C1—N1—C4	110.91 (13)	C6—C5—C51	118.64 (14)
C9—N2—C6	109.00 (12)	C4—C5—C51	115.41 (14)
N1—C1—C10^i	127.69 (13)	N2—C6—C5	126.21 (13)
N1—C1—C2	105.98 (14)	N2—C6—C7	111.76 (13)
C10^i—C1—C2	126.33 (14)	C5—C6—C7	122.02 (13)
C3—C2—C1	108.39 (15)	C8—C7—C6	103.71 (13)
C2—C3—C4	108.53 (14)	C7—C8—C9	103.20 (13)
N1—C4—C5	127.38 (14)	N2—C9—C10	126.31 (14)
N1—C4—C3	106.17 (13)	N2—C9—C8	112.33 (13)
C5—C4—C3	126.44 (14)	C10—C9—C8	121.36 (14)
C6—C5—C4	125.95 (13)	C9—C10—C1^i	126.30 (14)

Symmetry code: (i) $2 - x, -y, -z$.

The pyrrole H atom was located in a difference map and refined using isotropic displacement parameters. Other H atoms were placed in calculated positions and refined using a riding model. The *meso*-butyl chain located at C5 was disordered. The two outer C atoms (C13 and C14) were each refined as disordered over two positions with equal occupancies. H atoms were modelled accordingly.

Data collection: *P*3 (Siemens, 1990). Cell refinement: *P*3. Data reduction: *XDISK* in *SHELXTL-Plus* (Siemens, 1994). Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELX*97.

This work was supported by grants from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Se543/2-4 and /3-1).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1301). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1919–1921

o-Nitrobenzaldehyde Isonicotinoylhydrazone

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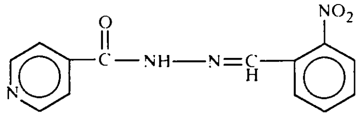
(*Received 26 November 1997; accepted 24 June 1998*)

Abstract

The title compound, $C_{13}H_{10}N_4O_3$, is planar and exists in the keto tautomeric form. The crystal packing is stabilized by weak intermolecular hydrogen bonds involving the N3···N4 and C2···O1 atoms of neighbouring molecules.

Comment

Photochromism based on tautomerism by hydrogen transfer in anils, *aci*-nitro and related compounds has been the subject of extensive study (Chichibabin *et al.*, 1925; Ellam *et al.*, 1974; Dürr & Bouas-Laurent, 1990; Kimura *et al.*, 1993; Hadjoudis, 1994; Lambi *et al.*, 1995). Although the title compound has been prepared and its photochromic properties described (Ellam *et al.*, 1974), its crystal structure has not been reported. Hence, we report herein the crystal structure of *o*-nitrobenzaldehyde isonicotinoylhydrazone, (I).



(I)

The N2—C7 [1.264 (3) Å] and N2—N3 [1.373 (3) Å] distances correspond to N=C double and N—N single bonds, respectively. These are comparable to those in 2,2′-azinodimethyldiphenol [1.285 (7) and 1.386 (9) Å; Xu *et al.*, 1994] and *p*-nitrobenzaldehyde nicotinoylhydrazone monohydrate [1.274 (2) and 1.376 (2) Å; Lu *et al.*, 1996]. The C8=O3 double bond distance [1.212 (3) Å] falls within the normal range for C=O double bonds (Lu *et al.*, 1996) suggesting that the molecule is in the keto form. The molecule is planar except for the nitro group [torsion angle O1—N1—C1—C2 −38.9 (4)°]. An intramolecular hydrogen bond exists between C7 and O2 [C7···O2 2.850 (3) Å], while weak intermolecular N3—H3*A*···N4($1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$) [3.101 (3) Å] and C2—H2···O1($2 - x, -1 - y, 1 - z$)

[3.297 (4) Å] hydrogen bonds exist. The hydrogen-bonding scheme is very different from that found in *p*-nitrobenzaldehyde nicotinoylhydrazone monohydrate, where a molecule of water of crystallization is extensively involved (Lu *et al.*, 1996). Also, the hydrogen-bonding scheme is different from that found in *p*-nitrobenzaldehyde isonicotinoylhydrazone (Fun *et al.*, 1997).

