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Structure of (9*SR*,10*RS*,11a*SR*,21*SR*,22*RS*,23a*SR*)-5,6,9,10,11,11a,17,18,21,22,23,23a-Dodecahydro-9,21-dimethyl-25-phenyl-10,22-methano-8*H*,12*H*,20*H*,24*H*-cycloocta[1″,2″:3,2;6″,5″:2′,3′]-diquinolizino[7,8-*b*:8′,7′-*b*′]diindole-9,21-diol 5·4-Hydrate

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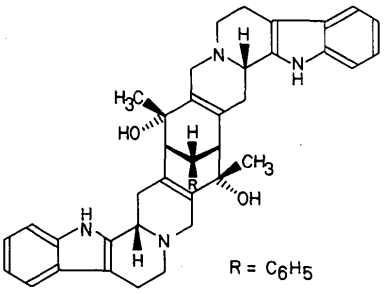
Abstract. $C_{43}H_{44}N_4O_2.5{\cdot}4H_2O$, $M_r = 746{\cdot}13$, monoclinic, $P2_1/n$, $a = 10{\cdot}967\ (2)$, $b = 13{\cdot}181\ (2)$, $c = 28{\cdot}268\ (6)$ Å, $\beta = 98{\cdot}12\ (2)°$, $V = 4045\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}209$ g cm^{-3}, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) = $0{\cdot}69$ cm^{-1}, $F(000) = 1600$, room temperature, $R(F) = 0{\cdot}054$ for 3286 independent observed reflections. The rigid molecule consists of ten fused rings and contains a hydrophilic cavity flanked by two hydroxyl and two amine groups. This cavity contains two hydrate molecules. Three additional water molecules are involved in a network of intermolecular hydrogen bonds. A partly occupied, disordered sixth water molecule mainly serves space-filling purposes.

Introduction. The synthesis of the title compound has been reported by Teuber, Quintanilla-Licea & Bats (1989). The compound consists of two identical indoloquinolizine groups bridged by a bicyclo-[3.3.1]nonadiene system. To prove its structure an X-ray analysis was performed.



Experimental. Yellow transparent prisms from methanol, crystal dimensions 0·25 × 0·31 × 0·60 mm, Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, cell constants from the setting angles of 25 reflections with $8 < \theta < 12°$, systematic extinctions corresponded to space group $P2_1/n$, quadrant up to $2\theta = 40°$, h: 0→10, k: 0→12, l: −27→26, 4036 reflections measured, 3776 independent reflections, 3286 reflections with $I > \sigma(I)$ used, three standard reflections every 5500 s remained stable, no absorption correction, averaging of $0kl$ and $0k\bar{l}$ reflections, $R(F)_{int} = 0{\cdot}016$. The structure was determined by *MULTAN*80 (Main *et al.*, 1980) and completed by difference Fourier syntheses. Five remaining electron density maxima between 2·6 and 4·8 e Å^{-3} were identified as water molecules. H atoms of the main molecule were taken from a difference synthesis and included in the structure refinement with fixed isotropic thermal parameters. H atoms of the water molecules could not be located. A residual electron density peak of 0·62 e Å^{-3} was identified as a partly occupied, loosly bound water molecule. Its population refined to $p = 0{\cdot}42\ (1)$. The large value of the isotropic thermal parameter [$U = 0{\cdot}44\ (1)$ Å^2] shows this molecule to be considerably disordered. A refinement of the occupancy factors of water molecules O(6) and O(7) revealed full occupancy despite rather large thermal parameters. The structure was refined on F using the weighting scheme $w(F) = 4F/[\sigma^2(F^2) + (0{\cdot}03F^2)^2]$ to $R(F) = 0{\cdot}054$, $wR(F) = 0{\cdot}058$, $S = 2{\cdot}445$, extinction coefficient $g = 14\ (2) \times 10^{-8}$, $(\Delta/\sigma)_{max} = 0{\cdot}2$ for 3286 contributing reflections and 493 variables. The final difference density was less than 0·4 e Å^{-3}. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were performed with the *SDP* program system (Enraf–Nonius, 1986).

