Instrumental Achievements

Crystal Structure of 2,6-Dioxa-14,18-diazatricyclo[18,4,0,$0^{7,12}$]-tetracosa-7,9,11,20,22,24(1)-hexaene

Tuncer HÖKELEK,*† Nurcan AKDURAN,* Elif Ece KAYA, and Zeynel KILIÇ****

**Department of Physics, Hacettepe University, 06532 Beytepe-Ankara, Turkey*
***Department of Chemistry, Ankara University, 06100 Tandoğan-Ankara, Turkey*

(Received December 2, 1999; Accepted April 28, 2000)

Macrocyclic multidentate N_2O_2 donor-type ligands have been investigated previously as potential metal-ion-selective reagents.[1,2] A series of these investigations have involved the synthetic, thermodynamic and structural properties of selective complex formation of a number of transition metal ions.[3] There are only a few reports about the structures of the free macrocyclic multidentate N_2O_2 and N_2O_3 donor-type ligands.[4-6]

The title compound was prepared from the reduction of the reaction product of 1,5-bis(2-formylphenyl)-1,5-dioxapentane (2.84 g, 0.01 mol) and 1,3-diaminopropane (0.74 g, 0.01 mol) by $NaBH_4$ (2.00 g, 0.05 mol) in THF–MeOH mixture (1:1). The residue was dissolved in $CHCl_3$–light petroleum (1:1) and set aside for crystallization at ambient temperature [m.p. 91˚C and yield 1.4 g (49%)].

Table 1 Crystal and experimental data

Formula: $C_{20}H_{26}N_2O_2$	
Formula weight = 326.44	
Crystal system: monoclinic	
Space group: $P2_1/a$	$Z = 4$
a = 9.593(1)Å	
b = 18.143(1)Å	
c = 10.581(1)Å	
β = 95.23(1)˚	
V = 1834.0(1)Å^3	
D_x = 1.182 g/cm^3	
D_m = 1.165 g/cm^3	
μ(Cu K$_\alpha$) = 0.57 mm^{-1}	
T = 293 K	
F(0 0 0) = 704	
Colorless	
Crystal size: 0.20 × 0.25 × 0.30 mm	
λ(Cu K$_\alpha$) = 1.54184Å	
$2\theta_{max}$ = 148.7˚	
R = 0.041	
wR = 0.048	
$(\Delta/\sigma)_{max}$ = 0.01	
$(\Delta\rho)_{max}$ = 0.16 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.13 eÅ^{-3}	
No. of reflections used = 2252	
No. of parameters=301	
Goodness-of-fit=0.94	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS software	
Structure determination: MolEN	
Treatment of hydrogen atoms: difference synthesis and geometric calculation	
Refinement: full matrix	

† To whom correspondence should be addressed.

The structure determination was carried out in order to estimate the relative macrocyclic ring hole size of the molecule. The intramolecular distances N1···O1 4.057(3) and N2···O2 5.058(3)Å may reflect the size of the hole of the macrocyclic ring. When only the N and O atoms are taken into account, the mean N···O distance is 4.558(3)Å. A least-squares plane defined by O1, O2, N1 and N2 has maximum deviations to either side of the plane of 0.338(2) (O1), –0.310(2) (O2), 0.383(2) (N1) and –0.412(2) (N2). The relative macrocyclic inner-hole size, estimated as twice the mean distance of the donor atoms from their centroid, is approximately 1.57 Å, using the 'modified covalent radii' of the N sp^2 (0.66 Å) and O sp^3 (0.76 Å) atoms as in the literature method.[2] There is an intramolecular hydrogen bond between N1 and N2 atoms [N···N

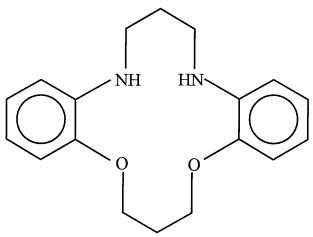

Fig. 1 Chemical structure.

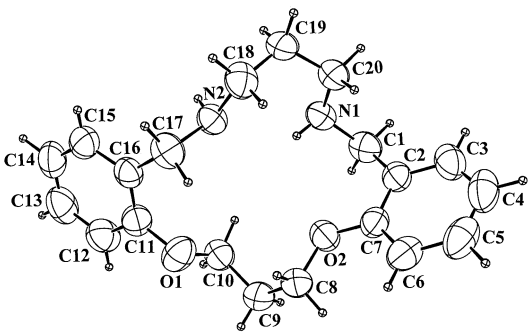

Fig. 2 Molecular structure of the title compound with atom-numbering scheme. The thermal ellipsoids are drawn at the 20% probability level.

