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3,15-Dimethyl-18-(1-propynyl)-16-oxapentacyclo[10.4.2.0^{2,11}.0^{3,8}.0^{15,18}]octadeca-4,7-dien-6-one

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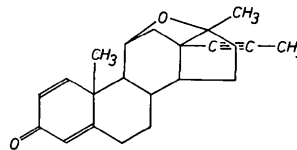
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Abstract. C₂₂H₂₆O₂, $M_r = 322.45$, monoclinic, $P2_1$, $Z = 4$, $a = 20.383$ (10), $b = 7.316$ (8), $c = 12.094$ (15) Å, $\beta = 90.74$ (6)°, $U = 1803$ (5) Å³, $D_x = 1.188$, $D_m = 1.18$ (2) Mg m⁻³ by flotation in aqueous K₂H₉I₄, $\mu(\text{Mo } K\alpha) = 0.069$ mm⁻¹. The structure was solved, *via* the $h0l$ projection, by direct methods and refined to $R = 0.056$ for 2902 unique diffractometer data [$F > \sigma(F)$]. The two virtually identical molecules in the asymmetric unit exhibit a steroid-like arrangement of three six- and one five-membered rings, with an additional transannular ether linkage.

Introduction. The title compound (I) was synthesized (at Roussel Uclaf, Romainville, France) according to a new rearrangement described by Teutsch, Lang, Smolik, Mornon & Delettré (1981). The crystals were of mediocre quality, so that out of the 4685 unique reflexions measured for $2\theta < 56^\circ$ with a Siemens computer-controlled diffractometer (Hoppe, 1965), Zr-filtered Mo $K\alpha$ radiation and crystal $0.75 \times 0.25 \times 0.2$ mm only 2902 had $F > \sigma(F)$. The crystal orientation and cell parameters were determined automatically by a 'systematically random' peak-search procedure described by Kobelt & Paulus (1979). After a number of fruitless attempts, the structure was solved by multiresolution tangent refinement, with several initial phases taken from a solution of the centrosymmetric

projection as recommended by Boeyens (1977). The structure was refined by least squares [2902 data, 433 parameters, $w = 1/\sigma^2(F)$] to $R = \sum \Delta / \sum F_o = 0.056$ and $R_g = [\sum w\Delta^2 / \sum wF_o^2]^{1/2} = 0.033$. A riding model with idealized geometry (C–H 0.96 Å), and temperature factors fixed at 1.2 times the equivalent isotropic values for the C atoms to which they were attached, was employed for the H atoms; the remaining atoms were refined anisotropically. The ten largest peaks in a final difference electron density synthesis were between 0.14 and 0.17 e Å⁻³. Calculations were performed with a Nova 3/12 computer and the *SHELXTL* programs written by GMS.



Discussion. Coordinates and selected molecular dimensions are given in Tables 1–3.* The two molecules in

* Lists of structure factors, anisotropic temperature factors and hydrogen atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36193 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å²) calculated from the anisotropic ones

E.s.d.'s are in parentheses.

