kontinuierlicher Übergang bis zum Fehlen der N(4)—C(8) Bindung (III) nachgewiesen werden kann. Hierbei werden Winkelwerte um C(8) von nahezu 120° (Planarität) dem Zustand III zugeordnet, während kleinere Werte für den Zustand II sprechen.

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Structure of *trans*-13a,21b-Dimethoxy-2,3,5,6,8,9,11,12,13a,21b-decahydrophenanthro[9,10-*b*][1,4,7,10,13]pentaoxacyclopentadecene

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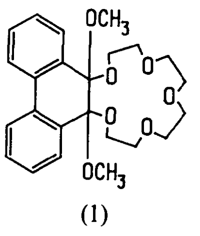
Abstract. $C_{24}H_{30}O_7$, M_r = 430·50, monoclinic, $P2_1/n$, a = 8·293 (3), b = 14·382 (6), c = 19·001 (7) Å, β = 96·42 (3)°, V = 2252 (2) Å^3, Z = 4, D_x = 1·270 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·09 mm^{-1}, F(000) = 920, T = 291 (1) K, final R = 0·085 for 2057 unique observed [$F \geq 6{\cdot}0\sigma(F)$] diffractometer data. The methoxy groups are in *trans* position with respect to the remainder of the molecule, which is almost planar [max. deviation from planarity 0·668 (6) Å]. The mean C—C and C—O distances in the 15-membered heterocycle are 1·515 (10) and 1·406 (9) Å respectively and agree with those in 1,4,7,10,13,16-hexaoxacyclooctadecane [Dunitz & Seiler (1974). *Acta Cryst.* B**30**, 2739–2741].

Experimental. A solution of 10 g 2,3,5,6,8,9,11,12-octahydrophenanthro[9,10-*b*][1,4,7,10,13]pentaoxacyclopentadecene (Boujlel & Simonet, 1979) in absolute methanol containing 2 g potassium hydroxide was submitted to electrolysis with efficient agitation until the starting material could no longer be observed by thin-layer chromatography (4–5 h). The temperature of the solution was kept in the range 283–293 K and the current density 0·0125–0·025 A cm^{-1}. The methanol was evaporated under vacuum and the residue was diluted with diethyl ether. After filtering over a short Al_2O_3 column (basic, activity III), the diethyl ether was evaporated and the oily residue recrystallized from diisopropyl ether. After 4 weeks the yield was 200 mg of crystals of (1) (1·7%), m.p. 380–380·5 K, calculated C 66·96, H 7·02%, found C 66·93, H 7·20%. Crystal size ~ 0·16 × 0·21 × 0·16 mm, D_m not determined, ω–2θ scan, scan speed 1·00–4·51° min^{-1} in θ, scan width (1·2 + dispersion)°; Nicolet $R3m/V$ diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 26 reflections up to 2θ = 21·82°; ω scans of low-order reflections along the three crystal axes showed acceptable mosaicity; six standard reflections (200, 040, 002, $\bar{2}00$, $0\bar{4}0$, $00\bar{2}$)



(1)

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Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* (Å^2 × 10^4)

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

	x	y	z	U_{eq}
O(1)	0·3320 (5)	0·8623 (3)	0·9181 (2)	578
C(2)	0·2228 (8)	0·7994 (5)	0·9454 (4)	651
C(3)	0·3144 (9)	0·7622 (6)	1·0132 (4)	668
O(4)	0·2506 (7)	0·6781 (4)	1·0359 (3)	826
C(5)	0·128 (1)	0·6852 (7)	1·0786 (4)	862
C(6)	−0·030 (1)	0·6432 (7)	1·0482 (4)	882
O(7)	−0·0946 (6)	0·6963 (5)	0·9913 (3)	994
C(8)	−0·2408 (9)	0·6587 (7)	0·9561 (5)	981
C(9)	−0·2972 (8)	0·7189 (7)	0·8960 (4)	834
O(10)	−0·2035 (5)	0·7077 (4)	0·8409 (3)	744
C(11)	−0·2088 (7)	0·7810 (5)	0·7916 (4)	541
C(12)	−0·0721 (6)	0·8501 (5)	0·8081 (3)	521
O(13)	0·0775 (4)	0·8026 (3)	0·7990 (2)	470
C(13a)	0·2209 (6)	0·8541 (4)	0·7897 (3)	403
C(13b)	0·1988 (7)	0·9155 (4)	0·7240 (3)	436
C(14)	0·0751 (7)	0·8986 (5)	0·6690 (3)	557
C(15)	0·0601 (8)	0·9566 (6)	0·6092 (3)	656
C(16)	0·1645 (9)	1·0283 (6)	0·6038 (4)	681
C(17)	0·2894 (8)	1·0432 (5)	0·6571 (3)	592
C(17a)	0·3102 (7)	0·9874 (5)	0·7171 (3)	479
C(17b)	0·4480 (7)	1·0004 (5)	0·7730 (3)	492
C(18)	0·5889 (8)	1·0472 (5)	0·7591 (4)	626
C(19)	0·7179 (8)	1·0573 (6)	0·8122 (4)	682
C(20)	0·7082 (8)	1·0245 (5)	0·8782 (4)	636
C(21)	0·5701 (7)	0·9766 (5)	0·8924 (3)	542
C(21a)	0·4398 (6)	0·9643 (4)	0·8405 (3)	450
C(21b)	0·2858 (7)	0·9135 (4)	0·8563 (3)	457
O(22)	0·3432 (4)	0·7884 (3)	0·7867 (2)	515
C(23)	0·3227 (8)	0·7253 (5)	0·7283 (4)	612
O(24)	0·1592 (4)	0·9778 (3)	0·8648 (2)	505
C(25)	0·1968 (8)	1·0490 (5)	0·9171 (4)	697

