those compounds listed in Table VI that have been structurally but not magnetically characterized, as well as to obtain new examples for analysis.

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Supplementary Material Available: Tables of atomic thermal parameters, bond lengths and angles in the ligands, and observed and calculated structure amplitudes for both structures (36 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of the Primary-Amine-Substituted Phosphines $(C_6H_5NH)_3P$ and $[(C_6H_5NH)_2P]_2NC_6H_5$

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The new primary-amine-substituted diphosphines $[(C_6H_5NH)_2P]_2NC_6H_5$ and $(C_6H_5NH)_3P$ have been obtained from the transamination of $[(C_2H_5)_2N]_3$ with aniline. ^{31}P NMR spectral evidence for intermediate formation of $[(C_2H_5)_2N]_2P(NHC_6H_5)$ and $[(C_2H_5)_2N]P(NHC_6H_5)_2$ has been obtained. The structure of $[(C_6H_5NH)_2P]_2NC_6H_5$ as the diethyl ether monosolvate and $(C_6H_5NH)_3P$ have been established by single-crystal X-ray studies. Crystals of $(C_6H_5NH)_3P$ are hexagonal, space group $P6_3$, with $a = b = 11.449$ (3) Å, $c = 7.488$ (2) Å, $Z = 2$, $d_{calcd} = 1.20$ g cm^{-3}, and $d_{obsd} = 1.21$ g cm^{-3} (20 °C, Mo Kα). The crystal structure, solved by direct methods, refined anisotropically to $R_F = 0.053$ and $R_{wF} = 0.071$ and 935 independent observed reflections. $(C_6H_5NH)_3P$ has C_3 molecular symmetry. The C–N and P–N distances and N–P–N angles are 1.393 (10) Å, 1.697 (7) Å, and 99.5 (4)°, respectively. Crystals of $[(C_6H_5NH)_2P]_2NC_6H_5\cdot(C_2H_5)_2O$ are monoclinic, space group $P2_1/n$, with $a = 9.193$ (4) Å, $b = 21.154$ (8) Å, $c = 16.624$ (5) Å, $\beta = 96.64$ (3)°, $Z = 4$, $d_{calcd} = 1.23$ g cm^{-3}, and $d_{obsd} = 1.25$ g cm^{-3} (20 °C, Mo Kα). The crystal structure, solved by direct methods, refined anisotropically to $R_F = 0.075$ and $R_{wF} = 0.085$ for 1403 independent observed reflections. $[(C_6H_5NH)_2P]_2NC_6H_5$ has approximate C_{2v} molecular symmetry in the crystal, a structure in which the N_2P–N–PN_2 conformation is twisted slightly from eclipsed phorphorus lone-pair electrons. Mean bond distances are as follows: C_6H_5(H)N–P, 1.70 (1) Å; C_6H_5N–P, 1.67 (1) Å; C–N, 1.41 (1) Å. Mean bond angles are as follows: C_6H_5(H)N–P–NHC_6H_5, 94.9 (5)°; C_6H_5(H)N–P–NC_6H_5, 105.3 (6)°; P–N–P, 117.7 (5)°; P–N(H)–C_6H_5, 121.1 (5)°; P–N–C, 124.9 (5)°. $(C_6H_5NH)_3P$ is stable in the solid; in solution it reacts rapidly to establish equilibrium with $[(C_6H_5NH)_2P]_2NC_6H_5$ and $C_6H_5NH_2$. $[(C_6H_5NH)_2P]_2NC_6H_5$ in the absence of $C_6H_5NH_2$ is stable for extended periods in solution, reacting only slowly to more highly condensed products.

