Synthesis, Solid-State Structures, and Aggregation Motifs of Phosphines and Phosphine Oxides Bearing One 2-Pyridone Ring

Motohiro Akazome, Shihomi Suzuki, Yoshiaki Shimizu, Keiichiro Henmi, and Katsuyuki Ogura*

Department of Materials Technology, Faculty of Engineering, Chiba University, 1-33 Yayoicho, Inageku, Chiba 263-8522, Japan

katsu@planet.tc.chiba-u.ac.jp

Received March 21, 2000

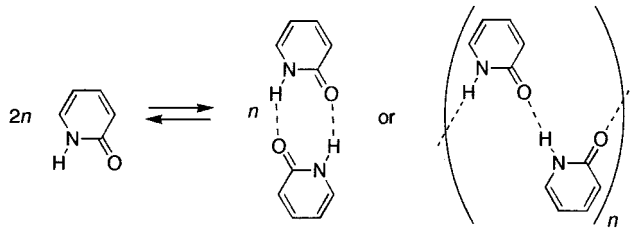
Three phosphines and their corresponding oxides bearing one 2-pyridone ring and two benzene rings were synthesized. Their single-crystal X-ray analyses exhibited three kinds of molecular aggregation: bimolecular aggregates, chiral one-dimensional structures, and achiral one-dimensional structures. In the bimolecular aggregate of (2-oxo-1,2-dihydro-*x*-pyridyl)diphenylphosphines (x = 3: **2a** and 6: **2c**), cyclic dimers that are derived from two 2-pyridone rings are observed. In contrast, (2-oxo-1,2-dihydro-5-pyridyl)diphenylphosphine (**2b**) molecules form a chiral one-dimensional chain via intermolecular hydrogen bonding. In the case of phosphine oxides, their oxygen always acts as a hydrogen acceptor of the hydrogen bonding. Thus, (2-oxo-1,2-dihydro-*x*-pyridyl)diphenylphosphine oxides (x = 3: **3a** and 5: **3b**) form hydrogen bonds intermolecularly between the oxygen atom on the phosphoryl group and the hydrogen atom on nitrogen to construct a chiral or an achiral one-dimensional chain. Interestingly, (2-oxo-1,2-dihydro-6-pyridyl)diphenylphosphine oxide (**3c**) exists as a 2-hydroxypyridine form (enol form) in a crystalline state, and intermolecular hydrogen bonds between the phosphoryl oxygen and the hydroxy proton construct an achiral one-dimensional chain.

Introduction

Crystal engineering to design and control crystal packing arrangement has emerged as one of the most active fields in chemistry.[1,2] A 2-pyridone ring is known to play an important role in supramolecular chemistry. This is because the molecules bearing 2-pyridone rings form intermolecular hydrogen bonds to control the conformation and geometry of their aggregation; two aggregation motifs of 2-pyridones were reported: a cyclic dimer[3,4] and a one-dimensional chain[5] (Scheme 1). Recently, Wuest et al. utilized the hydrogen-bonding ability of the 2-pyridone rings to produce molecular tectonics that construct beautiful three-dimensional assemblies, molecular aggregate, and self-replication.[6]

Against this background, we were interested in developing a three-dimensional packing structure via hydrogen bonds of phosphines and phosphine oxides bearing one 2-pyridone ring, because phosphines are well-known to be a good ligand for transition metal complexes. However, introduction of a 2-pyridone ring into phosphines and phosphine oxides had received less attention except for (2-oxo-1,2-dihydro-6-pyridyl)diphenylphosphine ligands.[7,8] First, we synthesized three phosphines and three phosphine oxides (Scheme 2), and their aggregation was elucidated in solid state by means of single-crystal X-ray analyses.

Scheme 1



Results and Discussion

Syntheses of Phosphines (2a−c) and Phosphine Oxides (3a−c). The synthetic routes leading to phosphines **2a**−**c** and phosphine oxides **3a**−**c** are summarized in Scheme 2. The starting 2-benzyloxy-*x*-bromopyridines

(1) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

(2) *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon Press: Oxford, 1996; Vol. 6.

(3) (a) Beak, P.; Covington, J. B.; Smith, S. G.; White, J. M.; Zeigler, J. M. *J. Org. Chem.* **1980**, *45*, 1354. (b) Beak, P. *Acc. Chem. Res.* **1977**, *10*, 185. (c) Hammes, G. G.; Park, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 956. (d) Krackov, M. H.; Lee, C. M.; Mautner, H. G. *J. Am. Chem. Soc.* **1965**, *87*, 892.

(4) (a) Held, A.; Pratt, D. W. *J. Am. Chem. Soc.* **1990**, *112*, 8629. (b) Held, A.; Champagnem, B. B.; Pratt, D. W. *J. Chem. Phys.* **1991**, *95*, 8732. (c) Held, A.; Pratt, D. W. *J. Chem. Phys.* **1992**, *96*, 4869.

(5) (a) Yang, H. W.; Craven, B. M. *Acta Crystallogr.* **1998**, *B54*, 912. (b) Penfold, B. R. *Acta Crystallogr.* **1953**, *6*, 591.

