Synthesis and Crystal Structure of a Novel Compound: 1-[[2-(1,3-Diphenyl-1*H*-naphtho [1,2-*e*][1,3]oxazin-2-yl)cyclohexylamino]phenylmethyl]-naphthalen-2-ol

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The reaction of (1*R*,2*R*)-1,2-diaminocyclohexane with 2-naphthol and benzaldehyde gave the title compound, 1-[[2-(1,3-diphenyl-1*H*-naphtho[1,2-*e*][1,3]oxazin-2-yl)cyclohexylamino]phenylmethyl]naphthalen-2-ol (**2**), under solvent-free condition. The results of an X-ray single crystal analysis indicate that there are five chiral centers and two different types of intramolecular hydrogen bonds in the title compound. One is a O-H...N hydrogen bond, and the other is a N-H...N hydrogen bond.

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Optically active 1,2-diaminocyclohexane and its derivatives have been widely used as chiral ligands of catalyst for asymmetric reactions, as effective host compounds for the isolation or optical resolution of organic guest molecules through the formation of crystalline inclusion complexes, as

chiral stationary phases for chromatographic separation, and as chelating agents for many minerals and metals.¹⁻⁵ The wide-ranging and important applications of these compounds in organic synthesis have stimulated great interest in developing efficient methods for their preparation. Recently, during the course of a one-pot synthesis of derivative **1** of the 1,2-diaminocyclohexane, it was found that the reaction of (1*R*,2*R*)-1,2-diaminocyclohexane with 2-naphthol and benzaldehyde under solvent-free condition did not afford the desired product; accidentally, a novel compound was obtained. In order to obtain a clear understanding of the structural feature of this novel compound (**2**), we also obtained its single crystals suitable for an X-ray crystallographic study by recrystallization from a methanol solution. In this paper, we wish to report on the synthesis and crystal structure of **2**.

Fig. 1 Chemical structure diagrams of **1** and **2**.

Fig. 2 Molecular structure diagram of **2**. Hydrogen atoms are omitted for clarity.

Table 1 Crystallographic data and structure refinement parameters

Formula:	C ₄₇ H ₄₂ N ₂ O ₂
Formula weight:	666.83
Crystal system:	monoclinic
Space group:	<i>P</i> 2 ₁ <i>Z</i> = 2
<i>a</i> =	10.1499 (10) Å
<i>b</i> =	13.9316 (14) Å
<i>c</i> =	13.1515 (13) Å
<i>V</i> =	1858.7 (3) Å ³
<i>D</i> _{calc} =	1.191 g/cm ³
No. of reflections used =	4346 [<i>I</i> > 2σ(<i>I</i>)]
2θ _{max} =	56.4° with Mo <i>K</i> _α
<i>R</i> ₁ =	0.0457; <i>wR</i> ₂ = 0.0813
(Δρ) _{max} =	0.000 eÅ ⁻³
(Δρ) _{max} =	0.142 eÅ ⁻³
(Δρ) _{min} =	-0.133 eÅ ⁻³
Measurement:	Bruker SMART CCD
Program system:	SHELXL-97
Structure determination:	direct methods (SHELXS-97)
Refinement:	full-matrix least-squares on <i>F</i> ²

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O(1)	3543(2)	5657(2)	3777(2)	58(1)
O(2)	1149(2)	5570(1)	8185(1)	49(1)
N(1)	1684(2)	6666(2)	4605(2)	38(1)
N(2)	727(2)	6304(1)	6551(1)	33(1)
C(1)	1980(3)	6845(2)	6444(2)	35(1)
C(2)	2388(3)	7524(2)	7310(2)	47(1)
C(3)	3693(4)	8011(3)	7117(3)	60(1)
C(4)	3644(4)	8551(3)	6121(2)	58(1)
C(5)	3269(3)	7873(2)	5257(2)	48(1)
C(6)	1962(3)	7379(2)	5419(2)	36(1)
C(7)	1410(2)	7079(2)	3568(2)	37(1)
C(8)	2600(2)	7021(2)	2894(2)	38(1)
C(9)	2675(3)	7661(2)	2044(2)	47(1)
C(10)	1787(4)	8412(2)	1853(3)	62(1)
C(11)	1862(5)	8998(3)	1023(3)	88(1)
C(12)	2858(6)	8847(4)	333(3)	111(2)
C(13)	3727(5)	8151(4)	478(3)	98(2)
C(14)	3682(3)	7514(3)	1322(2)	65(1)
C(15)	4577(3)	6754(3)	1482(3)	72(1)
C(16)	4531(3)	6180(3)	2291(3)	60(1)
C(17)	3519(3)	6308(2)	3014(2)	46(1)
C(18)	259(2)	6547(2)	3057(2)	37(1)
C(19)	399(3)	5624(2)	2700(2)	48(1)
C(20)	-656(3)	5150(3)	2235(2)	61(1)
C(21)	-1851(3)	5596(3)	2127(2)	60(1)
C(22)	-2001(3)	6507(3)	2478(2)	55(1)
C(23)	-947(3)	6992(2)	2942(2)	43(1)
C(24)	-423(2)	6846(2)	6917(2)	35(1)
C(25)	-364(2)	6901(2)	8071(2)	38(1)
C(26)	-1112(3)	7608(2)	8602(2)	41(1)
C(27)	-1975(3)	8258(2)	8101(3)	50(1)
C(28)	-2680(3)	8918(2)	8625(3)	64(1)
C(29)	-2542(4)	8954(3)	9684(3)	75(1)
C(30)	-1731(4)	8349(3)	10190(3)	69(1)
C(31)	-995(3)	7651(2)	9675(2)	52(1)
C(32)	-151(3)	6991(2)	10195(2)	58(1)
C(33)	522(3)	6320(2)	9692(2)	53(1)
C(34)	396(3)	6276(2)	8622(2)	40(1)
C(35)	827(3)	5427(2)	7110(2)	39(1)
C(36)	1803(3)	4724(2)	6695(2)	42(1)
C(37)	1579(4)	4404(2)	5696(2)	53(1)
C(38)	2432(5)	3766(2)	5273(3)	71(1)
C(39)	3489(4)	3428(3)	5816(4)	77(1)
C(40)	3733(3)	3726(2)	6795(4)	72(1)
C(41)	2875(3)	4386(2)	7243(3)	52(1)
C(42)	-1698(2)	6394(2)	6499(2)	39(1)
C(43)	-1968(3)	6381(2)	5466(2)	48(1)
C(44)	-3124(3)	5971(2)	5073(3)	60(1)
C(45)	-4008(3)	5566(3)	5705(3)	61(1)
C(46)	-3747(3)	5575(3)	6723(3)	69(1)
C(47)	-2609(3)	5986(2)	7121(3)	57(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

