Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2197 measured reflections
2099 independent reflections
1436 observed reflections [$I > 2\sigma(I)$]
$R_{\text{int}} = 0.011$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 6$
$l = -18 \rightarrow 16$
3 standard reflections monitored every 150 reflections frequency: 100 min intensity decay: 0.2%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.063$
$S = 2.44$
1436 reflections
110 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ 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)

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

	x	y	z	B_{eq}
O(4)	0.5150 (1)	0.2463 (3)	0.9667 (1)	4.41 (6)
O(91)	0.8791 (1)	0.6570 (3)	0.5324 (1)	5.56 (8)
O(92)	0.9793 (1)	0.3118 (3)	0.5893 (1)	4.45 (6)
C(1)	0.7515 (2)	0.2227 (4)	0.7873 (1)	3.27 (7)
C(2)	0.7621 (2)	0.4047 (4)	0.8581 (1)	3.93 (8)
C(3)	0.6842 (2)	0.4147 (4)	0.9180 (1)	3.76 (8)
C(4)	0.5936 (2)	0.2381 (3)	0.9068 (1)	3.04 (7)
C(5)	0.5801 (2)	0.0538 (4)	0.8370 (1)	3.51 (7)
C(6)	0.6593 (2)	0.0477 (3)	0.7777 (1)	3.55 (7)
C(7)	0.8353 (2)	0.2222 (4)	0.7207 (2)	4.37 (9)
C(8)	0.8163 (2)	0.4444 (4)	0.6544 (1)	3.91 (8)
C(9)	0.8995 (2)	0.4622 (4)	0.5886 (1)	3.27 (7)

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

O(4)—C(4)	1.389 (2)	C(2)—C(3)	1.383 (3)
O(91)—C(9)	1.294 (2)	C(3)—C(4)	1.375 (3)
O(92)—C(9)	1.211 (2)	C(4)—C(5)	1.374 (3)
C(1)—C(2)	1.378 (3)	C(5)—C(6)	1.388 (3)
C(1)—C(6)	1.384 (3)	C(7)—C(8)	1.494 (3)
C(1)—C(7)	1.511 (3)	C(8)—C(9)	1.499 (2)
C(2)—C(1)—C(6)	117.7 (2)	C(4)—C(5)—C(6)	119.2 (2)
C(2)—C(1)—C(7)	120.5 (2)	C(1)—C(6)—C(5)	121.5 (2)
C(6)—C(1)—C(7)	121.8 (2)	C(1)—C(7)—C(8)	112.4 (2)
C(1)—C(2)—C(3)	121.9 (2)	C(7)—C(8)—C(9)	115.6 (2)
C(2)—C(3)—C(4)	119.2 (2)	O(91)—C(9)—O(92)	123.4 (2)
O(4)—C(4)—C(3)	119.6 (2)	O(91)—C(9)—C(8)	113.2 (2)
O(4)—C(4)—C(5)	119.7 (2)	O(92)—C(9)—C(8)	123.4 (2)
C(3)—C(4)—C(5)	120.7 (2)		

Data collection and cell refinement: *MSC/AFC Data Collection and Refinement Software* (Rigaku Corporation, 1988). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Programs used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). Program used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: AS1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethyl Pentaspiro[2.0.2.0.0.2.0.2.0.1]tetradeca-14-ylideneacetate, $C_{18}H_{22}O_2$

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Abstract

The title molecule has a *Z* configuration at the exocyclic C═C double bond. The four-membered ring and the COOEt group are almost coplanar. The unusual distribution of bond lengths in the polycyclic system is a result of the electron-withdrawing effect of the COOEt group.

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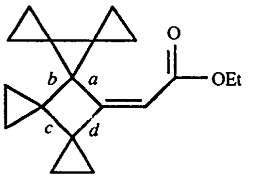
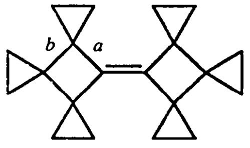
Comment

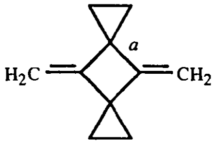
As part of a structural investigation of triangulanes [hydrocarbons constructed exclusively of spiroconjugated cyclopropane (CP) rings] and their derivatives (Lukin, Kozhushkov, Zefirov, Yufit & Struchkov, 1993, and references therein), we report here an X-ray study of (1).



(1)



(2)



(3)

The aim of the work was to determine the molecular configuration at the exocyclic C═C double bond and the effect of the COOEt group on the polycyclic system of (1) by comparing its geometry with that reported for the related molecules (2) and (3) (Boese, 1992).

