

Acta Cryst. (1997). **C53**, 380–381

Diethyl 3-(1-Morpholinyl)-2,8-cyclooctadiene-1,2-dicarboxylate

SÜHEYLA ÖZBEY^a AND NAZAN TUNOĞLU^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*

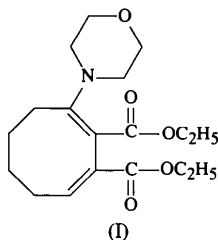
(Received 17 June 1996; accepted 21 October 1996)

Abstract

The 2,8-cyclooctadiene moiety of the title compound, C₁₈H₂₇NO₅, has a *cis,cis* configuration. The morpholinyl ring adopts an almost ideal chair conformation.

Comment

Enamines comprise a group of useful intermediates in several organic syntheses (Cook, 1969). Reactions of enamines of cyclic ketones with activated acetylenes is a suitable method for ring enlargement (Lown & Akhtar, 1973; Reinhoudt & Kouwenhoven, 1972). Different products can be obtained by changing the type of cyclic enamine and the acetylene (Özbeý, Temel, Tunođlu & Uludađ, 1996). 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.



The structural results show that the title molecule has a *cis,cis* configuration of the 1,3-diene moiety. The torsion angles for the C=C—C=C part of the eight-membered ring are C7—C8—C1—C2 3.0 (5), C8—C1—C2—C3 42.9 (4) and C1—C2—C3—C4 24.4 (4)°. These values and the bond distances in Table 1 show that there is some conjugation between the double bonds in the *cis,cis*-1,3-diene moiety. The conformation of the eight-membered ring is similar to that of dimethyl *cis,cis*-7,8-dihydro-6-(1-pyrrolidinyl)-2H-thiocine-4,5-dicarboxylate (Reinhoudt *et al.*, 1984) in which the corresponding torsion angles for the double bonds are -3.7 (2) and -17.4 (2)°, and the double-bond lengths are 1.340 (3) and 1.386 (2) Å. In the present

compound, the carboxylate groups attached to the C2 and C1 atoms are oriented with torsion angles C3—C2—C9—O2 and C8—C1—C12—O4 of -159.4 (3) and 32.1 (4)°, respectively. The morpholinyl ring has an almost ideal chair conformation. The perpendicular distances of the two chair atoms in the *para* positions N1 and O5 from the plane of the other four atoms of the six-membered morpholinyl ring are -0.580 (3) and 0.659 (3) Å, respectively. The torsion angle C4—C3—N1—C15 is -162.1 (3)°.

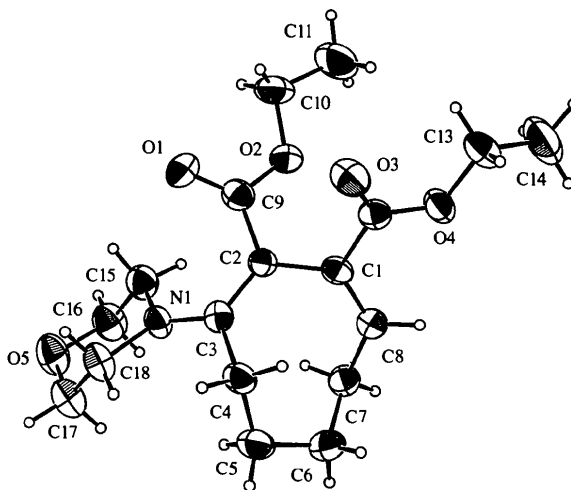


Fig. 1. The molecular structure of C₁₈H₂₇NO₅ with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

Experimental

A solution of diethyl acetylenedicarboxylate (5.46 mmol in 15 ml benzene) was added over a period of 2 h to a solution of morpholinylcyclohexene (5.46 mmol in 10 ml benzene) at 278–280 K to yield the title compound. The reaction mixture was stirred for 6 h after which the solvent was removed under reduced pressure. Column chromatography of the residue [ethyl acetate–benzene (1:4)] afforded the pure product (yield 56%; m.p. 427 K).

Crystal data

C₁₈H₂₇NO₅
M_r = 337.42
 Triclinic
 P1
a = 8.6903 (12) Å
b = 10.3999 (14) Å
c = 11.9025 (13) Å
 α = 68.481 (1)°
 β = 71.813 (1)°
 γ = 64.844 (1)°
V = 889.98 (15) Å³
Z = 2
D_s = 1.259 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 8–18°
 μ = 0.091 mm⁻¹
T = 295 K
 Prismatic
 0.56 × 0.24 × 0.16 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.02$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 26.3^\circ$
Absorption correction: none	$h = -10 \rightarrow 9$
3808 measured reflections	$k = -12 \rightarrow 0$
3392 independent reflections	$l = -14 \rightarrow 13$
1805 reflections with $I > \sigma(I)$	3 standard reflections frequency: 120 min intensity decay: 0.2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R = 0.0401$	$\Delta\rho_{\text{max}} = 0.241 \text{ e } \text{Å}^{-3}$
$wR = 0.0419$	$\Delta\rho_{\text{min}} = -0.116 \text{ e } \text{Å}^{-3}$
$S = 1.26$	Extinction correction: none
1805 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
217 parameters	
H atoms: see below	
$w = 1/[\sigma^2(F^2) + (0.04F^2)^2]$	

