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Structure and Absolute Configuration of 21α-Bromo-3-methoxy-19-nor-1,3,5(10),17(20),20-pregnapentaene, $C_{21}H_{25}BrO$

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Abstract. $M_r = 373{\cdot}33$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}030\,(4)$, $b = 13{\cdot}286\,(6)$, $c = 27{\cdot}41\,(1)$ Å, $U = 3652\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}358$ Mg m^{-3}, μ(Mo $K\alpha$) = 2·39 mm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å, $T = 295$ K, $F(000) = 1552$, $R = 0{\cdot}067$ for 3013 diffractometer data with $I \geq 2{\cdot}5\sigma(I)$. Except for the methoxy-group geometries the two independent molecules are structurally equivalent; they have their Br atoms in the 21α-position, which implies that the Lowe–Brewster rules do not apply in this case.

Introduction. When elaborating a stereoselective route to 1-haloallenes by reacting optically active 2-propynyl methanesulfonates with lithium dihalocuprates it was found that the reaction of mestranol methanesulfonate with lithium dibromocuprate proceeds stereospecifically (Elsevier, Meijer, Tadema, Stehouwer, Bos, Vermeer & Runge, 1982; Elsevier, Bos, Vermeer, Spek & Kroon, 1984). The structure assignment of the steroidal allene obtained could not reliably be made by application of the Lowe–Brewster rules (Lowe, 1965; Brewster, 1967) since in many cases these rules do not apply to trisubstituted allenes (Bertrand, Gil & Kumar, 1980; Elsevier, Meijer, Westmijze, Vermeer & van Dijck, 1982). In order to assess the absolute stereochemistry of the allene formation we determined the molecular structure of the title compound by X-ray crystallography.

Experimental. Plate-shaped crystal (001–00$\bar{1}$: 0·058; 110–$\bar{1}\bar{1}$0: 0·594; 1$\bar{1}$0–$\bar{1}$10: 0·575 mm), grown from a methanol solution. Enraf–Nonius CAD-4F diffractometer; Zr-filtered Mo $K\alpha$ radiation; $2\theta_{\max} = 46°$, $-h$, $\pm k,l$; $\omega/2\theta$ scan mode. Total of 5920 reflections scanned; 3013 observed [$I > 2{\cdot}5\sigma(I)$]. Two reference reflections (0$\bar{2}$4 and $\bar{2}$03) with individual fluctuations up to 5% from the average showed an overall decay of 17% during the 80 h of X-ray exposure. Corrections for the decay, Lorentz and polarization factors and for absorption (Gaussian integration with 264 grid points; min. and max. corrections 1·150 and 3·220). Unit-cell dimensions calculated from setting angles (2θ, ω, κ, φ) of 16 centered reflections. Structure determined by the usual heavy-atom techniques after location of the two Br atoms from a Patterson map. Blocked full-matrix least-squares refinement on F (positional and anisotropic thermal parameters for non-H atoms, one overall isotropic thermal parameter for H atoms refined in the riding mode on the carrying atoms). Convergence at $R = 0{\cdot}067$, $wR = 0{\cdot}078$, $S = 2{\cdot}37$; $w = 1{\cdot}424/[\sigma^2(F) + 0{\cdot}0022|F|^2]$. $(\Delta/\sigma)_{\max} = 1{\cdot}2$. Min. and max. residual electron density $-0{\cdot}84$ and $0{\cdot}88$ e Å^{-3}: interpreted as residual absorption effects. The enantiomeric structure was refined separately. It converged to $R = 0{\cdot}085$ and could be rejected at a significance level much lower than 0·005. Moreover, the absolute configuration is consistent with that defined by reference to the steroid moiety.

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Scattering factors from Cromer & Mann (1968), anomalous-dispersion corrections from Cromer & Liberman (1970). Calculations carried out either on the CDC-Cyber 175 computer of the University of Utrecht with programs of the *APOLLO* (data reduction and correction by A. L. Spek) and *EUCLID* [calculations of geometrical data and illustrations (Spek, 1982)] packages or on the in-house Eclipse S/230 minicomputer using the programs of a modified version of *SHELX76* (Sheldrick, 1976).

