overlap between the adjacent molecules, which can also have some effect on the twist angle between the phenyl rings, as in 2,2',3,4',5'-pentachloro-4-methoxybiphenyl (Rissanen, Valkonen & Mannila, 1988). There are no intermolecular contacts shorter than the sums of the van der Waals radii.

The authors thank Dr Tarmo Humppi for synthesizing the compound.

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# Functionalized Hydrocarbons with Condensed Ring Skeletons. I. Tricyclo[7.4.0.0²,⁶]tridecane Skeleton

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**Abstract.** Dimethyl 1,2-cis-1,9-trans-11-benzyloxymethyl-2-methoxymethoxy-1-methyltricyclo[7.4.0.-0²,⁶]tridec-7-ene-4,4-dicarboxylate, $C_{28}H_{38}O_7$, $M_r = 486.57$, triclinic, $P\bar{1}$, $a = 12.822$ (2), $b = 15.560$ (1), $c = 6.5851$ (7) Å, $\alpha = 85.73$ (1), $\beta = 96.42$ (1), $\gamma = 98.26$ (1)°, $V = 1289.71$ Å³, $D_x = 1.253$ Mg m⁻³, $Z = 2$, $\lambda(\text{Mo }K\bar{\alpha}) = 0.71069$ Å, $\mu = 0.0924$ mm⁻¹, $F(000) = 524$, room temperature, final $R = 0.043$ for 4285 observed reflexions. The title compound possesses a condensed ring skeleton closely related to the B, C, and D rings of steroid-like molecules. Ring B adopts a chair conformation with the methyl group axial at C(1), ring C has a boat conformation owing to the double bond between C(7)—C(8) and ring D has a β-envelope conformation, with the benzyloxymethyl group equatorial at C(11). The relative stereochemistry is trans for the BC junction, syn for the orientation of the methyl and methoxymethyl groups, and trans for the CD junction (T–S–T).
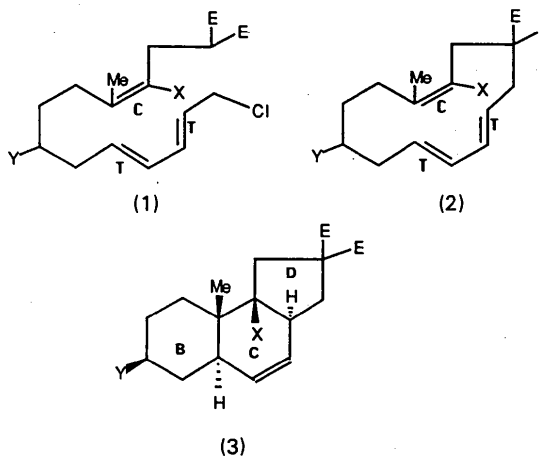
Fig. 1. Molecular schemes ($X = \text{OCH}_2\text{OCH}_3$, $Y = \text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$, $E = \text{COOCH}_3$).

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**Introduction.** This work is part of a more general study on the conformational properties of tricyclic molecules obtained from transannular Diels–Alder reaction (Beattig, Dallaire, Pitteloud & Deslongchamps, 1987; Beattig, Marinier, Pitteloud & Deslongchamps, 1987) on 13-membered macrocyclic trienes. The transannular Diels–Alder reaction on a macrocyclic triene seems a powerful strategy for the construction of complex polycyclic molecules among which many natural-product structures are known (Tokuyama, Daly & Witkop, 1969; Birch, Richards, Smith, Harris & Whalley, 1959). The title compound (3) was obtained as one of the major products of the macrocyclization of the allylic chloride (1) (Bérubé & Deslongchamps,