Primary-amine-substituted phosphines, because of their N–H bond functionality, are potential intermediates for the synthesis of a wide variety of aminophosphine compounds; however, because of their high reactivity they are seldom isolated. Trissubstituted phosphines, i.e., $(RNH)_3P$ (R = H, alkyl, aryl), often invoked as reaction intermediates, are sufficiently labile to have eluded isolation and unambiguous structural characterization.[2-7]

Trianilinophosphine has been reported,[8-10] but the early accounts of its isolation appear doubtful.[6,11] Recently, Trishin and co-workers[12] reported preparation of $(C_6H_5NH)_3P$ by $[(C_2H_5)_2N]_3P$–$C_6H_5NH_2$ transamination according to eq 1;

$$[(C_2H_5)_2N]_3P + 3C_6H_5NH_2 \rightarrow 3(C_2H_5)_2NH + (C_6H_5NH)_3P \quad (1)$$

however, their characterization data were insufficient to leave characterization unequivocal and their study did not establish properties of $(C_6H_5NH)_3P$ in solution. Recently, we have reexamined the reaction of $[(C_2H_5)_2N]_3P$ with aniline, in order to clarify the nature of the reaction products. We find that the products are $(C_6H_5NH)_3P$ (**1**) and a new diphosphine $[(C_6H_5NH)_2P]_2NC_6H_5$ (**2**). Preliminary accounts of this work have been reported.[13] Our study of the isolation, solution behavior, and X-ray structural characterization of these compounds is reported below.

Experimental Section

Apparatus and Materials. All manipulations requiring inert atmosphere were carried out in N$_2$-flushed glovebags or standard Schlenk apparatus.[14] Infrared, ^{1}H NMR (90.0 MHz), and mass spectra were obtained with a Perkin-Elmer 337G, a Varian EM390, and a Varian MAT CH-5 spectrometers, respectively. Phosphorus-31 NMR spectra were obtained with a JEOL-PFT 100 spectrometer equipped with standard probe accessories. ^{1}H NMR chemical shifts were measured relative to internal $(CH_3)_4Si$; values downfield from the standard given positive (+δ) values. ^{31}P NMR chemical shifts were measured relative

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to external H_3PO_4; downfield chemical shifts are given negative ($-\delta$) values. Single-crystal X-ray data were collected at ambient temperature with a Syntex P$\bar{1}$ automated diffractometer equipped with a graphite monochromator. Elemental analyses and molecular weight measurements were performed by Huffman Analytical Laboratory, Wheatridge, CO.

$[(C_2H_5)_2N]_3P$[15] was prepared as reported earlier. Toluene, benzene, and $(C_2H_5)_2O$ were dried over $LiAlH_4$. Aniline ($C_6H_5NH_2$) was distilled from CaH_2 and stored over activated molecular sieves (Linde, 5 Å).

Reaction materials from the reactions below were characterized by comparison of their physical and/or spectral properties with those reported in the literature or with samples prepared independently in our laboratories. Mass spectral data, in the sections below, refer to the major peak in the envelope in quesion.

Preparation of $(C_6H_5NH)_3P$ (1). Aniline (16.7 g, 0.18 mol) was added dropwise to $[(C_2H_5)_2N]_3P$ (14.8 g, 0.06 mol) under N_2 at room temperature. The reaction mixture was heated for 6 h at 55 °C. Periodically volatile components were removed in vacuo. A total of 13 g (0.15 mol) of volatile material, characterized as $(C_2H_5)_2NH$, was collected. The reaction mixture when allowed to cool to room temperature solidified. Unreacted $C_6H_5NH_2$ was removed in vacuo. The solid was extracted with 150 mL of diethyl ether and the solution filtered from a small amount of suspended solids. After 15 h of standing at 5 °C under N_2, crystals of **1** form. Collection of the first fraction yielded pure **1**, mp 95–96 °C (ca. 10% yield). Further crystallization yields samples contaminated with **2**. Anal. Calcd for $C_{18}H_{18}N_3P$: C, 70.34; H, 5.90; N, 13.68. Found: C, 70.45; H, 5.85; N, 13.73. Infrared absorptions (KBr pellet) occur at 3110 (vs), 2990 (sh), 2430 (m), 1920 (w), 1840 (sh), 1785 (w), 1715 (sh), 1615 (s), 1495 (vs), 1405 (s), 1325 (w), 1275–1285 (s, d), 1240 (m), 1160 (vs), 1085 (m), 1040 (s), 970 (s), 940 (vs), 890 (s), 750 (s), 695 (vs), 620 (m), 520 (m), 512 (m), 455 (s), and 415 (sh, w) cm^{-1}. The ^{31}P NMR spectrum (C_6D_6) shows a singlet resonance at δ −73.9 ± 0.02. Owing to the presence of $C_6H_5NH_2$ and **2**, which are always present with **1** in solution and which may exchange NH protons with **1**, ^1H NMR spectral assignments for either the phenyl or NH resonances were not attempted. Thermolysis of **1** in the mass spectrometer inlet precluded obtaining suitable mass spectral data.

