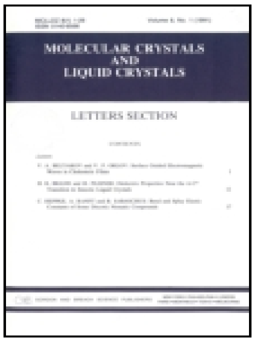

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Synthesis and Structure Analysis of N-diphenylphosphoryl-4-bromoaniline

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The title compound N-diphenylphosphoryl-4-bromoaniline was prepared from 4-bromoaniline and chlorodiphenylphosphine in the presence of triethylamine, and its structure was determined by X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/n$ with $a = 12.432(3)$, $b = 8.9512(18)$, $c = 15.150(3)$ Å, $\alpha = 90.00$, $\beta = 102.89(3)$, $\gamma = 90.00°$, $V = 1643.4(6)$ Å^3, and $Z = 4$.

Keywords Crystal structure; P-N ligand; synthesis

Introduction

In recent years, diphosphine ligands, such as monophosphanylamides [1, 2], diphosphanylamides [3, 4], diiminophosphinates [5, 6], have been received special attention due to their potential application in transition metal chemistry [7–9]. As a continuation of our studies on phosphine ligands [10, 11], we have obtained a colorless crystalline compound N-diphenylphosphoryl-4-bromoaniline. The route of the synthesis is shown in Scheme 1. Reaction of 4-bromoaniline with chlorodiphenylphosphine in the presence of triethylamine afforded the intermediate (4-bromoaniline)-diphenylphosphine, followed by oxidation to give the title compound N-diphenylphosphoryl-4-bromoaniline. The title compound was characterized by NMR and single crystal X-ray diffraction analysis.

Experimental

Synthesis of N-diphenylphosphoryl-4-bromoaniline: To a stirred mixture of 4-bromoaniline (1.71 g, 10 mmol) and triethylamine (3 mL, 21 mmol) in dichloromethane (30 mL) was slowly added chlorodiphenylphosphine (3.6 mL, 20 mmol) at 0°C. The new mixture was further stirred at room temperature for 2 hr and then was washed with water. The organic layer was dried over anhydrous sodium sulfate and then the solvent was removed at reduced pressure to give a yellow viscous solid. Recrystallization from ethanol afforded the title compound (1.56 g, 42%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.88–7.84 (m, 4H, *o*-PPh*H*), 7.58–7.53 (m, 2H, *p*-PPh*H*), 7.48–7.45 (m, 4H, *m*-PPh*H*), 7.24, 7.22, 6.89, 6.87 (AB q, $J = 9.0$ Hz, 4H, C_6H_4), 5.43 (d, $J_{\text{P-H}} = 8.5$ Hz, 1H, N*H*)

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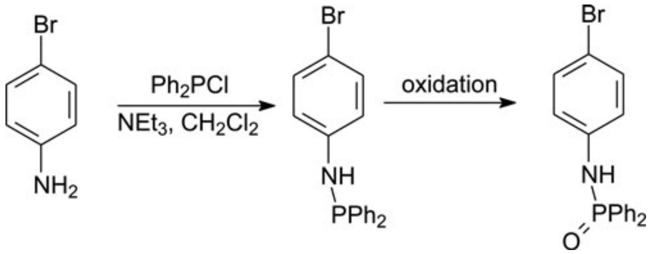

Scheme 1. Route of synthesis.

ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 18.82 (s) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 139.57 (s, *i*-BrPh*C*), 132.47 (d, $J = 2.6$ Hz, *o*-BrPh*C*), 132.17 (s, *p*-PPh*C*), 131.95 (d, $J_{\text{P-C}} = 10.0$ Hz, *m*-PPh*C*), 130.81 (d, $J_{\text{P-C}} = 29.0$ Hz, *i*-PPh*C*), 128.91 (d, $J_{\text{P-C}} = 13.1$ Hz, *o*-PPh*C*), 120.14 (d, $J = 6.6$ Hz, *m*-BrPh*C*), 114.41 (s, *p*-BrPh*C*) ppm.

Crystal structure determination: The crystal of title compound with dimensions of 0.20 mm ×0.18 mm × 0.12 mm was mounted on a Rigaku Saturn CCD area-detector

Table 1. Crystal data and structure refinement

Empirical formula	$C_{18}H_{15}BrNOP$
Formula weight	372.19
Crystal system	Monoclinic
Unit cell dimensions	
a (Å)	12.432(3)
b (Å)	8.9512(18)
c (Å)	15.150(3)
Unit cell angles (°)	
α	90
β	102.89(3)
γ	90
Volume (Å^3)	1643.4(6)
Z	4
Temperature (K)	293(2)
Space group	*P2(1)/n*
Wavelength (Å)	0.71073
Calculated density (g/cm^3)	1.500
Absorption coefficient (mm^{-1})	2.599
F(000)	748
Crystal size (mm)	0.20 × 0.18 × 0.12
Theta range for data collection (°)	1.92–27.84
Reflections collected	16304
Independent reflections	3866 [$R_{(\text{int})} = 0.0560$]
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.0968$

