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Bis(8-hydroxyquinolinium) squarate

Tonko Kolev,[a]
Snezana Sinadinovic Fiser,[b]
Michael Spiteller,[c]
William S. Sheldrick[d]* **and**
Heike Mayer-Figge[d]

[a]Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Building 9, 1113 Sofia, Bulgaria, [b]University of Novi Sad, Department of Petrochemical Engineering, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia and Montenegro, [c]Institut für Umweltforschung, Universität Dortmund, Otto-Hahn-Straße 6, D-44221 Dortmund, Germany, and [d]Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany

Correspondence e-mail:
william.sheldrick@rub.de

Key indicators

Single-crystal X-ray study
T = 566 K
Mean σ(C–C) = 0.005 Å
R factor = 0.060
wR factor = 0.152
Data-to-parameter ratio = 11.6

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

The title compound, $2C_9H_8NO_2^+ \cdot C_4O_4^{2-}$, contains a dianion with approximately D_{4h} symmetry [C—C = 1.465 (4)–1.470 (4) Å and C—O = 1.248 (4)–1.264 (4) Å]. Individual dianions are linked to four neighbouring 8-hydroxyquinolinium cations by O···H—N [2.666 (4) and 2.681 (4) Å] and O···H—O [2.596 (3) and 2.605 (3) Å] hydrogen bonds to generate a polymeric chain.

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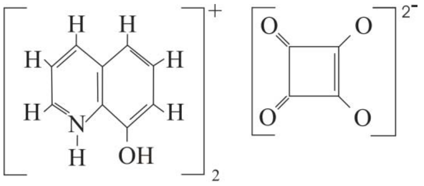
Comment

In the course of our continuing spectroscopic and structural studies of selected 'push–pull' substituted pyridinium betaines of squaric acid, having non-linear optical (NLO), photorefractive and electro-optical properties (Nalwa *et al.*, 1997; Wolff & Wortmann, 1999; Chemla & Zyss, 1987; Bosshard *et al.*, 1995), the crystal structure of the title compound bis(8-hydroxyquinolinium) squarate, $(8H_2Q)_2Sq$, (I), has been determined. We were, in fact, attempting to prepare 8-hydroxyquinolinium hydrogensquarate ($8H_2Q^+ \cdot HSq^-$), which can be easily transformed into the corresponding betaine of squaric acid, but isolated (I) instead in quantitative yield.



(I)

This interesting result provides a textbook example of a reagent that has wide interactive selectivity, particularly through pH control. The analytical applications of the formation of (I) are being investigated and will be published at a later date. Protonation of the heterocyclic N atom of 8-hydroxyquinoline takes place in the presence of relatively strong organic acids and the resulting $[8H_2Q]^+$ cation also participates in hydrogen-bonding interactions. The structures of many complexes of 8-hydroxyquinoline including $Pd(8Q)_2$ (Prout & Wheeler, 1966), $K(8Q) \cdot 8HQ$ and $K(8H_2Q)(8Q)_2$ (Hughes & Truter, 1979), and the $[H_2Q]^+$ salts of, respectively, 2-nitrobenzoic acid, 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid (Smith *et al.*, 2001), 5-sulfosalicylic acid (Smith, Wermuth & Healy, 2004), 8-hydroxy-7-iodoquinoline-5-sulfonic acid (Smith, Wermuth & White, 2004), salicylic acid (Singh *et al.*, 2000; Smith, Wermuth & White, 2003), 2-nitrobenzoic acid, 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid (Smith *et al.*, 2000). The structural chemistry of metal squarates has been summarized up to 1990 in a review (Lee & Wang, 1996). Squaric acid, $H_2C_4O_4$ (H_2Sq), is known to have a

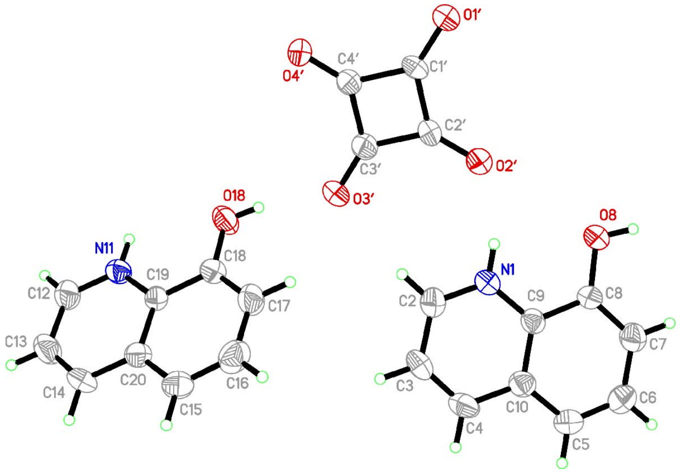


Figure 1
The molecular structure of 8-quinolinium squarate with the labelling of non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

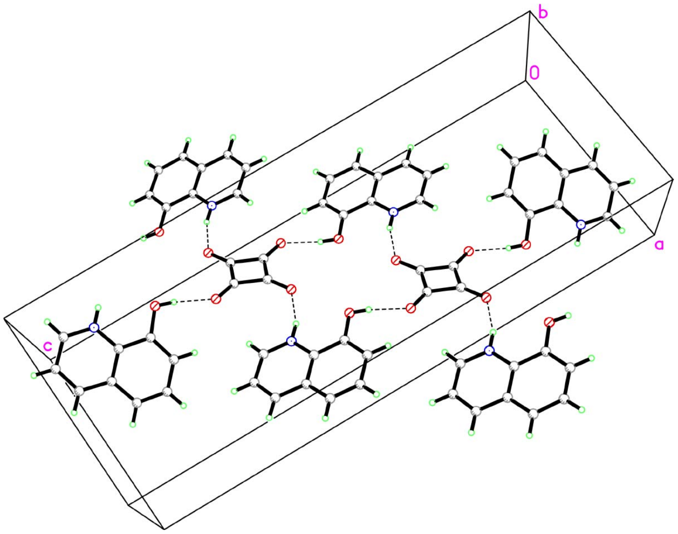


Figure 2
Hydrogen bonding (dashed lines) between molecules of (I).

