

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: MU1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2-Dimethyl-5-(2-methyl-4-phenyl-3,4-diaza-2-butenylidene)-1,3-dioxane-4,6-dione

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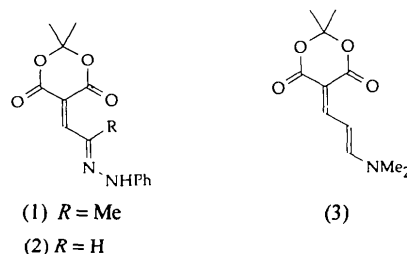
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Abstract

The molecular conformation of the title compound, $C_{15}H_{16}N_2O_4$, is described in terms of three planar sections which are mutually twisted. The main intermolecular contacts are $N-H \cdots O$ hydrogen bonds where the $O \cdots N$ separation is 3.063 (3) Å.

Comment

The study of the structure of the title compound, (1), was undertaken to determine whether there were conformational reasons for its ready cyclization to give a 3-oxopyridazinecarboxylic acid upon thermolysis in solution, while the corresponding unsubstituted compound (2) is recovered unchanged under similar conditions (McNab & Stobie, 1982). The structure of (1) is also related to that of the propenylidene Meldrum's acid derivative (3), which we have described recently (Blake, McNab & Monahan, 1991).



The conjugated system from C5 to N10 in (1) is exclusively *trans*, as found for (3), and so the cyclization reaction cannot be explained by a ground-state proximity of N10 and C4.

A feature of the structure of (3) is that electron delocalization occurs along the propenyl chain such that the lengths of all the C—C and C=C bonds are comparable [1.385 (8)–1.409 (8) Å]. In the case of (1), the system is much more localized [C=C 1.355 (3), C—C 1.439 (3) Å], partly due to poorer electron donation from the hydrazone N atom N10 compared with the terminal amino group in (3), and also partly due to the non-planarity of the system (see below). This reduced electron donation is also reflected in the lengths of the C4—C5 and C5—C6 bonds [both 1.469 (3) Å], which are substantially longer than the corresponding values for (3) [1.449 (8), 1.417 (8) Å].

The presence of the C8M methyl substituent in (1) has a dramatic effect on the angles subtended at C8 and C5. Non-bonded contacts between the C8M methyl group and O4 lead to widening of the C7—C8—C8M and C8M—C8—N9 angles to 125.7 (2) and 123.7 (2)°, respectively, with a concomitant reduction in the C7—C8—N9 angle to 110.5 (2)°. The C4—C5—C7 angle is widened to 126.0 (2)°, compared with an angle of 120.9 (5)° in (3). This distortion is almost entirely at the expense of the endocyclic C4—C5—C6 angle [116.5 (2)°, compared with 121.7 (5)° in (3)]. A similar trend at C5 has been noted for the corresponding angles in the dimethylaminomethylene Meldrum's acid, which has analogous steric constraints (Blake, McNab & Monahan, 1991). In (1), the two exocyclic N—C—C angles involving the phenyl group differ significantly, possibly because of repulsion between the *ortho* H6P atom and the lone pair on N9.

The molecular conformation of (1) can be described in terms of three planar sections: the phenyl ring, the five-atom chain C5—C7—C8—N9—N10 with its C8M substituent, and four atoms (O1, O3, C4 and C6) of the Meldrum's acid ring. The angle between the normals to the phenyl ring and the chain is 10.2 (2)° and the angle between the normals to the chain and the plane of the Meldrum's acid ring is 20.5 (2)°. In contrast, there is a much greater degree of coplanarity between the chain and the Meldrum's acid ring in (3). The mean deviation from the plane of the chain is 0.058 Å, while the four atoms defining the Meldrum's acid plane

are essentially coplanar (mean deviation 0.0013 Å). Within the Meldrum's acid ring, C5 is displaced in one direction from the plane by 0.276(3) Å, while O4 and O6 are displaced in the opposite direction by 0.330(3) and 0.244(3) Å, respectively; the greater deviation of O4 may be explained by the proximity of C8M. These distortions may be sufficient to lower the activation energy for bond rotation relative to that in the unsubstituted compound (2) so that thermal cyclization may take place.

The principal intermolecular contacts are hydrogen bonds between N10—H10 and O6 at $(x, 1+y, z)$, which link the molecules to form chains parallel to the *b* axis.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0397$
 $wR(F^2) = 0.1394$
 $S = 1.124$
 1845 reflections
 185 parameters
 H10 was constrained to lie 1.00 Å from N10; other H atoms were placed in calculated positions.
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.367$

$\Delta\rho_{\max} = 0.216 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.200 \text{ e } \text{Å}^{-3}$
 Extinction correction:
 SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.046 (9)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

