Acta Cryst. (1988). C**44**, 352–355

Structure of the Designed Macrocycle 1,4,11,20-Tetraoxa[4]orthobenzeno[2](2,6)pyridino[2]metabenzenophane

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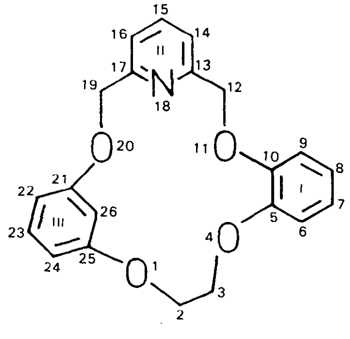
(*Received* 24 *April* 1987; *accepted* 1 *October* 1987)

Abstract. $C_{21}H_{19}NO_4$, $M_r = 349{\cdot}4$, monoclinic, $P2_1/c$, $a = 9{\cdot}113$ (2), $b = 16{\cdot}868$ (5), $c = 12{\cdot}280$ (3) Å, $\beta = 109{\cdot}69$ (2)°, $V = 1777{\cdot}5$ (8) Å^3, $Z = 4$, $D_x = 1{\cdot}306$, $D_m = 1{\cdot}28$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·53 cm^{-1}, $F(000) = 736$, $T = 293$ K, $R = 0{\cdot}052$ for 1516 reflections with $I > 3\sigma(I)$. The title compound is a designed crown ether, consisting of a 16-membered macrocyclic ring, which is flanked with a pyridine ring, and resorcinolic and catecholic ring systems. The macrocycle has a distorted cavity which, owing to its limited dimensions, is not suitable for accommodating uncharged organic guests (ethanol, propenol *etc.*) through, for example, formation of hydrogen-bond contacts with the ring hetero atoms.

Introduction. Crown ether compounds have several unique properties including complexation of cations and uncharged molecules (Weber & Vögtle, 1981*a*,*b*). Whereas the chemistry of crown cation complexes has been elaborated up to a high level (Izatt, Bradshaw, Nielsen, Lamb, Christensen & Sen, 1985), it is still difficult to suggest a crown which is a specific host for neutral (uncharged) guest molecules (Vögtle, Müller & Watson, 1984; Weber, 1987). Recently we projected a new strategy aimed at reducing this problem (Weber, Josel, Puff & Franken, 1985) and reported the directed formation of crystalline inclusion compounds (Weber, Franken, Puff & Ahrendt, 1986). One of the general conclusions emerging from this work is that the presence of aromatic building blocks in specified positions of the macrocycle can produce a concave and rigid (*e.g.* 'dentist chair') conformation of the host molecule (Weber & Jones, 1983).

The present investigation was undertaken in order to establish the effect on conformational behaviour of exchanging a catecholic for a resorcinolic group, *e.g.* at one of the flanking benzyl positions of the pyridine ring of the title compound (1). An X-ray analysis of (1) might, therefore, provide structural information as to its inability to form inclusion compounds compared to similar crown hosts (Weber, Vögtle, Josel, Newkome & Puckett, 1983).



(1)

Experimental. The title compound was synthesized following the general procedure described previously (Weber, Josel, Puff & Franken, 1985) and recrystallized from acetone. A suitable crystal for structure determination was grown from dimethylformamide. Density by flotation method. Preliminary studies for the cell dimensions and space-group determination were carried out by photographic methods. More accurate cell dimensions were obtained using a Rigaku automatic diffractometer by a least-squares fit of the 2θ values of 25 general reflections. 3D data of 2550 reflections were collected, 1516 considered observed [$I > 3\sigma(I)$]. Three standard reflections measured every hundred reflections during data collection varied less than 4%. Crystal dimensions 0·55 × 0·35 × 0·20 mm.

