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## Synthesis and X-ray Structural Characterization of Two Polymorphic Forms of Bis(anilino)phosphine Oxide, $(C_6H_5NH)_2P(O)H$

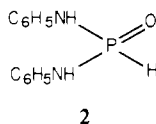
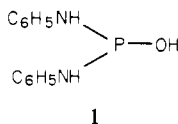
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Bis(anilino)phosphine oxide,  $(C_6H_5NH)_2P(O)H$ , is obtained along with aniline from the controlled hydrolysis of  $(C_6H_5NH)_3P$  or  $[(C_6H_5NH)_2P]_2NC_6H_5$ . No evidence for formation of the isomeric  $(C_6H_5NH)_2POH$ , either in solution or in the solid, has been obtained.  $(C_6H_5NH)_2P(O)H$  crystallizes in two polymorphic forms, each of which has been characterized by X-ray crystallography. Form I crystallizes from  $CH_2Cl_2$  or  $CHCl_3$  and is monoclinic (mp 160–161 °C), in space group  $C2/c$ , with unit cell parameters  $a = 17.929$  (7) Å,  $b = 5.232$  (2) Å,  $c = 24.804$  (6) Å,  $\beta = 103.59$  (3)°,  $V = 2262$  (2) Å<sup>3</sup>, and  $Z = 8$ . Form II crystallizes from  $C_2H_5OH$  and is orthorhombic (mp 151–152 °C), in space group  $Pnma$ , with unit cell parameters  $a = 7.702$  (3) Å,  $b = 26.723$  (9) Å,  $c = 5.558$  (3) Å,  $V = 1144$  (1) Å<sup>3</sup>, and  $Z = 4$ . Forms I and II each contain four intermolecular hydrogen bonds between  $C_6H_5NH$  hydrogen atoms and oxygen atoms of neighboring molecules. Form I contains hydrogen-bonded pairs of  $(C_6H_5NH)_2P(O)H$  molecules, each pair hydrogen bonded to another pair in the lattice. Form II contains linear head-to-tail hydrogen bonding between molecules. Both polymorphs have typical and similar intramolecular bond distances and angles: P–O, 1.475 (2) Å (I) and 1.471 (4) Å (II); mean P–N, 1.639 (3) Å (I) and 1.642 (4) Å (II);  $\angle N-P-N$ , 105.6 (15)° (I) and 100.4 (3)° (II); mean  $\angle N-P-O$ , 114.0 (14)° (I) and 116.3 (2)° (II). Form I appears to be thermodynamically more stable than form II.

### Introduction

A compound of composition  $(C_6H_5NH)_2POH$  from the hydrolysis of  $(C_6H_5NH)_2POC_6H_5$  has been reported by Goldschmidt and Obermeier;<sup>2</sup> however, its characterization as either of two possible structural isomers, **1** or **2**, was not



accomplished. Subsequently, Ginet and Geoffroy measured the unit cell parameters of the compound crystallized from ethanol and characterized it as orthorhombic, space group  $Pna2_1$  (mp 152 °C).<sup>3</sup> The molecular structure was not determined.

Recently, we have found that hydrolysis of anilino-phosphines, e.g.,  $(C_6H_5NH)_3P$ ,<sup>4,5</sup>  $[(C_6H_5NH)_2P]_2NC_6H_5$ ,<sup>5</sup> and  $[(C_6H_5NH)PNC_6H_5]_3$ ,<sup>6</sup> yields material characterized spectrally in solution as  $(C_6H_5NH)_2P(O)H$  (**2**), but which crystallizes not only in the orthorhombic form but also in a monoclinic form (mp 160–161 °C). Because there existed the possibility that the crystalline forms had different molecular structures,

and because of the potential usefulness of compounds **1** or **2** in further syntheses, we undertook a detailed study of the synthesis and crystallization properties of  $(C_6H_5NH)_2POH$ . Our results are reported below.

### Experimental Section

**Apparatus and Materials.** All inert-atmosphere manipulations were carried out in  $N_2$ -flushed glovebags and standard Schlenk-type glassware.<sup>7</sup> Infrared (4000–400  $cm^{-1}$ ) and mass spectra were obtained with Perkin-Elmer 337G and Varian MAT CH-5 spectrometers, respectively. Proton NMR spectra at 90.0 MHz were obtained on a Varian EM390 spectrometer. Chemical shifts were measured relative to internal  $(CH_3)_4Si$ ;  $+\delta$  values are downfield from the standard. <sup>31</sup>P NMR spectra were obtained at 40.5 MHz with a JEOL PFT-100 Fourier transform spectrometer equipped with standard probe accessories. Chemical shifts were measured relative to external  $H_3PO_4$ ;  $-\delta$  values are downfield from the standard. Elemental analyses were carried out by Huffman Analytical Laboratories, Wheatridge, CO.

$(C_6H_5NH)_3P$ <sup>4,5</sup> and  $[(C_6H_5NH)_2P]_2NC_6H_5$ <sup>5</sup> were prepared as described elsewhere. Benzene, toluene, and hexane were distilled from  $LiAlH_4$  before use. Chloroform and  $CH_2Cl_2$  were distilled from  $P_4O_{10}$ . Dimethyl sulfoxide was dried over 4-Å Linde molecular sieves.

