N-Protected Macrocycles with NO₂S₂ Donor Set

Il YOON, Ji-Eun LEE, Yongri JIN, Joobeom SEO, Ki-Min PARK, and Shim Sung LEE[†]

Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University,
Chinju 660-701, S. Korea

The single crystals of *N*-protected NO₂S₂ macrocycles with tosyl (I) and Boc (II) groups were prepared and their crystal structures were analyzed. Compound I exhibits a folded and twisted conformation due to intramolecular H-bondings as well as the π - π stacking interaction. In contrast, compound II is fully stretched because of the *exo*-orientation of two sulfur donors to the cavity.

(Received April 8, 2005; Accepted August 5, 2005; Published on web October 24, 2005)

Besides changing the cavity size that will vary a binding selectivity, the introduction of hetero atoms into the homoleptic macrocyclic ligands results in dramatic changes in both binding ability and geometry of the complexes.¹ We have been interested in the syntheses of new thioxa-² or thioxaaza-macrocyclic ligands³ and their supramolecular complexes with soft metal ions. As an extension of our synthetic programs, the title compounds I and II are the important precursors for the parent macrocycle and the *N*-functionalized macrocyclic derivatives.³ Herein, we report their crystal structures.

Compound I was prepared by the coupling reaction between 1,2-bis(2-(chloromethyl)phenoxy)ethane and *N,N*-bis(2-mercaptoethyl)-4-methylbenzenesulfonamide, employing Cs₂CO₃ in DMF under a high dilution condition. Compound II was prepared according to our previous method.² Single crystals of I and II suitable for crystallography were prepared by the vapor diffusion of diethyl ether into the dichloromethane solution and slow evaporation from ethyl acetate solution, respectively. The crystal and experimental data are given in Table 1. The structures were solved by direct methods and refined with anisotropic temperature factors for non-hydrogen atoms. All hydrogen atoms were located from different Fourier maps and were not refined. The atomic coordinates for non-hydrogen atoms are listed in Table 2. The selected bond lengths and bond angles are summarized in Table 3. The molecular structures and the atomic numbering are given in Fig. 2.

The conformations of the ring cavities in the two molecules are very different. Compound I exhibits folded and twisted conformation due to intramolecular H-bonding as well as the π - π stacking interaction. Moreover, the ethylene unit between S1

and N1 is disordered over two positions with occupancies of 0.71 [C8'-C9] and 0.29 [C8'-C9'] which allow several C-H...O type H-bondings⁴ (dashed lines in Fig. 2a) [C8-H...O1: 2.533 Å, C9'-H...O1: 2.460 Å, C9-H...O3: 2.511 Å (not shown) and C10-H...O4: 2.614 Å]. In addition, the weak intramolecular edge-to-face π - π stacking⁵ [82.82(6)°, C22-H...ring centeroid (C1-C6): 3.009 Å] is observed. Otherwise, II is fully stretched because two sulfur donors positioned exodentate to the ring cavity. Accordingly, the S...S distance of II [6.002(2)Å] is larger than that of I [5.470(1)Å]. In the packing structure of II,

Table 1 Crystal and experimental data for I and II

	I	II
Formula	C ₂₇ H ₃₁ NO ₄ S ₃	C ₂₅ H ₃₃ NO ₄ S ₂
Formula weight	529.71	475.64
Temperature	293(2)K	298(2)K
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	4
<i>a</i>	9.3136(9)Å	8.805(3)Å
<i>b</i>	11.2417(11)Å	9.710(9)Å
<i>c</i>	14.3042(14)Å	29.90(3)Å
α	109.074(2)°	
β	106.588(2)°	91.749(2)°
γ	96.526(2)°	
<i>V</i>	1320.6(2)Å ³	2554.3(4)Å ³
<i>D_x</i>	1.332 g/cm ³	1.237 g/cm ³
2 θ _{max}	56.66°	56.60°
<i>R</i>	0.0454	0.0644
<i>wR</i>	0.1357	0.2316
No. of reflections used	3964 [$>2\sigma(I)$]	2333 [$>2\sigma(I)$]
Diffraction system	Bruker SMART CCD system	Bruker SMART CCD system
Structure determination	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix

CCDC 277539 (I) and 252326 (II) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fig. 1 Chemical structures for I and II.