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0108-2701/88/020352-04$03.00

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters of the non-*H *atoms*

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

	x	y	z	B_{eq}(Å^2)
O(1)	1·0649 (6)	0·2401 (3)	0·1913 (5)	4·8
C(2)	1·2288 (10)	0·2271 (5)	0·2199 (7)	5·5
C(3)	1·3089 (9)	0·2662 (5)	0·3326 (7)	5·5
O(4)	1·2807 (6)	0·3494 (3)	0·3152 (4)	4·7
C(5)	1·3077 (9)	0·3948 (5)	0·4127 (7)	4·0
C(6)	1·4199 (9)	0·3773 (5)	0·5188 (8)	4·7
C(7)	1·4385 (10)	0·4275 (6)	0·6128 (7)	5·5
C(8)	1·3450 (11)	0·4923 (6)	0·5996 (8)	5·3
C(9)	1·2335 (9)	0·5112 (5)	0·4946 (7)	4·3
C(10)	1·2144 (9)	0·4617 (5)	0·4012 (6)	3·7
O(11)	1·1085 (6)	0·4727 (3)	0·2916 (4)	4·0
C(12)	0·9979 (9)	0·5347 (5)	0·2766 (6)	4·2
C(13)	0·8961 (8)	0·5319 (5)	0·1516 (6)	3·1
C(14)	0·9175 (8)	0·5848 (4)	0·0725 (5)	3·8
C(15)	0·8305 (9)	0·5751 (5)	−0·0430 (7)	4·3
C(16)	0·7242 (9)	0·5141 (5)	−0·0758 (7)	4·1
C(17)	0·7085 (9)	0·4644 (5)	0·0089 (7)	3·4
N(18)	0·7914 (7)	0·4721 (3)	0·1220 (5)	3·4
C(19)	0·5920 (8)	0·3969 (5)	−0·0228 (7)	4·5
O(20)	0·6212 (6)	0·3425 (3)	−0·1034 (4)	4·4
C(21)	0·7476 (9)	0·2930 (5)	−0·0646 (7)	4·0
C(22)	0·7738 (10)	0·2444 (5)	−0·1488 (7)	4·8
C(23)	0·9006 (11)	0·1946 (5)	−0·1170 (7)	5·4
C(24)	1·0021 (10)	0·1907 (5)	−0·0044 (8)	4·8
C(25)	0·9731 (10)	0·2389 (5)	0·0773 (7)	4·7
C(26)	0·8463 (9)	0·2897 (4)	0·0492 (7)	3·6

Table 2. *Bond lengths* (Å) *and angles* (°)

O(1)–C(2)	1·431 (11)	C(13)–N(18)	1·351 (9)
O(1)–C(25)	1·368 (9)	C(14)–C(15)	1·381 (8)
C(2)–C(3)	1·484 (11)	C(15)–C(16)	1·377 (12)
C(3)–O(4)	1·430 (12)	C(16)–C(17)	1·380 (12)
O(4)–C(5)	1·371 (10)	C(17)–N(18)	1·345 (10)
C(5)–C(6)	1·391 (10)	C(17)–C(19)	1·515 (12)
C(5)–C(10)	1·391 (12)	C(19)–O(20)	1·438 (11)
C(6)–C(7)	1·395 (13)	O(20)–C(21)	1·372 (9)
C(7)–C(8)	1·362 (14)	C(21)–C(22)	1·401 (13)
C(8)–C(9)	1·383 (11)	C(21)–C(26)	1·385 (10)
C(9)–C(10)	1·382 (12)	C(22)–C(23)	1·374 (12)
C(10)–O(11)	1·379 (8)	C(23)–C(24)	1·382 (11)
O(11)–C(12)	1·421 (9)	C(24)–C(25)	1·384 (13)
C(12)–C(13)	1·503 (9)	C(25)–C(26)	1·386 (11)
C(13)–C(14)	1·381 (11)		