Preparation of $[(C_6H_5NH)_2P]_2NC_6H_5$ (2). Typically, a reaction mixture from the $[(C_2H_5)_2N]_3P$–$C_6H_5NH_2$ reaction (above) was dissolved in diethyl ether. The solution was cooled to 5 °C to cause precipitation of **1**. A fraction of the diethyl ether was removed, the solution cooled to −10 °C, and fractions of precipitate of **1** and **2** collected. Repetition of this procedure removes **1** from the solution and leaves essentially pure **2**. Repeated recrystallization from diethyl ether yields pure **2** as the diethyl ether monosolvate (mp 115–116 °C; 50–60% yield). Anal. Calcd for $C_{34}H_{39}N_5P_2O$: C, 72.31; H, 6.96; N, 12.41; P, 5.48. Found: C, 72.25; H, 6.41; N, 12.62; P, 5.51. Infrared absorptions (KBr pellet) occur at 3250–2860 (complex, s), 2425 (m), 2370 (w), 1610 (s), 1480 (vs), 1410 (s), 1325 (m), 1300 (s), 1285 (m), 1242 (s), 1190 (w), 1162 (vs), 1110 (w), 1088 (m), 1005 (w), 970 (s), 943 (vs), 885 (s), 828 (w), 748 (vs), 695 (s), 615 (w), 520 (w), 510 (w), and 457 (s) cm^{-1}. A ^{31}P NMR (C_6D_6) singlet resonance occurs at δ −67.8 ± 0.02. The ^1H NMR spectrum (toluene-d_8) exhibits resonances at δ 7.24–6.65 (complex, area 25, phenyl), δ 3.99 ± 0.05 (s, area 4, NH), 3.25 (quartet, area 4, CH_2), and 1.08 (t, area 6, CH_3). Sample decomposition in the spectrometer inlet precluded obtaining characteristic mass spectral data.

Equilibration Studies. Samples of solid **1**, adjudged pure by melting point and X-ray crystallographic analysis, were dissolved in benzene, toluene, diethyl ether, and chloroform solvents at ambient temperature. In each case, by the time the ^{31}P NMR spectrum could be obtained, the solutions contained two resonances at δ −74 and −68 in an approximate 1:2 area ratio (Figure 1C). In addition, small resonances due to yet uncharacterized subsequent condensation products appeared and slowly increased in intensity. The ^1H NMR spectrum showed the presecence of $C_6H_5NH_2$. Because condensation reactions occurred slowly after the initial equilibration, quantitative measurement of equilibrium prameters was not attempted.

To the sample of pure **2** in toluene in an NMR tube was added a large excess of aniline, and the mixture was heated at 50 °C. After 3 h, the ^{31}P NMR spectra showed one singlet peak at δ −70.9, attributable to $(C_6H_5NH)_3P$ in aniline solution. Addition of more $C_6H_5NH_2$ caused the resonance to shift to still lower field. Removal of $C_6H_5NH_2$ and toluene in vacuo from samples cooled to 20 °C, yielded solid **1**, containing small quantities of **2**. However, upon dissolution in solvent, reequilibration to a **1**–**2** mixture occurs.

