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STRUCTURE AND CONFORMATIONAL ANALYSIS OF A MACROCYCLIC LIGAND: [24, 26-DIOXO-3,6,14,17-TETRAAZAPENTACYCLO (21.0.1 1,19 .1 3,6 .1 8,12 .1 14,17)HEXACOSAN-1(23),8(25),9,1 HEXAENE]

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STRUCTURE AND CONFORMATIONAL ANALYSIS OF A MACROCYCLIC LIGAND: [24, 26-DIOXO-3,6,14,17-TETRAAZAPENTACYCLO (21.0.$1^{1,19}$.$1^{3,6}$.$1^{8,12}$.$1^{14,17}$)HEXACOSAN-1(23),8(25),9,11,19,21-HEXAENE]†

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24,26-Dioxo-3,6,14,17-tetraazapentacyclo((21.0.$1^{1,19}$.$1^{3,6}$.$1^{8,12}$.$1^{14,17}$) hexacosan-1(23),8(25),9,11,19,21-hexaene, $C_{22}H_{24}N_4O_2$, FW = 376.45, monoclinic, $P2_1/n$, a = 11.144(2) Å, b = 6.395(1) Å, c = 13.562(3) Å, β = 95.81(1)°, V = 961.5(3) Å^3, Z = 2, D_{col} = 1.300 Mg/m^3, μ = 0.685 mm^{-1}, F(000) = 400, λ (CuKα) = 1.5418 Å final R1 and wR2 are 0.0409 and 0.1547, respectively. The macro ligand consists of two phenyl rings and two five-membered rings forming the walls of the central cavity which has roughly a square cross-section. The orientation of the phenyl ring is antiperiplanar and approximately perpendicular to the diazacyclopentanone ring which adopts envelope conformation. The molecules are stabilized by C-H…O and C-H…π types of intermolecular interactions in addition to van der Waals forces.

Keywords: macro ligand; diazacyclopentanone; crystal structure; conformation; hydrogen bonding

INTRODUCTION

Macrocyclic ligands are closed system compounds containing a minimum of nine atoms with at least three donor atoms [1]. They are two types: The

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first type are those systems which chiefly contain nitrogen, sulphur, phosphorus, and arsenic as donors and which tend to have considerable affinity for transition and other heavy metals but form less stable complexes with ions of the alkali and alkaline earth metals. The second type consists of a large group of cyclic compounds incorporating numbers of ether functions as donors. Such crown polyethers show strong complexing ability towards alkali and alkaline earth ions, but their tendency to coordinate to transition metal ions is less.

There are a number of factors affecting the formation and thermodynamic stabilities of these ion-macrocycle complexes, and thus there exist unusual opportunities for the synthesis of macrocyclic molecules which exhibit a high degree of selectivity in metal binding. Their hydrophobic exteriors allow them to solubilize ionic substances in nonaqueous solvents and in membrane media [2].

Macrocylic ligands are used as models for protein-metal binding sites in a substantial array of metalloproteins in biological systems—as synthetic ionophores, as models to study the magnetic exchange phenomenon, as therapeutic reagents in chelate therapy for the treatment of metal intoxication, as cyclic antibiotics actions to specific metal complexation, and to the guest-host interactions and in catalysis [3].

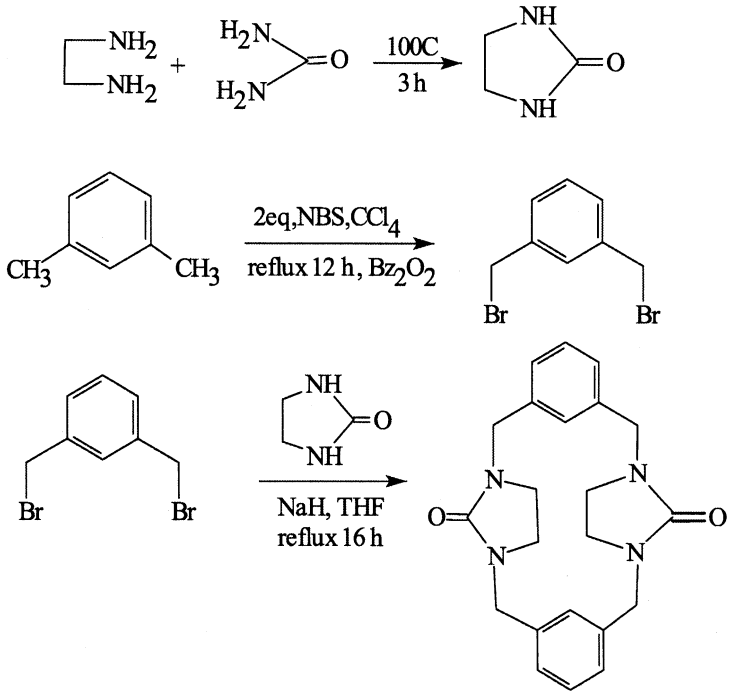
Macrocyclic ligands have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid-liquid or solid-solid phase transfer reactions, dissolution in apolar solvents of metal and organic salts, preparation of ionselective electrodes, isotope separation, and in the understanding of some natural processes through mimicry of metalloenzymes.

