

Crystal Structure of a 6-Hydroxynaphtho [2,1-*b*] -3H-1,4-thiazin-2(1*H*)-one Derivative

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Abstract

The title compound was prepared from the reaction of Orange I and thioglycolic acid and its structure was characterized by X-ray diffraction. This compound crystallizes in monoclinic, space group *C2/c* with cell parameters of $a = 15.786(4) \text{ \AA}$, $b = 8.586(4) \text{ \AA}$, $c = 23.952(4) \text{ \AA}$, $\beta = 97.98(2)^\circ$, and $Z = 8$; the final residual factor is $R1 = 0.043$ for 1586 reflections.

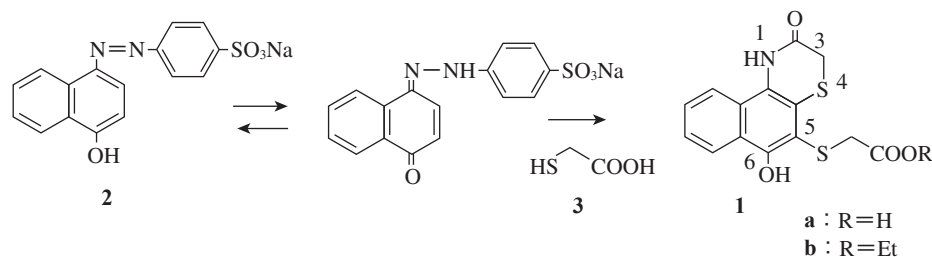
Much interest in benzothiazinone nucleus has been generated from both synthetic and pharmacological aspects for these decades, because some benzothiazinones have shown remarkable activities, such as a Ca^{2+} antagonist and an aromatase inhibitor.^{1,2)} During the course of our continuous investigation on nucleophilic addition of sulfur to azo dyes,^{3,4)} we obtained a naphthothiazinone **1a** by one step from the reaction of Orange I **2** with thioglycolic acid **3** (Scheme 1)⁵⁾. Since the usual spectroscopic techniques did not permit an identification of the framework of **1a**, the crystal structure of **1b** as an ester of **1a** was determined by X-ray analysis.

Compound **1b** was prepared as follows: A solution of **2** (0.57 mmol) and **3** (2.85 mmol) in water (40 ml) was refluxed for 2 h. The completion of the reaction was generally indicated by disappearance of origi-

nal red color. After cooling, filtration of resulting pale brown precipitates and recrystallization from ethanol afforded **1a** in 62% yield. The esterification of **1a** with EtOH/HCl readily occurred to afford an ethyl ester **1b** in 80% yield. Recrystallization from ethanol affords crystals appropriate for X-ray analysis.

X-ray analysis of a colorless crystal was performed on a four-cycle diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71069 \text{ \AA}$). The detailed measurement conditions and the crystal data are listed in Table 1. The intensity data were collected at 300 K using the $\omega - 2\theta$ scan technique. Of the 4098 reflections collected, 3953 were unique ($R_{\text{int}} = 0.024$).

The crystal structure was solved by direct methods with MITHRIL. The non-hydrogen atoms were refined anisotropically. The coordinates of the hydrogen atoms were determined by a calculation. All of the hy-



