

The R^*R^* diastereomer shows a shorter hydrogen bond between the O atom of the sulfinyl group and the H atom of the hydroxy group at O(4) ($-x, 1-y, 2-z$); the distance is 1.97 (4) Å. These observations are in agreement with the IR spectra of the solids which have OH peaks at 3400 and 3250 cm^{-1} for the S^*R^* and R^*R^* diastereomers respectively. The O...O(4) distances in S^*R^* and R^*R^* are 2.866 (1) and 2.807 (5) Å respectively.

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Structures of Four Tricyclo[3.3.0.0^{3,7}]octanes and a 4-Oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane Derivative

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Abstract. *N,N*-Dimethyl-6-methylenetricyclo[3.3.0.0^{3,7}]octane-2-carboxamide (1), $\text{C}_{12}\text{H}_{17}\text{NO}$, $M_r = 191.27$, monoclinic, $P2_1/c$, $a = 11.213$ (2), $b = 6.168$ (1), $c = 15.268$ (3) Å, $\beta = 95.07$ (1)°, $V = 1051.8$ (6) Å³, $Z = 4$, $D_x = 1.21$ Mg m^{-3} , $\mu = 0.071$ mm^{-1} , $F(000) = 416$, $T = 298$ K, final $R = 0.047$ for 1782 observed reflections. 4,6-Diisopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (2), $\text{C}_{14}\text{H}_{18}\text{O}$, $M_r = 202.30$, monoclinic, $P2_1/n$, $a = 9.532$ (1), $b = 9.218$ (1), $c = 13.496$ (2) Å, $\beta = 97.57$ (1)°, $V = 1175.5$ (5) Å³, $Z = 4$, $D_x = 1.14$ Mg m^{-3} , $\mu = 0.065$ mm^{-1} , $F(000) = 440$, $T = 208$ K, final $R = 0.041$ for 2244 observed reflections. 4,6,8-Triisopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-ol (3), $\text{C}_{17}\text{H}_{24}\text{O}$, $M_r = 244.38$, monoclinic, $P2_1/c$, $a = 8.618$ (1), $b = 22.054$ (5), $c = 7.871$ (1) Å, $\beta = 93.24$ (1)°, $V = 1493.6$ (7) Å³, $Z = 4$, $D_x = 1.09$ Mg m^{-3} , $\mu = 0.061$ mm^{-1} , $F(000) = 536$, $T = 223$ K, final $R = 0.049$ for 2211 observed reflections. 6,8-Diisopropylidenetricyclo[3.3.0.0^{3,7}]octane-2-spiro-1'-cyclopentane-4-one (4), $\text{C}_{18}\text{H}_{24}\text{O}$, $M_r = 256.39$, monoclinic, $P2_1/c$, $a = 11.796$ (3), $b = 11.483$ (2), $c = 11.312$ (2) Å, $\beta = 96.10$ (2)°, $V = 1523.6$ (7) Å³, $Z = 4$, $D_x = 1.12$ Mg m^{-3} , $\mu = 0.062$ mm^{-1} , $F(000) =$

560, $T = 223$ K, final $R = 0.047$ for 2467 observed reflections. 3-Isopropyl-8,9-diisopropylidene-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (5), $\text{C}_{17}\text{H}_{24}\text{O}$, $M_r = 244.38$, triclinic, $P\bar{1}$, $a = 9.675$ (2), $b = 12.997$ (2), $c = 6.454$ (1) Å, $\alpha = 91.14$ (2), $\beta = 100.51$ (2), $\gamma = 70.34$ (2)°, $V = 750.7$ (3) Å³, $Z = 2$, $D_x = 1.08$ Mg m^{-3} , $\mu = 0.060$ mm^{-1} , $F(000) = 268$, $T = 295$ K, final $R = 0.046$ for 2486 observed reflections. The radiation used for compounds (1) to (5) was $\text{Mo K}\alpha$, $\lambda = 0.7107$ Å. The cage-like molecules are highly strained with the consequence that the C—C bridging bonds are distinctly lengthened to 1.606 (2)–1.621 (2) Å.

