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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.043
 wR factor = 0.112
Data-to-parameter ratio = 12.2

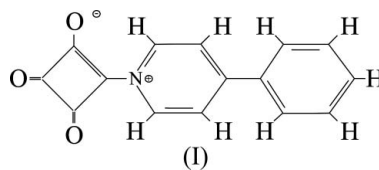
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

4-Phenylpyridinium betaine of squaric acid

The title compound, 4-phenylpyridinium-3-squarate, $\text{C}_{15}\text{H}_9\text{NO}_3$, exhibits an interplanar angle between the pyridinium and squarate rings of 0.6 (1°). It displays 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 31.6 (1°). The bond lengths within the squarate system represent average values for the two possible resonance structures, with a central typical carbonyl bond [1.203 (2) Å] flanked by two longer 'semicarboxyl' bonds of lengths 1.228 (2) and 1.221 (2) Å.

Comment

The substituted pyridinium betaines of squaric acid are of considerable current interest as potential organic nonlinear optical (NLO) materials (Nalwa *et al.*, 1997; Wolff & Wortmann 1999; Chemla & Zyss, 1987; Bosshard *et al.* 1995). In the course of our ongoing synthetic, spectroscopic and structural studies of selected 'push-pull' substituted pyridinium betaines of squaric acid, having nonlinear optical (NLO), photo-refractive and electro-optical properties, the crystal structure of the title compound, (I), has been determined.



It is known that certain classes of organic compounds (Wolff & Wortmann 1999; Bosshard *et al.* 1995) exhibit very pronounced NLO and electro-optical effects. Their non-linearity is based on the presence of molecular units containing strongly delocalized π electron systems with donor and acceptor groups sited at opposite ends of the molecule. Among such materials, the substituted betaines play an important role because of their dipolar ground-state electronic structure. The conversion of the N atom of 4-phenylpyridine into the corresponding pyridinium betaine provides a means of enhancing the charge-transfer transition at the molecular level, and this is a prerequisite for the design of efficient second- and third-order nonlinear optical materials.

We have studied the UV-vis spectra of a representative series of 3- and 4-substituted compounds of this class (Kolev, Yancheva & Stoyanov, 2004), which allowed us to characterize their distinct negative solvatochromism, typical for compounds with a dipolar electronic ground-state structure. The characteristic squarate bands in the IR and Raman spectra of (I) coincide to within $2\text{--}3$ cm^{-1} with those

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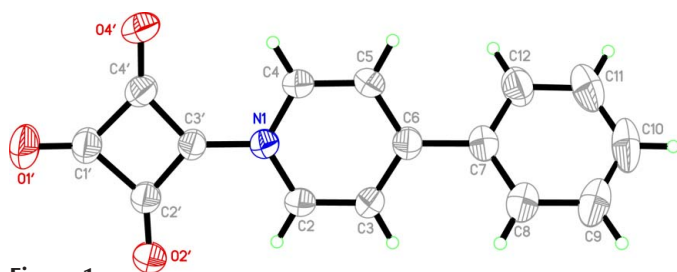


Figure 1
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

previously presented for the FT-IR spectrum (KBr pellet) of the 4-methoxypyridinium betaine of squaric acid (Kolev, Wortmann *et al.*, 2004). The strong IR band at 1784 cm^{-1} and weak Raman band at 1782 cm^{-1} can be assigned to the 'pure' C=O stretching vibration, while the bands at 1733 (s) (IR) and 1732 (w) cm^{-1} (Raman) are attributed to the asymmetric vibration of the two 'semicarbonyl' groups. The strong bands at 1634 (s) cm^{-1} (Raman) and 1637 (vs) (IR) can be assigned to the symmetric vibration of the same groups, and the most intense band in the FT-IR spectrum of (I), at 1621 cm^{-1} , which is also intense in the Raman spectrum at 1619 cm^{-1} , can be assigned to the radial vibration 8a. The frequency of this mode is predicted by both the B3LYP and RHF methods (Kolev *et al.*, 2003). Its high intensity is obviously due to the vibronic coupling between the carbonyl vibrations and the aromatic modes in (I).

The distances in the squarate ring system of (I) represent average values for the two possible resonance structures. This leads to partial double-bond character for C2'–C3' [$1.420\text{ (2)}\text{ \AA}$] and C3'–C4' [$1.427\text{ (2)}\text{ \AA}$] and single-bond character for C1'–C2' [$1.529\text{ (2)}\text{ \AA}$] and C1'–C4' [$1.529\text{ (3)}\text{ \AA}$]. The C1'–O1' carbonyl group has a bond length of $1.203\text{ (2)}\text{ \AA}$, corresponding to the vibrational frequency at 1784 cm^{-1} (IR) and 1782 cm^{-1} (Raman). The bond lengths of the two 'semicarbonyl' bonds C2'–O2' and C4'–O4' are 1.228 (2) and $1.221\text{ (2)}\text{ \AA}$, respectively. Repulsion between atoms H3 and H8 of the pyridinium ring and atoms H5 and H12, respectively, of the phenyl moiety leads to an interplanar angle of 31.6 (1)° . In contrast, the pyridinium and squarate ring systems are effectively coplanar, with a dihedral angle of only 0.6 (1)° .