[†] To whom correspondence should be addressed.
E-mail: sslee@gsnu.ac.kr

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for I and II

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Compound I					Compound II				
S(1)	-3205(1)	11233(1)	3511(1)	69(1)	S(1)	9002(1)	6680(1)	1462(1)	68(1)
S(2)	2803(1)	13415(1)	4341(1)	69(1)	S(2)	10395(1)	2115(2)	184(1)	99(1)
S(3)	1334(1)	9235(1)	2747(1)	58(1)	O(1)	13428(3)	5721(3)	1344(1)	73(1)
O(1)	-2627(2)	10701(1)	871(1)	53(1)	O(2)	14277(4)	3683(4)	701(1)	102(1)
O(2)	290(2)	12544(1)	1487(1)	61(1)	O(3)	9208(3)	415(3)	1480(1)	83(1)
O(3)	522(2)	9138(2)	1701(1)	85(1)	O(4)	7567(3)	2149(2)	1600(1)	56(1)
O(4)	2958(2)	9384(2)	3083(2)	82(1)	N(1)	9720(3)	2563(3)	1247(1)	56(1)
N(1)	980(2)	10469(2)	3542(1)	54(1)	C(1)	13241(4)	6613(4)	1696(1)	54(1)
C(1)	-3378(2)	9500(2)	729(2)	45(1)	C(2)	14252(5)	6663(4)	2058(2)	70(1)
C(2)	-3328(2)	8357(2)	-5(2)	55(1)	C(3)	14039(5)	7576(4)	2401(2)	70(1)
C(3)	-4124(3)	7197(2)	-88(2)	61(1)	C(4)	12820(5)	8443(5)	2384(2)	69(1)
C(4)	-4958(3)	7157(2)	553(2)	65(1)	C(5)	11794(5)	8386(4)	2030(1)	60(1)
C(5)	-5004(2)	8297(2)	1286(2)	58(1)	C(6)	11968(4)	7468(3)	1683(1)	47(1)
C(6)	-4236(2)	9482(2)	1384(2)	47(1)	C(7)	10794(4)	7401(4)	1302(1)	55(1)
C(7)	-4371(2)	10719(2)	2138(2)	54(1)	C(8)	9501(5)	4904(4)	1576(1)	65(1)
C(8)	-1278(4)	11474(3)	3460(2)	50(1)	C(9)	9240(5)	4002(4)	1173(1)	56(1)
C(9)	-712(4)	10262(4)	3394(3)	62(1)	C(10)	11215(4)	2131(4)	1101(2)	72(1)
C(8')	-1540(13)	10393(9)	3587(7)	68(3)	C(11)	11172(6)	1301(4)	675(2)	92(2)
C(9')	-381(11)	11041(9)	3301(6)	59(3)	C(12)	11861(5)	3344(5)	53(2)	78(1)
C(10)	2059(3)	11099(2)	4632(2)	65(1)	C(13)	13399(4)	2738(4)	3(1)	56(1)
C(11)	3376(3)	12148(2)	4779(2)	78(1)	C(14)	13732(5)	1907(5)	-357(1)	68(1)
C(12)	3028(3)	12863(2)	3061(2)	59(1)	C(15)	15143(6)	1387(5)	-413(2)	84(2)
C(13)	2749(2)	13833(2)	2557(2)	50(1)	C(16)	16283(6)	1636(5)	-102(2)	80(1)
C(14)	3877(3)	14929(2)	2848(2)	61(1)	C(17)	15999(5)	2415(5)	264(2)	72(1)
C(15)	3669(3)	15813(2)	2372(2)	66(1)	C(18)	14563(5)	2957(4)	317(1)	62(1)
C(16)	2310(3)	15620(2)	1600(2)	62(1)	C(19)	14984(5)	4916(4)	763(2)	72(1)
C(17)	1150(2)	14539(2)	1281(2)	56(1)	C(20)	14872(5)	5603(6)	1179(2)	86(2)
C(18)	1367(2)	13649(2)	1760(2)	48(1)	C(21)	8844(4)	1613(4)	1444(1)	52(1)
C(19)	-984(2)	12163(2)	537(2)	58(1)	C(22)	6442(4)	1252(4)	1815(1)	56(1)
C(20)	-1721(2)	10776(2)	233(2)	57(1)	C(23)	7138(5)	568(6)	2224(2)	98(2)
C(21)	508(2)	7845(2)	2893(2)	55(1)	C(24)	5814(5)	244(5)	1483(2)	89(2)
C(22)	-973(3)	7159(2)	2242(2)	70(1)	C(25)	5236(6)	2267(6)	1943(2)	108(2)
C(23)	-1627(3)	6095(2)	2383(4)	80(1)					
C(24)	-840(4)	5683(2)	3142(2)	76(1)					
C(25)	632(3)	6376(2)	3780(2)	75(1)					
C(26)	1320(3)	7454(2)	3665(2)	63(1)					
C(27)	-1573(4)	4504(3)	3263(3)	116(1)					

