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(Z)-Methyl 2-methoxyimino-3-oxobutanoateJin-Yong Lu,^{a,b} Wei-Zheng Shen,^a Hans Preut^{a*} and Hans-Dieter Arndt^{a,b*}^aFakultät Chemie, Technische Universität Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany, and ^bMax-Planck-Institut für Molekulare Physiologie, Otto-Hahn-Strasse 11, 44221 Dortmund, Germany

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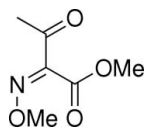
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.028; wR factor = 0.058; data-to-parameter ratio = 8.6.

The title compound, $\text{C}_6\text{H}_9\text{NO}_4$, was prepared stereoselectively as a precursor for 1-azadienes in a study of hetero-Diels-Alder reactions. The configuration of the $\text{C}=\text{N}$ double bond was found to be *Z*, corroborating earlier assignments of similar compounds based only on NMR and IR spectroscopic analysis.

Related literature

For related literature, see: Buehler (1967); Corrêa & Moran (1999); Fletcher *et al.* (2006); François *et al.* (2004); Jirman *et al.* (1990); Karabatsos & Taller (1968); Levy & Nelson (1972); Lu & Arndt (2007).



Experimental

Crystal data

 $\text{C}_6\text{H}_9\text{NO}_4$
 $M_r = 159.14$

 Orthorhombic, $Pna2_1$
 $a = 8.3410$ (17) Å

 $b = 13.410$ (3) Å
 $c = 7.2900$ (15) Å
 $V = 815.4$ (3) Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 291$ (1) K
 $0.2 \times 0.2 \times 0.2$ mm

Data collection

 Nonius KappaCCD diffractometer
 Absorption correction: none
 3104 measured reflections

 899 independent reflections
 536 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.057$
 $S = 1.09$
 899 reflections
 104 parameters

 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.08$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.11$ e Å⁻³

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2698).

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supporting information

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(Z)-Methyl 2-methoxyimino-3-oxobutanoate

Jin-Yong Lu, Wei-Zheng Shen, Hans Preut and Hans-Dieter Arndt

S1. Comment

Oxime geometry has been found to be important for determining their reactivity in cycloadditions and pericyclic reactions (*e.g.* François *et al.*, 2004). The title compound, (I), was prepared in the study of hetero-Diels–Alder reactions to form 3-hydroxy-pyridines (Lu & Arndt, 2007; Fletcher *et al.*, 2006).

The crystal structure of (I) (Fig. 1) verifies earlier studies by NMR and IR (Buehler, 1967; Karabatsos & Taller, 1968; Levy & Nelson, 1972; Jirman *et al.*, 1990; Corrêa & Moran, 1999) of *Z*-configured oximes and forms a basis for further studies in the field. Interestingly, the C1/O2/O4 carboxyl group in (I) adopts a dihedral angle of 93° with respect to the coplanar N?C—C?O π -system, which indicates complete absence of electronic conjugation.

S2. Experimental

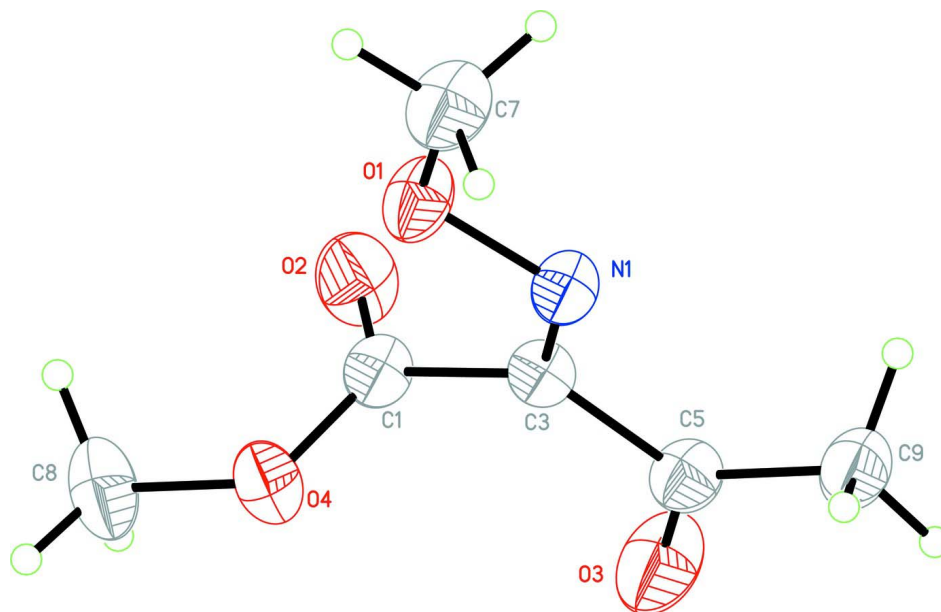
A stirred solution of 7.25 g (50.0 mmol) of *Z*-Methyl 2-(hydroxyimino)-3-oxobutanoate (Lu & Arndt, 2007; Fletcher *et al.*, 2006) in anhydrous acetone (50 ml) was cooled to 273 K and potassium carbonate (3.8 g, 27.5 mmol) was added, followed by dimethyl sulfate (5.70 ml, 60.0 mmol). The stirred reaction mixture was warmed to room temperature over 2 h and kept stirring for 10 h (TLC control). The reaction mixture was filtered and the solid residue was rinsed with acetone (3 × 10 ml). The combined filtrates were evaporated to dryness, redissolved in Et₂O (100 ml), washed with sat. NaCl solution (3 × 40 ml) and dried with Na₂SO₄. Concentration and purification by column chromatography (100 g SiO₂, EtOAc/light petroleum $v/v = 1:8$) gave 7.60 g (47.8 mmol, 96%) of the title compound as a colourless oil which crystallized on standing as colourless cubes.

