1,3,2-dioxaborinan-2-ol, average 1·363 Å (Kuribayashi, 1973). The Si—O bond length, 1·634 (2) Å, is exactly the same as that in $(H_3Si)_2O$ (Almenningen *et al.*, 1963) but slightly longer than the value of 1·616 (1) Å observed in $(Ph_3Si)_2O$ (Glidewell & Liles, 1977). Other $(X_3Si)_2O$ compounds (X = F, Cl) have *d*(Si—O) values of 1·580 (25) Å (Airey, Glidewell, Rankin, Robiette, Sheldrick & Cruickshank, 1970) and 1·592 (10) Å (Airey, Glidewell, Robiette & Sheldrick, 1971), respectively. Although there has been extensive discussion in the literature about the role of π bonding in Si—O bonds, it is generally agreed that there is no simple correlation between *d*(Si—O) and Si—O—Si angles and the amount of π bonding. A similar situation appears to pertain in boron–oxygen chemistry if we compare the data from the present work on the (triphenylsiloxy)-dioxaborinane derivative and the data from the 4,6-dimethyl-1,3,2-dioxaborinan-2-ol (Kuribayashi, 1973). In these compounds the heterocyclic BO_2C_3 entities are virtually identical as are the exocyclic B—O bond lengths [B—OSi 1·363 (5) and B—OH 1·365 (7) Å respectively]. However, in the first compound a 'π-bonding' $SiPh_3$ group is present whereas in the second the H atom clearly cannot participate in π bonding. Therefore other steric and/or electronic effects must be operating to equalize the observed B—O bond lengths. The C—C and C—O bond lengths are all normal. The Ph_3Si group has an irregular propeller conformation (angles between the phenyl ring planes and the relevant O—Si—C planes are 43·0, 19·7 and 64·4°); there are no untoward intermolecular contacts.

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References

AIREY, W., GLIDEWELL, C., RANKIN, D. W. H., ROBIETTE, A. G., SHELDRICK, G. M. & CRUICKSHANK, D. W. J. (1970). *Trans. Faraday Soc.* **66**, 551–556.

AIREY, W., GLIDEWELL, C., ROBIETTE, A. G. & SHELDRICK, G. M. (1971). *J. Mol. Struct.* **8**, 413–422.

ALMENNINGEN, A., BASTIANSEN, O., EWING, V., HEDBERG, K. & TRÆTTEBERG, M. (1963). *Acta Chem. Scand.* **17**, 2455–2460.

FRENZ, B. A. (1983). *SDP-Plus Structure Determination Package.* College Station, Texas, USA, and Enraf–Nonius, Delft, The Netherlands.

GLIDEWELL, C. & LILES, D. C. (1977). *Acta Cryst.* **B34**, 124–128.

GUNDERSEN, G. & VAHRENKAMP, H. (1976). *J. Mol. Struct.* **33**, 79–89.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Pres. (Present distributor Kluwer Academic Publishers, Dordrecht.)

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

KONIG, H., HOPPE, R. & JANSEN, M. (1979). *Z. Anorg. Chem.* **449**, 91–101.

KURIBAYASHI, S. (1973). *Bull. Chem. Soc. Jpn*, **46**, 1045–1048.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

ZACHARIASEN, W. H. (1954). *Acta Cryst.* **7**, 305–310.

Acta Cryst. (1990). C**46**, 1254–1256

Functionalized Hydrocarbons with Condensed Ring Skeletons. V. Substituted 1,2-Dimethyltricyclo[8.4.0.0^{2,7}]tetradec-8-ene