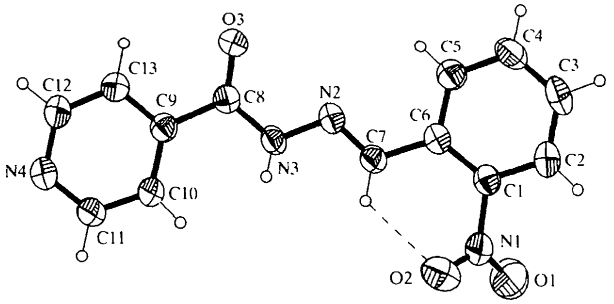


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I) at the 50% probability level. H atoms are drawn as circles of an arbitrary radius.

Experimental

The title compound was synthesized by refluxing *o*-nitrobenzaldehyde with stoichiometric quantities of isonicotinoyl hydrazine in an ethanol solution for 3 h. Diffraction quality crystals were obtained by recrystallization from ethanol.

Crystal data

$C_{13}H_{10}N_4O_3$
$M_r = 270.25$
Monoclinic
$P2_1/c$
$a = 7.4860$ (4) Å
$b = 10.889$ (1) Å
$c = 15.456$ (1) Å
$\beta = 94.916$ (6)°
$V = 1255.3$ (2) Å^3
$Z = 4$
$D_x = 1.430$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4$–13°
$\mu = 0.106$ mm^{-1}
$T = 300$ (2) K
Parallelepiped
0.36 × 0.18 × 0.18 mm
Pale orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.951$, $T_{\max} = 0.981$
4906 measured reflections
2462 independent reflections

1432 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.063$
$\theta_{\max} = 25.97°$
$h = -9 \rightarrow 0$
$k = -13 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections frequency: 60 min intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.145$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.216$ e Å^{-3}
$\Delta\rho_{\min} = -0.205$ e Å^{-3}

$S = 0.990$
2462 reflections
221 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—N1	1.206 (3)	C1—C6	1.389 (3)
O2—N1	1.216 (3)	C2—C3	1.367 (4)
O2—C7	2.850 (3)	C2—O1^{ii}	3.297 (4)
O3—C8	1.212 (3)	C3—C4	1.373 (4)
N1—C1	1.461 (3)	C4—C5	1.375 (4)
N2—C7	1.264 (3)	C5—C6	1.386 (3)
N2—N3	1.373 (3)	C6—C7	1.466 (3)
N3—C8	1.354 (3)	C8—C9	1.503 (3)
N3—N4^{i}	3.101 (3)	C9—C13	1.378 (3)
N4—C11	1.329 (3)	C9—C10	1.384 (3)
N4—C12	1.334 (3)	C10—C11	1.367 (4)
C1—C2	1.380 (4)	C12—C13	1.382 (4)
O1—N1—O2	122.9 (3)	C5—C6—C7	120.1 (2)
O1—N1—C1	118.3 (2)	C1—C6—C7	124.2 (2)
O2—N1—C1	118.7 (2)	N2—C7—C6	118.9 (2)
C7—N2—N3	116.0 (2)	O3—C8—N3	123.3 (2)
C8—N3—N2	118.3 (2)	O3—C8—C9	121.1 (2)
C11—N4—C12	116.0 (2)	N3—C8—C9	115.6 (2)
C2—C1—C6	123.3 (2)	C13—C9—C10	117.3 (2)
C2—C1—N1	115.5 (2)	C13—C9—C8	117.8 (2)
C6—C1—N1	121.2 (2)	C10—C9—C8	124.8 (2)
C3—C2—C1	118.8 (3)	C11—C10—C9	119.5 (3)
C2—C3—C4	119.9 (3)	N4—C11—C10	124.2 (2)
C3—C4—C5	120.4 (3)	N4—C12—C13	123.9 (3)
C4—C5—C6	121.9 (3)	C9—C13—C12	119.0 (2)
C5—C6—C1	115.7 (2)		

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $2 - x, -1 - y, 1 - z$.