Compounds containing nitrogen donor atoms have been used as models to explain metal ion–macrocycle reactions in biological systems [4]. The azacyclophanes show high substrate specificity due to their intrinsic geometrical requirements for host-guest interactions, which give them the potential to be the superior enzyme models [4]. Due to the above said importance, the macrocylic ligand [24,26-dioxo-3,6,14,17-tetraazapentacyclo ($21.0.1^{1,19}.1^{3,6}.1^{8,12}.1^{14,17}$)hexacosan-1(23), 8(25),9,11,19,21-hexaene], which possesses both the nitrogen and the ether group, was structurally characterized.

EXPERIMENTAL

Synthesis

Equal moles of ethylene diamine and urea were refluxed for 3 h and allowed to cool. The product imidazoline-2-one was crystallized from benzene. A fresh N-bromo succinimide was added to m-xylene in CCl_4. This mixture



SCHEME 1 Synthetic route for the macro ligand.

was refluxed and added few milligrams of benzoyl peroxide, which was then cooled and the precipitate obtained was washed. A solution of diazone (in THF) was added to a suspension of sodium hydride (in THF), refluxed, and cooled. The dibromide (in THF) solution was added to the reaction mixture periodically at nitrogen atmosphere in room temperature. This mixture was refluxed for 16 h and cooled. Dilute hydrochloric acid was added to the mixture and the precipitate was washed with water. The cyclophane was recrystallized from methylene chloride (Scheme 1).

X-Ray Data Collection

Transparent parallelopiped-shaped crystal of dimension $0.3 \times 0.22 \times 0.28$ mm was chosen for the intensity data collection on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated CuKα ($\lambda = 1.5418$ Å) radiation. Accurate unit cell parameters were obtained from 25 reflections in the range $15 \leq \theta \leq 25°$ from least-squares refinement. The intensities were measured to a maximum θ of 72.37° by $\omega/2\theta$ scan mode. Three standard reflections monitored for every hundred reflections

for intensity check showed little or no decay ($< 1\%$) throughout data collection. Out of 1973 ($R_{int} = 0.0183$) independent reflections collected, 1813 reflections with $I \geq 2\sigma(I)$ were used for structure analysis. The intensities were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods using the program SHELXS97 [5] and was refined on F^2 by full-matrix least-squares procedures using the program SHELXL97 [6]. The nonhydrogen atoms were refined anisotropically and all the hydrogens were identified from the difference Fourier map. The final cycle of refinement converged to $R1 = 0.0409$ and $wR2 = 0.1547$ for the observed reflections. The geometrical calculations and the figures were done by using the programs PLATON [7] and ZORTEP [8]. The crystal data and the other relevant parameters are given in Table 1. The atomic coordinates with their equivalent isotropic displacement factors for nonhydrogen atoms are presented in Table 2.

TABLE 1 Crystal Data

Empirical formula	$C_{22}H_{24}N_4O_2$
Formula weight	376.45
Temperature	293(2) K
Wavelength	1.5418 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a	11.144(2) Å
b	6.395(1) Å
c	13.562(3) Å
β	95.81(1)°
Volume	961.5(3) $Å^3$
Z, Calculated density	2, 1.300 Mg/m^3
Absorption coefficient	0.685 mm^{-1}
F(000)	400
Theta range for data collection	5.41 to 72.37°
Index ranges	$0 \leq h \leq 13$
	$0 \leq k \leq 7$
	$-16 \leq 1 \leq 16$
Reflections collected/unique	1973/1813 [R(int) = 0.0183]
Completeness to $\theta = 72.37$	95.5%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1813/0/176
Goodness-of-fit on F^2	1.113
Final R indices [$1 > 2\sigma(I)$]	$R1 = 0.0409$, $wR2 = 0.1547$
R indices (all data)	$R1 = 0.0530$, $wR2 = 0.1665$
Extinction coefficient	0.053(5)
Largest diff. peak and hole	0.217 and −0.216e. $Å^{-3}$