(6) (a) Su, D.; Wang, X.; Simard, M.; Wuest, J. D. *Supramol. Chem.* **1995**, *6*, 171. (b) Dycharme, Y.; Wuest, J. D. *J. Org. Chem.* **1988**, *53*, 5787. (c) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696. (d) Wang, X.; Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12119. (e) Gallant, M.; Viet, M. T. P.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 721. (f) Boucher, É.; Simard, M.; Wuest, J. D. *J. Org. Chem.* **1995**, *60*, 1408. (g) Persica, F.; Wuest, J. D. *J. Org. Chem.* **1993**, *58*, 95. (h) Gallant, M.; Viet, M. T. P.; Wuest, J. D. *J. Org. Chem. Soc.* **1991**, *56*, 2284.

(7) Newkome, G. R.; Hager, D. C. *J. Org. Chem.* **1978**, *43*, 947.

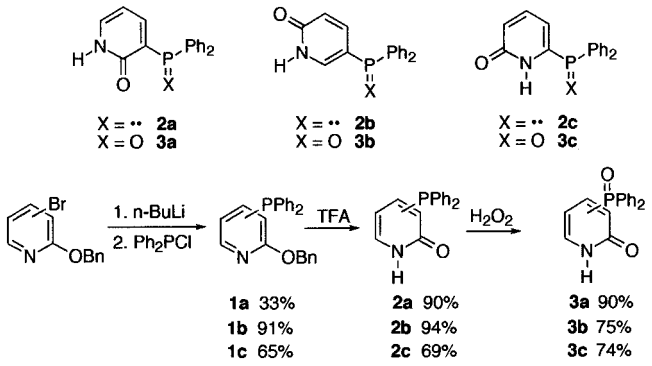
(8) **3a** as ligands: (a) Mashima, K.; Tanaka, M.; Tani, K.; Nakamura, A.; Takeda, S.; Mori, W.; Yamaguchi, K. *J. Am. Chem. Soc.* **1997**, *115*, 44307. (b) Mashima, K.; Tanaka, M.; Kaneda, Y.; Fukumoto, A.; Mizumoto, H.; Tani, K.; Nakano, H.; Nakamura, A.; Sekiguchi, T.; Kamada, K.; Ohta, K. *Chem. Lett.* **1997**, 411. (c) Mashima, K.; Nakano, H.; Nakamura, A. *J. Am. Chem. Soc.* **1996**, *118*, 9083. (d) Nakano, H.; Nakamura, A.; Mashima, K. *Inorg. Chem.* **1996**, *35*, 4007. (e) Mashima, K.; Nakano, H.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 11632.

10.1021/jo000417n CCC: $19.00
Published on Web 09/21/2000

Table 1. Crystal Structure Data for 2a−c and 3a−c

	compounds					
	2a	**2b**	**2c**	**3a**	**3b**	**3c**
mol formula	$C_{17}H_{14}NOP$	$C_{17}H_{14}NOP$	$C_{17}H_{14}NOP$	$C_{17}H_{14}NO_2P$	$C_{17}H_{14}NO_2P$	$C_{17}H_{14}NO_2P$
M_w	279.30	279.30	279.30	295.30	295.30	295.30
crystal system	triclinic	orthorhombic	triclinic	monoclinic	orthorhombic	orthorhombic
space group	*P*-1 (No. 2)	$P2_12_12_1$ (No. 19)	*P*-1 (No. 2)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	*Pcab* (No. 61)
a (Å)	9.381(2)	11.795(3)	8.548(2)	14.964(6)	12.492(6)	14.078(4)
b (Å)	11.507(4)	15.010(5)	9.172(2)	10.398(4)	12.660(5)	16.280(3)
c (Å)	14.703(4)	7.939(2)	10.283(2)	9.575(4)	9.181(3)	12.795(3)
α (deg)	69.91(2)	90	69.71(1)	90	90	90
β (deg)	75.59(2)	90	74.93(1)	98.41(3)	90	90
γ (deg)	88.71(3)	90	79.49(1)	90	90	90
V (Å^3)	1440.2(8)	1405.6(7)	726.4(2)	1474(1)	1542(1)	2932.5(9)
Z	4	4	2	4	4	8
D_{calc}	1.288	1.319	1.277	1.33	1.350	1.337
unique reflecns	5476	1342	2763	2805	1370	2788
of which $I > 1.5\sigma$	4879	1204	2528	2316	1293	1882
R	4.3	5.4	6.4	4.3	2.9	5.6
*R*w	5.0	5.8	8.9	4.9	3.3	6.0

Scheme 2



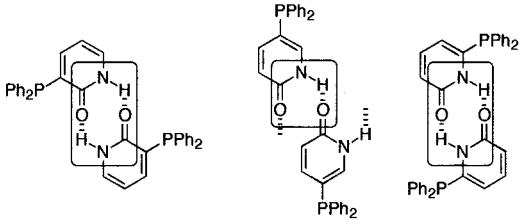
($x = 3$, 5, and 6) were prepared according to the literature method.[6b,f,9] Lithiation of the 2-benzyloxy-*x*-bromopyridines followed by coupling with chlorodiphenylphosphine gave **1a−c**, which were deprotected with TFA to afford **2a−c**. Further oxidation of **2a−c** with hydrogen peroxide gave **3a−c**.