	Molecule 1				Molecule 2			
	x	y	z	B _{eq} [*]	x	y	z	B _{eq} [*]
O(1)	0.0236 (1)	0.1424 (4)	0.7138 (2)	4.6 (1)	0.6339 (1)	-0.2968 (3)	0.6899 (2)	3.8 (1)
O(2)	0.2262 (1)	0.6429 (4)	0.3190 (2)	7.0 (1)	0.7202 (2)	0.1885 (5)	1.2017 (2)	11.7 (1)
C(1)	0.0318 (2)	0.0244 (5)	0.8110 (3)	4.5 (1)	0.5782 (2)	-0.3988 (5)	0.6426 (2)	3.8 (1)
C(2)	0.0945 (2)	0.1005 (5)	0.8667 (3)	3.9 (1)	0.5198 (2)	-0.3179 (5)	0.7048 (3)	3.7 (1)
C(3)	0.0900 (2)	0.3039 (5)	0.8417 (3)	4.9 (1)	0.5394 (2)	-0.1168 (5)	0.7156 (3)	4.2 (1)
C(4)	0.0686 (2)	0.2937 (5)	0.7211 (3)	4.1 (1)	0.6107 (2)	-0.1432 (5)	0.7543 (2)	3.8 (1)
C(5)	0.1304 (1)	0.2574 (4)	0.6523 (2)	3.3 (1)	0.6110 (1)	-0.1890 (5)	0.8773 (2)	3.5 (1)
C(6)	0.1539 (1)	0.0628 (5)	0.6773 (2)	3.6 (1)	0.5826 (2)	-0.3807 (5)	0.8911 (2)	3.6 (1)
C(7)	0.1482 (2)	0.0003 (5)	0.7994 (3)	3.7 (1)	0.5228 (2)	-0.4265 (5)	0.8149 (3)	4.2 (1)
C(8)	0.1230 (2)	-0.1964 (5)	0.8006 (3)	5.0 (1)	0.5317 (2)	-0.6218 (5)	0.7729 (3)	4.6 (1)
C(9)	0.0486 (2)	-0.1743 (5)	0.7768 (3)	5.2 (1)	0.5819 (2)	-0.6007 (5)	0.6783 (3)	5.0 (1)
C(10)	0.2212 (1)	0.0320 (5)	0.6296 (2)	4.9 (1)	0.5679 (2)	-0.4167 (5)	1.0115 (2)	5.0 (1)
C(11)	0.2184 (2)	0.0610 (5)	0.5043 (3)	4.7 (1)	0.6305 (2)	-0.3919 (5)	1.0835 (3)	5.7 (1)
C(12)	0.1892 (1)	0.2439 (5)	0.4755 (2)	3.4 (1)	0.6628 (2)	-0.2097 (6)	1.0610 (3)	4.8 (1)
C(13)	0.2207 (2)	0.3571 (5)	0.4088 (3)	4.0 (1)	0.6760 (2)	-0.0915 (6)	1.1427 (3)	6.2 (1)
C(14)	0.1971 (2)	0.5413 (6)	0.3820 (3)	5.0 (1)	0.7070 (2)	0.0865 (7)	1.1252 (3)	7.2 (2)
C(15)	0.1360 (2)	0.5953 (5)	0.4347 (3)	5.1 (1)	0.7189 (2)	0.1338 (7)	1.0119 (3)	6.2 (1)
C(16)	0.1056 (2)	0.4860 (5)	0.5028 (3)	4.8 (1)	0.7045 (2)	0.0223 (6)	0.9285 (3)	5.4 (1)
C(17)	0.1245 (1)	0.2910 (5)	0.5262 (2)	3.7 (1)	0.6776 (2)	-0.1686 (5)	0.9423 (2)	4.0 (1)
C(18)	0.1015 (2)	0.0550 (5)	0.9844 (3)	4.6 (1)	0.4557 (2)	-0.3443 (5)	0.6483 (2)	4.1 (1)
C(19)	0.1087 (2)	0.0207 (6)	1.0781 (3)	5.0 (1)	0.4047 (2)	-0.3651 (5)	0.6034 (3)	4.4 (1)
C(20)	0.1195 (2)	-0.0236 (6)	1.1954 (2)	7.2 (2)	0.3408 (1)	-0.3927 (6)	0.5491 (3)	5.5 (1)
C(21)	-0.0310 (2)	0.0357 (6)	0.8777 (3)	6.6 (1)	0.5777 (2)	-0.3721 (6)	0.5188 (2)	5.1 (1)
C(22)	0.0688 (1)	0.1735 (6)	0.4725 (2)	5.3 (1)	0.7135 (2)	-0.2962 (5)	0.8988 (3)	5.6 (1)

* B_{eq} = equivalent isotropic temperature factor, defined as $\frac{8}{3} \pi^2$ times the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths (Å)

