

$S = 1.37$
2303 reflections
172 parameters
H atoms: see below
Weighting scheme: see below

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Kuş, C., Göker, H., Ayhan, G. & Ertan, R. (1996). *Farmaco*, **51**, 413–417.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Nishina, K., Mikawa, K., Maekawa, N., Takao, Y., Shiga, M. & Obara, H. (1996). *Anesth. Analg.* **82**, 832–836.
Panneerselvam, K. & Soriano-García, M. (1996). *Acta Cryst.* **C52**, 1799–1801.
Preston, P. N. (1974). *Chem. Rev.* **74**, 279–314.
Ram, S., Wise, D. S., Wotring, L. L., McCall, J. W. & Townsend, L. B. (1992). *J. Med. Chem.* **35**, 539–547.
Tuñçbilek, M., Göker, H., Ertan, R., Eryiit, R., Kendi, E. & Altanlar, N. (1997). *Arch. Pharm.* **330**, 372–376.
Vasudevan, K. T., Puttaraja & Kulkarni, M. V. (1994). *Acta Cryst.* **C50**, 1286–1288.

Table 1. Selected geometric parameters (\AA , $^\circ$)

C11—C2	1.711 (2)	N3—C2	1.296 (2)
C12—C5	1.748 (2)	N3—C9	1.391 (2)
C13—C14	1.746 (2)	C8—C9	1.400 (3)
N1—C2	1.361 (3)	C10—C11	1.518 (3)
N1—C8	1.383 (2)	C14—C15	1.367 (3)
N1—C10	1.464 (2)		
C2—N1—C8	104.9 (1)	C4—C5—C6	123.5 (2)
C2—N1—C10	129.0 (1)	N1—C8—C9	105.4 (1)
C8—N1—C10	126.1 (1)	N3—C9—C8	110.6 (1)
C2—N3—C9	103.0 (2)	N1—C10—C11	113.0 (2)
C11—C2—N1	121.0 (1)	C13—C14—C13	119.2 (2)
N1—C2—N3	116.2 (2)	C13—C14—C15	119.1 (2)
C12—C5—C4	117.9 (2)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	H...A	D...A	D—H...A
C10—H101...C11	2.79	3.184 (3)	106
C13—H13...C12 ⁱ	2.92	3.639 (3)	133
C10—H101...C13 ⁱⁱ	2.86	3.668 (2)	143

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, -y, 1 - z$.

The weighting scheme used was as follows: $w = 1.0$ if $F > \text{threshold}$; $w = [\text{threshold}/F]^2$ if $F \geq \text{threshold}$; $w = 0$ if $F^2 < \text{cutoff} \times \sigma F^2$; where $\text{threshold} = 332.77$ and $\text{cutoff} = 3.0$. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically 0.95 \AA from the corresponding C atoms. For all H atoms a riding model was used with $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1993). Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SIR in MolEN. Program(s) used to refine structure: LSFM in MolEN. Molecular graphics: ORTEP in MolEN. Software used to prepare material for publication: MolEN and PARST95 (Nardelli, 1995).

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey. Support under Grant TBAG-1226 is also gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1364). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, G. D., Brammer, L., Orpen, G. A. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, S1–19.
Awouters, F. H. L., Niemegeers, C. I. E. & Janssen, P. A. J. (1983). *Arzneim. Forsch. (Drug Res.)* **33**, 381–388.
Enraf–Nonius (1993). CAD-4 EXPRESS. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). MolEN. An Interactive Intelligent System for Crystal Structure Analysis. Enraf–Nonius, Delft, The Netherlands.
Kendi, E., Özbeý, S., Tuñçbilek, M. & Göker, H. (1998). *Acta Cryst.* **C54**, 854–856.

Acta Cryst. (1999). **C55**, 245–248

4-Chloro-2-[2-(dimethylamino)ethylamino-methyl]phenol and 2-[2-(dimethylamino)-ethylaminomethyl]-6-methoxyphenol

LIAN EE KHOO,^a HONG JUAN HU^a AND ALAN HAZELL^b

^aSchool of Science, Nanyang Technological University, 469 Bukit Timah Road, Singapore 259756, Singapore, and
^bDepartment of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark. E-mail: ach@kemi.aau.dk

(Received 27 July 1998; accepted 21 September 1998)

