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Diethyl 3-Piperidino-2,7-cycloheptadiene-1,2-dicarboxylate

Süheyla Özbey,[a] Alime Temel,[a] Nazan Tunoğlu[b] and Nesimi Uludağ[b]

[a]*Department of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and* [b]*Department of Chemistry, Hacettepe University, Beytepe 06532, Ankara, Turkey. E-mail: sozbey@eti.cc.hun.edu.tr*

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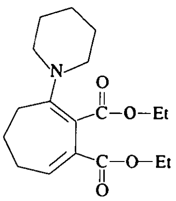
Abstract

The 2,7-cycloheptadiene moiety of the title compound, $C_{18}H_{27}NO_4$, has a *cis,cis* configuration. The piperidine ring adopts an almost-ideal chair conformation.

Comment

Enamines comprise an important class of compounds. Derived from cyclic ketones, they undergo [2 + 2] cycloaddition reactions with electron-deficient acetylenes, producing a ring enlargement by two C atoms (Brannock, Burpitt, Goodlett & Thweatt, 1963, 1964; Reinhoudt & Kouwenhoven, 1974, 1976). The reaction proceeds through the formation of an intermediate cyclobutene adduct that undergoes rearrangement with expansion of the carbocyclic ring. A wide variety of products can be obtained by changing the type of cyclic enamine and the acetylene (Reinhoudt *et al.*, 1984). Also, the polarity of the solvent used influences the route of the reaction. Pyrolidine, piperidine and morpholine enamines of cyclic ketones, such as cyclopentanone, cyclohexanone and α-tetralone, may react with diethyl acetylenedicarboxylate (DEAD) under mild conditions to afford the corresponding cyclobutene adduct and, in certain cases, the fused cyclobutenes undergo thermal isomerization to yield cyclic dienamines. We report here the crystal structure of the thermal rearrangement product, (I), of the cycloadduct obtained by the reaction of 1-piperidinyl cyclopentene with DEAD.



(I)

The structure determination of the title compound, (I), showed that the heptadiene moiety has a *cis,cis* configuration. The torsion angles for the C═C—C═C part of the seven-membered ring are C2—C1═C7—C6 = 1.6 (3), C3═C2—C1═C7 = 41.5 (3) and C1—C2═C3—C4 = 13.8 (2)°. These values are indicative of a *cis,cis*-1,3-diene moiety with little conjugation between the double bonds [C1═C7 = 1.332 (3) and C2═C3 = 1.379 (3) Å]. The C1—C2 and C6—C7 bonds are somewhat shorter than a single C—C bond (Table 2). The torsion angles and bond lengths may be compared with those of methyl 2-(1-pyrrolidinyl)-*cis,cis*-1,6-cycloheptadiene-1-carboxylate (Vos *et al.*, 1986) in which the corresponding torsion angles about the double bonds are 4.0 and −20.3°, and the double-bond lengths are 1.334 (2) and 1.396 (2) Å.

The piperidine ring has an almost-ideal chair conformation. The perpendicular distances of the two chair atoms in *para* positions, N1 and C16, from the plane of the other four atoms of the six-membered piperidine ring are 0.630 (2) and −0.659 (3) Å, respectively, close to the expected value of 0.726 Å. In the piperidine ring, bond lengths and angles agree well with those reported by Herbstein, Schwotzer, Addae-Mensah, Torto & Woode (1981) and Bellver & Lopez-Castro (1990).

The carboxylate groups are oriented with torsion angles C3—C2—C8—O2 = −159.2 (1) and C7—C1—C11—O4 = −156.1 (2)°

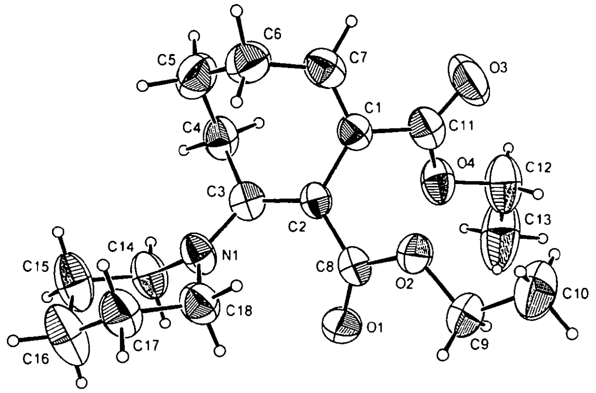


Fig. 1. *ORTEP* (Johnson, 1965) drawing of $C_{18}H_{27}NO_4$ with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

Experimental

1-Piperidinocyclopentene was allowed to react with an equimolar amount of diethyl acetylenedicarboxylate (DEAD) in benzene at 278–280 K for 2–3 h, after which the solution was refluxed for 4 h. The solvent was evaporated and the remaining material was purified by column chromatography [ethyl acetate–toluene (1:1)]. The solid was recrystallized in hexane; yield: 43%, m.p. 329 K.

