O(2A)—C(7A)	1.269 (6)	Cl(1C)—C(2C)	1.720 (5)
C(1A)—C(2A)	1.391 (6)	Cl(2C)—C(4C)	1.740 (5)
C(1A)—C(6A)	1.381 (6)	Cl(3C)—C(6C)	1.729 (5)
C(1A)—C(7A)	1.498 (6)	O(1C)—C(7C)	1.244 (6)
C(2A)—C(3A)	1.364 (6)	O(2C)—C(7C)	1.241 (6)
C(3A)—C(4A)	1.377 (6)	C(1C)—C(2C)	1.371 (6)
C(4A)—C(5A)	1.389 (6)	C(1C)—C(6C)	1.393 (7)
C(5A)—C(6A)	1.385 (6)	C(1C)—C(7C)	1.501 (6)
Cl(1B)—C(2B)	1.735 (5)	C(2C)—C(3C)	1.381 (7)
Cl(2B)—C(4B)	1.734 (5)	C(3C)—C(4C)	1.371 (8)
Cl(3B)—C(6B)	1.727 (5)	C(4C)—C(5C)	1.383 (7)
O(1B)—C(7B)	1.233 (6)	C(5C)—C(6C)	1.372 (7)
O(2B)—C(7B)	1.250 (6)	O(2A')· · ·O(1A)	2.664 (3)
C(1B)—C(2B)	1.390 (6)	O(2A')· · ·H(1A)	1.69 (3)
C(1B)—C(6B)	1.392 (7)	Cl(2C)· · ·Cl(2B'')	3.437 (2)
C(1B)—C(7B)	1.503 (6)		

C(2A)—C(1A)—C(6A)	117.6 (4)	C(3B)—C(4B)—C(5B)	121.8 (5)
C(2A)—C(1A)—C(7A)	121.7 (4)	C(4B)—C(5B)—C(6B)	118.2 (5)
C(6A)—C(1A)—C(7A)	120.7 (4)	Cl(3B)—C(6B)—C(1B)	118.5 (3)
Cl(1A)—C(2A)—C(1A)	119.2 (3)	Cl(3B)—C(6B)—C(5B)	118.9 (4)
Cl(1A)—C(2A)—C(3A)	118.4 (3)	C(1B)—C(6B)—C(5B)	122.5 (4)
C(1A)—C(2A)—C(3A)	122.3 (4)	O(1B)—C(7B)—O(2B)	124.9 (5)
C(2A)—C(3A)—C(4A)	118.4 (4)	O(1B)—C(7B)—C(1B)	117.3 (4)
Cl(2A)—C(4A)—C(3A)	119.0 (4)	O(2B)—C(7B)—C(1B)	117.8 (4)
Cl(2A)—C(4A)—C(5A)	119.0 (3)	C(2C)—C(1C)—C(6C)	117.6 (4)
C(3A)—C(4A)—C(5A)	122.0 (4)	C(2C)—C(1C)—C(7C)	121.2 (4)
C(4A)—C(5A)—C(6A)	117.6 (4)	C(6C)—C(1C)—C(7C)	121.2 (4)
Cl(3A)—C(6A)—C(1A)	120.4 (3)	Cl(1C)—C(2C)—C(1C)	119.2 (4)
Cl(3A)—C(6A)—C(5A)	117.5 (3)	Cl(1C)—C(2C)—C(3C)	118.1 (4)
C(1A)—C(6A)—C(5A)	122.1 (4)	C(1C)—C(2C)—C(3C)	122.6 (4)
O(1A)—C(7A)—O(2A)	125.1 (4)	C(2C)—C(3C)—C(4C)	117.7 (4)
O(1A)—C(7A)—C(1A)	118.2 (4)	Cl(2C)—C(4C)—C(3C)	119.0 (4)
O(2A)—C(7A)—C(1A)	116.7 (4)	Cl(2C)—C(4C)—C(5C)	118.8 (4)
C(2B)—C(1B)—C(6B)	116.6 (4)	C(3C)—C(4C)—C(5C)	122.2 (5)
C(2B)—C(1B)—C(7B)	121.4 (4)	C(4C)—C(5C)—C(6C)	118.2 (5)
C(6B)—C(1B)—C(7B)	122.0 (4)	Cl(3C)—C(6C)—C(1C)	119.3 (3)
Cl(1B)—C(2B)—C(1B)	118.8 (4)	Cl(3C)—C(6C)—C(5C)	119.0 (4)
Cl(1B)—C(2B)—C(3B)	119.0 (4)	C(1C)—C(6C)—C(5C)	121.7 (4)
C(1B)—C(2B)—C(3B)	122.1 (4)	O(1C)—C(7C)—O(2C)	124.4 (5)
C(2B)—C(3B)—C(4B)	118.8 (4)	O(1C)—C(7C)—C(1C)	117.8 (4)
Cl(2B)—C(4B)—C(3B)	119.1 (4)	O(2C)—C(7C)—C(1C)	117.8 (4)
Cl(2B)—C(4B)—C(5B)	119.1 (4)		