Abstract

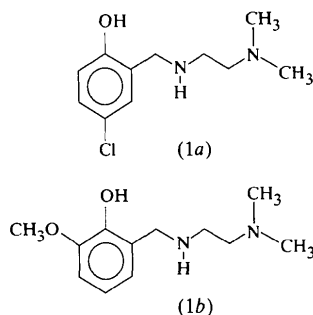
The structures of the title compounds, $\text{C}_{11}\text{H}_{17}\text{ClN}_2\text{O}$, (1a), and $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2$, (1b), show that unlike the related 4-nitro compound, the phenolic H atoms do not migrate to the amino groups. In both compounds, there are intermolecular hydrogen bonds between the phenolic O atoms and the amino group of neighbouring molecules [$\text{N} \cdots \text{O}$ 2.656 (3) for (1a) and 2.696 (2) \AA for (1b)] and weak bifurcated hydrogen bonds involving the imino H atoms [$\text{N1} \cdots \text{O1}$ 3.005 (2) and $\text{N1} \cdots \text{N2}$ 2.910 (3) \AA for (1a), and 3.111 (2) and 2.894 (3) \AA for (1b)]. The differences in structure are attributed to the acidities of the phenolic groups.

Comment

Brzezinski *et al.* (1990) reported IR continuum studies which showed that the phenolic proton of disubstituted *ortho* Mannich bases of the formula $\text{HOC}_6\text{H}_3(\text{CH}_2\text{NR}_2)_2$ exhibit an intra/intermolecular proton transfer equilibrium, $\text{O—H} \cdots \text{N} \rightleftharpoons \text{O} \cdots \text{H—N}$, between the phenolic O atom and the amino N atom. It was further reported that the differences between the intra- and intermolecular hydrogen-bonded systems of 2- $\text{HOC}_6\text{H}_3\text{XCH}_2\text{NR}_2$

are dependent on the pK_a values of these bases (Rospenk & Sobczyk, 1989). A recent crystal structure determination of 2-HOC₆H₃XCH₂NHR', [(1*c*); X = 4-NO₂, R' = CH₂CH₂NMe₂] confirmed that the phenolic proton was shifted to the amino N atom and that it takes part in both intra- and intermolecular O··H—N hydrogen bonds (Hazell *et al.*, 1997). This shift of a proton is due to the nitro substituent increasing the acidity of the phenolic group, *cf.* the related 4-NO₂C₆H₄OH for which $pK_a = 7.16$ as compared to 9.99 for phenol itself (Serjeant & Dempsey, 1979).

We report here the crystal structures of the title compounds, (1*a*) (X = 4-Cl, R' = CH₂CH₂NMe₂) and (1*b*) (X = 6-CH₃O, R' = CH₂CH₂NMe₂), which have



more weakly acidic phenolic groups (*cf.* $pK_a = 9.41$ for 4-ClC₆H₄OH and 9.98 for 2-CH₃OC₆H₄OH). The structures (Figs. 1 and 2) show that the phenolic H atom is not shifted to the amino N atom of the molecule as was the case for (1*c*). In both structures there are intermolecular hydrogen bonds linking the molecules in chains, O—H···N'(x, -y, $\frac{1}{2} + z$) = 2.656 (3) Å in (1*a*) and O—H···N'($\frac{1}{2} - x$, $\frac{1}{2} + y$, z) = 2.696 (2) Å in (1*b*). These bonds are both longer than that of 2.644 (3) Å in (1*c*), the O···N distance varying inversely with the acidity of the phenolic O atom. Whereas (1*c*) exhibited a strong intramolecular hydrogen bond

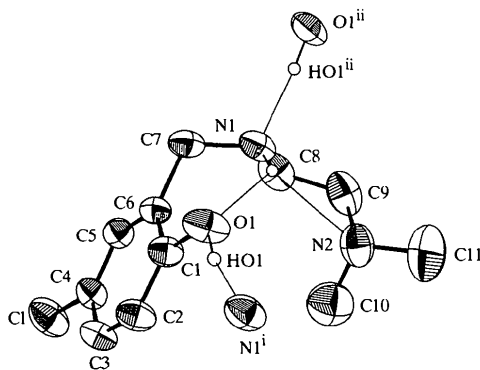


Fig. 1. View of (1*a*) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms of the phenolic and amino groups are drawn as small circles of an arbitrary radius. Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $x, -y, z - \frac{1}{2}$.