**Preparation of  $(C_6H_5NH)_2P(O)H$ .** To a chloroform solution of  $(C_6H_5NH)_3P$  (5.0 mmol) or  $[(C_6H_5NH)_2P]_2NC_6H_5$  (3.0 mmol) was added slowly with stirring at 5 mmol of  $H_2O$  in an  $H_2O-CHCl_3$  solution. After 1 h, chloroform and aniline were removed in vacuo. Recrystallization of the resulting solid from  $CHCl_3$  or  $CH_2Cl_2$  yielded pure  $(C_6H_5NH)_2P(O)H$ , form I (monoclinic, mp 160–161 °C, 60% yield). Anal. Calcd for  $C_{12}H_{13}N_2PO$ : C, 62.06; H, 5.64; N, 12.06. Found: C, 62.11; H, 5.52; N, 12.00. Repeated recrystallization from ethanol yielded pure  $(C_6H_5NH)_2P(O)H$ , form II (orthorhombic, mp 151–152 °C).

(1) To whom correspondence should be addressed.

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Table I. Crystal Data

	form I	form II
formula	(C <sub>6</sub> H <sub>5</sub> NH) <sub>2</sub> P(O)H	(C <sub>6</sub> H <sub>5</sub> NH) <sub>2</sub> P(O)H
<i>M<sub>r</sub></i>	232.223	232.223
mp, °C	161–162	152
space group <sup>a</sup>	C2/c	Pnma
<i>a</i> , Å	17.929 (7)	7.702 (3)
<i>b</i> , Å	5.232 (2)	26.723 (9)
<i>c</i> , Å	24.804 (6)	5.558 (3)
β, deg	103.59 (3)	90.0
<i>V</i> , Å <sup>3</sup>	2262 (2)	1144 (1)
<i>d<sub>c</sub></i> , g cm <sup>-3</sup>	1.364	1.348
<i>d<sub>o</sub></i> , g cm <sup>-3</sup>	1.36	1.34
<i>Z</i>	8	4
<i>F</i> (000)	976	488
μ(Mo Kα), cm <sup>-1</sup>	2.27	2.23

<sup>a</sup> The systematic absences and equivalent positions for C2/c, No. 15, and Pnma, No. 62, are found in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965; Vol. I, pp 101, 151. <sup>b</sup> Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

(C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H is soluble in (CH<sub>3</sub>)<sub>2</sub>SO, moderately soluble in C<sub>2</sub>H<sub>5</sub>OH, and slightly soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and toluene. It reacts slowly with protic solvents.

In several series of reactions, H<sub>2</sub>O in CHCl<sub>3</sub> was added slowly to solutions of [(C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P]<sub>2</sub>NC<sub>6</sub>H<sub>5</sub> in toluene and the <sup>31</sup>P NMR spectra of the solutions were monitored periodically. The resonance due to (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H at δ 1.10 appeared immediately. No other resonances were seen. As the consumption of [(C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P]<sub>2</sub>NC<sub>6</sub>H<sub>5</sub> neared completion, additional resonances appeared in the δ 1.0–2.0 region, which are attributed to the hydrolysis of (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H and/or condensation of (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H to higher molecular weight products.

**Spectra.** Infrared spectral absorptions for (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H (form I or II; KBr pellet) occur at 3185 (s), 2980 (w, sh), 2415 (m), 1930 (w), 1845 (w), 1709 (w), 1602 (s), 1497 (vs), 1402 (s), 1322 (m), 1294 (m), 1280 (s), 1165 (vs), 1078 (w, sh), 1002 (w), 971 (w, sh), 941 (vs), 887 (s), 840 (w), 824 (w), 801 (w), 749 (vs), 695 (s), 618 (m), and 455 (m) cm<sup>-1</sup>.

Forms I and II yield identical mass spectra. The spectra are variable, depending on the spectrometer inlet temperature; however, a strong parent peak at *m/e* 232, attributable to (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H<sup>+</sup>, is seen along with a series of less intense higher mass envelopes characteristic of phenylamido-containing phosphorus species expected from the pyrolysis of (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H.

Nuclear magnetic resonance spectral data: <sup>1</sup>H spectrum ((CD<sub>3</sub>)<sub>2</sub>SO, 30 °C) δ 7.50–6.50 (complex multiplet, phenyl, relative area 10), 8.18 (doublet, NH, relative area 2, <sup>2</sup>*J*<sub>PNH</sub> = 9.0 ± 0.1 Hz), and 7.34 (doublet, rel area 1, PH, <sup>1</sup>*J*<sub>PH</sub> = 600 ± 4 Hz); <sup>31</sup>P (CHCl<sub>3</sub>, 24 °C) δ 1.10 ± 0.05 (doublet of triplets, <sup>1</sup>*J*<sub>PH</sub> = 610 ± 4 Hz, <sup>2</sup>*J*<sub>PNH</sub> = 7.8 ± 0.2 Hz).

