The Crystal Structure of *N, N'*-Disubstituted-2,6-bis(tosylaminomethyl)pyridine

Yoshiharu NAKANO,*† Hiroki SUDA,* Tohru KOBAYASHI,* Yuki FUJII,* Li DONGFENG,** and Tsuyoshi YAITA***

*Faculty of Science, Ibaraki University, Bunkyo 2-1-1, Mito 310-8512, Japan

**School of Biotechnology, 17#Yanan Road, Changchun, Jilian Province, China

***Department of Materials Science, Japan Atomic Energy Research Institute, Ibaraki 319-1195, Japan

The crystal structure of *N, N'*-diphenyl-2,6-bis(tosylaminomethyl)pyridine **3a** and *N, N'*-dibenzyl-2,6-bis(tosylaminomethyl)pyridine **3b** were determined. The structures were solved by the direct method and refined to $R = 0.040$ and $R = 0.039$, respectively. Tosylamide **3a** has a symmetric structure, but **3b** has a complicated asymmetric conformation, unexpectedly. All oxygen atoms of the tosyl group are opposite side to the pyridine nitrogen.

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The radiotoxic inventories of nuclear waste increase along with the increasing electric supply annually. A simplification of the management strategy can be expected, if the 5f elements are separated from the wastes and the fission products are transmuted into short-lived products (4f elements). Among the many separation methods, liquid-liquid extraction using extracting ligands with sp^2 -nitrogen is expected to be a good choice. Tridentate ligands, such as 2,6-bisbenzimidazol-2-ylpyridine, are used as separating agents due to good separation factor (more than 100). We also expect triamines **4a** and **4b** (see Fig. 1), which contain a pyridine ring, to be favorable materials for versatile ligand and synthetic blocks of macrocyclic materials.

Both triamines are expected to be prepared from primary amines according to the well-known easy procedures shown in Fig. 1. Since almost all triamines are usually liquid, crystalline ditosylamides have to be identified completely. The two ditosylamides of 2,6-bis(aminomethyl)pyridine were recrystallized from a mixture of chloroform and hexane to give single crystals. We report here on the crystal structure of two derivatives, **3a** and **3b** (**3a** R = Phenyl and **3b** R = CH₂Ph).

The crystal structure was solved by the direct method² and refined using a package program, CrystalStructure.³ All of the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were determined from a difference Fourier map and were refined isotropically. A hydrogen atom of **3b**, H(33) was used as a riding model. Table 1 gives the crystal and experimental data. The final positional parameters of **3a** and **3b** are listed in Tables 2a and 2b,

respectively. The selected bond distances and torsion angles of the two sulfonylamides are shown in Table 3a and 3b. The ORTEP drawings of the two tosylamides are shown in Fig. 2a and 2b.

The ORTEP drawings of the amides show that three-dimensional conformations of the compounds seem to be determined mostly by a steric interaction and dipole-dipole interaction. Tosylamide **3a** has relatively simple and symmetric conformation, as expected, but **3b** has a very complicated asymmetric structure. Since the lone pairs of nitrogen in the aminomethyl groups delocalize to the tosyl groups in both samples, the S–N bond may have some multiplicity. Due to

Table 1 Crystallographic data

Compounds	3a (R = Ph)	3b (R = CH ₂ Ph)
Formula	C ₃₃ H ₃₁ N ₃ O ₄ S ₂	C ₃₃ H ₃₅ N ₃ O ₄ S ₂
fw	600.77	483.40
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /c
Radiation:	Mo K α (0.71069 Å)	
T = 298K		
a/Å	28.847 (9)	14.352 (5)
b/Å	10.210 (4)	24.860 (10)
c/Å	22.576 (6)	9.467 (2)
α /deg	90.0	90.0
β /deg	114.38 (2)	106.57 (2)
γ /deg	90.0	90.0
V/Å ³	6056 (3)	3236 (1)
Z	8	4
$D_{\text{calc}}/\text{g cm}^{-3}$	1.311	1.284
R^a, R_w^b (p-factor)	0.040, 0.057 (0.10)	0.039, 0.058 (0.05)
No. of reflections used	4449	4400
μ/cm^{-1}	2.18	2.07
$2\theta_{\text{max}}$	55.0	55.0
$(\Delta/\sigma)_{\text{max}}$	0.000	0.000
$(\Delta\rho)_{\text{max}}/\text{eÅ}^{-3}$	0.20	0.24
$(\Delta\rho)_{\text{min}}/\text{eÅ}^{-3}$	–0.37	–0.22
Crystal size/mm	0.50 × 0.50 × 0.55	0.68 × 0.62 × 0.68
Measurement	Rigaku AFC7R	Rigaku AFC7R

Fig. 1 Preparative processes of **3a** and **3b**.