Discussion. The positional parameters are reported in Table 1, the bond lengths and angles in Table 2. Fig. 1 shows the molecule and the atomic numbering scheme.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53054 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and equivalent values of the anisotropic thermal parameters*

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

	x	y	z	U_{eq}(Å^2)
O(1)	0·6653 (2)	0·1624 (2)	0·61422 (8)	0·0505 (8)
O(2)	0·9455 (2)	0·3746 (2)	0·72799 (7)	0·0491 (8)
O(3)	0·6758 (3)	0·4046 (2)	0·7122 (1)	0·084 (1)
O(4)	0·6420 (3)	0·4010 (3)	0·6050 (1)	0·102 (1)
O(5)	0·5445 (3)	0·6267 (4)	0·5887 (1)	0·144 (1)
O(6)	0·5097 (5)	0·3155 (5)	0·5120 (2)	0·213 (3)
O(7)	0·5220 (5)	0·0980 (5)	0·5279 (2)	0·219 (3)
N(1)	0·6012 (2)	0·2120 (2)	0·74978 (9)	0·0407 (8)
N(2)	0·7335 (2)	0·2439 (2)	0·87755 (9)	0·0414 (8)
N(3)	0·8784 (3)	0·4380 (2)	0·58314 (9)	0·0410 (9)
N(4)	0·8372 (3)	0·3263 (2)	0·46133 (9)	0·0514 (9)
C(1)	0·9690 (3)	0·1909 (3)	0·7164 (1)	0·039 (1)
C(2)	0·8384 (3)	0·1821 (3)	0·7290 (1)	0·036 (1)
C(3)	0·7445 (3)	0·1495 (3)	0·6980 (1)	0·035 (1)
C(4)	0·7576 (3)	0·1132 (3)	0·6481 (1)	0·038 (1)
C(5)	0·8876 (3)	0·1332 (3)	0·6350 (1)	0·0346 (9)
C(6)	0·9029 (3)	0·2406 (3)	0·6178 (1)	0·035 (1)
C(7)	0·9482 (3)	0·3151 (3)	0·6469 (1)	0·036 (1)
C(8)	0·9976 (3)	0·2995 (3)	0·6992 (1)	0·040 (1)
C(9)	0·9840 (3)	0·1089 (3)	0·6784 (1)	0·037 (1)
C(10)	0·8211 (3)	0·2085 (3)	0·7798 (1)	0·045 (1)
C(11)	0·6928 (3)	0·1833 (3)	0·7911 (1)	0·040 (1)
C(12)	0·6166 (3)	0·1445 (3)	0·7101 (1)	0·048 (1)
C(13)	0·4733 (3)	0·2043 (3)	0·7603 (1)	0·051 (1)
C(14)	0·4492 (3)	0·2876 (3)	0·7950 (1)	0·052 (1)
C(15)	0·5495 (3)	0·2832 (3)	0·8367 (1)	0·041 (1)
C(16)	0·6584 (3)	0·2366 (3)	0·8341 (1)	0·040 (1)
C(17)	0·6698 (3)	0·2955 (3)	0·9087 (1)	0·041 (1)
C(18)	0·5536 (3)	0·3215 (3)	0·8839 (1)	0·039 (1)
C(19)	0·4704 (3)	0·3747 (3)	0·9080 (1)	0·047 (1)
C(20)	0·5051 (4)	0·4000 (3)	0·9549 (1)	0·057 (1)
C(21)	0·6205 (4)	0·3745 (3)	0·9784 (1)	0·061 (1)
C(22)	0·7053 (3)	0·3225 (3)	0·9562 (1)	0·052 (1)
C(23)	0·8685 (3)	0·2582 (3)	0·5649 (1)	0·042 (1)
C(24)	0·9114 (3)	0·3604 (3)	0·5490 (1)	0·040 (1)
C(25)	0·9586 (3)	0·4215 (3)	0·6290 (1)	0·044 (1)
C(26)	0·8975 (4)	0·5417 (3)	0·5658 (1)	0·054 (1)
C(27)	0·8036 (4)	0·5669 (3)	0·5228 (1)	0·058 (1)
C(28)	0·7997 (3)	0·4817 (3)	0·4877 (1)	0·046 (1)
C(29)	0·8499 (3)	0·3906 (3)	0·5003 (1)	0·043 (1)
C(30)	0·7777 (3)	0·3792 (3)	0·4225 (1)	0·051 (1)
C(31)	0·7527 (3)	0·4767 (3)	0·4382 (1)	0·051 (1)
C(32)	0·6930 (4)	0·5449 (3)	0·4048 (1)	0·068 (1)
C(33)	0·6616 (4)	0·5142 (4)	0·3580 (1)	0·080 (1)
C(34)	0·6888 (4)	0·4173 (4)	0·3441 (1)	0·082 (1)
C(35)	0·7465 (4)	0·3475 (4)	0·3761 (1)	0·075 (1)
C(36)	1·1129 (3)	0·0912 (3)	0·6663 (1)	0·042 (1)
C(37)	1·1511 (3)	0·1216 (3)	0·6236 (1)	0·051 (1)
C(38)	1·2668 (3)	0·0960 (3)	0·6135 (1)	0·062 (1)
C(39)	1·3471 (3)	0·0388 (3)	0·6448 (1)	0·062 (1)
C(40)	1·3105 (3)	0·0095 (3)	0·6877 (1)	0·057 (1)
C(41)	1·1957 (3)	0·0355 (3)	0·6980 (1)	0·046 (1)
C(42)	0·7254 (3)	0·0010 (3)	0·6430 (1)	0·054 (1)
C(43)	1·1353 (3)	0·3207 (3)	0·7086 (1)	0·052 (1)
O(8)†	0·641 (3)	0·113 (2)	0·4536 (9)	0·44 (1)

