

(S)-2,2',6,6'-Tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine-(2S,3S)-(+)-dibenzoyl-L-tartaric acid-chloroform (1/1/1)

Hua Chen,^{a,b} Jing Wu,^{a,c}
Rongwei Guo,^a Chihung Yeung^a
and Zhongyuan Zhou^{a,d*}

^aDepartment of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, People's Republic of China, ^bDepartment of Chemistry, Sichuan University, Chengdu, People's Republic of China, ^cDepartment of Chemistry, Hangzhou Teacher College, Hangzhou, People's Republic of China, and ^dChengdu Institute of Organic Chemistry, Chinese Academy of Science, Chengdu, People's Republic of China

Correspondence e-mail:
bczyzhou@inet.polyu.edu.hk

Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.053
wR factor = 0.147
Data-to-parameter ratio = 18.4

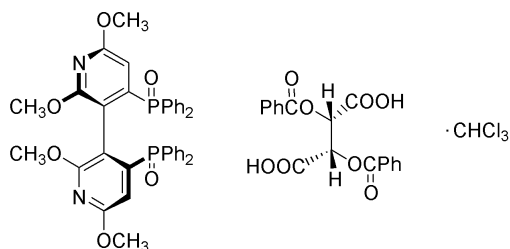
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title cocrystal, $\text{C}_{38}\text{H}_{34}\text{N}_2\text{O}_6\text{P}_2 \cdot \text{C}_{18}\text{H}_{14}\text{O}_8 \cdot \text{CHCl}_3$, (I), reveals that the crystals are built up of infinite chains in which (–)-2,2',6,6'-tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine, (II), and (+)-dibenzoyl-L-tartaric acid, (III), are connected in an alternating fashion through two intermolecular hydrogen bonds between O atoms of the $\text{P}=\text{O}$ groups in (II) and H atoms of the COOH groups in (III).

Comment

Transition-metal-catalysed asymmetric hydrogenation reactions are one of the most efficient methods for preparing a wide range of enantiomerically pure compounds. The possibility of discovering catalysts with improved utility, activity and selectivity by designing new ligands plays a crucial role in this research area. Consequently, the number of novel chiral ligands for catalytic asymmetric hydrogenation is growing rapidly. In this context, chiral bisphosphines (*e.g.* Dipamp, BINAP, DIOP, DuPhos *etc.*) are among the most useful and versatile ligands (Lin *et al.*, 2001). In contrast to the tremendous success achieved in the use of chiral arylphosphine ligands in Rh- and Ru-catalysed asymmetric reactions, chiral phosphine ligands containing heterocyclic moieties, such as pyridyl groups, have been relatively unexplored.

Recently, we have developed a chiral dipyridylphosphine ligand, namely 2,2',6,6'-tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine, (II) (P-Phos; Pai *et al.*, 2000), which was found to be very effective in the Ru-catalysed asymmetric hydrogenation of 2-(6'-methoxy-2'-naphthyl)propenoic acid and β -ketoesters (Pai *et al.*, 2000).



(I)

The key step in the synthesis of P-Phos is the optical resolution of racemate (II) with optically active (+)-dibenzoyl-L-tartaric acid [(+)-DBT], (III), as a resolving reagent (Takaya *et al.*, 1988), which is remarkably efficient and highly selective. After several trials with our experimental modifications, the optically pure dipyridylphosphine oxides (*R*)-(II) and (*S*)-(II) were obtained in high enantiopurity. Thus, when a solution of

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(2*S*,3*S*)-(+)-DBT in ethyl acetate was added to a boiling solution of racemic (II) in dichloromethane, a 1:1 complex of (–)-(II) and (+)-DBT [(–)-(II)–(+)-DBT, (I)] precipitated as a crystalline solid. From internal comparison with (2*S*,3*S*)-(+)-DBT, the absolute configuration of (–)-II was determined to be *S*.

The crystal structure of (I) (Fig. 1) also contains a disordered chloroform molecule in the asymmetric unit. The dihedral angle between the least-squares planes of the two pyridyl rings is 75.9(1)°. Crystals are built up of infinite chains in which equimolar amounts of (–)-(II) and (+)-DBT are connected in an alternating manner through two intermolecular hydrogen bonds formed between O9 and O14 of the P=O groups of (–)-(II) and H atoms of the COOH groups of (+)-DBT. The O4···O14ⁱ and O6···O9ⁱⁱ distances are 2.554 (2) and 2.551 (2) Å, respectively [symmetry codes: (i) 1 – *x*, *y* – ½, ½ – *z*; (ii) ½ + *x*, ½ – *y*, 1 – *z*; Fig. 2 and Table 1]. The low solubility of (I) is attributable to the observed polymeric structure.

Experimental

To a boiling solution of racemic (II) (Pai *et al.*, 2000) (1.87 g, 2.76 mmol) in chloroform (28 ml) was added a solution of (–)-DBT, (III), in ethyl acetate (28 ml). The mixture was refluxed until a white solid formed and then allowed to stand at ambient temperature overnight. The solid product was dried at room temperature under vacuum to give a 1:1 complex of (*R*)-(II) and (–)-DBT (93% yield). The mother liquor, which contained the (*S*)-(II)–(+)-DBT complex, was concentrated to dryness to give a solid material. This was dissolved in chloroform (10 ml) and then treated with 10% aqueous NaOH (10 ml). The mixture was extracted with two portions of chloroform (25 ml). Evaporation of the solvent gave crude (*S*)-(II), which was dissolved in refluxing chloroform (15 ml), and to this solution was added a solution of (+)-DBT in ethyl acetate (20 ml). The mixture was stirred at reflux temperature until the white precipitate formed and was then allowed to stand at room temperature overnight. The white precipitate was dried to give the pure (*S*)-(II)–(+)-DBT complex (92% yield). The crystal used for the data collection was obtained by slow evaporation from chloroform–ethyl acetate (1:1) saturated solution at room temperature.

