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(2α,5α)-1,5,6,9,9-Pentabromo-7-methoxy-2,3,3a,4,5,6-hexahydro-3a,6-methanoazulen-2-ol

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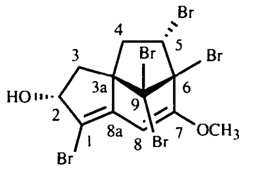
Abstract

The X-ray structure analysis of the title compound, $C_{12}H_{11}Br_5O_2$, established the presence of the 2,3,3a,4,5,6-hexahydro-3a,6-methanoazulene ring system, which was produced by a reaction sequence involving unexpected skeletal rearrangement processes.

Comment

We have been examining the utility of [5.3.1]propellanes (Banwell, Gable, Phyland & Peters, 1995; Banwell, Gable, Halton & Phyland, 1994) as precursors to the *AB* ring system of the potent antimitotic agent paclitaxel (taxol^{TM}) (Nicolaou, Dai & Guy, 1994). In this respect, we attempted the allylic bromination of the [5.3.1]propelladiene 6,9,9-tribromo-7-methoxy-2,3-dihydro-1*H*-3a,8a-methanoazulene (Banwell, Gable, Phyland & Peters, 1995) in the hope of installing functionality at the C4 positon within this framework. Both NMR and mass spectrometric analyses of the major product, however, suggested that a much more extensive reaction, including skeletal rearrangement, had occurred. As a result of the intervention of such manifold processes, the X-ray analysis of the compound, (I), was carried out.



(I)

The perhydro-3a,6-methanoazulene skeleton is found embedded within the framework of a large number of compounds and some 80 of these have been subjected to X-ray analysis. These include many gibberellins (Kutschabsky & Adam, 1983; Baynham, Hanson, Hitchcock & de Oliveira, 1990), certain pagodanes (Prakash *et al.*, 1988), some derivatives of zizaene-type sesquiterpenes (Ghisalberti, White & Willis, 1976; Coates, Farney, Johnson & Paul, 1969) and a number of alkaloidal materials (Sasaki & Hirata, 1971; Zheng *et al.*, 1987; Yoshino & Litaka, 1966; Cygler, Przybylska & Edwards, 1982; Arbain, Byrne, Cannon, Patrick & White, 1990). The structures of several mono-unsaturated perhydro-3a,6-methanoazulenes have also been established by X-ray analysis (Tochtermann *et al.*, 1993), but the title compound appears to represent the first example of a doubly unsaturated system for which the structure has been determined crystallographically. The present study shows that both the six-membered ring and the saturated five-membered ring adopt envelope conformations. The cyclopentenyl ring is slightly twisted from planarity. Shortest contacts to neighbouring molecules involve hydrogen bonding between the O(1) H atom and O(2^{i}) at a distance of 2.15 Å [O(1)···O(2^{i}) 2.958 (7); symmetry code: (i) $1-x, y, z$] and a non-bonding interaction between atoms Br(91) and O(1^{ii}) of 2.928 (6) Å [symmetry code: (ii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. The mode of formation of compound (I) is unusual and is the subject of ongoing study.

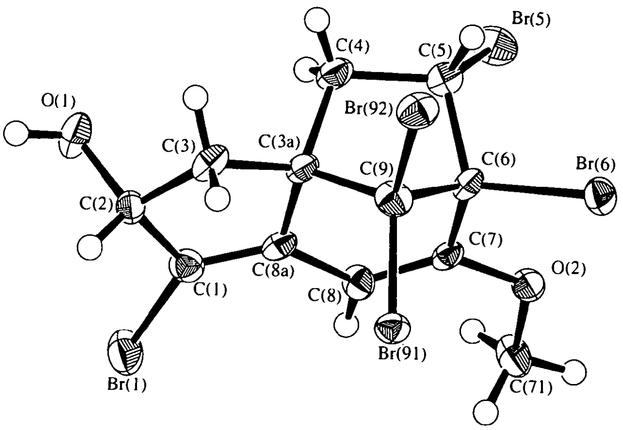


Fig. 1. A view of (I) showing the labelling of the non-H atoms, with displacement ellipsoids at the 50% probability level and H atoms drawn as circles of arbitrary radii.

Experimental

The title compound was prepared by irradiating with white light a CCl_4 solution of 6,9,9-tribromo-7-methoxy-2,3-dihydro-1*H*-3a,8a-methanoazulene (Banwell, Gable, Phyland & Peters, 1995) containing *N*-bromosuccinimide and a trace of benzoyl peroxide. The cooled reaction mixture was filtered, the filtrate concentrated under reduced pressure and the residue subjected to chromatography (silica gel, 15% ether/85% hexane elution). Concentration of the appropriate fractions [R_f 0.1 (33% dichloromethane/67% hexane)] afforded the title compound which was recrystallized from chloroform (m.p. 511–512.5 K).