polymeric layer structure with planar molecules connected through strong intermolecular O—H···O′ hydrogen bonds with a distance of only 2.649 Å. The most studied type of metal squarate structure is that of [M(Sq)(H_2O)$_4$], with two bridging [Sq]$^{2-}$ ligands at *trans* positions, which forms an infinite chain structure. The squarate dianion [Sq]$^{2-}$ is an interesting cyclic ligand with aromaticity (Lee & Wang, 1996) and a potential D_{4h} symmetry. As a bridging ligand it can adopt a μ_2-, μ_3- or μ_4-mode between metal ions. In our previous investigations, it was shown that the hydrogensquarate salt of *R*-(−)-1-phenylglycine forms infinite chains of [HSq]$^-$ anions along the *b* axis (Angelova, Petrova *et al.*, 1996). In contrast, in L-argininium hydrogensquarate, the [HSq]$^-$ anions participate in hydrogen-bonded dimers (Angelova, Velikova *et al.*, 1996). An anionic dimer structure was also found in 4-phenylpyridinium hydrogensquarate (Kolev *et al.*, 2004).

The vibrational bands in the IR and Raman spectra of (I) coincide within 2–3 cm^{-1}. The band belonging to the O—H stretching vibration of the cation is tentatively assigned to 3200 cm^{-1}. In the Raman spectrum, it appears as a shoulder of the strong band at 3075 cm^{-1} belonging to the C—H stretching vibration of the aromatic ring. The weak band at 1806 cm^{-1} and the middle ones at 1585 and 1499 cm^{-1} are attributed to the mixed vibration of the squarate dianion. Strong bands at 1633 and 1603 cm^{-1} are assigned to the radial vibrations 8*a* and 8*b* of the aromatic ring, and the strong Raman bands at 1383 (*vs*) and 1066 (*s*) cm^{-1} to the mixed C—C and C—O vibrations of the squarate ring. The strongest band in the Raman spectrum at 104 cm^{-1} and additional strong bands at 85 and 71 cm^{-1} belong to the lattice vibrations of the crystal. The squarate dianion adopts a nearly perfect resonance structure with approximately D_{4h} symmetry. All C—C distances coincide within 0.005 Å: C1′—C2′ = 1.465 (5) Å, C2′—C3′ = 1.465 (4) Å, C3′—C4′ = 1.468 (4) Å and C4′—C1′ = 1.470 (4) Å. The small differences in the C—O bond lengths can be explained by their differing interactions with H-bonds donors. Compound (I) exhibits the strong interactions listed in Table 1, which also includes two weaker O···H—C interactions. As depicted in Fig. 2, the hydrogen-bonding pattern leads to a chain structure for (I).

Experimental

The title compound was synthesized by adding a methanolic solution of 8HQ to an aqueous solution of squaric acid in a 1:1 molar ratio with continuous stirring and heating under reflux. A yellow precipitate was obtained from the resulting dark-yellow solution after 60 min. The product was filtered off after cooling and recrystallized from dimethylformamide to afford (I) in 89% yield. The purity of the compound was confirmed by elemental analysis and mass spectrometry, IR and UV–vis spectrometry. The absorption maximum of (I) is at 386 nm in methanol and 396 nm in dimethylformamide. Yellow single crystals, suitable for X-ray analysis, were grown from dimethylformamide at room temperature over a period of two weeks.

Crystal data

$2C_9H_8NO^+\cdot C_4O_4^{2-}$
$M_r = 404.37$
Monoclinic, $P2_1/c$
$a = 9.578$ (3) Å
$b = 7.3024$ (17) Å
$c = 25.656$ (5) Å
$\beta = 94.830$ (13)°
$V = 1788.1$ (6) Å^3
$Z = 4$

$D_x = 1.502$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 reflections
$\theta = 7.5$–15°
$\mu = 0.11$ mm^{-1}
$T = 566$ (2) K
Prism, yellow
0.42 × 0.36 × 0.28 mm

Data collection

Siemens *P*4 four-circle diffractometer
Profile-fitted ω scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL-Plus*; Sheldrick, 1995)
$T_{\min} = 0.930$, $T_{\max} = 0.973$
4380 measured reflections
3152 independent reflections

1640 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 8$
$l = -30 \rightarrow 30$
3 standard reflections every 100 reflections intensity decay: 2%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.152$
$S = 0.99$
3152 reflections
272 parameters
H-atom parameters constrained.

$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0063 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O1$'^{\rm i}$	0.93	2.56	3.168 (4)	123
O8—H8···O1$'^{\rm i}$	0.82	1.78	2.596 (3)	172
N1—H1···O2$'$	0.86	1.84	2.666 (4)	159
C17—H17···O3$'$	0.93	2.48	3.138 (4)	128
O18—H18···O3$'$	0.82	1.79	2.605 (3)	169
N11—H11···O4$'^{\rm ii}$	0.86	1.87	2.681 (4)	157

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

H atoms were included as riding on their parent atoms, with C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom).

Data collection: *Siemens R3m/V User's Guide* (Siemens, 1989); cell refinement: *Siemens 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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