Introduction. Tricyclo[3.3.0.0^{3,7}]octane (bisnoradamantane, stellane) (8) (Vogt, Suter & Hoover, 1968; Gleiter, Sigwart & Kissler, 1989) is the framework structure of compounds (1) to (4). One bridging C atom of (1) and three bridging C atoms in (2) to (4) are sp^2 hybridized. The polycyclic system (8) is also a subgroup of the tetracyclic compound (5). The stellane derivatives (1) to (5) were synthesized in order to understand the observed (Gleiter, Sigwart & Kissler, 1989) Cope-type rearrangement in these systems. Single-crystal X-ray structure determinations were undertaken to confirm the structures

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Table 1. Crystallographic and experimental details for compounds (1) to (5)

	(1)	(2)	(3)	(4)	(5)
Crystal shape	Needle	Prism	Needle	Prism	Prism
Crystal size (mm)	0.35 × 0.4 × 0.5	0.5 × 0.5 × 0.45	0.35 × 0.45 × 0.5	0.5 × 0.5 × 0.5	0.5 × 0.4 × 0.35
Solvents	Hexane	n-Pentane/ ether/CH ₂ Cl ₂	Petrol ether/ ether/CH ₂ Cl ₂	Petrol ether/ ether	n-Pentane/ ether
Reflections used for measuring lattice parameters					
Number	50	90	73	67	46
θ range (°)	10–18	10–28	10–18	10–22	11–21
Range of h	0 to 15	0 to 12	0 to 10	0 to 15	–12 to 12
k	0 to 8	0 to 12	0 to 29	0 to 15	0 to 17
l	–22 to 22	–17 to 17	–11 to 11	–14 to 14	–8 to 8
Monitor reflections	223, 324	323̄, 511̄, 136	292̄, 372̄, 332	324, 443, 451	522̄, 243̄, 291̄
Fluctuation (%)	3.7	2.5	2.6	1.6	16.8
Number of unique data	2462	2831	3546	3647	3592
Observed reflections	1782	2244	2211	2467	2486
Criterion	I ≥ 3σ(I)	I ≥ 2.5σ(I)	I ≥ 2.5σ(I)	I ≥ 2.5σ(I)	I ≥ 2.5σ(I)
Number of parameters	195	208	209	259	268
Final R	0.047	0.041	0.049	0.047	0.046
wR	0.065	0.053	0.057	0.059	0.059
S	2.85	2.42	2.28	2.52	2.50
(Δσ) _{max}	0.01	0.01	0.01	0.02	0.03
(Δρ) _{max} (e Å ⁻³)	0.24	0.22	0.25	0.32	0.22

of (1) to (5) and to examine the effects of strain on the molecular geometry.

Experimental. Crystallographic data and details of intensity measurements and structure refinements of (1) to (5) are given in Table 1. The crystals were grown at 253 K. Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo K α radiation by the ω -2 θ -scan technique with a variable scan rate, up to $\sin \theta/\lambda = 0.66 \text{ \AA}^{-1}$. Unit-cell parameters were refined using sets of 46–90 reflections with $\theta = 10$ –22°. The structures of (1), (2) and (5) were solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and the *SDP* program system (B. A. Frenz & Associates, Inc., 1982). The structures of (3) and (4) were solved with the program *SIR88* (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) and the program package *MolEN* (Fair, 1990). The refinements were performed by full-matrix least squares minimizing F , $w = 1/\sigma^2(F)$. H atoms were located in difference Fourier synthesis and refined with isotropic temperature factors. Lorentz and polarization corrections were applied. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The structure solution of (1) succeeded in the space group *P1*. The coordinates of the four molecules were refined up to an *R* value of about 0.20 and then reduced to the space group *P2₁/c*. Two reflections were excluded from refinement for (4) owing to extinction effects. Calculations were carried out on a PDP 11/44 computer and a MicroVAX 3100 computer. Figures were drawn using *ORTEP* (Johnson, 1976) and formulas by the program *PLT* (Reich, 1990). The semiempirical calculations were carried out with *MINDO/3* (Bingham, Dewar & Lo,

1975; Bischof, 1976), *MNDO/2* (Dewar & Thiel, 1977; Bischof & Friedrich, 1982) and *AM1* (Dewar, Zoebisch, Healy & Stewart, 1985) on an HP 9000/835 Turbo SRX workstation.

Discussion. Final positional and thermal parameters of (1) to (5) are given in Table 2.* The molecular structures of (1) to (5) with the atom-numbering schemes and selected bond distances are shown in Figs. 1 to 5. Selected bond angles and torsion angles are listed in Table 3.

Tricyclo[3.3.0.0^{3,7}]octane (8) is a member in the series of tricyclic alkanes of the general formula C_{2n+4}H_{4n+4} with $n = 2$. Other members are tricyclo[1.1.0.0^{2,4}]butane (tetrahedrane) (6) ($n = 0$), tricyclo[2.2.0.0^{2,5}]hexane (7) ($n = 1$), tricyclo[4.4.0.0^{3,8}]decane (twistane) (9) ($n = 3$) and tricyclo[5.5.0.0^{4,10}]dodecane (10) ($n = 4$) (Fig. 6). A characteristic feature of these molecules is the crosswise arrangement of the central bridging bonds.

