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 $R = 0{\cdot}044$ and $wR = 0{\cdot}021$. Weights based on counting statistics were used. The max. Δ/σ ratio was 0·407, min. and max. electron densities in final difference map were $-0{\cdot}190$ and $0{\cdot}160\,\text{e}\,\text{Å}^{-3}$. Atomic scattering factors from *NRCVAX*.

Discussion. Table 1 gives the final atomic parameters with their B_{eq} 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.

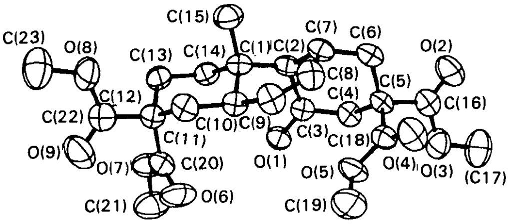

Fig. 2. *ORTEP* perspective view (Johnson, 1976) and atom numbering.

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 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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* 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.

References

Bérubé, G. & Deslongchamps, P. (1987). *Tetrahedron Lett.* **28**, 5255–5258.

Gabe, E. J., Lee, F. L. & Le Page, Y. (1985). *The NRCVAX Crystal Structure System.* In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 167–174. Oxford: Clarendon Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lamothe, S., Ndibwami, A. & Deslongchamps, P. (1988). *Tetrahedron Lett.* **29**, 1639–1640.

Marinier, A. & Deslongchamps, P. (1988). *Tetrahedron Lett.* **29**. In the press.

Michel, A. G., Proulx, M. & Michel-Dewez, N. (1988). *Acta Cryst.* C**44**, 1646–1648.

Acta Cryst. (1989). C**45**, 327–329

Functionalized Hydrocarbons with Condensed Ring Skeletons. III. A Tricyclo[8.4.0.0^{2,7}]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^{2,7}]tetradec-8-ene-5,5,12,12-tetracarboxylate, $C_{24}H_{34}O_8$, $M_r = 450{\cdot}53$, monoclinic, $P2_1/n$, $a = 9{\cdot}3930\,(20)$, $b = 23{\cdot}1260\,(20)$, $c = 11{\cdot}162\,(3)$ Å, $\beta = 93{\cdot}180\,(20)°$, $V = 2420{\cdot}90$ Å^3, $Z = 4$, $D_x = 1{\cdot}236$ Mg m^{-3}, $\lambda(\text{Mo}\ K\bar{\alpha}) = 0{\cdot}70930$ Å, $\mu = 0{\cdot}09$ mm^{-1}, $F(000) = 967{\cdot}90$, room temperature, final $R = 0{\cdot}065$ for 1342 observed reflections. The

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tricyclic compound possesses a condensed ring skeleton closely related to the *A*, *B* and *C* rings of steroid-like molecules. Rings *A* and *C* adopt a chair conformation with the C(1) methyl group axial and the C(7) methyl group equatorial; ring *B* prefers a half-chair conformation in this molecule. The relative stereochemistry is *trans* for the *AB* ring junction, *syn* between the C(1) methyl and C(2) proton and *cis* for the *BC* ring junction (abbreviated to *T–S–C*).

Introduction. In earlier communications (Michel, Proulx & Michel-Dewez, 1988; Michel, Boulay & Marinier, 1989), we have reported the conformational properties and X-ray data of two tricyclic molecules having a tridecane skeleton. The syntheses of these molecules (Bèrubé & Deslongchamps, 1987; Marinier & Deslongchamps, 1988) were a continuation of earlier general studies (Lamothe, Ndibwami & Deslongchamps, 1988*a*,*b*) demonstrating the power of the transannular Diels–Alder reaction of macrocycles in polycyclic molecule construction. In a similar fashion compound (3) (Fig. 1), a possible natural product precursor, was synthesized *via* the macrocyclization product (2) of the allylic chloride triene (1) (Fig. 1).

The transannular Diels–Alder reaction is expected, for stereoelectronic reasons, to take place *via* a boat-like transition state (Lamothe *et al.*, 1988*a*). Consequently, the conformational restraints imposed on a macrocycle by its triene configuration determine the feasibility of, and relative stereochemistries in, Diels–Alder adducts. A molecular model of (2) suggests that a single boat-like Diels–Alder transition state could be obtained, from which a tricycle of *T–S–C* relative stereochemistry and therefore variable conformation would result. The crystallographic study presented herein was undertaken to determine the relative stereochemistry and exact conformation of (3).