Table 1. *Fractional coordinates* $(\times 10^4)$ *and equivalent B values for nonhydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | $B_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| C(1) | 2593 (1) | 5460 (1) | 9605 (3) | 2·64 |
| C(2) | 2334 (1) | 4446 (1) | 9322 (3) | 2·65 |
| C(3) | 2012 (1) | 3819 (1) | 11137 (3) | 3·11 |
| C(4) | 2309 (1) | 2917 (1) | 10677 (3) | 2·81 |
| C(5) | 2927 (1) | 3097 (1) | 8740 (3) | 3·12 |
| C(6) | 3309 (1) | 4065 (1) | 8780 (3) | 2·63 |
| C(7) | 3782 (1) | 4576 (1) | 7010 (3) | 3·08 |
| C(8) | 4003 (1) | 5422 (1) | 7205 (3) | 3·14 |
| C(9) | 3770 (1) | 5769 (1) | 9148 (3) | 2·73 |
| C(10) | 4068 (1) | 6747 (1) | 9287 (3) | 3·23 |
| C(11) | 3909 (1) | 7052 (1) | 11375 (3) | 3·31 |
| C(12) | 2822 (1) | 6684 (1) | 12077 (3) | 3·68 |
| C(13) | 2526 (1) | 5705 (1) | 11812 (3) | 3·22 |
| C(14) | 1852 (1) | 5960 (1) | 8108 (3) | 3·56 |
| C(15) | 4107 (2) | 8041 (1) | 11364 (3) | 3·90 |
| O(16) | 3348 (1) | 8371 (1) | 9879 (2) | 4·08 |
| C(17) | 3566 (2) | 9274 (1) | 9351 (3) | 4·26 |
| C(18) | 2844 (2) | 9487 (1) | 7484 (3) | 3·65 |
| C(19) | 2271 (2) | 10180 (1) | 7405 (3) | 4·72 |
| C(20) | 1615 (2) | 10372 (2) | 5675 (4) | 5·94 |
| C(21) | 1530 (2) | 9879 (2) | 4000 (4) | 5·84 |
| C(22) | 2096 (2) | 9185 (2) | 4074 (3) | 5·26 |
| C(23) | 2746 (2) | 8995 (1) | 5793 (3) | 4·49 |
| O(24) | 1575 (1) | 4277 (1) | 7538 (2) | 3·30 |
| C(25) | 485 (2) | 4203 (1) | 7754 (3) | 4·19 |
| O(26) | 11 (1) | 3337 (1) | 7866 (2) | 4·64 |
| C(27) | −68 (2) | 2943 (2) | 5948 (4) | 5·95 |
| C(28) | 1355 (1) | 2219 (1) | 10337 (3) | 3·31 |
| O(29) | 1199 (1) | 1736 (1) | 8969 (2) | 4·51 |
| O(30) | 716 (1) | 2198 (1) | 11822 (2) | 4·13 |
| C(31) | −289 (2) | 1623 (2) | 11555 (4) | 5·38 |
| C(32) | 3062 (1) | 2583 (1) | 12431 (3) | 3·30 |
| O(33) | 3544 (1) | 3002 (1) | 13755 (2) | 5·58 |
| O(34) | 3191 (1) | 1762 (1) | 12215 (2) | 4·65 |
| C(35) | 3964 (2) | 1402 (2) | 13691 (4) | 5·58 |
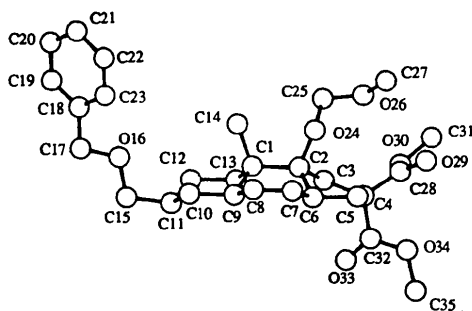