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) Involving Nonhydrogen Atoms

Atom	x	y	z	*U(eq)
C1	8236(2)	7735(3)	6422(1)	52(1)
C2	10593(2)	1979(4)	2920(2)	64(1)
N3	9516(1)	2341(3)	3402(1)	61(1)
C4	8861(2)	721(4)	3842(2)	69(1)
C5	7811(2)	1876(4)	4215(2)	67(1)
N6	7892(1)	3925(2)	3794(1)	56(1)
C7	7038(2)	5558(4)	3897(1)	59(1)
C8	7091(2)	6514(3)	4924(1)	50(1)
C9	6045(2)	7232(3)	5275(2)	61(1)
C10	6083(2)	8164(4)	6197(2)	68(1)
C11	7172(2)	8419(3)	6765(2)	62(1)
C12	8903(2)	4170(3)	3328(1)	47(1)
O13	9202(1)	5751(2)	2912(1)	69(1)
C14	8182(2)	6770(3)	5506(1)	50(1)}

*U(eq) = (1/3)Σ_i Σ_j a_i*a_j* $\mathbf{a_i.a_j}$

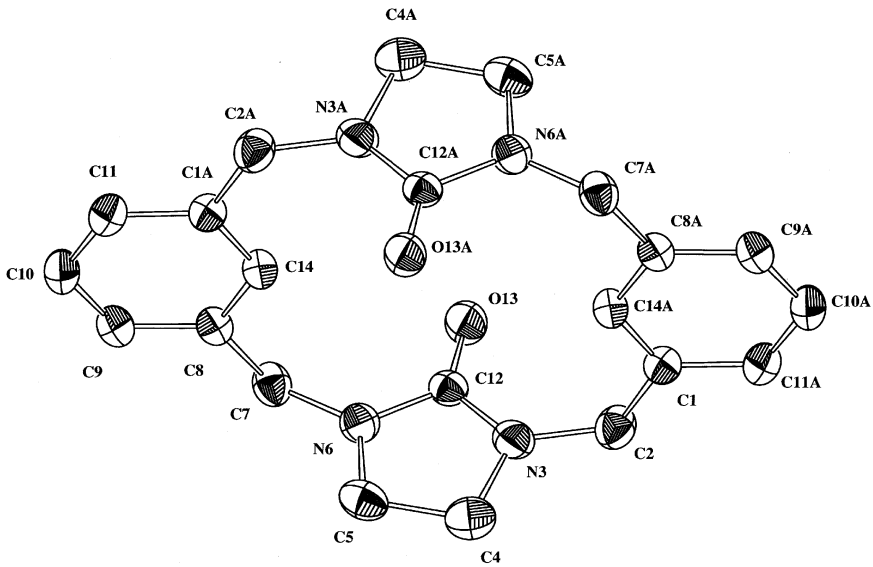


FIGURE 1 ZORTEP plot of the macro ligand showing the thermal displacement ellipsoids at 30% probability level.