C(25)–O(1)–C(2)	118·4 (5)	C(14)–C(15)–C(16)	119·5 (6)
O(1)–C(2)–C(3)	107·7 (6)	C(15)–C(16)–C(17)	118·4 (6)
C(2)–C(3)–O(4)	106·8 (6)	C(16)–C(17)–N(18)	123·2 (6)
C(3)–O(4)–C(5)	116·6 (9)	C(16)–C(17)–C(19)	120·3 (6)
O(4)–C(5)–C(6)	124·0 (6)	C(17)–N(18)–C(13)	116·7 (5)
O(4)–C(5)–C(10)	116·2 (4)	C(17)–C(19)–O(20)	112·3 (5)
C(6)–C(5)–C(10)	119·8 (7)	C(19)–O(20)–C(21)	118·6 (5)
C(5)–C(6)–C(7)	119·5 (7)	O(20)–C(21)–C(22)	115·6 (6)
C(6)–C(7)–C(8)	119·5 (7)	O(20)–C(21)–C(26)	123·9 (6)
C(7)–C(8)–C(9)	121·8 (7)	C(21)–C(22)–C(23)	119·0 (6)
C(8)–C(9)–C(10)	118·8 (7)	C(22)–C(23)–C(24)	121·8 (7)
C(9)–C(10)–O(11)	125·4 (6)	C(23)–C(24)–C(25)	118·9 (7)
C(9)–C(10)–C(5)	120·3 (6)	C(24)–C(25)–C(26)	122·0 (6)
C(10)–O(11)–C(12)	117·3 (5)	C(24)–C(25)–O(1)	123·4 (6)
O(11)–C(12)–C(13)	106·0 (5)	C(25)–C(26)–C(21)	118·7 (5)
C(12)–C(13)–C(14)	120·9 (6)	C(22)–C(21)–O(26)	120·4 (7)
C(12)–C(13)–N(18)	115·8 (5)	O(1)–C(25)–C(24)	123·4 (7)
C(13)–C(14)–C(15)	118·8 (6)		

Mo $K\alpha$ radiation; $h = -12\rightarrow 12$, $k = 0\rightarrow 18$, $l = 0\rightarrow 15$; scan range 3–55°, ω scan for $2\theta \leq 30°$, ω–2θ scan for $2\theta > 30°$. Background and Lp corrections were applied; no absorption correction as μ was small. Most of the non-H atoms were obtained with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); remaining atoms based on Fourier methods. Refinements were carried out with *SHELX*76 (Sheldrick, 1976), initially with isotropic temperature factors. The quantity minimized was $w[(|F_o|) - (|F_c|)]^2$ with weights $w = 1/\sigma_F^2$, σ_F computed from counting statistics; the refinement converged at an R of 0·14. Further refinements were carried out with anisotropic temperature factors. Most of the H atoms were obtained from a difference Fourier map computed at $R = 0·10$. The remaining H atoms were fixed. H atoms were included in the structure-factor calculations but were not refined and isotropic B values were assigned to the atom to which they were bonded. The refinement converged at an R of 0·052, $wR = 0·040$.[*] $(\Delta/\sigma)_{max} = 0·6$ in the final refinement cycle. The goodness-of-fit parameter $S = 1·40$. The maximum and minimum peak heights in the final difference Fourier map were +0·19 and −0·21 e Å^{-3} respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Fractional coordinates of the non-H atoms are given in Table 1, and bond lengths and angles in Table 2.

Discussion. *Conformation of the macrocycle.* Fig. 1 shows different views of the ring conformation of molecule (1). The overall geometry of (1) is different from the 'chair' form usually found for this class of compounds (Weber & Jones, 1983; Weber, 1984). The difference can be attributed to the linking position of ring III being 1,3 in (1) instead of 1,2.

The torsion angles of the macrocyclic ring were expected to be *anti* (for C–X–C–C, X = O, N), ±*gauche* (for O–C–C–O) and *syn* (at 1,2-disubstituted benzene) as is usually observed for benzo crown compounds (Hilgenfeld & Saenger, 1982). However, the macrocycle has an unusual conformation around ring III with the endocyclic torsion angles C(19)–O(20)–C(21)–C(26) = 2·7 (11)° and C(17)–C(19)–O(20)–C(21) = 72·3 (8)°, which causes this ring to tilt away from ring I and towards the pyridine ring, thus making it difficult to adopt a strain-free 'chair' conformation. Also, this causes C(26) to point inside the cavity of the macrocycle and makes the shape of this cavity irregular. The endocyclic torsion angles of the macrocycle are indicated in Fig. 1(*a*).[*] Starting from the O(1)–C(2) bond the macrocycle has the