Structural Feature of Three Phosphines (2a−c) and Their Oxides (3a−c). The crystal structures of three phosphines (**2a−c**) and three phosphine oxides (**3a−c**) were analyzed by single-crystal X-ray analyses. Since three polymorphs are known for triphenylphosphine oxide (Ph_3PO),[10] it is unclear whether polymorphism is possible for these compounds. Crystal data and the selected bond lengths are given in Tables 1 and 2. In the crystal of **2a**, two crystallographically independent molecules are present in an asymmetric unit. These molecules, which are labeled as P(A) and P(B), are very similar to each other in conformation. As is apparent from Table 2, the selected bond lengths of 2-pyridone rings are very similar except for **3c**, which has a 2-hydroxypyridine moiety instead of a 2-pyridone ring (vide infra).

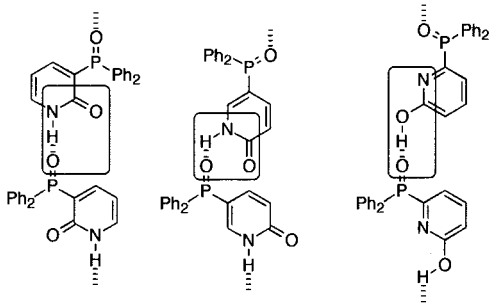
All of these phosphines and their oxides, except for **3c**, have propeller-type conformation where one 2-pyridone ring and two phenyl groups rotate in one direction, more or less.

Among **2a−c**, **3a**, **3b**, Ph_3PO,[10] triphenylphosphine (Ph_3P),[11] and diphenyl(2-pyridyl)phosphine [Ph_2(2-Py)P],[12] several conformational similarities were observed. For example, the conformations of **2a** and **2c** are similar to that of Ph_2(2-Py)P ($P2_1/n$), and the conformations of **3a** and **2b** are similar to that of Ph_3PO (*Pcab* and $P2_1/c$) and Ph_3P[11] ($P2_1/a$). Furthermore, **3b** and Ph_3PO ($P2_1/c$) have very similar conformation. Regardless of the phosphines or phosphine oxides, their torsion angles of the similar conformations are different within ca. 20°.

Table 2. Selected Bond Lengths



	2a [P(A)]	**2a [P(B)]**	**2b**	**2c**
C-O / Å	1.234(1)	1.242(1)	1.233(3)	1.244(2)
C-N / Å	1.374(1)	1.373(1)	1.374(4)	1.377(2)
hydrogen bond / Å	2.7611(7) O•••N	2.7976(8) O•••N	2.856(3) O•••N	2.776(1) O•••N



	3a	**3b**	**3c**
C-O / Å	1.231(1)	1.229(2)	1.340(3)
C-N / Å	1.379(1)	1.383(2)	1.322(3)
hydrogen bond / Å	2.7910(5) O•••N	2.732(1) O•••N	2.682(2) O•••O

(9) Serio Duggan, A. J.; Grabowski, E. J. J.; Russ, W. K. *Synthesis* **1980**, 573.

(10) (a) Brock, C. P.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 6964. (b) Bondoli, G.; Bortolozzo, G.; Clemente, D. A.; Croatto, U.; Panattoni, C. *J. Chem. Soc. A* **1970**, 2778−2780. (c) Ruban, G.; Zabel, V. *Cryst. Struct. Comm.* **1976**, *5*, 671. (d) Spek, A. L. *Acta Crystallogr.* **1987**, *C43*, 1233.

(11) Daly, J. J. *J. Chem. Soc.* **1964**, 3799.

(12) Charland, J.-P.; Roustan, J.-L.; Ansari, N. *Acta Crystallogr.* **1989**, *C45*, 680.

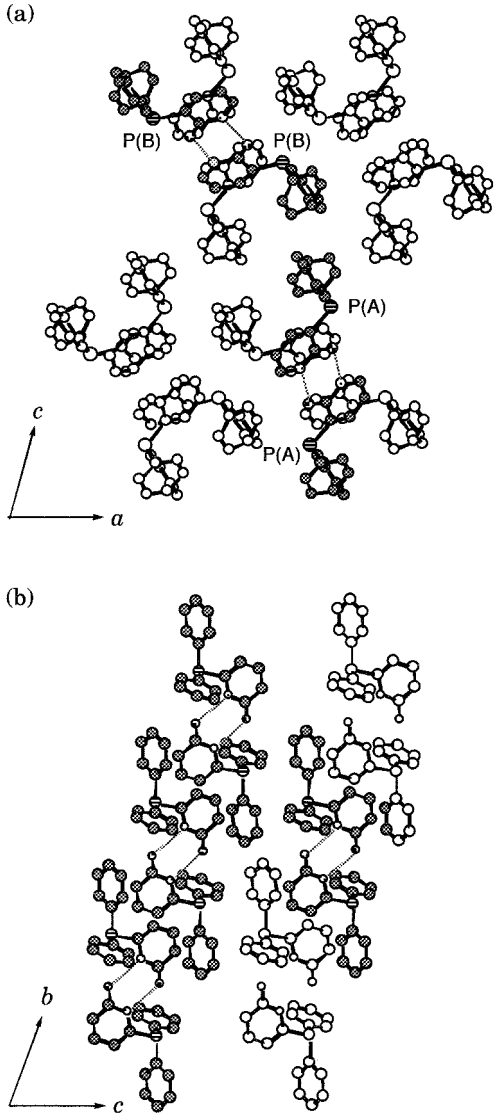


Figure 1. Two molecular aggregation by hydrogen bonds. (a) Crystal structure of **2a**. (b) Crystal structure of **2c**. Hydrogen atoms are omitted for clarity.

