Synthesis of a new macrocyclic compound and its self-assembly

PAN, Zhi-Quan[a,b,c](潘志权) **LUO, Qin-Hui**[*,a,c](罗勤慧) **LONG, De-Liang**[c](龙德良)
CHEN, Jiu-Tong[c](陈久桐)

[a] *Coordination Chemistry Institute and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, Jiansu 210093, China*

[b] *Wuhan Institute of Chemical Technology, Wuhan, Hubei 430073, China*

[c] *Fuzhou State Key Laboratory of Structure Chemistry, Fuzhou, Fujian 350002, China*

A new macrocyclic compound has been synthesized by condensation of pyridine-1-oxide-2, 6-dialdehyde with diethylenetriamine. The self-assemly behaviours were studied by X-ray diffraction. The results show that the self-assembly were controlled by intermolecular hydrogen bonds and π-π stacking effects.

Keywords Macrocycle, self-assembly, supramolecule

There has been a great deal of interests in "short-strong" or "low-barrier" hydrogen bonds and π-π interactions in recent years.[1] DeSantis and co-workers predicted a roughly planar structure for cyclopeptides made up of *D* and *L* amino acids.[2] A lot of tube-shaped structures with nanometer dimension have been constructed.[3-8] But only a few papers have been presented for Schiff-base macrocyclic molecules to construct nanotubes through molecular self-assembly.[9,10] We synthesized a macrocyclic compound ($L \cdot 4H_2O$) by (2 + 2) condensation of pyridine-1-oxide-2,6-dialdehyde (o-dfp) with diethylenetriamine (deta).[11] The molecular stacking forms tube-shaped structure by intermolecular hydrogen bonds. A three-dimensional layer structure in crystal was obtained by molecular self-assembly. The structural features in solid state are dictated by directional hydrogen bonding and π-π interaction. Although some of the ring-contracted forms in the presence of and the absence of metal ions[12-15] have been reported for Schiff base macrocycles, there are no hydrogen bonds existing in the molecules.

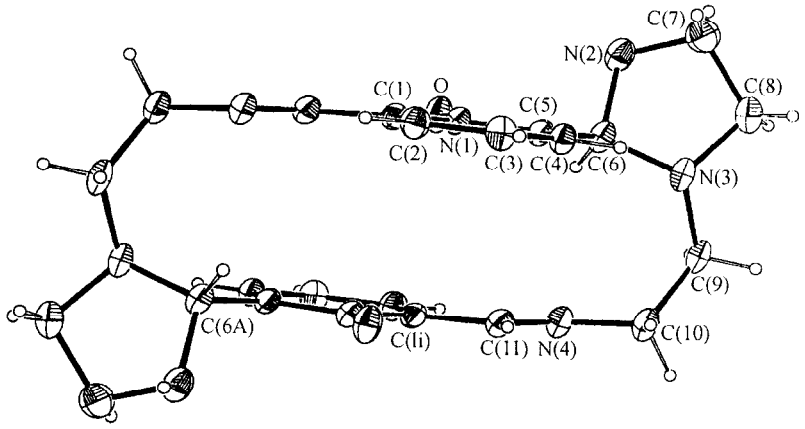

Fig. 1 A perspective view of macrocyclic compound L.

Received July 13, 1999; accepted September 24, 1999.

Project supported by the National Natural Science Foundation of China (No. 2957106) and the Foundation of Department of Education (No. 96028424).

A decrease in the ring size from 24- to 18- membered ring is displayed here, which was demonstrated by X-ray crystal analysis[16] (Fig. 1). Each molecule contains a symmetry centre and two chiral carbon atoms (C(6), C(6A)) at symmetric site. The two pyridine rings are parallel each other with a dihedral angle $0 \pm 0.12°$, and both are nearly perpendicular to macrocyclic plane with angles of 91.8°. The pyridine ring and oxygen atom of pyridine oxide are coplanar with the maximum deviation of 0.0007 nm. The approximate planes of imidazole rings are vertical to the pyridine plane. The distance of 0.324 nm between two pyridine rings shows a intramolecular π-π interaction which increases the stability of imidazole rings.

