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Dimethyl 7-oxo-3-(pyrrolidin-1-yl)cyclo-octa-2,8-diene-1,2-dicarboxylate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.004 Å
R factor = 0.044
wR factor = 0.099
Data-to-parameter ratio = 11.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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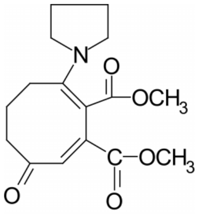
The title compound, $C_{16}H_{21}NO_5$, consists of a substituted 2,8-cyclooctadiene ring linked to a pyrrolidine ring through the N atom of the five-membered ring. The 2,8-cyclooctadiene moiety has a *cis,cis* configuration. The pyrrolidine ring adopts a twist conformation. A few interatomic close contacts seem to influence the shape of the molecule.

Comment

Enamines were developed in the early nineteen-sixties and, ever since, have appeared to be a very important class of compounds (Cook, 1969; Hickmott, 1982). The (2 + 2)-cycloaddition reactions of enamines of cyclic ketones with electron-deficient acetylenes is an established method in organic synthesis, resulting in ring enlargement by two C atoms (Kuehne, 1969; Reinhoudt, 1977). These reactions involve the formation of fused cyclobutenes, which may then undergo thermal rearrangement to yield cyclic 1,3-dienamines.

Enamines derived from cyclic ketones and secondary heterocyclic amines are useful intermediates, frequently used in (2 + 2)-cycloaddition reactions (Tunoğlu & Okay, 1996, 2000). During the course of our investigations of the reactions between unsubstituted cyclic enamines and electron-deficient acetylenes, such as dimethyl acetylenedicarboxylate (DMAD), we have synthesized, in good yield, a number of stable crystalline products (Tunoğlu & Uludağ, 1997). We have also been interested in the synthesis of new cycloadducts, starting with cyclic diketones, such as 1,3-cyclohexanedione, which, when reacted with pyrrolidine, gives 3-(pyrrolidin-1-yl)-2-cyclohexen-1-one in quite high yield (99%) because of the delocalization of the lone pair of electrons on the N atom through the double bond of the ring and the carbonyl group, as reported in the literature (Ishikawa *et al.*, 2001).



(I)

The structure determination of the title compound, (I), was undertaken in order to establish the configuration of the octadiene moiety and to compare the values obtained with reported structural results.

As shown in Fig. 1, the title compound consists of substituted 2,8-cyclooctadiene and pyrrolidine moieties. The eight-membered ring has a *cis,cis* configuration. The torsion angles

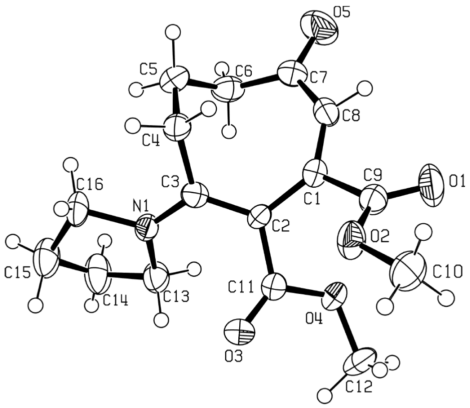


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

for the C═C—C═C part of the eight-membered ring [C2—C1—C8—C7 = −8.2 (5)°, C3—C2—C1—C8 = −41.4 (4)° and C1—C2—C3—C4 −11.8 (4)°] and the bond distances (Table 1) show evidence of some conjugation between the double bonds [C1═C8 = 1.347 (4) Å and C2═C3 = 1.398 (3) Å] in the *cis,cis*-2,8-diene moiety. The C1—C2 [1.454 (3) Å] and C7—C8 [1.457 (4) Å] bonds are somewhat shorter than a normal single C—C bond (Table 1).

The conformation of the eight-membered ring is similar to that of dimethyl *cis,cis*-7,8-dihydro-6-(1-pyrrolidinyl)-2*H*-thiocine-4,5-dicarboxylate (Reinhoudt *et al.*, 1984) in which the corresponding torsion angles about the double bonds are −3.7 (2) and −17.4 (2)°, and the double bonds are 1.340 (3) and 1.386 (2) Å in length.

Methyl atoms C10 and C12 are at distances of 0.045 (4) and 0.246 (4) Å from the carboxylate planes C9/O1/O2 and C11/O3/O4, respectively. The orientations of the carboxylate groups may be described by the torsion angles C8—C1—C9—O2 and C3—C2—C11—O4 of 143.5 (2) and 157.6 (2)°, respectively.

The pyrrolidine ring has a twist conformation, with atoms C14 and C15 displaced by 0.411 (5) and −0.196 (3) Å, respectively, from the plane of the other three ring atoms. The orientation of the five-membered ring with respect to the eight-membered ring may be described by the torsion angle C4—C3—N1—C13 of 157.1 (3)°.

