Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Jin-Yong Lu,[a,b] Wei-Zheng Shen,[a] Hans Preut[a]* and Hans-Dieter Arndt[a,b]*

[a]Fakultät Chemie, Technische Universität Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany, and [b]Max-Planck-Institut für Molekulare Physiologie, Otto-Hahn-Strasse 11, 44221 Dortmund, Germany
Correspondence e-mail: hans.preut@udo.edu, hans-dieter.arndt@mpi-dortmund.mpg.de

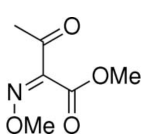
Received 31 January 2008; accepted 13 February 2008

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.058; data-to-parameter ratio = 8.6.

The title compound, $C_6H_9NO_4$, was prepared stereoselectively as a precursor for 1-azadienes in a study of hetero-Diels–Alder reactions. The configuration of the C=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

$C_6H_9NO_4$
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) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 291 (1) K
0.2 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
3104 measured reflections
899 independent reflections
536 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 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
$\Delta\rho_{\rm max}$ = 0.08 e Å^{-3}
$\Delta\rho_{\rm min}$ = −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).

Funding by the Deutsche Forschungsgemeinschaft (Emmy–Noether grant Nos. AR493-1 and -2 to HDA), the Fonds der Chemischen Industrie, and the IMPRS Chemical Biology (to JYL and WZS) is gratefully acknowledged.

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

References

Buehler, E. (1967). *J. Org. Chem.* **32**, 261–265.
Corrêa, I. R. Jr & Moran, P. J. S. (1999). *Tetrahedron*, **55**, 14221–14232.
Fletcher, M. D., Hurst, T. E., Miles, T. J. & Moody, C. J. (2006). *Tetrahedron*, **62**, 5454–5463.
François, D., Madden, A. & Murray, W. V. (2004). *Org. Lett.* **6**, 1931–1934.
Jirman, J., Lycka, A. & Ludwig, M. (1990). *Collect. Czech. Chem. Commun.* **55**, 136–146.
Karabatsos, G. J. & Taller, R. A. (1968). *Tetrahedron*, **24**, 3347–3360.
Levy, G. C. & Nelson, G. L. (1972). *J. Am. Chem. Soc.* **94**, 4897–4901.
Lu, J.-Y. & Arndt, H.-D. (2007). *J. Org. Chem.* **72**, 4205–4212.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2008). E**64**, o602 [**doi:10.1107/S1600536808004376**]

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

J.-Y. Lu, W.-Z. Shen, H. Preut and H.-D. Arndt

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.

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 Et_2O (100 ml), washed with sat. NaCl solution (3 × 40 ml) and dried with Na_2SO_4. Concentration and purification by column chromatography (100 g SiO_2, 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 (SiO_2, EtOAc/cyclohexane = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.38 (3*H*, s, C(O)CH3), 3.85 (3*H*, s, =$NOCH_3$), 4.08 (3*H*, s, $COOCH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 25.1 (C(O)CH_3), 52.5 ($COOCH_3$), 64.4 ($NOCH_3$), 149.9 (C=N), 161.5 ($COOCH_3$), 192.7 (C(O)CH_3); IR (KBr): ν = 3009w, 2951w, 1744 s, 1683 s, 1596 s, 1241 s, 1021 s, 841 s cm^{-1}; HRMS (EI): m/*Z* calc. for $C_6H_9NO_4$ [M^+]: 159.0532, found: 159.0524.

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.

Figures

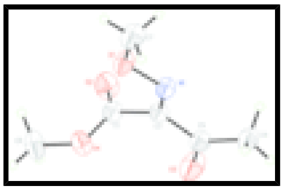


Fig. 1. The molecular structure of (I) with displacement ellipsoids shown at the 30% probability level (arbitrary spheres for the H atoms).

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

Crystal data

$C_6H_9NO_4$	F_{000} = 336
M_r = 159.14	D_x = 1.296 Mg m^{-3}
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2c -2n	Cell parameters from 3104 reflections
a = 8.3410 (17) Å	θ = 3.0–27.5º
b = 13.410 (3) Å	μ = 0.11 mm^{-1}
c = 7.2900 (15) Å	T = 291 (1) K
V = 815.4 (3) Å^3	Cube, colourless
Z = 4	0.2 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer	899 independent reflections
Radiation source: fine-focus sealed tube	536 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.045
Detector resolution: 19 vertical, 18 horizontal pixels mm^{-1}	θ_{max} = 26.4º
T = 291(1) K	θ_{min} = 3.9º
213 frames via ω–rotation (Δω = 1%) and two times 40 s per frame (four sets at different κ–angles) scans	h = −10→10
Absorption correction: none	k = −16→16
3104 measured reflections	l = −9→9

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.027	H-atom parameters constrained
$wR(F^2)$ = 0.057	$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.09	$(\Delta/\sigma)_{max}$ < 0.001
899 reflections	$\Delta\rho_{max}$ = 0.08 e Å^{-3}

104 parameters	$\Delta\rho_{min}$ = −0.11 e Å^{-3}
1 restraint	Extinction correction: SHELXL97 (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	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 > 2sigma(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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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)
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

Fig. 1