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Diethyl 7-oxo-3-(pyrrolidin-1-yl)cycloocta-2,8-diene-1,2-dicarboxylate

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Key indicators

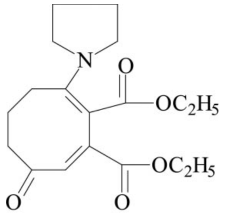
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.117
Data-to-parameter ratio = 9.9

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

The title compound, $C_{18}H_{25}NO_5$, 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 an envelope conformation. A few interatomic close contacts seem to influence the shape of the molecule.

Comment

The [2 + 2]-cycloaddition reaction, which is the key step in the synthesis of several natural products such as steganacin and macrocyclic musks, has been employed frequently in organic synthesis as it provides a method of ring enlargement of cyclic ketones by two C atoms. In addition, both cyclobutene derivatives and the cycloisomerization products can be used as monomers in the synthesis of conducting polymers (Kavuklu *et al.*, 2002; Şenöz & Tunoğlu, 1999). Today, conducting polymers are technologically important, since they have a widespread usage in making high-density energy batteries and sensors.



(I)

The [2 + 2]-cycloaddition reactions of enamines were developed in the early 1960 s and, since then, the products have been a very important class of compounds (Cook, 1969; Hickmott, 1982). Products derived from cyclic ketones with various electron-deficient acetylenes such as dimethyl acetylenedicarboxylate (DMAD) and diethyl acetylenedicarboxylate (DEAD) have been reported (Huebner *et al.*, 1963; Reinhoudt & Kouwenhoven, 1976). These reactions proceed by the formation of cyclobutene adducts, which then thermally isomerize to 1,3-dienamine.

The cyclobutene derivatives are formed readily in most of the [2 + 2]-cycloaddition reactions; however, very rarely they can be isolated as stable cycloadducts (Tunoğlu & Uludağ, 1997; Tunoğlu & Okay, 2000). In recent years, these compounds have been used in many areas (Reinhoudt & Kouwenhoven, 1976; Fex *et al.*, 1976).

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.

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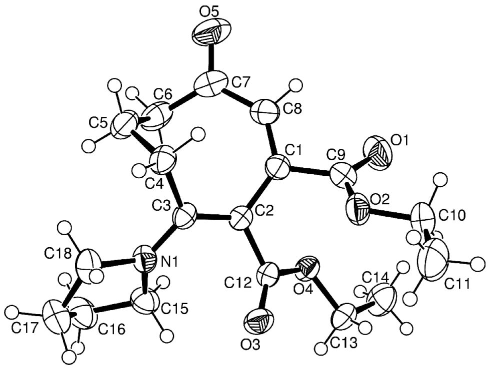

Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

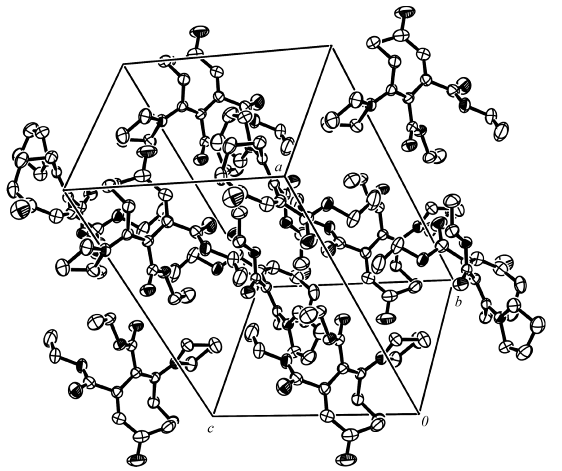

Figure 2
A view of the molecular packing.

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 for the C═C—C═C part of the eight-membered ring [C2—C1—C8—C7 = −5.3 (4)°, C3—C2—C1—C8 −34.7 (3)° and C1—C2—C3—C4 −11.9 (3)°] and the bond distances (Table 1) show evidence of some conjugation between the double bonds [C1═C8 = 1.348 (3) Å and C2═C3 = 1.398 (2) Å] in the *cis,cis*-2,8-diene moiety. The C1—C2 [1.462 (3) Å] and C7—C8 [1.464 (3) 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 7-oxo-3-(pyrrolidin-1-yl)cycloocta-2,8-diene-1,2-dicarboxylate, (II) (Hökelek *et al.*, 2003), and dimethyl *cis,cis*-7,8-dihydro-6-(1-pyrrolidinyl)-2*H*-thiocine-4,5-dicarb\\-forcelb]oxylate (Reinhoudt *et al.*, 1984), in which the corresponding torsion angles about the double bonds are −8.2 (5) and −11.8 (4)°, and −3.7 (2) and −17.4 (2)°, respectively; the corresponding double bond lengths are 1.347 (4) and 1.398 (3) Å, and 1.340 (3) and 1.386 (2) Å, respectively.

The lone pair of electrons on the N atom is delocalized through the double bond of the 2,8-cyclooctadiene ring and the carbonyl group, as reported in the literature (Ishikawa *et al.*, 2001). The effects of the diethyl and dimethyl carboxylate groups on the 2,8-cyclooctadiene rings in (I) and (II) are clear when the corresponding bond angles are compared (Table 2).

Ethyl atoms C10/C11 and C13/C14 are at distances of 0.073 (3)/0.045(4) and 0.237 (3)/0.262(3) Å from the carboxylate planes C9/O1/O2 and C12/O3/O4, respectively. The orientations of the carboxylate groups may be described by the torsion angles C8—C1—C9—O2 and C3—C2—C12—O4 of 136.4 (2) and 157.8 (2)°, respectively.