Crystal data

$C_{18}H_{27}NO_4$
$M_r = 321.416$

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

Monoclinic
$P2_1/c$
$a = 12.274\,(1)$ Å
$b = 8.086\,(1)$ Å
$c = 19.097\,(2)$ Å
$\beta = 108.24\,(1)^\circ$
$V = 1800.1\,(3)$ Å^3
$Z = 4$
$D_x = 1.186$ Mg m^{-3}
D_m not measured

Cell parameters from 23 reflections
$\theta = 8$–18°
$\mu = 0.083$ mm^{-1}
$T = 295$ K
Prism
0.60 × 0.32 × 0.24 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5509 measured reflections
4655 independent reflections
2657 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 23.2^\circ$
$h = 0 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity decay: 0.1%

Refinement

Refinement on F
$R = 0.0425$
$wR = 0.0433$
$S = 1.22$
2657 reflections
289 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$

$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O1	0.5802 (1)	0.3332 (2)	0.13852 (7)	4.95 (3)
O2	0.69585 (9)	0.1769 (2)	0.09532 (6)	4.18 (3)
O3	0.8433 (1)	−0.1853 (2)	0.19765 (9)	6.94 (5)
O4	0.7890 (1)	0.0447 (2)	0.24203 (7)	5.05 (4)
N1	0.3701 (1)	0.1215 (2)	0.12180 (8)	4.00 (4)
C1	0.6462 (1)	−0.1055 (2)	0.15510 (9)	3.52 (5)
C2	0.5683 (1)	0.0377 (2)	0.14288 (9)	3.14 (4)
C3	0.4620 (1)	0.0192 (2)	0.15224 (9)	3.53 (4)
C4	0.4396 (2)	−0.1340 (3)	0.1911 (1)	4.46 (5)
C5	0.4109 (2)	−0.2835 (3)	0.1399 (1)	5.47 (6)
C6	0.4872 (2)	−0.2925 (3)	0.0902 (1)	4.91 (6)
C7	0.6085 (2)	−0.2565 (3)	0.1317 (1)	4.41 (5)
C8	0.6106 (1)	0.1971 (2)	0.12621 (9)	3.64 (5)
C9	0.7564 (2)	0.3257 (3)	0.0890 (1)	5.40 (6)
C10	0.8522 (2)	0.2791 (3)	0.0608 (1)	7.50 (7)
C11	0.7691 (2)	−0.0892 (3)	0.1985 (1)	4.49 (5)
C12	0.9082 (2)	0.0783 (4)	0.2830 (1)	7.15 (7)
C13	0.9112 (2)	0.2143 (4)	0.3325 (2)	10.9 (1)
C14	0.2873 (2)	0.1650 (3)	0.1596 (1)	4.96 (6)
C15	0.1663 (2)	0.1467 (3)	0.1092 (1)	6.57 (7)
C16	0.1474 (2)	0.2486 (4)	0.0405 (1)	7.22 (7)
C17	0.2364 (2)	0.2050 (3)	0.0035 (1)	5.14 (6)
C18	0.3565 (2)	0.2192 (3)	0.0556 (1)	4.56 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C8	1.209 (2)	C2—C3	1.379 (3)
O2—C8	1.362 (2)	C2—C8	1.461 (3)
O2—C9	1.439 (3)	C3—C4	1.513 (3)
O3—C11	1.201 (3)	C4—C5	1.525 (3)
O4—C11	1.341 (2)	C5—C6	1.530 (3)
O4—C12	1.452 (2)	C6—C7	1.480 (3)
N1—C3	1.373 (2)	C9—C10	1.486 (4)
N1—C14	1.462 (3)	C12—C13	1.444 (4)
N1—C18	1.456 (3)	C14—C15	1.503 (2)
C1—C2	1.473 (3)	C15—C16	1.504 (3)
C1—C7	1.332 (3)	C16—C17	1.517 (4)
C1—C11	1.483 (2)	C17—C18	1.503 (2)
C8—O2—C9	115.1 (2)	C5—C6—C7	111.5 (2)
C11—O4—C12	116.3 (2)	C1—C7—C6	123.0 (2)
C3—N1—C14	122.8 (2)	O1—C8—O2	121.3 (2)
C3—N1—C18	123.3 (2)	O1—C8—C2	127.5 (2)
C14—N1—C18	113.0 (1)	O2—C8—C2	111.3 (2)
C2—C1—C7	121.8 (1)	O2—C9—C10	107.8 (2)
C2—C1—C11	121.0 (2)	O3—C11—O4	122.6 (2)
C7—C1—C11	117.0 (2)	O3—C11—C1	125.3 (2)
C1—C2—C3	119.2 (2)	O4—C11—C1	112.0 (2)
C1—C2—C8	118.1 (2)	O4—C12—C13	108.0 (2)
C3—C2—C8	122.6 (2)	N1—C14—C15	111.1 (2)
N1—C3—C2	124.4 (2)	C14—C15—C16	110.8 (2)
N1—C3—C4	116.7 (2)	C15—C16—C17	110.0 (2)
C2—C3—C4	118.5 (2)	C16—C17—C18	111.9 (2)
C3—C4—C5	112.1 (2)	N1—C18—C17	110.8 (2)
C4—C5—C6	111.8 (2)		

All H atoms were located geometrically 0.95 Å from their parent atoms and refined; displacement parameters were fixed at $1.3U_{\rm eq}$ of the parent atom.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965) in *MolEN*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1385). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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