

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(1*S*,2*S*,5*S*)-2-Methyl-3-oxo-5-(prop-1-en-2-yl)cyclohexane-1-carbonitrile

 Marcos L. Rivadulla,^a Alioune Fall,^a María González^a and Maria J. Matos^{b*}
^aDepartamento de Química Orgánica, Facultade de Química, Universidade de Vigo, E-36310 Vigo, Spain, and ^bDepartamento de Química Orgánica, Facultade de Farmacia, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Correspondence e-mail: mariacmatos@gmail.com

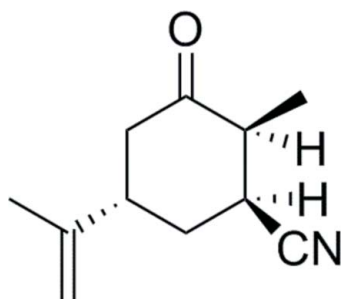
Received 19 April 2013; accepted 24 April 2013

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.052; wR factor = 0.164; data-to-parameter ratio = 21.6.

The molecule of the title compound, $\text{C}_{11}\text{H}_{15}\text{NO}$, contains a cyclohexanone ring, three defined stereocenters and an exocyclic double bond. The crystal structure is the result of a study on the Michael addition reaction of (*S*)-carvone with sodium cyanide using ionic liquids as the reaction medium and so the absolute configuration is known from the chemistry. The six-membered ring is in a chair conformation.

Related literature

For recent review of Ionic liquids as solvents, see: Welton (1999); Wasserscheid & Keim (2000).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{15}\text{NO}$	$V = 1109.1(3) \text{ \AA}^3$
$M_r = 177.24$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 5.2892(8) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 10.7213(16) \text{ \AA}$	$T = 293 \text{ K}$
$c = 19.559(3) \text{ \AA}$	$0.60 \times 0.56 \times 0.42 \text{ mm}$

Data collection

Bruker SMART 1000 CCD diffractometer	7138 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1995)	2590 independent reflections
$T_{\min} = 0.861$, $T_{\max} = 1.000$	2112 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	120 parameters
$wR(F^2) = 0.164$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.24 \text{ e \AA}^{-3}$
2590 reflections	$\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Bruker, 2007); software used to prepare material for publication: PLATON (Spek, 2009).

This work was supported financially by the Xunta de Galicia (No. EXPTE. CN 2012/184). The work of the MS and Single-crystal X-ray Diffraction divisions of the research support service of the University of Vigo (CACTI) is also gratefully acknowledged. MG thanks the University of Vigo for a PhD fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GO2087).

References

- Bruker (2007). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1995). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
- Spek, A. L. (2009). Acta Cryst. D65, 148–155.
- Wasserscheid, P. & Keim, W. (2000). Angew. Chem. Int. Ed. 39., 3772–3789.
- Welton, T. (1999). Chem. Rev. 99, 2071–2084.

supplementary materials

Acta Cryst. (2013). E69, o799 [doi:10.1107/S1600536813011197]

(1*S*,2*S*,5*S*)-2-Methyl-3-oxo-5-(prop-1-en-2-yl)cyclohexane-1-carbonitrile

Marcos L. Rivadulla, Alioune Fall, María González and Maria J. Matos

Comment

Ionic Liquids (ILs) have been attracting considerable attention in the last decade as a new media due to their unique physical and chemical properties (Welton, 1999, Wasserscheid and Keim, 2000). They are often preferred as being more environmentally friendly than traditional organic solvents. The range of known and available ILs has been rapidly growing and nowadays many ILs are commercially available. In accordance with current trends in academic and industrial research, in recent years our research group has also began to work towards the replacement of toxic volatile organic solvents with ILs. In the title compound, I, (Fig. 1), it is observed that the six-membered ring adopts the usual chair conformation. The C1–C2 bond of the cyclohexanone moiety adopts a *cis* configuration. The dihedral angle between the main plane of the cyclohexanone ring (defined for C1–C3–C4–C6) and the main plane of the lateral chain (defined for C5–C7–C8–C9) is 73.97°. The C5–C7–C8–C9 atoms of the lateral chain are co-planar but show large thermal motion. The absolute configuration was established according to the configuration of the starting material.

Experimental

Over a stirring solution of (S)-(+)-Carvone (104 μ L; 0.67 mmol) in the ionic liquid [TMG][LAC] (1 mL), NaCN (39.15 mg; 0.8 mmol) was added. The mixture was stirred at 60 °C for 12 h. Then the reaction was cooled at room temperature and was quenched with water (15 mL) and extracted with AcOEt. The organic layer was washed with a aqueous solution of HCl (10%) (2x10 ml) and brine (2x10 mL), then was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel (5% AcOEt/hexane) to afford the two desired diastereoisomeric compounds (116 mg; 86/14; 99%). The title compound, was crystallized using a mixture of 30% AcOEt/hexane.