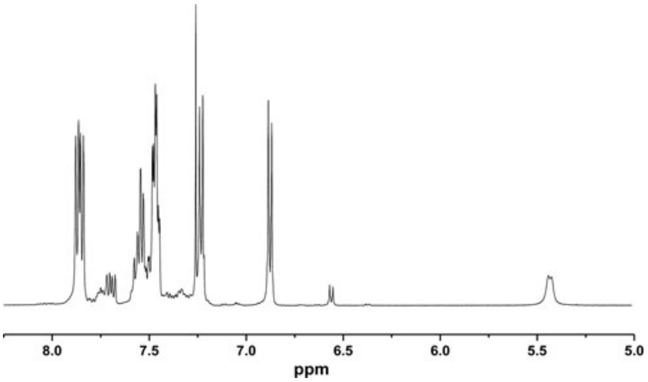

Figure 1. ^{1}H NMR spectra.

diffractometer with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a phi and scan modes at 293(2) K in the range of $1.92^\circ \leq \theta \leq 27.84^\circ$. A summary of crystal data is presented in Table 1.

The structure was solved by direct methods with SHELXS-97 [12] and refined by the full-matrix least squares method on F^2 data using SHELXL-97 [13]. H atoms were added at calculated positions and refined using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameters of their parent atoms, and C–H distances were restrained to 0.96 Å for methyl H atoms, while N—H distances were set to 0.86 Å.

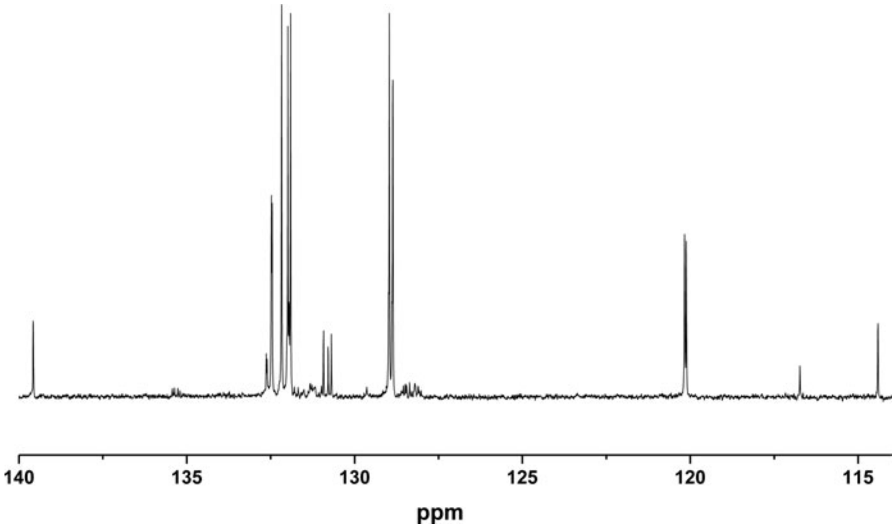

Figure 2. ^{13}C{^{1}H} NMR spectra.

Table 2. Selected bond lengths (Å) and bond angles (°)

Bond lengths			
Br(1)-C(16)	1.906(3)	P(1)-O(1)	1.4835(18)
P(1)-N(1)	1.657(2)	P(1)-C(7)	1.796(3)
P(1)-C(1)	1.798(3)	N(1)-C(13)	1.424(4)
Bond angles			
O(1)-P(1)-N(1)	117.49(12)	O(1)-P(1)-C(7)	112.40(12)
N(1)-P(1)-C(7)	100.51(13)	O(1)-P(1)-C(1)	110.92(13)
N(1)-P(1)-C(1)	106.12(12)	C(7)-P(1)-C(1)	108.61(13)

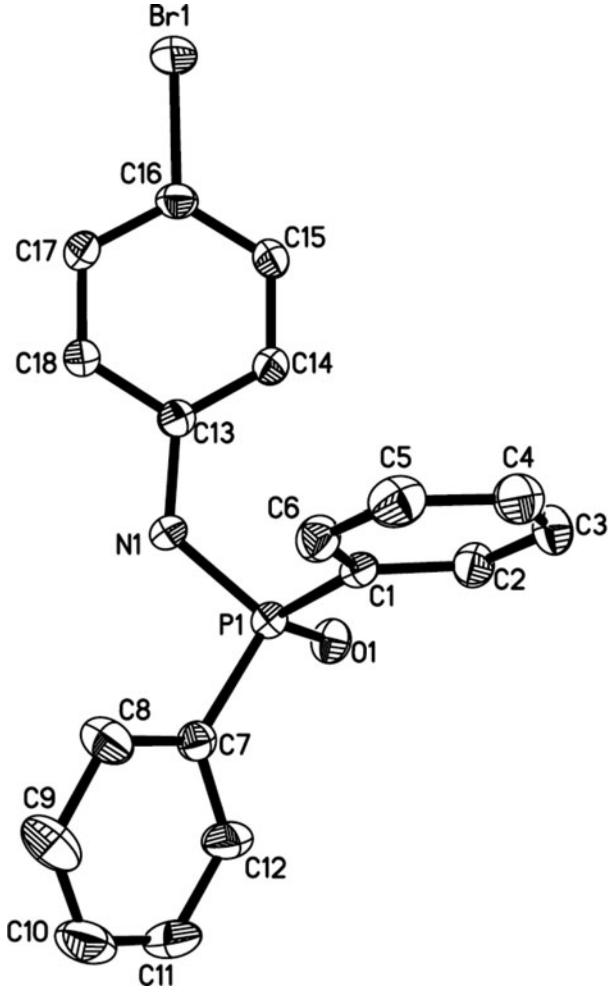

Figure 3. ORTEP view of the title compound.