For the unsubstituted hydrocarbons, X-ray structural data are not available and even for simple derivatives there are very few experimentally determined structures known. Information about the structural properties of these molecules can be obtained by semiempirical quantum-mechanical calculations (Table 4).

Tricyclo[3.3.0.0^{3,7}]octane (8) can be considered in three different ways. In relation to the synthetic precursors it may be looked on as a norbornane with a methylene bridge connecting the 1 and 3 positions (Fig. 7a). From another perspective, (8) consists of

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55484 (121 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1003]

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

Compound (1)	x	y	z	U_{eq}
O	0.1006 (1)	0.3471 (2)	0.6251 (1)	62 (1)
N	-0.0158 (1)	0.6428 (2)	0.6312 (1)	43 (1)
C(1)	0.2911 (1)	0.5464 (2)	0.5470 (1)	41 (1)
C(2)	0.1774 (1)	0.6732 (2)	0.5658 (1)	38 (1)
C(3)	0.2492 (1)	0.8444 (2)	0.6238 (1)	42 (1)
C(4)	0.2960 (1)	0.6930 (3)	0.6990 (1)	47 (1)
C(5)	0.3729 (1)	0.5568 (3)	0.6395 (1)	45 (1)
C(6)	0.4582 (1)	0.7401 (3)	0.6240 (1)	47 (1)
C(7)	0.3671 (1)	0.8810 (3)	0.5719 (1)	45 (1)
C(8)	0.3478 (1)	0.7236 (3)	0.4927 (1)	47 (1)
C(9)	0.0846 (1)	0.5408 (2)	0.6095 (1)	40 (1)
C(10)	-0.1042 (1)	0.5210 (3)	0.6757 (1)	54 (1)
C(11)	-0.0511 (1)	0.8612 (3)	0.6036 (1)	53 (1)
C(12)	0.5730 (2)	0.7682 (3)	0.6480 (1)	65 (1)
Compound (2)				
C(1)	0.8847 (1)	0.3418 (1)	0.0308 (1)	29 (1)
C(2)	0.9901 (1)	0.2568 (1)	-0.0224 (1)	28 (1)
C(3)	1.0517 (1)	0.1631 (1)	0.0665 (1)	24 (1)
C(4)	1.1154 (1)	0.2952 (1)	0.1248 (1)	22 (1)
C(5)	0.9750 (1)	0.3675 (1)	0.1389 (1)	25 (1)
C(6)	0.9237 (1)	0.2448 (1)	0.2007 (1)	26 (1)
C(7)	0.9130 (1)	0.1304 (1)	0.1191 (1)	27 (1)
C(8)	0.7936 (1)	0.2065 (1)	0.0473 (1)	34 (1)
O(9)	1.0159 (1)	0.2592 (1)	-0.1076 (1)	39 (1)
C(10)	1.2489 (1)	0.3358 (1)	0.1525 (1)	25 (1)
C(11)	1.3743 (1)	0.2461 (1)	0.1326 (1)	33 (1)
C(12)	1.2850 (1)	0.4751 (1)	0.2087 (1)	38 (1)
C(13)	0.8970 (1)	0.2401 (1)	0.2950 (1)	30 (1)
C(14)	0.9094 (1)	0.3722 (2)	0.3617 (1)	40 (1)
C(15)	0.8531 (1)	0.1027 (2)	0.3434 (1)	43 (1)
Compound (3)				
C(1)	0.8183 (2)	0.0869 (1)	0.7277 (2)	30 (1)
C(2)	0.7991 (2)	0.0319 (1)	0.6057 (2)	32 (1)
C(3)	0.8449 (2)	0.0684 (1)	0.4477 (2)	28 (1)
C(4)	0.7080 (2)	0.1114 (1)	0.4407 (2)	29 (1)
C(5)	0.7492 (2)	0.1424 (1)	0.6115 (2)	29 (1)
C(6)	0.8977 (2)	0.1709 (1)	0.5516 (2)	27 (1)
C(7)	0.9833 (2)	0.1112 (1)	0.5255 (2)	26 (1)
C(8)	0.9917 (2)	0.0941 (1)	0.7133 (2)	28 (1)
O(9)	0.6517 (2)	0.0040 (1)	0.5912 (2)	44 (1)
C(10)	0.5917 (2)	0.1194 (1)	0.3251 (2)	37 (1)
C(11)	0.5810 (2)	0.0852 (1)	0.1595 (3)	48 (1)
C(12)	0.4625 (2)	0.1635 (1)	0.3482 (3)	59 (1)
C(13)	0.9398 (2)	0.2284 (1)	0.5309 (2)	31 (1)
C(14)	0.8346 (3)	0.2806 (1)	0.5714 (3)	46 (1)
C(15)	1.0938 (2)	0.2463 (1)	0.4674 (3)	42 (1)
C(16)	1.1129 (2)	0.0889 (1)	0.8249 (2)	33 (1)
C(17)	1.0953 (3)	0.0762 (1)	1.0112 (3)	47 (1)
C(18)	1.2768 (2)	0.0969 (1)	0.7737 (3)	49 (1)
Compound (4)				
C(1)	0.6509 (1)	0.1927 (1)	0.7565 (1)	34 (1)
C(2)	0.5668 (1)	0.1318 (1)	0.8279 (1)	32 (1)
C(3)	0.6520 (1)	0.0927 (1)	0.9316 (1)	28 (1)
C(4)	0.7055 (1)	0.0080 (1)	0.8486 (1)	28 (1)
C(5)	0.7548 (1)	0.1011 (1)	0.7727 (1)	32 (1)
C(6)	0.8341 (1)	0.1523 (1)	0.8744 (1)	33 (1)
C(7)	0.7411 (1)	0.1988 (1)	0.9437 (1)	30 (1)
C(8)	0.6857 (1)	0.2890 (1)	0.8501 (1)	33 (1)
O(9)	0.4655 (1)	0.1147 (1)	0.8083 (1)	45 (1)
C(10)	0.7026 (1)	-0.1074 (1)	0.8403 (1)	31 (1)
C(11)	0.6496 (2)	-0.1829 (1)	0.9280 (2)	45 (1)
C(12)	0.7517 (2)	-0.1717 (1)	0.7417 (2)	43 (1)
C(13)	0.9468 (1)	0.1472 (2)	0.8972 (2)	45 (1)
C(14)	1.0205 (2)	0.0896 (2)	0.8127 (2)	66 (1)
C(15)	1.0088 (2)	0.1970 (2)	1.0082 (2)	69 (1)
C(16)	0.5870 (1)	0.3598 (1)	0.8924 (2)	39 (1)
C(17)	0.6415 (2)	0.4721 (1)	0.9471 (2)	44 (1)
C(18)	0.7611 (2)	0.4763 (2)	0.9117 (2)	62 (1)
C(19)	0.7648 (2)	0.3857 (2)	0.8138 (2)	48 (1)
Compound (5)				
C(1)	0.1111 (1)	0.3361 (1)	0.4259 (2)	43 (1)
C(2)	0.0522 (1)	0.4243 (1)	0.2426 (2)	45 (1)
C(3)	0.2072 (1)	0.4255 (1)	0.2219 (2)	42 (1)
C(4)	0.2643 (1)	0.4482 (1)	0.4458 (2)	39 (1)
C(5)	0.2638 (1)	0.3432 (1)	0.5486 (2)	40 (1)
C(6)	0.3730 (1)	0.2614 (1)	0.4325 (2)	39 (1)