Table I. Crystal Data for **1** and **2**

	1	2
formula	$C_{18}H_{18}N_3P$	$C_{30}H_{29}N_5P_2\cdot C_4H_{10}O$
M_r	307.337	595.67
space group[a]	hexagonal, $P6_3$	monoclinic, $P2_1/n$
a, Å[b]	11.449 (3)	9.913 (4)
b, Å	11.449 (3)	21.154 (8)
c, Å	7.488 (2)	16.624 (5)
α, deg	90	90
β, deg	90	96.64 (3)
γ, deg	120	90
V, Å^3	849.5 (4)	3211 (2)
d_c, g cm^{-3}	1.20	1.23
d_o, g cm^{-3}	1.21	1.25
Z	2	4
$F(000)$	324	1264
μ(Mo Kα), mm^{-1}	0.166	0.175

[a] The systematic absences and equivalent positions for $P6_3$, No. 173, are found in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. I, p 280. The nonstandard setting $P2_1/n$ was chosen to avoid a β angle of 114°. The systematic absences are $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$). The equivalent positions for $P2_1/n$ are x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; and $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$.
[b] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

Data Collection and Structure Analysis for 1 and 2. Crystals of **1** (0.4 × 0.2 × 0.2 mm) and **2** (0.5 × 0.3 × 0.3 mm) (**2** as $(C_2H_5)_2O$ solvate), crystallized from diethyl ether, were mounted and coated with epoxy resin. The crystals are extremely air sensitive. Cell parameters were determined on the diffratometer and were refined by least-squares fit of the parameters to 15 reflections for both **1** and **2**. Crystal data are summarized in Table I.

Data for both compounds were collected at room temperature with graphite-monochromatized Mo Kα radiation. θ–2θ scan techniques as programed by Syntex were employed. Background measurements, collected with the stationary-crystal stationary-counter technique, were made at the beginning and end of each scan for a total period equal to half the scan time. The data sets, monitored every 100 measurement cycles, showed a decline of approximately 10% and 20% for **1** and **2**, respectively, over the course of the experiment. Data were corrected for this decline and for Lorentz and polarization effects.[16] No corrections were made for absorption, the maximum error based on the crystal dimensions being less than 4% (for **1**) and 3% (for **2**) in F_o. For **1**, of 935 reflections measured in the range $3.0 < 2\theta < 40.0°$, 442 were determined to be significant; for **2** over the same range, 2166 measured, 1403 were significant.[17] All calculations except for final structure factor calculations were carried out with only significant reflections.

For **1** the position of the phosphorus was thought, on the basis of geometry, to be at the special position $^1/_3$, $-^1/_3$, z as opposed to 0, 0, z because the latter required that the phosphorus atoms be separated by only 3.74 Å. This short contact seemed unreasonable. However, a Patterson map based on $F_o{}^2$ showed no peaks corresponding to a phosphorus at either special position. A sharpened Patterson based on E^2-1 confirmed the phosphorus position to be $^1/_3$, $-^1/_3$, and z. A difference map based on only the phosphorus atom revealed no additional atoms. The phosphorus was then used in the MULTAN 78

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(16) RLP = $1/Lp = (2.0 \sin\theta \cos\theta)/\{0.5[(\cos^2 2\theta_m + \cos^2 2\theta)/(1 + \cos^2 2\theta_m)] + 0.5\,[(\cos 2\theta_m + \cos^2 2\theta)/(1 + \cos 2\theta_m)]\}$, where θ and θ_m are the Bragg angles for the crystal and the monochromator ($2\theta_m = 26.6°$). The fractional mosacity of the monochromator is assumed to be 0.5.

(17) A reflection was taken as significant when $F_o{}^2 > 3.0\sigma(F_o{}^2)$. $\sigma(F_o{}^2) = \mathrm{RLP}\{\mathrm{TSC} + \mathrm{BACK} + [\mathrm{P(TSC - BACK)}]^2\}^{1/2}$, 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, 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).