Mp = 335–337 K; $R_f = 0.46$ (SiO₂, EtOAc/cyclohexane = 1:2); ¹H NMR (400 MHz, CDCl₃) $\delta = 2.38$ (3H, s, C(O)CH₃), 3.85 (3H, s, =NOCH₃), 4.08 (3H, s, COOCH₃); ¹³C NMR (100.6 MHz, CDCl₃) $\delta = 25.1$ (C(O)CH₃), 52.5 (COOCH₃), 64.4 (NOCH₃), 149.9 (C=N), 161.5 (COOCH₃), 192.7 (C(O)CH₃); IR (KBr): $\nu = 3009w, 2951w, 1744 s, 1683 s, 1596 s, 1241 s, 1021 s, 841 s$ cm⁻¹; HRMS (EI): m/z calc. for C₆H₉NO₄ [M^+]: 159.0532, found: 159.0524.

S3. Refinement

Anomalous dispersion was negligible and Friedel pairs were merged before refinement.

The H atoms were placed in calculated positions, with C—H = 0.96 Å and were refined as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$; the methyl groups were allowed to rotate but not to tip.

**Figure 1**

The molecular structure of (I) with displacement ellipsoids shown at the 30% probability level (arbitrary spheres for the H atoms).

(Z)-Methyl 2-methoxyimino-3-oxobutanoate*Crystal data*C₆H₉NO₄ $M_r = 159.14$ Orthorhombic, *Pna*2₁

Hall symbol: P 2c -2n

 $a = 8.3410 (17) \text{ \AA}$ $b = 13.410 (3) \text{ \AA}$ $c = 7.2900 (15) \text{ \AA}$ $V = 815.4 (3) \text{ \AA}^3$ $Z = 4$ $F(000) = 336$ $D_x = 1.296 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3104 reflections

 $\theta = 3.0\text{--}27.5^\circ$ $\mu = 0.11 \text{ mm}^{-1}$ $T = 291 \text{ K}$

Cube, colourless

 $0.2 \times 0.2 \times 0.2 \text{ mm}$ *Data collection*

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 19 vertical, 18 horizontal
pixels mm⁻¹213 frames via ω -rotation ($\Delta\omega = 1^\circ$) and two
times 40 s per frame (four sets at different κ -
angles) scans

3104 measured reflections

899 independent reflections

536 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.045$ $\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 3.9^\circ$ $h = -10 \rightarrow 10$ $k = -16 \rightarrow 16$ $l = -9 \rightarrow 9$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.027$ $wR(F^2) = 0.057$ $S = 1.09$

