Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368
Editors: **W. Clegg and D. G. Watson**

The pyridinium-betaine of squaric acid

Tsonko Kolev, Denitsa Yancheva, Boris Shivachev and Rosica Petrova

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

The pyridinium-betaine of squaric acid

Tsonko Kolev,[a] Denitsa Yancheva,[a] Boris Shivachev[b] and Rosica Petrova[c]*

[a]Bulgarian Academy of Sciences, Institute of Organic Chemistry, Acad G. Bonchev Str. build. 9, 1113 Sofia, Bulgaria, [b]Bulgarian Academy of Sciences, CL of Mineralogy and Crystallography, Acad G. Bonchev Str. build. 107, 1113 Sofia, Bulgaria, and [c]Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan
Correspondence e-mail: rosica@yamaguchi-u.ac.jp

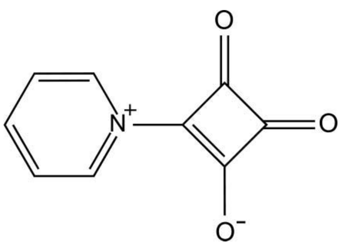
Received 7 June 2007; accepted 13 June 2007

Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.003 Å; R factor = 0.053; wR factor = 0.133; data-to-parameter ratio = 15.0.

In the title compound, 3,4-dioxo-2-(pyridinium-1-yl)cyclobut-1-enolate, $C_9H_5NO_3$, molecules are connected three-dimensionally through nonclassical C—H···O and π–π interactions [3.220 (3) Å] between the oppositely charged squarate and pyridinium fragments. Classical hydrogen-bonding interactions are not observed. In the unit cell, only half an independent molecule is present and a twofold rotation axis passes through the pyridinium ring and the opposite CO group.

Related literature

For related literature, see: Chemla & Zyss (1987); Kolev *et al.* (2001, 2002, 2004); Kolev, Wortmann *et al.* (2005); Kolev, Yancheva *et al.* (2005); Schmidt *et al.* (1984); Uçar *et al.* (2005); Wolff & Wortmann (1999).



Experimental

Crystal data

$C_9H_5NO_3$
M_r = 175.14
Orthorhombic, *Pbcn*
a = 5.0654 (2) Å
b = 18.8003 (17) Å
c = 8.1609 (4) Å
V = 777.17 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 290 (2) K
0.40 × 0.36 × 0.36 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
3425 measured reflections
942 independent reflections
559 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
3 standard reflections
frequency: 120 min
intensity decay: −5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.134
S = 1.03
942 reflections
63 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—HC4···O1^{i}	0.94	2.36	3.036 (3)	129
C5—HC5···O2^{ii}	1.01	2.64	3.218 (3)	116

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

RP thanks the Japan Society for the Promotion of Science (JSPS) for financial support. This work has been supported by the Bulgarian National Fund of Scientific Research Program ‘Improving Research Potential (Grants for Young Researchers)’ contract X-1510/F-1212.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2179).

References

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Chemla, D. & Zyss, J. (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, edited by D. Chemla & J. Zyss, pp. 23–187. New York: Academic Press.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Kolev, T., Wortmann, R., Spiteller, M., Sheldrick, W. S. & Mayer-Figge, H. (2004). *Acta Cryst.* E**60**, o1449–o1450.
Kolev, T., Wortmann, R., Spiteller, M., Sheldrick, W. S. & Mayer-Figge, H. (2005). *Acta Cryst.* E**61**, o1090–o1092.
Kolev, T., Yancheva, D., Kleb, D. C., Schurmann, M., Preut, H. & Bleckmann, P. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 65–66.
Kolev, T., Yancheva, D., Schürmann, M., Kleb, D.-C., Preut, H. & Spiteller, M. (2002). *Acta Cryst.* E**58**, o1267–o1268.
Kolev, T., Yancheva, D., Shivachev, B., Petrova, R. & Spiteller, M. (2005). *Acta Cryst.* C**61**, o213–o215.
Schmidt, A., Becker, U. & Aimene, A. (1984). *Tetrahedron Lett.* pp. 4475–4478.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Uçar, I., Bulut, A., Yeşilel, O. Z., Odabaşoglu, M. & Büyükgüngör, O. (2005). *Acta Cryst.* C**61**, o148–o150.
Wolff, J. J. & Wortmann, R. (1999). *Organic Materials for Second-Order Non-Linear Optics*, in *Advances in Phyical Organic Chemistry*, Vol. 32, edited by R. Bethel, pp. 121–217. London: Academic Press.