**Data Collection and Structure Analysis for (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H, Forms I and II.** Crystals of forms I (0.3 mm × 0.4 mm × 0.5 mm) and II (0.2 mm × 0.3 mm × 0.6 mm) were mounted and coated with epoxy resin. Cell parameters were determined on the diffractometer and were refined by a least-squares fit of the parameters to 15 centered reflections. Crystal data are summarized in Table I. Positional and thermal parameters for atoms of forms I and II are given in Tables II and III. Data collection: temperature, 290–295 K; radiation, Mo Kα, graphite monochromatized; scan mode, θ–2θ; minimum 2θ, 2.0°; maximum 2θ, 50.0°; scan speed, 2.0–24.0° min<sup>-1</sup>; scan range, 0.9° below 2θ for Kα<sub>1</sub> to +1.1° above 2θ for Kα<sub>2</sub>; background mode, stationary crystal–stationary counter; background time/scan time, 0.5; data points measured, 2200 (form I) and 1255 (form II); data points observed (*F*<sub>o</sub><sup>2</sup> > 3.0σ(*F*<sub>o</sub><sup>2</sup>)), 1316 (form I) and 652 (form II). The data sets, monitored every 100 measurement cycles, showed no significant variations over the course of the experiments. Data were corrected for Lorentz and polarization effects.<sup>8</sup>

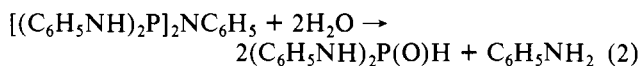
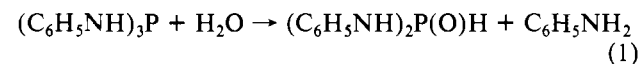
(8) RLP = 1/*Lp* = 2.0 sin θ cos θ/[0.5{(cos<sup>2</sup> 2θ<sub>m</sub> + cos<sup>2</sup> 2θ)/(1 + cos<sup>2</sup> 2θ<sub>m</sub>)} + 0.5{(cos 2θ<sub>m</sub> + cos<sup>2</sup> 2θ)/(1 + cos 2θ<sub>m</sub>)}], where θ and θ<sub>m</sub> are the Bragg angles for the crystal and the monochromator (2θ<sub>m</sub> = 26.6°). The fractional mosaicity of the monochromator is assumed to be 0.5.

All calculations were carried out by using only significant reflections<sup>9</sup> and scattering curves for neutral atoms.<sup>11</sup> All programs were contained in or derived from Syntex data reduction routines, the MULTAN 78 package,<sup>12</sup> and the Northwestern crystallographic computing package of Dr. J. A. Ibers.

Full-matrix least-squares refinement procedures minimizing Σw(|*F*<sub>o</sub> – |*F*<sub>c</sub>||<sup>2</sup>) were used. *R<sub>F</sub>* = Σ(|*F*<sub>o</sub> – |*F*<sub>c</sub>||)/Σ|*F*<sub>o</sub> and *R<sub>wF</sub>* = [Σw(|*F*<sub>o</sub> – |*F*<sub>c</sub>||<sup>2</sup>)/Σw(*F*<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>. The standard deviation of an observation of unit weight is defined as [Σw(|*F*<sub>o</sub> – |*F*<sub>c</sub>||<sup>2</sup>)/(NO – NV)]<sup>1/2</sup>, where NO is the number of observations and NV the number of variables. The weights, *w*, were calculated from counting statistics as *w* = 1/σ<sup>2</sup>(*F*<sub>o</sub>) = 4*F*<sub>o</sub><sup>2</sup>/σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>). σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) is defined in ref 9. In both cases hydrogen atoms were located from a difference map calculated after anisotropic refinement. These were included in the final refinements with fixed isotropic thermal parameters.<sup>10</sup> At convergence of the final refinement the following conditions held: number of variables, 184 (form I) and 96 (form II); ratio of observations to parameters, 7:1; esd of an observation of unit weight, 1.501 (form I) and 1.910 (form II); *R<sub>F</sub>* and *R<sub>wF</sub>*, 0.039 and 0.047 (form I) and 0.049 and 0.062 (form II); final difference map, featureless.

## Results and Discussion

**Synthesis of (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H.** (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H forms readily from the hydrolysis of (C<sub>6</sub>H<sub>5</sub>NH)<sub>3</sub>P or [(C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P]<sub>2</sub>NC<sub>6</sub>H<sub>5</sub> according to eq 1 and 2. If water addition is



controlled carefully, e.g., by its slow addition in an H<sub>2</sub>O–C–HCl<sub>3</sub> solution, subsequent hydrolysis of (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H to more highly hydrolyzed products can be minimized. Typically, yields of (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H in excess of 60% are obtained.

The <sup>31</sup>P NMR spectral data confirm that (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H in solution is the phosphine oxide **2** and not the hydroxyphosphine **1**. The chemical shift of (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H (δ 1.10) occurs in the region associated unequivocally with P(V) oxide species, the large <sup>1</sup>*J*<sub>PH</sub> coupling constant (590–610 Hz) is consistent with that of a directly bonded hydrogen,<sup>13</sup> and the δ<sub>p</sub> and <sup>1</sup>*J*<sub>PH</sub> data agree well with those reported previously for [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>N]<sub>2</sub>P(O)H,<sup>14</sup> also characterized in solution as the phosphine oxide. The δ<sub>p</sub>, <sup>1</sup>*J*<sub>PH</sub>, and <sup>2</sup>*J*<sub>PNH</sub> values for (C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P(O)H are somewhat solvent and temperature dependent; however, such a dependency is not surprising in an extensively hydrogen-bonded system. This dependency is being studied currently in detail and will be the subject of a later report.