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $\frac{3}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H· · ·A	D—H	H· · ·A	D· · ·A	D—H· · ·A
O(1A)—H(1A)· · ·O(2A^i)	0.98 (3)	1.69 (3)	2.664 (3)	172 (3)
O(1B)—H(1B)· · ·O(2C)	0.98 (3)	1.71 (2)	2.661 (3)	166 (3)
O(1C)—H(1C)· · ·O(2B)	0.98 (3)	1.72 (3)	2.693 (3)	176 (3)

Symmetry codes: (i) $1 - x, 2 - y, -z$.

All H atoms were found in difference Fourier maps and the non-carboxyl H atoms were allowed to refine as riding models; their average temperature factor was allowed to refine. The positional parameters of each of the carboxyl H atoms were refined, but these atoms were constrained to be 0.98 Å from their respective O atoms; the temperature factors of the carboxyl H atoms were held constant.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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(3aR,3bS,4aR,4bR,5aR,5bS)-4,4,8,8-Tetrabromo-2,2-dimethylperhydrodicyclopropa-[e,g][1,3]benzodioxole-3b-carbonitrile

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Abstract

The X-ray crystal structure of the title compound, $C_{12}H_{11}Br_4NO_2$, reveals that the two three-membered rings are in an *anti* relationship to one another.

Comment

In connection with a program (Banwell & Dupuche, 1994) directed towards exploiting microbially derived and enantiopure *cis*-1,2-dihydrocatechols (arene-*cis*-diols) in chemical synthesis (Brown & Hudlicky, 1993), we had occasion to subject the acetonide derivative of benzonitrile-*cis*-diol to reaction with dibromocarbene. In addition to obtaining significant quantities of the expected mono-adduct, (1), small amounts of a single bis-adduct, (2), were produced. Resubjection of purified (1) to reaction with dibromocarbene afforded good yields of the same bis-adduct (2) as observed originally, thus proving the former compound is the precursor to the latter. Inspection of molecular models suggested that both faces of the C=C double bond within (1) are sterically hindered [one by the *endo*-bromine at C(6) and the other by the *endo*-methyl at C(2)] and, therefore, it was not clear as to the stereochemical outcome of the reaction leading to adduct (2). NMR spectroscopic analysis of (2) was not informative in this regard so the compound was subjected to single-crystal X-ray analysis.

(1)   (2)
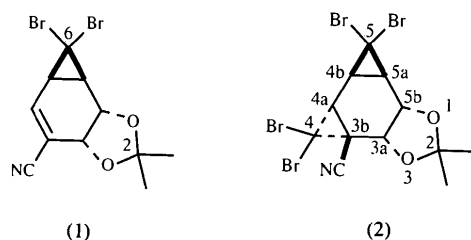
These data establish that the two cyclopropyl moieties are in an *anti* relationship to one another. Furthermore, since it was clear from NMR spectroscopic studies that (1) contains a trisubstituted C=C double bond and as it is the proven precursor to (2), the present study also provides definitive proof as to the structure of (1).
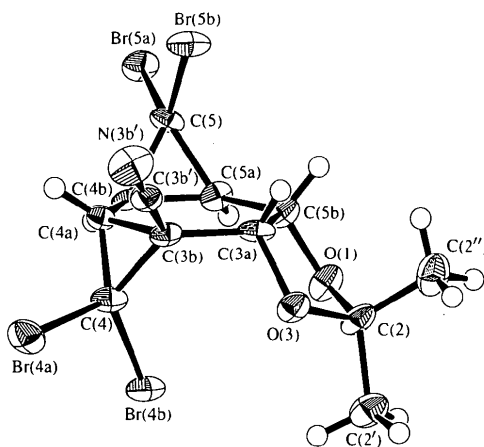

Fig. 1. View of the title compound showing the labelling of all non-H atoms. Thermal ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radius.

Experimental

Compound (1) was treated with a mixture of bromoform (*ca* 13 mol equivalents), benzene, 50% *w/v* aqueous sodium hydroxide and triethylbenzylammonium chloride at 291 K for 40 h then subjected to standard work-up conditions. The crude reaction product was subjected to flash chromatography (silica gel, 5:1 petroleum spirit/ethyl acetate elution) and concentration of the appropriate fractions (R_f 0.72) gave a white crystalline solid. Recrystallization of this material from chloroform/diethyl ether mixtures then afforded compound (2), m.p. 492–493 K.