Table II. Positional Parameters for $(C_6H_5NH)_3P$ (**1**) and $[(C_6H_5NH)_2P]_2NC_6H_5 \cdot O(C_2H_5)_2$ (**2**)

atom	*x*/*a*	*y*/*b*	*z*/*c*
	(a) Compound 1		
P	1/3	2/3	0.870
N	0.4310 (8)	0.8151 (7)	0.7630 (11)
C(1)	0.5526 (10)	0.9176 (12)	0.8308 (19)
C(2)	0.5960 (14)	1.0513 (16)	0.7861 (17)
C(3)	0.7171 (19)	1.1524 (14)	0.849 (3)
C(4)	0.7979 (15)	1.1244 (17)	0.9644 (21)
C(5)	0.7560 (16)	0.9939 (19)	1.0073 (19)
C(6)	0.6365 (17)	0.8915 (12)	0.9402 (18)
	(b) Compound **2**		
P(1)	−0.1977 (4)	0.281 09 (17)	−0.003 38 (20)
P(2)	0.0473 (5)	0.215 03 (18)	−0.059 65 (20)
O(1)	−0.2583 (12)	0.3637 (5)	0.2000 (5)
N(1)	−0.1771 (13)	0.3575 (4)	0.0281 (5)
N(2)	−0.2921 (11)	0.2595 (5)	0.0742 (6)
N(3)	−0.0330 (11)	0.2474 (4)	0.0185 (5)
N(4)	0.2180 (11)	0.2423 (5)	−0.0501 (5)
N(5)	0.0925 (14)	0.1398 (5)	−0.0295 (6)
C(1)	−0.3738 (22)	0.4021 (9)	0.2179 (10)
C(2)	−0.1599 (24)	0.3465 (9)	0.2701 (11)
C(3)	−0.4832 (17)	0.4152 (7)	0.1446 (9)
C(4)	−0.0642 (22)	0.3973 (10)	0.3054 (12)
C(11)	−0.1665 (14)	0.4090 (7)	−0.0227 (8)
C(12)	−0.1905 (14)	0.4695 (6)	0.0064 (7)
C(13)	−0.1812 (15)	0.5220 (6)	−0.0422 (8)
C(14)	−0.1476 (17)	0.5162 (7)	−0.1208 (10)
C(15)	−0.1234 (17)	0.4560 (8)	−0.1514 (9)
C(16)	−0.1336 (15)	0.4015 (6)	−0.1017 (9)
C(21)	−0.3768 (14)	0.2063 (6)	0.0781 (7)
C(22)	−0.3570 (16)	0.1526 (7)	0.0299 (8)
C(23)	−0.4478 (18)	0.1002 (7)	0.0348 (9)
C(24)	−0.5511 (16)	0.0982 (7)	0.0858 (9)
C(25)	−0.5723 (16)	0.1506 (7)	0.1348 (8)
C(26)	−0.4848 (15)	0.2029 (6)	0.1291 (8)
C(31)	0.0477 (12)	0.2503 (6)	0.0908 (7)
C(32)	0.0206 (13)	0.2034 (6)	0.1560 (7)
C(33)	0.0967 (14)	0.2059 (6)	0.2349 (8)
C(34)	0.1921 (15)	0.2546 (7)	0.2555 (8)
C(35)	0.2179 (14)	0.3019 (6)	0.2016 (8)
C(36)	0.1431 (14)	0.2993 (6)	0.1219 (8)
C(41)	0.2672 (15)	0.2980 (6)	−0.0855 (8)
C(42)	0.3887 (16)	0.3300 (7)	−0.0550 (8)
C(43)	0.4359 (17)	0.3835 (7)	−0.0907 (9)
C(44)	0.3629 (18)	0.4058 (7)	−0.1626 (9)
C(45)	0.2405 (19)	0.3744 (8)	−0.1957 (9)
C(46)	0.1875 (16)	0.3205 (7)	−0.1596 (9)
C(51)	0.0311 (15)	0.0872 (6)	−0.0711 (8)
C(52)	0.1186 (14)	0.0317 (6)	−0.0691 (7)
C(53)	0.0612 (16)	−0.0223 (7)	−0.1117 (8)
C(54)	−0.0715 (16)	−0.0207 (7)	−0.1546 (8)
C(55)	−0.1602 (16)	0.0342 (7)	−0.1590 (8)
C(56)	−0.1036 (15)	0.0870 (6)	−0.1145 (8)