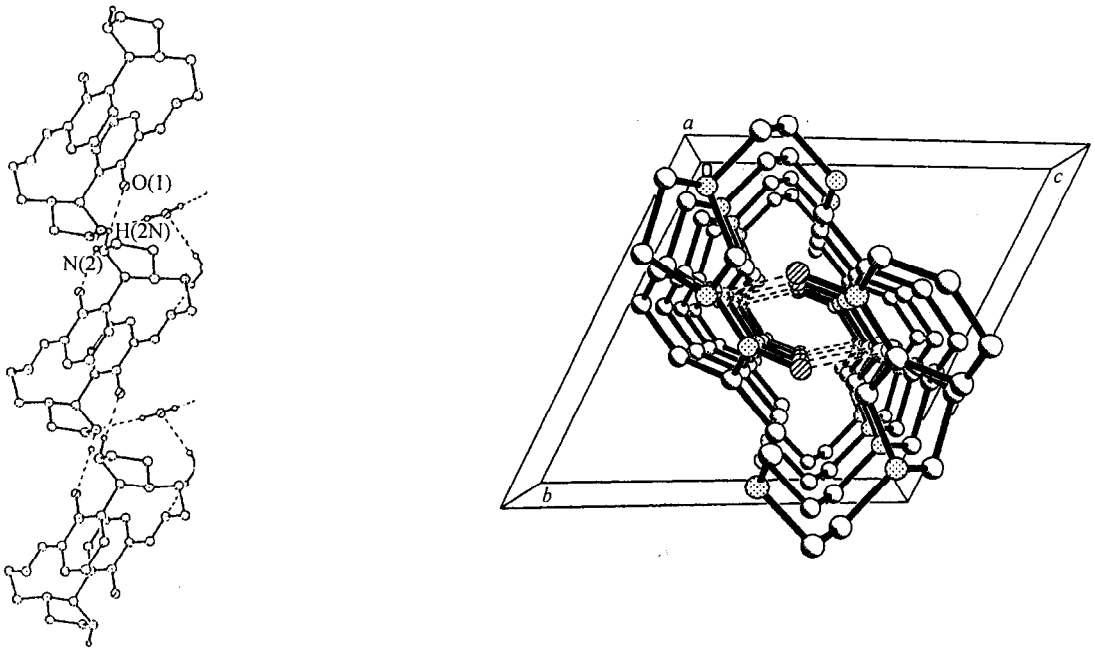

Fig. 2 Molecular stacking diagram of macrocycle showing one-dimensional tubular structure. Hydrogen-bonding interaction is shown with dotted lines.

Fig. 2 shows a one-dimensional tube-shaped structure, which is controlled by directional hydrogen bonding. Because there are hydrogen atoms attached to nitrogen in the contracted rings oriented at a right angle to the aromatic rings which contain the strong electron donors in proper position. The intermolecular hydrogen bonds can be formed between stacking rings. Each macrocycle is linked by intermolecule hydrogen bonding between the hydrogen atoms of imine at imidazole ring and oxygen atoms of N-oxide at the nearest macrocyclic molecule (N(Im)—H···O(Py)). In addition, intermolecule hydrogen bonding also involves the hydrogen and oxygen atoms of two waters as well as nitrogen atoms of imine group N(2) in one molecule and N(4) in an adjacent molecule to it (Fig. 2b). The average distance of hydrogen bonding is 0.2946(3) nm, which indicates that there is a strong interaction between two macrocycles. The lengths and angles of hydrogen bonds are listed in Table 1. To optimize hydrogen bonding interaction, the macrocycle planes are parallel and are ellipsed with respect to one another, the cavities of macrocycles form inclined tubular structure, the angle between the tube and the macrocyclic planes is about 57.30°. The distance between centres of two adjacent macrocyclic planes is about 0.86969 nm. The cross section area of the tube is about 0.326×0.800 nm^2.

Table 1 Bond lengths (nm) and angles (°) of hydrogen bonds

Hydrogen bond*	H···X	Y—H···X	Angle
O(1)(H(1B)···O(2) $1	0.1908(3)	0.2995(3)	172.81(8)
O(1)(H(1A)···N(2) $2	0.1035(3)	0.2883(3)	161.55(8)
O(2)(H(2A)···N(4) $3	0.1906(3)	0.2963(3)	172.56(8)
N(2)(H(2N)···O $4	0.2020(2)	0.2918(2)	165.41(6)
O(2)(H(2B)···O(1)	0.2154(3)	0.2838(3)	176.60(7)

* $1 $-x+2$, $-y$, $-z+1$; $2 $-x+1$, $-y$, $-z+1$; $3 $x+1$, $y-1$, z; $4 $-x$, $-y+1$, $-z+1$.