The structure shows a number of close contacts: O3···H132(C13) = 2.22 (2), O1···H81(C8) = 2.50 (3), O1^{i}···H51(C5) = 2.51 (2), O5^{i}···H161(C16) = 2.57 (3), O3^{ii}···H162(C16) = 2.64 (3), O5^{iii}···H103(C10) = 2.62 (3), O4^{iv}···H142(C14) = 2.65 (3) and O1^{v}···H102(C10) = 2.60 (3) Å [symmetry codes: (i) $x + \frac{1}{2}, \frac{3}{2} - y, z + \frac{1}{2}$; (ii) $1 - x, 1 - y, -z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $-x, 1 - y, 1 - z$; (v) $-x, -y, -z$]. These interactions may have an influence on the bond lengths and angles and also the shape of the molecule.

Experimental

A solution of dimethyl acetylenedicarboxylate (DMAD) (5 mmol in 5 ml toluene) was added, over a period of 30 min, to a solution of 3-(pyrrolidin-1-yl)-2-cyclohexen-1-one (5 mmol in 20 ml toluene) at 273–278 K, yielding the title compound, (I). The reaction mixture was stirred for a further 2 h in an ice bath, after which the solvent was removed under reduced pressure. Column chromatography of the residue (ethyl acetate) afforded the pure product, which was then recrystallized from methanol (53% yield; m.p. 434 K).

Crystal data

$C_{16}H_{21}NO_5$
$M_r = 307.34$
Monoclinic, $P2_1/n$
$a = 9.3947$ (18) Å
$b = 14.195$ (3) Å
$c = 11.7723$ (11) Å
$\beta = 99.213$ (12)°
$V = 1549.7$ (4) Å^3
$Z = 4$
$D_x = 1.317$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10–22°$
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Plate, yellow
0.35 × 0.25 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: none
3141 measured reflections
2994 independent reflections
1327 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.051$
$\theta_{\max} = 26.3°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.099$
$S = 0.91$
2994 reflections
263 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O4—C11	1.367 (3)	C3—C4	1.503 (4)
O4—C12	1.444 (4)	C4—C5	1.530 (4)
O2—C9	1.334 (3)	C9—C1	1.526 (3)
O2—C10	1.454 (3)	C1—C8	1.347 (4)
O3—C11	1.209 (3)	O5—C7	1.221 (3)
N1—C3	1.337 (3)	C13—C14	1.512 (4)
N1—C13	1.472 (4)	C16—C15	1.505 (4)
N1—C16	1.481 (3)	C5—C6	1.522 (4)
C2—C3	1.398 (3)	C8—C7	1.457 (4)
C2—C1	1.454 (3)	C7—C6	1.498 (4)
C2—C11	1.462 (3)	C14—C15	1.493 (4)
O1—C9	1.193 (3)		
C11—O4—C12	116.0 (3)	C8—C1—C9	111.6 (2)
C9—O2—C10	115.8 (2)	C2—C1—C9	117.4 (2)
C3—N1—C13	124.7 (2)	O3—C11—O4	121.7 (2)
C3—N1—C16	124.7 (2)	O3—C11—C2	127.4 (2)
C13—N1—C16	109.8 (2)	O4—C11—C2	110.9 (2)
C3—C2—C1	122.5 (2)	N1—C13—C14	103.4 (3)
C3—C2—C11	120.3 (2)	N1—C16—C15	104.3 (2)
C1—C2—C11	116.1 (2)	C6—C5—C4	113.0 (2)
N1—C3—C2	124.2 (2)	C1—C8—C7	132.1 (3)
N1—C3—C4	115.7 (2)	O5—C7—C8	118.0 (3)
C2—C3—C4	119.9 (2)	O5—C7—C6	119.6 (3)
C3—C4—C5	111.9 (2)	C8—C7—C6	122.4 (3)
O1—C9—O2	124.3 (2)	C7—C6—C5	113.7 (3)
O1—C9—C1	124.8 (3)	C15—C14—C13	103.6 (3)
O2—C9—C1	110.9 (2)	C14—C15—C16	103.8 (3)
C8—C1—C2	131.1 (2)		

Atoms H10*A*, H10*B*, H10*C*, H15*A* and H15*B* were positioned geometrically at distances of 0.96 (CH_3) and 0.97 Å (CH_2) from the parent C atoms, and a riding model was used during the refinement

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process. U_{iso}(H) values were set equal to $1.5U_{eq}$ (CH_3) and $1.2U_{eq}$ (CH_2) of the carrier atoms. The remaining H atoms were located in a difference synthesis and refined isotropically [C—H = 0.87 (3)–1.08 (4) Å].

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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