We obtained no evidence for the formation of the hydroxyphosphine **1** either as a minor product or as a reaction intermediate under the conditions of our experiments. Upon addition of H<sub>2</sub>O to (C<sub>6</sub>H<sub>5</sub>NH)<sub>3</sub>P or [(C<sub>6</sub>H<sub>5</sub>NH)<sub>2</sub>P]<sub>2</sub>NC<sub>6</sub>H<sub>5</sub>,

(9) A reflection was taken as significant when *F*<sub>o</sub><sup>2</sup> > 3.0σ(*F*<sub>o</sub><sup>2</sup>). σ(*F*<sub>o</sub><sup>2</sup>) = RLP/[TSC + BACK + {P(TSC – BACK)}<sup>2</sup>]<sup>1/2</sup>, where TSC is the total number of counts accumulated during the measurement scan, BACK is the total number of counts accumulated during the background measurement, and RLP is defined above; *P*, a damping factor, was given a value of 0.04 [Busing, W. R.; Levy, H. A. *J. Chem. Phys.* 1957, 26, 563. Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* 1967, 6, 197].

(10) The isotropic thermal parameters for the hydrogens were set to be 1 greater than those of the atom to which they were attached.

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Table II. Positional and Thermal Parameters for the Atoms of  $(C_6H_5NH)_2P(O)H$  (I)

atom	x	y	z	$B_{11}^a$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P1	0.65618 (5)	0.08316 (15)	0.04131 (3)	3.16 (4)	2.27 (3)	2.40 (3)	-0.01 (3)	0.97 (2)	-0.05 (3)
O1	0.70538 (12)	0.3058 (4)	0.06121 (8)	4.57 (11)	2.52 (9)	3.10 (10)	-0.70 (9)	1.37 (8)	-0.57 (8)
N1	0.66373 (15)	-0.1593 (5)	0.08378 (10)	3.91 (13)	2.13 (11)	2.43 (10)	0.19 (9)	1.17 (9)	-0.17 (9)
N2	0.67235 (15)	-0.0323 (5)	-0.01610 (10)	3.40 (13)	3.02 (12)	2.53 (11)	-0.64 (10)	1.15 (9)	-0.30 (9)
C11	0.65237 (17)	-0.1505 (5)	0.13859 (11)	3.20 (14)	2.23 (12)	2.37 (12)	-0.56 (11)	0.50 (10)	-0.33 (10)
C12	0.60823 (21)	0.0403 (6)	0.15447 (13)	4.66 (18)	3.06 (15)	2.91 (15)	0.45 (13)	1.12 (13)	-0.09 (12)
C13	0.59674 (22)	0.0418 (7)	0.20766 (14)	5.19 (20)	3.26 (16)	3.35 (16)	0.20 (15)	1.58 (14)	-0.44 (14)
C14	0.62886 (21)	-0.1426 (7)	0.24515 (14)	5.03 (19)	4.07 (17)	2.68 (14)	-0.79 (15)	1.51 (13)	-0.34 (13)
C15	0.67295 (22)	-0.3310 (7)	0.22966 (14)	5.03 (19)	3.80 (17)	2.93 (15)	-0.08 (15)	0.84 (13)	0.56 (13)
C16	0.68473 (19)	-0.3350 (6)	0.17625 (13)	3.83 (17)	2.87 (14)	3.02 (14)	0.08 (12)	1.04 (12)	0.18 (12)
C21	0.62745 (16)	-0.2000 (5)	-0.05499 (12)	2.67 (13)	2.28 (12)	2.57 (13)	0.12 (11)	0.69 (10)	0.03 (11)
C22	0.57460 (18)	-0.3660 (6)	-0.04171 (13)	3.59 (16)	3.31 (15)	2.56 (13)	-0.19 (12)	0.92 (12)	0.01 (12)
C23	0.53437 (20)	-0.5339 (7)	-0.08112 (14)	3.76 (17)	3.59 (16)	3.42 (15)	-0.78 (13)	0.63 (13)	-0.24 (13)
C24	0.54546 (21)	-0.5369 (7)	-0.13383 (14)	4.30 (18)	3.71 (17)	3.27 (15)	-0.34 (14)	0.41 (13)	-0.83 (14)
C25	0.59702 (21)	-0.3676 (7)	-0.14758 (14)	4.82 (18)	4.51 (18)	2.63 (14)	-0.39 (15)	1.12 (13)	-0.63 (14)
C26	0.63779 (19)	-0.1995 (7)	-0.10877 (13)	3.96 (17)	3.68 (15)	2.69 (14)	-0.27 (14)	1.21 (12)	-0.04 (13)

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
H1P1	0.5845 (20)	0.144 (7)	0.0291 (14)	3.5	H1C16	0.7144 (24)	-0.469 (8)	0.1673 (17)	4.1
H1N1	0.6839 (23)	-0.285 (8)	0.0762 (17)	3.6	H1C22	0.5654 (22)	-0.366 (8)	-0.0061 (17)	3.8
H1N2	0.7052 (24)	0.050 (8)	-0.0286 (17)	3.8	H1C23	0.4964 (23)	-0.649 (9)	-0.0709 (17)	4.6
H1C12	0.5834 (24)	0.146 (8)	0.1292 (17)	4.3	H1C24	0.5154 (24)	-0.643 (8)	-0.1610 (18)	4.8
H1C13	0.5691 (24)	0.183 (8)	0.2160 (17)	4.8	H1C25	0.6069 (23)	-0.367 (8)	-0.1847 (18)	4.7
H1C14	0.6196 (24)	-0.133 (8)	0.2819 (18)	4.6	H1C26	0.6722 (25)	-0.077 (8)	-0.1180 (17)	4.3
H1C15	0.6996 (25)	-0.459 (9)	0.2535 (18)	4.7					