† O(8) has an occupancy factor 0·42 (1).

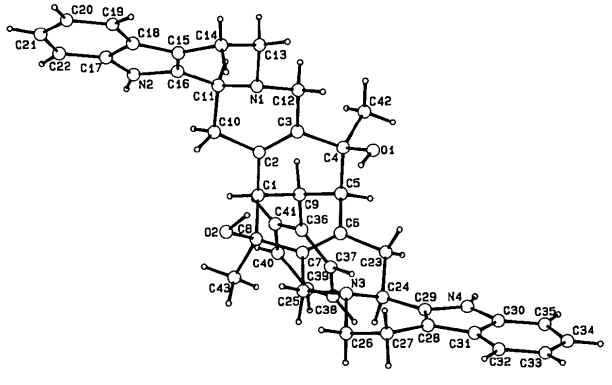

Fig. 1. View of the molecule along the pseudo-twofold axis, showing the numbering scheme.

Table 2. *Bond distances* (Å) *and angles* (°)

O(1)—C(4)	1·445 (4)	C(11)—C(16)	1·499 (5)
O(2)—C(8)	1·448 (4)	C(13)—C(14)	1·519 (5)
N(1)—C(11)	1·478 (4)	C(14)—C(15)	1·494 (4)
N(1)—C(12)	1·461 (4)	C(15)—C(16)	1·354 (5)
N(1)—C(13)	1·478 (4)	C(15)—C(18)	1·422 (4)
N(2)—C(16)	1·382 (4)	C(17)—C(18)	1·407 (4)
N(2)—C(17)	1·377 (4)	C(17)—C(22)	1·390 (4)
N(3)—C(24)	1·486 (4)	C(18)—C(19)	1·401 (5)
N(3)—C(25)	1·476 (4)	C(19)—C(20)	1·368 (5)
N(3)—C(26)	1·477 (4)	C(20)—C(21)	1·385 (5)
N(4)—C(29)	1·380 (4)	C(21)—C(22)	1·376 (6)
N(4)—C(30)	1·382 (4)	C(23)—C(24)	1·517 (5)
C(1)—C(2)	1·529 (5)	C(24)—C(29)	1·498 (4)
C(1)—C(8)	1·558 (5)	C(26)—C(27)	1·515 (5)
C(1)—C(9)	1·548 (5)	C(27)—C(28)	1·493 (5)
C(2)—C(3)	1·327 (4)	C(28)—C(29)	1·348 (5)
C(2)—C(10)	1·514 (4)	C(28)—C(31)	1·425 (4)
C(3)—C(4)	1·516 (4)	C(30)—C(31)	1·399 (5)
C(3)—C(12)	1·492 (5)	C(30)—C(35)	1·375 (5)
C(4)—C(5)	1·545 (5)	C(31)—C(32)	1·399 (5)
C(4)—C(42)	1·522 (5)	C(32)—C(33)	1·378 (5)
C(5)—C(6)	1·514 (5)	C(33)—C(34)	1·381 (7)
C(5)—C(9)	1·537 (4)	C(34)—C(35)	1·379 (6)
C(6)—C(7)	1·331 (4)	C(36)—C(37)	1·392 (5)
C(6)—C(23)	1·507 (4)	C(36)—C(41)	1·391 (5)
C(7)—C(8)	1·515 (4)	C(37)—C(38)	1·381 (5)
C(7)—C(25)	1·501 (5)	C(38)—C(39)	1·381 (5)
C(8)—C(43)	1·522 (5)	C(39)—C(40)	1·385 (6)
C(9)—C(36)	1·519 (5)	C(40)—C(41)	1·375 (5)
C(10)—C(11)	1·523 (5)		