Fig. 2. *PLUTO* perspective view and atom numbering.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·585 (2) | C(12)–C(13) | 1·535 (3) |
| C(1)–C(9) | 1·573 (2) | C(15)–O(16) | 1·423 (2) |
| C(1)–C(13) | 1·545 (3) | O(16)–C(17) | 1·418 (2) |
| C(1)–C(14) | 1·539 (3) | C(17)–C(18) | 1·500 (3) |
| C(2)–C(3) | 1·541 (2) | C(18)–C(19) | 1·386 (3) |
| C(2)–C(6) | 1·545 (3) | C(18)–C(23) | 1·382 (3) |
| C(2)–O(24) | 1·453 (2) | C(19)–C(20) | 1·379 (3) |
| C(3)–C(4) | 1·564 (3) | C(20)–C(21) | 1·376 (4) |
| C(4)–C(5) | 1·563 (3) | C(21)–C(22) | 1·380 (4) |
| C(4)–C(28) | 1·523 (2) | C(22)–C(23) | 1·369 (3) |
| C(4)–C(32) | 1·530 (3) | O(24)–C(25) | 1·407 (2) |
| C(5)–C(6) | 1·517 (2) | C(25)–O(26) | 1·397 (2) |
| C(6)–C(7) | 1·496 (2) | O(26)–C(27) | 1·431 (3) |
| C(7)–C(8) | 1·318 (3) | C(28)–O(29) | 1·198 (2) |
| C(8)–C(9) | 1·501 (3) | C(28)–O(30) | 1·341 (2) |
| C(9)–C(10) | 1·522 (3) | O(30)–C(31) | 1·460 (2) |
| C(10)–C(11) | 1·532 (3) | C(32)–O(33) | 1·191 (2) |
| C(11)–C(12) | 1·535 (3) | C(32)–O(34) | 1·333 (2) |
| C(11)–C(15) | 1·523 (3) | O(34)–C(35) | 1·450 (3) |
| | | | |
| C(2)–C(1)–C(9) | 108·5 (1) | C(10)–C(11)–C(12) | 112·8 (1) |
| C(2)–C(1)–C(13) | 113·3 (1) | C(10)–C(11)–C(15) | 110·4 (2) |
| C(2)–C(1)–C(14) | 110·6 (1) | C(12)–C(11)–C(15) | 111·8 (2) |
| C(9)–C(1)–C(14) | 109·0 (1) | C(11)–C(12)–C(13) | 113·3 (1) |
| C(13)–C(1)–C(14) | 109·5 (1) | C(1)–C(13)–C(12) | 112·6 (1) |
| C(1)–C(2)–C(3) | 120·1 (1) | C(11)–C(15)–O(16) | 107·8 (1) |
| C(1)–C(2)–C(6) | 111·7 (1) | C(15)–O(16)–C(17) | 114·7 (1) |
| C(1)–C(2)–O(24) | 110·4 (1) | O(16)–C(17)–C(18) | 108·4 (1) |
| C(3)–C(2)–C(6) | 100·5 (1) | C(17)–C(18)–C(19) | 121·1 (2) |
| C(3)–C(2)–O(24) | 109·8 (1) | C(17)–C(18)–C(23) | 120·3 (2) |
| C(6)–C(2)–O(24) | 102·7 (1) | C(19)–C(18)–C(23) | 118·6 (2) |
| C(2)–C(3)–C(4) | 105·7 (1) | C(18)–C(19)–C(20) | 120·5 (2) |
| C(3)–C(4)–C(5) | 105·4 (1) | C(19)–C(20)–C(21) | 120·2 (2) |
| C(3)–C(4)–C(28) | 113·6 (1) | C(20)–C(21)–C(22) | 119·5 (2) |
| C(3)–C(4)–C(32) | 110·7 (1) | C(21)–C(22)–C(23) | 120·3 (2) |
| C(5)–C(4)–C(28) | 111·4 (1) | C(18)–C(23)–C(22) | 120·9 (2) |
| C(5)–C(4)–C(32) | 107·7 (1) | C(2)–O(24)–C(25) | 119·1 (2) |
| C(28)–C(4)–C(32) | 107·9 (1) | O(24)–C(25)–O(26) | 112·1 (2) |
| C(4)–C(5)–C(6) | 102·4 (1) | C(25)–O(26)–C(27) | 112·4 (2) |
| C(2)–C(6)–C(5) | 103·4 (1) | C(4)–C(28)–O(29) | 125·5 (2) |
| C(2)–C(6)–C(7) | 111·0 (1) | C(4)–C(28)–O(30) | 110·6 (1) |
| C(5)–C(6)–C(7) | 122·2 (2) | O(29)–C(28)–O(30) | 123·9 (2) |
| C(6)–C(7)–C(8) | 115·3 (2) | C(28)–O(30)–C(31) | 116·1 (1) |
| C(7)–C(8)–C(9) | 117·2 (2) | C(4)–C(32)–O(33) | 125·9 (2) |
| C(1)–C(9)–C(8) | 111·5 (1) | C(4)–C(32)–O(34) | 111·3 (1) |
| C(1)–C(9)–C(10) | 111·8 (1) | O(33)–C(32)–O(34) | 122·5 (2) |
| C(8)–C(9)–C(10) | 114·8 (1) | C(32)–O(34)–C(35) | 116·1 (1) |
| C(9)–C(10)–C(11) | 112·5 (2) | | |

1987). This reaction was described as a transannular Diels–Alder reaction of compound (2). It was expected that the *trans–trans* diene and *cis* dienophile of (2) would give two different tricycles having *T–S–T* and *C–S–C* stereochemistry. The present crystallographic study was undertaken to determine the exact conformation of (3), expected to be the *T–S–T* isomer. The molecular formulae for (1), (2) and (3) are given in Fig. 1.

