We are grateful to Professor Joachim Pickardt for the data collection and determining the cell dimensions. Support by Bayer AG and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71624 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1057]

References

Bachi, M. D., Gross, A. & Frolow, F. (1982). *J. Org. Chem.* **47**, 765–767.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Radha, A. (1985). *Z. Kristallogr.* **171**, 225–228.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for Crystal Structure Solution.* Univ. of Göttingen, Germany.
Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Wheatley, P. J. (1962). *J. Chem. Soc.* p. 3636.
Zingaro, R. A. & Meyers, E. A. (1980). *Cryst. Struct. Commun.* **9**, 1167–1172.

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Molecular Structure and Absolute Configuration of (*P*)-7-Phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole

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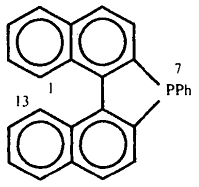
Abstract

An X-ray diffraction study of a crystal of the title compound, $C_{26}H_{17}P$, showed that the naphthyl rings bend away from each other and deviate significantly from planarity; the whole molecule has helical chirality. The crystal chosen for the crystallographic analysis had *P* absolute configuration, indicating that spontaneous resolution had occurred during crystallization.

Comment

Many effective and useful asymmetric catalyses using optically active transition-metal complexes have been developed (Nugent, RajanBabu & Burk, 1993). The 2,2′-binaphthyl group is considered to be a highly suitable moiety for endowing ligands with effective chirality (Kagan, 1985). In the course of our studies on the development of new chiral ligands for effective asymmetric catalysis using transition-metal complex catalysts, we have synthesized a monodentate phosphine ligand, (±)-7-phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole (I), representing a new type of chiral phosphine based on the binaphthyl moiety, and have made a preliminary report of its preparation, properties and X-ray analysis (Tani, Tashiro & Yamagata, 1992). Recently, the preparation and properties of the same compound and the X-ray crystallographic analysis of the arsenic analogue were reported (Watson, Willis & Wild, 1993). Here we report the full details of the results of the crystallographic analysis of the title compound for comparison with that of the arsenic analogue.



(I)

The phosphine (I) was prepared from the reaction of dichlorophenylphosphine with a slight excess of (±)-2,2′-dilithio-1,1′-binaphthyl, analogously to the method reported in the literature (Watson, Willis & Wild, 1993), and was isolated in 60% yield after crystallization from ethanol as pale yellow crystals, m.p. 430.5–432 K. For the X-ray crystallographic study, a single crystal grown from methanol was used.

The molecular structure and a stereoscopic view are shown in Figs. 1 and 2, respectively. The molecular structure and the crystal dimensions are similar to those reported for the arsenic analogue (Watson, Willis & Wild, 1993). Although the five-membered phosphole ring and each benzene ring in the binaphthyl moieties are almost planar, the naphthyl rings are bent significantly away from each other, making the compound chiral. The maximum shifts from the calculated mean planes are 0.084 (4) Å for the phosphole five-membered ring and 0.075 (4) Å for the benzene rings. The crystal chosen for the X-ray analysis belonged to the enantiomeric space group $P2_1$ and the absolute configuration was determined to be *P*. This result indicates that spontaneous resolution had occurred during crystallization, although compound (I) racemized easily in solution at room temperature, as indicated by the temperature-dependent ^{13}C NMR study [$\Delta G^{\ddagger}$ 59.4 kJ mol^{-1} at 253 K (Tani, Tashiro & Yamagata, 1992)]. The dihedral angles between the benzene rings (plane 2, plane 4) and the phosphole ring (plane 1) are 6.67 (9) and 12.03 (9)°, respectively. Each napthalene moiety is also folded considerably at the C—C bond fusing two benzene rings; the dihedral angle between plane 2 and plane 3 is 12.2 (2)° and that between plane 4 and plane 5 is 9.6 (1)°. The phenyl ring (plane 6) is almost perpendicular [92.9 (2)°] to the phosphole ring (plane 1). The dihedral angles between rings are summarized in Table 3. The dihedral angle between the outer benzene rings and that between the inner pair are 38.2 (2) and 18.7 (2)°, respectively, which are similar to those reported for the arsenic analogue [39.3 and 20.4°, respectively (Watson, Willis & Wild, 1993)]. The distance between H(8) and H(13) is 2.33 (5) Å. The average distance of the P—C bonds [1.823 (7) Å] is shorter by 0.12 Å than that of the As—C bonds in the arsole [1.947 (10) Å (Watson, Willis & Wild, 1993)]; this difference is close to the difference of the covalent radii of P and As.

