Crystal Structure of *N,N'*-Diethyl-*N,N'*-[[4,4'-dihydroxy-1,1'-binaphthalene]-3,3'-diyl]bisbenzamide

Tsuyoshi FUJIMOTO,[†] Mitsunobu DOI, Misa TABE, Takako YAMAGUCHI, and Yoshikazu FUJITA

Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 669-1094, Japan

The crystal structure of *N,N'*-diethyl-*N,N'*-[[4,4'-dihydroxy-1,1'-binaphthalene]-3,3'-diyl]bisbenzamide was determined. This compound was synthesized from a reaction between *N*-ethyl-2-naphthylamine (NENA) and benzoylperoxide. The torsion angle between the two-ring system (C5-C4-C24-C25) is 129.0(2)°. The length of the inter-ring C4-C24 bond is 1.488(3)Å. The amide bonds in the ethylbenzamide groups have *cis* stereochemistry.

(Received February 16, 2005; Accepted May 24, 2005; Published on web July 29, 2005)

We have reported a sensitive and selective spectrophotometric determination of copper(II) and benzoylperoxide (BPO) with *N*-ethyl-2-naphthylamine (NENA) by using the selective catalytic action of copper(II) in the reaction between NENA and BPO.¹ In this paper, the reaction between NENA and BPO was

presumed to be *N*-benzoylation and *O*-hydroxylation of NENA; however, the molecular structure of the reaction product (NENA-BPO) has not been fully explained. For the purpose of clarifying the structure of NENA-BPO, we carried out an X-ray analysis.

Equivalent molar amounts of NENA and BPO were dissolved

Fig. 1 Synthesis and chemical structure of the title compound.

Table 1 Crystal and experimental data

Formula:	C ₃₈ H ₃₂ N ₂ O ₄
Formula weight	= 580.66
Crystal system:	monoclinic
Space group:	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i>	= 14.045(4)Å
<i>b</i>	= 14.957(4)Å
<i>c</i>	= 15.626(5)Å
<i>V</i>	= 2983.2(2)Å ³
<i>T</i>	= 220 K
<i>D_x</i>	= 1.293 g cm ⁻³
<i>F</i> (000)	= 1224
θ _{max}	= 26.73° with Mo <i>K</i> _α
No. of reflections (<i>I</i> > 2σ(<i>I</i>))	= 4187
<i>R</i> (<i>I</i> > 2σ(<i>I</i>))	= 0.0691
<i>wR</i> (<i>I</i> > 2σ(<i>I</i>))	= 0.1771
(Δ/ <i>σ</i>) _{max}	< 0.001
Δρ _{max}	= 0.645 eÅ ⁻³
Δρ _{min}	= -0.227 eÅ ⁻³
Measurement:	Bruker AXS SMART APEX
Program system:	SAINT+
Structure determination:	SHELXS97
Refinement:	full-matrix (SHELXL97)

Table 2 Atomic coordinates and equivalent isotropic thermal parameters (*U*_{eq})

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
C1	0.4973(2)	0.7780(1)	0.1426(1)	0.0238(4)
O1	0.4018(1)	0.7819(1)	0.1450(1)	0.0334(4)
C2	0.5851(2)	0.7426(1)	0.2135(1)	0.0233(4)
N2	0.5774(1)	0.7083(1)	0.2962(1)	0.0252(4)
C3	0.6811(2)	0.7411(1)	0.2059(1)	0.0234(4)
C4	0.6945(2)	0.7804(1)	0.1323(1)	0.0227(4)
C5	0.6053(2)	0.8224(1)	0.0596(1)	0.0247(4)
C6	0.6113(2)	0.8711(2)	-0.0160(2)	0.0337(5)
C7	0.5240(2)	0.9098(2)	-0.0838(2)	0.0439(6)
C8	0.4263(2)	0.9037(2)	-0.0804(2)	0.0447(6)
C9	0.4170(2)	0.8593(2)	-0.0079(2)	0.0342(5)
C10	0.5055(2)	0.8182(1)	0.0632(1)	0.0249(4)
C11	0.5370(2)	0.6167(2)	0.2922(2)	0.0336(5)
C12	0.6222(2)	0.5480(2)	0.3168(2)	0.0536(7)
C13	0.6176(2)	0.7518(1)	0.3799(1)	0.0256(5)
O13	0.6179(1)	0.7160(1)	0.4512(1)	0.0361(4)
C14	0.6659(2)	0.8426(1)	0.3861(1)	0.0267(5)
C15	0.7620(2)	0.8577(2)	0.4618(2)	0.0352(5)
C16	0.8126(2)	0.9390(2)	0.4713(2)	0.0464(7)
C17	0.7678(2)	1.0063(2)	0.4073(2)	0.0471(7)
C18	0.6702(2)	0.9933(2)	0.3342(2)	0.0449(6)
C19	0.6192(2)	0.9121(2)	0.3228(2)	0.0347(5)
C21	0.9948(2)	0.7760(1)	0.1149(1)	0.0242(4)
O21	1.0897(1)	0.7774(1)	0.1119(1)	0.0351(4)
C22	0.9032(2)	0.7503(1)	0.0407(1)	0.0229(4)
N22	0.9083(1)	0.7193(1)	-0.0444(1)	0.0255(4)
C23	0.8077(2)	0.7511(1)	0.0491(1)	0.0236(4)
C24	0.7990(2)	0.7794(1)	0.1293(1)	0.0224(4)
C25	0.8934(2)	0.8074(1)	0.2078(1)	0.0238(4)
C26	0.8941(2)	0.8413(2)	0.2932(1)	0.0300(5)
C27	0.9843(2)	0.8700(2)	0.3646(2)	0.0366(6)
C28	1.0797(2)	0.8688(2)	0.3553(2)	0.0373(6)
C29	1.0832(2)	0.8380(2)	0.2748(2)	0.0325(5)
C30	0.9911(2)	0.8055(1)	0.2000(1)	0.0253(4)
C31	0.9473(2)	0.6284(2)	-0.0419(2)	0.0329(5)
C32	0.8634(2)	0.5593(2)	-0.0573(2)	0.0482(7)
C33	0.8670(2)	0.7635(1)	-0.1274(1)	0.0258(5)
O33	0.8636(1)	0.7277(1)	-0.1999(1)	0.0360(4)
C34	0.8228(2)	0.8554(1)	-0.1317(1)	0.0281(5)
C35	0.7296(2)	0.8751(2)	-0.2090(2)	0.0422(6)
C36	0.6866(2)	0.9598(2)	-0.2177(2)	0.0575(8)
C37	0.7360(3)	1.0247(2)	-0.1535(2)	0.0621(9)
C38	0.8299(3)	1.0067(2)	-0.0774(2)	0.0503(7)
C39	0.8727(2)	0.9222(2)	-0.0661(2)	0.0351(5)

