

$Q = 0.543(6) \text{ \AA}$ ,  $\varphi = 137.4(7)^\circ$ ,  $\theta = 71.9(6)^\circ$  for molecule *B*. The rings have a conformation between  ${}^3S_4$ ,  ${}^3E$  and  ${}^3B$  rather than corresponding to any stable conformation. Puckering analysis shows that the pyranoid ring is under considerable strain, while the strain in the furanoid ring is less because of the smaller deviation from the stable conformation.

The crystal packing does not reveal particularly short contacts.

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## Functionalized Hydrocarbons with Condensed Ring Skeletons. II. A 3-Oxotricyclo[8.4.0.0<sup>2,7</sup>]tetradec-8-ene

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**Abstract.** Tetramethyl 1,10-*trans*-1,2-*cisoid*-2,7-*cis*-1-methyl-3-oxotricyclo[8.4.0.0<sup>2,7</sup>]tetradec-8-ene-5,5-, 12,12-tetracarboxylate,  $C_{23}H_{30}O_9$ ,  $M_r = 450.49$ , triclinic,  $P\bar{1}$ ,  $a = 8.701(3)$ ,  $b = 12.6690(10)$ ,  $c = 12.7403(10) \text{ \AA}$ ,  $\alpha = 114.300(10)$ ,  $\beta = 99.127(10)$ ,  $\gamma = 107.988(10)^\circ$ ,  $V = 1149.71 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.301 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.70930 \text{ \AA}$ ,  $\mu = 0.09 \text{ mm}^{-1}$ ,  $F(000) = 479.95$ , room temperature, final  $R = 0.044$  for 1937 observed reflections. The tricyclic compound has a ring skeleton closely related to the *ABC* rings in steroids. Rings *A* and *C* adopt a chair conformation with the methyl group axial at C(1), while ring *B* has a half-chair conformation. The relative stereochemistry is *trans* for the *AB* ring junction, *syn* between Me–C(1) and H–C(2) and *cis* for the *BC* ring junction (*T–S–C*).

**Introduction.** In an earlier communication (Michel, Proulx & Michel-Dewez, 1988), we have reported the conformational properties and the X-ray data of a

tricyclic molecule having a tridecane skeleton. The synthesis of this molecule (Bérubé & Deslongchamps, 1987) was part of a general study of transannular Diels–Alder reactions, which demonstrates that the transannular Diels–Alder reaction on a macrocyclic triene is a powerful strategy for the construction of complex polycyclic molecules.

During the course of this study, compound (1) (Fig. 1), a possible intermediate in corticoid synthesis, was prepared (Marinier & Deslongchamps, 1988). Macrocyclization of the allylic chloride (2) (Fig. 1) to give triene (3) was followed by transannular Diels–Alder reaction resulting in the formation of (4). The relative stereochemistry of four [C(10), C(1), C(2), C(7)] of the five asymmetric centers in tricycle (4) can be predicted (Lamothe, Ndibwami & Deslongchamps, 1988). With a *trans–cis* diene and a *cis* dienophile, the transannular Diels–Alder reaction is expected to give a tricycle having *T–S–C* relative stereochemistry. Removal of the benzyl protective group and oxidation of the resulting alcohol (5) gave the ketone (1). This ketone, which is expected to have the same relative stereochemistry as

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(4) (*T-S-C*), was used for the crystallographic analysis. The present crystallographic study was undertaken to determine this relative stereochemistry.

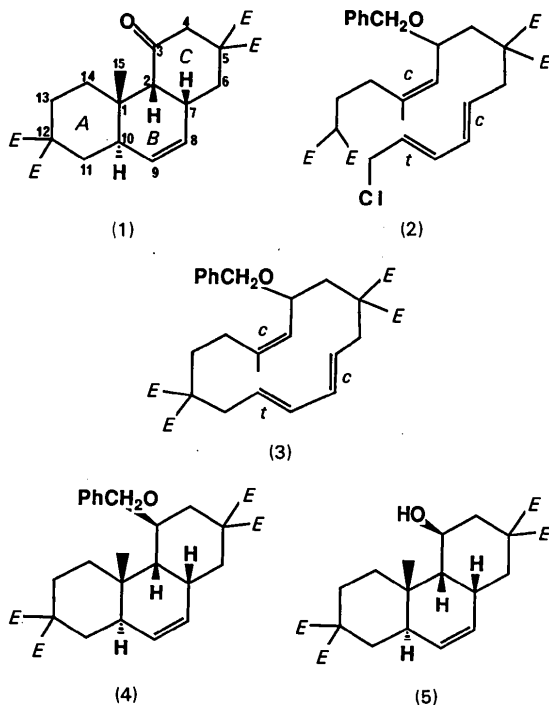


Fig. 1. Synthetic scheme. *E* = CO<sub>2</sub>Me.