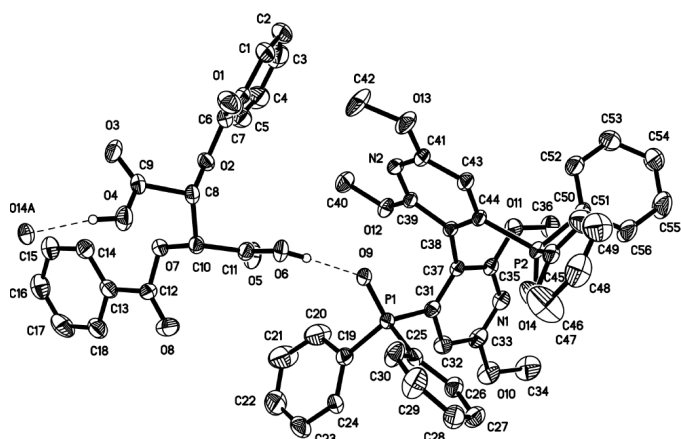


Figure 1

The molecular structure of (I), showing displacement ellipsoids at the 30% probability level (Bruker, 1995).

Crystal data

C₃₈H₃₄N₂O₆P₂·C₁₈H₁₄O₈·CHCl₃
M_r = 1154.27
 Orthorhombic, *P*2₁2₁2₁
a = 10.0967 (10) Å
b = 21.000 (2) Å
c = 27.390 (3) Å
V = 5807.6 (10) Å³
Z = 4
D_x = 1.320 Mg m^{–3}

Mo *K*α radiation
 Cell parameters from 6132 reflections
 θ = 1–27.5°
 μ = 0.28 mm^{–1}
T = 294 (2) K
 Block, colorless
 0.28 × 0.28 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.926, *T_{max}* = 0.947
 39 041 measured reflections

13 342 independent reflections
 8576 reflections with *I* > 2σ(*I*)
R_{int} = 0.043
 θ_{max} = 27.5°
h = –13 → 11
k = –23 → 27
l = –30 → 35

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.053
wR(*F*²) = 0.147
S = 1.01
 13 342 reflections
 725 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.014$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 5987 Friedel pairs
 Flack parameter = 0.05 (8)

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O4–H4···O14 ⁱ	0.82	1.75	2.554 (2)	166
O6–H6···O9 ⁱⁱ	0.82	1.76	2.551 (2)	162

Symmetry codes: (i) 1 – *x*, *y* – ½, ½ – *z*; (ii) ½ + *x*, ½ – *y*, 1 – *z*.

H atoms were included in the riding model approximation, with C–H and O–H distances of 0.93–0.98 and 0.82 Å and a *U_{iso}*(H) of 1.2 or 1.5 times *U_{eq}* of the atom to which they were bound. Two of the Cl atoms in the solvent CHCl₃ molecule are disordered and were each

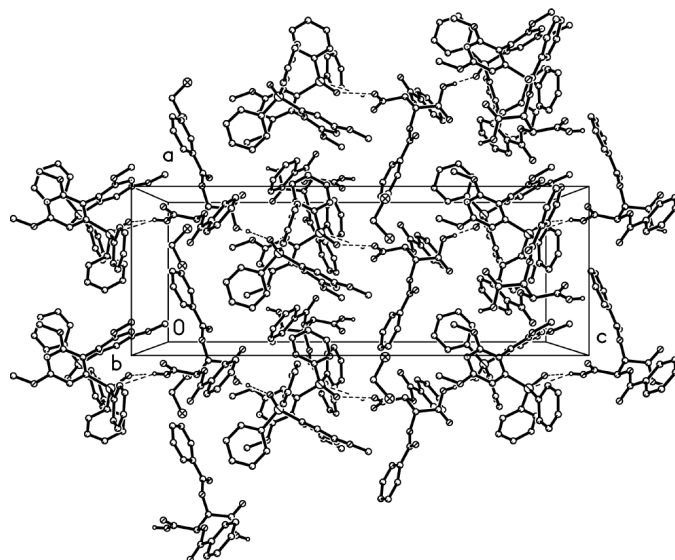


Figure 2

Packing diagram for (I). The chloroform molecules have been omitted.

modeled over two positions with site occupancies of 0.587 (2) and 0.413 (2).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SHELXTL-NT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

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References

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Lin, G. Q., Li, Y. M. & Chan, A. S. C. (2001). In *Principles and Applications of Asymmetric Synthesis*. New York: Wiley.
- Pai, C. C., Lin, C. W., Lin, C. C., Chen, C. C., Chan, A. S. C. & Wong, W. T. (2000). *J. Am. Chem. Soc.* **122**, 11513–11514.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Siemens (1995). *SMART* (Version 5.0) and *SHELXTL-NT* (Version 5.10). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Takaya, H., Akutagawa, S. & Noyori, R. (1988). *Org. Synth. Collect.* Vol. VIII, 57–63.