The molecules of (I) are linked by weak intermolecular C3–H3...O4', C6–H6...O2' and C10–H10...O1' hydrogen bonds (Table 1) into lamellar networks. The participating O2' and O4' atoms are partially negatively charged, owing to the resonance distribution depicted in the scheme.

Experimental

Compound (I) was synthesized according to the general literature procedure of Schmidt *et al.* (1984). Squaric acid (1 g, 8.7 mmol) was dissolved in acetic anhydride (30 ml) by continuous stirring and heating under reflux. A solution of 4-phenylpyridine (1.55 g, 8.7 mmol) dissolved in acetic anhydride (10 ml) was then added. A red precipitate was obtained from the resulting dark red solution after 30 min of heating and subsequent evaporation of half the

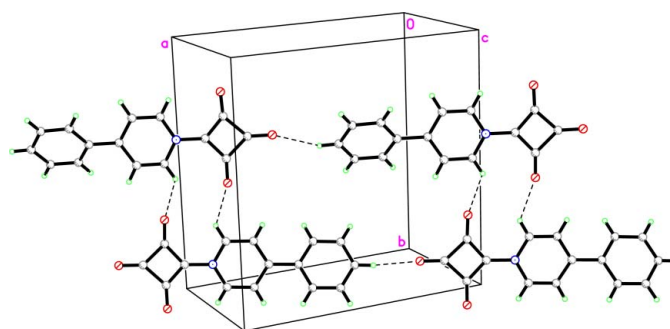


Figure 2
The hydrogen bonding between molecules of (I) (dashed lines).

solvent. The product was filtered off after cooling and recrystallized from dimethylformamide to afford (I) in 93% yield. The purity of the compound was confirmed by elemental analysis, mass spectrometry, and IR and UV-vis spectroscopy. The UV-vis absorption maximum is observed for (I) at 386 nm in methanol and 396 nm in dimethylformamide. Orange-red single crystals, suitable for X-ray analysis, were grown from ethanol at room temperature over a period of three weeks.

Crystal data

$\text{C}_{15}\text{H}_9\text{NO}_3$	$D_x = 1.389\text{ Mg m}^{-3}$
$M_r = 251.23$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 15 reflections
$a = 12.852\text{ (3)}\text{ \AA}$	$\theta = 7.5\text{--}15^\circ$
$b = 12.924\text{ (3)}\text{ \AA}$	$\mu = 0.10\text{ mm}^{-1}$
$c = 7.236\text{ (2)}\text{ \AA}$	$T = 293\text{ (2)}\text{ K}$
$\beta = 91.49\text{ (2)}^\circ$	Prism, orange-red
$V = 1201.4\text{ (5)}\text{ \AA}^3$	$0.34 \times 0.26 \times 0.21\text{ mm}$
$Z = 4$	

Data collection

Siemens P4 four-circle diffractometer	1455 reflections with $I > 2\sigma(I)$
Profile-fitted ω scans	$R_{\text{int}} = 0.038$
Absorption correction: ψ scan (XPREP in SHELXTL-Plus; Sheldrick, 1995)	$\theta_{\text{max}} = 25.0^\circ$
$T_{\text{min}} = 0.957$, $T_{\text{max}} = 0.983$	$h = -15 \rightarrow 15$
2889 measured reflections	$k = -15 \rightarrow 1$
2112 independent reflections	$l = -1 \rightarrow 8$
	3 standard reflections every 100 reflections intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.0499P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.112$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.13\text{ e \AA}^{-3}$
2112 reflections	$\Delta\rho_{\text{min}} = -0.16\text{ e \AA}^{-3}$
173 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.037 (6)

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
C6–H6...O2 ⁱⁱ	0.93	2.38	3.082 (2)	132
C3–H3...O4 ⁱⁱⁱ	0.93	2.62	3.138 (2)	116
C10–H10...O1 ⁱⁱⁱ	0.93	2.47	3.330 (3)	154

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

H atoms were positioned geometrically and treated as riding, with C–H distances of 0.93 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *R3m/V User's Guide* (Siemens, 1989); cell refinement: *R3m/V User's Guide*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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