Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

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

	x	y	z	$U_{\rm eq}$
P1	0.53981 (6)	0.17359 (3)	0.46447 (5)	0.0230 (2)
O2	0.5371 (2)	0.1058 (1)	0.3195 (1)	0.0311 (6)
O3	0.3418 (2)	0.2200 (1)	0.4860 (2)	0.0320 (6)
C4	0.6229 (3)	0.1193 (1)	0.6704 (2)	0.0261 (8)
C5	0.7956 (2)	0.0515 (1)	0.6675 (2)	0.0240 (8)
C6	1.0012 (2)	0.0967 (1)	0.6716 (2)	0.0264 (8)
O7	1.1326 (2)	0.0893 (1)	0.7914 (2)	0.0426 (8)
O8	1.0124 (2)	0.1422 (1)	0.5284 (2)	0.0445 (8)
N9	0.7994 (2)	−0.0114 (1)	0.8177 (2)	0.0267 (7)
O10	0.3335 (2)	0.3935 (1)	0.6046 (2)	0.0310 (7)

Table 2. *Geometric parameters* (Å, °)

P1—O2	1.501 (1)	C5—C6	1.524 (2)
P1—O3	1.515 (1)	C5—N9	1.484 (2)
P1—C4	1.808 (2)	C6—O7	1.202 (2)
C4—C5	1.531 (2)	C6—O8	1.303 (2)
O2—P1—O3	116.7 (1)	C4—C5—N9	110.3 (1)
O2—P1—C4	109.3 (1)	C6—C5—N9	109.0 (1)
O3—P1—C4	106.8 (1)	C5—C6—O7	123.4 (2)
P1—C4—C5	115.8 (1)	C5—C6—O8	110.4 (1)
C4—C5—C6	112.7 (1)	O7—C6—O8	126.1 (2)
O2—P1—C4—C5	40.1 (1)	C4—C5—C6—O7	114.4 (2)
O3—P1—C4—C5	167.2 (1)	C4—C5—C6—O8	−66.3 (2)
P1—C4—C5—C6	78.8 (2)	N9—C5—C6—O7	−8.5 (2)
P1—C4—C5—N9	−159.1 (1)	N9—C5—C6—O8	170.8 (1)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	A	$D\cdots A$	$\mathrm{H}\cdots A$	D—$\mathrm{H}\cdots A$
O8	H15	O3$^{\rm i}$	2.536 (2)	1.69 (3)	172 (3)
N9	H16	O10$^{\rm ii}$	2.807 (2)	1.72 (2)	167 (2)
N9	H17	O2$^{\rm iii}$	2.752 (2)	2.02 (2)	156 (2)
N9	H18	O10$^{\rm iv}$	2.830 (2)	1.82 (2)	163 (2)
O10	H19	O3	2.735 (2)	1.98 (3)	172 (3)
O10	H20	O2$^{\rm v}$	2.719 (2)	1.70 (4)	173 (3)

Symmetry code: (i) $1+x, y, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1-x, -y, 1-z$; (iv) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

2-Amino-2-carboxyethylphosphinic acid (1) was prepared by the method of Dingwall, Ehrenfreund & Hall (1989) and crystals were obtained by recrystallization from water/methanol. All non-H atoms were found by direct methods, and all H atoms were located in difference electron density maps. In the final full-matrix least-squares refinement coordinates of all atoms were adjusted along with anisotropic thermal parameters for non-H atoms and isotropic temperature factors for H atoms.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71251 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1053]

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Functionalized Hydrocarbons with Condensed Ring Skeletons. XIV. A Dioxotricyclo[8.4.0.0^{2,7}]tetradec-6-ene

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Abstract

The structure of methyl 1,2-*trans*-1,10-*cis*-8,14-dioxotricyclo[8.4.0.0^{2,7}]tetradec-6-ene-1-carboxylate consists of three angularly fused six-membered rings, *A*, *B* and *C*. The tricyclic compound has a *cis A*/*B* ring junction and an *anti* arrangement between the C(9) proton and the C(10) methoxycarbonyl substituent. Rings *A* and *B* adopt chair

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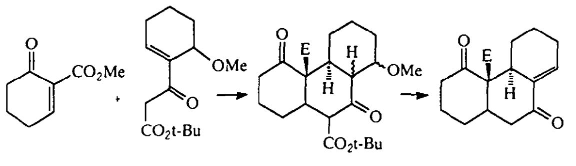
conformations while ring *C* prefers a flattened-chair conformation.

Comment

Decalins have been used extensively as intermediates in the synthesis of natural products. Highly stereoselective syntheses of *cis,cis*-decalins *via* a base-catalyzed [2 + 4] cycloaddition of substituted Nazarof reagents were recently reported (Lavallée, Spino, Ruel, Hogan & Deslongchamps, 1992). The present X-ray structure determination is part of the discussion of the mechanistic aspect of these reactions. The application of the synthetic strategy based on the cycloaddition to give tricyclic aldehydes failed for compound (3). Therefore its molecular structure was determined in order to explain such behavior and to confirm its relative stereochemistry. The compound was prepared from the cycloaddition-decarboxylation of the cyclic Nazarof reagent (2) and 2-methoxycarbonyl-2-cyclohexenone (1) (Lavallée, Spino, Ruel, Hogan & Deslongchamps, 1992). These authors supplied us with a suitable crystal for X-ray diffraction analysis.