[†] To whom the correspondence should be addressed.
E-mail: rinshoukagaku_fujimoto1@yahoo.co.jp

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

Fig. 2 ORTEP drawing of the title compound with atom labeling. The thermal ellipsoids are drawn at the 50% probability level.

in 50-times molar of benzene and stirred on an ice bath for 20 min. The product was then extracted with 0.1 M sodium hydroxide, and a white powder was subsequently filtered by acidifying with a 1 M hydrochloric acid solution. The reaction is shown in Fig. 1.

Crystals of NENA-BPO were grown from an aqueous methanol solution. A crystal with a size of $0.4 \times 0.30 \times 0.05$ mm was used for diffraction experiments (Table 1). The structure was solved by a direct method with SHELXS97.² Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated at the ideal positions and isotropically included in calculations of the structure factors. The atomic parameters for non-hydrogen atoms are listed in Table 2.

As expected, NENA-BPO is a product that resulted from the *N*-benzoylation and *O*-hydroxylation of NENA; however, it differs from 2-*N*-ethylbenzamido-1-naphthol as we estimated in the previous paper.¹ It has become clear that an oxidative

Table 3 Selected bond length (Å) and angles (°)

C1	O1	1.359(2)	C22	N22	1.436(2)		
C2	N2	1.436(2)	C31	N22	1.461(3)		
C11	N2	1.474(3)	C31	C32	1.510(3)		
C11	C12	1.499(4)	C33	O33	1.236(2)		
C13	O13	1.234(2)	C33	N22	1.353(3)		
C13	N2	1.355(3)	C33	C34	1.497(3)		
C13	C14	1.503(3)	C4	C24	1.488(3)		
C21	O21	1.354(2)					
N2	C11	C12	112.0(2)	N22	C31	C32	111.9(2)
O13	C13	N2	120.3(2)	O33	C33	N22	120.3(2)
O13	C13	C14	120.2(2)	O33	C33	C34	120.0(2)
N2	C13	C14	119.4(2)	N22	C33	C34	119.7(2)
C13	N2	C2	122.6(2)	C33	N22	C22	124.3(2)
C13	N2	C11	119.1(2)	C33	N22	C31	119.1(2)
C2	N2	C11	117.8(2)	C22	N22	C31	116.0(2)

dimerization is also involved in the reaction, and NENA-BPO is the 4,4'-dimer of 2-*N*-ethylbenzamido-1-naphthol. The molecular structure is shown in Fig. 2. The torsion angle between the two-ring system (C5-C4-C24-C25) is $129.0(2)^\circ$. The length of the inter-ring C4-C24 bond [1.488(3) Å] suggests that it is essentially a single bond. A somewhat interesting feature is that the amide bonds in the ethylbenzamide groups have *cis* stereochemistry, which is probably due to interactions of the bulky benzene rings. Selected bond lengths and angles are listed in Table 3.

References

1. I. Mori, T. Fujimoto, Y. Fujita, and T. Matsuo, *Talanta*, **1995**, 42, 77.
2. SHELXS-97, G. M. Sheldrick, **1997**, University of Goettingen, Germany.