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

Table III. Positional and Thermal Parameters for the Atoms of  $(C_6H_5NH)_2P(O)H$  (II)

atom	x	y	z	$B_{11}^a$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P1	0.82268 (20)	1/4	0.02192 (29)	3.28 (7)	3.26 (7)	3.11 (8)	0	-0.26 (7)	0
O1	0.6349 (5)	1/4	-0.0266 (7)	3.40 (20)	4.08 (20)	4.62 (22)	0	-0.72 (19)	0
N1	0.9337 (5)	0.20276 (13)	-0.0882 (7)	4.15 (19)	3.17 (16)	4.51 (20)	-0.01 (14)	1.20 (15)	0.25 (15)
C1	0.8938 (5)	0.15222 (15)	-0.0442 (7)	2.69 (16)	3.48 (18)	3.12 (19)	0.00 (15)	-0.29 (15)	0.27 (17)
C2	0.9513 (6)	0.11640 (16)	-0.2078 (8)	3.52 (22)	3.68 (18)	3.38 (20)	-0.29 (17)	0.24 (18)	0.11 (18)
C3	0.9144 (6)	0.06611 (16)	-0.1695 (9)	3.99 (24)	4.26 (23)	4.27 (24)	0.15 (18)	-0.07 (20)	-0.33 (20)
C4	0.8218 (6)	0.05134 (16)	0.0305 (9)	4.29 (21)	3.29 (19)	5.19 (26)	-0.62 (19)	-0.37 (24)	0.73 (22)
C5	0.7649 (6)	0.08673 (19)	0.1918 (8)	4.02 (24)	4.66 (24)	3.64 (24)	-0.36 (18)	0.20 (19)	0.80 (22)
C6	0.8016 (6)	0.13658 (17)	0.1563 (8)	3.81 (22)	3.94 (21)	3.32 (21)	0.12 (18)	0.20 (18)	0.01 (18)

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
H1P1	0.849 (5)	1/4	0.256 (6)	4.1	H1C4	0.797 (7)	0.0231 (20)	0.062 (10)	5.2
H1N1	0.994 (7)	0.2155 (17)	-0.214 (10)	5.0	H1C5	0.702 (7)	0.0787 (19)	0.333 (9)	5.2
H1C2	1.015 (7)	0.1233 (18)	-0.361 (9)	4.6	H1C6	0.781 (7)	0.1603 (17)	0.267 (10)	4.8
H1C3	0.967 (6)	0.0438 (19)	-0.289 (9)	5.2					

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

the first resonance detected in the  $^{31}\text{P}$  NMR spectrum is that of  $(C_6H_5NH)_2P(O)H$ . Further addition of  $H_2O$  yields, besides  $(C_6H_5NH)_2P(O)H$ , only other yet-uncharacterized P(V) hydrolysis products. Thus, although hydrolysis of  $(C_6H_5NH)_2P$  or  $[(C_6H_5NH)_2P]_2NC_6H_5$  may proceed via cleavage of P-N bonds to form the hydroxyphosphine **1**, it must be unstable relative to **2** and may rearrange rapidly to **2** via an Arbuzov-type process.<sup>15</sup>

**Structure of  $(C_6H_5NH)_2P(O)H$ .** Crystallization of  $(C_6H_5NH)_2P(O)H$  from chloroform, methylene chloride, or benzene yields monoclinic crystals (form I), space group  $C2/c$ . Crystallization of the same compound from ethanol yields orthorhombic crystals (form II). Although the unit cell parameters observed in our study of form II ( $a = 7.702$ ,  $b = 26.723$ ,  $c = 5.558$  Å) correspond closely to those reported by Ginet and Geoffroy ( $a = 7.71$ ,  $b = 5.55$ ,  $c = 26.75$  Å), we find that the crystal is best characterized in the centrosymmetric space group  $Pnma$ , rather than the acentric space group  $Pna2_1$ , which they reported. Forms I and II of  $(C_6H_5NH)_2P(O)H$  melt at 160–161 and 151–152 °C, respectively. Upon melting

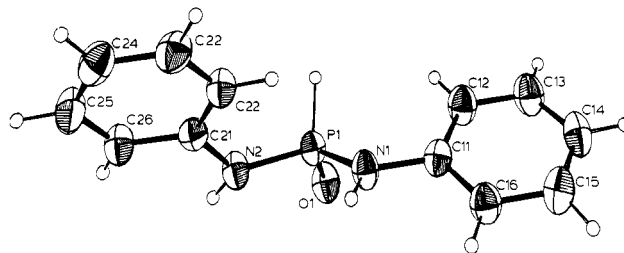


Figure 1. Molecular structure of  $(C_6H_5NH)_2P(O)H$ , form I. Nonhydrogen atoms are shown as 50% probability ellipsoids. Hydrogen atoms are included on an arbitrary scale for clarity.

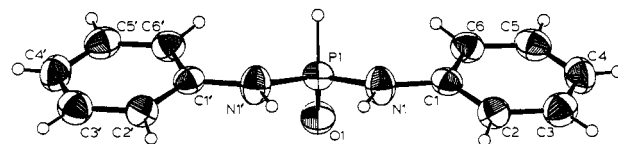


Figure 2. Molecular structure of  $(C_6H_5NH)_2P(O)H$ , form II. Nonhydrogen atoms are shown as 50% probability ellipsoids. Hydrogen atoms are included on an arbitrary scale for clarity. The atoms denoted by the single prime mark are at symmetry position  $x, 0.5 - y, z$ .