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles defining the macrocyclic ring system have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44416 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[*] See deposition footnote.

conformation $a'g^- \; aa'saag^+ \; aaa^* \; g^+ \; saaa'$. Fig. 1(*b*) gives a side view of the molecule and illustrates the 'distorted-chair' conformation. Fig. 1(*c*) shows the opposite face of the molecule to that in Fig. 1(*a*). This side of the molecule provides a cavity, but the pyridine N atom (which is supposed to be the most efficient hydrogen-bond acceptor) points away to the convex side of the molecule (Fig. 1*a*). This unfavourable factor prevents any hydrogen-bonded host–guest interactions.

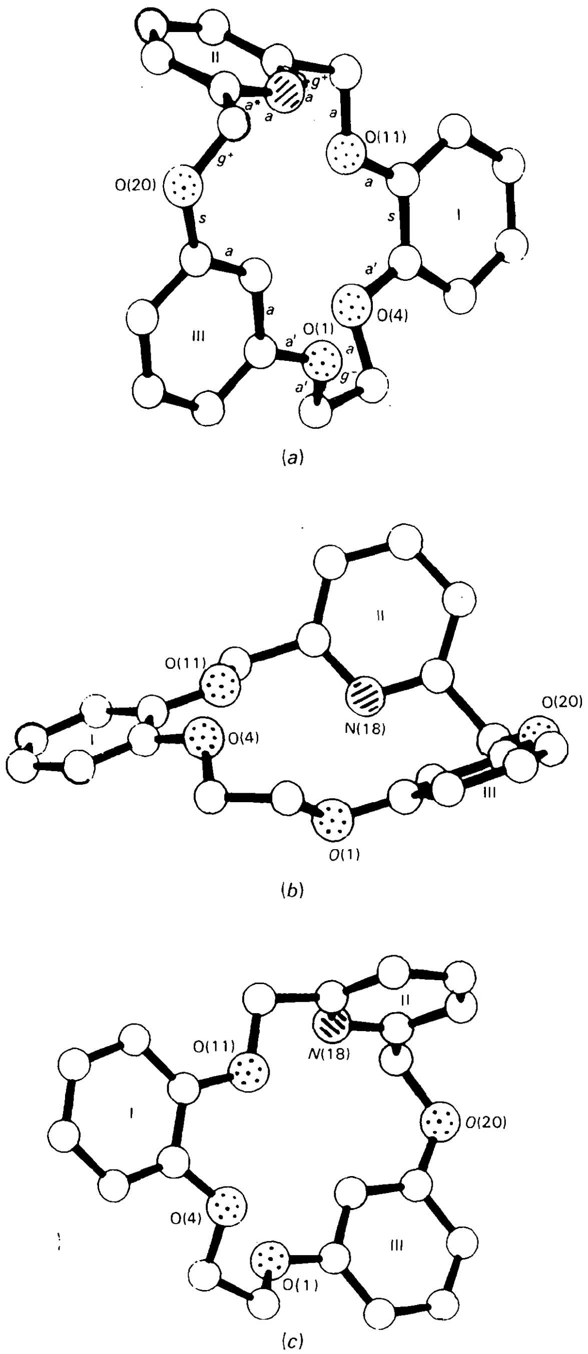

Fig. 1. Molecular structure of (1): (*a*) view of the convex side, (*b*) side view, (*c*) view of the concave side.

In this context it is of interest to refer to the behaviour of linear oligo ethers with aromatic donor end groups (Vögtle & Weber, 1979), which have been found to complex with uncharged guest molecules like urea and thiourea through weak N—H···O hydrogen bonds. They form an interesting comparative study in that the N atoms of the 'guest' molecules are hydrogen-bond 'donors', and these structures even demonstrate the existence of bifurcated hydrogen bonds (Chacko, Narasimhan & Saenger, 1984; Suh & Saenger, 1978).

