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4-Dimethylaminopyridinium-1-squarate

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.086
Data-to-parameter ratio = 15.0

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

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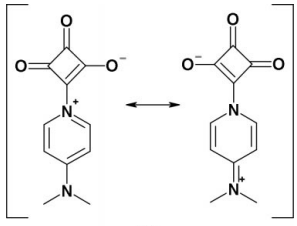
The crystal structure of the title compound, alternatively known as 4-dimethylaminopyridinium-betaine of squaric acid or 4-dimethylaminopyridiniumtrioxocyclobutylide, $C_{11}H_{10}N_2O_3$, contains a half molecule in the asymmetric unit. The nearly planar molecule [maximum deviation from planarity 0.077 (2) Å] is perpendicular to a mirror plane.

Comment

The title compound, (I), due to its negative solvatochromism, is supposed to be a good candidate for non-linear optical and electro-optical applications. The UV–vis spectra were measured in the following solvents: dichlorethane (368, 389, 445 nm), ethanol (357, 372, 422 nm), acetonitrile (364, 384, 440 nm), water (352, 364 nm) and 1-methylpyrrolidin-2-one (370, 389, 452 nm). The conversion of the N atom of 4-dimethylaminopyridine into the corresponding pyridinium betaine affords a way to enhance the charge-transfer transition on the molecular level, a requisite for the design of efficient second- and third-order non-linear optical materials.



(I)

The molecular geometry, determined by X-ray diffraction, lies between the two resonance structures shown in the chemical diagram.

There are no classical hydrogen bonds in the crystal, but there are some possible intra- and intermolecular non-classical hydrogen bonds. An intramolecular hydrogen bond connects an aromatic C—H group with an O atom [C4—H4···O2: C—H = 0.93 Å, H···O = 2.58 Å, $D\cdots A$ = 3.223 (2) Å and C4—H4···O2 = 127°]. The methyl groups are connected by intermolecular non-classical hydrogen bonds to O atoms [C7—H7A···O2($-x-1$, $-y+2$, $-z$): C—H = 0.96 Å, H···O = 2.58 Å, $D\cdots A$ = 3.510 (2) Å and C7—H7A···O2 = 162°; C7—H7B···O1 ($x-2$, y, $z-1$): C—H = 0.96 Å, H···O = 2.48 Å, $D\cdots A$ = 3.417 (2) Å and C7—H7B···O1 = 166°.

Experimental

The title compound was synthesized according to a general procedure described by Schmidt *et al.* (1984). Squaric acid (1 g, 8.7 mmol) was dissolved in 30 ml acetic anhydride by continuous stirring and heating

under reflux. A solution of 4-dimethylaminopyridine (1.36 g, 8.7 mmol) was added. After a few minutes the solution turned dark yellow. A yellow precipitate was obtained from the resulting dark-yellow solution after 30 min of heating and evaporation of half the solvent. The product was filtered off after cooling and recrystallized from ethanol (yield 90%, m.p. >600 K). The purity of the compound was confirmed by elemental analysis, IR, UV–vis and mass spectrometry. Yellow transparent crystals were grown from ethanol by slow evaporation at room temperature over a period of two weeks.

Crystal data

$C_{11}H_{10}N_2O_3$	D_x = 1.400 Mg m^{-3}
M_r = 218.21	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 4542 reflections
a = 4.1031 (4) Å	θ = 3.9–27.5°
b = 12.1158 (12) Å	μ = 0.10 mm^{-1}
c = 10.4553 (10) Å	T = 291 (1) K
β = 95.171 (6)°	Plate, yellow
V = 517.64 (9) Å^3	0.25 × 0.15 × 0.07 mm
Z = 2	

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.029
ω scans	θ_{max} = 27.5°
Absorption correction: none	$h = -5 \rightarrow 5$
4542 measured reflections	$k = -15 \rightarrow 15$
1243 independent reflections	$l = -13 \rightarrow 13$
514 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.086	$(\Delta/\sigma)_{max} < 0.001$
S = 0.91	$\Delta\rho_{max}$ = 0.12 e Å^{-3}
1243 reflections	$\Delta\rho_{min}$ = −0.15 e Å^{-3}
83 parameters	

H atoms were placed in calculated positions, with U_{iso} values constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. The methyl groups were allowed to rotate but not to tip.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97, *PARST*95 (Nardelli, 1995) and *PLATON* (Spek, 2001).

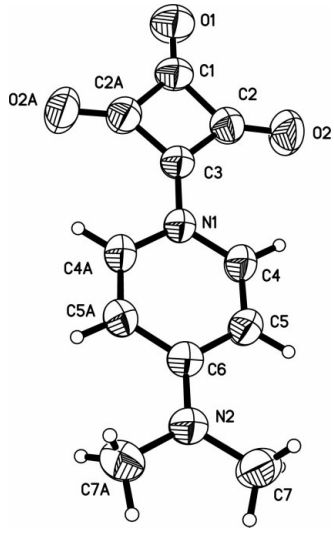


Figure 1
View of the title compound, showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as circles of arbitrary radii. The suffix A denotes a symmetry-generated atom $(x, \frac{3}{2} - y, z)$.

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