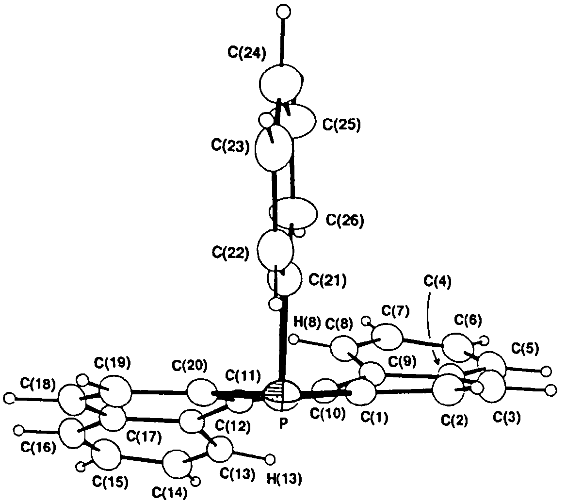


Fig. 1. Molecular structure of the title compound (*ORTEP*II; Johnson, 1976).

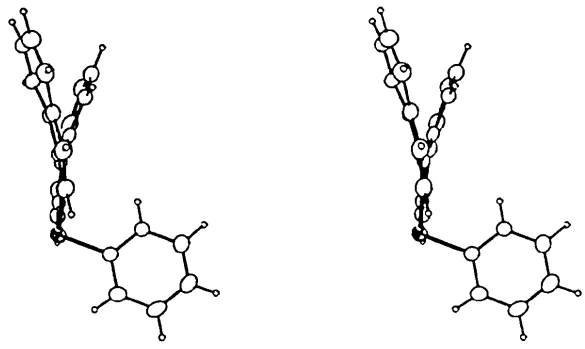


Fig. 2. A stereoview of the title compound.

Experimental

Crystal data

$C_{26}H_{17}P$
M_r = 360.39
Monoclinic
$P2_1$
a = 10.9127 (9) Å
b = 7.9906 (8) Å
c = 10.8248 (9) Å
β = 93.456 (7)°
V = 942.2 (1) Å^3
Z = 2
D_x = 1.270 Mg m^{-3}
D_m = 1.234 (1) Mg m^{-3}
D_m measured by flotation in aqueous CsCl

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 21–23°
μ = 1.31 mm^{-1}
T = 293 (1) K
Plate
0.80 × 0.60 × 0.10 mm
Pale yellow
Crystal source: crystallization from methanol

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.832, $T_{\max}$ = 0.999
2876 measured reflections
2785 independent reflections
2665 observed reflections [$F_o > 3.0\sigma(F_o)$]

$R_{\rm int}$ = 0.015
$\theta_{\max}$ = 60°
$h = -12 \rightarrow 12$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 150 reflections intensity variation: not significant

Refinement

Refinement on F
R = 0.0386
wR = 0.0463
S = 1.771
2665 reflections
311 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max}$ = 0.0001
$\Delta\rho_{\max}$ = 0.35 e Å^{-3}
$\Delta\rho_{\min}$ = −0.29 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
P	0.16836 (7)	0.2500	0.31413 (6)	0.0467 (4)
C(1)	0.3232 (3)	0.1856 (4)	0.2837 (2)	0.0415 (16)
C(2)	0.4156 (3)	0.1392 (4)	0.3738 (3)	0.0510 (19)
C(3)	0.5289 (3)	0.0966 (5)	0.3386 (3)	0.0540 (19)
C(4)	0.5589 (3)	0.1148 (4)	0.2134 (3)	0.0467 (16)
C(5)	0.6805 (3)	0.0874 (5)	0.1785 (4)	0.0580 (20)
C(6)	0.7143 (3)	0.1319 (5)	0.0643 (4)	0.0607 (22)
C(7)	0.6294 (3)	0.2087 (4)	−0.0200 (3)	0.0537 (19)
C(8)	0.5096 (3)	0.2285 (5)	0.0079 (3)	0.0448 (15)
C(9)	0.4686 (3)	0.1728 (4)	0.1234 (2)	0.0394 (14)
C(10)	0.3442 (3)	0.1885 (3)	0.1582 (2)	0.0372 (14)
C(11)	0.2311 (2)	0.2249 (4)	0.0806 (2)	0.0363 (14)
C(12)	0.2059 (3)	0.1976 (3)	−0.0506 (2)	0.0377 (14)
C(13)	0.2792 (3)	0.0964 (4)	−0.1236 (3)	0.0440 (16)
C(14)	0.2504 (3)	0.0753 (5)	−0.2475 (3)	0.0535 (19)
C(15)	0.1474 (3)	0.1536 (5)	−0.3047 (3)	0.0587 (20)
C(16)	0.0708 (3)	0.2443 (5)	−0.2362 (3)	0.0537 (17)

C(17)	0.0951 (2)	0.2629 (4)	−0.1066 (2)	0.0441 (15)
C(18)	0.0076 (3)	0.3419 (5)	−0.0336 (3)	0.0514 (18)
C(19)	0.0253 (3)	0.3431 (4)	0.0926 (3)	0.0490 (17)
C(20)	0.1364 (2)	0.2839 (4)	0.1491 (2)	0.0412 (15)
C(21)	0.1965 (3)	0.4622 (4)	0.3742 (2)	0.0445 (16)
C(22)	0.1322 (3)	0.5198 (5)	0.4718 (3)	0.0480 (18)
C(23)	0.1480 (3)	0.6812 (5)	0.5157 (3)	0.0548 (19)
C(24)	0.2276 (4)	0.7864 (5)	0.4611 (3)	0.0621 (21)
C(25)	0.2940 (4)	0.7311 (5)	0.3644 (3)	0.0693 (22)
C(26)	0.2790 (4)	0.5694 (5)	0.3221 (3)	0.0600 (21)