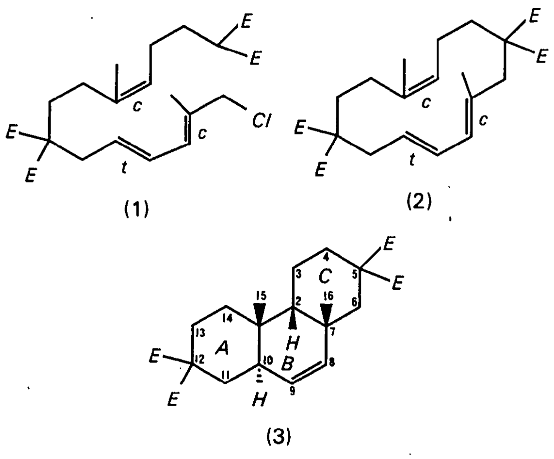

Fig. 1. Synthetic scheme. $E = COOCH_3$.

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

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
O(1)	5608 (6)	5021 (3)	7294 (5)	5·86
O(2)	3468 (6)	5385 (2)	6851 (5)	5·42
O(3)	2766 (5)	6448 (2)	8576 (5)	4·64
O(4)	3089 (5)	5602 (2)	9524 (5)	4·09
O(5)	4331 (5)	8935 (2)	12769 (5)	4·84
O(6)	4706 (6)	9472 (3)	11157 (5)	4·87
O(7)	3827 (5)	8624 (2)	8893 (5)	5·04
O(8)	2446 (5)	8299 (2)	10304 (5)	5·02
C(1)	6568 (8)	7385 (3)	10319 (6)	3·01
C(2)	6751 (7)	6848 (3)	9461 (7)	3·22
C(3)	5772 (7)	6933 (3)	8311 (7)	3·27
C(4)	5456 (7)	6402 (3)	7533 (6)	2·94
C(5)	4914 (8)	5893 (3)	8298 (7)	2·81
C(6)	6083 (7)	5759 (3)	9253 (7)	3·18
C(7)	6503 (8)	6264 (3)	10139 (7)	3·21
C(8)	5379 (8)	6310 (3)	11055 (6)	2·99
C(9)	4796 (8)	6795 (4)	11396 (7)	3·56
C(10)	5067 (7)	7370 (4)	10817 (6)	2·90
C(11)	4797 (8)	7882 (4)	11637 (7)	3·86
C(12)	4884 (8)	8455 (3)	10906 (7)	3·09
C(13)	6339 (7)	8498 (3)	10361 (7)	3·36
C(14)	6727 (7)	7960 (4)	9634 (6)	3·43
C(15)	7747 (7)	7380 (3)	11335 (6)	3·84
C(16)	7900 (7)	6043 (3)	10778 (6)	4·33
C(17)	4717 (9)	5380 (4)	7434 (7)	3·70
C(18)	3183 (9)	4928 (4)	5989 (8)	6·52
C(19)	3456 (9)	6033 (4)	8805 (7)	3·61
C(20)	1798 (8)	5689 (3)	10130 (7)	5·47
C(21)	4619 (8)	8972 (4)	11756 (8)	3·19
C(22)	4491 (9)	9979 (3)	11888 (8)	5·35
C(23)	3689 (9)	8472 (4)	9908 (7)	3·59
C(24)	1252 (8)	8248 (4)	9456 (7)	6·67

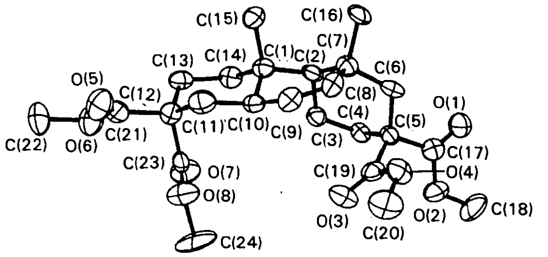

Fig. 2. *ORTEP* perspective view (Johnson, 1976) and atom numbering of (3).

Experimental. Crystal 0·20 × 0·20 × 0·10 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized Mo $K\bar{\alpha}$ radiation; cell parameters were obtained by least-squares procedure on 18 reflections with 2θ in the range 20·0–30·0°. The $\theta/2\theta$ scan mode was used for data collections at a constant speed of 4° min^{-1}. A total of 3123 reflections was collected (2947 independent) up to $2\theta_{max} = 44°$, corresponding to $9 \geq h \geq -9$, $23 \geq k \geq 0$, $11 \geq l \geq 0$, 1342 reflections satisfying $I \geq 2\sigma(I)$ were considered as observed. No correction was made for absorption. 62 standard reflections, 0·5% 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