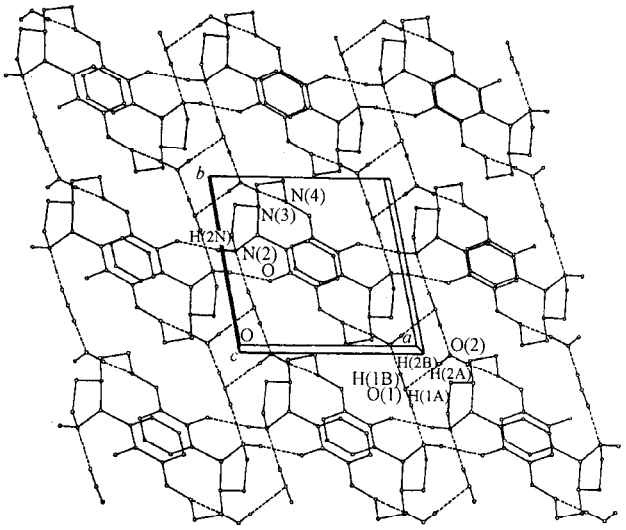

Fig. 3 Molecular stacking diagram showing two-dimensional sheet structure. Hydrogen-bonding interaction is shown with dotted lines.

As shown in Fig. 3, the tube stacking is parallel to one another, forming a two-dimensional sheet structure. The distance between the adjacent tubes is about 0.908 nm. The two tubes are held together by hydrogen bonding (N(4)---H(2A)-O(2), O(2)---H(1B)-O(1) and N(2)---H(1A)(O(1)). Four water molecules between tubes form a eight-membered ring by means of hydrogen bonding, and the hydrogen atoms interact with N(2) and N(4) of four macrocycles.

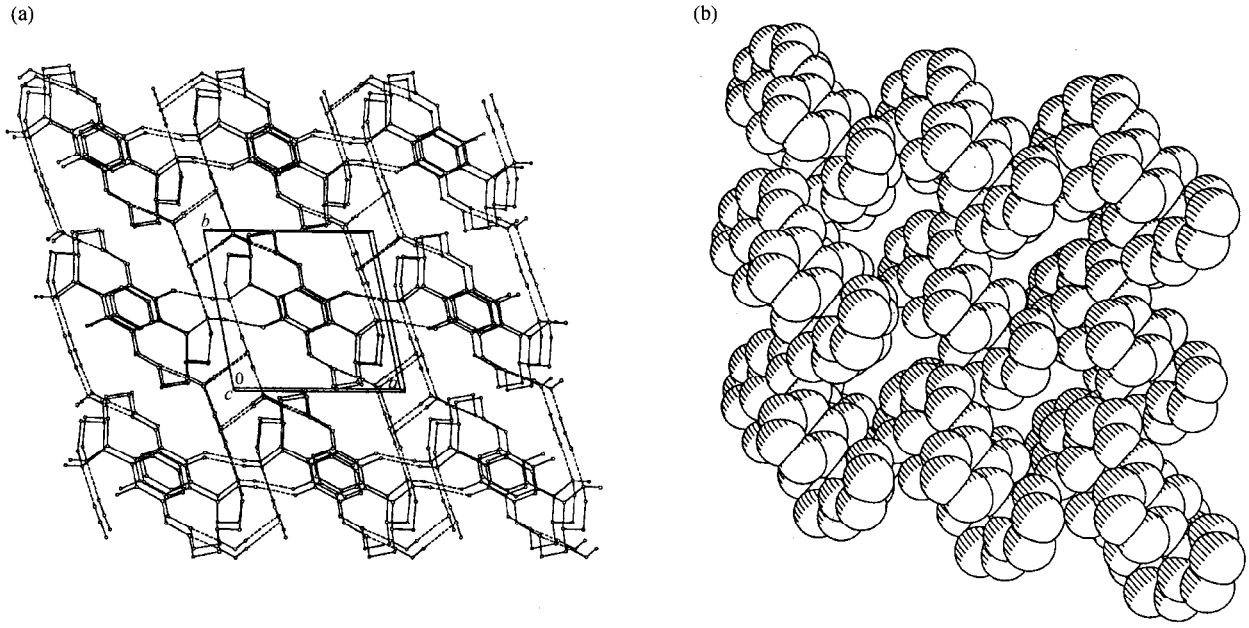

Fig. 4 (a) Molecular stacking diagram showing π-π interaction in macrocycles. (b) A view into the pores of the three-dimensional layer structure. The water molecules were omitted for clarity.

The π-π stacking interaction of pyridine rings and Van der Waals force make the sheets forming a three-dimensional layer structure (Fig. 4). The distance between two layers is also 0.324 nm, which is equal to that of two pyridine rings at the same macrocycle. There is no hydrogen bonding between two layers, but the

sheet packing in C axis by means of π-π interaction and Van der Waals force forms a porous structure filled with water molecules. The across section area is about 0.385 nm^2. Therefore self-assembly of this macrocyclic three-dimensional layer structure is not dominated only by directional hydrogen bonding but also by π-π interaction.

