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10,22,25,26-Tetraazatricyclo-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),9,11,13(26),21,23-hexaene, *trans*-$O\{(CH_2)_2O[2,4\text{-}(C_4H_2N_2)]O(CH_2)_2\}_2O$, a 2:2 Multiheteromacrocycle Possessing 2,4-Pyrimidino Subunits

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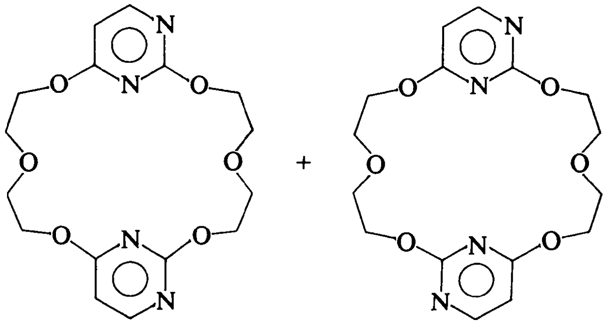
Abstract. $C_{16}H_{20}N_4O_6$, monoclinic, $P2_1/c$, a = 10·688 (2), b = 4·952 (3), c = 16·315 (4) Å, β = 99·06 (2)°, Z = 2, d_c = 1·421 Mg m^{-3}. R = 0·032 for 833 observed reflections measured by a diffractometer. The compound (m.p. 444–446 K) is the centrosymmetric *anti* isomer and exists in the crystal in a conformation such that only a small cavity exists in the center of the molecule. Atoms directed towards the cavity are two methylene H atoms, two pyrimidino N atoms, and two polyether O atoms. In both cases of polyether linkage to the pyrimidine nucleus the C—O—C group lies in the plane of the pyrimidine, directed *cis* in one case and *trans* in the other.

Introduction. During the course of our studies of macrocycles containing various subheterocyclic rings (Newkome, Sauer, Roper & Hager, 1977; Newkome, Nayak, McClure, Danesh-Khoshboo & Broussard-Simpson, 1977; Newkome & Nayak, 1978; Newkome, Danesh-Khoshboo, Nayak & Benton, 1978), we successfully incorporated a 2,4-pyrimidino moiety into a crown ether macrocyclic ring (Newkome, Nayak, Otemaa, Van & Benton, 1978). Reaction of 2,4-dichloropyrimidine with the dianion of diethylene glycol afforded two isomeric 2:2 macrocycles (m.p. 444–446 and 436–438 K) as well as a mixture of 3:3 macrocycles. Standard spectral (NMR, IR, UV) data afforded little assistance in the structural differentiation of these dimers [(I) *syn* and (II) *anti*]. It was also of interest to ascertain the directivity of the N electrons and intermolecular relationships. For these reasons, we herein report the structure of (II), the 444–446 K melting 2:2 macrocycle.



(I) *syn* (II) *anti*

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Intensity data were obtained from a colorless crystal of dimensions 0·19 × 0·33 × 1·03 mm sealed in a thin-walled glass capillary and mounted on an Enraf–Nonius CAD-4 automatic diffractometer. One quadrant of data with $2 \le 2\theta \le 50°$ was collected, using Mo $K\alpha$ radiation (λ = 0·71073 Å). Variable scan speeds were employed in the ω–2θ scans, with the scan speed adjusted to yield a net intensity of approximately 4000 counts. Two reflections (200 and 004) were remeasured every 50 measurements as standards; they exhibited no significant decrease in intensity. A total of 1768 unique reflections were measured in this manner, of which 833 were treated as observed by the criterion $F_o^2 \ge 3\sigma(F_o^2)$. Data were corrected for background, Lorentz, and polarization effects, but not for absorption, and placed on an absolute scale by statistical methods.

