

arranged in sheets parallel to (021) and the sheets are related by the inversion centres at $z = 0.5$. Molecules from neighbouring sheets are bonded *via* N(5)—H(N5)···N(2) hydrogen bridges and form dimers across the centre of symmetry. The N—H···N bond has the following geometry: N(5)—H(N5) 0.79 (2), H(N5)···N(2) 2.31 (3), N(5)···N(2) 3.094 (4) Å, N(5)—H(N5)···N(2) 171 (2)°. There is no indication of any other hydrogen bond and all intermolecular distances between non-hydrogen atoms are greater than the sum of the corresponding van der Waals radii.

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Structure of 11,14,27,30,35,38,43,46-Octaoxa-1,8,17,24-tetraazapentacyclo-[22.8.8.8¹⁷.2^{3,6}.2^{19,22}]dopentaconta-3,5,19,21,49,51-hexaene,* C₄₀H₆₄N₄O₈, a Tricyclic Macrocyclic Featuring Two [18]-N₂O₄ Binding Subunits and Two Benzene Bridges

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Abstract. $M_r = 728.98$, $P\bar{1}$, $a = 8.823$ (3), $b = 8.813$ (4), $c = 13.859$ (3) Å, $\alpha = 87.40$ (1), $\beta = 84.05$ (1), $\gamma = 85.19$ (1)°, $V = 1067.3$ Å³, $Z = 1$, $D_x = 1.134$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.0735$ mm⁻¹, $F(000) = 396$, $T = 293$ K, final $R = 0.048$ for 2124 observed reflections. The title compound is a tricyclic cryptand with an internal cavity defined by two parallel 18-membered [C₁₂H₂₄N₂O₄] macrocyclic units bridged by two parallel phenyl rings. The structure is consistent with the results obtained for a similar compound with two naphthalene bridges. However, the conformation of the macrocyclic subunit differs significantly from that of the free monocyclic analogue.

* Note that the preferred IUPAC numbering used in the nomenclature of the title compound differs slightly from the numbering used elsewhere in this paper.

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Introduction. An intriguing feature of the tricyclic cryptands containing two binding subunits is their ability to encapsulate diammonium salts and to form dinuclear metal complexes. Even more fascinating is the possibility of inserting one or several anions in the central cavity of the dinuclear complex (Lehn, 1980). These new coordination processes depend primarily on the rigidity of the cryptand, on the dimension of its central cavity and on the size of each binding subunit. Some of these parameters can be accurately determined following a crystallographic analysis. We have thus investigated the crystal structure of the title compound, a tricyclic macrocycle containing two [18]-N₂O₄ macrocyclic binding subunits, hereafter designated as compound (I). While this work was in progress, a short description of the structure of a similar ligand with two naphthalene bridges [hereafter designated as compound

(II) was published (Pascard, Riche, Cesario, Kotzyba-Hibert & Lehn, 1982). The crystal structures of the [18]-N₂O₄ monocycle, 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane [compound (III)] and of its potassium salt have also been reported (Herceg & Weiss, 1972; Moras, Metz, Herceg & Weiss, 1972). All these structures are briefly compared in the present paper.

Experimental. (I) synthesized by high-dilution condensation (Kotzyba-Hibert, Lehn & Vierling, 1980; Vögtle, Puff, Friedrichs & Müller, 1982); colorless prismatic crystals (selected crystal: 0.35 × 0.26 × 0.22 mm) obtained from acetonitrile; Enraf-Nonius CAD-4 diffractometer, monochromatic Mo K α radiation, cell dimensions by least squares from angle data for 25 reflections; 5934 reflections (2968 unique measured, θ - 2θ scan ($2 < \theta < 25^\circ$); two reflections monitored showed no crystal decomposition; intensities corrected for Lorentz-polarization effects, not for absorption; scattering factors and anomalous-dispersion corrections for non-hydrogen atoms from *International Tables for X-ray Crystallography* (1974); structure solved by direct methods and Fourier techniques that established unequivocally space group $P\bar{1}$; full-matrix least-squares refinement minimizing $(|F_o| - |F_c|)^2$, 2124 independent reflections ($R_{\text{int}} = 0.030$) with $F^2 \geq 3\sigma(F^2)$; all non-hydrogen atoms treated anisotropically, H-atom positions calculated on the basis of sp^2 or sp^3 geometry and C-H = 1.087 Å and assigned $B_{\text{iso}} = 5.0 \text{ \AA}^2$; final $R = 0.048$, $R_w = 0.054$, unit weights; in the last cycle, $\Delta \leq 0.01\sigma$, goodness-of-fit ratio $S = 0.771$; max. and min. $\Delta\rho$ excursions in final difference Fourier map: 0.17 and -0.15 e \AA^{-3} ; programs used are part of the Enraf-Nonius (1981) *Structure Determination Package*.