Refinement

In (I) H atoms were placed in calculated positions and treated as riding atoms with C—H(tertiary), 0.98 Å, C—H₂(secondary), 0.97 Å, C=C—H₂(terminal), 0.93 Å, with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ and C—H(methyl), 0.96 Å, with $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$.

The H atoms attached to atom C11 were located on a final difference map. Atoms C8 and C9 show large thermal motion and, as a result, their contact distances to atom C7 are shorter than would be expected. Since the C7—C8 distance was longer than the C7—C9 distance C8 was assumed to be the methyl carbon. The H atoms attached to C8 and C9 could not be clearly seen on a final difference map.

Since no atom in the structure had an atomic number greater than 8 the absolute configuration could not be determined with MoK α radiation hence the Flack parameter is meaningless.

Computing details

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 2008); molecular graphics: *SHELXTL* (Bruker, 2007); software used to prepare material for publication: *PLATON* (Spek, 2009).

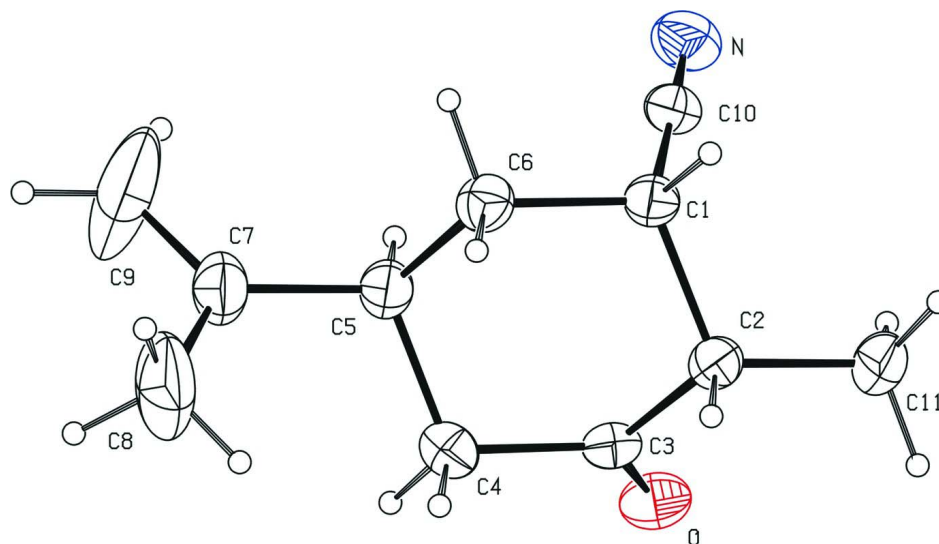


Figure 1

The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

(1*S*,2*S*,5*S*)-2-Methyl-3-oxo-5-(prop-1-en-2-yl)cyclohexane-1-carbonitrile

Crystal data

$C_{11}H_{15}NO$

$M_r = 177.24$

Orthorhombic, $P2_12_12_1$

$a = 5.2892$ (8) Å

$b = 10.7213$ (16) Å

$c = 19.559$ (3) Å

$V = 1109.1$ (3) Å³

$Z = 4$

$F(000) = 384$

$D_x = 1.061$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3155 reflections

$\theta = 2.8$ – 26.9°

$\mu = 0.07$ mm⁻¹

$T = 293$ K

Prism, colourless

$0.60 \times 0.56 \times 0.42$ mm

Data collection

Bruker SMART CCD area-detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1995)