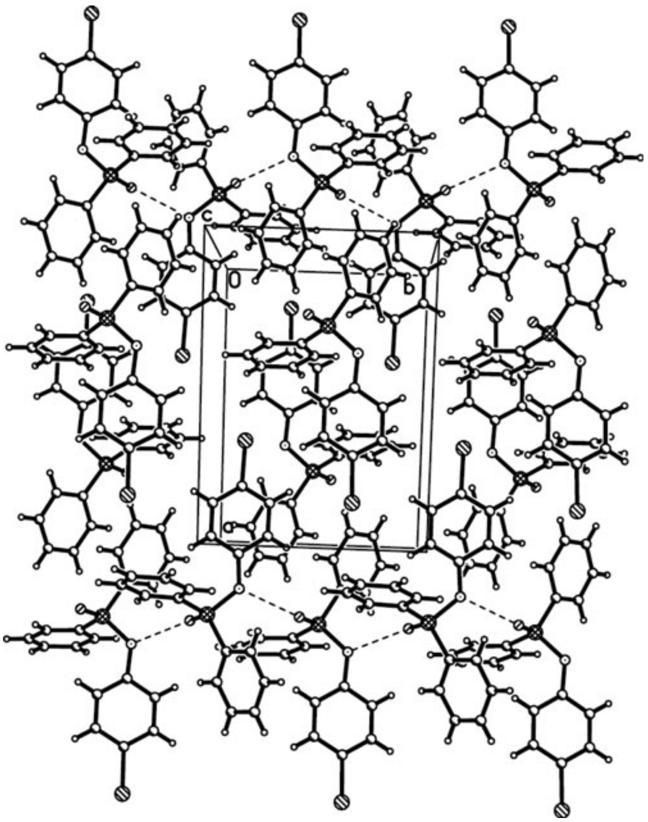

Figure 4. Packing diagram of the title compound.

Results and Discussion

Spectral Analysis

As shown in Fig. 1, the ^{1}H NMR spectra showed three multiplets for phenyl hydrogen atoms of PPh_2 group, an AB quadruplet for phenyl hydrogen atoms of aniline, and a doublet at 5.43 ppm with a coupling constant $J_{\text{P-H}} = 8.5$ Hz for its NH group.

As shown in Fig. 2, the $^{13}C\{^1H\}$ NMR spectra displayed two singlets at 139.57 and 114.41 ppm and two doublets at 132.47 and 120.14 ppm for phenyl carbons of aniline and one singlet at 132.17 ppm and three doublets at 131.95, 130.81, and 128.91 ppm for phenyl carbons of PPh_2 group.

Crystal Structure

The molecular structure of the title compound was determined by X-ray crystallography. While ORTEP view is shown in Fig. 3, selected bond lengths and angles are presented in Table 2, respectively. The title compound crystallizes in the monoclinic space group P2(1)/*n*, having one molecule in the asymmetric unit and four molecules in the unit cell. The bond length of P1-N1 [1.657(2) Å] is slightly longer than that of [$Ph_2P(O)NH(2,6\text{-}Me_2C_6H_3)$] [1.6455(19) Å] [6], whereas the bond lengths of P1-C1 [1.798(3) Å] and P1-C7 [1.796(3) Å] are slightly shorter than those of [$Ph_2P(O)NH(2,6\text{-}Me_2C_6H_3)$] [1.809(3) and 1.804 Å] [6]. The P—O bond length [1.4835(18) Å] is in good agreement with the double bond and comparable with $2,6\text{-}{}^iPr_2C_6H_3NHP(O)Ph_2$ [1.4736(19) Å] [14]. The phosphorus atom is sp^3 hybridized and occupies a tetrahedral geometry. The bond angles O1-P1-N1 [117.49(12)°], O1-P1-C7 [112.40(12)°], N1-P1-C7 [100.51(13)°], O1-P1-C1 [110.92(13)°], N1-P1-C1 [106.12(12)°], and C7-P1-C1 [108.61(13)°] are comparable to the ideal angle (109.5°) for tetrahedral arrangements.

As shown in the packing of the title compound (Fig. 4), there are intermolecular N—H···O hydrogen bonds in the crystal structure to stabilize the solid state structure.

Conclusions

In summary, the title compound N-diphenylphosphoryl-4-bromoaniline has been prepared and structurally characterized by NMR and X-ray crystallography.

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Supplemental Materials

Supplemental materials are available for this article. Go to the publisher's online edition of Molecular Crystals and Liquid Crystals to view the free supplemental file: Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 974662 for the title compound. Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk

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