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	B_{eq}/Å^2
C1	0.6585(2)	0.1741(1)	0.6298(2)	5.20(5)
C2	0.7842(2)	0.1376(1)	0.6978(2)	4.48(4)
C3	0.7791(3)	0.1122(1)	0.8204(2)	5.45(5)
C4	0.8899(3)	0.0765(2)	0.8852(2)	6.42(6)
C5	1.0103(3)	0.0662(2)	0.8287(3)	6.88(7)
C6	1.0200(3)	0.0912(2)	0.7065(3)	6.29(6)
C7	0.9075(2)	0.1264(1)	0.6417(2)	4.86(5)
C8	0.9199(2)	0.0999(1)	0.4240(2)	5.17(5)
C9	0.9478(2)	0.1381(2)	0.3031(2)	5.89(6)
C10	0.8289(2)	0.1836(1)	0.2439(2)	5.51(5)
C11	0.6092(2)	0.1556(1)	0.1240(2)	4.39(4)
C12	0.6053(1)	0.2213(1)	0.0569(2)	5.47(5)
C13	0.4984(3)	0.2335(2)	-0.0373(2)	6.58(6)
C14	0.3942(3)	0.1832(2)	-0.0625(2)	7.10(7)
C15	0.3964(3)	0.1194(2)	0.0077(2)	6.08(6)
C16	0.5025(2)	0.1034(1)	0.1018(2)	4.58(4)
C17	0.5031(2)	0.0341(1)	0.1791(2)	5.22(5)
C18	0.3430(2)	0.0793(1)	0.3284(2)	5.02(5)
C19	0.3264(2)	0.0945(1)	0.4667(2)	5.19(5)
C20	0.4266(2)	0.1502(1)	0.5299(2)	5.45(5)
N1	0.5675(2)	0.12089(9)	0.5591(2)	4.30(4)
N2	0.4745(2)	0.0422(1)	0.3119(2)	4.55(4)
O1	0.7148(2)	0.13482(9)	0.2125(1)	5.45(3)
O2	0.9200(2)	0.15411(9)	0.5215(2)	5.92(4)

$B_{eq} = (8\pi^2/3)\,\Sigma_i\Sigma_j U_{ij}\, a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Bond distances (Å) and angles (°)

C1-C2	1.500 (3)	C11-C16	1.398 (3)
C7-C2	1.387 (3)	C16-C17	1.500 (3)
C7-O2	1.383 (3)	C17-N2	1.464 (3)
O2-C8	1.425 (3)	N2-C18	1.453 (3)
C8-C9	1.501 (4)	C18-C19	1.512 (3)
C9-C10	1.498 (3)	C19-C20	1.509 (3)
C10-O1	1.424 (3)	C20-N1	1.459 (3)
O1-C11	1.386 (2)	N1-C1	1.460 (3)
C9-C10-O1	107.1(2)	C1-N1-C20	111.5(2)
C16-C11-O1	114.4(2)	C12-C11-O1	124.9(2)
C11-O1-C10	119.6(2)	C19-C20-N1	112.9(2)
O2-C8-C9	108.1(2)	C7-C2-C1	122.7(2)
C18-C19-C20	115.6(2)	C2-C1-N1	111.8(2)
C17-C16-C11	120.6(2)	O2-C7-C2	119.3(2)
C6-C7-O2	119.7(2)	C18-N2-C17	113.8(2)
N2-C17-C16	116.6(2)	C8-C9-C10	115.0(2)
C7-O2-C8	114.8(2)	N2-C18-C19	111.7(2)

Table 4 Torsion angles (°)

C11-O1-C10-C9	-159.9(2)	C1-N1-C20-C19	-175.2(2)
O1-C10-C9-C8	-62.0(3)	N1-C20-C19-C18	-75.5(3)
C10-C9-C8-O2	-72.5(3)	C20-C19-C18-N2	67.5(3)
C9-C8-O2-C7	-174.7(2)	C19-C18-N2-C17	-173.1(2)
C2-C1-N1-C20	160.6(2)	C18-N2-C17-C16	55.5(3)

3.041(3) and H2··N1 2.40(2)Å]. The configuration of the macrocyclic ring is given by the torsion angles (Table 4).

The positions of H51, H61, H121, H141 and H151 atoms were calculated geometrically 0.95 Å from the corresponding atoms, and a riding model was used in the refinement process. The remaining ones were obtained from the difference map and refined isotropically.

References

1. L. F. Lindoy, in "*Process in Macrocyclic Chemistry*", **1987**, Vol. 3, Wiley, New York, 53.
2. K. R. Adam, A. J. Leong, L. F. Lindoy, H. C. Lip, B. W. Skelton, and A. H. White, *J. Am. Chem. Soc*., **1983**, *105*, 4645.
3. K. Henrick, L. F. Lindoy, M. McPartlin, P. A. Tasker, and M. P. Wood, *J. Am. Chem. Soc*., **1984**, *106*, 1641.
4. P. S. K. Chia, A. Ekstrom, I. Liepa, L. F. Lindoy, M. McPartlin, S. V. Smith, and P. A. Tasker, *Aust. J. Chem*., **1991**, *44*, 737.
5. T. Hökelek, Z. Kılıç, and S. Bilge, *Acta Crystallogr*., **1999**, *C55*, 248.
6. T. Hökelek, Z. Kılıç, and S. Bilge, *Acta Crystallogr*., **1999**, *C55*, 381.