C(11)—N(1)—C(12)	108·1 (3)	C(14)—C(15)—C(16)	122·1 (3)
C(11)—N(1)—C(13)	112·4 (2)	C(14)—C(15)—C(18)	130·4 (3)
C(12)—N(1)—C(13)	109·2 (3)	C(16)—C(15)—C(18)	107·5 (3)
C(16)—N(2)—C(17)	108·0 (3)	N(2)—C(16)—C(11)	124·5 (3)
C(24)—N(3)—C(25)	107·4 (2)	N(2)—C(16)—C(15)	109·9 (3)
C(24)—N(3)—C(26)	111·2 (3)	C(11)—C(16)—C(15)	125·5 (3)
C(25)—N(3)—C(26)	109·5 (2)	N(2)—C(17)—C(18)	107·9 (3)
C(29)—N(4)—C(30)	107·8 (3)	N(2)—C(17)—C(22)	130·2 (3)
C(2)—C(1)—C(8)	112·2 (3)	C(18)—C(17)—C(22)	121·9 (3)
C(2)—C(1)—C(9)	107·7 (3)	C(15)—C(18)—C(17)	106·7 (3)
C(8)—C(1)—C(9)	112·4 (3)	C(15)—C(18)—C(19)	134·2 (3)
C(1)—C(2)—C(3)	122·3 (3)	C(17)—C(18)—C(19)	119·2 (3)
C(1)—C(2)—C(10)	116·8 (2)	C(18)—C(19)—C(20)	118·8 (3)
C(3)—C(2)—C(10)	120·8 (3)	C(19)—C(20)—C(21)	121·1 (4)
C(2)—C(3)—C(4)	123·5 (3)	C(20)—C(21)—C(22)	122·2 (3)
C(2)—C(3)—C(12)	121·9 (3)	C(17)—C(22)—C(21)	117·0 (3)
C(4)—C(3)—C(12)	114·6 (3)	C(6)—C(23)—C(24)	112·8 (3)
O(1)—C(4)—C(3)	108·9 (3)	N(3)—C(24)—C(23)	107·7 (3)
O(1)—C(4)—C(5)	110·4 (3)	N(3)—C(24)—C(29)	107·2 (3)
O(1)—C(4)—C(42)	104·0 (2)	C(23)—C(24)—C(29)	113·0 (3)
C(3)—C(4)—C(5)	112·4 (2)	N(3)—C(25)—C(7)	111·8 (3)
C(3)—C(4)—C(42)	110·1 (3)	N(3)—C(26)—C(27)	110·9 (3)
C(5)—C(4)—C(42)	110·7 (3)	C(26)—C(27)—C(28)	108·6 (3)
C(4)—C(5)—C(6)	112·6 (3)	C(27)—C(28)—C(29)	121·6 (3)
C(4)—C(5)—C(9)	109·1 (3)	C(27)—C(28)—C(31)	131·3 (3)
C(6)—C(5)—C(9)	110·8 (3)	C(29)—C(28)—C(31)	107·1 (3)
C(5)—C(6)—C(7)	122·7 (3)	N(4)—C(29)—C(24)	123·5 (3)
C(5)—C(6)—C(23)	116·0 (3)	N(4)—C(29)—C(28)	110·2 (3)
C(7)—C(6)—C(23)	121·3 (3)	C(24)—C(29)—C(28)	126·3 (3)