Table 2. *Molecular geometry*

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

O(1)–C(17)	1·195 (8)	C(2)–C(7)	1·570 (9)
O(2)–C(17)	1·310 (8)	C(3)–C(4)	1·524 (8)
O(2)–C(18)	1·443 (8)	C(4)–C(5)	1·557 (9)
O(3)–C(19)	1·178 (8)	C(5)–C(6)	1·519 (8)
O(4)–C(19)	1·337 (8)	C(5)–C(17)	1·532 (9)
O(4)–C(20)	1·436 (7)	C(5)–C(19)	1·545 (9)
O(5)–C(21)	1·181 (8)	C(6)–C(7)	1·567 (9)
O(6)–C(21)	1·339 (9)	C(7)–C(8)	1·514 (9)
O(6)–C(22)	1·450 (8)	C(7)–C(16)	1·547 (9)
O(7)–C(23)	1·199 (8)	C(8)–C(9)	1·314 (9)
O(8)–C(23)	1·334 (9)	C(9)–C(10)	1·506 (9)
O(8)–C(24)	1·431 (7)	C(10)–C(11)	1·527 (9)
C(1)–C(2)	1·584 (9)	C(11)–C(12)	1·560 (9)
C(1)–C(10)	1·543 (8)	C(12)–C(13)	1·530 (8)
C(1)–C(14)	1·546 (9)	C(12)–C(21)	1·554 (9)
C(1)–C(15)	1·540 (8)	C(12)–C(23)	1·538 (9)
C(2)–C(3)	1·549 (8)	C(13)–C(14)	1·540 (9)

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

C(17)–O(2)–C(18)	117·0 (6)	C(8)–C(7)–C(16)	108·5 (6)
C(19)–O(4)–C(20)	115·5 (6)	C(7)–C(8)–C(9)	124·9 (7)
C(21)–O(6)–C(22)	113·8 (6)	C(8)–C(9)–C(10)	123·1 (7)
C(23)–O(8)–C(24)	118·2 (6)	C(1)–C(10)–C(9)	110·7 (6)
C(2)–C(1)–C(10)	109·4 (6)	C(1)–C(10)–C(11)	112·6 (6)
C(2)–C(1)–C(14)	111·0 (6)	C(9)–C(10)–C(11)	112·9 (6)
C(2)–C(1)–C(15)	110·0 (6)	C(10)–C(11)–C(12)	109·3 (6)
C(10)–C(1)–C(14)	108·2 (6)	C(11)–C(12)–C(13)	109·7 (6)
C(10)–C(1)–C(15)	111·6 (6)	C(11)–C(12)–C(21)	108·6 (6)
C(14)–C(1)–C(15)	106·6 (6)	C(11)–C(12)–C(23)	110·1 (6)
C(1)–C(2)–C(3)	108·7 (6)	C(13)–C(12)–C(21)	111·7 (6)
C(1)–C(2)–C(7)	111·0 (6)	C(13)–C(12)–C(23)	110·0 (6)
C(3)–C(2)–C(7)	114·3 (6)	C(21)–C(12)–C(23)	106·7 (6)
C(2)–C(3)–C(4)	117·2 (6)	C(12)–C(13) C(14)	113·6 (6)
C(3)–C(4)–C(5)	110·9 (6)	C(1)–C(14)–C(13)	113·7 (6)
C(4)–C(5)–C(6)	107·1 (6)	O(1)–C(17)–O(2)	123·7 (8)
C(4)–C(5)–C(17)	105·8 (6)	O(1)–C(17)–C(5)	124·0 (7)
C(4)–C(5)–C(19)	111·4 (6)	O(2)–C(17)–C(5)	112·4 (7)
C(6)–C(5)–C(17)	110·0 (6)	O(3)–C(19)–O(4)	125·5 (8)
C(6)–C(5)–C(19)	114·0 (6)	O(3)–C(19)–C(5)	125·4 (8)
C(17)–C(5)–C(19)	108·3 (6)	O(4)–C(19)–C(5)	109·1 (7)
C(5)–C(6)–C(7)	115·9 (6)	O(5)–C(21)–O(6)	124·4 (8)
C(2)–C(7)–C(6)	112·1 (6)	O(5)–C(21)–C(12)	125·5 (8)
C(2)–C(7)–C(8)	113·2 (6)	O(6)–C(21)–C(12)	110·0 (7)
C(2)–C(7)–C(16)	111·2 (6)	O(7)–C(23)–O(8)	122·9 (7)
C(6)–C(7)–C(8)	108·5 (6)	O(7)–C(23)–C(12)	125·4 (8)
C(6)–C(7)–C(16)	102·8 (6)	O(8)–C(23)–C(12)	111·7 (7)