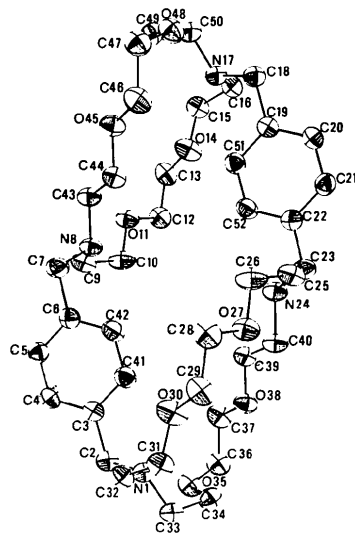


Fig. 1. Molecular geometry and labeling scheme in C₄₀H₆₄N₄O₈. Atoms are depicted by their 40% probability ellipsoids.

Discussion. A perspective view of tricycle (I) together with the atom-labeling scheme is shown in Fig. 1. The asymmetric unit contains half of the molecule which is centered on the $1(f)\bar{1}$ site ($\frac{1}{2}, 0, \frac{1}{2}$). Final fractional coordinates are in Table 1.* Selected bond lengths, valence angles and torsion angles are in Table 2.

The overall tricyclic conformation may be described in terms of four molecular planes bridged by four methyl C atoms. The two parallel mean planes of the [18]-N₂O₄ subunits (least-squares planes through the six heteroatoms) are 6.22 (3) Å apart and partially overlap each other. The two phenyl rings are planar within the limits of the e.s.d.'s and lie 2.12 (1) Å away from each other. These rings are completely free of overlap. The bridging carbons, C(7) and C(23), are in the plane of the phenyl ring to which they are attached, while C(2) and C(18) are 0.100 (4) Å out of the plane. The dihedral angle between one [18]-N₂O₄ mean plane and one phenyl plane is 96.8 (4)°. Another angle of interest, the angle between the axis C(3)-C(6) [or C(19)-C(22)] of one of the phenyl rings and the mean plane of one [18]-N₂O₄ subunit is 136.7 (4)°. The corresponding distances and angles for (II) are 7.65 (6) and 2.92 (3) Å, 97.6 (7) and 135.7 (8)°, respectively.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete bond length and angle data and least-squares plane equations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38997 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

	$B_{\text{eq}} = \frac{1}{3} \text{trace } \bar{B}$			
	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
C(2)	0.1321 (4)	0.2735 (4)	0.1842 (3)	3.77 (5)
C(3)	0.1260 (4)	0.2377 (4)	0.2920 (3)	3.22 (5)
C(4)	0.0212 (4)	0.3147 (4)	0.3563 (3)	3.77 (5)
C(5)	0.0219 (4)	0.2883 (4)	0.4561 (3)	4.00 (5)
C(6)	0.1280 (4)	0.1842 (4)	0.4930 (3)	3.66 (5)
C(42)	0.2319 (5)	0.1049 (5)	0.4281 (3)	4.43 (6)
C(41)	0.2318 (4)	0.1306 (4)	0.3288 (3)	4.17 (5)
C(7)	0.1304 (4)	0.1523 (5)	0.6009 (3)	4.49 (6)
N(8)	0.2832 (3)	0.1682 (3)	0.6306 (2)	3.84 (4)
C(9)	0.3114 (5)	0.3317 (5)	0.6306 (3)	4.76 (6)
C(10)	0.4783 (5)	0.3628 (4)	0.6190 (3)	5.11 (6)
O(11)	0.5430 (3)	0.3363 (3)	0.7079 (2)	4.38 (4)
C(12)	0.6980 (5)	0.3722 (4)	0.6988 (3)	4.77 (6)
C(13)	0.7647 (4)	0.3352 (4)	0.7926 (3)	4.64 (5)
O(14)	0.7974 (3)	0.1756 (3)	0.8004 (2)	5.33 (4)
C(15)	0.8703 (4)	0.1281 (4)	0.8844 (3)	4.42 (5)
C(16)	0.9338 (4)	-0.0355 (4)	0.8714 (3)	3.89 (5)
N(17)	0.8123 (3)	-0.1413 (3)	0.8728 (2)	3.41 (4)
C(50)	0.7434 (4)	-0.1790 (4)	0.9705 (3)	4.15 (5)
C(49)	0.5762 (5)	-0.2070 (5)	0.9716 (3)	4.50 (6)
O(48)	0.5640 (3)	-0.3478 (3)	0.9246 (2)	4.65 (4)
C(47)	0.4139 (5)	-0.3713 (4)	0.9030 (3)	4.68 (6)
C(46)	0.3807 (5)	-0.3074 (4)	0.8048 (3)	4.98 (6)
O(45)	0.3529 (3)	-0.1441 (3)	0.8085 (2)	4.42 (4)
C(44)	0.3295 (5)	-0.0794 (4)	0.7145 (3)	4.32 (6)
C(43)	0.3033 (4)	0.0934 (4)	0.7260 (3)	4.03 (5)

Replacing naphthalene bridges by benzene bridges thus brings about only minor structural changes, except, of course, for a modification of the size of the central cavity.