(1) (2) (3)

(E = CO_2Me)

The enone (3) is a potential intermediate for the synthesis of many terpenoid natural products including the quassinoids, some of which display interesting and potent biological activities and antineoplastic properties. The experimentally observed molecular structure corresponds to the most stable form of possible conformers. Among the two half-chair conformations that the cyclohexene ring can adopt, one will have the ring substituent occupying an equatorial position and the other an axial position. The latter will be destabilized by angle strain and steric hindrance. The relative stereochemistry of this adduct is *cis* for the *A*/*B* ring junction, the proton at C(9) being *anti* to the methoxycarbonyl group at C(10). The *A* and *B* rings have chair conformations. Ring *C* is a flattened chair; the double bond at $\Delta^{8,11}$ is located in the flat region of the six-membered ring, the related torsion-angle values being 179.9 (3) and 0.6 (2)° for C(7)—C(8)—C(11)—C(12) and C(9)—C(8)—C(11)—C(12), respectively. The methoxycarbonyl sp^2 O(3) atom is eclipsed by C(9); the C(9)—C(10)—C(15)—O(3) torsion angle value is −0.1 (1)°, the O(4) atom being close to the C(5) H atom [2.38 (1) Å]. No unusually short contact distances were found.

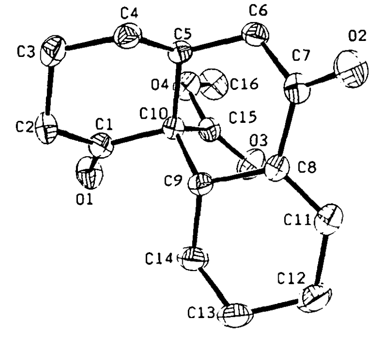


Fig. 1. *ORTEP* perspective view (Johnson, 1976) with thermal ellipsoids shown at 50% probability levels; H atoms are omitted for clarity.

Experimental

Crystal data

$C_{16}H_{20}O_4$
M_r = 276.33
Monoclinic
$P2_1/c$
a = 11.747 (4) Å
b = 9.2937 (10) Å
c = 12.983 (3) Å
β = 99.630 (19)°
V = 1397.4 (6) Å^3
Z = 4

D_x = 1.313 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.70930 Å
Cell parameters from 24 reflections
θ = 18.00–22.50°
μ = 0.09 mm^{-1}
T = 293 K
Colorless
0.30 × 0.30 × 0.30 mm
Prism

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1987 measured reflections
1817 independent reflections
1369 observed reflections [$I_{net} > 2.5\sigma(I_{net})$]

R_{int} = 0.008
θ_{max} = 22.44°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 13$
2 standard reflections
frequency: 30 min
intensity variation: none

Refinement

Refinement on F
Final R = 0.034
wR = 0.030
S = 1.85
1369 reflections
182 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.00005F^2]$
$(\Delta/\sigma)_{max}$ = 0.072
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 2.8 (6)

Data collection: *NRCCAD DATCOL* (Le Page, White & Gabe, 1986). Cell refinement: *NRCCAD TRUANG*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES DISANG*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

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

	x	y	z	U_{eq}
C(1)	0.07667 (18)	0.28196 (21)	0.30805 (15)	0.0414 (12)
C(2)	−0.01163 (17)	0.35408 (23)	0.22759 (15)	0.0497 (13)
C(3)	0.02621 (18)	0.36256 (24)	0.12066 (15)	0.0518 (13)
C(4)	0.14555 (18)	0.42841 (22)	0.12907 (14)	0.0434 (12)
C(5)	0.23452 (16)	0.34215 (20)	0.20246 (13)	0.0360 (11)
C(6)	0.35698 (17)	0.39795 (22)	0.20864 (14)	0.0419 (12)
C(7)	0.38607 (17)	0.52984 (21)	0.27399 (14)	0.0421 (12)
C(8)	0.33332 (17)	0.54353 (20)	0.37030 (14)	0.0355 (11)
C(9)	0.21532 (17)	0.47739 (21)	0.36962 (14)	0.0371 (12)
C(10)	0.20279 (15)	0.32846 (20)	0.31430 (13)	0.0335 (11)
C(11)	0.39058 (18)	0.61375 (22)	0.45178 (15)	0.0486 (13)
C(12)	0.34574 (21)	0.6341 (3)	0.55237 (16)	0.0663 (15)
C(13)	0.21702 (21)	0.6160 (3)	0.53733 (16)	0.0640 (15)
C(14)	0.18003 (20)	0.47775 (25)	0.47833 (16)	0.0578 (14)
C(15)	0.28031 (17)	0.21388 (21)	0.37415 (14)	0.0396 (11)
C(16)	0.33658 (22)	−0.03129 (24)	0.37017 (19)	0.0667 (16)
O(1)	0.04987 (13)	0.19434 (16)	0.36851 (11)	0.0630 (9)
O(2)	0.45437 (14)	0.61848 (17)	0.25206 (12)	0.0719 (10)
O(3)	0.34512 (12)	0.23023 (15)	0.45461 (10)	0.0600 (9)
O(4)	0.26837 (12)	0.08822 (14)	0.32253 (10)	0.0551 (9)