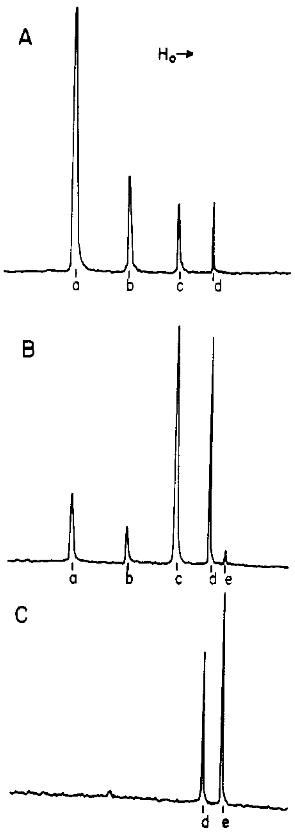

Figure 1. $[(C_2H_5)_2N]_3P$–$C_6H_5NH_2$ transamination series: (A) after 20 min at 25 °C, (B) after 1 h at 55 °C, and (C) after removal of $(C_2H_5N)_2H$, the final product mixture.

package as a known atom. The resulting *E* map revealed the position of the nitrogen atom. Repetition of this process revealed three carbons in the phenyl ring. The final three atoms were located with Fourier techniques. Isotropic refinement on this model converged at $R = 0.08$. Hydrogen atoms were located in a difference map based on this model. Inclusion of the hydrogen atoms in least-squares refinement,[18] with the phosphorus treated anisotropically and with hydrogen atoms held fixed, resulted in convergence at $R = 0.059$ and $R_w = 0.057$. Further refinement with all nonhydrogen atoms treated anisotropically converged at $R = 0.052$ and $R_w = 0.050$ for the observed data. The ratio of observations to variables (66) was 5/1. The esd of an observation of unit weight was 1.18. A structure factor calculation using all data gave $R = 0.136$ and $R_w = 0.071$. Final positional parameters for compound **1** are given in Table II. Thermal parameters are given in supplementary tables. Attempts to determine the absolute configuration of **1** using the imaginary component of the scattering factor for phosphorus ($\Delta f'' = 0.095$) were inconclusive.

Compound **2** was solved routinely with direct methods. The initial MULTAN 78 run revealed the position of 24 of the 42 atoms in the molecule. The remaining atoms were located by Fourier techniques. Isotropic least-square refinement of this model converged with $R = 0.11$. Additional refinement with nonphenyl atoms treated anisotropically and phenyl carbon atoms treated isotropically converged with $R = 0.088$ and $R_w = 0.099$. A difference map based on this model revealed the positions of all but the methyl hydrogens of the diethyl ether. Inclusion of these is fixed idealized positions resulted after further least-squares refinement in $R = 0.075$ and $R_w = 0.091$ with 229 variables; the ratio of observations to parameters was 4:1 with an esd of an observation of unit weight = 2.18. A structure factor calculation based on all data gave $R = 0.113$ and $R_w = 0.091$. Final positional and thermal parameters are give in Table II and supplementary tables, respectively.

For both compounds, the scattering factors used were for neutral atoms.[19] All calculations were carried out on the dual CDC 6400's at the University of Colorado Computing Center using programs contained in or based on Iber's Northwestern Univeristy computer package, the MULTAN 78 package,[20] and the Syntex data reduction routines.

Results and Discussion

Formation of $(C_6H_5NH)3P$ (1) and $[(C_6H_5NH)_2P]_2NC_6H_5$ (2). Reaction of $[(C_6H_5)_2N]_3P$ with $C_6H_5NH_2$ results in the stepwise replacement of $(C_2H_5)_2NH$, sequential formation of $[(C_2H_5)_2N]_2P(NHC_6H_5)$ and $[(C_2H_5)_2N]P(HNC_6H_5)_2$, and

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(18) The quantity minimized in the least-squares procedure was $\sum w(|F_o| - |F_c|)^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The standard deviation of an observation of unit weight is defined as $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV the number of variables. The weights, *w*, were calculated from counting statistics as $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$. $\sigma(F_o^2)$ is defined in ref 17.

