GENESTE, P., KAMENKA, J. M., ROQUES, R., DECLERCQ, J.-P. & GERMAIN, G. (1981). *Tetrahedron Lett.* **22**, 949–950.
JONES, L. A., BEAVER, R. W., SCHMOEGER, T. L., ORT, J. F. & LEANDER, J. D. (1981). *J. Org. Chem.* **46**, 3330–3333.
KIMURA, M. & OKABAYASHI, I. (1986). *J. Heterocycl. Chem.* **23**, 1287–1289.
NELSON, H. C. & SIMONSEN, S. H. (1981). *Acta Cryst.* A**37**, C168.
SHELDRICK, G. M. (1985). *SHELXTL User's Manual.* Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
SINGH, P., JONES, L. A. & COUCH, R. (1988). *Acta Cryst.* C**44**, 1976–1979.
SPARKS, R. A. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. A. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN, pp. 170–187. New York: Pergman Press.

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Complexation of Water by a 4-Phenylpyridohemispherand

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Abstract. 25,26-Dimethoxy-9,23-dimethyl-4-phenyl-13,16,19-trioxa-27-azoniatetracyclo[19.3.1.1^{2,6}.1^{7,11}]-heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene perchlorate–ethanol–water (1/1/1), $C_{33}H_{36}NO_5^+.ClO_4^-.C_2H_5OH.H_2O$, M_r = 690·2, orthorhombic, $Pca2_1$, a = 27·747 (5), b = 9·572 (3), c = 12·866 (4) Å, V = 3417 (3) Å^3, Z = 4, D_x = 1·39 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·69 cm^{-1}, $F(000)$ = 1464, T = 100 (5) K, final R = 6·5% for 2915 observed reflections. The water molecule is complexed in the cavity of the macrocycle with hydrogen bonds to the polyethylene oxy atoms adjacent to the outer phenyl rings of the terphenyl unit. The O atom of the water molecule accepts hydrogen bonds from the pyridinium proton and the OH proton of the ethanol molecule. The $HClO_4$ proton is transferred to the pyrido nitrogen.

Experimental. The title compound was prepared by dissolving 50 mg (0·09 mmol) of the 4-phenylpyridohemispherand (Dijkstra, den Hertog, van Steen, Zijlstra, Skowronska-Ptasinska, Reinhoudt, van Eerden & Harkema, 1987) in 2 ml of ethanol and the slow addition of 0·5 ml of 70% $HClO_4$. Slow evaporation of solvent afforded colorless crystals of the complex suitable for X-ray diffraction, m.p. 496 K (dec.).

Intensities were measured at 100 (5) K on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å). Lattice parameters determined by least squares from 25 centered reflections $6 < \theta < 13°$. A total of 2915 independent reflections up to $\theta = 25°$ ($0 \le h \le 33$, $0 \le k \le 12$, $0 \le l \le 16$) were measured in the $\theta/2\theta$ scan mode [scan speed 0·046° s^{-1}, scan width (θ) 1·5°]; 2021 considered observed [$F_o^2 > 2\sigma(F_o^2)$]. The intensity loss of three standard reflections measured every hour was less than 1·3%, correction for which was applied. No absorption correction.

H atoms of the macrocycle were placed in calculated positions and treated as riding on their parent atoms (bond distance 0·95 Å, B_{iso} = 4·0 Å^2), with the exception of the methyl hydrogens. These atoms and the H atoms of the water molecule were found from a difference Fourier synthesis. Positions of these atoms were refined. Hydrogens of the ethanol group could not be located (probably due to the large thermal motions). These hydrogens were not included in the refinement. In order to fix the origin in the c direction, the z parameter of the Cl atom has been fixed.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares. Weights for each reflection in the refinement (on F) were calculated from $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$; the value of the instability factor p was determined as 0·04. The number of parameters refined was 457: scale factor, isotropic extinction factor [final value 2·4 (7) × 10^{-9}], positional and anisotropic thermal parameters for the non-H atoms positional parameters of some H atoms.