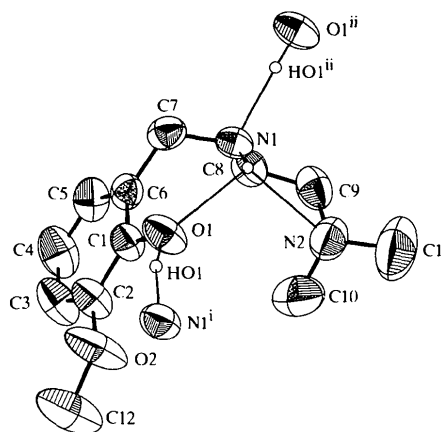


Fig. 2. View of (1*b*) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms of the phenolic and amino groups are drawn as small circles of an arbitrary radius. Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z$.

[O1···N2 = 2.662 (4) Å], here there are weak bifurcated hydrogen bonds involving the imino H atom HN1 [N1···O1 3.005 (2) and N1···N2 2.910 (3) Å for (1*a*), and N1···O1 3.111 (2) and N1···N2 2.894 (3) Å for (1*b*)]. The change in N···O distances is reflected in the C1—C6—C7—N1 torsion angles, 67.5 (3), 71.2 (2) and 48.9 (4)° in (1*a*), (1*b*) and (1*c*), respectively. Bond distances and angles have the expected values, the phenolic C—O distances are 1.352 (3) Å in (1*a*) and 1.348 (2) Å in (1*b*), *i.e.* they lack the double-bond character which was observed in (1*c*) [C—O = 1.295 (3) Å].

Experimental

The title compounds, (1*a*) and (1*b*), were prepared by reducing the corresponding Schiff base analogue with NaBH₄ in boiling ethanol (Shukla *et al.*, 1994). Yellow crystals of (1*a*), m.p. 335–338 K, and off-white crystals of (1*b*), m.p. 337–339 K, were isolated in 61 and 13% yields, respectively. Both (1*a*) and (1*b*) were found to have satisfactory elemental CHN analysis after recrystallization in petroleum ether 60–80°C.

Compound (1*a*)

Crystal data

C₁₁H₁₇ClN₂O

$M_r = 228.73$

Orthorhombic

Pbcn

$a = 21.935$ (1) Å

$b = 11.4354$ (7) Å

$c = 9.9743$ (6) Å

$V = 2501.9$ (2) Å³

$Z = 8$

$D_x = 1.214$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 5045

reflections

$\theta = 2.9$ – 26.8°

$\mu = 0.283$ mm⁻¹

$T = 295$ K

Block

$0.52 \times 0.21 \times 0.12$ mm

White

Data collection

Siemens SMART CCD diffractometer
 ω rotation scans with narrow frames
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.822$, $T_{\max} = 0.951$
 14 436 measured reflections

Refinement

Refinement on F
 $R = 0.041$
 $wR = 0.046$
 $S = 1.295$
 1499 reflections
 144 parameters
 H-atom parameters constrained

2569 independent reflections
 1499 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 26.8^\circ$
 $h = -24 \rightarrow 27$
 $k = -13 \rightarrow 13$
 $l = -11 \rightarrow 11$
 Intensity decay: none

$w = 1/[\sigma_{\text{cs}}(F^2) + 1.03F^2]^{1/2} - |F|$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.23(4) \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23(4) \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (1a)

C1—C4	1.751 (2)	C7—N1	1.472 (3)
O1—C1	1.352 (3)	N1—C8	1.469 (3)
C6—C7	1.505 (3)		
O1—C1—C2	123.4 (2)	C1—C6—C7	119.1 (2)
O1—C1—C6	116.8 (2)	C6—C7—N1	114.2 (2)
C1—C4—C3	120.0 (2)	C7—N1—C8	113.1 (2)
C1—C4—C5	119.3 (2)	N1—C8—C9	110.1 (2)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (1a)

D—H...A	D—H	H...A	D...A	D—H...A
O1—HO1...N1'	0.90 (3)	1.77 (3)	2.656 (3)	167 (3)
N1—HN1...O1	0.81 (2)	2.46 (2)	3.005 (2)	125 (2)
N1—HN1...N2	0.81 (2)	2.47 (2)	2.910 (2)	115 (1)

Symmetry code: (i) $x, -y, \frac{1}{2} + z$.

