

4-Dimethylaminopyridinium-1-squarate

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Key indicators

Single-crystal X-ray study

$T = 291\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.037

w R factor = 0.086

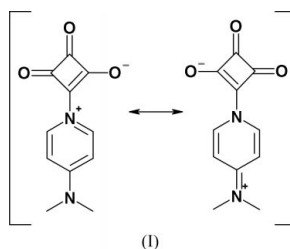
Data-to-parameter ratio = 15.0

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

The crystal structure of the title compound, alternatively known as 4-dimethylaminopyridinium-betaine of squaric acid or 4-dimethylaminopyridiniumtrioxocyclobutylide, $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_3$, contains a half molecule in the asymmetric unit. The nearly planar molecule [maximum deviation from planarity $0.077(2)\text{ \AA}$] 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: dichloroethane (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.



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...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...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...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

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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

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

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.029$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
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
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2]$
$wR(F^2) = 0.086$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1243 reflections	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
83 parameters	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$

H atoms were placed in calculated positions, with U_{iso} values constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and $1.2U_{\text{eq}}$ 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: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*, *PARST95* (Nardelli, 1995) and *PLATON* (Spek, 2001).

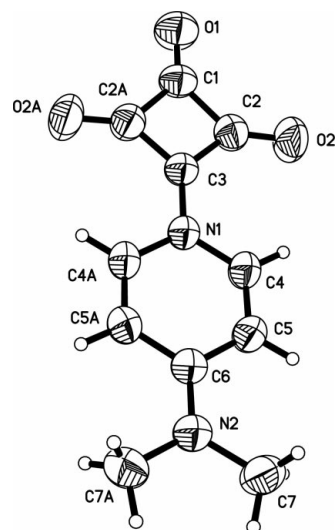


Figure 1

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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