Systematic absences $0k0$ with k odd and $h0l$ with l odd uniquely determine the space group to be $P2_1/c$. The structure was solved with difficulty by application of the multiple-solution direct-phasing method (Germain, Main & Woolfson, 1971), using the program *MULTAN* 74. Difficulties in the direct-phasing procedure arise from the pronounced degree of parallelism present in the seven-atom zigzag chain O(1) through C(7) (see Fig. 1), as well as the atoms C(2), C(3), and N(2), which lie in the same plane. This hypersymmetry causes systematic trends in the set of normalized structure factors which are not corrected by routine renormalization procedures based on parity class. This difficulty was circumvented by renormalizing the data using spherically averaged molecular fragments recognized from early E maps.

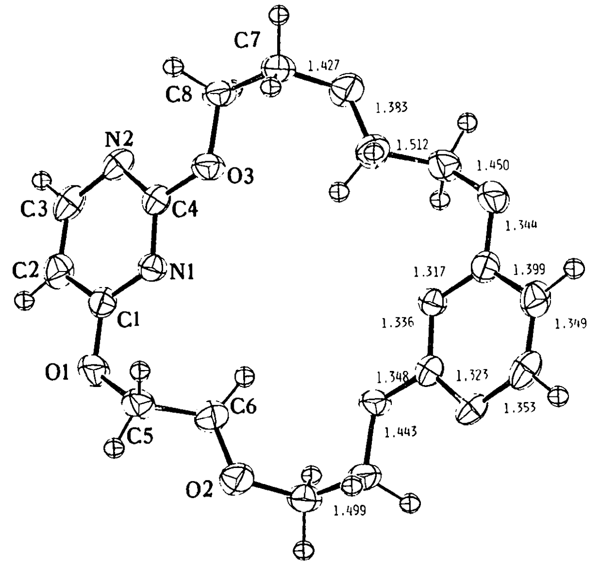

Fig. 1. An *ORTEP* (Johnson, 1965) diagram of the macrocycle showing bond distances (Å) and the atom numbering. Nonhydrogen atoms are illustrated by 40% probability thermal ellipsoids and hydrogen atoms by spheres of arbitrary radius. Standard deviations in distances are 0·002 to 0·003 Å.

Full-matrix least-squares refinement, treating nonhydrogen atoms as anisotropic and H atoms as isotropic, led to convergence with R = 0·032 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$), R_w = 0·032 $\{R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\}$, and goodness-of-fit = 1·16 $\{\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ for NO = 833 observations and NV = 158 variables$\}$. The weights (w) were calculated from counting statistics and adjusted by adding a term (0·02 × intensity)^2. Unobserved data were given zero weight in the refinement. Refined positional parameters are listed in Table 1.*

Discussion. Macrocycle (II) is illustrated in Fig. 1, on which the numbering scheme, as well as important distances, are given. Bond angles and torsion angles are given in Table 2. The molecule was established to be the *anti* isomer, with no indication of possible disorder involving the *syn* isomer causing the crystallographic centrosymmetry. Bond distances and angles are reasonable; in particular, the dimensions of the aromatic ring are comparable with those of pyrimidine itself (Wheatley, 1960), with small differences attributed to the 2,4-disubstitution. An interesting point arises concerning the linkage of polyether chains to the pyrimidine moieties. In both cases, the linkage is essentially planar, as O(1) and C(5) as well as O(3) and C(8) lie closely in

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34074 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (×10^4 *for* H *atoms and* ×10^5 *for nonhydrogen atoms*)

	x	y	z
N(1)	25774 (13)	50223 (34)	3421 (9)
N(2)	35531 (15)	63129 (34)	17136 (9)
O(1)	35234 (12)	18272 (30)	−3771 (8)
O(2)	−6728 (13)	101642 (34)	16422 (8)
O(3)	16735 (12)	81030 (27)	10479 (7)
C(1)	35170 (18)	33222 (45)	3097 (12)
C(2)	45324 (20)	29861 (51)	9576 (14)
C(3)	44865 (21)	45288 (51)	16338 (15)
C(4)	26645 (17)	64119 (40)	10504 (11)
C(5)	25028 (21)	22280 (61)	−10661 (13)
C(6)	−12982 (26)	91309 (75)	9015 (16)
C(7)	4864 (23)	115394 (52)	15884 (15)
C(8)	16294 (22)	97505 (53)	17719 (13)
H(2)	5170 (18)	1652 (42)	893 (11)
H(3)	5121 (17)	4360 (36)	2097 (10)
H(51)	2351 (19)	4305 (49)	−1175 (12)
H(52)	2807 (16)	1441 (36)	−1542 (11)
H(61)	−767 (32)	7877 (74)	733 (22)
H(62)	−1412 (29)	10469 (70)	489 (19)
H(71)	432 (16)	12299 (35)	1022 (10)
H(72)	546 (17)	12958 (42)	2023 (11)
H(81)	2449 (17)	10910 (39)	1883 (11)
H(82)	1560 (15)	8576 (36)	2255 (10)