From these results, replacement of the phenyl or pyridyl group by one 2-pyridone ring did not influence the typical propeller-type conformation. More surprisingly, even intermolecular hydrogen bonding between the 2-pyridone rings did not compel their conformation to change. The intriguing conformation of **3c** may be based on a unique hydrogen network and/or packing (shown in Figure 4).

Molecular Aggregation of Phosphines (2a−c) by Hydrogen Bonding between 2-Pyridones. In crystals of **2a** and **2c**, the molecules aggregate by bimolecular hydrogen bonds to form a dimeric structure (Figure 1). Hydrogen bonding distances are summarized in Table 2. Since these have a space group of *P*-1, two phosphine molecules in the dimer are a mirror image of each other and are centrosymmetric. The stacking of the dimeric aggregates constructs these crystals.

In contrast, **2b** forms a one-dimensional chain of hydrogen bonds between 2-pyridone rings, which is 2_1 helical columnar (shown as *P*-form of **2b** in Figure 2). Since the space group of **2b** crystal is $P2_12_12_1$ (chiral), the 2_1 helical columns stacked side by side in opposite direction. This is similar to the case of 2-pyridone itself,

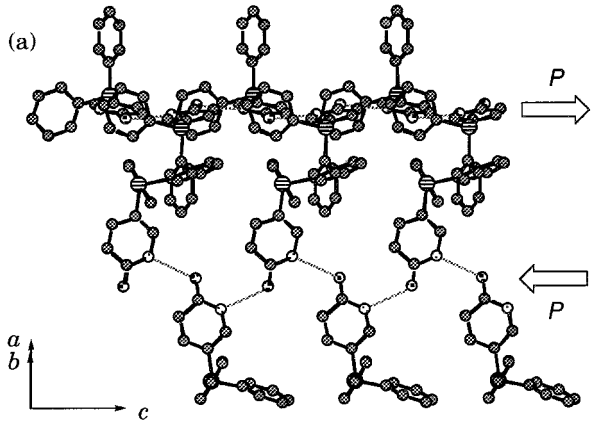


Figure 2. Hydrogen-bonding columnar structure of **2b** (chiral). Hydrogen atoms are omitted for clarity.

which has been reported to afford the crystals ($P2_12_12_1$) with 2_1 helical columns via hydrogen bonds (Scheme 1).[5]

Molecular Aggregation of Phosphine Oxides (3a−c) by Hydrogen Bonding between 2-Pyridones and Phosphine Oxides. Crystals of **3a** have a 2_1 helical chain, which comprises intermolecular hydrogen bonds between the phosphoryl oxygen and the pyridone *N*-proton (Figure 3a). In this case, the oxygen atom of the phosphoryl groups worked as a good hydrogen acceptor[13,14] to disrupt self-aggregation of the 2-pyridone rings. One-dimensional hydrogen-bonding chains of the *P*-form and *M*-form of **3a** align side by side so that the crystals become achiral (space groups $P2_1/n$).

In a manner similar to that of **2b**, the crystals of its oxide **3b** have a space group of $P2_12_12_1$, and chiral 2_1 helical chains were constructed by means of hydrogen bonds (Figure 3b).

In crystals (space groups *Pcab*) of **3c**, a 2_1 helical chain via hydrogen bonds was also formed, and the helical chains paired with the opposite 2_1 helical chain and, in result, became achiral (Figure 4).

Fixation of the Enol Form of 3c in Solid State. It should be noted that **3c** adopts an enol form in solid state, but a keto form predominates in solution. The bond distances in Table 2 strongly supported the hydroxypyridine skeleton. The C−O bond (1.340(3) Å) is fairly longer than other C−O bonds (1.229(2)−1.244(2) Å), and the C−N bond (1.322(3) Å) is shorter than other C−N bonds (1.373(1)−1.382(2) Å).

The IR spectra of **2a−c**, **3a**, and **3b** in crystalline state show an absorption peak in the range between 1631 and 1684 cm^{-1}, which corresponds with absorption of 2-pyridone carbonyl. The absorption is similar to that (1650 cm^{-1}) of 2-pyridone in solid state.[15] Although **3c** in solid state exhibited no absorption in this range, a chloroform solution of **3c** showed a strong absorbent peak at 1665 cm^{-1}. Etter et al. reported a quite similar phenomenon, namely, that triphenylphosphine oxide compels an enolizable amide into an enol form by the hydrogen bond.[14] The present tautomerism was also detected by ^{13}C NMR spectra as summarized in Figure 5. Most of the compounds listed herein show that the chemical shifts of their solid states are comparable with those of their

(13) Etter, M. C.; Baures, P. W. *J. Am. Chem. Soc.* **1988**, *110*, 639.
(14) Etter, M. C.; Gillard, R. D.; Gleason, W. B.; Rasmussen, J. K.; Duerst, R. W.; Johnson, R. B. *J. Org. Chem.* **1986**, *51*, 5405.
(15) Mason, S. F. *J. Chem. Soc.* **1957**, 4874.