(15) Hall, D.; Emsley, J. "The Chemistry of Phosphorus"; Harper and Row: London, 1976.

**Table IV.** Nonphenyl Structural Parameters for  $(C_6H_5NH)_2P(O)H$  for  $(C_6H_5NH)_2P(O)H$ 

form I		form II	
(a) Bond Distances (Å)			
P1-N1	1.634 (3)	P1-N1	1.643 (4)
P1-N2	1.634 (3)		
P1-O1	1.475 (2)	P1-O1	1.471 (4)
P1-H1P1	1.29 (4)	P1-H1P1	1.32 (3)
N1-C11	1.422 (4)	N1-C1	1.407 (5)
N2-C21	1.408 (4)		
N1-H1H1	0.79 (4)	N1-H1H1	0.91 (5)
N2-H1H2	0.84 (4)		
(b) Bond Angles (Deg)			
N1-P1-O1	116.4 (1)	N1-P1-O1	116.3 (2)
N2-P1-O1	111.6 (1)		
N1-P1-H1P1	106 (2)	N1-P1-H1P1	106.7 (9)
N2-P1-H1P1	105 (2)		
O1-P1-H1P1	112 (2)	O1-P1-H1P1	109 (2)
N1-P1-N2	105.6 (1)	N1-P1-N1'	100.4 (3)
C11-N1-P1	125.6 (2)	C1-N1-P1	124.0 (3)
C21-N2-P1	129.5 (2)		
C11-N1-H1N1	115 (3)	C1-N1-H1N1	127 (3)
C21-N2-H1N2	114 (3)		
P1-N1-H1N1	118 (3)	P1-N1-H1N1	105 (3)
P1-N2-H1N2	114 (3)		

**Table V.** Phenyl-Group Structural Parameters for  $(C_6H_5NH)_2P(O)H$ 

(a) Form I, Bond Distances (Å)			
C11-C12	1.387 (4)	C21-C22	1.381 (4)
C12-C13	1.382 (4)	C22-C23	1.384 (4)
C12-H1C12	0.88 (4)	C22-H1C22	0.94 (4)
C13-C14	1.370 (5)	C23-C24	1.368 (5)
C13-H1C13	0.94 (4)	C23-H1C23	0.98 (4)
C14-C15	1.374 (5)	C24-C25	1.380 (5)
C14-H1C14	0.97 (4)	C24-H1C24	0.94 (4)
C15-C16	1.390 (5)	C25-C26	1.380 (5)
C15-H1C15	0.95 (4)	C25-H1C25	0.95 (4)
C16-C11	1.374 (4)	C26-C21	1.389 (4)
C16-H1C16	0.94 (4)	C26-H1C26	0.95 (4)
(b) Form I, Bond Angles (Deg) <sup>a</sup>			
C16-C11-C12	119.4 (3)	C26-C21-C22	119.0 (3)
C11-C12-C13	119.9 (3)	C21-C22-C23	120.2 (3)
C12-C13-C14	120.7 (3)	C22-C23-C24	120.9 (3)
C13-C14-C15	119.6 (3)	C23-C24-C25	119.0 (3)
C14-C15-C16	120.2 (3)	C24-C25-C26	120.8 (3)
C15-C16-C11	120.2 (3)	C25-C26-C21	120.0 (3)
(c) Form II, Bond Distances (Å)			
C1-C2	1.393 (5)	C4-C5	1.375 (6)
C2-C3	1.390 (6)	C5-C6	1.376 (6)
C3-C4	1.378 (6)	C6-C1	1.386 (6)
(d) Form II, Bond Angles (Deg) <sup>a</sup>			
C6-C1-C2	118.7 (4)	C3-C4-C5	119.6 (4)
C1-C2-C3	119.9 (4)	C4-C5-C6	120.5 (4)
C2-C3-C4	120.4 (4)	C5-C6-C1	120.8 (4)

<sup>a</sup> Angles involving phenyl hydrogens are not listed. Angles range from 115 (3) to 125 (3)<sup>o</sup>; mean angle 120 (3)<sup>o</sup>.

and refreezing, I remelted at 160–161 °C, whereas when II was melted and refrozen, its melting point began to increase and the range became broader. Thus it appears that in the process II is converting to I and that I may represent the thermodynamically more stable form of  $(C_6H_5NH)_2P(O)H$  in the temperature range involved.

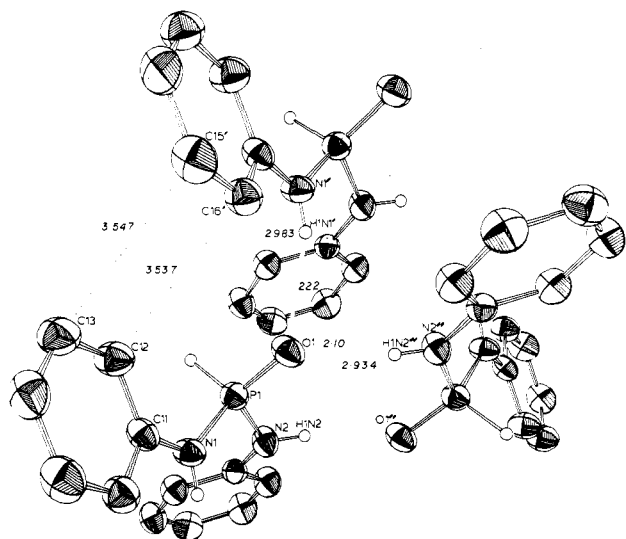
The structure of  $(C_6H_5NH)_2P(O)H$  in both forms I (Figure 1) and II (Figure 2) is that of a phosphine oxide (2), the two crystalline forms being examples of conformational polymorphs.<sup>16</sup> The molecule consists of two anilino moieties, an oxygen atom, and a hydrogen atom bonded to a four-coor-

