: (iii) $1 - x, -1 - y, -2 - z$].

[†] Present address: Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208, USA.

and in L-argininium hydrogen squarate (Angelova *et al.*, 1996). The dipyridinium dications of (I) and (II) lie in a plane, with maximum deviations of 0.003 (3) Å for (I) and 0.004 (1) Å for (II). The bond lengths in the dipyridinium moieties are similar to the literature values [Cambridge Structural Database (CSD), Version 5.20; Allen *et al.*, 1987].

Figs. 3 and 4 show the packing diagrams of (I) and (II), respectively, viewed along the *c* axis. The squarate monoanions and the dipyridinium dications form an infinite one-dimensional molecular tape structure along the [120] direction and are connected *via* an intermolecular N—H···O hydrogen bond [N1—H1···O1 2.636 (4) Å for (I) and N1—H1···O2 2.655 (2) Å for (II); see Tables 3 and 4]. The conformation of these molecular tapes is flat and almost linear. The squarate monoanions and the pyridine rings of the dipyridinium dications are almost coplanar [the dihedral angles between the two ring planes are 8.9 (2)° for (I) and 10.2 (1)° for (II)].

The most remarkable feature of the molecular tapes is the existence of a ten-membered hydrogen-bonded dimer of the squarate monoanions within the tapes. The two squarate monoanions are linked by two intermolecular O—H···O hydrogen bonds [O4—H4···O3ⁱⁱ 2.511 (3) Å for (I) and O1—H1A···O4^{iv} 2.503 (2) Å for (II); symmetry codes: (ii) 2 - *x*, -*y*, 1 - *z*; (iv) -*x*, 1 - *y*, -*z*] and are coplanar. The dimensions of the squarate dimer fit those of the dipyridyl-type ligands, as shown in Figs. 3 and 4. The squarate monoanion dimer is rare, and we have found only eight examples in the CSD (Angelova *et al.*, 1996; Bernardinelli *et al.*, 1989; Bock *et al.*, 1998; Braga *et al.*, 1999; Braga & Grepioni, 1998; Kanters *et al.*, 1991; Karle *et al.*, 1996; MacLean *et al.*, 1999). In all other

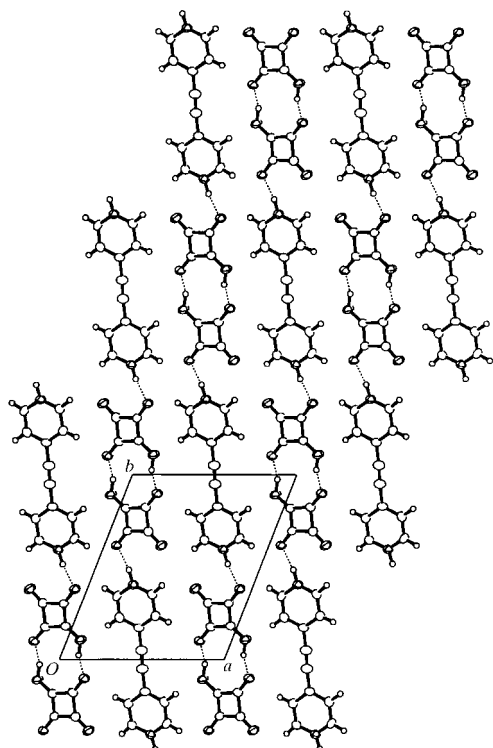


Figure 3
The packing diagram of (I) viewed along the *c* axis. Dotted lines show the intermolecular hydrogen bonds.

squarate structures, the squarate monoanions are linked by a single intermolecular O—H···O hydrogen bond and no ten-membered rings are formed.

Each component molecule forms a segregated stack along the *c* axis. The interstack distances of the squarate plane and the dipyridinium plane for (I) and (II) are 3.21 (1) and 3.40 (1) Å, respectively. The flat conformation of the molecular tapes is favourable for close packing of the tapes and of the segregated stack.