C(6)—C(7)—C(8)	123·7 (3)	N(4)—C(30)—C(31)	107·7 (3)
C(6)—C(7)—C(25)	121·2 (3)	N(4)—C(30)—C(35)	129·1 (4)
C(8)—C(7)—C(25)	115·0 (3)	C(31)—C(30)—C(35)	123·2 (3)
O(2)—C(8)—C(1)	109·9 (3)	C(28)—C(31)—C(30)	107·1 (3)
O(2)—C(8)—C(7)	109·9 (3)	C(28)—C(31)—C(32)	134·8 (4)
O(2)—C(8)—C(43)	103·8 (3)	C(30)—C(31)—C(32)	118·1 (3)
C(1)—C(8)—C(7)	111·6 (3)	C(31)—C(32)—C(33)	119·2 (4)
C(1)—C(8)—C(43)	110·7 (3)	C(32)—C(33)—C(34)	120·7 (4)
C(7)—C(8)—C(43)	110·7 (3)	C(33)—C(34)—C(35)	121·8 (4)
C(1)—C(9)—C(5)	106·3 (3)	C(30)—C(35)—C(34)	116·9 (4)
C(1)—C(9)—C(36)	117·2 (3)	C(9)—C(36)—C(37)	123·7 (3)
C(5)—C(9)—C(36)	114·2 (3)	C(9)—C(36)—C(41)	118·7 (3)
C(2)—C(10)—C(11)	113·0 (3)	C(37)—C(36)—C(41)	117·5 (3)
N(1)—C(11)—C(10)	108·9 (3)	C(36)—C(37)—C(38)	120·4 (3)
N(1)—C(11)—C(16)	107·5 (3)	C(37)—C(38)—C(39)	121·5 (4)
C(10)—C(11)—C(16)	114·5 (3)	C(38)—C(39)—C(40)	118·4 (3)
N(1)—C(12)—C(3)	111·3 (3)	C(39)—C(40)—C(41)	120·2 (3)
N(1)—C(13)—C(14)	109·7 (3)	C(36)—C(41)—C(40)	122·0 (3)
C(13)—C(14)—C(15)	107·8 (3)		

The molecule consists of two identical parts, related by a pseudo-twofold axis passing through the bridging atom C(9) and bisecting the C(1)—C(9)—C(5) angle. Torsion angles among related

Table 3. *Hydrogen bonds* (Å, °) *and possible hydrogen bonds* (Å)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H—*A*	Symmetry
O(1)—H(O1)···O(4)	0·80 (4)	2·40 (4)	3·163 (4)	160 (3)	*x,y,z*
O(2)—H(O2)···O(3)	1·01 (3)	2·02 (4)	2·955 (4)	153 (3)	*x,y,z*
N(2)—H(O3)···O(5)	1·05 (4)	1·94 (4)	2·927 (5)	155 (3)	$1{\cdot}5-x,-0{\cdot}5+y,1{\cdot}5-z$