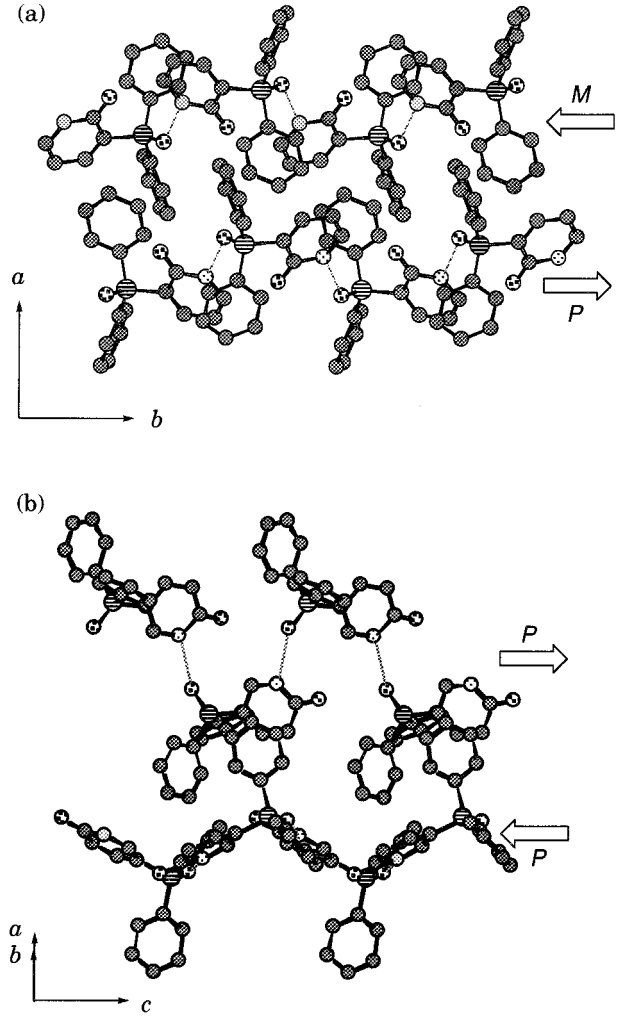


Figure 3. (a) Hydrogen-bonding columnar structure of **3a** (achiral). (b) Hydrogen-bonding columnar structure of **3b** (chiral). Hydrogen atoms are omitted for clarity.

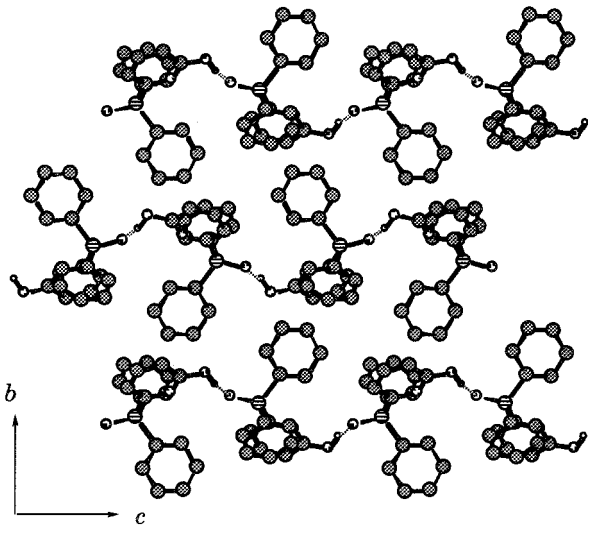


Figure 4. Crystal structure of (2-hydroxy-6-pyridyl)diphenylphosphine oxide as a tautomer of **3c**; *b*−*c* plane. Hydrogen atoms except for the hydroxy group are omitted for clarity.

solution states. However, the ^{13}C NMR spectrum of **3c** in solid state was different from that in a solution. Since the chemical shifts of the 3- and 6-carbons of the 2-pyridone ring are quite different from those of the