**Table VI.** Least-Squares Planes,<sup>a</sup> Deviations from Planarity, and Interplane Angles in  $(C_6H_5NH)_2P(O)H$ 

atom	dev, Å	atom	dev, Å
Form I			
Plane 1: $13.8x + 2.97y + 2.67z = 8.90$			
C11* <sup>b</sup>	0.008 (3)	C15*	-0.002 (4)
C12*	0.009 (4)	C16*	0.006 (3)
C13*	-0.003 (4)	N1*	-0.008 (3)
C14*	-0.008 (4)		
Plane 2: $12.1x - 3.61y + 2.41z = 8.19$			
C21*	-0.012 (3)	C25*	0.002 (4)
C22*	-0.020 (3)	C26*	-0.020 (3)
C23*	0.005 (4)	N2*	-0.019 (3)
C24*	0.023 (4)		
Plane 3: $16.3x + 1.11y + 3.30z = 10.9$			
P1*	0.000 (1)	C11*	0.001 (3)
N1*	-0.005 (3)	H1N1*	0.16 (4)
Plane 4: $6.70x - 4.07y + 9.98z = 4.47$			
P1*	0.000 (1)	C21*	-0.001 (3)
N2*	0.005 (3)	H1N2*	-0.234
Plane 5: $-15.0x + 2.03y + 14.3z = -9.06$			
P1*	0.00	O1*	0.00
N1*	0.00	N2	-1.296
Plane 6: $10.6x - 3.18y + 9.37z = 7.07$			
P1*	0.00	O1*	0.00
N2*	0.00	N1	1.248
Plane 7: $-16.8x + 1.52y + 0.491z = -11.3$			
N1*	0.00	H1P1	1.76
N2*	0.00	C11	0.231
O1*	0.00	C21	0.478
P1	0.475		
Form II			
Plane 8: $6.56x - 2.62y + 2.86z = 5.35$			
C1*	-0.003 (4)	C5*	-0.004 (5)
C2*	0.001 (4)	C6*	0.005 (4)
C3*	-0.000 (4)	N1*	0.000 (4)
C4*	0.002 (5)		
Plane 9: $4.59x + 0.334y + 4.46z = 3.96$			
P1*	-0.000 (2)	C1*	-0.001 (4)
N1*	-0.006 (4)	H1N1*	-0.27 (5)
Plane 10: $1.21x + 13.8y - 4.68z = 4.33$			
P1*	0.00	O1*	0.00
N1*	0.00	N1' <sup>c</sup>	1.30
Plane 11: $1.13x + 0.0y + 5.50z = 0.573$			
N1*	0.00	P1H1	1.80
N1'*	0.00	C1	0.197
O1*	0.00	P1	0.479
		C1'	0.197
dihedral angles (deg) between planes			
planes	angle	planes	angle
Form I			
1-3	22.4	2-7	152.3
2-4	22.8	3-7	149.5
3-5	122.6	4-7	132.8
4-6	15.9	5-7	35.6
1-7	127.8	6-7	146.9
Form II			
8-9	22.9	9-11	28.2
9-10	124.9	10-11	144.1
8-11	50.7		

<sup>a</sup> The planes are calculated according to: Hamilton, W. C. *Acta Crystallogr.* 1961, 14, 185. <sup>b</sup> Atoms with an asterisk are those used to calculate the plane. <sup>c</sup> Atoms marked with a prime are related by a symmetry operation.

(16) Bernstein, J.; Hagler, A. T. *Mol. Cryst. Liq. Cryst.* 1979, 50, 223. Hagler, A. T.; Bernstein, J. *J. Am. Chem. Soc.* 1978, 100, 6349.



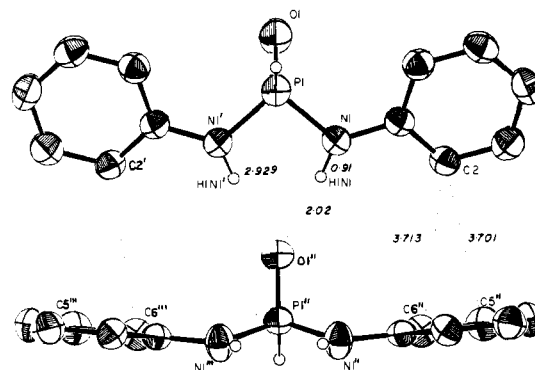
**Figure 3.** View of three molecules in the unit cell of  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$ , form I, showing intermolecular contacts. The molecule denoted by the single prime mark is at symmetry position  $x, 1.0 + y, z$ ; the molecule denoted by double prime marks is at symmetry position  $1.5 - x, 0.5 - y, -z$ . For clarity, only hydrogen atoms H1P1, H1N1, and H1N2 are shown.

dinate distorted tetrahedral phosphorus atom. Form I has  $C_1$  molecular symmetry. Form II has  $C_s$  crystallographic and molecular symmetry, with P1, O1, and H1P1 being on the mirror plane of symmetry.