$T_{\min} = 0.861$, $T_{\max} = 1.000$

7138 measured reflections

2590 independent reflections

2112 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -6 \rightarrow 6$

$k = -13 \rightarrow 13$

$l = -19 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.164$

$S = 1.04$

2590 reflections

120 parameters

0 restraints

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

$$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2 + 0.0575P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. ¹H-NMR (CDCl₃, δ): δ(eq) 4.83 (2H, J=26.07 Hz, H-9), 3.35–3.32 (1H, m, H-3), 2.82–2.74 (1H, m, H-5), 2.63–2.55 (2H, m, H-2 + H_{eq}-4), 2.32–2.24 (2H, m, H_{ax}-4 + H_{eq}-6), 1.99–1.92 (1H, m, H_{ax}-6), 1.77 (3H, d, J=6.70 Hz, H₃-7) δ(ax) 4.94 (1H, s, H-9), 4.65 (1H, s, H-9), 2.84–2.81 (1H, m, H-5), 2.69–2.63 (2H, m, H-3 + H_{eq}-4) 2.58–2.49 (2H, m, H-2 + H_{ax}-4), 2.35–2.18 (2H, m, H_{eq}+_{ax}-6), 1.75 (3H, s, H-10); 1.25 (3H, d, J=6.70 Hz, H-7). ¹³C-NMR (CDCl₃, δ): δ(eq) 206.73 (C-1), 145.55 (C-8), 118.65 (C-11), 111.16 (CH₂-9), 45.79 (CH₂-4), 45.05 (CH-2), 42.25 (CH-5), 35.67 (CH-3), 32.85 (CH₂-6), 20.53 (CH₃-10), 12.59 (CH₃-7); δ(ax) 207.23 (C-1), 144.76 (C-8), 120.54 (C-11), 113.88 (CH₂-9), 46.70 (CH₂-4), 40.35 (CH-5), 31.96 (CH-3), 30.52 (CH₂-6), 21.89 (CH₃-10), 13.50 (CH₃-7). **IR–** (CDCl₃, ν(cm⁻¹)): 2974, 2936, 2359, 2237, 1709, 1447, 1379, 898. **MS (EI⁺) (m/z, %):** 162.99 ([C₁₁H₁₄O]⁺, 4); 178.12 ([M+1]⁺, 57); 200.10 ([M+Na]⁺, 100); 201.05 (12); 201.10 (16); 210 (10); 216 (5). **HRMS:** 177.2429 calculated for C₁₁H₁₅NO and found 177.1145.

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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O	0.1359 (3)	0.16426 (13)	0.97088 (8)	0.0752 (4)
N	0.1851 (4)	−0.20500 (17)	0.92433 (12)	0.0888 (6)
C1	0.5822 (3)	−0.06508 (16)	0.94292 (9)	0.0573 (4)
H1	0.7132	−0.1143	0.9659	0.069*
C2	0.5121 (4)	0.04653 (16)	0.99035 (8)	0.0588 (4)
H2	0.6689	0.0917	1.0002	0.071*
C3	0.3426 (3)	0.13420 (15)	0.95095 (9)	0.0564 (4)
C4	0.4468 (4)	0.17830 (18)	0.88397 (11)	0.0705 (5)
H4A	0.5991	0.2266	0.8919	0.085*
H4B	0.3243	0.2320	0.8617	0.085*
C5	0.5082 (4)	0.06743 (17)	0.83708 (9)	0.0625 (4)
H5	0.3501	0.0222	0.8288	0.075*
C6	0.6881 (4)	−0.02143 (19)	0.87410 (10)	0.0646 (5)
H6A	0.8484	0.0203	0.8816	0.078*
H6B	0.7192	−0.0935	0.8454	0.078*
C7	0.6110 (5)	0.1083 (2)	0.76790 (12)	0.0885 (7)
C8	0.7980 (8)	0.2010 (4)	0.76281 (18)	0.1574 (17)
H8A	0.7514	0.2597	0.7280	0.236*
H8B	0.9568	0.1631	0.7511	0.236*
H8C	0.8137	0.2434	0.8058	0.236*
C9	0.5180 (13)	0.0550 (7)	0.71081 (16)	0.263 (4)
H9A	0.5776	0.0796	0.6681	0.316*
H9B	0.3943	−0.0063	0.7141	0.316*
C10	0.3602 (4)	−0.14556 (16)	0.93301 (10)	0.0642 (5)

C11	0.4019 (6)	0.0058 (2)	1.05820 (10)	0.0901 (7)
H11A	0.2379	-0.0301	1.0509	0.135*
H11B	0.3870	0.0768	1.0879	0.135*
H11C	0.5111	-0.0550	1.0789	0.135*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O	0.0629 (8)	0.0698 (8)	0.0928 (10)	0.0087 (7)	0.0027 (7)	-0.0158 (7)
N	0.1012 (14)	0.0644 (10)	0.1009 (14)	-0.0174 (11)	0.0103 (12)	-0.0007 (9)
C1	0.0587 (9)	0.0538 (8)	0.0594 (9)	0.0115 (7)	0.0018 (7)	-0.0007 (7)
C2	0.0646 (10)	0.0575 (8)	0.0542 (8)	0.0038 (8)	-0.0016 (8)	-0.0046 (7)
C3	0.0598 (9)	0.0453 (7)	0.0641 (9)	-0.0001 (7)	-0.0026 (8)	-0.0111 (6)
C4	0.0820 (13)	0.0565 (9)	0.0729 (11)	0.0033 (9)	-0.0021 (10)	0.0073 (8)
C5	0.0656 (10)	0.0669 (10)	0.0549 (9)	-0.0066 (9)	0.0005 (8)	0.0009 (8)
C6	0.0609 (10)	0.0682 (10)	0.0647 (9)	0.0022 (9)	0.0111 (8)	-0.0039 (8)
C7	0.1031 (17)	0.0994 (15)	0.0630 (11)	-0.0087 (15)	0.0083 (12)	0.0114 (11)
C8	0.179 (3)	0.205 (4)	0.0891 (19)	-0.075 (4)	0.014 (2)	0.044 (2)
C9	0.358 (9)	0.365 (8)	0.0663 (17)	-0.233 (8)	0.047 (3)	-0.045 (3)
C10	0.0789 (12)	0.0467 (8)	0.0669 (10)	0.0016 (9)	0.0094 (9)	0.0003 (7)
C11	0.129 (2)	0.0840 (13)	0.0578 (10)	0.0202 (15)	0.0180 (12)	-0.0017 (10)