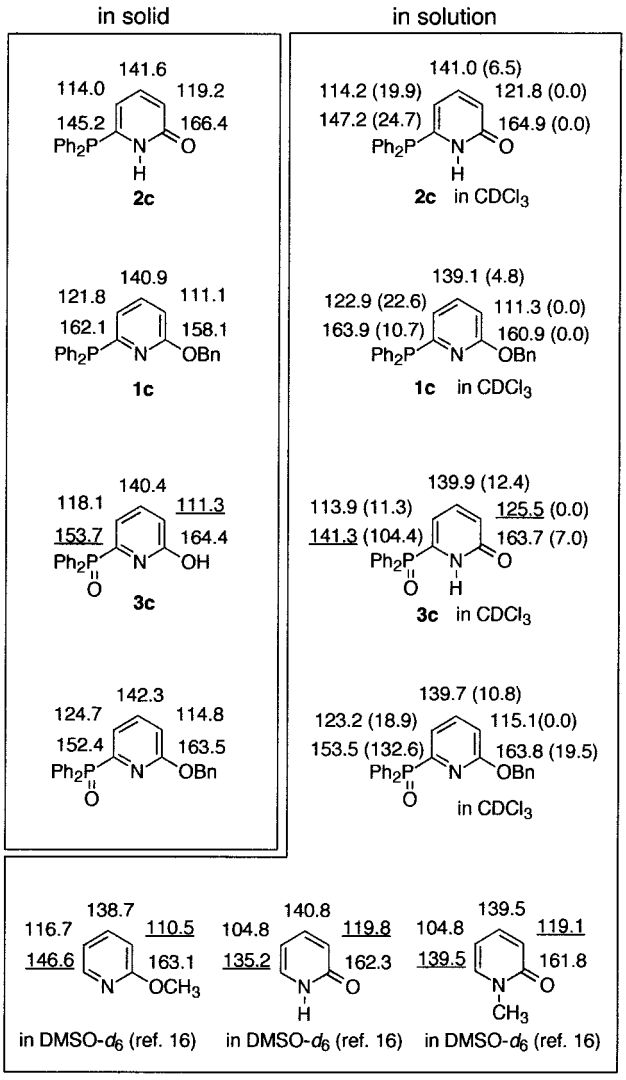


Figure 5. Chemical shift (ppm) of ^{13}C NMR spectra of **1c**, **2c**, **3c**, and related compounds in solid and solution. Coupling constants (J_{CP}, Hz) are shown in parentheses.

2-hydroxypyridine structure (marked underlines in Figure 5), the enol form in solid **3c** was supported again. A similar change in chemical shift was reported in the parent 2-pyridone ring as depicted in Figure 5.[16]

Conclusion

Three phosphines (**2a**−**c**) and their corresponding oxides (**3a**−**c**) bearing one 2-pyridone ring and two benzene rings were synthesized, and their crystal structures and aggregation motifs by means of hydrogen bonds were elucidated by single-crystal X-ray analyses. In the cases of the phosphines **2a** and **2c**, two molecules of 2-pyridones aggregate so as to construct a cyclic dimer. The crystals of **2b** showed a one-dimensional chain like those of 2-pyridone.

In case of the phosphine oxides (**3a**−**c**), the oxygen atom of the phosphoryl groups serves as a good acceptor of hydrogen bonding to link a neighboring molecule. As a result, the phosphine oxides have a chiral or an achiral one-dimensional chain by means of hydrogen bonds. The phosphine oxide **3c** showed a keto−enol tautomerism:

(16) Vögeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1973**, *5*, 551.

the keto form was observed in solution, but the enol form was found in solid state.

Now we are investigating the application of these phosphines as ligands of transition metals.

Experimental Section

General Methods. Melting points are measured on a hot stage or TG-DTA and are uncorrected. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solution were recorded at 300 and 75 MHz, respectively. ^{13}C CP/MAS NMR spectra were recorded at a frequency of 75.50 MHz, rotor spinning speed of 3.5 or 4.0 kHz, 1024 scans, pulse interval of 10 s, contact time of 5 ms, and spectral width of 29 940 Hz. Elemental analyses were performed at Chemical Analysis Center, Chiba University, Japan.

2-Benzyloxy-3-bromopyridine,[6b,9] 2-benzyloxy-5-bromopyridine,[6f,9] and 2-benzyloxy-6-bromopyridine[6b,9] were prepared according to the literature procedures.

Synthesis of the Phosphine 1a. A Typical Procedure. *n*-Butyllithium (1.6 M in hexane, 2.0 mL, 3.2 mmol) was added dropwise to a stirred solution of 2-benzyloxy-3-bromopyridine (0.62 g, 2.3 mmol) in dry THF (10 mL) at −78 °C under N_2 and stirred for 30 min. Then chlorodiphenylphosphine (0.6 mL, 3.3 mmol) was added to the solution, which was stirred at −78 °C for 30 min and warmed to room temperature. After 1 h, water was added and further extracted with chloroform. The combined organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification by column chromatography on silica gel (hexane/chloroform 1:3) gave **1a** (0.28 g, 0.76 mmol, 33%) as a colorless solid: mp 142.1−146.1 °C (hot stage); ^{1}H NMR ($CDCl_3$) δ 5.34 (s, 2H), 6.80 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 5.1 Hz, 1H), 6.97−7.40 (m, 16H), 8.13 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.9 Hz, 1H). Anal. Calcd for $C_{24}H_{20}NOP\cdot0.5H_2O$: C, 76.18; H, 5.59; N, 3.70. Found: C, 76.45; H 5.46; N, 3.32.

Phosphine 1b: colorless solid; mp 66.8−68.2 °C (hot stage); ^{1}H NMR ($CDCl_3$) δ 5.38 (s, 2H), 6.80 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.27−7.47 (m, 15H), 7.51 (ddd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 5.9 Hz, $^4J_{HH}$ = 2.3 Hz, 1H), 8.13 (dd, $^3J_{HP}$ = 4.7 Hz, $^4J_{HH}$ = 2.3 Hz, 1H). Anal. Calcd for $C_{24}H_{20}NOP\cdot0.1H_2O$: C, 77.66; H, 5.48; N, 3.78. Found: C, 77.51; H, 5.40; N, 3.76.

