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2-(3-Benzoyl-1-pyridinio)-3,4-dioxocyclobutenolate

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2-(3-Benzoyl-1-pyridinio)-3,4-dioxo-
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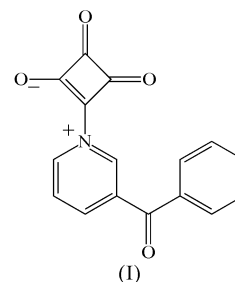
The title compound, $C_{16}H_9NO_4$, also known as the 3-benzoylpyridinium betaine of squaric acid, exhibits a dipolar electronic ground-state structure with a positively charged pyridinium fragment and a negatively charged squarate moiety. In the molecule, the two aromatic rings are twisted by $56.03(2)^\circ$ relative to one another. The three-dimensional packing of the molecules is stabilized by $C-H\cdots O$ short contacts.

Comment

The substituted pyridinium betaines of squaric acid are of particular interest as potential organic non-linear optical (NLO) materials (Chemla & Zyss, 1987; Nalwa *et al.*, 1997; Wolff & Wortmann, 1999). In the course of our detailed study of squaric acid derivatives, the syntheses and structural characterizations of the 4-benzoyl (Kolev *et al.*, 2001), 4-dimethylamino (Kolev, Yancheva *et al.*, 2002) and 4-methoxy analogues (Kolev, Wortmann *et al.*, 2004) have been published. In view of the very interesting chemical structures of these molecules, density functional theory calculations of the electronic structure and UV-vis spectroscopic studies have been carried out (Kolev *et al.*, 2003; Kolev, Stamboliyska *et al.*, 2004; Kolev, Yancheva & Stoyanov, 2004). The electro-optical absorption measurements (EOAM) demonstrate that the studied series of compounds possess hyperpolarizabilities exceeding that of the reference substance, *p*-nitroaniline, both in absolute and relative values. These results are due to be published shortly. In this paper, we report the structural characteristics of the 3-benzoylpyridinium betaine of squaric acid, (I).

The molecular structure of (I) is dipolar, with the positive and the negative charges situated on the pyridinium and squarate groups, respectively (Fig. 1). One of the C—O bonds within the squarate system has a value of $1.204(4)$ Å, typical

for a carbonyl group. The remaining two C—O bonds are longer and have similar values [$1.219(3)$ and $1.220(4)$ Å], indicating that the negative charge is equally distributed between atoms O2 and O3. This charge repartition also affects the cyclobutene C—C distances, with two of them being shorter than the other two, with respective values of $1.426(4)/1.430(4)$ and $1.527(5)/1.533(4)$ Å. A similar deformation of the squarate moiety is known for the 4-benzoyl derivative (Kolev *et al.*, 2001). The squarate and pyridinium rings are nearly coplanar, with a dihedral angle of $4.1(2)^\circ$. Similar values of this angle have been observed in previously described structures of this type. The dihedral angle between the aromatic rings is $56.03(2)^\circ$. This is comparable with the corresponding value in 4-dimethylamino-4'-nitrobenzophenone (Kolev, Schurmann *et al.*, 2002) and differs significantly from that in the 4-benzoyl derivative (Kolev *et al.*, 2001), where the aromatic rings are nearly perpendicular.



The molecule of (I) is Λ shaped, *i.e.* the rings are mutually twisted (Nalwa *et al.*, 1997). In the crystal structure, the molecules face each other in an alternate end-to-end fashion, so that opposite shoulders of the molecules are adjacent to each other. There are a number of intermolecular interactions stabilizing the three-dimensional packing of the molecules. We consider two of them as non-classical hydrogen bonds, namely the contacts between the negatively charged squarate O atoms and the pyridinium H atoms (Table 1). These contacts are likely to occur due to the greater mobility of H atoms within

