

**(S)-2,2'-Bis(4-nitro-2-pyridyloxy)-1,1'-binaphthalene**

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**Key indicators**

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

$R$  factor = 0.037

w $R$  factor = 0.092

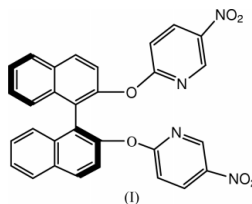
Data-to-parameter ratio = 7.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{30}\text{H}_{18}\text{N}_4\text{O}_6$ , is formed when two 4-nitro-2-pyridyl units link, in a *trans* fashion, to the two O atoms of optically active (*S*)-BINOL (1,1'-bi-2-naphthol). The molecule exhibits some dramatic deviations from planarity due to the steric hindrance caused by the presence of the two nitro-pyridyloxy moieties. C—H...O hydrogen bonding between adjacent molecules links them into a chain-like structure.

**Comment**

The designed synthesis of functional supramolecular complexes has received much attention, because of the interesting structural topologies of these complexes and their potential application in materials science (Kitagawa & Kondo, 1998; Swiegers & Maleftse, 2002). The structures and functional properties of complexes can be adjusted by changing and controlling the type, angle and size of the spacers between coordination sites in the bridging ligands (Breuning *et al.*, 2001; Fujita, 1998; Leininger *et al.*, 2000). Rigid or flexible spacers, such as alkyl and aryl groups as well as organometallic complexes, have been employed in association with metal coordination sites (Hong *et al.*, 2000; Horikoshi *et al.*, 2002; Sun *et al.*, 2000; Wang *et al.*, 2002). From the viewpoint of constructing functional supramolecules, it may be more valuable to introduce functional spacer groups directly into organic ligands..



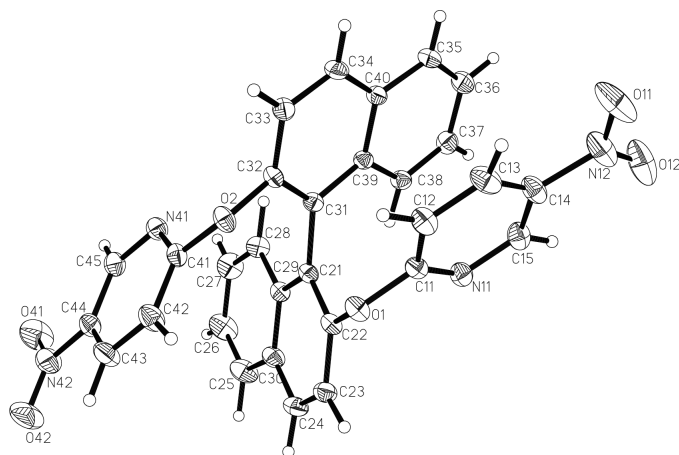
Optically active 1,1'-bi-2-naphthol (BINOL) derivatives have been used successfully in asymmetric catalysis, molecular recognition and optical materials (Lee & Lin, 2002; Noyori, 2002; Pu, 1998). Their success is due to the fact that the axial chirality of the ligands can be well expressed in the steric environment of the active sites, and the chiral configuration of BINOL molecules is known to be stable at high temperature over extended periods of time. Thus, BINOL may be used as a preferred starting material or auxiliary for the synthesis of homochiral functional supramolecular complexes. Here we report the synthesis and crystal structure of a homochiral organic ligand, namely (*S*)-2,2'-bis(4-nitro-2-pyridyloxy)-1,1'-binaphthalene [(*S*)-*L*], (I).

As shown in Fig. 1, the ligand (*S*)-*L* is composed of two 4-nitro-2-pyridyl units linked, in a *trans* fashion, to the two O

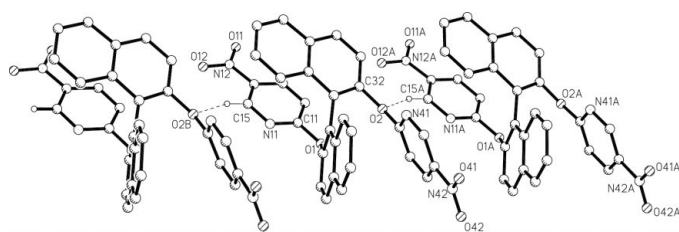
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**Figure 1**  
View of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**  
The one-dimensional chain formed through C—H...O hydrogen bonds.

atoms (2,2'-) of the optically active (*S*)-BINOL. The bond distances of C11—O1 and C41—O2 are 1.362 (3) and 1.363 (3) Å, respectively. The separation between atoms O1 and O2 is 3.028 Å, similar to that reported in 2,2'-O-substituted complexes (Goldberg, 1980). Considerable twisting between the two naphthyl groups produces a dihedral angle of 105.2°, which compares well with the angle of 101.7° found in (*S*)-BINOL itself (Mori *et al.*, 1993; Toda *et al.*, 1997). The naphthyl groups are also highly twisted with respect to their covalently linked pyridyl groups, with dihedral angles of 96.7 and 110.3°. These twists may be ascribed to steric repulsion, resulting in the two nitropyridyl units lying on opposite sides of the binaphthyl backbone. Both nitro groups are approximately coplanar with their linked pyridyl rings, with dihedral angles of 1.0 and 4.7°, respectively. The absolute configuration of (I) could not be reliably determined from the experimental X-ray data. The (*S*) assignment was based on the negative value of the optical rotation of BINOL, and from the known configurations of the starting materials.