Table 1. Final coordinates ( $\times 10^4$ ) and equivalent *B* values (with *e.s.d.*'s in parentheses) of the title compound

$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
O(1)	1685 (3)	59 (2)	5968 (2)	4.44
O(2)	-1481 (3)	3073 (3)	8654 (3)	7.54
O(3)	673 (3)	3931 (3)	8114 (2)	6.35
O(4)	2711 (3)	3603 (2)	10190 (2)	5.90
O(5)	3484 (3)	2708 (2)	8561 (2)	5.39
O(6)	5675 (3)	-798 (2)	6443 (2)	6.93
O(7)	3956 (3)	-2482 (2)	4657 (2)	5.43
O(8)	3607 (3)	-4250 (3)	6771 (2)	6.15
O(9)	5707 (4)	-3390 (3)	6210 (3)	8.40
C(1)	875 (4)	-1608 (3)	7020 (3)	3.72
C(2)	89 (4)	-643 (3)	7119 (3)	3.74
C(3)	813 (4)	231 (3)	6620 (3)	3.44
C(4)	327 (4)	1349 (4)	6907 (3)	4.12
C(5)	516 (4)	2111 (3)	8251 (3)	3.54
C(6)	-424 (5)	1208 (4)	8661 (3)	4.52
C(7)	160 (5)	134 (4)	8452 (3)	4.24
C(8)	1929 (5)	595 (4)	9323 (3)	4.79
C(9)	3065 (5)	154 (3)	9007 (3)	4.59
C(10)	2803 (4)	-822 (3)	7749 (3)	3.64
C(11)	3754 (4)	-1663 (3)	7725 (3)	4.25
C(12)	3541 (4)	-2583 (3)	6400 (3)	3.74
C(13)	1617 (5)	-3376 (3)	5634 (3)	4.13
C(14)	663 (4)	-2528 (3)	5702 (3)	4.03
C(15)	-14 (5)	-2410 (4)	7555 (4)	5.47
C(16)	-244 (5)	3077 (4)	8379 (3)	4.65
C(17)	94 (7)	4909 (5)	8165 (5)	7.92
C(18)	2374 (4)	2912 (3)	9132 (4)	4.28
C(19)	5264 (6)	3327 (5)	9353 (5)	7.98
C(20)	4515 (5)	-1831 (4)	5866 (4)	4.37
C(21)	4851 (7)	-1890 (5)	4042 (5)	8.04
C(22)	4416 (5)	-3445 (4)	6433 (3)	4.90
C(23)	4345 (7)	-5094 (5)	6886 (5)	7.52

Table 2. Molecular geometry

(a) Intramolecular bond lengths (Å) with *e.s.d.*'s in parentheses

O(1)-C(3)	1.211 (4)	C(2)-C(3)	1.518 (5)
O(2)-C(16)	1.183 (5)	C(2)-C(7)	1.553 (5)
O(3)-C(16)	1.332 (5)	C(3)-C(4)	1.520 (5)
O(3)-C(17)	1.457 (5)	C(4)-C(5)	1.530 (5)
O(4)-C(18)	1.189 (5)	C(5)-C(6)	1.516 (5)
O(5)-C(18)	1.323 (4)	C(5)-C(16)	1.526 (5)
O(5)-C(19)	1.461 (6)	C(5)-C(18)	1.542 (5)
O(6)-C(20)	1.195 (5)	C(6)-C(7)	1.534 (5)
O(7)-C(20)	1.326 (5)	C(7)-C(8)	1.520 (6)
O(7)-C(21)	1.449 (6)	C(8)-C(9)	1.317 (6)
O(8)-C(22)	1.317 (5)	C(9)-C(10)	1.492 (5)
O(8)-C(23)	1.449 (6)	C(10)-C(11)	1.532 (5)
O(9)-C(22)	1.191 (5)	C(11)-C(12)	1.546 (5)
C(1)-C(2)	1.548 (5)	C(12)-C(13)	1.550 (5)
C(1)-C(10)	1.543 (5)	C(12)-C(20)	1.519 (5)
C(1)-C(14)	1.539 (5)	C(12)-C(22)	1.521 (5)
C(1)-C(15)	1.533 (5)	C(13)-C(14)	1.532 (5)