	Molecule 1	Molecule 2
O(1)–C(1)	1.466 (4)	1.468 (4)
O(1)–C(4)	1.440 (4)	1.450 (4)
O(2)–C(14)	1.223 (4)	1.216 (5)
C(1)–C(2)	1.541 (5)	1.536 (4)
C(1)–C(9)	1.551 (5)	1.540 (5)
C(1)–C(21)	1.525 (5)	1.510 (4)
C(2)–C(3)	1.522 (5)	1.529 (5)
C(2)–C(7)	1.556 (5)	1.552 (5)
C(2)–C(18)	1.467 (5)	1.479 (4)
C(3)–C(4)	1.519 (4)	1.534 (4)
C(4)–C(5)	1.542 (4)	1.525 (4)
C(5)–C(6)	1.531 (5)	1.527 (5)
C(5)–C(17)	1.548 (4)	1.567 (4)
C(6)–C(7)	1.551 (4)	1.555 (4)
C(6)–C(10)	1.512 (4)	1.514 (4)
C(7)–C(8)	1.528 (5)	1.528 (5)
C(8)–C(9)	1.548 (5)	1.553 (5)
C(10)–C(11)	1.531 (4)	1.544 (4)
C(11)–C(12)	1.504 (5)	1.513 (5)
C(12)–C(13)	1.328 (4)	1.337 (5)
C(12)–C(17)	1.500 (4)	1.501 (5)
C(13)–C(14)	1.466 (5)	1.464 (6)
C(14)–C(15)	1.461 (5)	1.437 (6)
C(15)–C(16)	1.309 (5)	1.328 (6)
C(16)–C(17)	1.504 (5)	1.511 (5)
C(17)–C(22)	1.559 (4)	1.540 (5)
C(18)–C(19)	1.168 (5)	1.176 (4)
C(19)–C(20)	1.468 (5)	1.464 (4)

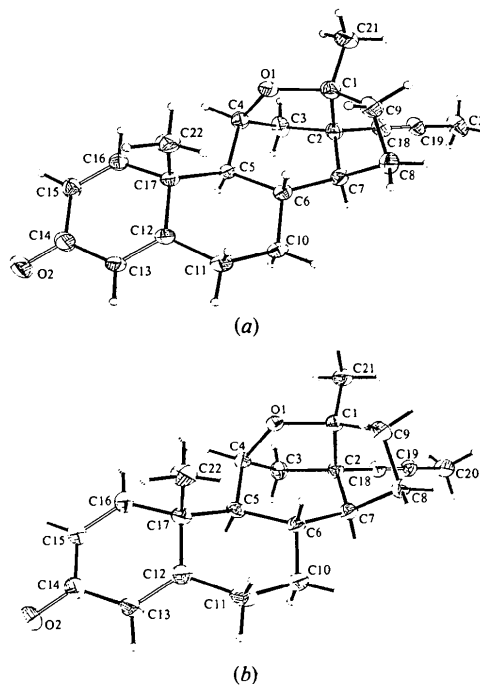
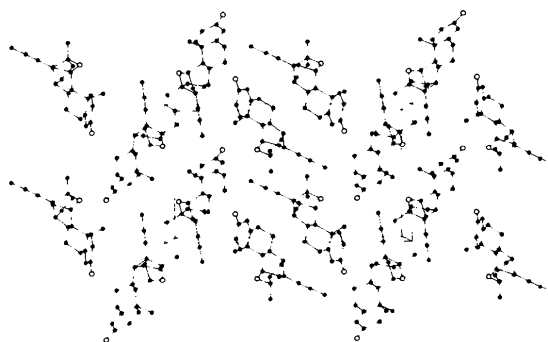


Fig. 1. The two independent molecules, showing 20% probability thermal ellipsoids for the non-hydrogen atoms, and atom numbering scheme. (a) Molecule 1. (b) Molecule 2.