Table 2 (cont.)

	x	y	z	U_{eq}
C(7)	0.2830 (1)	0.2960 (1)	0.2116 (2)	41 (1)
C(8)	0.1429 (1)	0.2658 (1)	0.2287 (2)	44 (1)
O(9)	0.0173 (1)	0.3472 (1)	0.0936 (2)	53 (1)
C(10)	0.2972 (1)	0.5341 (1)	0.5243 (2)	43 (1)
C(11)	0.2834 (2)	0.6301 (1)	0.3860 (3)	56 (1)
C(12)	0.3496 (2)	0.5433 (1)	0.7560 (3)	58 (1)
C(13)	0.5020 (1)	0.1820 (1)	0.5029 (2)	44 (1)
C(14)	0.5949 (2)	0.1103 (1)	0.3574 (3)	65 (1)
C(15)	0.5658 (2)	0.1582 (1)	0.7340 (3)	59 (1)
C(16)	0.1468 (2)	0.1493 (1)	0.1994 (3)	58 (1)
C(17)	0.1531 (3)	0.1195 (2)	-0.0293 (3)	89 (1)
C(18)	0.0178 (2)	0.1287 (2)	0.2740 (4)	97 (1)

Table 3. Selected bond and torsion angles ($^\circ$) for (1) to (5)

