

Functionalized Hydrocarbons with Condensed Ring Skeletons. VII. A Methyltricyclo[8.4.0.0^{2,7}]tetradec-8-ene

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Abstract. Trimethyl 1,10-*cis*-1,2-*transoid*-2,7-*cis*-1-methyltricyclo[8.4.0.0^{2,7}]tetradec-8-ene-5,12,12-tricarboxylate, C₂₁H₃₀O₆, *M_r* = 378.46, monoclinic, *P*2₁/*a*, *a* = 14.6080 (4), *b* = 6.0494 (2), *c* = 22.6001 (9) Å, β = 96.929 (3)°, *V* = 1982.57 (12) Å³, *Z* = 4, *D_x* = 1.268 Mg m⁻³, λ(Cu *K*α) = 1.54056 Å, μ = 0.72 mm⁻¹, *F*(000) = 816, room temperature, final *R* = 0.044 for 3068 observed reflections. The structure consists of three angularly fused six-membered rings *A*, *B* and *C*. The *AB* ring junction is *cis*, the structure is *anti* between the C11 proton and C12 methyl, and also *cis* for the *BC* ring junction (abbreviated to *CAC*). Rings *A* and *C* adopt chair conformations. A double bond is contained within the half-chair conformation of ring *B*.

Introduction. We reported earlier (Michel, Giguère, Deslongchamps & Michel-Dewez, 1990) the conformation of a parent tricyclic molecule obtained by a transannular Diels–Alder reaction on a macrocycle which had four esters and a tetrasubstituted dienophile. In order to understand and predict the stereochemical outcome of the Diels–Alder reaction we carried out the reaction on a macrocycle with the same geometry at the three double bonds but different substituents. This new macrocycle had three esters and a trisubstituted dienophile (Fig. 1). The transannular Diels–Alder reaction is expected, for stereoelectronic reasons, to take place *via* a boat-like transition state (Lamothe, Ndibwami & Deslongchamps, 1988). Moreover, the conformational restraints imposed on the transition state of the macrocycle in the reaction should result in the formation of a *CAC* (*cis-anti-cis*) relative stereochemistry on the tricyclic product. We also expected a mixture of two epimers, the major one with the C5 ester in the equatorial position and the minor epimer having the C5 ester in the axial position. Indeed, NMR and GC analyses of the mixture obtained

showed a ratio of 80:20 of two products. After acidification at 273 K, the composition of the mixture changed to a ratio of 1:1. The crystallographic study presented herein was undertaken to determine the relative stereochemistry and the position of the single ester on the major epimer obtained from the Diels–Alder reaction.

Experimental. Crystal 0.30 × 0.20 × 0.15 mm; Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Cu *K*α radiation, ω–2θ scan; lattice parameters refined from 25 reflections with 2θ range 60–80°; *hkl* range: –17–17, 0–6 and 0–27; two standard reflections were monitored every 60 min, without significant deviation; 2θ_{max} = 144°; 3803 unique measured reflections; 3068 observed with *I*_{net} > 2.5σ*I*_{net}; structure was solved by direct methods and refined with *NRCVAX* (Gabe, Lee & Le Page, 1985). All non-H atoms were located in the first Fourier *E* map. After subsequent least-squares refinement, all H atoms were found by Fourier difference synthesis except for those of C17 and C21 which were calculated. All non-H atoms were refined anisotropically. Thermal parameters for isotropic H atoms were refined. The last least-squares cycle was calculated with 57 atoms; 335 parameters using weights based on counting statistics. The residuals for all significant reflections are *R_F* = 0.044, *wR* = 0.033 and *S* = 2.737; max. Δ/σ = 0.457. In the final difference map, the deepest hole was –0.22 e Å⁻³ and the

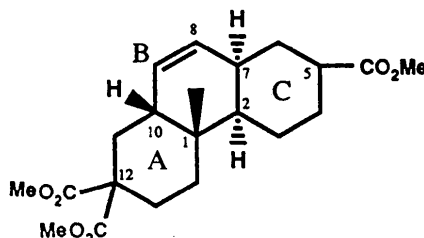


Fig. 1. IUPAC numbering (*E* = COOCH₃).