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

C(10)–C(1)–C(2)–C(3)	69·2 (6)	C(10)–C(1)–C(2)–C(7)	−57·4 (5)
C(14)–C(1)–C(2)–C(3)	−50·2 (5)	C(14)–C(1)–C(2)–C(7)	−176·8 (8)
C(2)–C(1)–C(10)–C(9)	53·6 (5)	C(2)–C(1)–C(10)–C(11)	−178·9 (9)
C(14)–C(1)–C(10)–C(9)	174·7 (9)	C(14)–C(1)–C(10)–C(11	−57·8 (5)
C(2)–C(1)–C(14)–C(13)	171·3 (8)	C(10)–C(1)–C(14)–C(13)	51·2 (5)
C(7)–C(2)–C(3)–C(4)	−38·4 (4)	C(1)–C(2)–C(3)–C(4)	−163·0 (8)
C(1)–C(2)–C(7)–C(8)	34·5 (4)	C(1)–C(2)–C(7)–C(6)	157·6 (8)
C(3)–C(2)–C(7)–C(6)	34·2 (4)	C(3)–C(2)–C(7)–C(8)	−89·0 (7)
C(3)–C(4)–C(5)–C(6)	−59·7 (5)	C(2)–C(3)–C(4)–C(5)	51·5 (5)
C(5)–C(6)–C(7)–C(2)	−48·1 (5)	C(4)–C(5)–C(6)–C(7)	60·4 (5)
C(6)–C(7)–C(8)–C(9)	−134·4 (9)	C(5)–C(6)–C(7)–C(8)	77·6 (6)
C(7)–C(8)–C(9)–C(10)	6·6 (4)	C(2)–C(7)–C(8)–C(9)	−9·3 (4)
C(8)–C(9)–C(10)–C(11)	−156·8 (9)	C(8)–C(9)–C(10)–C(1)	−29·5 (5)
C(9)–C(10)–C(11)–C(12)	−171·7 (9)	C(1)–C(10)–C(11)–C(12)	62·0 (6)
C(11)–C(12)–C(13)–C(14)	52·6 (5)	C(10)–C(11)–C(12)–C(13)	−57·2 (5)
C(12)–C(13)–C(14)–C(1)	−51·1 (5)		

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 $R = 0{\cdot}065$ and $wR = 0{\cdot}026$. Weights based on counting statistics were used. The max. Δ/σ ratio was 0·001. In the last *D* map the deepest hole was $-0{\cdot}230$ e Å^{-3} and the highest peak $0{\cdot}240$ e Å^{-3}. Atomic scattering factors from *NRCVAX*.

Discussion. Table 1 gives the final atomic parameters with their $B_{\rm eq}$ 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 results of the structure determination indicate that (3) has, indeed, a *T–S–C* relative stereochemistry. The *trans–cis* diene and *cis* dienophile of (2) allow the macrocycle to take a conformation leading to only one boat-like transition state in which the *T–S–C* relative stereochemistry of the resulting racemic adduct is determined. Unlike a conformationally rigid *trans–syn–trans* (*T–S–T*) transannular Diels–Alder adduct (Michel *et al.*, 1988), a *T–S–C* adduct is conformationally mobile; the *B* and *C* rings of the latter are analogous to a *cis*-decalin system in which steric interactions dictate the resulting conformation. Presumably after the Diels—Alder reaction, ring *B* adopts an energetically preferred half-chair conformation which compensates the pseudo-1,3-diaxial C(1) and C(7) methyl-group interaction. This allows ring *C* to adopt a chair conformation in which the C(7) methyl is equatorial, while the C(1) methyl necessarily takes an axial position on the chair conformation of ring *A*.

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* 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 51428 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bérubé, G. & Deslongchamps, P. (1987). *Tetrahedron Lett.* **28**, 5255–5258.

Gabe, E. J., Lee, F. L. & Le Page, Y. (1985). *The NRCVAX Crystal Structure System.* In *Crystallographic Computing* 3: *Data Collection, Structure Determination, Proteins, and Databases,* edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 167–174. Oxford: Clarendon Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lamothe, S., Ndibwami, A. & Deslongchamps, P. (1988*a*). *Tetrahedron Lett.* **29**, 1639–1640.

Lamothe, S., Ndibwami, A. & Deslongchamps, P. (1988*b*). *Tetrahedron Lett.* **29**, 1641–1644.

Marinier, A. & Deslongchamps, P. (1988). *Tetrahedron Lett.* **29**. In the press.

Michel, A. G., Boulay, G. & Marinier, A. (1989). *Acta Cryst.* C**45**, 325–327.

Michel, A. G., Proulx, M. & Michel-Dewez, N. (1988). *Acta Cryst.* C**44**, 1646–1648.