Phosphine 1c: colorless solid; mp 69.4−70.4 °C (hot stage); ^{1}H NMR ($CDCl_3$) δ 5.26 (s, 2H), 6.66 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 0.8 Hz, 1H), 6.78 (ddd, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 0.8 Hz, $^3J_{HP}$ = 2.3 Hz, 1H), 7.25−7.49 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 68.3, 111.3, 122.9 (d, $^2J_{CP}$ = 22.6 Hz), 128.5, 129.1, 129.2, 129.5 (d, $^2J_{CP}$ = 32.9 Hz), 135.1 (d, $^3J_{CP}$ = 19.4 Hz), 137.4 (d, $^1J_{CP}$ = 9.7 Hz), 138.3, 139.1 (d, $^3J_{CP}$ = 4.8 Hz), 160.9,163.9 (d, $^1J_{CP}$ = 10.7 Hz); ^{13}C NMR (solid) δ 66.0, 111.1, 121.8, 128.8, 129.7, 134.7, 137.4, 138.5, 140.9, 158.1, 162.1. Anal. Calcd for $C_{24}H_{20}NOP$: C, 78,04; H, 5.46; N, 3.79. Found: C, 77.66; H, 5.39; N, 4.00.

Synthesis of the Phosphine 2a. A Typical Procedure. A solution of **1a** (0.11 g, 0.30 mmol) in TFA (5 mL) was stirred at room temperature for 1.5 h. The reaction mixture was neutralized by saturated aqueous $NaHCO_3$ and then extracted with chloroform. The combined organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification by column chromatography on silica gel (hexane/ethyl acetate 1:2) gave **2a** (0.07 g, 0.27 mmol, 90%) as a colorless solid: mp 198 °C (TG-DTA); ^{1}H NMR ($CDCl_3$) δ 6.13 (t, $^3J_{HH}$ = $^3J_{HP}$ = 6.7 Hz, 1H), 6.86 (ddd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 3.5 Hz, $^4J_{HP}$ = 2.1 Hz, 1H), 7.26 (m, 1H), 7.30−7.37 (m, 10H), 13.1 (s(br), 1H); IR (KBr) 1631 cm^{-1}; IR ($CHCl_3$) 1634 cm^{-1}. Anal. Calcd for $C_{17}H_{14}NOP$: C, 73.11; H, 5.05; N, 5.02. Found: C, 72.57; H, 4.82; N, 4.95.

Phosphine 2b: colorless solid; mp 152 °C (TG-DTA); ^{1}H NMR ($CDCl_3$) δ 6.56 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.26−7.41 (m, 12H), 13.2 (s(br), 1H); IR (KBr) 1684, 1662 cm^{-1}; IR ($CHCl_3$) 1675, 1652 cm^{-1}. Anal. Calcd for $C_{17}H_{14}NOP$: C, 73.11; H, 5.05; N, 5.02. Found: C, 72.83, H, 4.95, N, 4.93.

Phosphine 2c: colorless solid; mp 195.5 °C (TG-DTA); ^{1}H NMR ($CDCl_3$) δ 6.21 (ddd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 5.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 6.48 (dd, $^3J_{HH}$ = 9.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.29−7.44 (m, 11H), 9.22 (s(br), 1H); ^{13}C NMR ($CDCl_3$) δ 114.2 (d, $^2J_{CP}$ = 19.9 Hz), 121.8, 130.0 (d, $^3J_{CP}$ = 7.5 Hz), 130.9, 133.6 (d, $^1J_{CP}$ = 9.7 Hz), 134.7 (d, $^2J_{CP}$ = 19.9 Hz), 141.0 (d, $^3J_{CP}$ = 6.5 Hz), 147.2 (d, $^1J_{CP}$ = 24.7 Hz), 164.9; ^{13}C NMR (Solid) δ 114.0, 119.2, 129.5, 132.0, 133.3, 135.3, 140.6, 145.2, 166.4; IR (KBr) 1643 cm^{-1}; IR ($CHCl_3$) 1654 cm^{-1}. Anal. Calcd for $C_{17}H_{14}NOP$: C, 73.11; H, 5.05, N, 5.02. Found: C, 73.21; H, 4.99; N, 4.96.

Preparation of the Phosphine Oxide 3a. A Typical Procedure. Hydrogen peroxide (30%, 1 mL) was added to a solution of **2a** (28 mg, 0.10 mmol) in chloroform/diethyl ether (1:1, 30 mL) and stirred at room temperature. After 3 h, water and chloroform were added. The aqueous layer was removed and further extracted with chloroform. The combined organic layer was dried (Na_2SO_4) and concentrated in vacuo. A colorless solid **3a** (27 mg, 0.09 mmol) was obtained in 90% yield: mp 147.6 °C (TG-DTA); ^{1}H NMR (d_4-MeOH) δ 6.58 (ddd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 6.4 Hz, $^4J_{HP}$ = 1.9 Hz, 1H), 7.48−7.83 (m, 11H), 8.23 (ddd, $^3J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 2.2 Hz, 1H); IR (KBr) 1667, 1640 cm^{-1}. Anal. Calcd for $C_{17}H_{14}NO_2P$: C, 69.15; H, 4.78; N, 4.74. Found: C, 68.96; H, 4.57; N, 4.73.

