For comparison, mean C—C(sp^3)—C and H—C(sp^3)—H angles for other large rings are 115·2 and 103·9° in cycloundecylmethyl 1-naphthylcarbamate (Russell & Sim, 1990) and 114·3 and 106·9° in *N*-(*p*-toluensulfonyl)azacyclotridecane (Sim, 1987*b*); in cyclodecane-1,6-diol the C—C—C angles are 113·4–120·1° and the H—C—H angles are 104·7–106·7° (Ermer, Dunitz & Bernal, 1973).

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Structural Studies of Mitomycins. IV. Structure of Albomitomycin A

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Abstract. [1*S*-(1α,2α,4β,5β,6α,6aα,10a*R*)]-2,3,6,6a,-7,10-Hexahydro-1,2,5-metheno-5,8-dimethoxy-9-methyl-7,10-dioxo-1*H*,5*H*-imidazo[2,1-*i*]indol-6-ylmethyl carbamate, $C_{16}H_{19}N_3O_6$, $M_r = 351{\cdot}36$, monoclinic, $P2_1$, $a = 10{\cdot}605\ (1)$, $b = 8{\cdot}342\ (2)$, $c = 9{\cdot}4889\ (7)$ Å, $\beta = 106{\cdot}416\ (7)°$, $V = 805{\cdot}2\ (3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}45$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}296$ cm^{-1}, $F(000) = 372$, $T = 293$ K, $wR = 0{\cdot}044$ for 1427 observed reflections with $F > 3\sigma(F)$. The title compound is one of the minor constituents from the fermentation broth of mitomycin A. The structure has a quite unusual fused-ring system for mitomycins. The quinone ring which is one of the important structural characteristics of the mitomycin family is reduced to a dihydroquinone in the title compound.

Introduction. Mitomycins are potent antitumour antibiotics and mitomycin C which is a member of the family has clinically been applied to various tumours successfully. Although mitomycin C is a prominent antitumor drug, we have been screening the minor constituents from the fermentation broth of mitomycins since 1977 to discover more effective and less toxic compounds. Albomitomycin A was discovered from the fermentation broth of mitomycin A by *Streptomyces caespitosus* (Kono, Saitoh, Shirahata, Arai & Ishii, 1987). Albomitomycin A is almost colourless as suggested by its name. Since the colours of most mitomycins are very deep the unusual pale colour of albomitomycin A implies that it should have a quite unique skeleton. If albomitomycin A has a new skeleton we may develop a new chemistry of mitomycins to discover more potent compounds. Therefore we have undertaken its structure determination. Since the compound was isolated as a minor constituent the sample was very small. In addition the structure is quite different from other members of the mitomycin family. Therefore it was extremely difficult to elucidate the chemical structure by normal spectroscopic methods (Kono, Saitoh, Shirahata, Arai & Ishii, 1987). The chloroform solution, which was left in a refrigerator for days, unexpectedly gave a few prismatic crystals and by use of these crystals we have successfully determined the unique structure unequivocally by X-ray analysis. The crystals were pale violet due to a trace amount of mitomycin A in the crystals.

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Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij} \mathbf{a}_i.\mathbf{a}_j$.