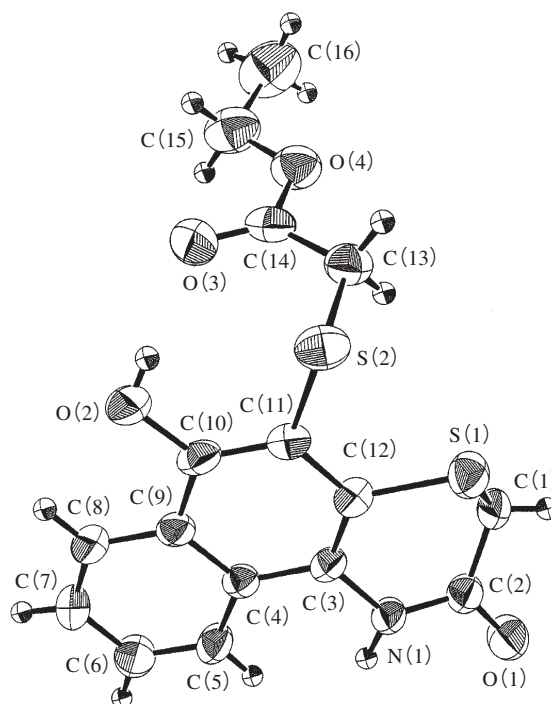
Scheme 1

Table 1. Crystal and experimental data

Chemical formula: C ₁₆ H ₁₅ NO ₄ S ₂
Formula weight = 349.42
T = 300K
Crystal system: monoclinic
Space group: C2/c Z = 8
a = 15.786(4) Å
b = 8.586(4) Å
c = 23.952(4) Å
β = 97.98(2)°
V = 3215(1) Å ³
D _x = 1.444 g/cm ³
Radiation: MoKα (λ = 0.71069 Å)
μ (MoKα) = 3.35 cm ⁻¹
F(000) = 1456
Crystal size = 0.30 × 0.20 × 0.20 mm
2θ _{max} = 55.0°
No. of reflections collected = 4098
No. of independent reflections = 3953
No. of reflections used = 1586 [I > 3.00 σ(I)]
Goodness-of-fit on F ² = 1.206
R indices [I > 3.00 σ(I)]: R1, wR2 = 0.043, 0.044
(ΔI/σ) _{max} = 0.07
(Δρ) _{max} = 0.24 e Å ⁻³
(Δρ) _{min} = -0.27 e Å ⁻³
Measurement: Rigaku AFC5R
Program system: TEXSAN ⁶⁾
Structure determination: direct methods (MITHRIL) ⁷⁾
Refinement: full-matrix least-squares
CCDC deposition number: ⁸⁾ 701870

drogen atoms were refined isotropically. The refined atomic parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 2. The selected bond lengths and bond angles are given in Table 3. An ORTEP drawing of compound **1b** is illustrated in Fig. 1.

The structure of **1** consists of 1-naphthol and 1,4-thiazinone rings, fused at the axis of C(3)–C(12). The formation of **1** seems to occur through addition of two molecules of thioglycolic acid to hydrazone form of Orange I and the loss of sulfanilic acid. S(2) deviates most remarkably from least squares of plane of the naphthalene ring among atoms bonded directly to the naphthalene ring [distances from the plane; S(1), 0.001(1) Å; S(2), 0.190(2) Å; N(1), 0.012(2) Å; O(2), 0.023(2) Å]. The deviation of S(2) from the plane is compatible with larger values of tor-

**Fig. 1.** ORTEP drawing of the title compound along with the atomic labeling scheme.**Table 2.** Final atomic coordinates and equivalent isotropic thermal parameters (B_{eq})

Atom	x	y	z	B_{eq} (Å ²)
S(1)	0.39268(8)	0.4386(1)	0.64413(5)	3.98(6)
S(2)	0.32682(8)	0.2358(1)	0.73988(5)	3.84(5)
N(1)	0.2551(2)	0.6046(4)	0.5678(1)	3.1(2)
O(1)	0.3522(2)	0.7397(4)	0.5270(1)	5.1(2)
O(2)	0.1377(2)	0.2796(4)	0.7440(1)	4.4(2)
O(3)	0.2502(2)	0.3814(4)	0.8371(1)	4.9(2)
O(4)	0.3680(2)	0.5072(4)	0.8750(1)	4.8(2)
C(1)	0.3988(4)	0.6327(7)	0.6177(2)	3.7(2)
C(2)	0.3335(3)	0.6648(5)	0.5668(2)	3.4(2)
C(3)	0.2270(3)	0.5248(5)	0.6134(2)	2.8(2)
C(4)	0.1376(2)	0.5252(5)	0.6188(2)	2.7(2)
C(5)	0.0754(3)	0.6048(6)	0.5815(2)	3.7(2)
C(6)	-0.0090(3)	0.6030(6)	0.5879(2)	4.1(2)
C(7)	-0.0355(4)	0.5241(6)	0.6332(2)	4.2(2)
C(8)	0.0216(3)	0.4457(6)	0.6706(2)	3.7(2)
C(9)	0.1091(3)	0.4416(5)	0.6639(2)	2.9(2)
C(10)	0.1696(3)	0.3571(5)	0.7021(2)	3.1(2)
C(11)	0.2547(3)	0.3564(5)	0.6956(2)	2.8(2)
C(12)	0.2834(2)	0.4429(5)	0.6512(2)	2.8(2)
C(13)	0.3768(4)	0.3728(8)	0.7916(2)	4.0(2)
C(14)	0.3236(3)	0.4187(6)	0.8359(2)	3.8(2)
C(15)	0.3224(5)	0.562(1)	0.9202(3)	5.7(3)
C(16)	0.384(1)	0.640(2)	0.9629(4)	7.5(5)