The dihedral angles between the aromatic planes are: I/II = 70 (1), I/III = 14 (1) and II/III = 88 (1)°. Heteroatoms are not coplanar which is further characteristic of the ring conformation that contrasts with the previous examples.

Bond distances and angles. There is only one aliphatic CH_2—CH_2 bond in this structure, namely the C(2)—C(3) bond, which is significantly shorter [1·484 (11) Å] than the normal value of 1·537 Å; this can be attributed to the 'macrocyclic effect' (Hilgenfeld & Saenger, 1982; Weber, Franken, Puff & Ahrendt, 1986). The mean C—C bond length of the catecholic and resorcinolic moieties is 1·385 (10) Å while the mean C(sp^2)—O and C(sp^3)—O bonds are 1·373 (5) and 1·430 (8) Å, respectively. The C(sp^2)—N bonds of the pyridine ring differ slightly [1·351 (9) and 1·345 (10) Å], but the difference is not significant. There is good agreement of bond lengths with those of a crown ether propanol inclusion compound studied by Weber, Josel, Puff & Franken (1985). The intramolecular distance between O(1) and O(4) is 2·750 (7) and the O(4)···O(11) contact is 2·562 (7) Å; the latter contact is short compared with the van der Waals O···O non-bonded contact distance of 2·8 Å and reflects the conformational strain of the macrocycle.

The mean values of bond angles are: C—O—C of the macrocycle, 117·7 (7)°; C—N—C of the pyridine ring, 116·7 (5)°; C—C—C of the phenylene groups, 120 (1)°. Considerable ring strain could be seen at C(5), C(10), C(13), C(17), C(21) and C(25); maximum distortion (from 120°) is noticed at C(10).

The structure investigation shows that (1) has a constricted void and hence cannot accommodate even a small organic 'guest'. This feature supports our chemical studies which showed that (1) could not be co-crystallized with usual guest molecules. The structural findings also show that incorporation of a resorcinol building block into a macrocyclic ring may have a disadvantageous effect on the conformation of an expectedly active 'host' molecule.

The authors thank Professors W. Saenger (Freie Universität Berlin) and F. Vögtle (Universität Bonn) for helpful discussions. KKC thanks the CSIR for financial support. EW acknowledges the financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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Acta Cryst. (1988). C**44**, 355–357

Structure of *N*-(Diethylaminothiocarbonyl)benzamidine

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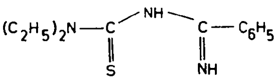
(*Received* 20 *January* 1987; *accepted* 10 *June* 1987)

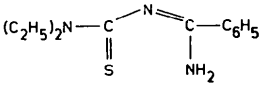
Abstract. $C_{12}H_{17}N_3S$, $M_r = 235\cdot4$, monoclinic, $P2_1$, $a = 5\cdot353\ (2)$, $b = 8\cdot440\ (3)$, $c = 14\cdot380\ (8)$ Å, $\beta = 95\cdot06\ (3)°$, $V = 647\cdot1$ Å^3, $Z = 2$, $D_x = 1\cdot21$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 1·88 cm^{-1}, $F(000) = 252$, room temperature. Final $R = 0\cdot079$ for 1164 unique observed reflections. The molecules have an approximate *Z,Z′* configuration. Both H atoms are bonded to the terminal N atom (enamine form). The C—S bond is intermediate between a double and a single bond. There exist two types of C—N bonds inside the molecule.

Introduction. Recently we reported the structure of 1,1-diethyl-3-thiobenzoylthiourea (Braun, Richter, Sieler, Beyer, Lindqvist, Yanovsky & Struchkov, 1987). As part of our study on the structure of *N*-chalcogenoacylthioureas we report here the structure of the title compound in which the chalcogen atom is formally substituted by an NH group which is isoelectronic to the chalcogen atom O [(I)]. The solution of the structure should provide information on the configuration and the tautomerism [(I) or (II)] as well as the bonding parameters.



$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-C_6H_5$

(I)



$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-N=\underset{\underset{NH_2}{|}}{C}-C_6H_5$

(II)

Experimental. The title compound was prepared according to the method of Beyer, Hartung & Widera

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