Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*S*)-(−)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl, a versatile chelating ligand

Matthew D. Jones,* Filipe A. Almeida Paz, John E. Davies and Brian F. G. Johnson

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

Correspondence e-mail: mdj22@cam.ac.uk

Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.004 Å
R factor = 0.042
wR factor = 0.088
Data-to-parameter ratio = 12.8

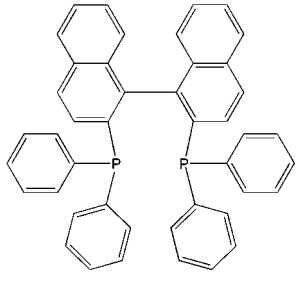
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 March 2003
Accepted 17 March 2003
Online 31 March 2003

The crystal structure of the title compound, [(*S*)-(−)-BINAP] or $C_{44}H_{32}P_2$, is enantiomorphous to the previously reported (*R*)-(+)-BINAP [Deeming *et al.* (1997). *Organometallics*, **16**, 6004–6009], with effectively no differences in the molecular geometry apart from being of opposite absolute configuration.

Comment

The ability to selectively form one enantiomer in preference to the other (asymmetric catalysis) is undoubtedly one of the major advances in modern drug design and synthesis. In 2000, the total worldwide sales of single-enantiomer compounds was 123 billion US dollars (Stinson, 2001). In recognition of the outstanding contributions to this field, Noyori received the Nobel Prize for Chemistry in 2001, with much of his work being centred around the different chiral forms of 2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl (BINAP) (Noyori, 2002). BINAP is a conformationally flexible atropisometric diphosphine, which is able to coordinate to several transition metal centres, such as rhodium (Ikariya *et al.*, 1985), ruthenium (Toriumi *et al.*, 1982) and palladium (Ozawa & Hayashi, 1992). Once BINAP is coordinated, the high steric hindrance around the metal centre affords complexes which are extremely potent for asymmetric hydrogenation (Noyori, 2002). An example of this is the synthesis of (−)-menthol, in which a [Rh-(*S*)-BINAP] derivative is utilized to induce chirality in the final product. A search in the Cambridge Structural Database (Allen, 2002) reveals that only the (*R*)-(+)-BINAP crystal structure has been reported so far (Deeming *et al.*, 1997). We report here the structure of the *S* enantiomer of this renowned organic ligand.



(I)

[(*S*)-(−)-BINAP], (I), crystallizes in the monoclinic space group $P2_1$, with one molecule in the asymmetric unit, as depicted in Fig. 1. Individual molecules of (*S*)-(−)-BINAP are spatially arranged in close packing along the *a* direction (Figs. 2 and 3). The structures of the *R* and *S* enantiomers are essentially the same, except for being of opposite absolute configuration (Deeming *et al.*, 1997).

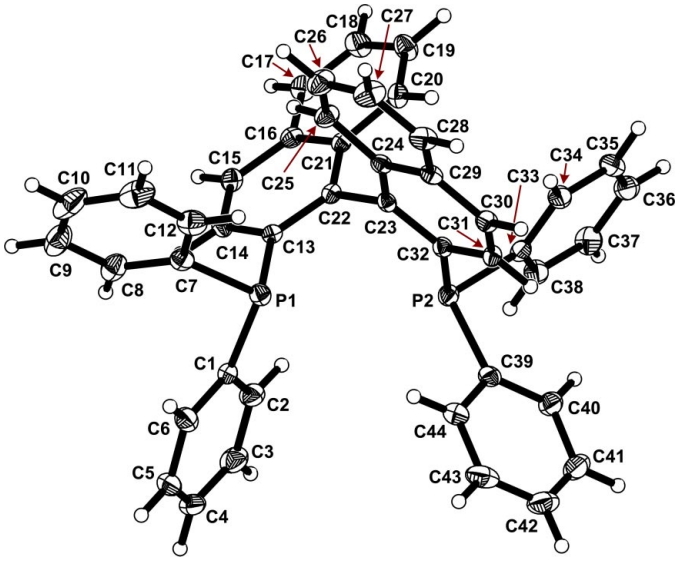


Figure 1
The molecular structure of (I), showing the labelling scheme for all non-H atoms. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres.

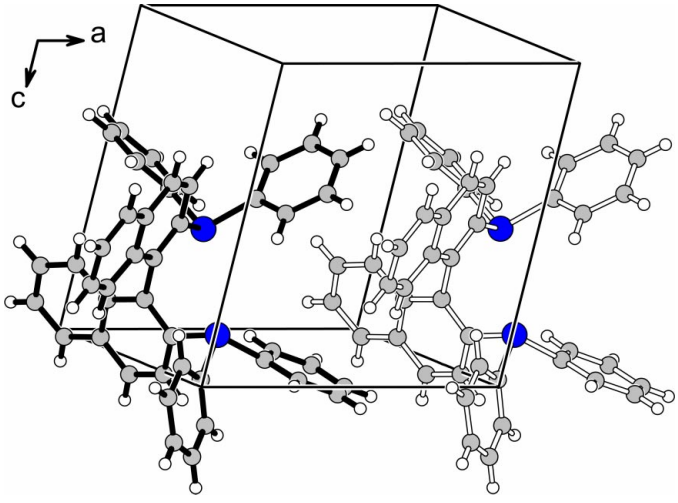


Figure 2
Crystal packing of two (filled and hollow bonds) molecules of (I).