Crystal data

$C_{12}H_{11}Br_4NO_2$	Cu $K\alpha$ radiation
$M_r = 520.84$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 25
$P2_1$	reflections
$a = 6.322\,(1)$ Å	$\theta = 48.9$–$50.0°$
$b = 13.476\,(1)$ Å	$\mu = 13.348$ mm^{-1}
$c = 9.115\,(2)$ Å	$T = 213\,(1)$ K
$\beta = 106.54\,(1)°$	Irregular
$V = 744.5\,(2)$ Å^3	$0.200 \times 0.160 \times 0.080$ mm
$Z = 2$	Colourless
$D_x = 2.323$ Mg m^{-3}	

Data collection

AFC-6*R* diffractometer	$R_{int} = 0.062$
$\omega/2\theta$ scans	$\theta_{max} = 60.05°$
Absorption correction:	$h = 0 \rightarrow 7$
empirical, based on	$k = 0 \rightarrow 15$
azimuthal (ψ) scans	$l = -10 \rightarrow 9$
(North, Phillips &	3 standard reflections
Mathews, 1968)	monitored every 150
$T_{min} = 0.610$, $T_{max} =$	reflections
1.000	intensity decay: insignifi-
1283 measured reflections	cant
1170 independent reflections	
1134 observed reflections	
$[I > 3.00\sigma(I)]$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.74$ e Å^{-3}
$R = 0.0272$	$\Delta\rho_{min} = -0.51$ e Å^{-3}
$wR = 0.0325$	Extinction correction:
$S = 2.798$	Zachariasen type 2
1134 reflections	Gaussian isotropic
171 parameters	Extinction coefficient:
H-atom parameters not	$1.5\,(3) \times 10^{-6}$
refined	Atomic scattering factors
$w = 4F_o^2/[\sigma^2(F_o^2)$	from *International Tables*
$+ (0.010F_o^2)^2]$	*for Crystallography* (1992,
$(\Delta/\sigma)_{max} = 0.0020$	Vol C, Tables 4.2.6.8 and
	6.1.1.4)

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

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

	x	y	z	U_{eq}
Br(4a)	0.0868 (2)	−0.0250	−0.1721 (1)	0.0355 (3)
Br(4b)	−0.1009 (2)	0.2429 (1)	−0.1830 (1)	0.0316 (3)

$C_{12}H_{11}Br_4NO_2$

Br(5a)	−0.3639 (2)	−0.2804	−0.8642 (1)	0.0301 (3)
Br(5b)	0.1380 (2)	−0.2185 (1)	−0.7381 (1)	0.0345 (3)
O(1)	0.111 (1)	−0.4359 (5)	−0.3539 (8)	0.029 (2)
O(3)	0.357 (1)	−0.3295 (6)	−0.2106 (7)	0.028 (2)
N(3b′)	0.515 (2)	−0.0495 (8)	−0.361 (1)	0.043 (3)
C(2)	0.309 (2)	−0.4334 (8)	−0.226 (1)	0.030 (3)
C(2′)	0.254 (2)	−0.4688 (9)	−0.085 (1)	0.036 (3)
C(2″)	0.491 (2)	−0.4889 (9)	−0.265 (1)	0.041 (3)
C(3a)	0.296 (2)	−0.2871 (9)	−0.3606 (10)	0.023 (3)
C(3b)	0.218 (2)	−0.1796 (8)	−0.355 (1)	0.021 (3)
C(3b′)	0.388 (2)	−0.1060 (8)	−0.353 (1)	0.026 (3)
C(4a)	−0.014 (2)	−0.1462 (8)	−0.448 (1)	0.021 (3)
C(4b)	−0.165 (1)	−0.2210 (8)	−0.544 (1)	0.021 (3)
C(4)	0.041 (2)	−0.1498 (8)	−0.282 (1)	0.025 (3)
C(5a)	−0.094 (2)	−0.3279 (8)	−0.552 (1)	0.024 (3)
C(5b)	0.135 (2)	−0.3640 (8)	−0.461 (1)	0.026 (3)
C(5)	−0.124 (1)	−0.2606 (8)	−0.6862 (10)	0.023 (3)

Table 2. Selected geometric parameters (Å, °)

