

2,2-Dimethyl-5-(*N*-methyl-*N*-methoxyaminomethylene)-1,3-dioxane-4,6-dioneAlexander J. Blake,^{a*} Hamish McNab^b and Kirsti Withell^b^aSchool of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England, and ^bDepartment of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

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Key indicators

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.043

wR factor = 0.119

Data-to-parameter ratio = 11.3

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

In the title compound, $\text{C}_9\text{H}_{13}\text{NO}_5$, the *N*-methoxy group adopts a conformation almost at right angles to the least-squares mean plane through the other two nitrogen substituents, in a direction opposite to that of the axial methyl substituent on the ring of the Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) moiety. There is an indication, at the limits of precision, that delocalization of the N-atom lone pair into the Meldrum's acid ring may be favoured in the direction of one of the two carbonyl groups. The structure is otherwise very similar to that of previously reported 2,2-dimethyl-5-(*N,N*-dimethylaminomethylene)-1,3-dioxane-4,6-dione [Blake *et al.* (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 2003–2010].

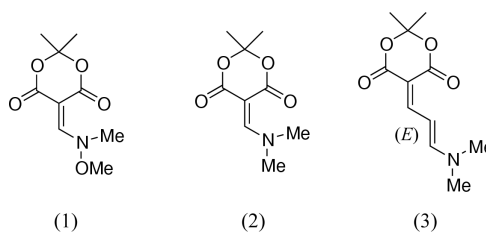
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Comment

The *N*-methoxy group N8—O10—C11 in the title compound, (1), adopts a conformation almost at right angles to the C7—N8—C9 plane [the dihedral angle is $89.3(2)^\circ$] in a direction opposite to that of the axial methyl substituent C2A on the Meldrum's acid ring (Fig. 1). The dihedral angle between the C4/C5/C6 and the C7/N8/C9 planes is $26.0(6)^\circ$. By comparison with its *N,N*-dimethyl analogue, (2) (Blake *et al.*, 1991), the methoxy group has comparatively little structural influence on the molecule as a whole. Thus, many of the values of the corresponding bond lengths and valence angles in (1) and (2) (including C5—C7 and C7—N8) lie within one s.u. of one another and most are within three s.u.'s. The sole significant exceptions appear to be the bond angles around N8. Thus, in (1), C7—N8—C9 is increased to $130.7(2)^\circ$ and C7—N8—O10 reduced to $115.1(2)^\circ$ from the corresponding values in (2), which are $123.0(3)^\circ$ and $121.2(3)^\circ$, respectively.



There is an indication, at the limit of the precision of our results, that delocalization of the N8 lone pair into the Meldrum's acid ring may be favoured in the direction of C5—C4—O4. Thus C4—C5 [1.437(4) Å] displays more double-bond character than C5—C6 [1.452(4) Å] and C4—O4 [1.218(3) Å] correspondingly displays more single-bond character than C6—O6 [1.208(3) Å]. Although this feature was not observed in the structure of (2), we have previously

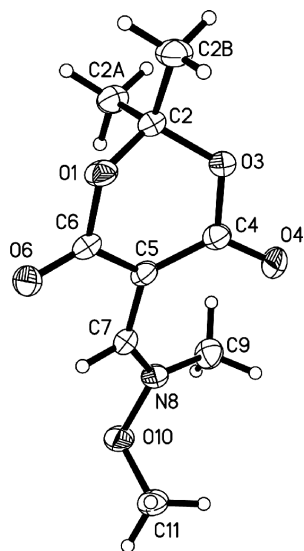


Figure 1

The molecular structure and atom-numbering scheme for 2,2-dimethyl-5-(*N*-methyl-*N*-methoxyaminomethylene)-1,3-dioxane-4,6-dione. Displacement ellipsoids are drawn at the 30% probability level.

made a similar observation in the structure of the vinyllogue (3) (Blake *et al.*, 1991). Interestingly, in this case, the preferred delocalization took place towards the other carbonyl group.

Experimental

The title compound was made by treatment of *N,O*-dimethylhydroxylamine hydrochloride with methoxymethylene Meldrum's acid in acetonitrile solution, in the presence of triethylamine (McNab & Withell, 2000). Crystals were grown from an ethanol solution.

Crystal data

$C_9H_{13}NO_5$
 $M_r = 215.20$
 Triclinic, $P\bar{1}$
 $a = 6.477$ (5) Å
 $b = 7.769$ (5) Å
 $c = 11.675$ (12) Å
 $\alpha = 98.04$ (7)°
 $\beta = 100.50$ (7)°
 $\gamma = 112.71$ (5)°
 $V = 518.4$ (7) Å³

$Z = 2$
 $D_x = 1.379$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 14 reflections
 $\theta = 5.5$ – 12.3 °
 $\mu = 0.11$ mm⁻¹
 $T = 150$ (2) K
 Cuboid, colourless
 $0.23 \times 0.19 \times 0.19$ mm

Data collection

Stoe Stadi-4 four-circle diffractometer
 ω - 2θ scans
 Absorption correction: none
 2066 measured reflections
 1580 independent reflections
 1259 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.022$

$\theta_{max} = 25.0$ °
 $h = -7 \rightarrow 6$
 $k = -8 \rightarrow 9$
 $l = 0 \rightarrow 13$
 3 standard reflections
 frequency: 60 min
 intensity decay: 12%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.119$
 $S = 1.12$
 1580 reflections
 140 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.537P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.21$ e Å⁻³
 $\Delta\rho_{min} = -0.24$ e Å⁻³

All H atoms were located from a ΔF synthesis, but they were included at geometrically calculated positions. For methyl H atoms C–H was fixed at 0.98 Å; for the remaining H atom this distance was 0.95 Å, and $U_{iso}(H) = xU_{eq}(C)$, with $x = 1.5$ for methyl H atoms and 1.2 for the other.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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