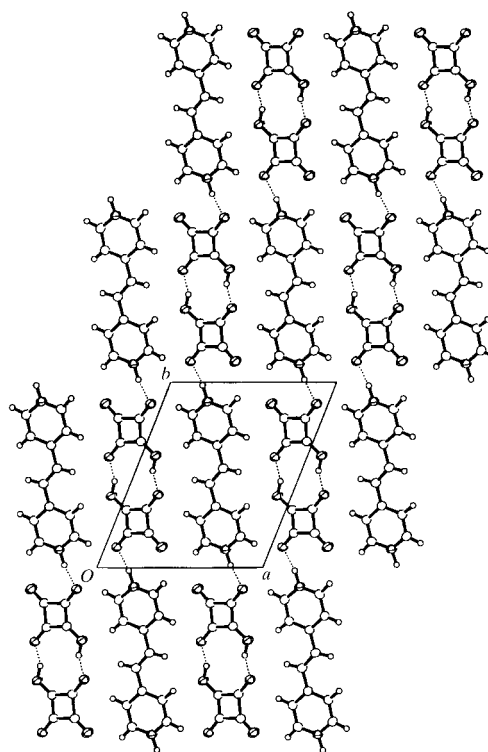


Figure 4
The packing diagram of (II) viewed along the *c* axis. Dotted lines show the intermolecular hydrogen bonds.

In conclusion, the supramolecular synthon (Desiraju, 1995) formed by a combination of squaric acid and dipyridyl-type ligands has been successfully used in the construction of linear hydrogen-bonded molecular tapes. The strong resemblance between the crystal structures of (I) and (II) suggests the robustness and reproducibility of this supramolecular synthon. Studies of the characterization of the physical properties of the cocrystals (I) and (II), and of the construction of new molecular architectures using squaric acid and other dipyridyl-type ligands, are now in progress.

Experimental

4,4'-Dipyridylacetylene was prepared according to the literature method of Tanner & Ludi (1980). Squaric acid and 1,2-bis(4-pyridyl)ethylene were commercially available and were purified by standard methods. Slow evaporation of a solution of squaric acid (0.05 mmol) and the dipyridyl-type ligand (0.05 mmol) in methanol-water (1:1, 20 ml) gave crystals of (I) or (II) suitable for X-ray analysis.

Compound (I)

Crystal data

$C_{12}H_{10}N_2^{2+} \cdot 2C_4HO_4^-$	$Z = 1$
$M_r = 408.32$	$D_x = 1.555 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.221 (2) \text{ \AA}$	Cell parameters from 25 reflections
$b = 12.325 (3) \text{ \AA}$	$\theta = 13.1\text{--}14.8^\circ$
$c = 3.7951 (9) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\alpha = 97.24 (2)^\circ$	$T = 296 (2) \text{ K}$
$\beta = 98.49 (2)^\circ$	Prismatic, gold
$\gamma = 67.649 (18)^\circ$	$0.22 \times 0.15 \times 0.05 \text{ mm}$
$V = 436.06 (18) \text{ \AA}^3$	

Data collection

Rigaku AFC-7R diffractometer	$h = 0 \rightarrow 13$
$\omega/2\theta$ scans	$k = -14 \rightarrow 15$
2101 measured reflections	$l = -4 \rightarrow 4$
1992 independent reflections	3 standard reflections
788 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.048$	intensity decay: 0.8%
$\theta_{\text{max}} = 27.5^\circ$	

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2]$
$wR(F^2) = 0.141$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1992 reflections	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
160 parameters	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

O1—C1	1.255 (4)	C2—C3	1.505 (5)
O2—C2	1.215 (4)	C3—C4	1.427 (5)
O3—C3	1.240 (4)	C5—C6	1.383 (4)
O4—C4	1.306 (4)	C5—C9	1.397 (4)
N1—C7	1.328 (4)	C5—C10	1.436 (5)
N1—C8	1.329 (4)	C6—C7	1.367 (5)
C1—C4	1.415 (4)	C8—C9	1.377 (5)
C1—C2	1.483 (5)	C10—C10 ⁱ	1.181 (6)
C7—N1—C8	122.3 (3)	O4—C4—C3	136.5 (3)
O1—C1—C4	136.6 (3)	C1—C4—C3	93.5 (3)
O1—C1—C2	133.3 (3)	C6—C5—C9	119.4 (3)
C4—C1—C2	90.0 (2)	C6—C5—C10	119.2 (3)
O2—C2—C1	135.0 (3)	C9—C5—C10	121.4 (3)
O2—C2—C3	137.3 (3)	C7—C6—C5	119.1 (3)
C1—C2—C3	87.7 (3)	N1—C7—C6	120.4 (3)
O3—C3—C4	138.2 (3)	N1—C8—C9	120.3 (3)
O3—C3—C2	133.1 (3)	C8—C9—C5	118.4 (3)
C4—C3—C2	88.7 (2)	C10 ⁱ —C10—C5	176.2 (6)
O4—C4—C1	130.0 (3)		