Refinement converged at R = 6·5%, wR = 6·3%, S = 1·64, $(\Delta/\sigma)_{max}$ = 0·2. Largest peak on the final difference Fourier map 0·54 e Å^{-3} (in the perchlorate ion). All calculations were performed using *SDP*

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}(Å^2)
Cl	0·08729 (7)	0·0049 (2)	0·3979	2·25 (3)
O7	0·3167 (2)	0·2590 (6)	0·5637 (4)	2·4 (1)
O14	0·3607 (2)	0·4576 (5)	0·4297 (4)	2·6 (1)
O28	0·4206 (2)	0·4044 (5)	0·6275 (4)	2·3 (1)
O32	0·4642 (2)	0·4180 (5)	0·4088 (4)	2·3 (1)
O35	0·4041 (2)	0·2064 (6)	0·3148 (4)	2·4 (1)
O38	0·3003 (2)	0·2123 (6)	0·3430 (4)	2·4 (1)
O51	0·0822 (2)	−0·1355 (6)	0·4297 (5)	3·2 (1)
O52	0·1299 (2)	0·0152 (6)	0·3336 (5)	2·9 (1)
O53	0·0460 (3)	0·0430 (8)	0·3406 (6)	5·0 (2)
O54	0·0919 (2)	0·0947 (8)	0·4854 (6)	5·9 (2)
O100	0·3668 (2)	0·6430 (7)	0·2616 (5)	4·0 (2)
N11	0·3272 (2)	0·5247 (6)	0·6522 (5)	1·5 (1)
C1	0·2416 (3)	0·2442 (8)	0·4741 (7)	2·1 (2)
C2	0·1947 (3)	0·2874 (8)	0·4648 (7)	2·5 (2)
C3	0·1736 (3)	0·3904 (9)	0·5273 (7)	2·7 (2)
C4	0·2034 (3)	0·4525 (8)	0·6018 (7)	2·3 (2)
C5	0·2517 (3)	0·4121 (7)	0·6134 (6)	1·6 (2)
C6	0·2700 (3)	0·3046 (8)	0·5532 (6)	1·9 (2)
C8	0·3271 (3)	0·1850 (8)	0·6561 (7)	3·1 (2)
C9	0·1218 (3)	0·4382 (10)	0·5141 (7)	3·1 (2)
C10	0·2823 (3)	0·4966 (8)	0·6844 (6)	1·7 (2)
C12	0·3565 (3)	0·6150 (8)	0·7032 (6)	1·7 (2)
C13	0·3396 (3)	0·6754 (8)	0·7937 (6)	1·8 (2)
C14	0·2933 (3)	0·6491 (8)	0·8300 (6)	1·6 (2)
C15	0·2650 (3)	0·5527 (8)	0·7740 (6)	1·8 (2)
C16	0·2748 (3)	0·7180 (8)	0·9230 (6)	1·8 (2)
C17	0·3057 (3)	0·7668 (8)	1·0021 (7)	2·4 (2)
C18	0·2873 (3)	0·8242 (8)	1·0930 (7)	2·6 (2)
C19	0·2387 (3)	0·8407 (8)	1·1045 (7)	2·8 (2)
C20	0·2081 (3)	0·8019 (8)	1·0285 (7)	3·1 (2)
C21	0·2256 (3)	0·7414 (8)	0·9370 (7)	2·5 (2)
C22	0·4029 (3)	0·6479 (8)	0·6531 (6)	1·8 (2)
C23	0·4165 (3)	0·7864 (8)	0·6401 (6)	1·8 (2)
C24	0·4558 (3)	0·8237 (9)	0·5802 (7)	2·5 (2)
C25	0·4819 (3)	0·7189 (8)	0·5339 (7)	2·2 (2)
C26	0·4706 (3)	0·5781 (8)	0·5470 (6)	1·9 (2)
C27	0·4317 (3)	0·5427 (8)	0·6120 (7)	2·0 (2)
C29	0·4391 (4)	0·3585 (9)	0·7262 (7)	3·5 (2)
C30	0·4693 (3)	0·9760 (9)	0·5657 (7)	3·4 (2)
C31	0·4961 (3)	0·4628 (9)	0·4885 (7)	3·0 (2)
C33	0·4821 (3)	0·2928 (9)	0·3580 (7)	2·8 (2)
C34	0·4488 (3)	0·2556 (9)	0·2729 (7)	2·8 (2)
C36	0·3696 (3)	0·1884 (9)	0·2350 (7)	3·4 (2)
C37	0·3257 (3)	0·1200 (10)	0·2764 (8)	3·7 (2)
C39	0·2640 (3)	0·1397 (8)	0·4035 (7)	2·8 (2)
C101	0·4271 (5)	0·8201 (14)	0·2240 (20)	12·2 (7)
C102	0·4110 (5)	0·7216 (16)	0·2789 (17)	12·4 (5)