Table 2. *Selected geometric parameters* (Å, °)

P—C(1)	1.815 (3)	P—C(20)	1.819 (3)
P—C(21)	1.835 (3)	C(1)—C(10)	1.391 (4)
C(10)—C(11)	1.479 (4)	C(11)—C(20)	1.391 (4)
H(8)· · ·H(13)	2.33 (5)		
P—C(1)—C(2)	125.7 (2)	P—C(1)—C(10)	112.5 (1)
P—C(20)—C(11)	111.6 (2)	P—C(20)—C(19)	125.9 (2)
P—C(21)—C(22)	119.8 (2)	P—C(21)—C(26)	121.7 (3)
C(1)—P—C(20)	89.4 (1)	C(1)—P—C(21)	100.9 (1)
C(20)—P—C(21)	103.2 (1)	C(2)—C(1)—C(10)	121.8 (3)
C(1)—C(10)—C(9)	117.9 (2)	C(1)—C(10)—C(11)	112.2 (2)
C(9)—C(10)—C(11)	129.6 (3)	C(10)—C(11)—C(12)	129.1 (3)
C(10)—C(11)—C(20)	112.6 (2)	C(12)—C(11)—C(20)	118.1 (2)

Table 3. *Dihedral angles (°) between least-squares planes*

Plane 1: P, C(1), C(10), C(11), C(20). Plane 2 C(1)-C(4), C(9), C(10). Plane 3: C(4)-C(9). Plane 4: C(11), C(12), C(17)-C(20). Plane 5: C(12)-C(17). Plane 6: C(21)-C(26). Napl 1: C(1)-C(10). Napl 2: C(11)-C(20).

Plane 1—Plane 2	6.67 (9)	Plane 1—Plane 4	12.03 (9)
Plane 1—Plane 6	92.9 (2)	Plane 2—Plane 3	12.2 (2)
Plane 2—Plane 4	18.7 (2)	Plane 3—Plane 5	38.2 (2)
Plane 4—Plane 5	9.6 (1)	Napl 1—Napl 2	28.7 (1)

The positional parameters for all non-H atoms were determined by direct methods (Sheldrick, 1985). The refinements were carried out by full-matrix least-squares techniques (Imoto, 1990). All H atoms were located in a difference Fourier map. The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included in the calculation for the P atom (Cromer & Ibers, 1974). The refined structure showed *P* helicity. On the other hand, the enantiomeric structure gave *R* and *wR* values of 0.0494 and 0.0601. Thus, we decided that the title compound has the absolute configuration *P*. All calculations were carried out on an NEC ACOS 930S computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

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References

Cromer, D. T. & Ibers, J. A. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Imoto, H. (1990). *ANYBLK. Program for Least-Squares Refinement*. Department of Chemistry, Univ. of Tokyo, 113, Japan.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kagan, H. B. (1985). *Asymmetric Catalysis*, Vol. 5, edited by J. D. Morrison, pp. 1-6. New York: Academic Press.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351-359.

Nugent, W. A., RajanBabu, T. V. & Burk, M. J. (1993). *Science*, **259**, 479-483.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Tani, K., Tashiro, H. & Yamagata, T. (1992). *Abstracts of Symposium on Organometallic Chemistry, Japan*, pp. 178-180.

Watson, A. A., Willis, A. C. & Wild, S. B. (1993). *J. Organomet. Chem.* **445**, 71-78.

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5,6-Dihydroxy-7-methoxyflavone

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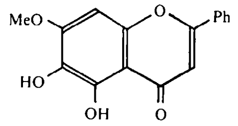
Abstract

The 5-hydroxy group of the title compound, 5,6-dihydroxy-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one, $C_{16}H_{12}O_5$, forms a cyclic intramolecular hydrogen bond O(3)—H···O(2), H···O = 1.71 (3) Å, with the carbonyl group. The heterocyclic ring is not coplanar with the phenyl ring. The C(7) methoxy group is in the plane of the γ-benzopyrone ring with the torsion angle C(11)—O(4)—C(7)—C(8) = 2.9 (3)°.

Comment

The dihedral angle of 12.2 (2)° between the phenyl ring and the γ-benzopyrone portion of the molecule (I) is significantly different from those of two related structures, 5-hydroxy-7-methoxyflavone (Shoja, 1989) and 5-hydroxyflavone (Shoja, 1990), with dihedral angles of 24.8 (2) and 5.7 (7)°, respectively. Given the wide range of dihedral angles and the fact that all three of these molecules contain hydrogen bonding, it is unlikely that any planarity is solely a



(I)