Table 2. *Geometric parameters* (Å, °)

C(1)—C(2)	1.501 (3)	C(8)—C(9)	1.515 (3)
C(1)—C(10)	1.532 (3)	C(8)—C(11)	1.326 (3)
C(1)—O(1)	1.2087 (24)	C(9)—C(10)	1.555 (3)
C(2)—C(3)	1.529 (3)	C(9)—C(14)	1.536 (3)
C(3)—C(4)	1.517 (3)	C(10)—C(15)	1.527 (3)
C(4)—C(5)	1.520 (3)	C(11)—C(12)	1.500 (3)
C(5)—C(6)	1.519 (3)	C(12)—C(13)	1.501 (4)
C(5)—C(10)	1.5635 (25)	C(13)—C(14)	1.522 (3)
C(6)—C(7)	1.497 (3)	C(15)—O(3)	1.1949 (23)
C(7)—C(8)	1.491 (3)	C(15)—O(4)	1.3420 (24)
C(7)—O(2)	1.2164 (24)	C(16)—O(4)	1.447 (3)
C(2)—C(1)—C(10)	117.41 (16)	C(8)—C(9)—C(14)	112.40 (16)
C(2)—C(1)—O(1)	121.86 (18)	C(10)—C(9)—C(14)	114.03 (16)
C(10)—C(1)—O(1)	120.68 (17)	C(1)—C(10)—C(5)	110.63 (14)
C(1)—C(2)—C(3)	112.51 (17)	C(1)—C(10)—C(9)	106.94 (15)
C(2)—C(3)—C(4)	111.16 (15)	C(1)—C(10)—C(15)	108.62 (15)
C(3)—C(4)—C(5)	111.27 (16)	C(5)—C(10)—C(9)	109.74 (15)
C(4)—C(5)—C(6)	113.52 (16)	C(5)—C(10)—C(15)	108.36 (15)
C(4)—C(5)—C(10)	112.30 (15)	C(9)—C(10)—C(15)	112.55 (14)
C(6)—C(5)—C(10)	110.46 (14)	C(8)—C(11)—C(12)	123.47 (20)
C(5)—C(6)—C(7)	115.72 (16)	C(11)—C(12)—C(13)	111.44 (17)
C(6)—C(7)—C(8)	117.23 (16)	C(12)—C(13)—C(14)	110.88 (19)
C(6)—C(7)—O(2)	121.25 (18)	C(9)—C(14)—C(13)	111.48 (18)
C(8)—C(7)—O(2)	121.43 (18)	C(10)—C(15)—O(3)	126.51 (18)
C(7)—C(8)—C(9)	117.95 (15)	C(10)—C(15)—O(4)	110.44 (15)
C(7)—C(8)—C(11)	118.98 (18)	O(3)—C(15)—O(4)	123.04 (18)
C(9)—C(8)—C(11)	123.07 (18)	C(15)—O(4)—C(16)	116.78 (16)
C(8)—C(9)—C(10)	112.31 (15)		

The structure was solved by the application of direct methods and refined using full-matrix least squares on F. All H-atom positional parameters were calculated and refined. Atomic scattering factors as stored in the *NRCVAX* program are those of Cromer & Waber (1974).

We thank Professor C. Spino (University of Victoria) for helpful discussions while preparing this manuscript.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71215 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1041]

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Functionalized Hydrocarbons with Condensed Ring Skeletons. XV. A (Methoxymethoxymethyl)tricyclo-[9.4.0.0^{2,8}]pentadec-9-ene

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Abstract

The tricyclic title compound, (*trans-anti-cis*)-tetramethyl 1-(methoxymethoxymethyl)tricyclo[9.4.0.0^{2,8}]pentadec-9-ene-5,5,13,13-tetracarboxylate, $C_{26}H_{38}O_{10}$, has a *trans-anti-cis* stereochemistry. Ring *A* adopts a chair conformation, ring *B* a half chair and ring *C* a twist chair. The methoxymethoxymethyl substituent adopts a *gauche-gauche* conformation.

Comment

The [6.6.7] tricyclic condensed ring structures, although less frequent than the [6.6.5] and [6.6.6] ones, constitute the skeletons of numerous natural products like the stemodanes, kauranes, stachanes and aphidicolins (Devon & Scott, 1972; Kametani, 1983).

The transannular Diels–Alder (TDA) reaction was used to synthesize a [6.6.7] tricyclic compound (1) starting from a 15-membered ring macrocycle triene with the

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