† To whom correspondence should be addressed.
E-mail: nyoshi@mx.ibaraki.ac.jp

a. $R = (|F_o| - |F_c|)/\Sigma|F_o|$, b. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = [\sigma^2(F_o) + (p^2/4)F_o^2]^{-1}$, $p = p$ -factor

Table 2a Atomic coordinates and B_{eq} of **3a**

Atom	x	y	z	B_{eq}
S(1)	0.94708(3)	-0.07990(7)	0.07179(3)	4.50(1)
S(2)	1.23324(2)	0.44859(7)	0.38520(3)	4.50(1)
O(1)	0.97228(8)	-0.2043(2)	0.0888(1)	6.06(5)
O(2)	0.92441(8)	-0.0394(2)	0.00531(8)	6.11(5)
O(3)	1.26213(8)	0.3316(2)	0.4099(1)	6.52(6)
O(4)	1.25745(7)	0.5632(2)	0.3751(1)	6.15(5)
N(1)	0.98968(8)	0.0305(2)	0.11152(9)	4.04(4)
N(2)	1.09410(7)	0.1506(2)	0.24241(8)	3.57(4)
N(3)	1.18735(8)	0.4075(2)	0.31395(9)	4.05(4)
C(1)	0.8557(1)	-0.0023(3)	0.0693(1)	4.21(5)
C(2)	0.8178(1)	-0.0027(3)	0.0917(1)	4.35(5)
C(3)	0.82264(9)	-0.0751(2)	0.1464(1)	4.14(5)
C(4)	0.7808(1)	-0.0790(4)	0.1698(2)	5.73(8)
C(5)	0.8673(1)	-0.1471(3)	0.1780(1)	4.48(6)
C(6)	0.9050(1)	-0.1488(3)	0.1557(1)	4.32(5)
C(7)	0.89926(9)	-0.0756(2)	0.1012(1)	3.77(5)
C(8)	0.97797(9)	0.1675(3)	0.0970(1)	4.09(5)
C(9)	0.9635(1)	0.2455(3)	0.1363(1)	5.19(7)
C(10)	0.9574(1)	0.3784(4)	0.1244(2)	6.42(9)
C(11)	0.9641(1)	0.4327(4)	0.0727(2)	6.77(9)
C(12)	0.9772(1)	0.3533(4)	0.0327(2)	6.8(1)
C(13)	0.9847(1)	0.2217(3)	0.0448(1)	5.49(7)
C(14)	1.0272(1)	0.0013(3)	0.1783(1)	4.34(6)
C(15)	1.07643(9)	0.0703(2)	0.1911(1)	3.60(5)
C(16)	1.1012(1)	0.0511(3)	0.1505(1)	4.21(5)
C(17)	1.1459(1)	0.1153(3)	0.1641(1)	4.59(6)
C(18)	1.1652(1)	0.1977(3)	0.2174(1)	4.36(6)
C(19)	1.13801(9)	0.2122(2)	0.2551(1)	3.69(5)
C(20)	1.1571(1)	0.2926(3)	0.3166(1)	4.68(6)
C(21)	1.16236(9)	0.5051(2)	0.2647(1)	3.93(5)
C(22)	1.1905(1)	0.5773(3)	0.2392(1)	5.12(7)
C(23)	1.1666(2)	0.6655(3)	0.1897(2)	7.1(1)
C(24)	1.1146(2)	0.6802(4)	0.1639(2)	8.3(1)
C(25)	1.0866(2)	0.6072(4)	0.1875(2)	7.6(1)
C(26)	1.1103(1)	0.5201(3)	0.2383(1)	5.52(7)
C(27)	1.20428(9)	0.4905(2)	0.4373(1)	3.88(5)
C(28)	1.1973(1)	0.6218(3)	0.4479(1)	5.19(7)
C(29)	1.1757(1)	0.6552(3)	0.4894(1)	5.74(7)
C(30)	1.1590(1)	0.5608(3)	0.5205(1)	5.03(6)
C(31)	1.1338(2)	0.6006(5)	0.5644(2)	7.3(1)
C(32)	1.1670(1)	0.4306(3)	0.5105(1)	4.77(6)
C(33)	1.1896(1)	0.3945(3)	0.4698(1)	4.21(5)

$$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$$

Fig. 2a An ORTEP drawing and numbering scheme of **3a**. Fig. 2b An ORTEP drawing and numbering scheme of **3b** (hydrogen atoms were hidden).

strong interactions of summated S-O vectors with a pyridine dipole, which is assumed to direct to the nitrogen atom, all of the oxygen atoms direct to the opposite side to the pyridine ring.