(b) Intramolecular valence angles (°) with *e.s.d.*'s in parentheses

C(16)-O(3)-C(17)	117.2 (3)	C(7)-C(8)-C(9)	123.8 (3)
C(18)-O(5)-C(19)	114.9 (3)	C(8)-C(9)-C(10)	124.4 (3)
C(20)-O(7)-C(21)	116.5 (3)	C(1)-C(10)-C(9)	110.4 (3)
C(22)-O(8)-C(23)	117.9 (3)	C(1)-C(10)-C(11)	112.4 (3)
C(2)-C(1)-C(10)	106.7 (3)	C(9)-C(10)-C(11)	113.4 (3)
C(2)-C(1)-C(14)	113.8 (3)	C(10)-C(11)-C(12)	110.8 (3)
C(2)-C(1)-C(15)	108.4 (3)	C(11)-C(12)-C(13)	110.2 (3)
C(10)-C(1)-C(14)	108.7 (3)	C(11)-C(12)-C(20)	109.5 (3)
C(10)-C(1)-C(15)	111.6 (3)	C(11)-C(12)-C(22)	108.3 (3)
C(14)-C(1)-C(15)	107.7 (3)	C(13)-C(12)-C(20)	112.6 (3)
C(1)-C(2)-C(3)	115.7 (3)	C(13)-C(12)-C(22)	110.8 (3)
C(1)-C(2)-C(7)	110.4 (3)	C(20)-C(12)-C(22)	105.3 (3)
C(3)-C(2)-C(7)	111.0 (3)	C(12)-C(13)-C(14)	111.9 (3)
O(1)-C(3)-C(2)	124.0 (3)	C(1)-C(14)-C(13)	112.9 (3)
O(1)-C(3)-C(4)	118.4 (3)	O(2)-C(16)-O(3)	124.0 (4)
C(2)-C(3)-C(4)	117.4 (3)	O(2)-C(16)-C(5)	125.8 (4)
C(3)-C(4)-C(5)	113.9 (3)	O(3)-C(16)-C(5)	110.2 (3)
C(4)-C(5)-C(6)	109.2 (3)	O(4)-C(18)-O(5)	126.2 (3)
C(4)-C(5)-C(16)	108.4 (3)	O(4)-C(18)-C(5)	122.3 (3)
C(4)-C(5)-C(18)	115.2 (3)	O(5)-C(18)-C(5)	111.5 (3)
C(6)-C(5)-C(16)	110.4 (3)	O(6)-C(20)-O(7)	123.2 (3)
C(6)-C(5)-C(18)	108.7 (3)	O(6)-C(20)-C(12)	125.4 (3)
C(16)-C(5)-C(18)	104.9 (3)	O(7)-C(20)-C(12)	111.4 (3)
C(5)-C(6)-C(7)	113.5 (3)	O(8)-C(22)-O(9)	123.0 (4)
C(2)-C(7)-C(6)	113.9 (3)	O(8)-C(22)-C(12)	112.4 (3)
C(2)-C(7)-C(8)	109.6 (3)	O(9)-C(22)-C(12)	124.6 (4)
C(6)-C(7)-C(8)	112.9 (3)		

(c) Selected torsional angles (°) with *e.s.d.*'s in parentheses

C(10)-C(1)-C(2)-C(3)	60.1 (2)	C(12)-C(13)-C(14)-C(1)	-55.0 (2)
C(14)-C(1)-C(2)-C(3)	-59.8 (2)	C(10)-C(1)-C(2)-C(7)	-67.0 (2)
C(2)-C(1)-C(10)-C(9)	52.4 (2)	C(14)-C(1)-C(2)-C(7)	173.1 (3)
C(14)-C(1)-C(10)-C(9)	175.6 (3)	C(2)-C(1)-C(10)-C(11)	-179.8 (3)
C(2)-C(1)-C(14)-C(13)	173.7 (3)	C(14)-C(1)-C(10)-C(11)	-56.6 (2)
C(1)-C(2)-C(3)-C(4)	-168.8 (3)	C(10)-C(1)-C(14)-C(13)	54.9 (2)
C(7)-C(2)-C(3)-C(4)	-42.1 (2)	C(1)-C(2)-C(7)-C(6)	174.0 (3)
C(1)-C(2)-C(7)-C(8)	46.5 (2)	C(3)-C(2)-C(7)-C(6)	44.4 (2)
C(3)-C(2)-C(7)-C(8)	-83.2 (2)	C(3)-C(4)-C(5)-C(6)	-51.8 (2)
C(2)-C(3)-C(4)-C(5)	47.5 (2)	C(5)-C(6)-C(7)-C(2)	-53.8 (2)
C(4)-C(5)-C(6)-C(7)	55.7 (2)	C(2)-C(7)-C(8)-C(9)	-14.2 (1)
C(5)-C(6)-C(7)-C(8)	72.0 (2)	C(7)-C(8)-C(9)-C(10)	2.2 (1)
C(6)-C(7)-C(8)-C(9)	-142.3 (3)	C(8)-C(9)-C(10)-C(11)	-149.4 (3)
C(8)-C(9)-C(10)-C(1)	-22.2 (2)	C(9)-C(10)-C(11)-C(12)	-175.7 (3)
C(1)-C(10)-C(11)-C(12)	58.1 (2)	C(11)-C(12)-C(13)-C(14)	53.8 (2)
C(10)-C(11)-C(12)-C(13)	-55.1 (2)		