supplementary materials

Acta Cryst. (2007). E**63**, o3259 [**doi:10.1107/S1600536807028887**]

The pyridinium-betaine of squaric acid

T. Kolev, D. Yancheva, B. Shivachev and R. Petrova

Comment

The title compound, (I), has been synthesized as part of our synthetic and structural investigations of new organic materials with nonlinear and electro-optical properties (Chemla & Zyss, 1987; Wolff & Wortmann, 1999). We already analyzed the crystal structures of a number of pyridinium-betaines of squaric acid (Kolev *et al.*, 2001, 2002, 2004; Kolev, Yancheva *et al.*, 2005; Kolev, Wortmann *et al.*, 2005), but without the essential member of the family, the unsubstituted compound, (I), their characterization remains incomplete. In order to provide relevant information on the changes observed upon substitution, we report its characteristic features.

The molecular features of (I) are similar to those in Kolev *et al.* (2001, 2002, 2004), Kolev, Yancheva *et al.* (2005), Kolev, Wortmann *et al.* (2005) and Uçar *et al.* (2005) with positive and negative charges situated on the pyridinium and squarate moiety, respectively (Scheme 1). The "semicarbonyl" C2—O1 bond length of 1.221 (2) Å shows the complete delocalization of the negative charge. In all reported structures the semi-carbonyl bond lengths, within the squarate fragment, are apparently unaffected by the substitution and their values vary around 1.22 Å. The C=O double bond length is also constant in reported structures with typical values around 1.201 Å. The pyridinium ring in (I) is planar with r.m.s deviation of 0.002 (2) Å and has partially quinoidal character reflected by the shorter C5—C6 and C8—C9 distances, most expressed in the 4-dimethylamino derivative (Kolev *et al.*, 2002).

The C(Sq)—N(py) bond length bond length of 1.403 (4) Å is also unaffected by the presence of different substitutes. From the studied compounds only in 3-acetoxy-2-(acetylamino)pyridinium-1-squarate (Uçar *et al.*, 2005) this value differs slightly and has a value of 1.422 (5) Å.

The dihedral angle between the squarate and pyridinium mean planes also show minor variations within the series of 3- and 4-substituted compounds, but differ significantly from the values for the 2-(3-benzoyl-1-pyridinio)-3,4-dioxocyclob-utenolate derivative (Kolev, Yancheva *et al.*, 2005), which is a sign that the conjugation between the molecular fragments is strongly decreased by the substitution at 2- and 3-position.

Similarly to the substituted pyridinium-betaines of squaric acid in the crystal structure of (I) molecules are connected through non-classical C—H···O hydrogen bonds (Table1) and π···π interactions between the oppositely charged squarate and pyridinium fragments [$Cg1\cdots O1^{iii}$ 3.220 (3) Å; *Cg*1 is the controid of the pyridinium ring; symmetry code: (iii) x, $1 - y$, $1/2 + z$]. A side-to-side $C4—HC4\cdots O1^{i}$ [symmetry code: (i) $-x$, $1 - y$, $-z$] interaction of squarate and pyridinium fragments build up straight chains replicating along the *c* axis. A bifurcated head-to-tail $C5—HC5\cdots O2^{ii}$ [symmetry code: (i) $-1/2 + x$, $-1/2 + y$, $1/2 - z$] interaction connects three-dimensionally the chains.

Practically in all derivatives of (I) the squarate carbonyl O atom forms a bifurcated bond. The only observed exception is for 3-benzoylpyridinium betaine of squaric acid (Kolev, Yancheva *et al.*, 2005) and could be explained by the steric effect of the phenyl substitute.

Experimental

The title compound was synthesized according to Schmidt *et al.* (1984). Crystal suitable for X-ray diffraction has been obtained after slow evaporation from water/ethanol mixture (1:1) at room temperature.

Refinement

Hydrogen atoms were located in a difference map. All H atoms were constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

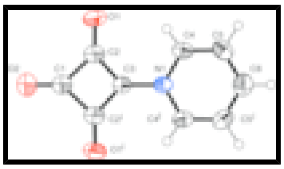


Fig. 1. View of the molecule and the atom-numbering scheme of (I) showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $1 - x, y, 1/2 - z$].