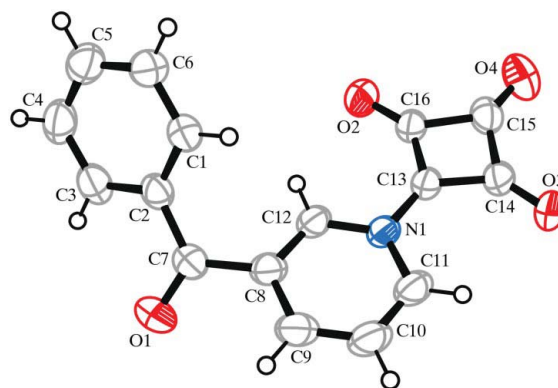


Figure 1

The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

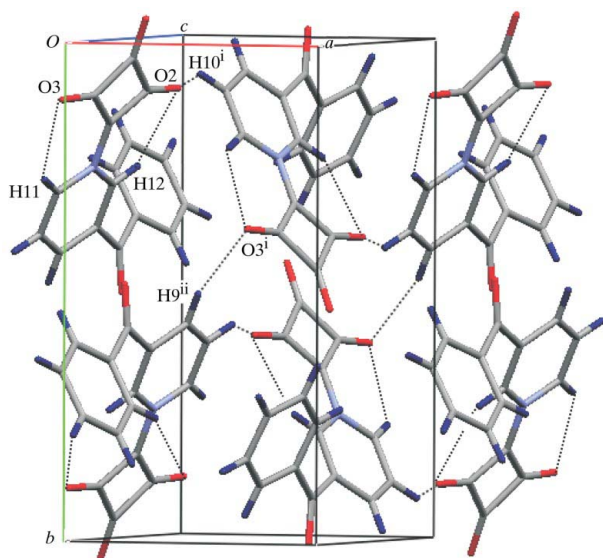


Figure 2
The molecular packing in (I), showing the C—H···O contacts as dotted lines. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-x, 1 - y, 1 - z$.]

the pyridinium ring caused by the electron-withdrawing N atom. A similar manner of hydrogen bonding is observed in the previously reported 4-benzoyl analogue, where the molecules are linked to form ribbons. In contrast, the molecules of the title compound are connected in a two-dimensional manner (Fig. 2).

It is interesting to note that the coplanarity of the squarate and pyridinium rings produces two additional short contacts, *viz.* C11···O3 and C12···O2 (Table 2), which could be regarded as intramolecular hydrogen bonds. Similar short contacts were found in the 4-benzoyl analog.

Experimental

The synthesis of (I) is described in our previous article (Kolev, Yancheva & Stoyanov, 2004). The crystals were grown by slow evaporation from an acetonitrile solution over a period of a week. IR (KBr pellet, ν , cm^{-1}): the $\nu_{\text{C—H}}$ vibrations of the pyridyl ring and benzoyl group appear at 3138 (w), 3130 (w), 3122 (w) and 3107 (w), and at 3092 (w) and 3033 (w), respectively. The very strong band at 1783 (s) is assigned to $\nu_{\text{C=O}}$ of the isolated carbonyl group of the squarate ring, while those at 1748 (s) and 1625 (s) correspond to the symmetric and asymmetric modes of the semicarboxyl groups. The pyridinium ring vibration 8a lies in the massif of the broad band at 1625 (s).

Crystal data

$\text{C}_{16}\text{H}_9\text{NO}_4$
 $M_r = 279.24$
Monoclinic, $P2_1/n$
 $a = 7.9319$ (11) Å
 $b = 13.6577$ (14) Å
 $c = 12.0890$ (12) Å
 $\beta = 103.903$ (12)°
 $V = 1271.3$ (3) Å³
 $Z = 4$
 $D_x = 1.459$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
 $\theta = 18.4$ – 19.6°
 $\mu = 0.11$ mm⁻¹
 $T = 290$ (2) K
Cubic, red
 $0.24 \times 0.24 \times 0.24$ mm

Table 1

Selected bond lengths (Å).

C2—C7	1.478 (4)	C14—O3	1.220 (4)
C7—O1	1.216 (4)	C14—C15	1.527 (5)
C7—C8	1.498 (4)	C15—O4	1.204 (4)
C13—C14	1.426 (4)	C15—C16	1.533 (4)
C13—C16	1.430 (4)	C16—O2	1.219 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
C9—H9···O3 ⁱ	0.93	2.59	3.225 (4)	125
C10—H10···O2 ⁱⁱ	0.93	2.60	3.215 (3)	124
C11—H11···O3	0.93	2.50	3.152 (5)	127
C12—H12···O2	0.93	2.54	3.191 (4)	127

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

Data collection

Enraf-Nonius CAD-4
diffractometer
Non-profiled $\omega/2\theta$ scans
6407 measured reflections
3063 independent reflections
1558 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.093$

$\theta_{\text{max}} = 28.0^\circ$
 $h = 0 \rightarrow 10$
 $k = -18 \rightarrow 18$
 $l = -15 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.236$
 $S = 1.04$
3063 reflections
190 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1235P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

H atoms were placed in idealized positions (C—H = 0.93 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1218). Services for accessing these data are described at the back of the journal.

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