Geometric parameters (\AA , $^\circ$)

O—C3	1.205 (2)	C5—C6	1.529 (3)
N—C10	1.137 (3)	C5—H5	0.9800
C1—C10	1.470 (3)	C6—H6A	0.9700
C1—C6	1.531 (3)	C6—H6B	0.9700
C1—C2	1.559 (2)	C7—C9	1.347 (5)
C1—H1	0.9800	C7—C8	1.406 (5)
C2—C3	1.510 (2)	C8—H8A	0.9600
C2—C11	1.513 (3)	C8—H8B	0.9600
C2—H2	0.9800	C8—H8C	0.9600
C3—C4	1.498 (3)	C9—H9A	0.9300
C4—C5	1.536 (3)	C9—H9B	0.9300
C4—H4A	0.9700	C11—H11A	0.9600
C4—H4B	0.9700	C11—H11B	0.9600
C5—C7	1.522 (3)	C11—H11C	0.9600
C10—C1—C6	110.83 (16)	C4—C5—H5	107.5
C10—C1—C2	109.82 (15)	C5—C6—C1	112.29 (15)
C6—C1—C2	112.06 (14)	C5—C6—H6A	109.1
C10—C1—H1	108.0	C1—C6—H6A	109.1
C6—C1—H1	108.0	C5—C6—H6B	109.1
C2—C1—H1	108.0	C1—C6—H6B	109.1
C3—C2—C11	113.48 (17)	H6A—C6—H6B	107.9
C3—C2—C1	108.38 (13)	C9—C7—C8	119.8 (3)
C11—C2—C1	113.08 (16)	C9—C7—C5	119.0 (3)
C3—C2—H2	107.2	C8—C7—C5	121.2 (2)
C11—C2—H2	107.2	C7—C8—H8A	109.5

C1—C2—H2	107.2	C7—C8—H8B	109.5
O—C3—C4	122.18 (18)	H8A—C8—H8B	109.5
O—C3—C2	122.69 (18)	C7—C8—H8C	109.5
C4—C3—C2	115.10 (16)	H8A—C8—H8C	109.5
C3—C4—C5	110.84 (15)	H8B—C8—H8C	109.5
C3—C4—H4A	109.5	C7—C9—H9A	120.0
C5—C4—H4A	109.5	C7—C9—H9B	120.0
C3—C4—H4B	109.5	H9A—C9—H9B	120.0
C5—C4—H4B	109.5	N—C10—C1	178.0 (2)
H4A—C4—H4B	108.1	C2—C11—H11A	109.5
C7—C5—C6	112.20 (17)	C2—C11—H11B	109.5
C7—C5—C4	112.55 (17)	H11A—C11—H11B	109.5
C6—C5—C4	109.32 (15)	C2—C11—H11C	109.5
C7—C5—H5	107.5	H11A—C11—H11C	109.5
C6—C5—H5	107.5	H11B—C11—H11C	109.5
C10—C1—C2—C3	-71.53 (18)	C3—C4—C5—C6	-55.5 (2)
C6—C1—C2—C3	52.1 (2)	C7—C5—C6—C1	-178.64 (18)
C10—C1—C2—C11	55.2 (2)	C4—C5—C6—C1	55.8 (2)
C6—C1—C2—C11	178.83 (19)	C10—C1—C6—C5	67.67 (19)
C11—C2—C3—O	-2.8 (2)	C2—C1—C6—C5	-55.4 (2)
C1—C2—C3—O	123.73 (18)	C6—C5—C7—C9	102.3 (5)
C11—C2—C3—C4	179.06 (17)	C4—C5—C7—C9	-133.9 (5)
C1—C2—C3—C4	-54.45 (19)	C6—C5—C7—C8	-78.4 (3)
O—C3—C4—C5	-120.6 (2)	C4—C5—C7—C8	45.4 (4)
C2—C3—C4—C5	57.6 (2)	C6—C1—C10—N	-58 (6)
C3—C4—C5—C7	179.12 (18)	C2—C1—C10—N	66 (6)