(1) has a *Z* configuration at the C(14)═C(15) double bond. The planar cyclobutane ring [Δ_{max} = 0.014 (4) Å] and the carbonyl group are almost coplanar; the dihedral angle between their planes is 4.5 (2)°. The bonds *a* and *d* in the cyclobutane ring of (1) are similar in length to *a* in (3) but shorter than *a* in (2) [1.503 (2) and 1.516 (2) Å, respectively]. The length of bond *b* is also equal to that in (2) [1.522 (2) Å] and in the 4-rotane molecule [1.525 (1) Å; Almenningen, Bastiansen, Cyvin, Cyvin, Fernholt & Romming, 1984], but bond *c* appears to be slightly shorter than *b*. Another unusual feature of (1) is the equivalence of vicinal and distal bond lengths in CP rings *A* and *B*. Similar distribution of CP bond lengths was found earlier (Yufit, Struchkov, Lukin, Kozhushkov & Zefirov, 1993) and was attributed to the combined influence of spiroconjugation of three- and four-membered rings and the electron-withdrawing substituent. The equivalence of bond lengths in CP rings *A* and *B* in (1) implies that there is some conjugation between these cycles and the π system of the exocyclic double bond; this conclusion is supported by the contraction of bond *c*. This unusual form of conjugation is not found in 4-rotane or (2); it is pronounced in (1), presumably due to the π-acceptor effect of the COOEt group. Another indication that the ethoxycarbonyl group strongly effects the geometry of the polycyclic system in (1) comes from the contraction of the C(8)—C(11) distance to 1.449 (4) Å in comparison with the standard value of 1.463 Å for such bonds in triangulanes (Lukin *et al.*, 1993, and references therein).

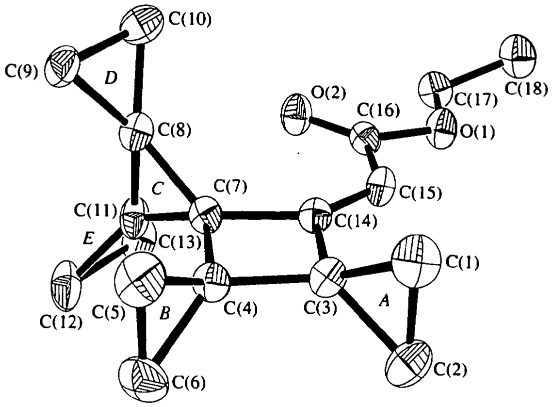


Fig. 1. View of (1). Displacement ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity.

In spite of the significant increase of the C(7)—C(14)—C(15), C(14)—C(15)—C(16) and C(15)—C(16)—O(2) bond angles, there are short intramolecular non-bonded contacts O(2)···C(13) [3.057 (4) Å] and O(2)···C(11) [3.274 (4) Å] in (1). The slight inequivalence of vicinal bond lengths in the terminal CP rings *D* and *E* is also worth noting.

Experimental

Crystal data

$C_{18}H_{22}O_2$
M_r = 270.4
Orthorhombic
Pccn
a = 15.685 (7) Å
b = 25.364 (9) Å
c = 7.579 (4) Å
V = 3015 (2) Å^3
Z = 8
D_x = 1.19 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 11–11.5°
μ = 0.08 mm^{-1}
T = 143 K
Transparent plate
0.05 × 0.04 × 0.02 mm
Colourless
Crystal source: ethanol

Data collection

Siemens *P*3/PC diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2652 measured reflections
2652 independent reflections
2272 observed reflections [$I > 2\sigma(I)$]

θ_{max} = 30°
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 35$
$l = 0 \rightarrow 9$
2 standard reflections monitored every 98 reflections intensity decay: 2%

Refinement

Refinement on F
R = 0.063
wR = 0.060
S = 1.52

$(\Delta/\sigma)_{max}$ = 0.042
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: none

2272 reflections
269 parameters
All H-atom parameters refined
Unit weights applied

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)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.1253 (1)	0.4182 (1)	0.0991 (2)	0.029 (1)
O(2)	−0.0077 (1)	0.4280 (1)	0.2073 (3)	0.030 (1)
C(1)	0.1724 (2)	0.3252 (1)	0.7301 (4)	0.035 (1)
C(2)	0.1504 (2)	0.2776 (1)	0.6225 (4)	0.034 (1)
C(3)	0.0864 (2)	0.3212 (1)	0.6430 (3)	0.023 (1)
C(4)	−0.0010 (2)	0.3197 (1)	0.7257 (4)	0.024 (1)
C(5)	−0.0233 (2)	0.3187 (1)	0.9179 (4)	0.037 (1)
C(6)	−0.0470 (2)	0.2730 (1)	0.8016 (4)	0.037 (1)
C(7)	−0.0322 (2)	0.3581 (1)	0.5854 (3)	0.022 (1)
C(8)	−0.0909 (2)	0.4043 (1)	0.6132 (4)	0.023 (1)
C(9)	−0.1237 (2)	0.4332 (1)	0.7701 (4)	0.030 (1)
C(10)	−0.0845 (2)	0.4622 (1)	0.6139 (4)	0.031 (1)
C(11)	−0.1183 (2)	0.3617 (1)	0.4990 (4)	0.026 (1)
C(12)	−0.1931 (2)	0.3264 (2)	0.4753 (5)	0.039 (1)
C(13)	−0.1526 (2)	0.3546 (1)	0.3192 (4)	0.031 (1)
C(14)	0.0548 (2)	0.3571 (1)	0.5009 (3)	0.021 (1)
C(15)	0.0963 (2)	0.3758 (1)	0.3613 (4)	0.025 (1)
C(16)	0.0631 (2)	0.4100 (1)	0.2197 (4)	0.024 (1)
C(17)	0.1034 (2)	0.4502 (1)	−0.0529 (4)	0.029 (1)
C(18)	0.1841 (2)	0.4718 (1)	−0.1283 (5)	0.039 (1)