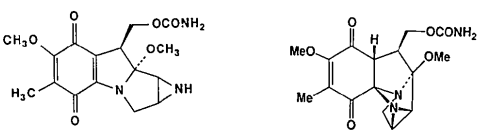
	x	y	z	B_{eq}(Å^2)
O(5)	0·6173 (2)	0·262	0·8438 (2)	4·67 (5)
O(7)	0·6319 (2)	−0·2418 (3)	0·6414 (2)	5·86 (5)
O(8)	0·3722 (2)	−0·2795 (3)	0·6416 (2)	5·12 (5)
O(9*a*)	0·0863 (2)	0·1864 (2)	0·6653 (2)	3·44 (4)
O(10*a*)	0·0030 (2)	−0·2982 (2)	0·9810 (2)	4·74 (4)
O(10)	0·1299 (2)	−0·2894 (2)	0·8268 (2)	3·29 (3)
N(1)	0·4005 (2)	0·1996 (3)	0·9358 (2)	2·97 (4)
N(4)	0·3196 (2)	0·1760 (2)	0·6803 (2)	2·80 (4)
N(10*a*)	0·0233 (2)	−0·5139 (3)	0·8451 (3)	4·03 (5)
C(1)	0·2549 (2)	0·2132 (3)	0·8904 (3)	3·05 (5)
C(2)	0·3354 (2)	0·3500 (3)	0·8678 (3)	3·39 (5)
C(3)	0·3306 (2)	0·3509 (3)	0·7080 (3)	3·52 (6)
C(4*a*)	0·4222 (2)	0·1093 (3)	0·8083 (3)	2·69 (5)
C(5)	0·5618 (2)	0·1363 (3)	0·7980 (3)	3·10 (5)
C(6)	0·6257 (2)	0·0121 (3)	0·7347 (3)	3·27 (5)
C(6*a*)	0·7557 (3)	0·0506 (4)	0·7113 (3)	4·84 (7)
C(7)	0·5698 (2)	−0·1341 (3)	0·7033 (3)	3·39 (5)
C(7*a*)	0·6328 (3)	−0·4060 (4)	0·6795 (4)	5·31 (7)
C(8*a*)	0·3788 (2)	−0·0660 (3)	0·8112 (2)	2·56 (4)
C(8)	0·4341 (3)	−0·1711 (3)	0·7133 (3)	3·22 (5)
C(9*a*)	0·2096 (2)	0·1287 (3)	0·7426 (3)	2·72 (5)
C(9*b*)	0·0383 (3)	0·1320 (4)	0·5165 (3)	5·19 (8)
C(9)	0·2271 (2)	−0·0535 (3)	0·7607 (3)	2·65 (5)
C(10*a*)	0·0488 (2)	−0·3630 (3)	0·8928 (3)	3·07 (5)
C(10)	0·1519 (2)	−0·1205 (3)	0·8603 (3)	2·99 (5)