As shown in Fig. 2, (*S*)-*L* molecules are linked into a chain structure through C—H...O hydrogen-bonding interactions [O2...H = 2.547 Å, O2...H—C15<sup>i</sup> = 144°; symmetry code: (i) *x*, *y* + 1, *z*; Desiraju & Steiner, 1999]. There are no other short contacts or noteworthy aryl–aryl interactions between adjacent molecules or between adjacent chains. It may be interesting to compare the crystal structure of (I) with that of (*S*)-BINOL, which crystallizes in the trigonal space group *P*3<sub>2</sub>. (*S*)-BINOL forms an infinite right-handed helical chain

arranged along a 3<sub>2</sub> screw axis through intermolecular O—H...O hydrogen bonds, with an O...O distance of 2.96 Å (Mori *et al.*, 1993; Toda *et al.*, 1997).

## Experimental

A mixture of (*S*)-BINOL (1.14 g, 4 mmol) and NaOH (0.32 g, 8 mmol) in MeOH (10 ml) was stirred for 6 h at room temperature. The solvent was removed under reduced pressure; the residue and 2-chloro-5-nitropyridine (1.40 g, 8.8 mmol) were dissolved in tetrahydrofuran (15 ml) and refluxed overnight. The resulting solution was diluted with EtOAc (20 ml) and then washed three times with water and once with brine; the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the residue was recrystallized from acetone/MeOH to afford colorless solid (*S*)-*L*. Slow evaporation of a methanol solution of (*S*)-*L* in air gave colorless crystals suitable for X-ray analysis.

## Crystal data

C<sub>30</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>

*M<sub>r</sub>* = 530.48

Triclinic, *P*1

*a* = 7.4573 (14) Å

*b* = 7.9472 (15) Å

*c* = 11.748 (2) Å

α = 96.859 (3)°

β = 104.061 (4)°

γ = 108.599 (3)°

*V* = 625.3 (2) Å<sup>3</sup>

*Z* = 1

*D<sub>x</sub>* = 1.409 Mg m<sup>-3</sup>

Mo Kα radiation

Cell parameters from 1879 reflections

θ = 3.0–27.5°

μ = 0.10 mm<sup>-1</sup>

*T* = 293 (2) K

Needle, colorless

0.38 × 0.17 × 0.10 mm

## Data collection

Siemens SMART CCD diffractometer

ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

*T<sub>min</sub>* = 0.980, *T<sub>max</sub>* = 0.990

4222 measured reflections

3405 independent reflections

2651 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.017

θ<sub>max</sub> = 27.5°

*h* = −9 → 9

*k* = −10 → 10

*l* = −13 → 15

## Refinement

Refinement on *F*<sup>2</sup>

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.037

*wR* (*F*<sup>2</sup>) = 0.092

*S* = 0.97

3405 reflections

434 parameters

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0549*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δσ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.16 e Å<sup>-3</sup>

Δρ<sub>min</sub> = −0.15 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

N11—C11	1.321 (3)	N42—O42	1.222 (4)
N11—C15	1.336 (4)	N42—C44	1.458 (4)
N12—O11	1.213 (5)	O1—C11	1.362 (3)
N12—O12	1.221 (5)	O1—C22	1.398 (3)
N12—C14	1.462 (4)	O2—C41	1.363 (3)
N41—C41	1.312 (3)	O2—C32	1.403 (3)
N41—C45	1.335 (4)	C21—C31	1.493 (4)
N42—O41	1.219 (4)		
O11—N12—O12	123.0 (4)	C11—O1—C22	118.1 (2)
O41—N42—O42	123.6 (3)	C41—O2—C32	120.5 (2)

H atoms were positioned geometrically (C—H bond fixed at 0.96 Å) and assigned isotropic displacement parameters, and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to

solve structure: *SHELXTL/PC* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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## References

- Breuning, E., Ziener, U., Lehn, J.-M., Wegelius, E. & Rissanen, K. (2001). *Eur. J. Inorg. Chem.* pp. 1515–1521.
- Desiraju, G. R. & Steiner, K. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press.
- Fujita, M. (1998). *Chem. Soc. Rev.* **27**, 417–425.
- Goldberg, I. (1980). *J. Am. Chem. Soc.* **102**, 4106–4113.
- Hong, M. C., Su, W. P., Cao, R., Fujita, M. & Lu, J. X. (2000). *Chem. Eur. J.* **6**, 427–431.
- Horikoshi, R., Mochida, T. & Moriyama, H. (2002). *Inorg. Chem.* **41**, 3017–3024.
- Kitagawa, S. & Kondo, M. (1998). *Bull. Chem. Soc. Jpn.* **71**, 1739–1753.
- Lee, S. J. & Lin, W. B. (2002). *J. Am. Chem. Soc.* **124**, 4554–4555.
- Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–908.
- Mori, K., Masuda, Y. & Kashino, S. (1993). *Acta Cryst. C* **49**, 1224–1227.
- Noyori, R. (2002). *Angew. Chem. Int. Ed.* **41**, 2008–2022.
- Pu, L. (1998). *Chem. Rev.* **98**, 2405–2494.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL/PC*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1994). *SMART* and *SAINTE*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sun, W. Y., Fan, J., Okamura, T. & Ueyama, N. (2000). *Inorg. Chem. Commun.* **3**, 541–544.
- Swiegers, G. F. & Maleftse, T. J. (2002). *Coord. Chem. Rev.* **225**, 91–121.
- Toda, F., Tanaka, K., Miyamoto, H., Koshima, H., Miyahara, I. & Hirotsu, K. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 1877–1885.
- Wang, R. H., Hong, M. C., Luo, J. H., Cao, R. & Weng, J. B. (2002). *Eur. J. Inorg. Chem.* pp. 3097–3100.