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Table 1. Final coordinates and B_{eq} values for non-H atoms, with e.s.d.'s in parentheses
$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
C1	0.80302 (12)	0.3582 (3)	0.35223 (8)	2.48 (8)
C2	0.82912 (16)	0.1747 (4)	0.31064 (9)	2.97 (10)
C3	0.88041 (14)	0.2552 (3)	0.25897 (8)	2.74 (9)
C4	0.97897 (14)	0.3231 (4)	0.27888 (9)	3.33 (10)
C5	1.02123 (14)	0.4916 (4)	0.25640 (9)	3.36 (10)
C6	0.97467 (13)	0.6467 (4)	0.21043 (8)	2.78 (8)
C7	1.03889 (16)	0.7390 (4)	0.16755 (10)	3.51 (10)
C8	1.06225 (14)	0.5719 (4)	0.12150 (9)	3.28 (9)
C9	0.97375 (16)	0.4800 (5)	0.08726 (10)	3.70 (11)
C10	0.91284 (16)	0.3762 (4)	0.13035 (10)	3.37 (10)
C11	0.88741 (13)	0.5405 (3)	0.17744 (8)	2.51 (8)
C12	0.82598 (12)	0.4375 (3)	0.22186 (8)	2.31 (7)
C13	0.79848 (14)	0.6192 (3)	0.26333 (9)	2.47 (8)
C14	0.74931 (14)	0.5419 (4)	0.31543 (9)	2.69 (8)
C15	0.73926 (15)	0.3366 (4)	0.18704 (10)	3.37 (10)
C16	0.73820 (14)	0.2625 (4)	0.39402 (9)	3.15 (9)
C17	0.66459 (22)	0.3389 (7)	0.48011 (13)	4.94 (15)
C18	0.88960 (13)	0.4325 (4)	0.39169 (8)	2.80 (9)
C19	0.99540 (19)	0.7212 (5)	0.41920 (13)	4.40 (13)
C20	1.12637 (16)	0.6655 (4)	0.08029 (10)	4.08 (11)
C21	1.1548 (3)	0.9682 (8)	0.01805 (17)	6.53 (19)
O1	0.69822 (11)	0.0905 (3)	0.38717 (7)	5.43 (9)
O2	0.72815 (10)	0.4014 (3)	0.43803 (6)	4.38 (7)
O3	0.93626 (10)	0.30746 (25)	0.42357 (6)	4.27 (7)
O4	0.90816 (9)	0.64748 (23)	0.38722 (6)	3.21 (6)
O5	1.09704 (12)	0.8566 (3)	0.05692 (7)	5.44 (9)
O6	1.19545 (13)	0.5826 (4)	0.06942 (10)	9.23 (13)

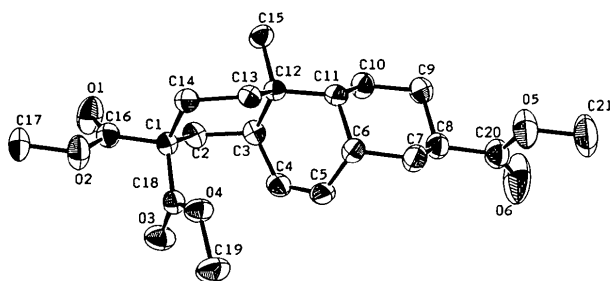


Fig. 2. ORTEP perspective view with crystallographic numbering.

highest peak 0.28 e \AA^{-3} . The secondary-extinction coefficient was $0.97 (3)$. Atomic scattering factors were from *NRCVAX*.

