N-Phenylated Pyridine-Containing N₂S₂ Macrocycle

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Single crystals of the N-phenylated 12-membered N₂S₂ macrocycle with a pyridine subunit were prepared and the crystal structure was analyzed. The title compound exhibits a chair-like conformation and the macrocyclic ring is folded over a pyridine subunit. Two S donors are exo-oriented to the macrocyclic ring cavity.

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Chromoionophores with a donor- π -acceptor concept play a major role in UV-Vis spectrophotometric analysis. Such

Fig. 1 Chemical structure.

functionalized dye molecules usually consist of a macrocyclic or acyclic ion-responsive receptor as a recognition unit and a color-changing signaling unit, which are covalently linked.¹ We have been interested in the syntheses of new thioxa- or thiaoxaaza-macrocyclic ligands and their supramolecular complexes with soft metal ions.^{2,3} As an extension of our programs, we are currently working on the synthesis of novel macrocyclic chromoionophores for the selective and quantitative detection of heavy metal ions, both for biological and environmental applications.⁴ Lippolis *et al.*⁵ have reported on the fluorescence chemosensors based on pyridine-N₂S₂ macrocycles exhibiting heavy metal ions selectivity. The title

Table 1 Crystal and experimental data

Formula	C ₁₇ H ₂₀ N ₂ S ₂
Formula weight	316.47
Temperature	173(2)K
Crystal system	triclinic
Space group	<i>P</i> 1
<i>Z</i>	2
<i>a</i>	9.1407(10)Å
<i>b</i>	9.8364(11)Å
<i>c</i>	10.7107(12)Å
α	65.688(2)°
β	77.638(2)°
γ	65.927(2)°
<i>V</i>	800.05(15)Å ³
<i>D_x</i>	1.314 g/cm ³
$2\theta_{\max}$	56.56°
<i>R</i>	0.0376
<i>wR</i>	0.1001
No. of reflections used	2805
Diffractionmeter	Bruker SMART CCD system
Structure determination	SHELXTL
Refinement	full-matrix
CCDC 299779 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data/request/cif .	

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
S(1)	10012(1)	5203(1)	7228(1)	38(1)
S(2)	4324(1)	2543(1)	9893(1)	30(1)
N(1)	8541(2)	1981(2)	9108(2)	28(1)
N(2)	5762(2)	5469(2)	6242(1)	28(1)
C(1)	8980(2)	1850(2)	11647(2)	35(1)
C(2)	9924(2)	2396(2)	10511(2)	34(1)
C(3)	9679(2)	2432(2)	9257(2)	29(1)
C(4)	10654(2)	3025(2)	7975(2)	35(1)
C(5)	7882(2)	5774(2)	7130(2)	31(1)
C(6)	7475(2)	5154(2)	6196(2)	30(1)
C(7)	5218(2)	4184(2)	7203(2)	29(1)
C(8)	4650(2)	4313(2)	8616(2)	27(1)
C(9)	6338(2)	1022(2)	9976(2)	31(1)
C(10)	7613(2)	1475(2)	10215(2)	27(1)
C(11)	7801(2)	1391(2)	11505(2)	32(1)
C(12)	4719(2)	6920(2)	5439(2)	24(1)
C(13)	5257(2)	8173(2)	4564(2)	29(1)
C(14)	4227(2)	9575(2)	3697(2)	34(1)
C(15)	2631(2)	9813(2)	3666(2)	37(1)
C(16)	2082(2)	8604(2)	4546(2)	34(1)
C(17)	3086(2)	7193(2)	5426(2)	29(1)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

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

S(1)-C(5)	1.8070(18)	C(5)-S(1)-C(4)	101.56(8)
S(1)-C(4)	1.827(2)	C(8)-S(2)-C(9)	101.84(8)
S(2)-C(8)	1.8103(17)	C(10)-N(1)-C(3)	118.40(14)
S(2)-C(9)	1.8299(18)	C(12)-N(2)-C(7)	122.30(14)
N(1)-C(10)	1.342(2)	C(12)-N(2)-C(6)	121.54(14)
N(1)-C(3)	1.345(2)	C(7)-N(2)-C(6)	116.14(14)
N(2)-C(12)	1.385(2)	S(1)-C(5)-C(6)-N(2)	173.62 (12)
N(2)-C(7)	1.458(2)	N(2)-C(7)-C(8)-S(2)	-169.36 (12)
N(2)-C(6)	1.461(2)	N(1)-C(3)-C(4)-S(1)	101.01 (16)
		S(2)-C(9)-C(10)-N(1)	-102.36 (16)

Fig. 2 Perspective view with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

compound in Fig. 1 is one of the important macrocyclic precursors for synthesizing macrocyclic chromoionophores that are *N*-functionalized with azobenzene, tricyanovinyl and other coloring moieties.⁶ Herein, we report on the preparation of its single crystals and crystal structure.

The title compound was synthesized by a mercaptan-tosylate coupling reaction of *N,N*-bis(2-mercaptoethyl)aniline with 2,6-ditosyloxymethylpyridine, employing Cs_2CO_3 as a base in DMF under high dilution condition. The synthetic procedure will be presented elsewhere. Single crystals suitable for crystallography were prepared by slow evaporation from a dichloromethane solution. The crystal and experimental data are given in Table 1. The structure was solved by direct methods and refined with anisotropic temperature factors for non-hydrogen atoms. All of the 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 structure along with the atomic numbering is given in Fig. 2.

In the crystal, the aliphatic portion of the macrocyclic unit is folded over the pyridine subunit. Two S donors have *exodentate* to the ring cavity, and the S1...S2 distance in the ring is as large as 6.373(1) Å, due to the repulsive interaction. The N1(py)...N2 distance in the ring is 3.899(2) Å. The dihedral angle between the pyridine and phenyl rings is 61.61(6)°. The S-C-C-N1(py) chains are arranged *gauche* [101.01(16) - 102.36(16)°], whereas those of S-C-C-N2 are arranged *anti* [169.36(12) - 173.62(12)°]. According to our previous work,⁶ the chromophoric moieties, such as the azobenzene and tricyanovinyl groups barely influence the conformation of the macrocyclic unit in the crystalline state. In packing, there is an intermolecular face-to-face type π - π stacking interaction between two pyridine rings with a centroid-to-centroid distance of 3.846 Å.

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