

Ethyl 4-cyclohexyl-7-(dicyanomethylene)-tricyclo[4.2.1.0^{2,5}]non-3-ene-3-carboxylateAlan J. Lough,^{a*} Robert W. Jordan^b and William Tam^b^aDepartment of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6, and ^bDepartment of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1Correspondence e-mail: alough@chem.utoronto.ca

Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
R factor = 0.064
wR factor = 0.179
Data-to-parameter ratio = 18.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The regio- and stereochemistry of the title compound, $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$, has been established by X-ray analysis. There are two independent molecules in the asymmetric unit, one of which is disordered.

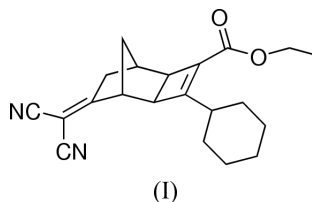
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Comment

Recently, we studied the remote substituent effects on ruthenium-catalysed [2 + 2]-cycloaddition reactions between 2-substituted 5-norbornenes and unsymmetrically substituted alkynes. Two different regio- and stereoisomers could be formed in the cycloadditions. When the substituent of the norbornene is a dicyanomethylene group, two regioisomers were obtained in a ratio of 15:1. These regioisomers were separated by fractional recrystallization. The regio- and stereochemistry of the major isomer, (I), has been established by our single-crystal X-ray diffraction analysis.



In the structure of (I), there are two molecules in the asymmetric unit, namely *A* and *B* (Figs. 1 and 2). In molecule *B*, atom C15 of the ethoxy group is disordered over three sites. The occupancies of the three disorder sites, named C15*B*, C15* and C15\$, are 0.50, 0.25 and 0.25, respectively (see Fig. 2). The three sites are the result of rotational disorder about the O2*B*–C14*B* bond. Torsion angles for C13–O2–C14–C15, which describes the disorder and contrasts the geometry of the ethoxy group in molecules *A* and *B*, are given in Table 1. In addition, there is a slight difference in the orientation of the cyclohexyl group in each of the independent molecules, which is described by the torsion angle C7–C6–C16–C17 (see Table 1).

Experimental

Addition of 2-dicyanomethylene-5-norbornene and ethyl 3-cyclohexylpropionate to $\text{Cp}^*\text{RuCl}(\text{COD})$ in THF at 298 K provided two regioisomers in a ratio of 15:1. Fractional recrystallization from an ethyl acetate/hexanes (1:4) mixture provided the major regioisomer, (I). Suitable crystals were grown from an ethyl acetate/hexanes (1:4) mixture.

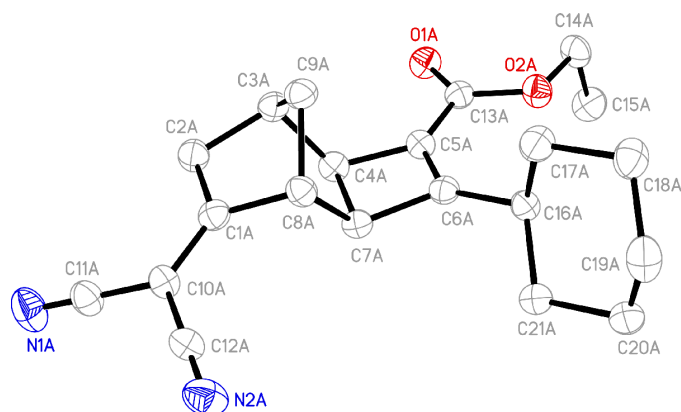


Figure 1
View of molecule *A* of (I), with the crystallographic labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

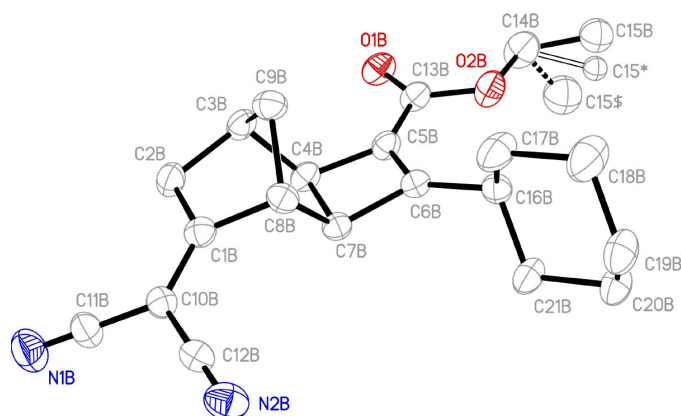


Figure 2
View of molecule *B* of (I), with the crystallographic labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor disorder components are shown with open and dashed bonds.

Crystal data

$C_{21}H_{24}N_2O_2$
 $M_r = 336.42$
 Triclinic, $P\bar{1}$
 $a = 11.6420$ (10) Å
 $b = 12.2348$ (11) Å
 $c = 13.5739$ (13) Å
 $\alpha = 104.761$ (5)°
 $\beta = 90.427$ (4)°
 $\gamma = 93.727$ (5)°
 $V = 1865.1$ (3) Å³

$Z = 4$
 $D_x = 1.198$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 16348 reflections
 $\theta = 2.6$ – 27.5 °
 $\mu = 0.08$ mm⁻¹
 $T = 150$ (1) K
 Plate, colourless
 $0.35 \times 0.30 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans and ω scans with κ offsets
 Absorption correction: none
 20141 measured reflections
 8463 independent reflections
 3937 reflections with $I > 2\sigma(I)$

$R_{int} = 0.100$
 $\theta_{max} = 27.6$ °
 $h = -15 \rightarrow 15$
 $k = -15 \rightarrow 15$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.180$
 $S = 0.98$
 8463 reflections
 456 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.26$ e Å⁻³
 $\Delta\rho_{min} = -0.30$ e Å⁻³
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.0087 (18)

Table 1

Selected torsion angles (°).

C13A–O2A–C14A–C15A	–87.4 (3)	C13B–O2B–C14B–C15\$	–114.0 (8)
C13B–O2B–C14B–C15B	169.6 (4)	C7A–C6A–C16A–C17A	–85.1 (3)
C13B–O2B–C14B–C15*	–159.9 (6)	C7B–C6B–C16B–C17B	–66.3 (4)

In the refinement, the bond lengths of the three disorder components (C14B–C15B, C14B–C15* and C14B–C15\$) were constrained to be equal, and the partial occupancy atoms were refined with isotropic displacement parameters. All H atoms were placed in calculated positions, with C–H distances ranging from 0.98 to 1.00 Å and included in the refinement in riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ (1.5 U_{eq} for methyl) of the carrier atom.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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