mation auf. Die Konformationen der CF_3-Gruppen sind aber unterschiedlich, wenn man einen Fünfring mit dem anderen vergleicht. Die Konformation der CF_3-Gruppen am Triazolring mit N(1) ist dergestalt, dass, wie in Fig. 2 ersichtlich, jeweils ein Fluoratom [F(1) bzw. F(6)] eine partielle Konformation einnimmt, die zwischen einer syn- und antiklinalen (Dunitz & Prelog, 1960) partiellen Konformation liegt (Torsionswinkel $\simeq 90°$). Die beiden anderen Fluoratome jeder CF_3-Gruppe bilden dann partielle Konformationen zwischen einer synperiplanaren und synklinalen aus (Torsionswinkel $\simeq 30°$). Die beiden statistischen Lagen jeder CF_3-Gruppe im Fünfring mit N(4) entstehen aus der Konformation am Fünfring mit N(1), indem man die CF_3-Gruppen um die C–C-Bindung sowohl nach links, wie nach rechts soweit verdreht, bis jeweils ein Fluoratom eine synperiplanare partielle Konformation (Torsionswinkel $\simeq 0°$) einnimmt.

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Polycyclic Hydrogen Bridges in Oxybis(2-methylene-6-methylpyridine N-oxide)

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Abstract. $C_{14}H_{16}N_2O_3.2H_2O$, $P2/c$, $a = 12.909$ (5), $b = 8.202$ (3), $c = 14.685$ (5) Å, $\beta = 104.24$ (4)°, $M_r = 296.33$, $Z = 4$, $d_c = 1.306$ Mg m^{-3}, $\mu = 0.843$ mm^{-1}. Linked by several hydrogen bridges, two molecules of the ligand and four water molecules are bound in a dimeric structure. These dimers are further linked to one another thus forming an endless chain of hydrogen bridges. The ether O atom is not involved in coordination.

Introduction. Acyclic ethers with two pyridine N-oxide moieties as rigid donor units are used in syntheses of crown-type polyethers (Newcomb, Timko, Walba & Cram, 1977). Also the N-oxides themselves are able to complex neutral molecules such as urea, thiourea etc. (Vögtle, Oepen, Rasshofer & Luppertz, 1979). In these complexes water molecules may replace urea stoichiometrically.

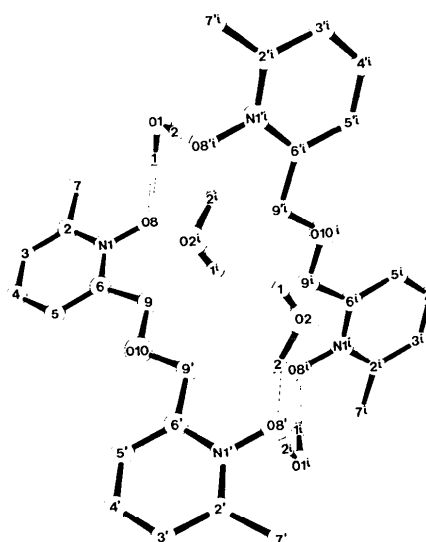* To whom correspondence should be addressed.

Fig. 1. View of the dimer (Johnson, 1965) with the numbering scheme. Radii are of arbitrary size; atoms indicated by (i) are related by $2 - x, y, 1.5 - z$.

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *of the non-hydrogen atoms and of the refined H atoms* $(\times 10^3)$ *and isotropic B values calculated from the anisotropic U values*

The mean e.s.d. for B is $\sim$0·2 Å^2 (0·9 Å^2 for H atoms).

	x	y	z	B (Å^2)
N(1)	12000 (2)	−4422 (4)	6363 (2)	4·3
C(2)	12743 (3)	−5263 (5)	6026 (3)	5·0
C(3)	12610 (3)	−5319 (5)	5061 (4)	5·7
C(4)	11774 (3)	−4532 (5)	4456 (3)	5·3
C(5)	11037 (3)	−3672 (5)	4830 (3)	4·4
C(6)	11173 (3)	−3625 (5)	5793 (3)	3·8
C(7)	13631 (3)	−6046 (6)	6728 (4)	6·9
O(8)	12100 (2)	−4356 (3)	7280 (2)	5·6
C(9)	10460 (3)	−2762 (5)	6285 (3)	4·1
O(10)	9635 (2)	−1977 (3)	5610 (2)	4·4
C(9')	8927 (3)	−1151 (5)	6057 (3)	4·3
O(8')	7412 (2)	492 (3)	6555 (2)	4·7
C(7')	5706 (3)	2100 (5)	5472 (3)	5·3
C(6')	8079 (3)	−380 (4)	5325 (2)	3·6
C(5')	7985 (3)	−465 (5)	4357 (2)	4·2
C(4')	7154 (3)	296 (5)	3750 (3)	4·6
C(3')	6397 (3)	1138 (5)	4087 (3)	4·4
C(2')	6485 (3)	1221 (5)	5052 (3)	4·0
N(1')	7316 (2)	453 (4)	5641 (2)	3·8
O(1)	13753 (3)	−2557 (4)	8412 (2)	6·6
O(2)	9025 (3)	2342 (5)	7786 (3)	8·5
H'(O1)	1320 (4)	−324 (7)	801 (4)	13·0
H"(O1)	1329 (4)	−184 (7)	849 (4)	13·0
H'(O2)	962 (4)	254 (6)	778 (5)	13·0
H"(O2)	846 (4)	180 (7)	709 (4)	13·0