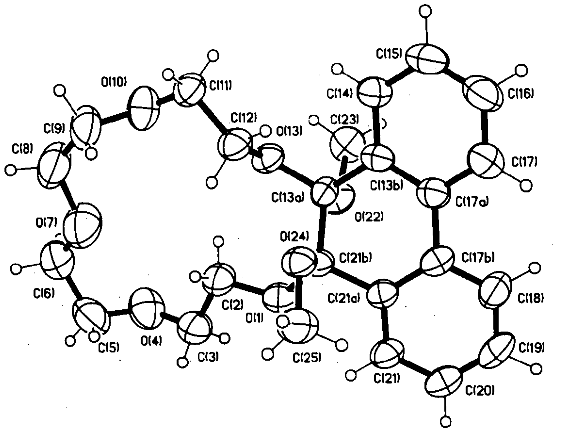

Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme.

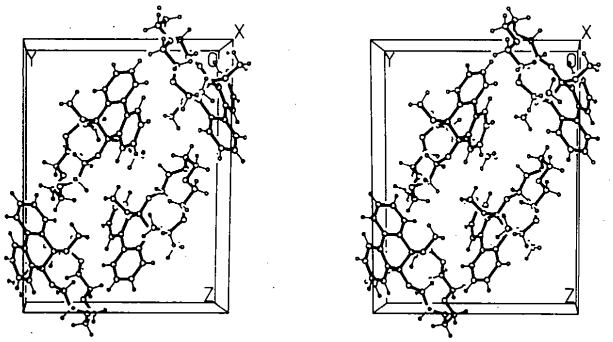

Fig. 2. Stereoscopic view (*SHELXTL-Plus* graphic) of the unit cell.

Table 2. *Bond distances* (Å), *bond angles* (°), *torsion angles* (°), *least-squares planes and dihedral angles* (°)

O(1)—C(2)	1·419 (9)	C(13b)—C(14)	1·401 (8)
O(1)—C(21b)	1·403 (7)	C(13b)—C(17a)	1·402 (9)
C(2)—C(3)	1·52 (1)	C(14)—C(15)	1·40 (1)
C(3)—O(4)	1·41 (1)	C(15)—C(16)	1·36 (1)
O(4)—C(5)	1·37 (1)	C(16)—C(17)	1·382 (9)
C(5)—C(6)	1·50 (1)	C(17)—C(17a)	1·388 (9)
C(6)—O(7)	1·38 (1)	C(17a)—C(17b)	1·483 (8)
O(7)—C(8)	1·42 (1)	C(17b)—C(18)	1·399 (9)
C(8)—C(9)	1·47 (1)	C(17b)—C(21a)	1·393 (9)
C(9)—O(10)	1·382 (9)	C(18)—C(19)	1·393 (9)
O(10)—C(11)	1·407 (9)	C(19)—C(20)	1·35 (1)
C(11)—C(12)	1·513 (9)	C(20)—C(21)	1·389 (9)
C(12)—O(13)	1·443 (7)	C(21)—C(21a)	1·390 (8)
O(13)—C(13a)	1·429 (7)	C(21a)—C(21b)	1·530 (8)
C(13a)—C(13b)	1·523 (8)	C(21b)—O(24)	1·422 (7)
C(13a)—C(21b)	1·571 (8)	O(22)—C(23)	1·430 (8)
C(13a)—O(22)	1·392 (7)	O(24)—C(25)	1·437 (8)