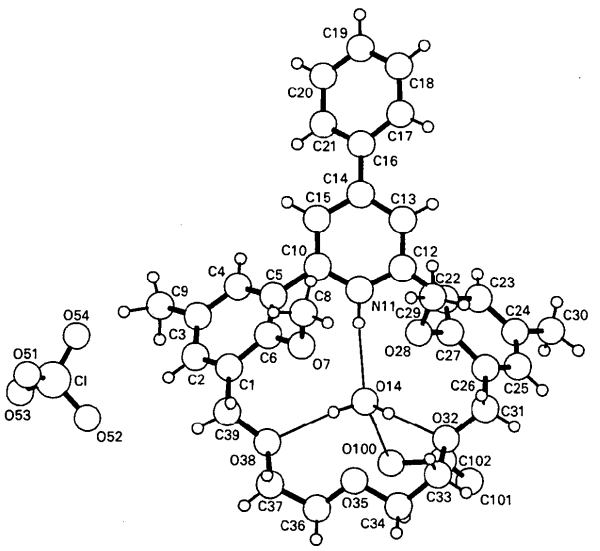

Fig. 1. View of the molecule with the atom-numbering scheme.

Table 2. *Bond distances* (Å) *and angles* (°) *for non-H atoms and torsion angles in the macrocycle* (°) *with e.s.d.'s in parentheses*

Cl—O51	1·413 (6)	C5—C10	1·49 (2)
Cl—O52	1·446 (6)	C10—C15	1·36 (2)
Cl—O53	1·410 (7)	C12—C13	1·38 (2)
Cl—O54	1·422 (8)	C12—C22	1·47 (2)
O7—C6	1·374 (9)	C13—C14	1·39 (1)
O7—C8	1·41 (2)	C14—C15	1·41 (2)
O28—C27	1·374 (9)	C14—C16	1·47 (1)
O28—C29	1·44 (2)	C16—C17	1·41 (1)
O32—C31	1·42 (2)	C16—C21	1·39 (1)
O32—C33	1·45 (2)	C17—C18	1·39 (1)
O35—C34	1·43 (2)	C18—C19	1·37 (1)
O35—C36	1·42 (2)	C19—C20	1·35 (1)
O38—C37	1·42 (2)	C20—C21	1·40 (1)
O38—C39	1·46 (2)	C22—C23	1·39 (2)
O100—C102	1·46 (2)	C22—C27	1·39 (2)
N11—C10	1·34 (1)	C23—C24	1·38 (1)
N11—C12	1·357 (9)	C24—C25	1·37 (1)
C1—C2	1·37 (1)	C24—C30	1·52 (1)
C1—C6	1·42 (1)	C25—C26	1·39 (1)
C1—C39	1·49 (1)	C26—C27	1·41 (2)
C2—C3	1·41 (1)	C26—C31	1·51 (1)
C3—C4	1·40 (1)	C33—C34	1·48 (1)
C3—C9	1·52 (1)	C36—C37	1·48 (1)
C4—C5	1·40 (2)	C101—C102	1·26 (3)
C5—C6	1·38 (2)		