Table 2. *Bond distances* (Å) *of the non-hydrogen atoms*

N(1)–C(2)	1·369 (6)	N(1')–C(2')	1·356 (4)
N(1)–C(6)	1·353 (4)	N(1')–C(6')	1·371 (5)
N(1)–O(8)	1·322 (4)	N(1')–O(8')	1·317 (4)
C(2)–C(3)	1·384 (7)	C(2')–C(3')	1·395 (6)
C(2)–C(7)	1·486 (6)	C(2')–C(7')	1·489 (6)
C(3)–C(4)	1·379 (6)	C(3')–C(4')	1·384 (6)
C(4)–C(5)	1·400 (7)	C(4')–C(5')	1·365 (5)
C(5)–C(6)	1·382 (6)	C(5')–C(6')	1·398 (5)
C(6)–C(9)	1·483 (6)	C(6')–C(9')	1·475 (5)
C(9)–O(10)	1·419 (4)	C(9')–O(10)	1·421 (5)

Table 3. *Bond angles* (°) *of the non-hydrogen atoms*

C(2)–N(1)–C(6)	122·4 (4)	C(2')–N(1')–C(6')	122·4 (3)
C(2)–N(1)–O(8)	119·2 (3)	C(2')–N(1')–O(8')	120·0 (3)
C(6)–N(1)–O(8)	118·4 (3)	C(6')–N(1')–O(8')	117·5 (3)
N(1)–C(2)–C(3)	117·7 (4)	N(1')–C(2')–C(3')	118·7 (4)
N(1)–C(2)–C(7)	117·1 (4)	N(1')–C(2')–C(7')	118·0 (3)
C(3)–C(2)–C(7)	125·2 (4)	C(3')–C(2')–C(7')	123·3 (3)
C(2)–C(3)–C(4)	121·6 (5)	C(2')–C(3')–C(4')	119·9 (3)
C(3)–C(4)–C(5)	118·9 (5)	C(3')–C(4')–C(5')	120·4 (4)
C(4)–C(5)–C(6)	119·1 (3)	C(4')–C(5')–C(6')	119·9 (4)
N(1)–C(6)–C(5)	120·2 (4)	N(1')–C(6')–C(5')	118·6 (3)
N(1)–C(6)–C(9)	114·8 (3)	N(1')–C(6')–C(9')	115·7 (3)
C(5)–C(6)–C(9)	125·1 (3)	C(5')–C(6')–C(9')	125·7 (3)
C(6)–C(9)–O(10)	109·0 (3)	C(6')–C(9')–O(10)	108·3 (3)
C(9)–O(10)–C(9')	110·5 (3)		

Colourless platelets were grown from a hot solution of the title compound in methanol/acetone (1:1) (Vögtle, Oepen, Rasshofer & Luppertz, 1979). Intensities for 2170 unique reflexions were obtained from a crystal 0·5 × 0·5 × 0·1 mm with a four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation with a θ–2θ step scan up to sin $\theta/\lambda = 0·57$ Å^{-1}. The structure was solved by direct methods (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined by full-matrix least squares (Sheldrick, 1976).

H-atom positions of the ligand were calculated from stereochemical considerations after each cycle. Isotropic temperature factors of all H atoms and coordinates only of the H atoms of the water molecules were allowed to vary during refinement.

Application of a weighting scheme based on counting statistics (Stout & Jensen, 1968) and a correction for extinction effects ($x = 0·0387$) (Sheldrick, 1976) led to $R_w = 0·076$ with all data included.

Atomic coordinates of all refined atoms are presented in Table 1;* a view of the dimer including the numbering scheme is shown in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34806 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Depending on their chain lengths, linear polyethers with terminal donor groups have been found to wrap around cations and neutral guest molecules in a circular or helical manner such that all hetero atoms are involved in coordination (Saenger & Reddy, 1979; Suh, Weber & Saenger, 1978). The short and rather rigid monoether of the title compound, however, shows a different coordination behaviour. The O(ether) atom does not participate in any interactions, but the two water molecules are each hydrogen bonded to the O atoms of the two *N*-oxide groups.

Bond distances and angles are listed in Tables 2 and 3 and show the pseudomirror through O(10) in the ligand. Similar to those in the structure of 8-hydroxyquinoline *N*-oxide (Desiderato, Terry, Freeman & Levy, 1971), angles N(1)–C(2)–C(7) and N(1')–C(2')–C(7') are slightly smaller than 120°, and angles C(3)–C(2)–C(7) and C(3')–C(2')–C(7') are widened, which may reflect some weak interactions between the methyl H atoms and O(8) or O(8'). Torsion angles are not given explicitly since they are all 'normal', *i.e.* either 0 or 180 (±3)°, resulting in a planar conformation of the ligand (all non-hydrogen atoms are coplanar to within 0·03 Å). Only if the ligand were to adopt a butterfly or a skew conformation, with at least one torsion angle forced to be *gauche*, could all three O atoms surround a guest molecule without steric hindrance.