A mixture of 2-naphthol (5.76 g, 40 mmol), (1*R*, 2*R*)-1,2-diaminocyclohexane (2.28 g, 20 mmol) and benzaldehyde (4.24 g, 40 mmol) was heated and stirred at 60°C for 4 h under an argon atmosphere using an oil bath until it became white solid. Heating was continued for another 2 h, and then cooling was performed to ambient temperature. The resulting white solid was crushed and stirred in a solution of ethanol for 0.5 h. The crude product was filtered and washed with ethanol. Recrystallization from methanol/chloroform (1:1) give 5.87 g (44.2%) of **2** as colorless prism crystals. The crystal and experimental data are listed in Table 1. The structure was solved by direct methods and expanded using successive Fourier techniques. In the final cycle full-matrix refinement

Table 3 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

Bond	Distance/ $\text{\AA}$	Bond	Angle/ $^\circ$
O(1)–C(17)	1.354(3)	C(6)–N(1)–C(7)	115.2(2)
O(2)–C(34)	1.383(3)	C(1)–N(2)–C(24)	117.12(19)
O(2)–C(35)	1.454(3)	C(1)–N(2)–C(35)	115.8(2)
N(1)–C(6)	1.481(3)	O(2)–C(35)–N(2)	113.2(2)
N(1)–C(7)	1.497(3)	O(2)–C(35)–C(36)	108.1(2)
N(2)–C(35)	1.427(3)	N(2)–C(35)–C(36)	113.9(2)
N(2)–C(24)	1.483(3)	C(24)–N(2)–C(35)	108.19(19)
N(2)–C(1)	1.490(3)	N(2)–C(24)–C(25)	110.1(2)
O(1)–H(41)	0.92(3)	N(2)–C(24)–C(42)	109.9(2)
N(1)–H(42)	0.86(2)	C(34)–O(2)–C(35)	113.1(2)

using SHELX 97, all non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The final positional parameters for non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3. The molecular structure of **2** is shown in Fig. 2 together with the atomic-labeling scheme.

As shown in Fig. 2, the crystal of the title compound **2** possesses five chiral centers including original two chiral centers (C(1) (*R*), C(6) (*R*)) and three new stereogenic centers (C(7) (*R*), C(24) (*S*) and C(35) (*R*)). N(2), C(24), C(25), C(34), O(2) and C(35) atoms constitute a new six-membered ring which is in chair conformation. The bond angles of the new six-membered ring are: 108.19(19)°(C(24)–N(2)–C(35)), 113.2(2)°(O(2)–C(35)–N(2)), 113.1(2)°(C(35)–O(2)–C(34)), 110.1(2)°(N(2)–C(24)–C(25)), 123.1(2)°(C(25)–C(34)–O(2)) and 120.3(2)°(C(24)–C(25)–C(34)), respectively. The former four bond angles are close to the theoretical value (109.5°) and the later two bond angles deviate from the theoretical value. In addition, there are two different types of intramolecular hydrogen bonds in the crystal. One is a O–H...N hydrogen bond; the other is a N–H...N hydrogen bond. The parameters of these two H-bonds are: O(1)–H(41)...N(1)(2.618 Å, 150.38°) and N(1)–H(42)...N(2)(2.813 Å, 113.48°).

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