	(1)	(2)	(3)	(4)	(5)
C(1)—C(2)—C(3)	93.2 (1)	97.5 (1)	93.9 (1)	97.4 (1)	95.1 (1)
C(1)—C(2)—C(9)	114.7 (1)				
C(1)—C(5)—C(4)	103.4 (1)	101.3 (1)	102.6 (1)	101.0 (1)	100.6 (1)
C(1)—C(5)—C(6)	102.2 (1)	102.4 (1)	101.4 (1)	103.5 (1)	100.7 (1)
C(1)—C(8)—C(7)	93.5 (1)	94.3 (1)	96.0 (1)	92.9 (1)	93.6 (1)
C(1)—C(8)—C(16)			133.1 (2)	115.7 (1)	127.6 (1)
C(1)—C(8)—C(19)				117.1 (1)	
C(2)—C(1)—C(5)	103.4 (1)	101.2 (1)	102.6 (1)	99.9 (1)	107.6 (1)
C(2)—C(1)—C(8)	97.3 (1)	94.0 (1)	96.1 (1)	96.1 (1)	77.7 (1)
C(2)—C(3)—C(4)	98.0 (1)	92.2 (1)	97.0 (1)	89.8 (1)	100.2 (1)
C(2)—C(3)—C(7)	102.7 (1)	101.5 (1)	102.4 (1)	102.3 (1)	96.3 (1)
C(2)—O(9)—C(8)					84.2 (1)
C(3)—C(2)—C(9)	117.0 (1)				
C(3)—C(4)—C(5)	93.6 (1)	96.7 (1)	96.1 (1)	96.1 (1)	96.7 (1)
C(3)—C(4)—C(10)					
C(3)—C(7)—C(6)	101.8 (1)	102.1 (1)	101.7 (1)	101.0 (1)	103.4 (1)
C(3)—C(7)—C(8)	103.3 (1)	102.4 (1)	102.5 (1)	102.8 (1)	97.0 (1)
C(4)—C(3)—C(7)	102.2 (1)	102.4 (1)	101.8 (1)	103.0 (1)	103.6 (1)
C(4)—C(5)—C(6)	94.5 (1)	95.4 (1)	94.0 (1)	94.9 (1)	98.1 (1)
C(5)—C(1)—C(8)	102.2 (1)	103.3 (1)	102.2 (1)	104.1 (1)	108.1 (1)
C(5)—C(4)—C(10)		131.5 (1)	132.2 (2)	131.9 (1)	132.6 (1)
C(5)—C(6)—C(7)	96.0 (1)	96.6 (1)	96.1 (1)	96.1 (1)	96.8 (1)
C(5)—C(6)—C(12)	132.1 (2)				
C(5)—C(6)—C(13)		131.5 (1)	132.0 (2)	130.7 (2)	131.4 (1)
C(6)—C(7)—C(8)	95.3 (1)	96.5 (1)	94.6 (1)	99.0 (1)	100.0 (1)
C(7)—C(6)—C(12)	131.9 (2)				
C(7)—C(6)—C(13)		131.9 (1)	131.8 (2)	132.9 (2)	131.7 (1)
C(7)—C(8)—C(16)			130.9 (2)	114.4 (1)	119.6 (1)
C(7)—C(8)—C(19)				115.8 (1)	
C(16)—C(8)—C(19)				101.7 (1)	
O(9)—C(2)—C(1)		131.9 (1)	117.1 (2)	131.9 (1)	91.8 (1)
O(9)—C(2)—C(3)		130.6 (1)	115.5 (1)	130.6 (1)	106.9 (1)
O(9)—C(8)—C(1)					90.8 (1)
O(9)—C(8)—C(7)					105.7 (1)
O(9)—C(8)—C(16)					114.2 (1)
C(2)—C(1)—C(5)—C(4)	-1.1 (1)	1.4 (1)	-2.3 (2)	0.6 (1)	9.2 (1)
C(6)—C(5)—C(1)—C(8)	1.9 (1)	0.2 (1)	0.2 (2)	1.7 (2)	-8.8 (1)
C(2)—C(3)—C(7)—C(8)	-1.0 (1)	2.5 (1)	-1.5 (2)	4.8 (1)	0.3 (1)
C(4)—C(3)—C(7)—C(6)	1.8 (1)	-2.1 (1)	1.0 (2)	-4.4 (1)	0.4 (2)

two six-membered rings [C(1), C(2), C(3), C(7), C(6), C(5) and C(1), C(8), C(7), C(3), C(4), C(5)], which are 1,4-bridged above and below the corresponding mean ring plane by a C atom [C(4), C(8) and C(2), C(6), respectively]. This kind of bridging fixes the six-membered carbon rings in twisted conformations (Fig. 7b). Finally, the polycyclic framework can be regarded as two interlocking bicyclo[3.3.0]octane systems. The connection between atoms C(3) and C(7) in the middle of the trimethylene groups represents the zero bridge of one bicyclo[3.3.0]octane unit (Fig. 7c) and the connection between atoms C(1) and C(5) represents that of the other. Therefore, the smallest rings in the molecule are five membered. The

molecular symmetry of tricyclo[3.3.0.0^{3,7}]octane (8) is D_{2d} .