Symmetry code: (i) $1 - x, 2 - y, 3 - z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots O1	0.98 (4)	1.68 (4)	2.636 (4)	165 (3)
O4—H4 \cdots O3 ⁱⁱ	1.04 (5)	1.52 (5)	2.511 (3)	157 (4)

Symmetry code: (ii) $2 - x, -y, 1 - z$.

Compound (II)

Crystal data

$C_{12}H_{12}N_2^{2+} \cdot 2C_4HO_4^-$	$Z = 1$
$M_r = 410.33$	$D_x = 1.575 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 10.2606 (9) \text{ \AA}$	Cell parameters from 22 reflections
$b = 12.2942 (17) \text{ \AA}$	$\theta = 13.9\text{--}42.6^\circ$
$c = 3.7749 (13) \text{ \AA}$	$\mu = 1.06 \text{ mm}^{-1}$
$\alpha = 97.845 (17)^\circ$	$T = 296 (2) \text{ K}$
$\beta = 98.444 (13)^\circ$	Prismatic, yellow
$\gamma = 67.259 (8)^\circ$	$0.25 \times 0.10 \times 0.08 \text{ mm}$
$V = 432.75 (17) \text{ \AA}^3$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.009$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 74.2^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.778, T_{\text{max}} = 0.920$	$k = -15 \rightarrow 15$
2052 measured reflections	$l = 0 \rightarrow 4$
1771 independent reflections	3 standard reflections
1468 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 2.9%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0919P)^2 + 0.0683P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
1771 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
164 parameters	
All H-atom parameters refined	

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

O1—C1	1.3138 (19)	C2—C3	1.491 (2)
O2—C2	1.2453 (19)	C3—C4	1.499 (2)
O3—C3	1.215 (2)	C5—C9	1.394 (2)
O4—C4	1.2440 (19)	C5—C6	1.400 (2)
N1—C7	1.340 (2)	C5—C10	1.470 (2)
N1—C8	1.342 (2)	C6—C7	1.369 (2)
C1—C2	1.425 (2)	C8—C9	1.378 (2)
C1—C4	1.432 (2)	C10—C10 ⁱⁱⁱ	1.320 (3)
C7—N1—C8	121.94 (13)	O4—C4—C3	133.73 (14)
O1—C1—C2	130.32 (14)	C1—C4—C3	88.84 (12)
O1—C1—C4	136.15 (14)	C9—C5—C6	118.14 (14)
C2—C1—C4	93.53 (12)	C9—C5—C10	119.34 (14)
O2—C2—C1	136.23 (14)	C6—C5—C10	122.51 (14)
O2—C2—C3	134.37 (14)	C7—C6—C5	119.41 (15)
C1—C2—C3	89.40 (12)	N1—C7—C6	120.71 (14)
O3—C3—C2	135.13 (15)	N1—C8—C9	119.52 (14)
O3—C3—C4	136.64 (15)	C8—C9—C5	120.27 (14)
C2—C3—C4	88.22 (11)	C10 ⁱⁱⁱ —C10—C5	125.34 (19)
O4—C4—C1	137.42 (14)		

Symmetry code: (iii) $1 - x, -1 - y, -2 - z$.

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A \cdots O4 ^{iv}	0.99 (2)	1.56 (2)	2.5033 (17)	156 (2)
N1—H1 \cdots O2	1.02 (3)	1.64 (3)	2.6546 (17)	170 (2)

Symmetry code: (iv) $-x, 1 - y, -z$.

All H atoms in both (I) and (II) were located in the Fourier map and were refined isotropically; the C–H ranges are 0.91 (3)–0.95 (4) and 0.96 (2)–0.99 (2) Å for (I) and (II), respectively.

For compound (I), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*. For compound (II), data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1995); cell refinement: *CAD-4 EXPRESS*. For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1134). Services for accessing these data are described at the back of the journal.

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