Data collection: *CAD*-4 *VAX*/*PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX*/*PC*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

We thank the State Science and Technology Commission and the National Nature Science Foundation of China for a major key research project and the Malaysian National Science Council for R&D (09-02-03-0004) for supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1206). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1921–1923

Two Macrocyclic Azacrown Ethers

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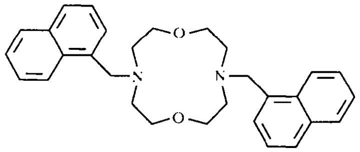
(Received 21 April 1998; accepted 28 May 1998)

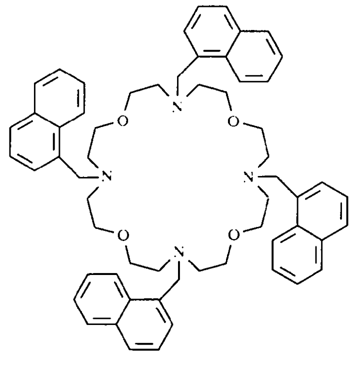
Abstract

The structures of two macrocyclic azacrown ethers, namely, 4,10-bis(1-naphthylmethyl)-1,7-dioxa-4,10-diazacyclododecane, $C_{30}H_{34}N_2O_2$, and 4,10,16,22-tetrakis(1-naphthylmethyl)-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetracosane as its bis(methylene dichloride) solvate, $C_{60}H_{68}N_4O_4.2CH_2Cl_2$, have been determined by single-crystal diffractometry. Both molecules are characterized by a cavity suitable for hosting cationic guests.

Comment

Over the past few years, the design of macrocyclic ligands has received increasing attention in view of the photochemical and photophysical properties characterizing the supramolecular adduct obtained by complexing the macrocycle with an appropriate electron acceptor (Lehn, 1995). We report here the structures of two diazacrown ethers, namely, 4,10-bis(1-naphthylmethyl)-1,7-dioxa-4,10-diazacyclododecane, (I), and 4,10,16,22-tetrakis(1-naphthylmethyl)-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetracosane as its bis(methylene dichloride) solvent, (II). These compounds were synthesized as part of a study of macrocycles complexing metal and ammonium cations (see, for example, Quici *et al.*, 1996).


(I)


(II)

Both compounds crystallize in a centrosymmetric space group with half a molecule in the asymmetric unit. In (I), the ether ring forms a cavity with transannular O1···O1^i and N4···N4^i distances of 4.231 (2) and 4.504 (2) Å, respectively. The shortest transannular contact is O1···C6 at 3.822 (2) Å. Here and elsewhere, the superscript refers to the symmetry-centre operation which completes the molecule, *i.e.* $-x$, $-y$, $1-z$. The ring adopts a chair–chair conformation with a dihedral angle of 6.0 (2)° between the plane containing atoms N4, C5 and C6, and the plane containing atoms O1, C2 and C3. The torsion angles of this ring are reported in Table 1. The least-squares plane of the naphthalene system forms a dihedral angle of 89.54 (8)° with the plane formed by atoms N4, C5 and C6. The geometric parameters of (I) were compared with those of a similar compound where the naphthalene is substituted by a benzene ring (Mendez *et al.*, 1992). The monoprotonated form of that compound proved suitable for complexing neutral guests such as alcohols. No relevant differences between (I) and that compound were found.

The structure of (II), which contains two CH_2Cl_2 solvent molecules, was determined at T = 245 K because at room temperature the crystals lose the solvent and collapse within a few days. The molecule is characterized by a large cavity having the following transannular distances: N1···N1^i = 9.619 (3), N7···N7^i = 8.313 (2), O4···O4^i = 8.129 (2) and O10···O10^i = 6.216 (2) Å. The shortest transannular contact is C9···C9^i of 5.266 (4) Å. The conformation of the macrocycle is determined by a sequence of essentially *trans* and *gauche* torsion angles; the torsion angles that significantly de-