Compound (1b)**Crystal data**

$\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2$
 $M_r = 224.310$
 Orthorhombic
Pbca
 $a = 15.9034(8) \text{ \AA}$
 $b = 10.5054(5) \text{ \AA}$
 $c = 16.1559(8) \text{ \AA}$
 $V = 2699.2(2) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.104 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 7440 reflections
 $\theta = 2.5\text{--}25.0^\circ$
 $\mu = 0.075 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Block
 $0.48 \times 0.40 \times 0.34 \text{ mm}$
 Yellow

Data collection

Siemens SMART CCD diffractometer
 ω rotation scans with narrow frames
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.872$, $T_{\max} = 0.985$
 19 817 measured reflections

3558 independent reflections
 1795 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 25.7^\circ$
 $h = -21 \rightarrow 21$
 $k = -14 \rightarrow 10$
 $l = -16 \rightarrow 21$

Refinement

Refinement on F
 $R = 0.048$
 $wR = 0.056$
 $S = 1.569$
 1872 reflections
 154 parameters
 H-atom parameters constrained
 $w = 1/[\sigma_{\text{cs}}(F^2) + 1.05F^2]^{1/2} - |F|$
 $(\Delta/\sigma)_{\text{max}} = 0.0013$

$\Delta\rho_{\text{max}} = 0.17(3) \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15(3) \text{ e } \text{\AA}^{-3}$
 Extinction correction: B-C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
 Extinction coefficient: $0.26(7) \times 10^3$
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. Selected geometric parameters (\AA , $^\circ$) for (1b)

O1—C1	1.348 (2)	N1—C8	1.460 (2)
O2—C2	1.369 (2)	N1—C7	1.463 (3)
O2—C12	1.379 (3)	C6—C7	1.505 (3)
C2—O2—C12	120.9 (2)	O2—C2—C3	125.2 (2)
C7—N1—C8	114.4 (2)	O2—C2—C1	114.4 (2)
O1—C1—C6	118.3 (2)	C1—C6—C7	119.2 (2)
O1—C1—C2	122.2 (2)	N1—C7—C6	115.0 (1)

Table 4. Hydrogen-bonding geometry (\AA , $^\circ$) for (1b)

D—H...A	D—H	H...A	D...A	D—H...A
O1—HO1...N1'	0.92 (3)	1.81 (3)	2.696 (2)	164 (2)
N1—HN1...O1	0.81 (2)	2.61 (2)	3.111 (2)	121 (1)
N1—HN1...N2	0.81 (2)	2.51 (2)	2.894 (3)	111 (1)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$.

Absorption corrections were made using a multi-scan technique (SADABS; Sheldrick, 1996), which in the case of (1b) gave a ratio of $T_{\text{max}}/T_{\text{min}}$ of 1.130 whereas the expected value is 1.011. This difference arises because the method corrects for errors other than absorption. H atoms were kept at calculated positions (C—H = 0.95 \AA) with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the atom to which they were attached, except for the H atoms of the phenolic and imino groups which were refined isotropically.

For both compounds, data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structures: SIR92 (Altomare *et al.*, 1994) and KRYSTAL (Hazell, 1995); program(s) used to refine structures: modified ORFLS (Busing *et al.*, 1962) and KRYSTAL; molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and KRYSTAL; software used to prepare material for publication: KRYSTAL.

Financial support from Nanyang Technological University [grant no. RP18/96(KLE)] is gratefully acknowledged. AH is indebted to the Carlsberg Foundation for the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1230). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
 Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–153.
 Brzezinski, B., Maciejewska, H., Zundel, G. & Kramer, R. (1990). *J. Phys. Chem.* **94**, 528–531.

- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII. Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Hazell, A. (1995). *KRYSTAL. An Integrated System of Crystallographic Programs*. Aarhus University, Denmark.
- Hazell, A., Overgaard, J., Konstmann Lausen, S., Hu, H. & Ee Khoo, L. (1997). *Acta Cryst.* **C53**, 640–641.
- Rospenk, M. & Sobczyk, L. (1989). *Magn. Reson. Chem.* **27**, 445–450.
- Serjeant, E. P. & Dempsey, B. (1979). *Ionization Constants of Organic Acids in Aqueous Solution*. IUPAC Chemical Data Series No. 23. Oxford: Pergamon Press.
- Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area-Detector Data*. University of Göttingen, Germany.
- Shukla, R., Bharadwaj, P. K., Hall, J. V. & Whitmire, K. H. (1994). *Polyhedron*, **13**, 2387–2394.
- Siemens (1995). *SMART and SAINT. Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). **C55**, 248–250