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

O(5)—C(5)	1·220 (3)	N(10*a*)—C(10*a*)	1·340 (3)
O(7)—C(7)	1·342 (4)	C(1)—C(2)	1·478 (4)
O(7)—C(7*a*)	1·416 (4)	C(1)—C(9*a*)	1·522 (3)
O(8)—C(8)	1·208 (4)	C(2)—C(3)	1·504 (5)
O(9*a*)—C(9*a*)	1·392 (3)	C(4*a*)—C(5)	1·528 (4)
O(9*a*)—C(9*b*)	1·433 (4)	C(4*a*)—C(8*a*)	1·536 (3)
O(10*a*)—C(10*a*)	1·207 (4)	C(5)—C(6)	1·457 (4)
O(10)—C(10*a*)	1·347 (3)	C(6)—C(6*a*)	1·491 (5)
O(10)—C(10)	1·450 (3)	C(6)—C(7)	1·353 (4)
N(1)—C(1)	1·486 (3)	C(7)—C(8)	1·502 (4)
N(1)—C(2)	1·489 (3)	C(8*a*)—C(8)	1·511 (4)
N(1)—C(4*a*)	1·497 (3)	C(8*a*)—C(9)	1·548 (4)
N(4)—C(3)	1·481 (3)	C(9*a*)—C(9)	1·536 (3)
N(4)—C(4*a*)	1·491 (3)	C(9)—C(10)	1·506 (4)
N(4)—C(9*a*)	1·503 (3)		
C(7)—O(7)—C(7*a*)	120·4 (3)	C(5)—C(6)—C(6*a*)	117·7 (2)
C(9*a*)—O(9*a*)—C(9*b*)	115·5 (2)	C(5)—C(6)—C(7)	120·4 (2)
C(10*a*)—O(10)—C(10)	115·2 (3)	C(6*a*)—C(6)—C(7)	121·8 (3)
C(1)—N(1)—C(2)	59·6 (2)	O(7)—C(7)—C(6)	117·5 (2)
C(1)—N(1)—C(4*a*)	100·9 (2)	O(7)—C(7)—C(8)	119·2 (2)
C(2)—N(1)—C(4*a*)	103·5 (2)	C(6)—C(7)—C(8)	122·7 (2)
C(3)—N(4)—C(4*a*)	102·8 (2)	C(4*a*)—C(8*a*)—C(8)	111·8 (2)
C(3)—N(4)—C(9*a*)	102·7 (2)	C(4*a*)—C(8*a*)—C(9)	102·7 (2)
C(4*a*)—N(4)—C(9*a*)	92·9 (2)	C(8)—C(8*a*)—C(9)	113·6 (2)
N(1)—C(1)—C(2)	60·3 (2)	O(8)—C(8)—C(7)	119·8 (3)
N(1)—C(1)—C(9*a*)	105·3 (2)	O(8)—C(8)—C(8*a*)	122·5 (3)
C(2)—C(1)—C(9*a*)	105·6 (2)	C(7)—C(8)—C(8*a*)	117·7 (3)
N(1)—C(2)—C(1)	60·1 (2)	O(9*a*)—C(9*a*)—N(4)	114·9 (2)
N(1)—C(2)—C(3)	108·7 (2)	O(9*a*)—C(9*a*)—C(1)	109·4 (3)
C(1)—C(2)—C(3)	107·1 (3)	O(9*a*)—C(9*a*)—C(9)	117·9 (2)
N(4)—C(3)—C(2)	98·8 (2)	N(4)—C(9*a*)—C(1)	99·4 (2)
N(1)—C(4*a*)—N(4)	103·1 (2)	N(4)—C(9*a*)—C(9)	102·8 (2)
N(1)—C(4*a*)—C(5)	110·5 (2)	C(1)—C(9*a*)—C(9)	111·0 (2)
N(1)—C(4*a*)—C(8*a*)	110·5 (3)	C(8*a*)—C(9)—C(9*a*)	100·6 (2)
N(4)—C(4*a*)—C(5)	112·9 (3)	C(8*a*)—C(9)—C(10)	118·0 (2)
N(4)—C(4*a*)—C(8*a*)	102·5 (2)	C(9*a*)—C(9)—C(10)	111·6 (2)
C(5)—C(4*a*)—C(8*a*)	116·2 (3)	O(10*a*)—C(10*a*)—O(10)	123·6 (2)
O(5)—C(5)—C(4*a*)	118·9 (2)	O(10*a*)—C(10*a*)—N(10*a*)	124·9 (3)
O(5)—C(5)—C(6)	121·6 (2)	O(10)—C(10*a*)—N(10*a*)	111·5 (2)
C(4*a*)—C(5)—C(6)	119·6 (2)	O(10)—C(10)—C(9)	107·7 (3)
C(8*a*)—C(9)—C(10)—O(10)	−86·5 (2)	C(10*a*)—O(10)—C(10)—C(9)	−171·6 (2)
C(10)—O(10)—C(10*a*)—O(10*a*)	−4·5 (3)	C(10)—O(10)—C(10*a*)—N(10*a*)	173·8 (2)
C(9*b*)—O(9*a*)—C(9*a*)—C(9)	−59·5 (3)	C(7*a*)—O(7)—C(7)—C(8)	−46·1 (4)
C(4*a*)—N(1)—C(1)—C(9*a*)	0·2 (2)	C(4*a*)—N(1)—C(2)—C(1)	94·8 (2)
C(4*a*)—N(1)—C(2)—C(3)	−4·6 (3)	N(1)—C(2)—C(3)—N(4)	31·4 (2)

Experimental. Crystal dimensions 0·30 × 0·20 × 0·20 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. ω–2θ scans. Cell dimensions from setting angles of 22 independent reflections with $9{\cdot}1 \le \theta \le 14{\cdot}8°$. 2153 reflections surveyed in the range $1 \le 2\theta \le 55°$; $-13 \le h \le 13$, $-\le k \le 10$, $0 \le l \le 12$; 1964 reflections were unique, 1362 observed with $F > 3\sigma$ (F). Three reference reflections monitored periodically showed no significant variation in intensity. Absorption correction was not applied. Structure solved using *MULTAN*/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier-map recycling. Refinement using the *SDP* package (Frenz, 1985), full-matrix least-squares refinement on F, with non-H atoms having anisotropic temperature factors. Most of the H atoms were located from difference Fourier syntheses but were not refined. $w = 4F_o^2/[\sigma^2(I_o) + (0{\cdot}04I_o)^2]^{1/2}$/Lp, final $R = 0{\cdot}030$, $wR = 0{\cdot}040$, $S = 1{\cdot}57$, maximum shift/e.s.d. in the final least-squares cycle = 0·03, maximum peak in the final difference map = 0·17 (4) e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final fractional coordinates and equivalent B values are listed in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53185 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



Mitomycin A Albomitomycin A

Fig. 1. Chemical structure of albomitomycin A and mitomycin A.