Table 3. Bond angles (°)

	Molecule 1	Molecule 2
C(1)—O(1)—C(4)	109.7 (2)	110.3 (2)
O(1)—C(1)—C(2)	102.9 (3)	102.4 (2)
O(1)—C(1)—C(9)	111.2 (3)	110.1 (2)
O(1)—C(1)—C(21)	107.7 (3)	108.4 (2)
C(2)—C(1)—C(9)	105.7 (3)	105.6 (3)
C(2)—C(1)—C(21)	116.5 (3)	116.1 (3)
C(9)—C(1)—C(21)	112.5 (3)	113.7 (3)
C(1)—C(2)—C(3)	102.6 (3)	102.1 (3)
C(1)—C(2)—C(7)	100.7 (3)	101.5 (3)
C(1)—C(2)—C(18)	114.4 (3)	114.2 (3)
C(3)—C(2)—C(7)	113.5 (3)	114.3 (3)
C(3)—C(2)—C(18)	114.8 (3)	113.2 (3)
C(7)—C(2)—C(18)	109.9 (3)	110.8 (3)
C(2)—C(3)—C(4)	99.1 (3)	98.7 (3)
O(1)—C(4)—C(3)	105.7 (3)	104.4 (2)
O(1)—C(4)—C(5)	111.1 (3)	110.9 (3)
C(3)—C(4)—C(5)	107.5 (3)	108.4 (2)
C(4)—C(5)—C(6)	108.0 (2)	108.2 (2)
C(4)—C(5)—C(17)	116.8 (2)	117.4 (2)
C(6)—C(5)—C(17)	111.2 (2)	111.1 (3)
C(5)—C(6)—C(7)	115.8 (3)	115.4 (3)
C(5)—C(6)—C(10)	110.3 (3)	110.1 (3)
C(7)—C(6)—C(10)	113.5 (3)	111.7 (3)
C(2)—C(7)—C(6)	114.9 (3)	114.8 (3)
C(2)—C(7)—C(8)	101.5 (3)	101.4 (3)
C(6)—C(7)—C(8)	108.4 (3)	107.6 (3)
C(7)—C(8)—C(9)	103.2 (3)	103.6 (3)
C(1)—C(9)—C(8)	105.5 (3)	105.7 (3)
C(6)—C(10)—C(11)	109.5 (3)	110.5 (3)
C(10)—C(11)—C(12)	111.2 (3)	111.2 (3)
C(11)—C(12)—C(13)	120.1 (3)	121.4 (3)
C(11)—C(12)—C(17)	117.2 (3)	116.2 (3)
C(13)—C(12)—C(17)	122.7 (3)	122.4 (4)
C(12)—C(13)—C(14)	123.2 (3)	123.5 (3)
O(2)—C(14)—C(13)	122.3 (3)	121.9 (4)
O(2)—C(14)—C(15)	122.1 (3)	122.6 (4)
C(13)—C(14)—C(15)	115.6 (3)	115.5 (4)
C(14)—C(15)—C(16)	121.5 (4)	122.6 (4)
C(15)—C(16)—C(17)	125.1 (3)	124.1 (3)
C(5)—C(17)—C(12)	108.0 (2)	106.1 (2)
C(5)—C(17)—C(16)	110.7 (3)	110.2 (3)
C(5)—C(17)—C(22)	111.7 (2)	112.8 (3)
C(12)—C(17)—C(16)	111.5 (3)	111.7 (3)
C(12)—C(17)—C(22)	110.0 (3)	111.0 (3)
C(16)—C(17)—C(22)	105.1 (3)	105.1 (3)
C(2)—C(18)—C(19)	178.3 (4)	180.0 (5)
C(18)—C(19)—C(20)	178.6 (4)	179.1 (3)

Fig. 2. Projection of the structure, viewed in perspective down *b*.

the asymmetric unit (Fig. 1) do not differ very significantly; a least-squares analysis in which one molecule was translated and rotated to fit the other gave a r.m.s. deviation between positions of the corresponding non-hydrogen atoms of 0.089 Å. The steroid skeleton of three six- and one five-membered rings is bridged by a transannular ether linkage [C(1)—O(1)—C(4)], and a methylethynyl group is attached to C(2). The molecules have been assigned the known absolute configuration of the starting materials; no attempt was made to establish the absolute configuration from the X-ray data. It had not proved possible to determine this structure by spectroscopic methods. The structure exhibits no unusual bond lengths and angles. The packing arrangement is shown in Fig. 2; the good resolution in this projection (perpendicular to *b*) undoubtedly facilitated its use in the structure determination.

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