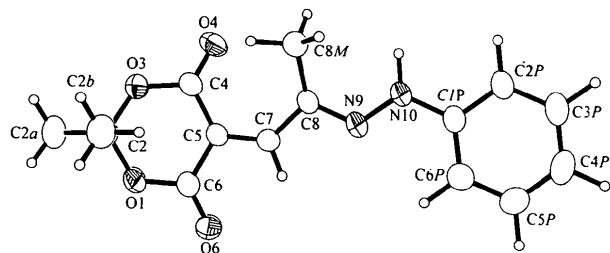


Fig. 1. A view of the molecule with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O1	0.2374 (2)	0.2956 (2)	0.82567 (12)	0.0474 (5)
C2	0.2004 (3)	0.4137 (2)	0.7209 (2)	0.0408 (6)
C2A	0.2316 (4)	0.3119 (3)	0.6290 (2)	0.0569 (7)
C2B	0.0055 (3)	0.5346 (3)	0.7267 (2)	0.0554 (7)
O3	0.3367 (2)	0.5016 (2)	0.69950 (11)	0.0439 (4)
C4	0.3673 (3)	0.5714 (2)	0.7839 (2)	0.0400 (6)
O4	0.4654 (2)	0.6617 (2)	0.76169 (13)	0.0602 (5)
C5	0.2926 (3)	0.5147 (2)	0.8982 (2)	0.0355 (5)
C6	0.2617 (3)	0.3502 (3)	0.9186 (2)	0.0412 (6)
O6	0.2589 (3)	0.2608 (2)	1.01041 (13)	0.0615 (5)
C7	0.2684 (3)	0.5915 (2)	0.9891 (2)	0.0384 (5)
C8	0.2622 (3)	0.7571 (2)	1.0000 (2)	0.0364 (5)
C8M	0.2414 (3)	0.9034 (3)	0.9051 (2)	0.0491 (6)
N9	0.2675 (2)	0.7654 (2)	1.10718 (14)	0.0381 (5)
N10	0.2704 (2)	0.9075 (2)	1.13387 (13)	0.0387 (5)
C1P	0.2730 (2)	0.9166 (2)	1.24865 (8)	0.0354 (5)
C2P	0.3019 (2)	1.05723 (14)	1.27502 (9)	0.0419 (6)
C3P	0.3058 (2)	1.06988 (15)	1.38855 (11)	0.0490 (6)
C4P	0.2809 (2)	0.9418 (2)	1.47570 (8)	0.0561 (7)
C5P	0.2520 (3)	0.8012 (2)	1.44930 (9)	0.0610 (7)
C6P	0.2481 (2)	0.78853 (15)	1.33577 (11)	0.0526 (6)

Experimental

The title compound was obtained by the reaction of PhNHN=C(Me)CHO with 2,2-dimethyl-1,3-dioxane-4,6-dione. Crystals were grown from ethanol (McNab & Stobie, 1982).

Crystal data

C₁₅H₁₆N₂O₄
 $M_r = 288.30$
 Triclinic
 $P\bar{1}$
 $a = 7.544 (3) \text{ Å}$
 $b = 8.576 (3) \text{ Å}$
 $c = 12.014 (7) \text{ Å}$
 $\alpha = 78.01 (3)^\circ$
 $\beta = 83.36 (3)^\circ$
 $\gamma = 71.41 (3)^\circ$
 $V = 719.6 (6) \text{ Å}^3$
 $Z = 2$
 $D_x = 1.330 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ Å}$
 Cell parameters from 12 reflections
 $\theta = 15\text{--}16^\circ$
 $\mu = 0.098 \text{ mm}^{-1}$
 $T = 295 (2) \text{ K}$
 Lath
 $0.75 \times 0.33 \times 0.075 \text{ mm}$
 Orange

Table 2. Selected geometric parameters (Å, °)

Data collection

Stoe Stadi-4 diffractometer
 ω - 2θ scans
 Absorption correction: none
 1858 measured reflections
 1847 independent reflections
 1499 observed reflections
 $[I > 2\sigma(I)]$

$R_{int} = 0.0116$
 $\theta_{\max} = 22.52^\circ$
 $h = -7 \rightarrow 8$
 $k = -8 \rightarrow 9$
 $l = 0 \rightarrow 12$
 3 standard reflections
 frequency: 120 min
 intensity decay: 2.0%