C(2)—O(1)—C(21b)	121·0 (5)	C(15)—C(16)—C(17)	119·6 (7)
O(1)—C(2)—C(3)	104·8 (6)	C(16)—C(17)—C(17a)	121·7 (6)
C(2)—C(3)—O(4)	113·2 (6)	C(13b)—C(17a)—C(17)	118·7 (6)
C(3)—O(4)—C(5)	116·5 (7)	C(17)—C(17a)—C(17b)	122·0 (6)
O(4)—C(5)—C(6)	114·4 (6)	C(13b)—C(17a)—C(17b)	119·3 (6)
C(5)—C(6)—O(7)	109·0 (7)	C(17a)—C(17b)—C(21a)	120·0 (5)
C(6)—O(7)—C(8)	113·1 (7)	C(17a)—C(17b)—C(18)	121·2 (6)
O(7)—C(8)—C(9)	108·7 (7)	C(18)—C(17b)—C(21a)	118·7 (6)
C(8)—C(9)—O(10)	111·4 (7)	C(17b)—C(18)—C(19)	120·3 (7)
C(9)—O(10)—C(11)	116·0 (6)	C(8)—C(19)—C(20)	120·9 (6)
O(10)—C(11)—C(12)	112·8 (5)	C(19)—C(20)—C(21)	119·4 (7)
C(11)—C(12)—O(13)	107·4 (5)	C(20)—C(21)—C(21a)	121·1 (6)
C(12)—O(13)—C(13a)	120·5 (5)	C(17b)—C(21a)—C(21)	119·5 (5)
O(13)—C(13a)—O(22)	105·9 (4)	C(21)—C(21a)—C(21b)	121·4 (5)
O(13)—C(13a)—C(21b)	113·3 (4)	C(17b)—C(21a)—C(21b)	119·1 (5)
O(13)—C(13a)—C(13b)	112·2 (4)	C(13a)—C(21b)—C(21a)	108·7 (5)
C(21b)—C(13a)—O(22)	102·4 (4)	O(1)—C(21b)—C(21a)	105·0 (5)
C(13b)—C(13a)—O(22)	112·5 (5)	O(1)—C(21b)—C(13a)	115·2 (5)
C(13b)—C(13a)—C(21b)	110·1 (5)	C(21a)—C(21b)—O(24)	110·8 (5)
C(13a)—C(13b)—C(17a)	119·0 (5)	C(13a)—C(21b)—O(24)	104·8 (4)
C(13a)—C(13b)—C(14)	121·4 (5)	O(1)—C(21b)—O(24)	112·5 (5)
C(14)—C(13b)—C(17a)	119·6 (5)	C(13a)—O(22)—C(23)	116·0 (5)
C(13b)—C(14)—C(15)	119·4 (6)	C(21b)—O(24)—C(25)	115·9 (5)
C(14)—C(15)—C(16)	120·8 (6)		

C(2)—O(1)—C(21b)—C(13a)	−54·8 (7)	O(7)—C(8)—C(9)—O(10)	74·3 (8)
C(21b)—O(1)—C(2)—C(3)	−177·4 (5)	C(8)—C(9)—O(10)—C(11)	−159·4 (6)
O(1)—C(2)—C(3)—O(4)	−160·4 (6)	C(9)—O(10)—C(11)—C(12)	94·8 (7)
C(2)—C(3)—O(4)—C(5)	−87·8 (8)	O(10)—C(11)—C(12)—O(13)	66·2 (6)
C(3)—O(4)—C(5)—C(6)	118·3 (8)	C(11)—C(12)—O(13)—C(13a)	161·0 (5)
O(4)—C(5)—C(6)—O(7)	−69·0 (9)	C(12)—O(13)—C(13a)—C(21b)	65·1 (6)
C(5)—C(6)—O(7)—C(8)	176·5 (7)	O(13)—C(13a)—C(21b)—O(1)	61·8 (6)
C(6)—O(7)—C(8)—C(9)	−178·9 (7)		