References

1. The two dithiolamides, **3a** and **3b** gave good results of elemental analyses data, NMR, and IR. Melting point: R = phenyl, 152 - 154°C, R = benzyl, 110 - 112°C.
2. A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, and G. Polidori, *J. Appl.*

Table 2b Atomic coordinates and B_{eq} of pytosbn **3b**

Atom	x	y	z	B_{eq}
S(1)	0.95573(4)	0.31946(3)	1.09339(7)	4.47(1)
S(2)	1.42545(5)	0.36981(3)	0.74015(8)	5.37(2)
O(1)	1.0003(1)	0.26899(8)	1.1426(2)	5.64(4)
O(2)	0.9200(1)	0.35195(8)	1.1911(2)	5.79(5)
O(3)	1.4739(2)	0.4163(1)	0.7060(3)	7.42(6)
O(4)	1.4458(1)	0.31784(9)	0.6920(2)	6.75(6)
N(1)	1.0367(1)	0.35567(8)	1.0464(2)	4.57(5)
N(2)	1.2724(1)	0.32352(8)	0.9976(2)	3.90(4)
N(3)	1.4512(1)	0.36734(8)	0.9185(2)	4.66(5)
C(1)	0.8588(2)	0.3086(1)	0.9337(3)	4.17(5)
C(2)	0.8514(2)	0.2605(1)	0.8574(3)	5.17(6)
C(3)	0.7768(2)	0.2537(1)	0.7295(3)	5.40(7)
C(4)	0.7095(2)	0.2939(1)	0.6744(3)	4.80(6)
C(5)	0.6311(2)	0.2861(2)	0.5313(4)	6.39(8)
C(6)	0.7167(2)	0.3408(1)	0.7551(3)	5.47(7)
C(7)	0.7899(2)	0.3486(1)	0.8827(3)	5.07(6)
C(8)	1.0153(2)	0.4129(1)	1.0115(4)	5.70(7)
C(9)	1.1061(2)	0.4467(1)	1.0642(3)	4.94(6)
C(10)	1.1452(3)	0.4720(1)	0.9666(4)	6.13(8)
C(11)	1.2290(3)	0.5020(1)	1.0153(6)	7.6(1)
C(12)	1.2740(3)	0.5070(1)	1.1606(6)	7.6(1)
C(13)	1.2360(3)	0.4822(2)	1.2594(5)	8.5(1)
C(14)	1.1520(3)	0.4523(1)	1.2115(4)	7.08(9)
C(15)	1.1015(2)	0.3290(1)	0.9726(3)	4.64(6)
C(16)	1.2047(1)	0.32366(9)	1.0695(2)	4.04(5)
C(17)	1.2272(2)	0.3183(1)	1.2211(3)	5.06(6)
C(18)	1.3228(2)	0.3128(1)	1.3013(3)	5.60(7)
C(19)	1.3929(2)	0.3131(1)	1.2282(3)	5.03(6)
C(20)	1.3656(1)	0.31808(9)	1.0771(3)	4.02(5)
C(21)	1.4401(2)	0.3164(1)	0.9923(3)	4.61(6)
C(22)	1.2990(2)	0.3809(1)	0.6702(3)	4.84(6)
C(23)	1.2637(2)	0.4325(1)	0.6548(3)	5.91(7)
C(24)	1.1640(3)	0.4406(2)	0.6084(4)	6.81(9)
C(25)	1.0996(2)	0.3982(2)	0.5766(3)	6.56(8)
C(26)	0.9912(3)	0.4075(3)	0.5327(6)	11.0(2)
C(27)	1.1369(2)	0.3469(2)	0.5902(3)	6.42(8)
C(28)	1.2362(2)	0.3376(1)	0.6367(3)	5.58(7)
C(29)	1.4546(2)	0.4171(1)	1.0023(3)	5.13(6)
C(30)	1.5391(2)	0.4177(1)	1.1417(3)	4.64(6)
C(31)	1.6310(2)	0.4000(1)	1.1411(4)	5.55(7)
C(32)	1.7073(2)	0.4010(1)	1.2679(4)	6.27(8)
C(33)	1.6942(3)	0.4192(1)	1.3967(4)	6.45(8)
C(34)	1.6036(3)	0.4361(1)	1.4004(4)	6.91(9)
C(35)	1.5268(2)	0.4351(1)	1.2734(4)	5.96(7)