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

O(1)—C(16)	1.353 (3)	C(7)—C(11)	1.504 (4)
O(1)—C(17)	1.450 (4)	C(7)—C(14)	1.507 (4)
O(2)—C(16)	1.204 (3)	C(8)—C(9)	1.490 (4)
C(1)—C(2)	1.497 (5)	C(8)—C(10)	1.471 (4)
C(1)—C(3)	1.506 (4)	C(8)—C(11)	1.449 (4)
C(2)—C(3)	1.500 (4)	C(9)—C(10)	1.523 (4)
C(3)—C(4)	1.507 (4)	C(11)—C(12)	1.487 (4)
C(3)—C(14)	1.496 (4)	C(11)—C(13)	1.476 (4)
C(4)—C(5)	1.499 (4)	C(12)—C(13)	1.522 (5)
C(4)—C(6)	1.502 (4)	C(14)—C(15)	1.330 (4)
C(4)—C(7)	1.522 (4)	C(15)—C(16)	1.474 (4)
C(5)—C(6)	1.503 (5)	C(17)—C(18)	1.494 (5)
C(7)—C(8)	1.505 (4)		
C(16)—O(1)—C(17)	116.9 (2)	C(7)—C(11)—C(8)	61.3 (2)
C(2)—C(1)—C(3)	59.9 (2)	C(7)—C(11)—C(12)	136.4 (3)
C(1)—C(2)—C(3)	60.4 (2)	C(8)—C(11)—C(12)	139.0 (3)
C(1)—C(3)—C(2)	59.7 (2)	C(7)—C(11)—C(13)	136.2 (2)
C(1)—C(3)—C(4)	129.4 (2)	C(8)—C(11)—C(13)	138.6 (3)
C(2)—C(3)—C(4)	129.3 (2)	C(12)—C(11)—C(13)	61.8 (2)
C(1)—C(3)—C(14)	124.8 (2)	C(11)—C(12)—C(13)	58.7 (2)
C(2)—C(3)—C(14)	126.6 (2)	C(11)—C(13)—C(12)	59.5 (2)
C(4)—C(3)—C(14)	90.8 (2)	C(3)—C(14)—C(7)	90.2 (2)
C(3)—C(4)—C(5)	128.1 (3)	C(3)—C(14)—C(15)	128.9 (2)
C(3)—C(4)—C(6)	127.9 (2)	C(4)—C(7)—C(8)	126.6 (2)
C(5)—C(4)—C(6)	60.1 (2)	C(4)—C(7)—C(11)	129.2 (2)
C(3)—C(4)—C(7)	89.2 (2)	C(8)—C(7)—C(11)	57.6 (2)
C(5)—C(4)—C(7)	128.0 (2)	C(4)—C(7)—C(14)	89.8 (2)
C(6)—C(4)—C(7)	128.2 (2)	C(8)—C(7)—C(14)	128.7 (2)
C(4)—C(5)—C(6)	60.0 (2)	C(11)—C(7)—C(14)	129.0 (2)
C(4)—C(6)—C(5)	59.8 (2)	C(7)—C(8)—C(9)	135.0 (2)
C(7)—C(8)—C(10)	137.3 (2)	C(7)—C(14)—C(15)	140.9 (2)
C(9)—C(8)—C(10)	61.9 (2)	C(14)—C(15)—C(16)	128.0 (2)
C(7)—C(8)—C(11)	61.2 (2)	O(1)—C(16)—O(2)	123.6 (2)
C(9)—C(8)—C(11)	137.9 (2)	O(1)—C(16)—C(15)	109.1 (2)
C(10)—C(8)—C(11)	140.0 (3)	O(2)—C(16)—C(15)	127.3 (3)
C(8)—C(9)—C(10)	58.5 (2)	O(1)—C(17)—C(18)	107.9 (2)
C(8)—C(10)—C(9)	59.6 (2)		

All calculations were performed using the *SHELXS*86 (PC version) programme (Robinson & Sheldrick, 1988) on an IBM PC/AT computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1327–1330

Structural Studies of Intermediates in the Synthesis of Mifepristone (RU 486). III. 3,3-Ethylenedioxy-5(10),9(11)-estradien-17-one

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Abstract

Crystallographic characterization of the title compound, $C_{20}H_{26}O_3$, an intermediate in the synthesis of mifepristone (RU 486), has helped establish the molecular structure and its conformation. An uncommon C(14)-envelope conformation is observed in the five-membered ring due to the presence of a trigonal C atom. The molecules form continuous intermolecular C—H$\cdots$O hydrogen-bonded chains arranged in a more or less zigzag shape along the *b* axis.

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