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Abstract. Tetramethyl 1,2-*trans*-1,10-*cis*-2,7-*cis*-1,2-dimethyltricyclo[8.4.0.0.^{2,7}]tetradec-8-ene-5,5,12,12-tetracarboxylate, $C_{24}H_{34}O_8$, M_r = 450·53, monoclinic, $A2/n$, a = 25·8320 (10), b = 6·8873 (3), c = 26·4287 (8) Å, β = 99·620 (3)°, V = 4635·88 Å^3, D_x = 1·291 Mg m^{-3}, Z = 8, λ(Cu $K\bar{\alpha}$) = 1·54056 Å, μ = 0·66 mm^{-1}, $F(000)$ = 1935·79, room temperature, final R = 0·044 for 3692 observed reflections. The tricyclic compound has the opposite configuration at C(10), from the triterpene saponins. The relative stereochemistry is *cis* for the *AB* ring junction, *anti* between C(1) methyl and C(2) methyl and *cis* for the *BC* ring junction (abbreviated to *CAC*).

Introduction. We have reported a general strategy for the synthesis of polycyclic compounds *via* the trans-

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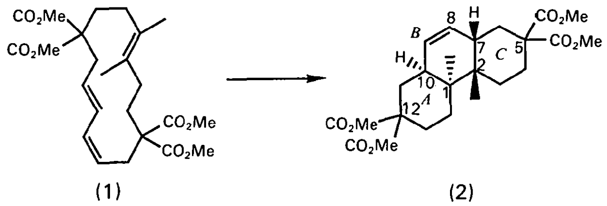
Table 1. *Fractional coordinates and B_{eq} values with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
O1	0·96553 (7)	0·8622 (4)	0·42900 (6)	8·31 (12)
O2	0·89018 (5)	0·75156 (24)	0·38980 (5)	4·36 (7)
O3	0·81448 (6)	0·62342 (25)	0·46603 (6)	4·86 (7)
O4	0·82311 (5)	0·94605 (22)	0·46102 (5)	4·29 (6)
O5	0·85828 (6)	1·11216 (19)	0·72060 (5)	4·12 (6)
O6	0·77952 (5)	0·97032 (18)	0·70172 (5)	3·63 (6)
O7	0·80975 (6)	0·56062 (21)	0·78680 (5)	4·58 (7)
O8	0·84964 (6)	0·83286 (20)	0·81759 (5)	4·30 (6)
C1	0·91411 (7)	0·6287 (3)	0·64757 (6)	2·74 (6)
C2	0·93399 (7)	0·6755 (3)	0·59524 (6)	2·78 (7)
C3	0·91192 (8)	0·5233 (3)	0·55430 (7)	3·31 (8)
C4	0·92227 (8)	0·5666 (3)	0·50032 (7)	3·39 (8)
C5	0·90163 (7)	0·7666 (3)	0·48076 (6)	2·88 (7)
C6	0·92394 (8)	0·9218 (3)	0·52039 (7)	3·13 (7)
C7	0·91476 (7)	0·8802 (3)	0·57566 (6)	2·83 (7)
C8	0·85865 (7)	0·9169 (3)	0·58103 (6)	2·97 (7)
C9	0·83163 (7)	0·8074 (3)	0·60851 (6)	2·95 (7)
C10	0·85320 (7)	0·6330 (3)	0·63889 (6)	2·70 (6)
C11	0·83079 (7)	0·6130 (3)	0·68894 (7)	2·78 (7)
C12	0·85182 (7)	0·76331 (24)	0·73028 (6)	2·66 (6)
C13	0·91238 (7)	0·7616 (3)	0·73890 (7)	3·08 (8)
C14	0·93417 (7)	0·7831 (3)	0·68883 (7)	3·09 (8)
C15	0·93348 (10)	0·4272 (3)	0·66747 (9)	3·95 (9)
C16	0·99434 (8)	0·6719 (4)	0·60271 (9)	4·04 (10)
C17	0·92279 (8)	0·8046 (3)	0·43078 (7)	3·48 (8)
C18	0·90821 (12)	0·7723 (5)	0·34091 (8)	4·75 (12)
C19	0·84176 (7)	0·7658 (3)	0·46884 (6)	3·23 (8)
C20	0·76653 (11)	0·9643 (7)	0·45142 (15)	6·80 (18)
C21	0·83158 (7)	0·9691 (3)	0·71710 (6)	2·88 (7)
C22	0·75676 (12)	1·1564 (4)	0·68498 (13)	5·24 (13)
C23	0·83357 (7)	0·7043 (3)	0·78040 (7)	3·00 (7)
C24	0·83804 (15)	0·7853 (5)	0·86788 (9)	5·33 (14)