References and notes

1. Garcia-Viloca, M.; Gonzalez-Lafont, A.; Lluch, J.M., *J. Am. Chem. Soc.*, **119**, 1081(1997).
2. DeSantis, P.; Morosetti, S.; Rizzo, R., *Macromolecules*, **7**, 52(1974).
3. Tans, S.J.; Devoret, M.H.; Dai, H.; Thess, A.; Smalley, R.E.; Geerligs, L.J.; Dekker, C., *Nature*, **386**, 474(1997).
4. Hartgernik, J.D.; Granja, J.R.; Milligan, R.A.; Ghadiri, M.R., *J. Am. Chem. Soc.*, **118**, 43(1996).
5. Khazanovich, N.; Granja, J.R.; McRee, D.E.; Milligan, R.A.; Ghadiri, M.R., *J. Am. Chem. Soc.*, **116**, 6011(1994).
6. Kobayashi, K.; Granja, J.R.; Ghadiri, M.R., *Angew. Chem., Int. Ed. Engl.*, **34**, 95(1995).
7. Clark, T.D.; Ghadiri, M.R., *J. Am. Chem. Soc.*, **117**, 12364(1995).
8. Tomasi, L.; Lorenzi, G.P., *Helv. Chim. Acta*, **70**, 1012(1987).
9. Engels, M.; Bashford, D.; Ghadiri, M.R., *J. Am. Chem. Soc.*, **117**, 9151(1995).
10. Gattuso, G.; Menzer, S.; Nepogodiev, S.A.; Stoddart, J.F.; Williams, D.J., *Angew. Chem., Int. Ed. Engl.*, **36**, 1451(1997).
11. A methanol solution (80 cm^3) containing diethylenetrimine (1.04 g, 0.01 mol) was added dropwise to a stirring methanol solution (150 cm^3) containing a stoichoimetric amount (1:1) of pyridine-1-oxide-2,6-dialdehyde (1.51 g, 0.01 mol) at room temperature. The mixture was refluxed for three hours, the colorless needle crystals were obtained and recrystalized from methanol. The cube crystals were obtained in yield 70% (1.78 g). ν_{max}(KBr): 3338(N-H), 3225, 3220(O-H), 1625(C = N), 1603(N-H) cm^{-1}. Anal. $C_{22}H_{36}N_8O_6$. Calcd. C, 51.96; H, 7.13; N, 22.20; H_2O, 14.16. Found: C, 51.74; H, 7.17; N, 22.20; H_2O, 13.90.
12. Rockcliffe, D.A.; Martell, A.E.; Reibenspies, J.H., *J. Chem. Soc., Dalton Trans.*, 167(1996).
13. Pietraszkiewicz, M.; Gasiorowski, R., *Chem. Ber.*, **123**, 405(1990).
14. Ashton, P.R.; Brown, C.L.; Menzer, S.; Nepogodiev, S.A.; Stoddart, J.F.; Williams, D.J., *Chem. Eur. J.*, **2**, 580(1996).
15. Drew, M.G.B.; Nelson, J.; Nelson, S.M., *J. Chem. Soc., Dalton Trans.*, 1678(1981).
16. Crystal data for [$(4H_2O$]: Colorless cube crystal with dimensions 0.5 × 0.35 × 0.08 mm, $C_{22}H_{36}N_8O_6$, Mr = 508.59, triclinic, space group $P\bar{1}$, a = 0.86969 (2), b = 0.907890 (10), c = 0.908280 (10) nm, α = 114.1670 (10)°, β = 104.229 (2)°, γ = 93.760 (2)°, V = 0.62293 (2) nm^3, Z = 1, T = 293 (2) K, ρ_c = 1.356 $g \cdot cm^{-3}$, θ_{max} = 25.12°, λ = 0.071073 nm, $\mu(M_oK_\alpha)$ = 0.942 cm^{-1}, F (000) = 272. Data were collected using a Simens SMART CCD area-detector diffractometer, and corrected for absorption by SADABS.[17] 3064 Reflections (2086 unique) were collected in range of $2.46 < \theta < 25.12°$. The exposure time of frame was 10 s. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions and refined as riding atoms with individual isotropic displacement parameters. Full-matrix least squares refinement on F^2 using SHELXTL 9318 with all independent data. The final circle gives R = 0.0506 and R_w = 0.1413 based on 2086 reflections [$I < 2\theta(I)$] (maximun and minimun residual electron densities 420 and −233 enm^{-3}, respectively). All calculations were performed on a INDY workstation.
17. Sheldrick, G.M., *SADABS*, University of Gottingen, Gottingen, 1996.
18. Sheldrick, G.M., *SHELXL 93*, University of Gottingen, 1993.

(SONG, J.P.; LING, J.)