Discussion. The final atomic coordinates of the non-H atoms together with their e.s.d.'s and equivalent isotropic thermal parameters are given in Table 1.* The structure appears to be isotructural with 3-methoxy-21α-methyl-19-nor-1,3,5(10),17(20),20-pregnapentaene [ORG2700] (Elsevier, Meijer, Westmijze, Vermeer & van Dijck, 1982), the methyl group being replaced by Br. Thus the structure presented here shows that the Br atom is in the α position. Based on the high $[\alpha]_D^{20\,^\circ C}$ value for the title compound, *viz* −173° ($c = 1{\cdot}10$ g dm^{-3}, $CHCl_3$), Lowe–Brewster rules predict the structure with the Br atom in the *β* position (Elsevier, Meijer, Tadema, Stehouwer, Bos, Vermeer & Runge, 1982). Apparently, the rules are also violated for this trisubstituted allene. Table 2 lists bond lengths and angles. Fig. 1 is a labeled perspective view of both independent molecules, which are structurally equivalent in every respect, except for the conformations of the methoxy groups. The torsion angles C(2)—C(3)—O—C(19) in molecules *A* and *B* are −15(2) and 9(2)° respectively; corresponding values in ORG2700 are −10(2) and 10(1)° respectively. The methoxy-group bonding shows great flexibility, with the sum of the C—O bond distances remaining practically constant. In molecule *A* C(3)—O = 1·44 (2) and C(19)—O = 1·33 (2) Å, whereas for molecule *B* these values are 1·40 (1) and 1·41 (1) Å respectively. For ORG2700 these distances show the same trend and are 1·52 (2), 1·30 (1) and 1·39 (1), 1·42 (1) Å respectively. However, in both cases the thermal motion in the methoxy group of molecule *A* is higher than that in molecule *B*, thus providing a possible explanation for this observed trend. The puckering of corresponding rings is nearly the same in both molecules as is indicated by the mean (standard deviation 0·4°) of the absolute values for the torsion angles. We find for molecule *A* (values for *B* in parentheses) ring *A*: 1·3 (0·9), ring *B*: 34·0 (34·8), ring *C*: 55·7 (56·8) and ring *D*: 27·3 (28·0)°. Similar values are found in ORG2700. The packing is shown in Fig. 2. The two independent molecules form nearly parallel

Table 1. *Final coordinates and equivalent isotropic thermal parameters*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$(Å^2)
Molecule *A*				
Br	−0·8046 (1)	0·2533 (1)	0·08985 (5)	0·0904 (5)
O(1)	0·212 (1)	0·2643 (7)	0·3649 (3)	0·120 (2)
C(1)	−0·094 (1)	0·3279 (8)	0·2929 (4)	0·074 (2)
C(2)	0·003 (1)	0·3332 (9)	0·3309 (5)	0·088 (2)
C(3)	0·110 (1)	0·2676 (9)	0·3282 (5)	0·082 (2)
C(4)	0·126 (1)	0·2004 (9)	0·2924 (5)	0·085 (2)
C(5)	0·035 (1)	0·1958 (8)	0·2560 (4)	0·071 (2)
C(6)	0·060 (1)	0·1227 (9)	0·2154 (5)	0·090 (2)
C(7)	−0·052 (1)	0·1069 (8)	0·1801 (5)	0·084 (2)
C(8)	−0·124 (1)	0·2063 (7)	0·1690 (4)	0·056 (2)
C(9)	−0·1852 (9)	0·2467 (7)	0·2161 (3)	0·057 (2)
C(10)	−0·0802 (9)	0·2603 (8)	0·2562 (4)	0·063 (2)
C(11)	−0·269 (1)	0·3408 (8)	0·2069 (4)	0·074 (2)
C(12)	−0·378 (1)	0·3248 (8)	0·1670 (4)	0·071 (2)
C(13)	−0·314 (1)	0·2843 (7)	0·1210 (4)	0·067 (2)
C(14)	−0·237 (1)	0·1916 (8)	0·1321 (4)	0·071 (2)
C(15)	−0·208 (1)	0·143 (1)	0·0842 (5)	0·096 (2)
C(16)	−0·341 (1)	0·156 (1)	0·0552 (5)	0·108 (2)
C(17)	−0·408 (1)	0·244 (1)	0·0821 (4)	0·083 (2)
C(18)	−0·228 (1)	0·3670 (9)	0·0973 (4)	0·087 (2)
C(19)	0·219 (2)	0·341 (1)	0·3960 (5)	0·118 (3)
C(20)	−0·530 (1)	0·2744 (9)	0·0717 (4)	0·081 (3)
C(21)	−0·650 (1)	0·3077 (8)	0·0602 (4)	0·078 (2)
Molecule *B*				
Br	0·8682 (1)	0·50785 (9)	0·47248 (5)	0·0961 (5)
O(1)	0·4620 (8)	−0·0580 (6)	0·1578 (3)	0·086 (2)
C(1)	0·4995 (9)	0·1096 (7)	0·2637 (4)	0·058 (2)
C(2)	0·449 (1)	0·0712 (8)	0·2200 (4)	0·068 (2)
C(3)	0·5023 (9)	−0·0137 (8)	0·2015 (4)	0·060 (2)
C(4)	0·6033 (9)	−0·0620 (7)	0·2248 (4)	0·053 (2)
C(5)	0·6586 (8)	−0·0270 (7)	0·2673 (3)	0·048 (2)
C(6)	0·772 (1)	−0·0803 (7)	0·2917 (4)	0·059 (2)
C(7)	0·8550 (9)	−0·0155 (7)	0·3249 (3)	0·059 (2)
C(8)	0·7639 (9)	0·0419 (6)	0·3602 (3)	0·049 (2)
C(9)	0·6699 (8)	0·1122 (6)	0·3318 (4)	0·049 (2)
C(10)	0·6049 (8)	0·0623 (7)	0·2885 (3)	0·045 (2)
C(11)	0·5748 (9)	0·1658 (7)	0·3676 (4)	0·061 (2)
C(12)	0·648 (1)	0·2249 (7)	0·4077 (4)	0·067 (2)
C(13)	0·7476 (9)	0·1573 (7)	0·4335 (3)	0·051 (2)
C(14)	0·8393 (8)	0·1051 (6)	0·3965 (3)	0·048 (2)
C(15)	0·953 (1)	0·0624 (8)	0·4279 (4)	0·066 (2)
C(16)	0·973 (1)	0·1446 (8)	0·4681 (5)	0·077 (2)
C(17)	0·8516 (9)	0·2091 (7)	0·4654 (4)	0·054 (2)
C(18)	0·6750 (9)	0·0832 (7)	0·4673 (4)	0·065 (2)
C(19)	0·372 (1)	−0·0015 (8)	0·1289 (4)	0·092 (2)
C(20)	0·8377 (9)	0·2972 (8)	0·4856 (4)	0·059 (2)
C(21)	0·8246 (9)	0·3864 (8)	0·5060 (4)	0·068 (2)