**Experimental.** Crystal 0.20 × 0.20 × 0.15 mm; Enraf-Nonius CAD-4 diffractometer; graphite-monochromatized Mo *K*α radiation; cell parameters were obtained by least-squares procedure on 15 reflections in the range 20 ≤ 2θ ≤ 30°. The θ/2θ scan mode was used for data collections at a constant scan speed of 4° min<sup>-1</sup>. A total of 2992 reflections was collected (2836 independent) up to 2θ<sub>max</sub> = 44°, corresponding to 9 ≥ *h* ≥ -9, 13 ≥ *k* ≥ 0, 13 ≥ *l* ≥ -13. 1937 reflections satisfying *I* > 2.5σ(*I*) were considered as observed. No correction was made for absorption. 60 standard reflections, 1% intensity variation.

The *NRCVAX* system (Gabe, Lee & Le Page, 1985) was used for all calculations. The structure was solved by the application of direct methods and refined by full-matrix least squares on *F*. Anisotropic thermal parameters were refined for non-H atoms. The H atoms were located from a difference map, but their positions were not refined. The final residuals obtained at convergence were *R* = 0.044 and *wR* = 0.021. Weights based on counting statistics were used. The max. *A*/*σ* ratio was 0.407, min. and max. electron densities in final difference map were -0.190 and 0.160 e Å<sup>-3</sup>. Atomic scattering factors from *NRCVAX*.

**Discussion.** Table 1 gives the final atomic parameters with their *B*<sub>eq</sub> values.\* Fig. 2 shows a perspective view and atom numbering of the molecule. Bond lengths and angles and selected torsion angles in the tricyclic skeleton are given in Table 2.

The data obtained verify the *T-S-C* relative stereochemistry of the tricycle. The rings *A* and *C* adopt a normal chair conformation. Although the transition state in the Diels-Alder reaction is expected to adopt a boat-like conformation (Lamothe *et al.*, 1988), ring *B* has a half-chair conformation. Since the *BC* rings are analogous to a *cis*-decalin system, the product is conformationally mobile. It is supposed that the

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51427 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

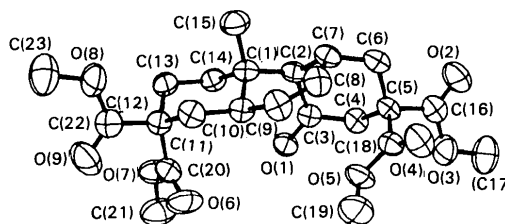


Fig. 2. ORTEP perspective view (Johnson, 1976) and atom numbering.

half-chair conformation, usually the preferred conformation for a cyclohexene ring, is adopted by ring *B* after the Diels-Alder reaction. The small steric interactions between the ketone group and both H-C(10) and H-C(14), in the observed conformation, appear to be negligible.

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## Functionalized Hydrocarbons with Condensed Ring Skeletons. III. A Tricyclo[8.4.0.0<sup>2,7</sup>]tetradec-8-ene

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**Abstract.** Tetramethyl 1,10-*trans*-1,2-*cisoid*-2,7-*cis*-1,7-dimethyltricyclo[8.4.0.0<sup>2,7</sup>]tetradec-8-ene-5,5,12,12-tetracarboxylate, C<sub>24</sub>H<sub>34</sub>O<sub>8</sub>, *M<sub>r</sub>* = 450.53, monoclinic,

*P*2<sub>1</sub>/*n*, *a* = 9.3930 (20), *b* = 23.1260 (20), *c* = 11.162 (3) Å, β = 93.180 (20)°, *V* = 2420.90 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.236 Mg m<sup>-3</sup>, λ(Mo Kα) = 0.70930 Å, μ = 0.09 mm<sup>-1</sup>, *F*(000) = 967.90, room temperature, final *R* = 0.065 for 1342 observed reflections. The

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