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Crystal data

$C_{12}H_{11}Br_5O_2$
$M_r = 586.74$
Monoclinic
$P2_1/c$
$a = 9.293\ (2)$ Å
$b = 12.992\ (3)$ Å
$c = 12.710\ (2)$ Å
$\beta = 97.67\ (2)°$
$V = 1520.8\ (5)$ Å^3
$Z = 4$
$D_x = 2.562$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 49.0–49.9°$
$\mu = 15.975$ mm^{-1}
$T = 213\ (1)$ K
Plate
$0.19 \times 0.15 \times 0.05$ mm
Colourless

Data collection

Rigaku AFC-6*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: face-indexed analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.125$, $T_{\max} = 0.352$
2553 measured reflections
2389 independent reflections

2134 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.0138$
$\theta_{\max} = 60.05°$
$h = 0 \rightarrow 10$
$k = -14 \rightarrow 0$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 150 reflections

Refinement

Refinement on F
$R = 0.0400$
$wR = 0.0485$
$S = 2.920$
2134 reflections
173 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.010F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.0150$

$\Delta\rho_{\max} = 1.08$ e Å^{-3}
$\Delta\rho_{\min} = -1.11$ e Å^{-3}
Extinction correction: Zachariasen (1967) type II, Gaussian isotropic
Extinction coefficient: $5\ (8) \times 10^{-7}$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br(1)	−0.13896 (9)	0.35605 (8)	−0.00348 (7)	0.0365 (3)
Br(5)	0.40029 (10)	0.62940 (7)	0.26253 (7)	0.0360 (3)
Br(6)	0.52269 (8)	0.37279 (7)	0.38586 (6)	0.0276 (3)
Br(91)	0.20033 (8)	0.21343 (6)	0.32343 (6)	0.0235 (3)
Br(92)	0.21162 (9)	0.37427 (7)	0.50870 (6)	0.0297 (3)
O(1)	−0.2511 (5)	0.4927 (4)	0.2001 (4)	0.031 (1)
O(2)	0.4586 (5)	0.3959 (4)	0.1600 (4)	0.025 (1)
C(1)	−0.0718 (8)	0.3821 (6)	0.1399 (6)	0.024 (3)
C(2)	−0.1762 (8)	0.3959 (6)	0.2199 (6)	0.023 (3)
C(3)	−0.0741 (8)	0.3967 (6)	0.3236 (6)	0.027 (3)
C(3a)	0.0777 (8)	0.4218 (6)	0.2969 (6)	0.021 (3)
C(4)	0.1324 (8)	0.5342 (6)	0.3160 (6)	0.026 (3)
C(5)	0.2991 (8)	0.5286 (6)	0.3388 (5)	0.022 (3)
C(6)	0.3340 (7)	0.4157 (6)	0.3129 (6)	0.021 (1)
C(7)	0.3254 (7)	0.3989 (5)	0.1933 (6)	0.019 (1)
C(71)	0.4584 (8)	0.3751 (7)	0.0493 (6)	0.034 (3)
C(8)	0.1993 (7)	0.3916 (6)	0.1322 (5)	0.021 (3)
C(8a)	0.0655 (8)	0.3951 (6)	0.1805 (6)	0.022 (3)
C(9)	0.2061 (8)	0.3586 (6)	0.3542 (5)	0.025 (3)

Table 2. *Selected geometric parameters (Å, °)*

Br(1)—C(1)	1.877 (8)	C(1)—C(2)	1.507 (10)
Br(5)—C(5)	1.945 (7)	C(1)—C(8a)	1.32 (1)
Br(6)—C(6)	1.953 (7)	C(3a)—C(8a)	1.509 (10)
Br(91)—C(9)	1.926 (8)	C(6)—C(7)	1.526 (9)
Br(92)—C(9)	1.968 (7)	C(8)—C(8a)	1.459 (10)
Br(1)—C(1)—C(2)	121.1 (5)	Br(6)—C(6)—C(9)	112.5 (5)
Br(1)—C(1)—C(8a)	125.5 (6)	C(5)—C(6)—C(9)	100.9 (5)
C(2)—C(1)—C(8a)	113.3 (7)	O(2)—C(7)—C(8)	126.0 (6)
C(1)—C(2)—C(3)	101.7 (6)	C(1)—C(8a)—C(3a)	110.8 (6)
C(3)—C(3a)—C(4)	117.2 (6)	C(1)—C(8a)—C(8)	131.6 (7)
C(3)—C(3a)—C(8a)	102.6 (6)	Br(91)—C(9)—Br(92)	107.5 (4)
C(3)—C(3a)—C(9)	117.3 (6)	Br(91)—C(9)—C(3a)	115.1 (5)
C(4)—C(3a)—C(9)	102.1 (6)	Br(91)—C(9)—C(6)	113.7 (5)
Br(5)—C(5)—C(4)	114.5 (5)	Br(92)—C(9)—C(3a)	109.3 (5)
Br(5)—C(5)—C(6)	113.8 (5)	Br(92)—C(9)—C(6)	111.7 (5)
Br(6)—C(6)—C(5)	111.7 (5)	C(3a)—C(9)—C(6)	99.4 (6)
Br(6)—C(6)—C(7)	110.9 (4)		

The θ scan width used was $(0.90 + 0.3\tan\theta)°$ at a speed of 8.0° min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts were accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were located from a difference map and fixed at ideal positions [C—H = 0.95 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$]. The structure was solved by Patterson methods and expanded using Fourier techniques (Beurskens *et al.*, 1992). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1993). *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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