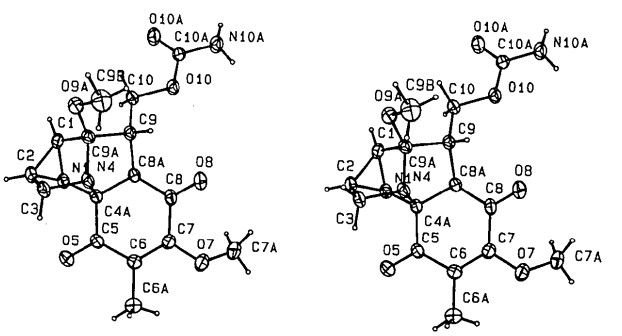


Fig. 2. *ORTEP*II (Johnson, 1976) stereoscopic drawing of albomitomycin A with thermal ellipsoids at 30% probability.

Discussion. The chemical structures of the title compound and mitomycin A are shown in Fig. 1. Bond lengths, angles and selected torsion angles are shown in Table 2. An *ORTEP*II (Johnson, 1976) drawing of the molecule is shown in Fig. 2.

N(1) is bonded to C(4*a*) and an H atom is bonded to C(8*a*). Therefore the molecule curls up and takes a more compact shape than mitomycin A. The quinone ring in mitomycin A is not present in albomitomycin A and the dihydroquinone ring takes a half-chair conformation. C(8*a*) deviates by 0·421 (1) Å from the least-squares plane defined by C(4*a*), C(5), C(6), C(7) and C(8). O(5) and O(8) deviate by 0·148 (2) and 0·379 (2) Å, respectively, from the plane on the opposite side as in mitomycin A (Hirayama & Shirahata, 1989). The significant deviation of this six-membered ring from planarity is obviously the main reason for the achromaticity of albomitomycin A.

Mitomycin A can be transformed to albomitomycin A in a protic solvent (Kono, Saitoh, Shirahata, Arai & Ishii, 1987). The transformation may occur through an intramolecular Michael reaction. In the crystal structure of mitomycin A (Hirayama & Shirahata, 1989), the lone-pair electrons of the N atoms of azirizine rings in the two independent molecules point towards C(4*a*) atoms. The average C(4*a*)···N(1)—C(1) angle and the average distance between C(4*a*) and N(1) in mitomycin A are 76·9° and 3·323 Å, respectively. In albomitomycin A they are 100·9° and 1·497 Å, respectively. These geometrical parameters suggest that the intramolecular reaction is not only governed by the geometrical prerequisite in the molecule but also by the electronic characteristics of the C(4*a*) atom.

There is an intermolecular hydrogen bond between the N(10*a*)(x, y, z) and O(10*a*)($-x$, $-1/2+y$, $2-z$) atoms [N(10*a*)···O(10*a*) = 2·948 (3) Å and N(10*a*)—H···O(10*a*) = 141 (3)°].

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Structure of the Biimidazole Dimer Obtained from a Bridged *N,N′*-Diimidazolyl Sulfone

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Abstract. (±)-4,4′-Bi(2-thia-1,3,6,12-tetraazatricyclo[9.3.0.0^{3,7}]tetradeca-4,6,11,13-tetraene 2,2-dioxide) (1), $C_{18}H_{18}N_8O_4S_2$, M_r = 470·52, monoclinic, $C2/c$, a = 24·444 (9), b = 5·468 (2), c = 15·282 (7) Å, β = 98·82 (4)°, V = 2018 Å^3, Z = 4, D_x = 1·55 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 2·96 cm^{-1}, $F(000)$ = 968, T = 296 K, R = 0·043 for 1190 observed [$I > 3\sigma(I)$] data. The title compound (1) is obtained from a copper-mediated homo-coupling of two symmetrical 2,2′-trimethylene-1,1′-diimidazolyl sulfone units. Only one diastereomer is obtained from this reaction, which is the racemic form. Each half of the molecule, containing the diimidazolyl sulfone groups, comprises an eight-membered ring in a boat–chair conformation. The two N—S bonds of (1) are statistically different, 1·645 (3) *versus* 1·672 (3) Å, and shorter than analogous imidazole N—S bond lengths in related structures. The standard deviation from planarity of the imidazole ring atoms in the biimidazole moiety is 0·006 Å, with a 78·3° dihedral angle between the rings. The S-bonded N atoms in the biimidazole group are slightly pyramidal, with the sum of the internal angles 356·8°. The other imidazole rings in the structure have a standard deviation from planarity of 0·007 Å, and there is no N-pyramidalization.

Introduction. In connection with synthetic efforts towards the preparation of macrocyclic ligands that

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