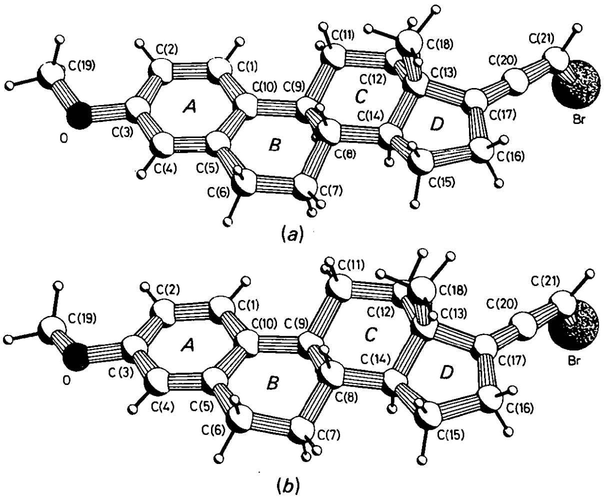

Fig. 1. Comparison and absolute configuration of the two independent molecules along with the labeling scheme of the atoms and rings. (*a*) Molecule *A*. (*b*) Molecule *B*.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39004 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Relevant bond distances* (Å) *and angles* (°)

	A	*B*		*A*	*B*		*A*	*B*
Br—C(21)	1·89 (1)	1·91 (1)	C(5)—C(6)	1·50 (2)	1·50 (1)	C(13)—C(14)	1·49 (1)	1·53 (1)
O(1)—C(3)	1·44 (2)	1·40 (1)	C(6)—C(7)	1·50 (2)	1·50 (1)	C(13)—C(17)	1·52 (2)	1·53 (1)
O(1)—C(19)	1·33 (2)	1·41 (1)	C(7)—C(8)	1·53 (1)	1·53 (1)	C(13)—C(18)	1·54 (2)	1·53 (1)
C(1)—C(2)	1·42 (2)	1·40 (2)	C(8)—C(9)	1·53 (1)	1·54 (1)	C(14)—C(15)	1·49 (2)	1·53 (1)
C(1)—C(10)	1·35 (2)	1·40 (1)	C(8)—C(14)	1·53 (1)	1·50 (1)	C(15)—C(16)	1·56 (2)	1·57 (2)
C(2)—C(3)	1·38 (2)	1·35 (1)	C(9)—C(10)	1·53 (1)	1·51 (1)	C(16)—C(17)	1·53 (2)	1·49 (1)
C(3)—C(4)	1·34 (2)	1·36 (1)	C(9)—C(11)	1·53 (1)	1·54 (1)	C(17)—C(20)	1·33 (2)	1·30 (1)
C(4)—C(5)	1·35 (2)	1·37 (1)	C(11)—C(12)	1·56 (1)	1·54 (1)	C(20)—C(21)	1·32 (2)	1·32 (1)
C(5)—C(10)	1·44 (1)	1·43 (1)	C(12)—C(13)	1·51 (1)	1·52 (1)			
C(3)—O(1)—C(19)	118 (1)	116·2 (8)	C(9)—C(8)—C(14)	107·6 (8)	107·7 (7)	C(14)—C(13)—C(17)	100·1 (9)	99·9 (7)
C(2)—C(1)—C(10)	120 (1)	121·5 (9)	C(7)—C(8)—C(14)	111·6 (8)	113·3 (7)	C(14)—C(13)—C(18)	112·6 (9)	113·1 (8)
C(1)—C(2)—C(3)	117 (1)	119 (1)	C(8)—C(9)—C(10)	111·7 (8)	113·4 (7)	C(17)—C(13)—C(18)	107·6 (9)	105·6 (8)
O(1)—C(3)—C(4)	114 (1)	114·8 (9)	C(8)—C(9)—C(11)	111·7 (8)	109·7 (8)	C(8)—C(14)—C(15)	119·5 (9)	122·4 (8)
C(2)—C(3)—C(4)	124 (1)	121 (1)	C(10)—C(9)—C(11)	113·5 (8)	115·9 (7)	C(13)—C(14)—C(15)	106 (1)	103·9 (7)
O(1)—C(3)—C(2)	122 (1)	124·3 (9)	C(1)—C(10)—C(5)	119 (1)	117·3 (8)	C(8)—C(14)—C(13)	114·7 (9)	112·8 (7)