annular Diels–Alder reaction on macrocyclic trienes (Lamothe, Ndibwami & Deslongchamps, 1988 *a*,*b*). Using this approach on the *cis-trans-trans* triene (1) the Diels–Alder reaction should take place *via* a boat-like transition state to afford only the *CAC* tricycle (2) since the other possible tricycle *TAT* cannot have its *B* ring in a boat conformation. The crystallographic study presented here was undertaken to verify the relative stereochemistry and the conformation of the product obtained. These results are essential to plan the total synthesis of triterpenes having pharmacological activities.



(1) (2)

Experimental. Crystal dimensions 0·10 × 0·15 × 0·20 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromator, Cu $K\bar{\alpha}$ radiation. Cell dimensions were obtained from 21 reflections with 2θ angle in the range 60·00–100·00°. The $\omega/2\theta$ scan mode was used for data collections at a constant scan speed of 4° min^{-1}. A total of 5131 reflections was collected (4556 independent) up to $2\theta_{max}$ =

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles of the condensed rings skeleton* (°)

O(1)—C(17)	1·182 (3)	C(2)—C(7)	1·5543 (25)
O(2)—C(17)	1·3081 (22)	C(2)—C(16)	1·539 (3)
O(2)—C(18)	1·4517 (25)	C(3)—C(4)	1·524 (3)
O(3)—C(19)	1·202 (3)	C(4)—C(5)	1·535 (3)
O(4)—C(19)	1·3354 (25)	C(5)—C(6)	1·540 (3)
O(4)—C(20)	1·447 (3)	C(5)—C(17)	1·5341 (24)
O(5)—C(21)	1·1974 (22)	C(5)—C(19)	1·526 (3)
O(6)—C(21)	1·3386 (22)	C(6)—C(7)	1·5453 (24)
O(6)—C(22)	1·448 (3)	C(7)—C(8)	1·501 (3)
O(7)—C(23)	1·1920 (23)	C(8)—C(9)	1·324 (3)
O(8)—C(23)	1·3365 (22)	C(9)—C(10)	1·500 (3)
O(8)—C(24)	1·448 (3)	C(10)—C(11)	1·5361 (24)
C(1)—C(2)	1·5869 (23)	C(11)—C(12)	1·5368 (24)
C(1)—C(10)	1·5510 (24)	C(12)—C(13)	1·543 (3)
C(1)—C(14)	1·5491 (25)	C(12)—C(21)	1·5303 (25)
C(1)—C(15)	1·538 (3)	C(12)—C(23)	1·5333 (23)
C(2)—C(3)	1·545 (3)	C(13)—C(14)	1·5293 (25)