This third way of looking at (8) gives a good explanation for the observed stretching of the bond lengths between the bridgehead atoms in the tricyclo[3.3.0.0^{3,7}]octane skeleton. In (1) to (4), bond lengths of the order of 1.606 (2) to 1.621 (2) Å are found for C(1)—C(5) and C(3)—C(7) bonds between bridgehead atoms. (Figs. 1 to 4). The lengthening of these bridging bonds is caused by the eclipsed conformation along these bonds (Table 3). Compared with

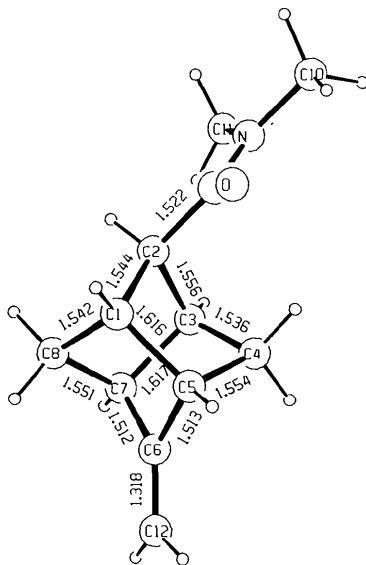


Fig. 1. The molecular structure and atom-numbering scheme of compound (1), with significant bond lengths (e.s.d.'s are 0.002 Å).

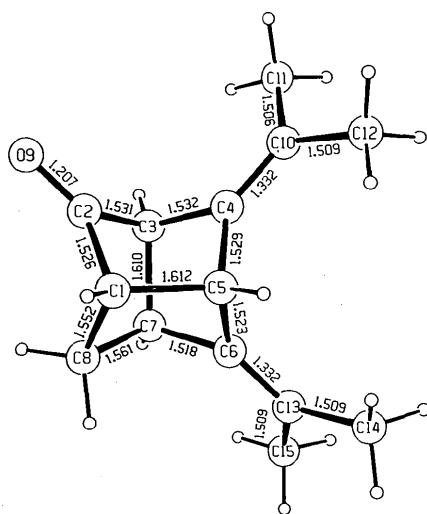


Fig. 2. The molecular structure and atom-numbering scheme of compound (2), with significant bond lengths (e.s.d.'s are 0.001 to 0.002 Å).

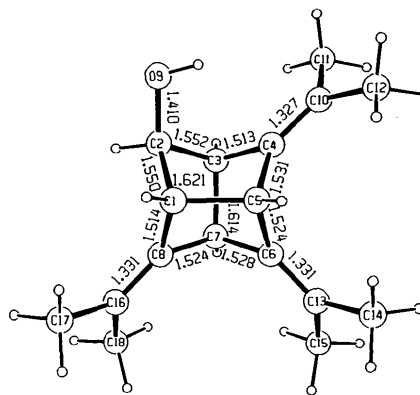


Fig. 3. The molecular structure and atom-numbering scheme of compound (3), with significant bond lengths (e.s.d.'s are 0.002 to 0.003 Å).

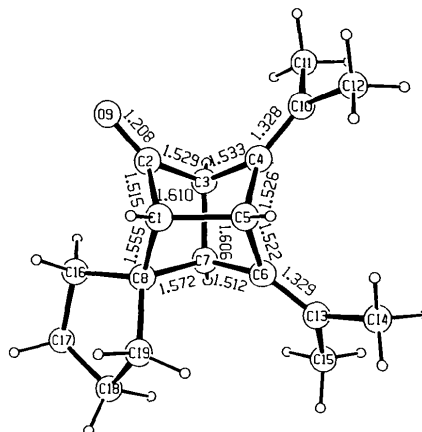


Fig. 4. The molecular structure and atom-numbering scheme of compound (4), with significant bond lengths (e.s.d.'s are 0.002 to 0.003 Å).