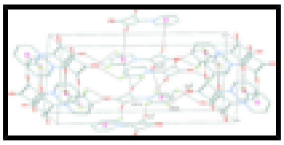


Fig. 2. A view of the molecular packing in (I). All H atoms not involved in the short contact interactions have been omitted for clarity [symmetry codes: (i) $-x, 1 - y, -z$; (ii) $-1/2 + x, -1/2 + y, 1/2 - z$; (iii) $x, 1 - y, 1/2 + z$].

3,4-dioxo-2-(pyridinium-1-yl)cyclobut-1-enolate

Crystal data

$C_9H_5NO_3$	D_x = 1.497 Mg m^{-3}
M_r = 175.14	Melting point: not measured K
Orthorhombic, *Pbcn*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2n 2ab	Cell parameters from 22 reflections
a = 5.0654 (2) Å	θ = 19.3–19.6º
b = 18.8003 (17) Å	μ = 0.12 mm^{-1}
c = 8.1609 (4) Å	T = 290 (2) K
V = 777.17 (9) Å^3	Prism, yellow
Z = 4	0.40 × 0.36 × 0.36 mm
F_{000} = 360	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.070
Radiation source: fine-focus sealed tube	$θ_{max}$ = 27.9º
Monochromator: graphite	$θ_{min}$ = 2.2º
T = 290(2) K	h = 0→6
Non–profiled ω/2θ scans	k = −24→24

Absorption correction: none	$l = -10 \rightarrow 10$
3425 measured reflections	3 standard reflections
942 independent reflections	every 120 min
559 reflections with $I > 2\sigma(I)$	intensity decay: −5%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.053$	H-atom parameters constrained
$wR(F^2) = 0.134$	$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.3645P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
942 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
63 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5000	0.64018 (18)	0.2500	0.0465 (8)
C2	0.3375 (4)	0.58204 (12)	0.1671 (3)	0.0408 (5)
C3	0.5000	0.53134 (15)	0.2500	0.0356 (6)
C4	0.3121 (4)	0.42083 (12)	0.1638 (3)	0.0411 (5)
HC4	0.1779	0.4499	0.1194	0.061 (7)*
C5	0.3098 (5)	0.34857 (13)	0.1636 (3)	0.0491 (6)
HC5	0.1706	0.3201	0.1032	0.059*
C6	0.5000	0.31182 (18)	0.2500	0.0531 (9)
HC6	0.5000	0.2609	0.2500	0.064*
N1	0.5000	0.45673 (12)	0.2500	0.0349 (6)
O1	0.1529 (3)	0.58096 (9)	0.0708 (2)	0.0557 (5)
O2	0.5000	0.70389 (12)	0.2500	0.0725 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0433 (18)	0.0490 (18)	0.0471 (18)	0.000	−0.0043 (16)	0.000
C2	0.0356 (11)	0.0494 (13)	0.0373 (11)	0.0003 (10)	−0.0020 (10)	0.0018 (10)
C3	0.0325 (15)	0.0415 (15)	0.0330 (14)	0.000	−0.0009 (13)	0.000
C4	0.0336 (10)	0.0505 (13)	0.0391 (11)	−0.0035 (11)	−0.0031 (10)	0.0002 (10)
C5	0.0430 (12)	0.0530 (14)	0.0512 (13)	−0.0102 (12)	0.0009 (12)	−0.0054 (11)
C6	0.051 (2)	0.0440 (17)	0.065 (2)	0.000	0.007 (2)	0.000
N1	0.0297 (12)	0.0429 (14)	0.0319 (12)	0.000	0.0000 (11)	0.000
O1	0.0484 (9)	0.0637 (11)	0.0549 (10)	0.0019 (9)	−0.0204 (8)	0.0061 (8)
O2	0.080 (2)	0.0418 (13)	0.096 (2)	0.000	−0.0218 (18)	0.000

Geometric parameters (Å, °)