$$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$$

Table 3a Bond lengths (Å) of **3a** (R = Ph)

atom	atom	distance	atom	atom	distance
S(1)	N(1)	1.635(2)	S(1)	C(7)	1.761(3)
S(2)	N(3)	1.661(2)	S(2)	C(27)	1.753(3)
N(1)	C(8)	1.445(3)	N(1)	C(14)	1.479(3)
N(2)	C(15)	1.337(3)	N(2)	C(19)	1.335(3)
N(3)	C(20)	1.477(4)	N(3)	C(21)	1.444(3)
C(14)	N(1)	1.479(3)	C(14)	C(15)	1.502(4)

Torsion angles (°) of 3a (R=Ph)					
Atom1	atom2	Atom3	Atom4	angle	
O(1)	S(1)	N(1)	C(8)	170.8(2)	
O(2)	S(1)	N(1)	C(8)	41.5(2)	
C(7)	S(1)	N(1)	C(8)	-73.6(2)	
O(3)	S(2)	N(3)	C(20)	52.8(2)	
O(4)	S(2)	N(3)	C(20)	-177.9(2)	
C(27)	S(2)	N(3)	C(20)	-62.0(2)	

Atom1	atom2	Atom3	Atom4	angle	
O(1)	S(1)	N(1)	C(14)	-37.4(2)	
O(2)	S(1)	N(1)	C(14)	-166.6(2)	
C(7)	S(1)	N(1)	C(14)	78.2(2)	
O(3)	S(2)	N(3)	C(21)	-157.5(2)	
O(4)	S(2)	N(3)	C(21)	-28.1(2)	
C(27)	S(2)	N(3)	C(21)	87.7(2)	

Table 3b Bond lengths (Å) of **3b** (R = benzyl)

atom	atom	distance	atom	atom	distance
S(1)	N(1)	1.630(2)	S(1)	C(1)	1.758(2)
S(2)	N(3)	1.624(2)	S(2)	C(22)	1.768(3)
N(1)	C(8)	1.473(4)	N(1)	C(15)	1.469(4)
N(2)	C(16)	1.335(3)	N(2)	C(20)	1.340(2)
N(3)	C(21)	1.476(4)	N(3)	C(29)	1.463(4)
C(8)	C(9)	1.511(4)	C(15)	C(16)	1.510(3)

Torsion Angles(°) of 3b (R=benzyl)					
atom1	atom2	atom3	atom4	angle	
O(1)	S(1)	N(1)	C(8)	-171.2(2)	
O(2)	S(1)	N(1)	C(8)	-42.3(2)	
C(1)	S(1)	N(1)	C(8)	72.6(2)	
O(3)	S(2)	N(3)	C(21)	-160.3(2)	
O(4)	S(2)	N(3)	C(21)	-30.8(2)	
C(22)	S(2)	N(3)	C(21)	84.6(2)	
S(1)	N(1)	C(15)	C(16)	-108.1(2)	
C(16)	N(2)	C(20)	C(21)	178.3(2)	

atom1	atom2	atom3	atom4	angle	
O(1)	S(1)	N(1)	C(15)	37.9(2)	
O(2)	S(1)	N(1)	C(15)	166.8(1)	
C(1)	S(1)	N(1)	C(15)	-78.3(2)	
O(3)	S(2)	N(3)	C(29)	39.5(2)	
O(4)	S(2)	N(3)	C(29)	169.0(2)	
C(22)	S(2)	N(3)	C(29)	-75.6(2)	
S(1)	N(2)	C(16)	C(21)	-179.0(2)	
C(16)	N(3)	C(21)	C(20)	-116.9(2)	

The sign of torsion angle is positive if when looking from atom 2 to atom 3 a clock-wise motion of atom 1 would superimpose it on atom 4.

Cryst., **1994**, 27, 435.

3. CrsytalStructure, Version 3.6.0 Crystal Strucutre Analysis Package, Rigaku and Rigaku/MS.