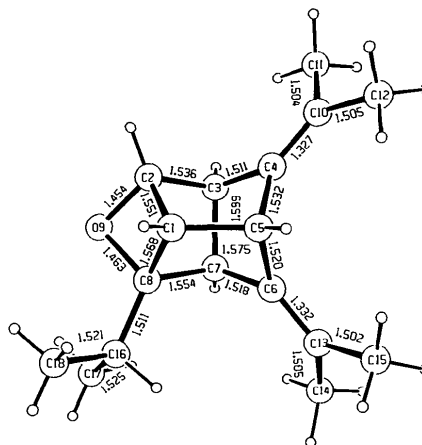


Fig. 5. The molecular structure and atom-numbering scheme of compound (5), with significant bond lengths (e.s.d.'s are 0.001 to 0.003 Å). The atom-numbering scheme does not correspond to IUPAC nomenclature.

Table 4. Bond lengths (Å) of the C—C zero bridges of tricyclic alkanes of the general formula $C_{2n+4}H_{4n+4}$ and their derivatives

Calculated for tricyclic alkanes (6) to (10)					Method
(6)	(7)	(8)	(9)	(10)	
1.502	1.578	1.618	1.595	1.589	MINDO/3 ^a
1.520	1.595	1.617	1.585	1.576	MINDO/2 ^b
1.494	1.598	1.608	1.550	1.536	AM1 ^c
Experimentally determined for derivatives of (6), (8) and (9) by X-ray crystallography					
(6) derivative	(8) derivative	(9) derivative			
1.487 ^d	1.616 ^e	1.540 ^f			
1.487 ^d	1.617 ^e	1.563 ^f			
1.494 ^e	1.610 ^e	1.584 ^f			
1.496 ^e	1.612 ^e	1.585 ^f			
	1.614 ^g				
	1.621 ^g				
	1.606 ^h				
	1.610 ⁱ				

References: (a) MINDO/3 (Bingham, Dewar & Lo, 1975; Bischof, 1976); (b) MINDO/2 (Dewar & Thiel, 1977; Bischof & Friedrich, 1982); (c) AM1 (Dewar, Zoebisch, Healy & Stewart, 1985); (d) tetra-*tert*-butyltricyclo[1.1.0.0^{2,3}]butane (Irgartinger, Goldmann, Jahn, Nixdorf, Rodewald, Maier, Malsch & Emrich, 1984); (e) compound (1); (f) (1*R*,6*S*,8*R*,10*R*)-8-(4-bromobenzenesulfonyloxy)-1,10-dimethyltricyclo[4.4.0.0^{3,5}]decan-2-one (Barnett & Yordy, 1975); (g) tetra-*tert*-butyltricyclo[1.1.0.0^{2,4}]butane argon clathrate (Irgartinger, Jahn, Maier & Emrich, 1987); (h) compound (2); (i) 1β,3,4β,6β,8-pentamethyl-9-*exo*-methylenetricyclo[4.4.0.0^{3,8}]decane-2,5-dione (Greenhough & Trotter, 1980); (j) compound (3); (k) compound (4).

experimentally determined values, the lengths of the central bridges of the unsubstituted hydrocarbon are in good agreement with the results of semiempirical quantum-mechanical calculations (Table 4). The lengthening of these bonds is in accord with the observed rearrangement of these compounds (Gleiter, Sigwart & Kissler, 1989). As anticipated, the molecule breaks at the weakest bond. In this connection it is interesting to note that a strong through-bond and through-space interaction between the *exo*-methylene moieties has been observed (Gleiter, Kissler & Ganter, 1987).

The remaining C—C bonds of the tricyclic cage are extended by 0.015 to 0.025 Å on average compared with the mean values of corresponding C—C bond types in open-chain compounds (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) because of strain effects. The cage-like basic framework in (1) to (4) is slightly distorted because of the different hybridizations (sp^2 and sp^3 , respectively) of the bridging C atoms. The bond angles reflect the highly strained nature of these molecules. Around the rings from C(1) to C(8), their values vary from 89.8 to 99.0°. The angles formed by a bond between two bridgehead atoms [C(1)—C(5), C(3)—C(7)] and a bond between a bridgehead atom and the neighbouring C atom have values in the range 99.9 to 104.1° (Table 3).