No.	Plane through atoms	Equation of the plane	χ^2
1	C(13b),C(14),C(15), C(16),C(17),C(17a)	$0{\cdot}648x-0{\cdot}615y-0{\cdot}449z=-14{\cdot}16$ Å	18·7
2	C(17b),C(18),C(19), C(20),C(21),C(21a)	$0{\cdot}429x-0{\cdot}861y-0{\cdot}271z=-15{\cdot}46$ Å	7·7
3	C(13a),C(13b),C(17a), C(17b),C(21a),C(21b)	$0{\cdot}668x-0{\cdot}710y-0{\cdot}224z=-12{\cdot}25$ Å	7240·8

Dihedral angles: 1,2 21·6 (1), 1,3 14·1 (2), 2,3 16·5 (1)°. Maximum deviation from planarity: plane 1: 0·016 (6), plane 2: 0·013 (8), plane 3: 0·332 (6) Å

recorded every 2·5 h, up to 12·7% intensity loss over 550·88 h of X-ray exposure; 16161 reflections measured, $3{\cdot}0 \le 2\theta \le 50{\cdot}0°$, $-10 \le h \le 10$, $-18 \le k \le 18$, $-23 \le l \le 23$; after averaging ($R_{\rm int} = 0{\cdot}022$): 3968 unique reflections, 2057 with $F \ge 6{\cdot}0\sigma(F)$; Lorentz–polarization correction, no absorption correction; systematic absences ($h0l$) $h + l = 2n + 1$, ($0k0$) $k = 2n + 1$ conform to space group $P2_1/n$; structure solution *via* direct methods, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C—H 0·96 Å); refinement on F with 2057 reflections and 281 refined parameters; $w = 1{\cdot}0/[\sigma^2(F) + (0{\cdot}001F^2)]$ which led to featureless analysis of variance in terms of $\sin\theta$ and F_o; $S = 2{\cdot}49$, $R = 0{\cdot}085$, $wR = 0{\cdot}091$ (for all data $R = 0{\cdot}162$, $wR = 0{\cdot}137$), $(\Delta/\sigma)_{\max} = 0{\cdot}004$, no extinction correction; largest peak in final ΔF map $\pm 0{\cdot}3$ (2) e Å^{-3}; atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography* (1974); the weakly reflecting crystal is the reason for the high R value; programs: *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987), *PCK*83 (Williams, 1984), *PLATON* (Spek, 1982), *MISSYM* (Le Page, 1987). The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view in Fig. 2. Positional parameters and the equivalent values of the anisotropic temperature factors for the non-H atoms are given in Table 1.* Bond lengths, bond angles, torsion angles, least-squares planes and dihedral angles are given in Table 2.

Related literature. Cram & Trueblood (1981) and Maverick, Seiler, Schweizer & Dunitz (1980).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52633 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1990). C**46**, 1349–1351

Structure of 5-Hydroxy-2-methyl-3-[1,2,3,4-tetrahydro-2-(1,4-dihydro-5-hydroxy-2-methyl-1,4-dioxo-3-naphthyl)-5-hydroxy-2-methyl-1,4-dioxo-3-naphthylmethyl]-1,4-napthoquinone Toluene Solvate*

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Abstract. $C_{34}H_{24}O_9.C_7H_8$, $M_r = 668{\cdot}7$, triclinic, $P\bar{1}$, $a = 9{\cdot}489$ (6), $b = 13{\cdot}020$ (13), $c = 14{\cdot}773$ (22) Å, $\alpha = 96{\cdot}22$ (10), $\beta = 98{\cdot}60$ (9), $\gamma = 113{\cdot}15$ (6)°, $V = 1631{\cdot}0$ Å^3, $Z = 2$, $D_x = 1{\cdot}36$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}51$ cm^{-1}, $F(000) = 700$, $T = 293$ K, $R = 0{\cdot}069$ for 4844 observed reflexions. The structure of the natural product consists of three plumbagin moieties plus an additional C atom. Two plumbagin units in the trimeric structure are inclined at 80° to each other about the C(9)—C(11) single bond. The third unit is linked in a *trans* arrangement to C(8) *via* a methylene group. The recrystallizing solvent, toluene, has been incorporated into the crystal.

Experimental. Red crystal, 1·10 × 1·10 × 0·64 mm. Nicolet $P3$ automated diffractometer, monochromated Mo $K\alpha$ radiation. Cell dimensions from setting angles of 12 independent reflexions with $2\theta \simeq 20°$. Data corrected for Lorentz and polarization effects, absorption ignored. 7930 unique intensities were measured with $2\theta \leq 60°$ with ω–2θ scans; 4844 reflexions had $F > 5\sigma(F)$. Range of hkl:

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* Plumbazeylanone toluene solvate.

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