Discussion. Table 1 gives the final atomic parameters with their B_{eq} values.* Fig. 2 shows the atom numbering and an ORTEP (Johnson, 1976) perspective view of the tricyclic compound. Bond lengths and angles are given in Tables 2(a) and 2(b). The crystal structure of the major epimer shows the expected *CAC* (*cis-anti-cis*) relative stereochemistry and the C5 ester in equatorial position. From these results and earlier work (Lamothe, Ndibwami &

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52927 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Molecular geometry

(a) Bond lengths (\AA) with e.s.d.'s in parentheses

C1—C2	1.532 (3)	C10—C11	1.534 (3)
C1—C14	1.544 (3)	C11—C12	1.555 (3)
C1—C16	1.530 (3)	C12—C13	1.529 (3)
C1—C18	1.525 (3)	C12—C15	1.535 (3)
C2—C3	1.540 (3)	C13—C14	1.525 (3)
C3—C4	1.513 (3)	C16—O1	1.194 (3)
C3—C12	1.547 (3)	C16—O2	1.324 (3)
C4—C5	1.324 (3)	C17—O2	1.457 (3)
C5—C6	1.501 (3)	C18—O3	1.1988 (25)
C6—C7	1.533 (3)	C18—O4	1.535 (3)
C6—C11	1.538 (3)	C19—O4	1.457 (3)
C7—C8	1.519 (3)	C20—O5	1.321 (3)
C8—C9	1.529 (3)	C20—O6	1.179 (3)
C8—C20	1.509 (3)	C21—O5	1.456 (3)
C9—C10	1.531 (3)		

(b) Valence angles ($^\circ$) with e.s.d.'s in parentheses

C2—C1—C14	109.80 (15)	C6—C11—C12	111.31 (14)
C2—C1—C16	108.85 (16)	C10—C11—C12	113.29 (17)
C2—C1—C18	108.78 (16)	C3—C12—C11	109.68 (15)
C14—C1—C16	107.03 (15)	C3—C12—C13	109.64 (15)
C14—C1—C18	115.78 (17)	C3—C12—C15	109.43 (17)
C16—C1—C18	106.37 (15)	C11—C12—C13	108.83 (16)
C1—C2—C3	114.58 (17)	C11—C12—C15	109.46 (15)
C2—C3—C4	113.13 (17)	C13—C12—C15	109.79 (16)
C2—C3—C12	111.79 (16)	C12—C13—C14	115.86 (17)
C4—C3—C12	112.09 (17)	C1—C14—C13	112.36 (16)
C3—C4—C5	124.48 (19)	C1—C16—O1	125.39 (19)
C4—C5—C6	123.61 (19)	C1—C16—O2	110.91 (18)
C5—C6—C7	113.85 (17)	O1—C16—O2	123.63 (19)
C5—C6—C11	110.75 (17)	C1—C18—O3	122.49 (19)
C7—C6—C11	112.36 (16)	C1—C18—O4	113.85 (16)
C6—C7—C8	113.32 (19)	O3—C18—O4	123.66 (18)
C7—C8—C9	110.04 (18)	C8—C20—O5	112.33 (19)
C7—C8—C20	112.36 (19)	C8—C20—O6	125.41 (23)
C9—C8—C20	111.97 (18)	O5—C20—O6	122.26 (21)
C8—C9—C10	110.36 (18)	C16—O2—C17	117.58 (20)
C9—C10—C11	112.58 (19)	C18—O4—C19	115.73 (18)
C6—C11—C10	110.56 (16)	C20—O5—C21	117.6 (3)

Deslongchamps, 1988) we can assume that during the Diels–Alder reaction the transition state which leads to the major epimer adopted a chair-boat-chair conformation with the C5 ester equatorial. As the intermediate formed is conformationally mobile, ring A will adopt another chair conformation to avoid eclipsing interactions between C11 and C12. This change leads to the structure observed with ring A as a chair, a half-chair conformation in ring B, while ring C, which is not affected by the conformational change, stays in a chair conformation. No close contacts were observed in the packing.

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