

4-Methoxypyridinium betaine of squaric acid

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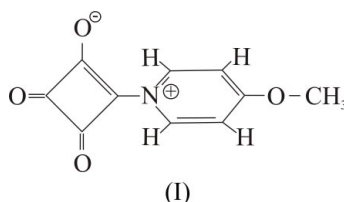
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.044
 wR factor = 0.107
Data-to-parameter ratio = 10.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, 4-methoxypyridinium-3-squarate or 2-(4-methoxypyridinio)-3,4-dioxocyclobut-1-en-1-olate, $\text{C}_{10}\text{H}_7\text{NO}_4$, exhibits an interplanar angle of $5.3(2)^\circ$. The bond lengths within the squarate system represent average values for the two possible resonance structures, with a central typical carbonyl bond [$1.209(3)$ Å] flanked by two longer 'semicarboxyl' bonds of length $1.230(3)$ Å.

Comment

In the course of our synthetic, spectroscopic and structural studies of some 'push-pull' substituted pyridinium betaines of squaric acid, having non-linear optical (NLO), photorefractive and electro-optical properties, the crystal structure of the title compound, the 4-methoxypyridinium betaine of squaric acid, has been determined. It is known that certain classes of organic compounds (Nalwa *et al.*, 1997; Wolff & Wortmann, 1999; Chemla & Zyss, 1987) exhibit very high 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 structure. The conversion of the N atom of 4-methoxypyridine into the corresponding pyridinium betaine provides a way of enhancing the charge transfer transition at the molecular level and this is a prerequisite for the design of efficient second- and third-order non-linear 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). In the course of this work, we could characterize the distinct negative solvatochromism, typical for compounds with a dipolar electronic ground-state structure.



The FT-IR spectrum (KBr pellet) of (I) is very similar to that of the dimethylaminopyridinium betaine of squaric acid, (II) (Kolev, Stamboliyska *et al.*, 2004). The strong band at 1796 cm^{-1} can be assigned to the 'pure' $\text{C}=\text{O}$ stretching vibration, while the bands at 1727 (s) and 1642 cm^{-1} (vs) are attributed to the symmetric and asymmetric vibrations of the two 'semicarboxyl' groups. The most intense band in the

Received 22 July 2004

Accepted 27 July 2004

Online 31 July 2004

FT-IR spectrum of (I), at 1625 cm^{-1} , practically coincides with that of (II) (1626 cm^{-1}) and is assigned to the radial vibration *8a*. The frequency of this mode is well predicted by both the B3LYP and RHF methods. Its high intensity is obviously due to the vibrational coupling between the carbonyl vibrations and the aromatic modes in (I) and (II).

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 C11–C12 [$1.426(3)\text{ \AA}$] and C11–C14 [$1.416(3)\text{ \AA}$] and single-bond character for C12–C13 [$1.528(3)\text{ \AA}$] and C13–C14 [$1.527(3)\text{ \AA}$]. The carbonyl group C13=O13 has a bond length of $1.209(3)\text{ \AA}$ corresponding to the IR frequency at 1796 cm^{-1} (KBr pellet). The bond lengths of the two ‘semi-carbonyl’ bonds C12–O12 and C14–O14 are both $1.230(3)\text{ \AA}$. A strong donor effect is observed for the 4-methoxy group. Conjugation between it and the positively charged strong acceptor N1 results in a shortening of the C13–O13 bond. The mean planes of the pyridinium and squarate ring systems are inclined at an angle of $5.3(2)^\circ$ with respect to one another.

Experimental

The title compound was synthesized according to a general literature procedure (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-methoxypyridine (1.23 g, 8.7 mmol) dissolved in acetic anhydride (10 ml) was then added. A yellow precipitate was obtained from the resulting dark-yellow solution after 45 min of heating and subsequent evaporation of half of the solvent. The product was filtered off after cooling and recrystallized from ethanol to afford (I) in 89% yield. The purity of the compound was confirmed by elemental analysis and mass spectrometry, IR and UV–vis spectrometry. Yellow single crystals suitable for X-ray analysis were grown from ethanol at room temperature over a period of two weeks.

Crystal data

$\text{C}_{10}\text{H}_7\text{NO}_4$	$D_x = 1.537\text{ Mg m}^{-3}$
$M_r = 205.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 14 reflections
$a = 4.5810(9)\text{ \AA}$	$\theta = 7.4\text{--}14.6^\circ$
$b = 11.744(2)\text{ \AA}$	$\mu = 0.12\text{ mm}^{-1}$
$c = 16.594(3)\text{ \AA}$	$T = 293(2)\text{ K}$
$\beta = 96.69(3)^\circ$	Block, yellow
$V = 886.6(3)\text{ \AA}^3$	$0.57 \times 0.27 \times 0.17\text{ mm}$
$Z = 4$	

Data collection

Siemens P4 four-circle diffractometer	1021 reflections with $I > 2\sigma(I)$
Profile-fitted ω scans	$R_{\text{int}} = 0.020$
Absorption correction: ψ scan (XPREP in SHELXTL-Plus; Sheldrick, 1995)	$\theta_{\text{max}} = 25.0^\circ$
$T_{\text{min}} = 0.963$, $T_{\text{max}} = 0.981$	$h = 0 \rightarrow 5$
1757 measured reflections	$k = 0 \rightarrow 13$
1553 independent reflections	$l = -19 \rightarrow 19$
	3 standard reflections every 100 reflections
	intensity decay: 2%

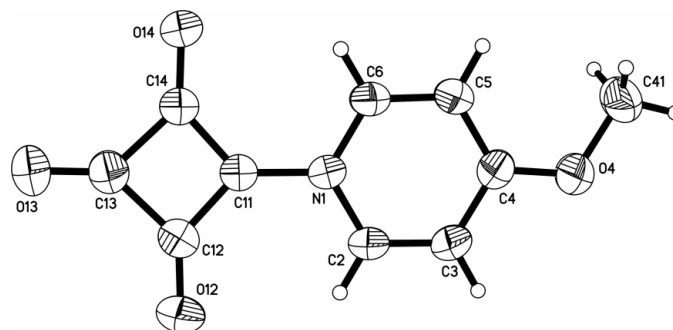


Figure 1

The molecular structure of (I), showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.1372P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.15\text{ e \AA}^{-3}$
1553 reflections	$\Delta\rho_{\text{min}} = -0.14\text{ e \AA}^{-3}$
142 parameters	Extinction correction: SHELXL97
Only H-atom U 's refined	Extinction coefficient: 0.0093 (19)

C–H distances are in the range $0.93\text{--}0.96\text{ \AA}$.

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.

TK, RW and MS thank the DAAD for a grant within the priority programme ‘Stability Pact South-Eastern Europe’, the Alexander von Humboldt Foundation and the Bulgarian National Fund for Research (grant No. X-1213).

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