Table 2. *Angles (°) and torsion angles (°) formed by bonded atoms*

Standard deviations in the bond angles are approximately 0·2°.

C(1)–N(1)–C(4)	114·5	N(2)–C(4)–O(3)	119·1
C(3)–N(2)–C(4)	112·9	C(1)–O(1)–C(5)	118·0
N(1)–C(1)–C(2)	123·3	O(1)–C(5)–C(6)	110·9
N(1)–C(1)–O(1)	119·3	C(5)–C(6)–O(2)	108·5
C(2)–C(1)–O(1)	117·3	C(6)–O(2)–C(7)	115·3
C(1)–C(2)–C(3)	115·3	O(2)–C(7)–C(8)	113·1
N(2)–C(3)–C(2)	124·8	C(7)–C(8)–O(3)	107·5
N(1)–C(4)–N(2)	129·2	C(8)–O(3)–C(4)	118·4
N(1)–C(4)–O(3)	111·7		

O(2′)–C(7)–C(8)–O(3)	77·0
C(7)–C(8)–O(3)–C(4)	176·7
C(8)–O(3)–C(4)–N(1)	180·0
O(3)–C(4)–N(1)–C(1)	−179·6
C(4)–N(1)–C(1)–O(1)	−179·8
N(1)–C(1)–O(1)–C(5)	1·9
C(1)–O(1)–C(5)–C(6)	−76·9
O(1)–C(5)–C(6)–O(2)	−143·6
C(6)–O(2)–C(7′)–C(8′)	−93·8

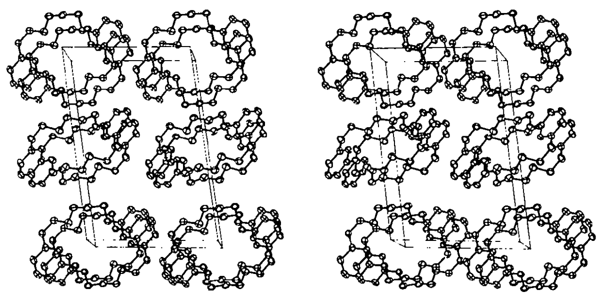

Fig. 2. Stereoscopic representation of the packing of molecules in the crystal, viewed approximately down the *b* axis. The outlined region is one unit cell. Hydrogen atoms have been omitted for clarity.

the plane of the aromatic ring. C(5) is, however, *cis* to N(1), while C(8) is *trans* to N(1). This difference is thought to be a result of both the steric constraints imposed by the presence of the H(2) atom on C(2) and the absence of a H atom on N(2), and more importantly the well-known preferred *syn* conformation of imidate esters. We believe this conformational influence to be an extremely important consideration in the design of macrocycles containing the 2,4-pyrimidino subunit as potential ligands.

A macrocycle, in order to sequester metal ions, must contain a cavity of suitable size, shape, and electronic character. The present molecule possesses a small cavity in the crystal. Six atoms are directed inward towards the center of the molecule: N(1), O(3), H(61), and their symmetry equivalents. Their distances from the center of symmetry are 2·72, 2·74, and 1·21 Å, respectively. The methylene H atom, in particular, diminishes the cavity size, but the molecule appears flexible enough to change conformation such as to remove H(61) from the interior of the cavity in solution.

Fig. 2 illustrates the packing of molecules in the crystal. Molecules are seen to stack along the short axis of the unit cell. No unusually close intermolecular contacts exist.

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