Br(4a)—C(4)	1.93 (1)	C(3a)—C(3b)	1.54 (1)
Br(4b)—C(4)	1.910 (10)	C(3a)—C(5b)	1.56 (1)
Br(5a)—C(5)	1.900 (9)	C(3b)—C(3b′)	1.46 (1)
Br(5b)—C(5)	1.930 (9)	C(3b)—C(4a)	1.54 (1)
O(1)—C(2)	1.45 (1)	C(3b)—C(4)	1.51 (1)
O(1)—C(5b)	1.41 (1)	C(4a)—C(4b)	1.49 (1)
O(3)—C(2)	1.43 (1)	C(4a)—C(4)	1.46 (1)
O(3)—C(3a)	1.43 (1)	C(4b)—C(5a)	1.52 (1)
N(3b′)—C(3b′)	1.13 (1)	C(4b)—C(5)	1.50 (1)
C(2)—C(2′)	1.50 (1)	C(5a)—C(5b)	1.53 (1)
C(2)—C(2″)	1.50 (2)	C(5a)—C(5)	1.49 (1)
C(2)—O(1)—C(5b)	107.7 (7)	C(4a)—C(4b)—C(5a)	121.4 (8)
C(2)—O(3)—C(3a)	107.9 (8)	C(4a)—C(4b)—C(5)	120.5 (8)
O(1)—C(2)—O(3)	102.1 (8)	C(5a)—C(4b)—C(5)	59.3 (7)
O(1)—C(2)—C(2′)	109.0 (9)	Br(4a)—C(4)—Br(4b)	110.4 (5)
O(1)—C(2)—C(2″)	110.0 (9)	Br(4a)—C(4)—C(3b)	116.0 (7)
O(3)—C(2)—C(2′)	108.8 (9)	Br(4a)—C(4)—C(4a)	117.7 (8)
O(3)—C(2)—C(2″)	110.8 (9)	Br(4b)—C(4)—C(3b)	122.6 (8)
C(2′)—C(2)—C(2″)	115.3 (10)	Br(4b)—C(4)—C(4a)	120.5 (7)
O(3)—C(3a)—C(3b)	110.2 (8)	C(3b)—C(4)—C(4a)	62.4 (6)
O(3)—C(3a)—C(5b)	104.4 (8)	C(4b)—C(5a)—C(5b)	121.6 (9)
C(3b)—C(3a)—C(5b)	119.0 (8)	C(4b)—C(5a)—C(5)	59.6 (6)
C(3a)—C(3b)—C(3b′)	113.4 (8)	C(5b)—C(5a)—C(5)	121.1 (8)
C(3a)—C(3b)—C(4a)	121.5 (8)	O(1)—C(5b)—C(3a)	103.4 (8)
C(3a)—C(3b)—C(4)	123.6 (8)	O(1)—C(5b)—C(5a)	108.7 (8)
C(3b′)—C(3b)—C(4a)	113.0 (9)	C(3a)—C(5b)—C(5a)	118.0 (9)
C(3b′)—C(3b)—C(4)	116.8 (9)	Br(5a)—C(5)—Br(5b)	111.4 (4)
C(4a)—C(3b)—C(4)	57.1 (6)	Br(5a)—C(5)—C(4b)	119.7 (7)
N(3b′)—C(3b′)—C(3b)	175 (1)	Br(5a)—C(5)—C(5a)	119.9 (7)
C(3b)—C(4a)—C(4b)	118.6 (9)	Br(5b)—C(5)—C(4b)	118.9 (7)
C(3b)—C(4a)—C(4)	60.4 (6)	Br(5b)—C(5)—C(5a)	117.6 (6)
C(4b)—C(4a)—C(4)	120.7 (8)	C(4b)—C(5)—C(5a)	61.1 (6)

The θ-scan width used was $(1.30 + 0.3\tan\theta)°$ at a speed of $32.0°\,\mathrm{min}^{-1}$ (in ω). The weak reflections were rescanned a maximum of four times and the counts 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 with $U_{iso} = 1.2U_{eq}(C)$. The structure was solved by direct methods using *SIR*92 (Altomare *et al.*, 1994) and expanded using Fourier techniques (Beurskens *et al.*, 1992).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1058). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structural Studies of Mitomycins. VII. Mitomycin G

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Abstract

The title compound, [1aS-(1aα,8aα,8bα)]-6-amino-1,1a,2,8,8a,8b-hexahydro-8a-methoxy-1,5-dimethyl-8-methyleneazirino[2′,3′:3,4]pyrrolo[1,2-a]indole-4,7-dione, $C_{15}H_{17}N_3O_3$, is a derivative of the mitomycins, which are antitumor antibiotics. The quinone O atoms deviate significantly from the least-squares plane of the quinone ring.

Comment

Mitomycins are potent antitumor antibiotics and the mitomycin C member of the family has been applied clinically to various tumors successfully. It is important to understand the relationships between the three-