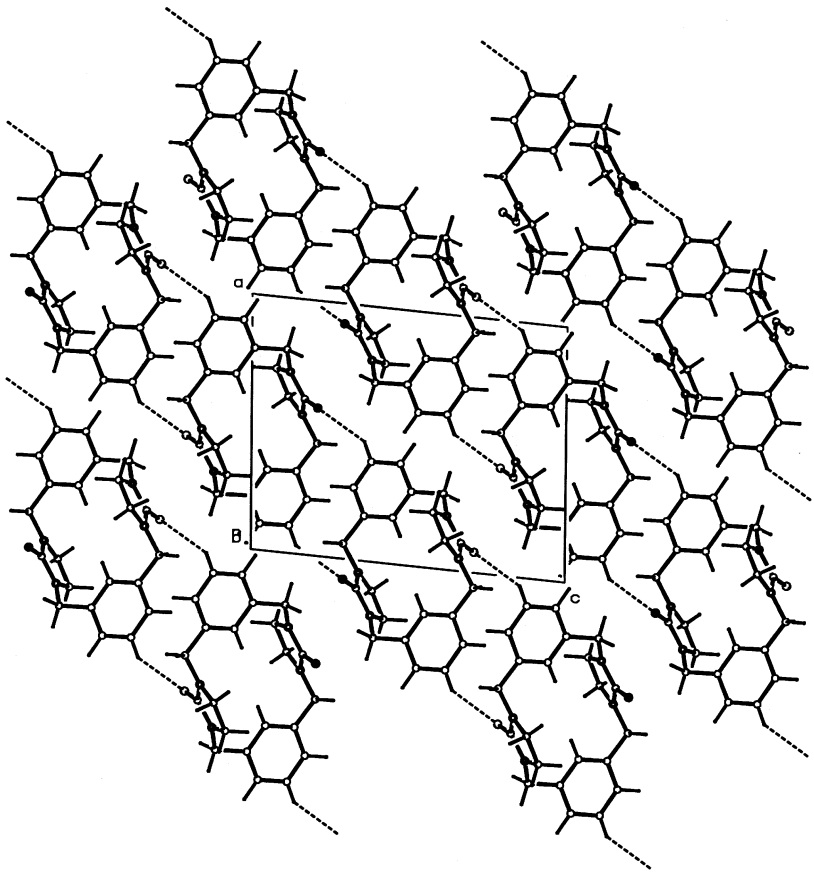


FIGURE 2 Packing of the molecules viewed down b-axis (dotted lines indicate the hydrogen bonds).

DISCUSSION

The perspective view of the molecule is shown in Figure 1. Only one half molecule is present in the asymmetric unit, and the unit cell has two molecules. The half of the molecule is related to the other half through its inversion center. The macro ligand consists of two phenyl rings and two five membered rings forming the walls of the central cavity. The bond lengths around this macrocyclic ring structure are comparable with the literature values [9,10].

The molecule has roughly a square cross-section, and the size of the cavity is approximately $4.96 \times 5.16\,\text{Å}^2$ measured between two parallel

TABLE 3 Possible Nonbonded Interactions (Hydrogen Bonds)

Donor-H . . . Acceptor	d(D-H)Å	d(D . . . A)Å	d(H . . . A)Å	< (DHA)°
C10 −H10 . . . O13^{i}	0.99(3)	3.357(3)	2.50(3)	144(2)
C5 −H5B . . . O13^{ii}	1.03(3)	3.544(3)	2.84(2)	126(2)
C4 −H4A . . . O13^{iii}	1.06(3)	3.454(3)	2.65(3)	132(2)
C7 −H7A . . . Cg^{iv}	1.00(2)	3.777(1)	3.03(1)	132(1)

Cg, Centroid of the diazacyclopentanone ring.

Equivalent positions: i), x−1/2, −y+1/2, +z+1/2; ii), −x+1/2+1, +y−1/2, −z+1/2; iii), x, +y−1, +z; iv), 3/2−x, 1/2+y, 1/2−z.

atoms of the molecule. Any metal ion introduced may be caught in the cavity of this macro ligand. Normally the orientations of the phenyl rings can be described as synperiplanar, synclinal, antiperiplanar, and anticlinal depending on the dihedral angle about the bond connecting the two rings or angle between the planes [11]. In this molecule the orientation of the phenyl rings is antiperiplanar as can be seen from the angle between the planes [180.0(1)°].

The diazacyclopentanone ring adopts envelope conformation with C4 atom deviating from the best plane by 0.152(2) Å. This is also confirmed by the asymmetry parameters which stand out to be $q_2 = 0.0943$ and $\varphi_2 = 40.40$ [12]. The phenyl ring is planar and approximately perpendicular to the diazacyclopentanone ring with the orientation angle of 89.19(9)°.

The C10 atom in the phenyl ring forms C-H . . . O type of intermolecular hydrogen bond with O13 atom of the diazacyclopentanone ring, and the C7 atom makes C-H . . . π intermolecular interaction with the phenyl ring. These interactions pack the molecule in the crystal in such a way that they are arranged in a linear polymer fashion (Fig. 2). Other than this the molecules are also stabilized by many C-H . . . O type of intermolecular interactions in addition to van der Waals forces (Table 3).

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