$$U_{eq} = (1/3)\sum_i U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

Fig. 2 Perspective views of (a) I and (b) II with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

the intermolecular C-H...O type H-bonding⁴ [C7-H...O=C: 2.557 Å] was also observed.

Acknowledgements

This work was supported by the Korea Research Foundation Grant (KRF-2004-015-C00250)

References

1. L. F. Lindoy, "The Chemistry of Macrocyclic Ligand

Table 3 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for I and II

Compound I		Compound II	
S(1)-C(7)	1.808(2)	S(1)-C(7)	1.804(4)
S(1)-C(8)	1.810(3)	S(1)-C(8)	1.810(4)
S(1)-C(8')	1.901(12)	S(2)-C(11)	1.786(6)
S(2)-C(11)	1.809(2)	S(2)-C(12)	1.809(5)
S(2)-C(12)	1.812(2)	O(1)-C(1)	1.379(4)
O(1)-C(1)	1.371(2)	O(1)-C(20)	1.381(5)
O(1)-C(20)	1.423(2)	O(2)-C(19)	1.360(5)
O(2)-C(18)	1.371(2)	O(2)-C(18)	1.378(5)
O(2)-C(19)	1.422(2)	N(1)-C(21)	1.351(4)
N(1)-C(10)	1.471(3)	N(1)-C(10)	1.460(5)
N(1)-C(9)	1.490(10)	N(1)-C(9)	1.475(5)
N(1)-C(9)	1.509(4)		
C(7)-S(1)-C(8)	101.78(12)	C(7)-S(1)-C(8)	102.14(18)
C(7)-S(1)-C(8')	107.8(3)	C(11)-S(2)-C(12)	102.2(2)
C(11)-S(2)-C(12)	99.91(12)	C(1)-O(1)-C(20)	117.2(3)
C(1)-O(1)-C(20)	117.86(15)	C(19)-O(2)-C(18)	118.0(3)
C(18)-O(2)-C(19)	117.75(15)	C(10)-N(1)-C(9)	119.0(3)
C(10)-N(1)-C(9)	114.6(3)		
C(10)-N(1)-C(9)	116.7(2)		
O(1)-C(20)-C(19)-O(2)	77.7(2)	O(1)-C(20)-C(19)-O(2)	-48.7(7)
S(1)-C(8)-C(9)-N(1)	-169.9(2)	S(1)-C(8)-C(9)-N(1)	176.6(3)
N(1)-C(10)-C(11)-S(2)	55.5(3)	N(1)-C(10)-C(11)-S(2)	61.1(5)

Complexes", 1989, Cambridge University Press, Cambridge.

2. Y. H. Lee and S. S. Lee, *J. Inclusion Phenom.*, **2001**, 39, 235.
3. Y. Jin, I. Yoon, J. Seo, J.-E. Lee, S.-T. Moon, J. Kim, S. W. Han, K.-M. Park, L. F. Lindoy, and S. S. Lee, *Dalton Trans.*, **2005**, 788.
4. G. R. Desiraju, *Acc. Chem. Res.*, **1996**, 29, 441.
5. W. B. Jennings, B. M. Farrell, and J. F. Malone, *Acc. Chem. Res.*, **2001**, 34, 885.