899 reflections

104 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.08 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.11 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.087 (6)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.14686 (19)	0.12432 (11)	0.8457 (2)	0.0633 (5)
O2	0.1931 (2)	0.03995 (12)	0.4285 (2)	0.0784 (6)
O3	0.4017 (2)	0.23981 (12)	0.3446 (3)	0.0923 (7)
O4	0.4114 (2)	0.03491 (11)	0.6049 (2)	0.0634 (5)
N1	0.19750 (19)	0.20788 (12)	0.7495 (3)	0.0536 (5)
C1	0.2847 (3)	0.07762 (15)	0.5349 (3)	0.0520 (6)
C3	0.2673 (2)	0.18321 (15)	0.5998 (3)	0.0463 (5)
C5	0.3291 (3)	0.26405 (17)	0.4804 (3)	0.0557 (6)
C7	0.0702 (3)	0.15466 (19)	1.0136 (3)	0.0749 (8)
H7A	0.0349	0.0967	1.0796	0.112*
H7B	-0.0205	0.1961	0.9857	0.112*
H7C	0.1449	0.1914	1.0875	0.112*
C8	0.4383 (4)	-0.06865 (16)	0.5537 (3)	0.0819 (9)
H8A	0.5226	-0.0960	0.6279	0.123*
H8D	0.4683	-0.0721	0.4268	0.123*
H8B	0.3416	-0.1061	0.5727	0.123*
C9	0.3008 (3)	0.37018 (15)	0.5307 (4)	0.0674 (7)
H9A	0.3481	0.4128	0.4397	0.101*
H9B	0.3484	0.3836	0.6480	0.101*
H9D	0.1875	0.3826	0.5367	0.101*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0881 (11)	0.0498 (9)	0.0519 (9)	-0.0045 (8)	0.0208 (9)	0.0002 (9)
O2	0.0868 (13)	0.0657 (11)	0.0828 (13)	0.0028 (9)	-0.0205 (12)	-0.0202 (11)
O3	0.1322 (17)	0.0691 (12)	0.0755 (13)	-0.0101 (10)	0.0492 (14)	-0.0068 (11)
O4	0.0676 (10)	0.0551 (9)	0.0675 (10)	0.0137 (8)	-0.0078 (9)	-0.0037 (9)
N1	0.0625 (12)	0.0471 (11)	0.0510 (12)	-0.0028 (9)	0.0046 (12)	0.0004 (10)

supporting information

C1	0.0601 (14)	0.0494 (13)	0.0467 (14)	-0.0018 (13)	0.0041 (14)	-0.0023 (13)
C3	0.0483 (12)	0.0491 (13)	0.0415 (12)	0.0010 (10)	-0.0001 (12)	-0.0037 (12)
C5	0.0615 (16)	0.0567 (15)	0.0490 (14)	-0.0031 (12)	0.0063 (13)	-0.0008 (13)
C7	0.0981 (19)	0.0731 (17)	0.0535 (16)	-0.0063 (16)	0.0276 (15)	-0.0040 (14)
C8	0.1075 (19)	0.0597 (17)	0.079 (2)	0.0278 (14)	0.0040 (16)	0.0008 (15)
C9	0.0773 (15)	0.0517 (14)	0.0732 (17)	-0.0057 (13)	0.0087 (13)	0.0009 (15)

Geometric parameters (Å, °)

O1—N1	1.387 (2)	C7—H7A	0.9600
O1—C7	1.440 (3)	C7—H7B	0.9600
O2—C1	1.200 (3)	C7—H7C	0.9600
O3—C5	1.205 (3)	C8—H8A	0.9600
O4—C1	1.306 (3)	C8—H8D	0.9600
O4—C8	1.455 (2)	C8—H8B	0.9600
N1—C3	1.281 (3)	C9—H9A	0.9600
C1—C3	1.500 (3)	C9—H9B	0.9600
C3—C5	1.483 (3)	C9—H9D	0.9600
C5—C9	1.489 (3)		
N1—O1—C7	109.67 (16)	O1—C7—H7C	109.5
C1—O4—C8	116.29 (19)	H7A—C7—H7C	109.5
C3—N1—O1	111.12 (17)	H7B—C7—H7C	109.5
O2—C1—O4	125.7 (2)	O4—C8—H8A	109.5
O2—C1—C3	122.6 (2)	O4—C8—H8D	109.5
O4—C1—C3	111.7 (2)	H8A—C8—H8D	109.5
N1—C3—C5	118.01 (19)	O4—C8—H8B	109.5
N1—C3—C1	123.8 (2)	H8A—C8—H8B	109.5
C5—C3—C1	118.1 (2)	H8D—C8—H8B	109.5
O3—C5—C3	117.4 (2)	C5—C9—H9A	109.5
O3—C5—C9	122.7 (2)	C5—C9—H9B	109.5
C3—C5—C9	119.9 (2)	H9A—C9—H9B	109.5
O1—C7—H7A	109.5	C5—C9—H9D	109.5
O1—C7—H7B	109.5	H9A—C9—H9D	109.5
H7A—C7—H7B	109.5	H9B—C9—H9D	109.5