C(3)—C(4)—C(5)	119 (1)	122·7 (9)	C(5)—C(10)—C(9)	118·5 (9)	121·6 (7)	C(14)—C(15)—C(16)	104 (1)	103·5 (8)
C(4)—C(5)—C(10)	121 (1)	118·4 (8)	C(1)—C(10)—C(9)	122·8 (9)	120·6 (8)	C(15)—C(16)—C(17)	102 (1)	105·0 (9)
C(6)—C(5)—C(10)	122 (1)	119·8 (8)	C(9)—C(11)—C(12)	112·9 (9)	113·2 (7)	C(13)—C(17)—C(20)	128 (1)	125·2 (8)
C(4)—C(5)—C(6)	118 (1)	121·8 (8)	C(11)—C(12)—C(13)	109·9 (8)	110·2 (8)	C(13)—C(17)—C(16)	109·8 (9)	109·1 (8)
C(5)—C(6)—C(7)	116 (1)	114·8 (8)	C(12)—C(13)—C(14)	110·0 (9)	110·6 (8)	C(16)—C(17)—C(20)	122 (1)	125·7 (9)
C(6)—C(7)—C(8)	111·0 (9)	109·8 (7)	C(12)—C(13)—C(17)	116·9 (9)	116·7 (8)	C(17)—C(20)—C(21)	178 (1)	180 (1)
C(7)—C(8)—C(9)	108·8 (8)	110·3 (8)	C(12)—C(13)—C(18)	109·5 (8)	110·5 (8)	Br—C(21)—C(20)	121·0 (9)	122·2 (8)

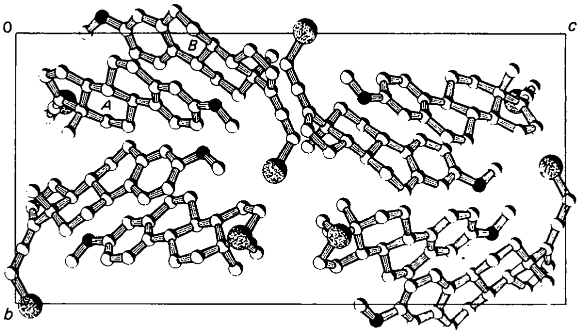

Fig. 2. Projection of the unit-cell contents down the *a* axis. The two independent molecules are indicated by *A* and *B* respectively.

pairs and are related by a pseudo-twofold axis running parallel to their medium axis of inertia.

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Structures of *tert*-Butyl 3-Nitroperbenzoate (I) and *tert*-Butyl 4-Nitroperbenzoate (II), $C_{11}H_{13}NO_5$

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Abstract. $M_r = 239\cdot2$. (I): monoclinic, $P2_1/c$, $a = 8\cdot462\,(4)$, $b = 17\cdot408\,(10)$, $c = 8\cdot279\,(4)$ Å, $\beta = 101\cdot56\,(4)°$, $V = 1194\cdot8$ Å^3, $Z = 4$, $D_m = 1\cdot30\,(5)$, $D_x = 1\cdot330$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot114$ mm^{-1}, $F(000) = 504$, $T = 293\,(1)$ K, $R = 0\cdot114$ for 1069 unique observed reflexions. (II): triclinic, $P\bar{1}$, $a = 6\cdot892\,(3)$, $b = 8\cdot077\,(4)$, $c = 11\cdot970\,(6)$ Å, $\alpha = 106\cdot94\,(4)$, $\beta = 102\cdot11\,(4)$, $\gamma = 93\cdot37\,(4)°$, $V =$

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