O51—C1—O52	108·2 (3)	C13—C14—C15	117·6 (8)
O51—C1—O53	108·4 (5)	C13—C14—C16	121·3 (7)
O51—Cl—O54	110·8 (5)	C15—C14—C16	121·3 (7)
O52—Cl—O53	110·4 (4)	C10—C15—C14	119·7 (7)
O52—Cl—O54	109·8 (4)	C14—C16—C17	121·8 (8)
O53—Cl—O54	109·4 (4)	C14—C16—C21	121·5 (8)
C6—O7—C8	115·8 (6)	C17—C16—C21	116·7 (7)
C27—O28—C29	110·1 (6)	C16—C17—C18	120·9 (8)
C31—O32—C33	111·1 (6)	C17—C18—C19	120·0 (8)
C34—O35—C36	110·7 (6)	C18—C19—C20	120·8 (8)
C37—O38—C39	111·7 (7)	C19—C20—C21	120·4 (8)
C10—N11—C12	122·4 (6)	C16—C21—C20	120·9 (8)
C2—C1—C6	117·9 (7)	C12—C22—C23	119·6 (7)
C2—C1—C39	123·2 (8)	C12—C22—C27	120·9 (7)
C6—C1—C39	119·0 (7)	C23—C22—C27	119·4 (8)
C1—C2—C3	124·0 (8)	C22—C23—C24	121·9 (7)
C2—C3—C4	116·5 (8)	C23—C24—C25	118·0 (8)
C2—C3—C9	122·9 (8)	C23—C24—C30	120·7 (8)
C4—C3—C9	120·5 (8)	C25—C24—C30	121·3 (8)
C3—C4—C5	121·5 (7)	C24—C25—C26	122·4 (7)
C4—C5—C6	119·6 (8)	C25—C26—C27	118·5 (7)
C4—C5—C10	117·5 (7)	C25—C26—C31	122·7 (8)
C6—C5—C10	122·7 (7)	C27—C26—C31	118·7 (8)
O7—C6—C1	117·8 (7)	O28—C27—C22	121·0 (7)
O7—C6—C5	121·7 (7)	O28—C27—C26	119·3 (7)
C1—C6—C5	120·3 (7)	C22—C27—C26	119·5 (7)
N11—C10—C5	116·7 (6)	O32—C31—C26	106·8 (7)
N11—C10—C15	120·8 (7)	O32—C33—C34	108·5 (7)
C5—C10—C15	122·4 (7)	O35—C34—C33	110·1 (8)
N11—C12—C13	118·0 (7)	O35—C36—C37	110·4 (7)
N11—C12—C22	116·6 (7)	O38—C37—C36	110·5 (7)
C13—C12—C22	125·2 (7)	O38—C39—C1	107·1 (6)
C12—C13—C14	121·5 (7)	O100—C102—C101	127 (2)

C33—O32—C31—C26	−171·1 (6)	C6—C1—C39—O38	−66·1 (9)
C31—O32—C33—C34	−177·2 (7)	C10—C5—C6—C1	−168·7 (7)
C36—O35—C34—C33	172·0 (7)	C6—C5—C10—N11	36·1 (11)
C34—O35—C36—C37	172·5 (7)	N11—C12—C22—C27	−46·1 (11)
C3—O38—C37—C36	−166·5 (7)	C12—C22—C27—C26	167·5 (7)
C37—O38—C39—C1	177·0 (7)	C31—C26—C27—C22	−169·6 (8)
C12—N11—C10—C5	171·4 (7)	C27—C26—C31—O32	71·9 (9)
C10—N11—C12—C22	−173·5 (7)	O32—C33—C34—O35	−70·1 (8)
C39—C1—C6—C5	173·5 (7)	O35—C36—C37—O38	70·1 (9)

Table 3. *Hydrogen-bond data* (Å, °)

Donor atom *D*	Hydrogen atom H	Acceptor atom *A*	*D*—H	*A*···H	*D*—H···*A*	*D*···*A*
O14	H14A	O38	0·96 (7)	2·13 (8)	174 (7)	2·909 (7)
O14	H14B	O32	0·99 (8)	1·94 (8)	163 (7)	3·093 (8)
N11	H11*	O14	0·950 (7)	2·174 (6)	158·4 (4)	3·077 (8)
O100		O14				2·803 (9)

* H11 was placed in a calculated position. Therefore the e.s.d. of bond lengths and angles involving H11 is determined by the uncertainty in the positions of the heavy atoms only.