**Experimental.** Crystal $0.30 \times 0.32 \times 0.23$ mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized Mo $K\bar\alpha$ radiation; lattice parameters determined from 25 medium-angle reflexions; $0 \le h \le 17$, $-21 \le k \le 20$, $-8 \le l \le 8$; one standard reflexion monitored every 80 reflexions without significant deviation; 6835 unique measured reflexions; 4285 observed with $F \ge 2\sigma(F)$; structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); molecular illustration drawn using *PLUTO* (Motherwell & Clegg, 1978); $\sum w(\Delta F)^2$ minimized; max. $\Delta/\sigma$ (for

$C_{28}H_{38}O_7$

non-H atoms) $= 0.46$; max. and min. electron densities in final difference map $0.10$ and $-0.12$ e $Å^{-3}$; H atoms calculated and kept unrefined for the last two cycles; all non-H atoms refined anisotropically; $R = 0.043$; $wR = 0.040$; block-diagonal least-squares refinement using *XTAL* (Stewart & Hall, 1985).

**Discussion.** Table 1 gives the atomic coordinates of the structure shown in Fig. 2.* Bond lengths and angles are given in Table 2. Ring *B* adopts a 'chair' conformation with C(9) $0.6$ Å above and C(12) $0.7$ Å below the least-squares plane of C(1), C(13), C(11) and C(10). The middle ring *C* adopts a boat-like conformation with C(9) and C(6), respectively, $0.61$ and $0.63$ Å above the least-squares plane of C(1), C(2), C(7) and C(8). Ring *D* can be described as a $\beta$-envelope similar to the other five-membered rings found in polycyclic structures (Cox, Mkandawire & Mallinson, 1981; Précigoux, Busetta & Geoffre, 1981; Précigoux, Leroy & Geoffre, 1980). The *BC* and *CD* junctions are both *trans*, and the methyl and methoxymethoxy groups are *syn*, leading to the *trans–syn–trans* stereochemistry. Such a

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* 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 51042 (60 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

conformation for the major isomer obtained by trans-annular Diels–Alder reaction is compatible with a boat-like transition state wherein the *C* ring would adopt a boat conformation.

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# Structure of 10,11-μ-Hydro-9-dimethylsulfido-7,8-dicarba-*nido*-undecaborane(11)

BY JILL COWIE, EWAN J. M. HAMILTON, JILL C. V. LAURIE AND ALAN J. WELCH

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**Abstract.** $C_4H_{17}B_9S$, $M_r = 194.53$, triclinic, $P\bar{1}$, $a = 8.7912$ (14), $b = 12.093$ (5), $c = 12.5617$ (19) Å, $\alpha = 107.53$ (3), $\beta = 101.019$ (13), $\gamma = 106.10$ (3)°, $V = 1167.2$ (8) Å$^3$, $Z = 4$, $D_x = 1.107$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.213$ mm$^{-1}$, $F(000) = 408$, 291 K, $R = 0.0480$ for 3580 observed reflections. There are two crystallographically independent molecules in the asymmetric fraction of the unit cell, which differ in respect of the torsion about the B(9)–S bond. The $\mu$-H atom bridges the B(10)–B(11) connectivity asymmetrically, favouring B(10), the less positively charged boron [average $\mu$-H–B(10) 1.165, average $\mu$-H–B(11) 1.35 Å].

**Introduction.** The synthesis of the title compound (1) was reported ten years ago (Plesek, Janousek & Hermanek, 1978). Spectroscopic study indicated that the SMe$_2$ unit was bound to B(9) of the *nido*-icosahedral {7,8-C$_2$B$_9$} polyhedron, but the position of the bridging H atom (shown to be either 9,10 or 10,11 bridging) was not unambiguously determined.

We are interested in (1) as a precursor of [9-SMe$_2$-*nido*-7,8-C$_2$B$_9$H$_{10}$]$^-$, a monoanionic carbaborane fully analogous to the ubiquitous [C$_5$H$_5$]$^-$ ligand. Since the position of the $\mu$-H atom in (1) may be important in the formation and structure of metal complexes of its anion, we have undertaken the present study.