Experimental

(*S*)-(−)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl was purchased from Aldrich (99.99% purity). Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from methanol.

Crystal data

$C_{44}H_{32}P_2$
M_r = 622.64
Monoclinic, $P2_1$
a = 9.1206 (2) Å
b = 18.7541 (7) Å
c = 9.9829 (3) Å
β = 103.206 (2)°
V = 1662.40 (9) Å^3
Z = 2
D_x = 1.244 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6595 reflections
θ = 1.0–25.0°
μ = 0.16 mm^{-1}
T = 180 (2) K
Block, white
0.23 × 0.21 × 0.16 mm

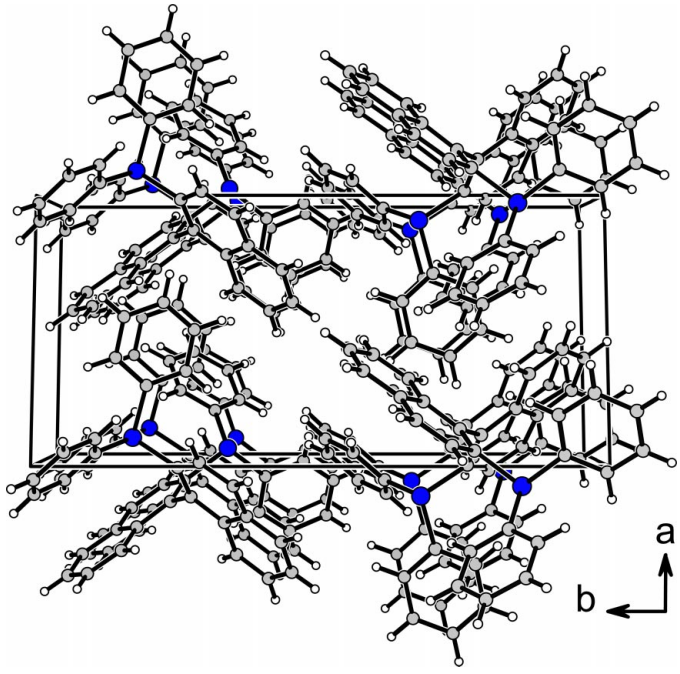


Figure 3
Perspective view of the crystal structure of (I) along the c direction.

Data collection

Nonius KappaCCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.934, T_{max} = 0.981
11117 measured reflections
5303 independent reflections
4457 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.1°
$h = -10 \rightarrow 10$
$k = -22 \rightarrow 20$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.088
S = 1.04
5303 reflections
415 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.2494P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.04 (8)

Table 1
Selected geometric parameters (Å, °).

P1—C1	1.828 (3)	P2—C39	1.841 (3)
P1—C13	1.838 (3)	P2—C32	1.843 (3)
P1—C7	1.837 (3)	C22—C23	1.504 (3)
P2—C33	1.832 (3)		
C1—P1—C13	103.59 (13)	C33—P2—C39	102.39 (13)
C1—P1—C7	102.88 (13)	C33—P2—C32	101.88 (12)
C13—P1—C7	101.83 (12)	C39—P2—C32	100.36 (13)

All H atoms were placed in calculated positions and allowed to ride during subsequent refinement, with U_{iso}(H) = 1.2U_{eq}(C). A total of 2287 Friedel pairs were used in the refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001);

molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the EPSRC for a studentship to MDJ and for their general financial support, ICI, for financial support, and the Newton Trust. We are also grateful to the Portuguese Foundation for Science and Technology (FCT) for financial support through PhD scholarship No. SFRH/BD/3024/2000, awarded to FAAP.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–58.
Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
Deeming, A. J., Speel, D. M. & Stchedroff, M. (1997). *Organometallics*, **16**, 6004–6009.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Ikariya, T., Ishii, Y., Kawano, H., Arai, T., Saburi, M., Yoshikawa, S. & Akutagawa, S. (1985). *Chem. Commun.* pp. 922–924.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Noyori, R. (2002). *Angew. Chem. Int. Ed.* **41**, 2008–2022.
Ozawa, F. & Hayashi, T. (1992). *J. Organomet. Chem.* **428**, 267–277.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Stinson, S. C. (2001). *Chem. Eng. News*, **79**, 45–47.
Toriumi, K., Ito, T., Takaya, H., Souchi, T. & Noyori, R. (1982). *Acta Cryst.* B**38**, 807–812.