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

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

S(1)	C(12)	1.757(4)	S(1)	C(1)	1.790(7)				
S(2)	C(11)	1.777(4)	S(2)	C(13)	1.809(5)				
C(12)	C(11)	1.422(5)	C(12)	C(3)	1.371(5)				
C(11)	C(10)	1.374(5)	C(9)	C(10)	1.425(6)				
N(1)	C(3)	1.413(6)	N(1)	C(2)	1.344(5)				
C(10)	O(2)	1.357(5)	O(3)	C(14)	1.208(5)				
O(4)	C(15)	1.459(7)	O(4)	C(14)	1.329(5)				
C(2)	O(1)	1.219(5)	C(2)	C(1)	1.510(6)				
C(13)	C(14)	1.493(7)							
C(12)	S(1)	C(1)	96.7(2)	C(11)	S(2)	C(13)	102.3(3)		
S(1)	C(12)	C(11)	118.7(3)	S(1)	C(12)	C(3)	120.3(3)		
C(11)	C(12)	C(3)	121.0(4)	S(2)	C(11)	C(12)	120.4(3)		
S(2)	C(11)	C(10)	119.3(3)	C(9)	C(4)	C(3)	119.1(4)		
C(4)	C(9)	C(8)	119.4(4)	C(4)	C(9)	C(10)	119.4(4)		
C(8)	C(9)	C(10)	121.2(4)	C(3)	N(1)	C(2)	126.2(4)		
C(12)	C(3)	C(4)	119.9(4)	C(12)	C(3)	N(1)	120.9(4)		
C(4)	C(3)	N(1)	119.2(4)	C(11)	C(10)	O(2)	123.4(4)		
C(9)	C(10)	O(2)	116.1(4)	C(15)	O(4)	C(14)	116.3(4)		
N(1)	C(2)	C(1)	116.2(4)	N(1)	C(2)	O(1)	122.7(4)		
C(1)	C(2)	O(1)	121.1(4)	S(2)	C(13)	C(14)	115.0(4)		
O(3)	C(14)	O(4)	123.3(5)	O(3)	C(14)	C(13)	125.7(5)		
O(4)	C(14)	C(13)	111.0(4)	S(1)	C(1)	C(2)	113.1(4)		
S(1)	C(12)	C(11)	C(10)	-179.8(3)	S(1)	C(12)	C(3)	C(4)	178.8(3)
S(1)	C(12)	C(3)	N(1)	1.1(6)	S(1)	C(1)	C(2)	N(1)	40.0(6)
S(1)	C(1)	C(2)	O(1)	-139.1(4)	S(2)	C(12)	C(11)	S(1)	4.3(5)
S(2)	C(11)	C(12)	C(3)	173.8(3)	S(2)	C(11)	C(10)	C(9)	-174.3(3)
S(2)	C(11)	C(10)	O(2)	5.5(6)	S(2)	C(13)	C(14)	O(3)	-5.7(8)
S(2)	C(13)	C(14)	O(4)	174.0(4)	C(12)	S(1)	C(1)	C(2)	-53.7(5)
C(12)	C(11)	S(2)	C(13)	83.9(4)	C(12)	C(11)	C(10)	O(2)	-178.8(4)
C(12)	C(3)	N(1)	C(2)	-28.5(6)	C(11)	S(2)	C(13)	C(14)	77.1(5)
C(11)	C(12)	S(1)	C(1)	-147.3(4)	C(11)	C(12)	C(3)	N(1)	-177.0(4)
C(4)	C(9)	C(10)	O(2)	-179.8(4)	C(4)	C(3)	N(1)	C(2)	153.8(4)
C(9)	C(4)	C(3)	N(1)	178.4(4)	C(3)	C(12)	S(1)	C(1)	34.6(4)
C(3)	N(1)	C(2)	C(1)	4.9(7)	C(3)	N(1)	C(2)	O(1)	-176.0(4)
C(8)	C(9)	C(10)	O(2)	1.2(6)	C(10)	C(11)	S(2)	C(13)	-100.5(4)

sion angles of S(2)-C(11)-C(12)-S(1) [4.3(2)°] and S(2)-C(11)-C(10)-O(2) [5.5(3)°] than that of S(1)-C(12)-C(3)-N(1) [1.1(2)°]. A bond length of S(1)-C(12) is slightly shorter than that of S(2)-C(11).

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graphic 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.