O1—C6	1.349 (3)	C5—C7	1.355 (3)
O1—C2	1.435 (3)	C5—C6	1.469 (3)
C2—O3	1.430 (2)	C6—O6	1.208 (3)
C2—C2A	1.499 (3)	C7—C8	1.439 (3)
C2—C2B	1.508 (3)	C8—N9	1.309 (3)
O3—C4	1.354 (2)	C8—C8M	1.490 (3)
C4—O4	1.206 (3)	N9—N10	1.330 (2)
C4—C5	1.469 (3)	N10—C1P	1.400 (2)
C6—O1—C2	118.2 (2)	C4—C5—C6	116.5 (2)
O3—C2—O1	109.1 (2)	O6—C6—O1	118.2 (2)
O3—C2—C2A	107.0 (2)	O6—C6—C5	125.5 (2)
O1—C2—C2A	105.9 (2)	O1—C6—C5	116.2 (2)
O3—C2—C2B	110.4 (2)	C5—C7—C8	132.9 (2)
O1—C2—C2B	110.6 (2)	N9—C8—C7	110.5 (2)
C2A—C2—C2B	113.5 (2)	N9—C8—C8M	123.7 (2)
C4—O3—C2	118.4 (2)	C7—C8—C8M	125.7 (2)
O4—C4—O3	118.2 (2)	C8—N9—N10	119.2 (2)
O4—C4—C5	125.6 (2)	N9—N10—C1P	119.06 (15)
O3—C4—C5	115.9 (2)	C6P—C1P—N10	121.38 (10)
C7—C5—C4	126.0 (2)	C2P—C1P—N10	118.60 (10)
C7—C5—C6	117.1 (2)		
C4—C5—C7—C8	16.6 (4)	C8M—C8—N9—N10	−5.9 (3)
C6—C5—C7—C8	−170.8 (2)	C8—N9—N10—C1P	179.0 (2)
C5—C7—C8—N9	−169.2 (2)	N9—N10—C1P—C6P	−8.5 (2)
C5—C7—C8—C8M	14.2 (4)	N9—N10—C1P—C2P	171.33 (13)
C7—C8—N9—N10	177.4 (2)		

The phenyl ring (C1P to C6P) was constrained as a regular hexagon with C—C distances of 1.390 Å. Data collection and cell refinement: *DIF4* (Stoe & Cie, 1988a). Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

We thank the SERC for funding towards the provision of a four-circle diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and torsion angles have been deposited with the IUCr (Reference: HA1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2*RS*)-4,4-Dimethyl-2-[(1*SR*)-1-phenylethyl]-1-pyrrolidinol

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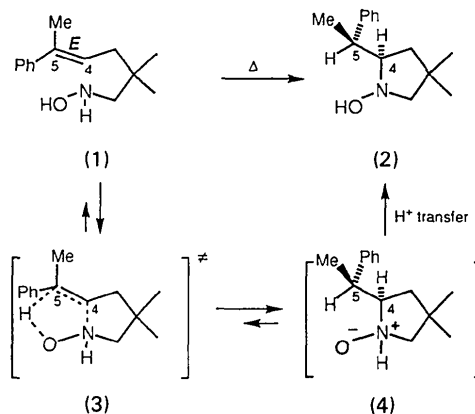
Abstract

In order to determine the stereospecificity of the thermal cyclization of [(*E*)-2,2-dimethyl-5-phenyl-4-hexenyl]hydroxylamine (1), the relative configuration of the title compound, C₁₄H₂₁NO, (2), has been established by single-crystal X-ray diffraction. The pyrrolidine ring adopts an envelope conformation with the N atom out

of the ring plane. The molecules form hydrogen-bonded pairs through a centre of inversion [O···N 2.808 (5) Å and O—H···N 160 (4)°].

Comment

The thermal cyclization of *N*-alkenylhydroxylamines, first reported by House and co-workers (House, Manning, Melillo, Lee, Haynes & Wilkes, 1976; House & Lee, 1976) and independently discovered by us (Oppolzer, Siles, Snowden, Bakker & Petrzilka, 1979), was initially proposed to occur *via* a radical chain mechanism. As an alternative to the thermal conversion of *N*-alkenyl-*N*-methylhydroxylamines to cyclic *N*-oxides, a retro-Cope elimination mechanism has also been postulated (Ciganek, 1990). However, compelling proof of either mechanism has not yet been presented.



In order to study the alkene faciality of this process, the (*E*)-5,5-disubstituted 4-alkenylhydroxylamine (1) was cyclized by heating it in degassed benzene under reflux (18 h) to provide the *N*-hydroxypyrrolidine (2) (m.p. 358–359 K) in 81% yield. Under analogous reaction conditions, the *Z* isomer of (1) gave an epimer of (2) (oil, yield 81%) without cross contamination (Oppolzer, Spivey & Bochet, 1994).

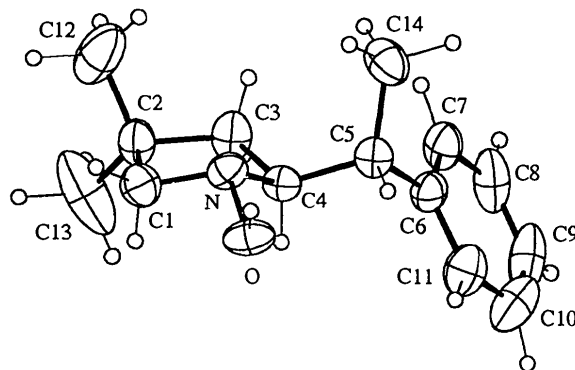


Fig. 1. View of the *N*-hydroxypyrrolidine (2) with the atomic labelling of non-H atoms shown. Ellipsoids are shown at the 30% probability level.