2,5,8-Trioxa-16,20-diazatricyclo[20.4.0.0^{9,14}]-hexacosane-9,11,13,15,20,22,24,26-octaene

TUNCER HÖKELEK,^{a*} ZEYNEL KILIÇ^b AND SELEN BİLGE^b

^aHacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and ^bAnkara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr

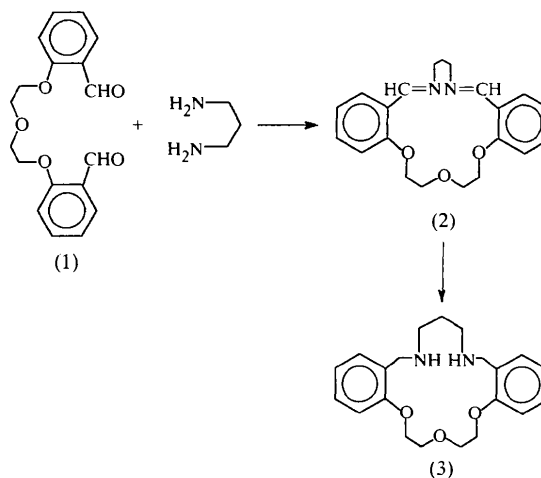
(Received 23 July 1998; accepted 25 September 1998)

Abstract

The title molecule, C₂₁H₂₄N₂O₃, an N₂O₃-type crown compound, is a crystallographically centrosymmetric multidentate Schiff base ligand containing two imine N and three ether O atoms. It has a short C=N imine bond length [1.254 (4) Å] and a narrow C—N—C angle [117.9 (3)°] compared with salicylaldimine and naphthaldimine Schiff bases.

Comment

Macrocyclic Schiff base ligands, such as the 16-membered ring composed of the —O_xN_y— donor type (where *x* = 2, 3 and *y* = 2, 3), have been investigated previously as potential metal-ion-selective reagents (Goodwin *et al.*, 1982; Lindoy *et al.*, 1993). A large number of these investigations has involved the synthetic, thermodynamic and/or structural properties of complex formation of a range of transition metal ions (Adam *et al.*, 1979, 1983; Fenton *et al.*, 1987). Some Schiff base complexes have also been used in catalytic reduction reactions (Tafesh & Weiguny, 1996). In 1983, Adam and co-workers synthesized compound (3), without isolating compound (2), from the reaction of (1) with 1,3-diaminopropane (see Scheme below). We have isolated compounds (2) and (3) separately. The structure determination of the title compound, (2), was undertaken in order to determine the effects of the macrocyclic ring on the C=N imine bond system and to compare the results obtained with those of acyclic salicylaldimine and naphthaldimine Schiff bases.



Since it has two N- and three O-donor atoms in the macrocyclic ring, compound (2) may be a potential metal-ion-selective reagent for transition, alkaline and alkaline earth metal ions. The molecule of (2) (Fig. 1) is crystallographically centrosymmetric and a half molecule occupies the asymmetric unit. The intramolecular distances C1···O2 6.690 (3), N1···O2 5.645 (2) and C3···O2 4.600 (3) Å reflect the size of the hole of the macrocyclic ring. The C1···O2 distance is larger than the N···N distance in the potassium complex of substituted diaza-18-crown-6 (6.253 Å; Gandour *et al.*, 1986). The N1=C3 imine bond is in the same plane as the benzene ring. The torsion angles O1—C10—C11—O2, C10—C11—O2—C11', N1—C2—C1—C2' and C3—N1—C2—C1 are -58.1 (7), -126.0 (4), -73.9 (2) and 127.3 (3)°, respectively [symmetry code: (') 1 - *x*, *y*, $\frac{1}{2}$ - *z*]. All of these correspond to a *gauche* conformation (Hilgenfeld & Saenger, 1982). The Csp³—Csp³ mean bond length is given in the literature as 1.524 (14) Å (Allen *et al.*, 1987) and in (2), the corresponding values are 1.387 (7) and 1.512 (4) Å. The C=N imine bond distance and the C—N—C angle are 1.254 (4) Å and 117.9 (3)°, respectively, which are small compared with values of 1.270 (3) Å and 123.6 (2)° found in 1,8-di(*N*-2-oxyphenylsalicylidene)-3,6-dioxaoctane (Yıldız *et al.*, 1998), 1.313 (8) Å and 122.5 (6)° found in 2-hydroxy-*N*-