Structural parameters for I and II are listed in Tables IV-VI. Bond distances and angles (Table IV) in I and II are closely similar. The P-O and P-H distances, 1.475 (2) and 1.29 (4) Å in I and 1.471 (4) and 1.320 (3) Å in II, are consistent with those of previously studied phosphoryl compounds.<sup>17</sup> Mean P-N distances of 1.639 (3) (I) and 1.642 (4) Å (II) are slightly shorter than those of  $(\text{NH}_2)_3\text{PO}$  [1.662 (2) Å],<sup>17</sup> an aminophosphine oxide known to be hydrogen bonded in the solid.

The geometry around nitrogen atoms is distorted from planar; mean hydrogen atom deviations from the P,C,N planes (planes 3, 4, and 9, Table VI) are 0.2 (I) and 0.3 Å (II). The sum of bond angles around nitrogen atoms are 358 (I) and 356° (II). The dihedral angles between P,N,C planes and  $\text{C}_6\text{N}$  planes (planes 1-3, 2-4, and 8-9), mean angle 22.4 (I) and 22.9° (II), are surprisingly similar in the two forms.

The most interesting structural features displayed by I and II are the characteristic intermolecular hydrogen-bonding patterns and the conformational properties with respect to groups around P-N bonds. The hydrogen-bonding patterns are seen in the partial unit cell diagrams of I (Figure 3) and II (Figure 4). In both forms, each  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$  molecule is hydrogen bonded by four hydrogen bonds to other  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$  molecules in the crystal. Every oxygen atom is involved in two hydrogen bonds and every anilino hydrogen atom is involved in one hydrogen bond. The pattern in I (Figure 3) consists of hydrogen-bonded  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$  dimer units bonded by a pair of hydrogen bonds,  $\text{O1} \cdots \text{H1N2}'$  and  $\text{H1N2} \cdots \text{O1}'$ , with each of the dimer units attached by two single hydrogen bonds to two other dimer units, e.g.,  $\text{O1} \cdots \text{H1N1}'$ . In contrast, in II (Figure 4) the pattern consists of a more linear head-to-tail arrangement of  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$  molecules, where each oxygen is bonded symmetrically to the two anilino hydrogen atoms of a nearby molecule, e.g.,  $\text{O1}'' \cdots \text{H1N1}$  and  $\text{O1}'' \cdots \text{H1N1}'$ . The hydrogen-bond angles are 161° for  $\angle \text{N2}-\text{H1N2} \cdots \text{O1}''$  and 170° for  $\angle \text{N1}'-\text{H1N1}' \cdots \text{O1}$



**Figure 4.** View of two molecules in the unit cell of  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$ , form II, showing intermolecular contacts. The atoms denoted by the prime marks are at symmetry positions  $x, 0.5 - y, z$  (single prime),  $-0.5 + x, 0.0 + y, -0.5 - z$  (double prime), and  $-0.5 + x, 0.5 - y, -0.5 - z$  (triple primes). For clarity only hydrogen atoms H1P1 and H1N1 are shown.

for I, and 173° for  $\angle \text{N1}-\text{H1N1} \cdots \text{O1}$  for II.

The conformational properties with respect to the distribution of groups around the P-N bonds of I and II are of interest. Examination of projections down N1-P1 and N2-P1 axes for I and N1'-P1 for II shows that the nearest eclipsing of bonds occurs in every case between an N-H bond and the P-N bond of the other nitrogen. If the lone-pair electrons of the anilino nitrogen atoms are assumed to be in a  $p_z$  orbital perpendicular to the approximate C,H,N,P planes, considerable differences in how these electrons are oriented relative to the other bonds of the system are seen. The electron pair on N1 in I is rotated approximately 30° from being eclipsed with the P=O bond and is rotated about 90° from the P-N2 bond. In contrast, the nitrogen  $p_z$  orbital of N2 is rotated approximately 90° from the P=O bond and is nearly aligned with the N1-P bond. In II, the nitrogen  $p_z$  orbital of N1' is about 90° from the P-N bond of the other nitrogen, P1-N1.

The orientation of the electron-occupied  $p_z$  orbital of the nitrogen atoms with respect to orbitals on phosphorus has been discussed recently in connection with the interpretation of photoelectron spectra of aminophosphines, aminophosphine oxides and sulfides, and metal-coordinated aminophosphines.<sup>18</sup> In these systems, the lowest energy conformation around P-N bonds is of interest to determine. In the  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$  systems, it is not possible to state which conformation around the P-N bonds represents a lowest energy conformation, because of the large orientational effect that hydrogen bonding must play in the crystal. It might be expected that hydrogen-bond effects would dominate other conformational energy effects. It seems that in the polymorphic  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$  system, hydrogen bonding may dominate and cause conformational effects around the P-N bonds, which are not necessarily lowest in energy and which may be quite different when seen in the absence of hydrogen bonding.

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**Registry No.**  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$ , 4671-85-6;  $(\text{C}_6\text{H}_5\text{NH})_3\text{P}$ , 15159-51-0;  $[(\text{C}_6\text{H}_5\text{NH})_2\text{P}]_2\text{NC}_6\text{H}_5$ , 73131-02-9.

**Supplementary Material Available:** Listings of structure factor amplitude data for  $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{H}$ , forms I and II (6 pages). Ordering information is given on any current masthead page.

(17) Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: London, 1974.

(18) Hargis, J. H.; Jennings, W. B.; Worley, S. D.; Tolley, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 13 and references cited therein.