Phosphine oxide 3b: colorless solid; mp 229.4 °C (TG-DTA); ^{1}H NMR ($CDCl_3$) δ 6.60 (dd, $^3J_{HH}$ = 10.1 Hz, $^4J_{HP}$ = 2.3 Hz, 1H), 7.27−7.71 (m, 12H), 13.0 (s(br), 1H); IR (KBr) 1673, 1650 cm^{-1}; IR ($CHCl_3$) 1680, 1656 cm^{-1}. Anal. Calcd for $C_{17}H_{14}NO_2P$: C, 69.15; H, 4.78; N, 4.74. Found: C, 69.11; H, 4.75; N 4.98.

Phosphine oxide 3c: colorless solid; mp 204 °C (TG-DTA), ^{1}H NMR ($CDCl_3$) δ 6.36 (ddd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.2 Hz, $^3J_{HP}$ = 9.2 Hz, 1H), 6.68 (dd, $^3J_{HH}$ = 9.3 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.38 (ddd, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.3 Hz, $^4J_{HP}$ = 4.2 Hz, 1H), 7.50−7.76 (m, 10H), 9.81 (s(br), 1H); ^{13}C NMR ($CDCl_3$) δ 113.9 (d, $^2J_{CP}$ = 11.3 Hz), 125.5, 129.8 (d, $^2J_{CP}$ = 12.3 Hz), 130.1 (d, $^1J_{CP}$ = 107.6 Hz), 132.9 (d, $^3J_{CP}$ = 10.3 Hz), 133.9 (d, $^4J_{CP}$ = 2.7 Hz), 139.9 (d, $^3J_{CP}$ = 12.4 Hz), 141.3 (d, $^1J_{CP}$ = 104.4 Hz), 163.7 (d, $^3J_{CP}$ = 7.0 Hz); ^{13}C NMR (solid) δ 111.3, 118.1, 131.0, 132.0, 134.7, 140.4, 153.7, 164.4; IR ($CHCl_3$) 1665 cm^{-1}. Anal. Calcd for $C_{17}H_{14}NO_2P$: C, 69.15; H, 4.78; N, 4.74. Found: C, 69.23; H, 4.71; N, 4.75.

(2-Benzyloxy-6-pyridyl)diphenylphosphine oxide: colorless solid; mp 142.1−146.1 °C (EtOH/hexane, hot stage); ^{1}H NMR ($CDCl_3$) δ 5.27 (s, 2H), 6.91 (ddd, $^3J_{HH}$ = 8.4 Hz, $^5J_{HP}$ = 1.8 Hz, $^4J_{HH}$ = 0.9 Hz, 1H), 7.26−7.33 (m, 6H), 7.37−7.44 (m, 3H), 7.49−7.54 (m, 2H), 7.73 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 4.1 Hz, 1H), 7.75−7.83 (m, 4H), 7.89 (ddd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 6.2 Hz, $^4J_{HH}$ = 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 68.6, 115.1, 123.2 (d, $^2J_{CP}$ = 18.9 Hz), 128.5, 128.7, 129.2 (d, $^2J_{CP}$ = 26.5 Hz), 129.2, 132.6 (d, $^4J_{CP}$ = 2.2 Hz), 132.9 (d, $^3J_{CP}$ = 9.4 Hz), 133.1 (d, $^1J_{CP}$ = 104.5 Hz), 137.9, 139.7 (d, $^3J_{CP}$ = 10.8 Hz), 153.5 (d, $^1J_{CP}$ = 132.6), 163 (d, $^3J_{CP}$ = 19.5); ^{13}C NMR (solid) δ 69.7, 114.8, 124.7, 128.7, 130.9, 133.1, 134.1, 135.0, 136.3, 142.3, 152.4, 136.5. Anal. Calcd for $C_{24}H_{20}NO_2P\cdot0.5C_2H_6O$: C, 73.50; H, 5.68; N, 3.43. Found: C, 73.20; H, 5.40; N, 3.38.

Crystal Structure Analysis. Single crystals of **2a**−**c** and **3a**−**c** were prepared by recrystallization from ethanol/hexane. Data collection was performed on a four-circle diffractometer with monochromated Cu Kα (λ = 1.54178 Å) radiation, and the X-ray intensities were measured up to 2θ = 140° at 298 K. The structures were solved and refined on direct methods (SIR 92[17] on a computer program package; maXus ver. 1.1 from Mac Science Co. Ltd.)

Acknowledgment. This work was supported by Grant-in-Aids for Research for the Future Program (JSPS-RFTF96P00304) and Encouragement of Young Scientists (11750733) from The Japan Society for the Promotion of Science.

Supporting Information Available: Tables of atomic coordinates and thermal parameters, bond lengths and angles, and ORTEP views of **2a**−**c** and **3a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO000417N

(17) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.