Table 1. Selected geometric parameters (Å , $^\circ$)

O1—C9	1.216 (4)	C1—C12	1.490 (3)
O2—C9	1.359 (3)	C2—C3	1.379 (4)
O2—C10	1.433 (4)	C2—C9	1.469 (5)
O3—C12	1.210 (3)	C3—C4	1.512 (5)
O4—C12	1.341 (3)	C4—C5	1.526 (4)
O4—C13	1.447 (3)	C5—C6	1.518 (4)
O5—C16	1.425 (3)	C6—C7	1.532 (5)
O5—C17	1.409 (5)	C7—C8	1.496 (4)
N1—C3	1.359 (4)	C10—C11	1.481 (4)
N1—C15	1.451 (5)	C13—C14	1.482 (4)
N1—C18	1.459 (3)	C15—C16	1.500 (4)
C1—C2	1.471 (4)	C17—C18	1.503 (4)
C1—C8	1.336 (5)		
C9—O2—C10	116.5 (2)	C4—C5—C6	114.1 (2)
C12—O4—C13	116.6 (2)	C5—C6—C7	114.2 (3)
C16—O5—C17	108.8 (3)	C6—C7—C8	114.4 (2)
C3—N1—C15	123.4 (2)	C1—C8—C7	127.3 (3)
C3—N1—C18	123.8 (3)	O1—C9—O2	121.8 (3)
C15—N1—C18	112.1 (3)	O1—C9—C2	127.0 (3)
C2—C1—C8	124.3 (2)	O2—C9—C2	111.1 (3)
C2—C1—C12	116.3 (3)	O2—C10—C11	107.0 (3)
C8—C1—C12	119.3 (3)	O3—C12—O4	122.7 (2)
C1—C2—C3	121.0 (3)	O3—C12—C1	124.5 (2)
C1—C2—C9	116.5 (2)	O4—C12—C1	112.8 (2)
C3—C2—C9	122.4 (3)	O4—C13—C14	107.2 (2)
N1—C3—C2	123.5 (3)	N1—C15—C16	111.0 (3)
N1—C3—C4	116.6 (2)	O5—C16—C15	112.5 (2)
C2—C3—C4	119.9 (3)	O5—C17—C18	112.0 (3)
C3—C4—C5	115.0 (2)	N1—C18—C17	111.3 (2)

All H atoms were geometrically located 0.95 Å from their parent atoms and included using a riding model; displacement parameters were fixed at $1.3U_{\text{eq}}$ of the parent atom.

Data collection: *CAD-4 Express* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1416). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Cook, A. G. (1969). In *Enamines: Synthesis, Structure and Reactions*. New York: Marcel Dekker.
- Enraf–Nonius (1993). *CAD-4 Express*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lown, J. W. & Akhtar, M. H. (1973). *Tetrahedron Lett.* **38**, 3727–3730.
- Özbeý, S., Temel, A., Tunođlu, N. & Uludađ, N. (1996). *Acta Cryst.* **C52**, 2890–2891.
- Reinholdt, D. N. & Kouwenhoven, C. G. (1972). *Tetrahedron Lett.* **51**, 5203–5204.
- Reinholdt, D. N., Verboom, W., Visser, G. W., Trompenaars, W. P., Harkema, S. & Hummel, G. J. (1984). *J. Am. Chem. Soc.* **106**, 1341–1350.

Acta Cryst. (1997). **C53**, 381–383

2-Amino-6-fluorobenzothiazole

JARAN JAI-NHUKNAN,^a ANASTAS G. KARIPIDES,^{a†} JOHN M. HUGHES^b AND JOSEPH S. CANTRELL^a

^aDepartment of Chemistry, Miami University, Oxford, Ohio 45056, USA, and ^bDepartment of Geology, Miami University, Oxford, Ohio 45056, USA. E-mail: jcantrel@miamiu.acs.muohio.edu

(Received 14 June 1995; accepted 20 November 1996)

Abstract

Crystals of 2-amino-6-fluoro-1,3-benzothiazole, $\text{C}_7\text{H}_5\text{FN}_2\text{S}$, have an amphiphilic layer-like structure. Each amino substituent donates two protons to hydrogen bonds and accepts one. The ring N atoms accept one proton. The F atoms are not involved in any hydrogen bonds.

Comment

We have been interested in the possibility that covalently bound F atoms might act as hydrogen-bond acceptors. The structure determination of the title compound, (I), was undertaken because it is an uncharged fluorinated organic molecule having hydrogen-bond donors.

† Deceased.