D···*A*	*D*···*A*	Symmetry
O(3)···O(4)	3·001 (4)	*x,y,z*
O(3)···N(1)	2·913 (4)	*x,y,z*
O(4)···O(5)	3·173 (6)	*x,y,z*
O(4)···O(6)	3·035 (6)	*x,y,z*
O(4)···N(3)	2·792 (4)	*x,y,z*
O(5)···O(6)	2·925 (7)	$1{\cdot}0-x,1{\cdot}0-y,1{\cdot}0-z$
O(6)···O(7)	2·901 (9)	*x,y,z*
O(7)···O(1)	2·839 (5)	*x,y,z*
O(7)···O(7′)	3·031 (8)	$1{\cdot}0-x,-y,1{\cdot}0-z$
O(7)···O(8)	2·64 (3)	*x,y,z*

bonds differ by less than 5°. Only the different substituents at C(9) lead to a local deviation of the molecular symmetry from C_2.

The overall shape of the rigid molecule is that of a V-shaped propeller. The V shape of the molecule is a consequence of the conformation of the bicyclo-[3.3.1]nona-2,6-diene group which has the conformation characteristic for this group (Radcliffe, Gutierrez, Blount & Mislow, 1984; Quast, Görlach, Stawitz, Peters, Peters & von Schnering, 1984).

The concave side of the molecule encloses a hydrophilic cavity (Fig. 2) flanked by the hydroxyl groups O(1) and O(2) and the pyramidal amine atoms N(1) and N(3). This cavity contains the hydrate molecules O(3) and O(4) which are tightly connected to the main molecule by a network of hydrogen bonds (Table 3). The hydrate molecules O(5), O(6) and O(7) form a second hydration sphere and contribute to the intermolecular bonding *via* a hydrogen bond between O(5) and the amino group N(2) of a neighboring molecule. The amino group N(4) is not involved in hydrogen bonding.

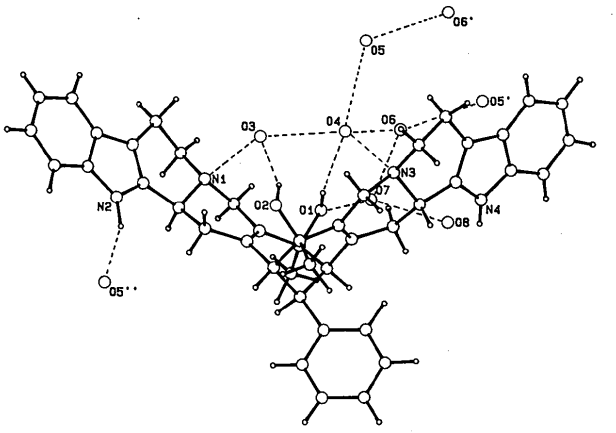

Fig. 2. View of the molecule showing the hydrophilic cavity and the hydrogen-bond network.

The partly occupied water molecule represented by O(8) has a contact distance of 2·64 (3) Å to O(7) indicating a possible hydrogen bond. However, O(8) has no other contact distances short enough for hydrogen bonding. Thus O(8) mainly serves space-filling purposes and does not contribute to the intermolecular bonding.

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Spiro[1,3-benzodioxole-2,9′(10′*H*)-phenanthren]-10′-one

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Abstract. $C_{20}H_{12}O_3$, $M_r = 300{\cdot}3$, triclinic, $P\bar{1}$, $a = 7{\cdot}908$ (4), $b = 8{\cdot}946$ (5), $c = 11{\cdot}402$ (7) Å, $\alpha = 69{\cdot}10$ (5), $\beta = 72{\cdot}31$ (4), $\gamma = 72{\cdot}14$ (4)°, $V = 699{\cdot}9$ (7) Å^3, $Z = 2$, $D_x = 1{\cdot}42$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}104$ mm^{-1}, $F(000) = 312$, $T = 133$ K, $R = 0{\cdot}072$ for 581 unique observed reflections.

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