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5-(*N*,*N*-Dimethylammoniomethyl)-2,2-dimethyl-4-oxido-6-oxo-6*H*-1,3-dioxine

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The title compound, $C_9H_{15}NO_4$, a Mannich base of Meldrum's acid, proves to be an inner salt.

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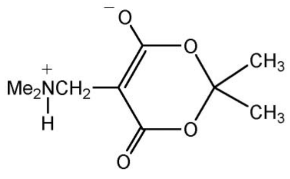
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.102
Data-to-parameter ratio = 9.5

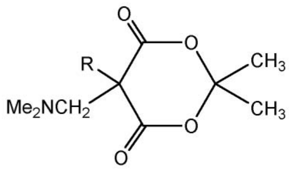
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Meldrum's acid and its 5-monosubstituted derivatives are versatile reagents with much stronger acidity than their corresponding acyclic malonates (McNab, 1978; Pihlaja & Seilo, 1968, 1969). According to our previous work (Li & Chen, 2000; Li *et al.*, 2001), there are also obvious differences between the aminomethyl derivatives, *i.e.* (I), the title compound, and (II), in their chemical and physical properties.



(I)



(II)

As described in our previous work (Li & Chen, 2000), (II) is soluble in polar organic solvents and can readily condense with some reactive methyl ketones. On the other hand, (I) is insoluble in most polar organic solvents but soluble in water. The IR spectrum of (I) exhibits a conjugated carbonyl absorption at 1680 cm^{-1} [1770 and 1730 cm^{-1} for (II)], and the ^{1}H NMR spectrum of (I) exhibits only one single peak at 1.64 p.p.m. for the two methyl groups on the dioxane ring [two single peaks at 0.9 and 1.7 p.p.m. for (II)]. Unlike (II), (I) is of low reactivity. All of these factors imply that (I) might be an inner salt (Li & Chen, 2000). In order to confirm this deduction, we examined (I) by X-ray structural analysis. The result shows that (I) is an inner salt. In the structure, the H atom originally attached to atom O3 is transferred to atom N1, and an N—H···O intramolecular hydrogen bond is formed (Fig. 1

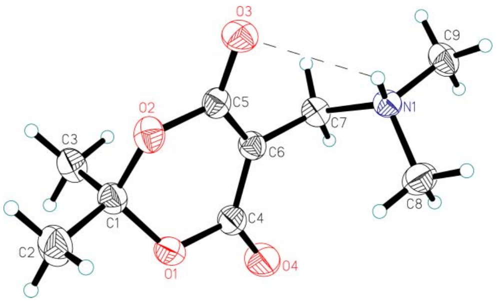


Figure 1
The molecular structure of (I) with the atom numbering, showing displacement ellipsoids at the 30% probability level.

and Table 2). There is also an intermolecular hydrogen bond, which is stronger (Table 2).

Experimental

$(Me_2N)_2CH_2$ (10 mmol) was added slowly to a stirred acetonitrile solution (20 ml) of Meldrum's acid (10 mmol) and acetic anhydride (11 mmol) with cooling. The mixture was stirred at room temperature for 30 min to complete the reaction. The precipitated crystals were collected, washed with acetonitrile and then recrystallized from water–acetone (1:1 *v*/*v*) to give single crystals with a yield of 95% (m.p. 433–434 K). IR (KBr, cm^{-1}): 2550, 1680, 1605, 1410, 1380, 1210. ^{1}H NMR (D_2O, p.p.m.): 1.64 (6H, *s*, C—CH_3, C—CH_3), 2.77 (6H, *s*, N—CH_3, N—CH_3), 3.84 (2H, *s*, CH_2), 4.67 (DHO). Analysis calculated for $C_9H_{15}NO_4$: C 53.72, H 7.51, N 6.96%; found: C 53.60, H 7.64, N 6.98%.

Crystal data

$C_9H_{15}NO_4$
$M_r = 201.22$
Triclinic, $P\bar{1}$
$a = 6.7922$ (5) Å
$b = 8.4862$ (8) Å
$c = 9.1518$ (8) Å
$\alpha = 99.810$ (6)°
$\beta = 101.532$ (3)°
$\gamma = 92.919$ (5)°
$V = 507.33$ (8) Å^3
$Z = 2$
$D_x = 1.317$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2555 reflections
$\theta = 3.0$–27.3°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.50 × 0.48 × 0.42 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: none
2699 measured reflections
1785 independent reflections
1519 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\rm max} = 25.0°$
$h = -7 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.102$
$S = 1.08$
1785 reflections
187 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 0.079P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O3—C5	1.2503 (16)	C6—C4	1.423 (2)
O4—C4	1.2196 (18)	C6—C5	1.3952 (19)
C4—C6—C7	121.08 (12)	O3—C5—C6	124.68 (12)
C5—C6—C4	120.87 (12)	O4—C4—C6	127.02 (13)
C5—C6—C7	117.43 (12)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3	0.86 (2)	2.51 (2)	3.0696 (16)	124 (1)
N1—H1···O3$^{\rm i}$	0.86 (2)	2.01 (2)	2.7740 (15)	148 (2)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

All H atoms were located in a difference Fourier map and refined isotropically [C—H = 0.94 (2)–1.010 (17) Å].

Data collection: *RAPID-AUTO* (Rigaku Corporation, 2001); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CrystalStructure*.

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