Table 4. *Distances* (Å) *and angles* (°) *within hydrogen*
bridges

Atoms indicated by (i) are related by $2 - x, y, 1\cdot5 - z$; the atom indicated by (ii) is related by $2 - x, 1 + y, 1\cdot5 - z$. $\angle H'(O1)-$ $O(1)-H''(O1) = 92(5)$, $\angle H'(O2)-O(2)-H''(O2) = 117(5)°$.

	$O\cdots O$	$O-H$	$O\cdots H$	$\angle O-H\cdots O$
O(1),O(8),H'(O1)	2·784 (6)	0·98 (5)	1·80 (5)	175 (5)
O(1),O(8')^i,H''(O1)	2·924 (5)	0·86 (6)	2·11 (5)	157 (5)
O(2),O(2)^i,H'(O2)	2·844 (7)	0·79 (6)	2·12 (5)	153 (5)
O(2),O(8'),H''(O2)	2·838 (5)	1·19 (5)	1·76 (5)	149 (5)
O(2),O(8)^{ii}	3·063 (5)	–	–	–

The present study reveals an intricate system of hydrogen bridges; from the contents of two asymmetric units related to each other by a twofold axis, a bridged dimeric structure with circles of hydrogen bonds is formed: two ligands are linked by four water molecules (see Fig. 1) which are located 2·26 (5) [O(1)] and 2·25 (5) Å [O(2)] from the planes of the ligands. A summary of all unique distances and angles within the system of cyclic hydrogen bridges is given in Table 4.

The H atoms of O(1) and O(1)^i are each coordinated to O(8) and O(8') of both ligands thus forming the outer circle of 24 atoms, 20 covalent bonds, and four hydrogen bridges. This arrangement is additionally stabilized by two more water molecules, O(2) and O(2)^i, which are mutually H-bonded and further coordinated to O(8') and O(8')^i, respectively. Thus two more circles of hydrogen bridges are formed each containing 18 atoms and sharing O(2) and O(2)^i. These two water molecules themselves might form the smallest hydrogen-bridge circle with only four atoms. This possibility is rather dubious, however, since the H'(O2)$\cdots$H'(O2)^i distance is only 1·4 (1) Å and becomes even shorter when theoretical H—O distances are assumed; also, the H$\cdots$O—H angle (27°) is rather small. Therefore, the alternative O(2)—H'(O2)$\cdots$O(2)^i or O(2)$\cdots$H'(O2)^i—O(2)^i bridges seem to be more reasonable. The resulting disorder of one H atom cannot be proved by X-ray methods and could not be found in Fourier maps but is probable because of the O(2)$\cdots$O(8)^{ii} distance of 3·063 Å. Interactions between these two atoms in both molecules of the dimer give rise to one more circle of hydrogen bridges containing four symmetry-related O(2), two O(1), and two O(8) and O(8') atoms. With the O(2) atoms serving as switches, an endless chain of cycles along b is formed (see Fig. 2).

Molecules generated by the inversion centre are stacked in an antiparallel arrangement 3·4 (1) Å apart (see Fig. 3). An approximate 50% overlap of the pyridine nuclei therefore allows additional $\pi\cdots\pi$ interactions between dimers. Thus the molecular packing is stabilized by endless hydrogen bonds along b and mutual O—H$\cdots$O and $\pi\cdots\pi$ interactions along c.

Only a small guest molecule with an ambivalent function as an electron donor and acceptor can be
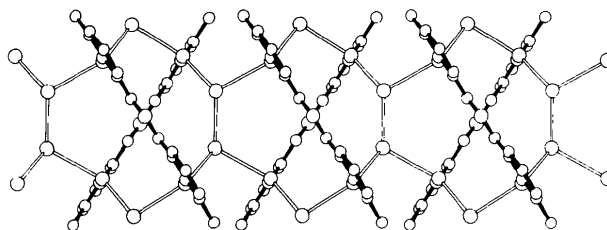

Fig. 2. View of the hydrogen-bonded dimers related by a translation of 1 along b. The two molecules of the dimer form a dihedral angle of 68 (3)°. For clarity, molecules generated by the inversion centre are omitted.
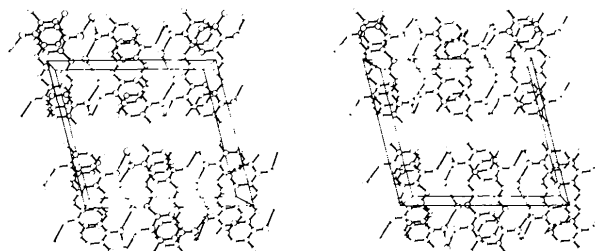

Fig. 3. Stereoscopic view of the cell (Johnson, 1965) down b showing the stacking of dimers.

involved in such an intricate system of interactions. This may explain why this ligand favours water coordination.

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