C(17)—O(2)—C(18)	116·84 (17)	C(6)—C(7)—C(8)	111·18 (15)
C(19)—O(4)—C(20)	115·84 (23)	C(7)—C(8)—C(9)	124·17 (17)
C(21)—O(6)—C(22)	115·75 (17)	C(8)—C(9)—C(10)	124·56 (16)
C(23)—O(8)—C(24)	116·02 (18)	C(1)—C(10)—C(9)	111·79 (14)
C(2)—C(1)—C(10)	109·57 (13)	C(1)—C(10)—C(11)	112·94 (14)
C(2)—C(1)—C(14)	110·80 (14)	C(9)—C(10)—C(11)	111·89 (15)
C(2)—C(1)—C(15)	110·32 (15)	C(10)—C(11)—C(12)	114·37 (14)
C(10)—C(1)—C(14)	107·62 (14)	C(11)—C(12)—C(13)	109·22 (14)
C(10)—C(1)—C(15)	109·36 (16)	C(11)—C(12)—C(21)	113·28 (14)
C(14)—C(1)—C(15)	109·11 (16)	C(11)—C(12)—C(23)	108·21 (14)
C(1)—C(2)—C(3)	109·70 (14)	C(13)—C(12)—C(21)	109·87 (14)
C(1)—C(2)—C(7)	110·03 (13)	C(13)—C(12)—C(23)	108·72 (14)
C(1)—C(2)—C(16)	110·69 (14)	C(21)—C(12)—C(23)	107·43 (14)
C(3)—C(2)—C(7)	108·80 (14)	C(12)—C(13)—C(14)	112·47 (14)
C(3)—C(2)—C(16)	109·04 (16)	C(1)—C(14)—C(13)	114·48 (15)
C(7)—C(2)—C(16)	108·54 (16)	O(1)—C(17)—O(2)	122·52 (17)
C(2)—C(3)—C(4)	114·89 (16)	O(1)—C(17)—C(5)	124·14 (17)
C(3)—C(4)—C(5)	112·65 (15)	O(2)—C(17)—C(5)	113·11 (15)
C(4)—C(5)—C(6)	108·94 (15)	O(3)—C(19)—O(4)	123·78 (18)
C(4)—C(5)—C(17)	106·83 (15)	O(3)—C(19)—C(5)	125·38 (18)
C(4)—C(5)—C(19)	110·45 (16)	O(4)—C(19)—C(5)	110·83 (16)
C(6)—C(5)—C(17)	108·69 (15)	O(5)—C(21)—O(6)	123·68 (17)
C(6)—C(5)—C(19)	113·21 (15)	O(5)—C(21)—C(12)	125·04 (16)
C(17)—C(5)—C(19)	108·52 (14)	O(6)—C(21)—C(12)	111·27 (14)
C(5)—C(6)—C(7)	114·53 (15)	O(7)—C(23)—O(8)	123·36 (16)
C(2)—C(7)—C(6)	113·07 (15)	O(7)—C(23)—C(12)	125·68 (16)
C(2)—C(7)—C(8)	112·41 (14)	O(8)—C(23)—C(12)	110·92 (15)

C10—C1—C2—C3	−59·5 (1)	C10—C1—C2—C7	60·1 (1)
C14—C1—C2—C3	−178·1 (2)	C14—C1—C2—C7	−58·5 (1)
C2—C1—C10—C9	−45·9 (1)	C2—C1—C10—C11	−173·2 (2)
C14—C1—C10—C9	74·6 (1)	C14—C1—C10—C11	−52·6 (1)
C2—C1—C14—C13	174·1 (2)	C10—C1—C14—C13	54·3 (1)
C1—C2—C3—C4	172·5 (2)	C7—C2—C3—C4	52·0 (1)
C1—C2—C7—C6	−169·7 (2)	C1—C2—C7—C8	−42·8 (1)
C3—C2—C7—C6	−49·5 (1)	C3—C2—C7—C8	77·4 (1)
C2—C3—C4—C5	−56·0 (1)	C3—C4—C5—C6	53·3 (1)
C4—C5—C6—C7	−52·8 (1)	C5—C6—C7—C2	53·0 (1)
C5—C6—C7—C8	−74·5 (1)	C2—C7—C8—C9	13·1 (1)
C6—C7—C8—C9	141·0 (2)	C7—C8—C9—C10	1·0 (1)
C8—C9—C10—C1	16·5 (1)	C8—C9—C10—C11	144·3 (2)
C1—C10—C11—C12	54·9 (1)	C9—C10—C11—C12	−72·3 (1)
C10—C11—C12—C13	−52·2 (1)	C11—C12—C13—C14	51·9 (1)
C12—C13—C14—C1	−56·1 (1)		