The conformation of the [18]-N₂O₄ subunit in tricycle (I) is also very similar to that observed in tricycle (II). Many of the corresponding valence and torsion angles are alike. However, this conformation is strongly distorted with respect to the highly symmetrical structure adopted by the monocyclic analogue (III). Significant differences appear among valence and torsion angles, the latter being either close to 60° (about aliphatic C—C bonds) or to 180° (about C—O and C—N bonds) in (III). Furthermore, all the heteroatoms of (III) are coplanar; the O atoms have their lone electron pairs directed toward the center of the internal cavity in an endodentate conformation while the two N atoms are exodentate with their lone electron pairs directed away from the internal cavity. There is little distortion of ligand (III) upon complexation with potassium: all heteroatoms remain in a planar array and the two N atoms become endodentate. However, significant structural modifications would have to take place if a metal ion is to be complexed by tricycle (I). The heteroatoms belonging to the [18]-N₂O₄ subunits are not coplanar. The N atoms are displaced by 0.372 (3) and 0.397 (3) Å on one side of each mean plane (through the heteroatoms) and the O atoms are at distances varying from 0.045 (3) to 0.345 (3) Å on the other side of the plane. Moreover, the lone electron pairs of the N atoms are directed toward the central cavity while the electron pairs of O(11) and O(14) [and O(27) and O(30)] point toward the internal cavity of the macrocyclic subunit. In addition, O(45) and O(48) [and O(32) and O(35)] adopt a very irregular exodentate arrangement.

In the crystal, no strong interaction is observed between the molecules, which are packed parallel to one another.

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Table 2. Selected intramolecular distances (Å), bond angles (°) and torsion angles (°)

N(8)—C(7)	1.469 (5)	C(2)—C(3)	1.508 (6)
N(8)—C(9)	1.483 (6)	C(6)—C(7)	1.511 (6)
N(8)—C(43)	1.471 (5)	O(11)...O(48)	6.610 (8)
N(17)—C(16)	1.477 (5)	O(14)...O(45)	5.006 (7)
N(17)—C(18)*	1.459 (3)	N(8)...N(17)	6.386 (8)
N(17)—C(50)	1.462 (6)	N(8)...N(1)*	7.130 (7)
C(7)—N(8)—C(9)	109.8 (4)	N(8)—C(9)—C(10)	114.5 (4)
C(7)—N(8)—C(43)	112.0 (3)	C(9)—C(10)—O(11)	110.9 (4)
C(9)—N(8)—C(43)	110.9 (3)	O(11)—C(12)—C(13)	109.7 (4)
C(16)—N(17)—C(50)	113.4 (3)	C(12)—C(13)—O(14)	108.0 (4)
C(16)—N(17)—C(18)*	109.9 (3)	O(14)—C(15)—C(16)	107.3 (4)
C(50)—N(17)—C(18)*	114.3 (3)	C(15)—C(16)—N(17)	112.5 (4)
C(10)—O(11)—C(12)	111.2 (4)	N(8)—C(43)—C(44)	109.2 (4)
C(13)—O(14)—C(15)	112.9 (3)	C(43)—C(44)—O(45)	106.3 (4)
C(44)—O(45)—C(46)	110.4 (4)	O(45)—C(46)—C(47)	109.3 (4)
C(47)—O(48)—C(49)	114.5 (4)	C(46)—C(47)—O(48)	112.8 (4)
C(3)—C(2)—N(1)*	112.3 (3)	O(48)—C(49)—C(50)	109.2 (4)
C(6)—C(7)—N(8)	110.8 (4)	N(17)—C(50)—C(49)	112.0 (4)
O(11)—C(10)—C(9)—N(8)	-79.4 (3)	C(50)—N(17)—C(16)—C(15)	-78.3 (3)
N(17)—C(16)—C(15)—O(14)	-67.6 (2)	C(13)—C(12)—O(11)—C(10)	-177.1 (4)
N(8)—C(43)—C(44)—O(45)	178.2 (3)	C(16)—C(15)—O(14)—C(13)	-166.1 (4)
O(48)—C(49)—C(50)—N(17)	69.8 (2)	C(43)—C(44)—O(45)—C(46)	-179.3 (4)
O(14)—C(13)—C(12)—O(11)	77.0 (3)	C(46)—C(47)—O(48)—C(49)	89.8 (3)
O(45)—C(46)—C(47)—O(48)	-76.2 (3)	C(12)—O(11)—C(10)—C(9)	-177.2 (4)
C(10)—C(9)—N(8)—C(43)	79.6 (3)	C(15)—O(14)—C(13)—C(12)	176.4 (4)
C(49)—C(50)—N(17)—C(16)	147.8 (3)	C(44)—O(45)—C(46)—C(47)	176.7 (4)
C(9)—N(8)—C(43)—C(44)	-160.2 (4)	C(47)—O(48)—C(49)—C(50)	-167.6 (4)

* N(1) and C(18) are related, by the inversion centre ($\frac{1}{2}$, 0, $\frac{1}{2}$), to reference atoms N(17) and C(2) of Table 1.

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