The pyrrolidine ring has an envelope conformation with atom C16 displaced by 0.621 (3) Å from the plane of the other four 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—C15 of 151.9 (2)°.

The structure reveals a number of close contacts: O3···H151(C15) = 2.25 (2) Å, O1···H81(C8) = 2.48 (2) Å, O1···H101(C10) = 2.51 (3) Å, $O5^{i}$···H41(C4) = 2.55 (3) Å, $O4^{ii}$···H101(C10) = 2.63 (3) Å and $O3^{iii}$···H161(C16) = 2.53 (3) Å [symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $x, \frac{3}{2}-y, z+\frac{1}{2}$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$]. These interactions may have an influence on the bond lengths and angles and also the shape of the molecule. The molecules are arranged parallel to the (011) plane (Fig. 2). Dipole–dipole and van der Waals forces are effective in molecular packing.

Experimental

A solution of diethyl acetylenedicarboxylate (DEAD) (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 2 h in an ice bath, after which the solvent was removed under reduced pressure. Column chromatography of the residue (silica gel, ethyl acetate) afforded the pure product, which was then recrystallized from methanol (64% yield; m.p. 393.5–394.7 K).

Crystal data

$C_{18}H_{25}NO_5$
M_r = 335.39
Monoclinic, $P2_1/c$
a = 16.3870 (16) Å
b = 9.5645 (12) Å
c = 11.3393 (19) Å
β = 82.044 (10)°
V = 1760.1 (4) Å^3
Z = 4

D_x = 1.266 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11–22°
μ = 0.09 mm^{-1}
T = 293 (2) K
Plate, yellow
0.40 × 0.25 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: none
3194 measured reflections
3124 independent reflections
2047 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019

$\theta_{\max}$ = 25.7°
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = -13 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.117
S = 1.02
3124 reflections
317 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.2352P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.15 e Å^{-3}
$\Delta\rho_{\min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O3—C12	1.204 (2)	C1—C9	1.518 (3)
O4—C12	1.357 (2)	C13—C14	1.492 (3)
O4—C13	1.453 (2)	O1—C9	1.201 (2)
O2—C9	1.337 (3)	O5—C7	1.224 (3)
O2—C10	1.461 (3)	C8—C7	1.464 (3)
C2—C3	1.398 (2)	C4—C5	1.535 (3)
C2—C1	1.462 (3)	C15—C16	1.516 (3)
C2—C12	1.479 (2)	C7—C6	1.495 (4)
N1—C3	1.338 (2)	C6—C5	1.530 (3)
N1—C15	1.468 (2)	C18—C17	1.511 (3)
N1—C18	1.479 (3)	C10—C11	1.469 (4)
C3—C4	1.506 (2)	C16—C17	1.515 (4)
C1—C8	1.348 (3)		
C12—O4—C13	115.6 (2)	O4—C13—C14	106.9 (2)
C9—O2—C10	115.5 (2)	O1—C9—O2	124.0 (2)
C3—C2—C1	123.6 (2)	O1—C9—C1	124.4 (2)
C3—C2—C12	119.7 (2)	O2—C9—C1	111.6 (2)
C1—C2—C12	116.0 (2)	C1—C8—C7	132.4 (2)
C3—N1—C15	125.5 (2)	C3—C4—C5	109.7 (2)
C3—N1—C18	124.4 (2)	N1—C15—C16	102.7 (2)
C15—N1—C18	109.8 (2)	O5—C7—C8	118.4 (2)
O3—C12—O4	122.2 (2)	O5—C7—C6	119.8 (2)
O3—C12—C2	126.9 (2)	C8—C7—C6	121.8 (2)
O4—C12—C2	110.8 (2)	C7—C6—C5	110.7 (2)
N1—C3—C2	123.6 (2)	C6—C5—C4	111.9 (2)
N1—C3—C4	115.7 (2)	N1—C18—C17	104.4 (2)
C2—C3—C4	120.5 (2)	O2—C10—C11	107.7 (2)
C8—C1—C2	131.8 (2)	C17—C16—C15	102.0 (2)
C8—C1—C9	111.2 (2)	C18—C17—C16	103.7 (2)
C2—C1—C9	117.0 (2)		
C3—C2—C12—O4	157.8 (2)	C3—C2—C1—C8	−34.7 (3)
C15—N1—C3—C4	151.9 (2)	C8—C1—C9—O2	136.4 (2)
C1—C2—C3—C4	−11.9 (3)	C2—C1—C8—C7	−5.3 (4)

Table 2
Comparison of bond angles (°) in the 2,8-cyclooctadiene ring of (I) and (II).

	(I)	(II)
C2—C1—C8	131.8 (2)	131.1 (2)
C1—C2—C3	123.6 (2)	122.5 (2)
C2—C3—C4	120.5 (2)	119.9 (2)
C3—C4—C5	109.7 (2)	111.9 (2)
C4—C5—C6	111.9 (2)	113.0 (2)
C5—C6—C7	110.7 (2)	113.7 (3)
C6—C7—C8	121.8 (2)	122.4 (3)
C7—C8—C1	132.4 (2)	132.1 (3)

H atoms were located in a difference map and refined isotropically [C—H = 0.95 (2)–1.03 (3) 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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