C1—O2	1.198 (4)	C4—N1	1.363 (2)
C1—C2	1.526 (3)	C4—HC4	0.9436
C2—O1	1.221 (2)	C5—C6	1.379 (3)
C2—C3	1.430 (3)	C5—HC5	1.0133
C3—N1	1.403 (4)	C6—HC6	0.9571
C4—C5	1.359 (3)		
O2—C1—C2	135.73 (12)	N1—C4—HC4	114.5
O2—C1—C2^{i}	135.73 (12)	C4—C5—C6	119.6 (2)
C2—C1—C2^{i}	88.5 (2)	C4—C5—HC5	122.3
O1—C2—C3	137.2 (2)	C6—C5—HC5	118.0
O1—C2—C1	135.2 (2)	C5^{i}—C6—C5	119.9 (3)
C3—C2—C1	87.55 (16)	C5^{i}—C6—HC6	120.1
N1—C3—C2^{i}	131.82 (11)	C5—C6—HC6	120.1
N1—C3—C2	131.82 (11)	C4—N1—C4^{i}	120.6 (3)
C2^{i}—C3—C2	96.4 (2)	C4—N1—C3	119.69 (13)
C5—C4—N1	120.1 (2)	C4^{i}—N1—C3	119.69 (13)
C5—C4—HC4	124.9		
O2—C1—C2—O1	0.9 (3)	N1—C4—C5—C6	−0.6 (3)
C2^{i}—C1—C2—O1	−179.1 (3)	C4—C5—C6—C5^{i}	0.28 (15)
O2—C1—C2—C3	180.0	C5—C4—N1—C4^{i}	0.29 (16)
C2^{i}—C1—C2—C3	0.0	C5—C4—N1—C3	−179.71 (16)
O1—C2—C3—N1	−0.9 (3)	C2^{i}—C3—N1—C4	177.06 (15)
C1—C2—C3—N1	180.0	C2—C3—N1—C4	−2.94 (15)
O1—C2—C3—C2^{i}	179.1 (3)	C2^{i}—C3—N1—C4^{i}	−2.94 (15)
C1—C2—C3—C2^{i}	0.0	C2—C3—N1—C4^{i}	177.06 (15)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C4—HC4···O1^{ii}	0.94	2.36	3.036 (3)	129
C5—HC5···O2^{iii}	1.01	2.64	3.218 (3)	116

Symmetry codes: (ii) −*x*, −*y*+1, −*z*; (iii) *x*−1/2, *y*−1/2, −*z*+1/2.

Fig. 1

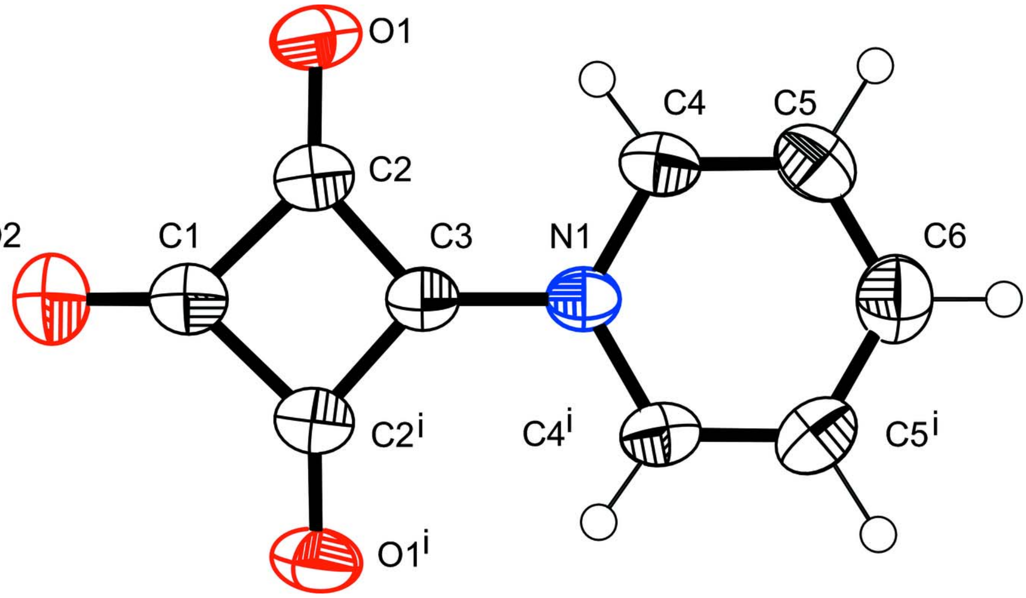


Fig. 2