(B. A. Frenz & Associates, Inc., 1983). Atomic scattering factors from *International Tables for X-ray Crystalloraphy* (1974, Vol. IV). Atomic parameters of non-H atoms are in Table 1.* Bond distances and angles and macrocyclic torsion angles are given in Table 2, whereas some important non-bonded distances and hydrogen bonds in the crystal structure of the complex are given in Table 3. Atom numbering in the macrocycle is shown in Fig. 1.

Related literature. Crystal structures of the uncomplexed 4-pyridohemispherand (Dijkstra, den Hertog, van Eerden, Harkema & Reinhoudt, 1988), the Na.picrate complex (Dijkstra, den Hertog, van Steen, Zijlstra, Skowronska-Ptasinska, Reinhoudt, van Eerden & Harkema, 1987) and the complex with malononitrile (van Eerden, Grootenhuis, Dijkstra van Staveren, Harkema & Reinhoudt, 1986) have been reported.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53289 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Upon complexation of water but also with Na^+ and malononitrile a rather strong reorganization takes place: in the crystal structure of the uncomplexed ligand the two methoxy groups are on either side of the mean macrocyclic plane, whereby one of the methoxy groups partly converges into the cavity which is partly filled by the methyl groups.

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References

B. A. Frenz & Associates, Inc. (1983). *SDP Structure Determination Package*. College Station, Texas, USA.

Dijkstra, P. J., den Hertog, H. J. Jr, van Eerden J., Harkema S. & Reinhoudt, D. N. (1988). *J. Org. Chem.* **53**, 374–382.

Dijkstra, P. J., den Hertog, H. J. Jr, van Steen, B. J., Zijlstra, S., Skowronska-Ptasinska, M., Reinhoudt, D. N., van Eerden, J. & Harkema, S. (1987). *J. Org. Chem.* **52**, 2433–2442.

Eerden, J. van, Grootenhuis, P. D. J., Dijkstra, P. J., van Staveren, C. J., Harkema, S. & Reinhoudt, D. N. (1986). *J. Org. Chem.* **51**, 3918–3920.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

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Structure of 1-(3-Methylphenyl)-4-(2-β-quinolylethyl)piperazine: Centhaquin

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Abstract. $C_{22}H_{25}N_3$, centrally active hypotensive agent, antihypertensive, $M_r = 331{\cdot}46$, monoclinic, $P2_1/c$, $a = 9{\cdot}122$ (2), $b = 22{\cdot}108$ (3), $c = 9{\cdot}165$ (2) Å, $\beta = 102{\cdot}20$ (1)°, $V = 1806{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}22$ g cm^{-3}, $\bar{\lambda}$(Cu $K\alpha$) = 1·54178 Å, $\mu = 5{\cdot}67$ cm^{-1}, $F(000) = 712$, room temperature, $R = 0{\cdot}043$ for 1360 observed reflections. The methylphenyl substituted nitrogen exhibits sp^2 character. The resonance of its axial lone pair with the phenyl ring is evidenced by the shortening of the bridge bond and by the almost parallel position of the phenyl ring and of the mean plane of the piperazine ring.

Experimental. White prisms, dimensions 0·20 × 0·15 × 0·08 mm. Density not measured. Unit-cell parameters and intensity data obtained on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation in ω/θ scan mode ($0 < \theta < 65°$). Cell dimensions refined by least-squares fitting of θ values of 25 reflections. No appreciable drop in intensity of two standard reflections ($\bar{2}10$, 040) checked every 5400 s. 3081 independent reflections collected in h, k, $\pm l$, range 0, 0, $\bar{10}$ to 10, 26, 10; 1360 unique reflections with $I \geq 3\sigma(I)$ used in subsequent calculations. Intensities corrected

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