The cage oxetane (5) (Fig. 5) is a derivative of 4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (11) (Fig. 7*d*), which can be constructed from the tricyclic system of (8) by the additional link through O(9) between C(2) and C(8). The oxetane ring is folded by 139.9° along

the C(2)⋯C(8) axis. Other derivatives of cage compound (11) (Harano, Okamoto, Yasuda, Ueyama & Kanematsu, 1983; Coxon, O'Connell & Steel, 1986; Carceller, Moyano, Serratos, Font-Altaba & Solans, 1986) also contain a significantly puckered oxetane. Oxetane derivatives generally have an almost planar conformation (Luger & Buschmann, 1984). The bond angles within the oxetane ring, C(2)—C(1)—C(8) 77.7, C(2)—O(9)—C(8) 84.2, O(9)—C(2)—C(1) 91.8 and O(9)—C(8)—C(1) 90.8° (Table 3), deviate considerably from the tetrahedral angle and demonstrate the strain in compound (5). In the oxetane ring the bond lengths are in good

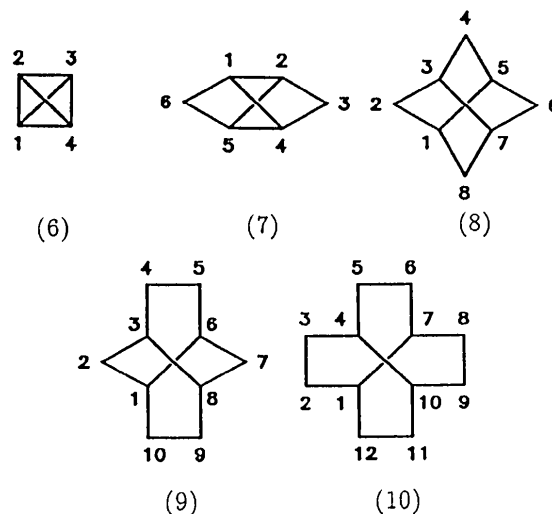


Fig. 6. Basic structures of some tricyclic alkanes of the general formula $C_{2n+4}H_{4n+4}$.

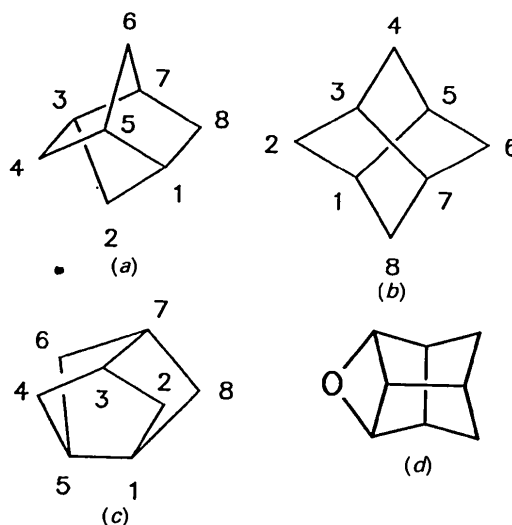


Fig. 7. Three different views, (a), (b) and (c), of the tricyclo[3.3.0.0^{3,7}]octane (8) molecule and the formula diagram (d) of 4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (11).

agreement with other oxetane systems (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The relatively strong *s* character of atom C(1) causes a shortening of the central C(1)—C(5) bond (1.575 Å) in comparison with the second zero bridge C(3)—C(7) (1.599 Å) in (5) and the analogous bonds of the tricyclo[3.3.0.0^{3,7}]octane system derivatives (1) to (4). Moreover, the deviation from the eclipsed conformation along this C(1)—C(5) bond of (5) is relatively large (Table 3) and, therefore, the stretching effect is reduced.

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Structure of Pregna-4,16-diene-7 α ,14 α -diol-3,20-dione

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Abstract. 7 α ,14 α -Dihydroxypregna-4,16-diene-3,20-dione, C₂₁H₂₈O₄, *M_r* = 344.45, orthorhombic, *P*2₁2₁2₁, *a* = 7.136 (1), *b* = 12.342 (1), *c* = 20.049 (3) Å, *V* = 1765.7 (3) Å³, *Z* = 4, *D_x* = 1.295 g cm⁻³, $\lambda(\text{Cu K}\alpha)$ = 1.5418 Å, μ = 6.7 cm⁻¹, *F*(000) = 744, *T* = 293 K, *R* = 0.048 for 1345 observations. The *A* ring may be described as in a 1 α ,2 β -half-chair conformation or a 1 α -sofa conformation. The *B* and *C* rings adopt normal chair conformations and the *D* ring has a 14 α -envelope conforma-

tion. The molecules are held together by a hydrogen bond [O(3)⋯O(7) = 2.767 Å].

Introduction. Microbial transformation has been used extensively for the introduction of functional groups into steroids in order to obtain biologically useful substances. Fermentation of pre-gna-4,16-diene-3,20-dione with the fungus *Murcor Piriformis* yielded the metabolites pre-gna-4,16-diene-7 α ,14 α -