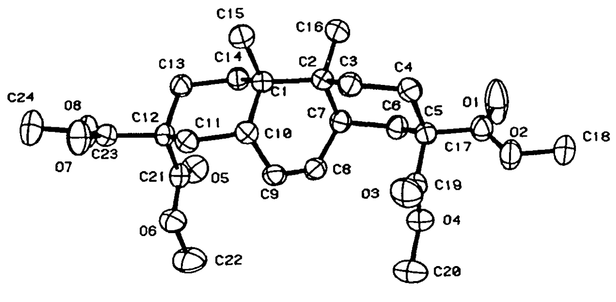


Fig. 1. *ORTEP* perspective view (Johnson, 1976), molecular formula and atomic numbering.

143·5°, corresponding to $-31 \leq h \leq 31$, $0 \leq k \leq 8$, $0 \leq l \leq 32$. 3692 reflections satisfying $I \geq 2{\cdot}5\,\sigma(I)$ were considered as observed. No correction was made for absorption, 62 standard reflections, 0·5% intensity variation. The *NRCVAX* system was used for all calculations (Gabe, Lee & LePage, 1985). 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, their positions and isotropic temperature factors were refined. The final residuals obtained at convergence* were $R = 0{\cdot}044$ and $wR = 0{\cdot}052$, $S = 2{\cdot}03$. Weights based on counting statistics were used. The maximum Δ/σ ratio was 0·220. In the last D map, the deepest hole was $-0{\cdot}390$ e Å^{-3}, and the highest peak 0·440 e Å^{-3}. Atomic scattering factors as stored in the *NRCVAX* program were those of Cromer & Waber (1974).

Discussion. Table 1 gives the final atomic parameters with their *B* values.† Bond lengths and angles are given in Tables 2(*a*) and 2(*b*). Selected torsion angles of the condensed rings skeleton are given in Table 2(*c*). Fig. 1 shows a perspective view and the atomic numbering of the molecule. The results of the structure determination indicate that (2) has a *CAC* relative stereochemistry. This observation confirms that during the Diels–Alder reaction, the macrocycle (1) leads to a conformationally mobile tricycle having a boat-like *B* ring and chair-like *A* and *C* rings. This transient conformer adopted a more stable conformation with a twisted boat *B* ring as observed in the crystal structure. It is interesting to notice here that the planes of both axial methoxycarbonyl groups symmetrically face the olefinic plane, as can be seen in Fig. 1. Such proximities between methoxycarbonyl and the olefinic moieties suggest further exploitation of the iodolactonization reaction and further desactivation leading to specific natural products. No abnormally short intermolecular contacts were noted in the crystal packing.

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* Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$.

† 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 52678 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cromer, D. T. & Waber, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, edited by J. A. Ibers & W. C. Hamilton, Table 2.2B, pp. 99–101. Birmingham: Kynoch Press.

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.

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Structure of 1-Methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine

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Abstract. $C_{30}H_{25}N$, $M_r = 399{\cdot}54$, monoclinic, $P2_1/c$, $a = 12{\cdot}581\,(5)$, $b = 13{\cdot}955\,(5)$, $c = 12{\cdot}885\,(4)$ Å, $\beta = 93{\cdot}63\,(3)°$, $V = 2258\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}17\,(1)$, $D_x = 1{\cdot}176\,(1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}063$ mm^{-1}, $F(000) = 848$, $T = 296$ K, $R = 0{\cdot}052$ for 2231 unique observed reflections. The planes of the phenyl rings at C1, C3, C3 and C5 make angles 51·5 (1), 56·9 (1), 75·6 (1) and 60·8 (1)° with the mean plane of the dihydropyridine ring, which is itself essentially planar. No significant intermolecular interactions are observed.

Introduction. The structure of the title compound has been studied in connection with the development of new materials suitable for recording media. The structure of the excited state may explain the differ-

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