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Table III. Structural Parameters for $(C_6H_5NH)_3P$ (1)

Bond Lengths, Å			
P-N	1.697 (7)	C(3)-C(4)	1.417 (19)
N-C(1)	1.393 (10)	C(4)-C(5)	1.360 (16)
C(1)-C(2)	1.392 (11)	C(5)-C(6)	1.377 (15)
C(2)-C(3)	1.369 (16)	C(6)-C(1)	1.404 (12)
Bond Angles, Deg			
N-P-N'	99.5 (4)	C(1)-C(2)-C(3)	120.0 (11)
P-N-C(1)	123.5 (8)	C(2)-C(3)-C(4)	121.2 (12)
N-C(1)-C(2)	119.7 (15)	C(3)-C(4)-C(5)	118.8 (14)
C(2)-C(1)-C(6)	117.9 (9)	C(4)-C(5)-C(6)	120.2 (15)
phenyl C-C-C[a]	120.0	C(5)-C(6)-C(1)	121.7 (11)

[a] Minimum and maximum deviation from average of −2.1 and +1.7 standard deviations.

finally formation of the completely transaminated products $(C_6H_5NH)_3P$ (**1**) and $[(C_6H_5NH)_2P]_2NC_6H_5$ (**2**) (eq 2–5).

$$[(C_2H_5)_2N]_3P + C_6H_5NH_2 \rightarrow (C_2H_5)_2NH + [(C_2H_5)_2N]_2P(HNC_6H_5) \quad (2)$$

$$[(C_2H_5)_2N]_2P(HNC_6H_5) + C_6H_5NH_2 \rightarrow (C_2H_5)_2NH + [(C_2H_5)_2N]P(HNC_6H_5)_2 \quad (3)$$

$$[(C_2H_5)_2N]P(HNC_6H_5)_2 + C_6H_5NH_2 \rightarrow (C_2H_5)_2NH + (C_6H_5NH)_3P \quad (4)$$

$$2(C_6H_5NH)_3P \rightleftharpoons [(C_6H_5NH)_2P]_2NC_6H_5 + C_6H_5NH_2 \quad (5)$$

This is demonstrated by observing the course of the reaction by monitoring periodically the ^{31}P NMR spectrum of reaction mixtures (Figure 1).

Immediately after mixing reagents, only the singlet resonance of $[(C_2H_5)_2N]_3P$ at δ −116.8 (resonance a) is present. After 20 min at 25 °C resonance b (δ −98.9) appears, followed successively upon further heating at 55 °C by resonances c (δ −82.7) and **d** (δ −71.4, assigned to **1**) (Figure 1A). Resonance d continues to increase in intensity and resonance e (δ −67.2, assigned to **2**) appears (Figure 1B). On the basis of comparisons of chemical shifts of b and c with those previously reported and the monotonic nature of the a–d resonance series,[21] b and c can be assigned to $[(C_2H_5)_2N]_2P(NHC_6H_5)$ and $[(C_2H_5)_2N]P(NHC_6H_5)_2$, respectively.

Of particular significance in the transamination reaction is that **2** (resonance e) appears very soon after **1** (resonance d) and while the concentration of $(C_2H_5)N$-containing phosphines (resonances a–c) is still high. In no case were we able to stop the reaction before formation of **2** becomes appreciable. Under conditions were $(C_2H_5)_2NH$ is removed in vacuo from the reaction mixture, the reactions in eq 2–4 are shifted to the right, and only **1** and **2** are obtained as products.

The product mixture from $[(C_2H_5)_2N]_3P$–$C_6H_5NH_2$ transamination in toluene at 60 °C is more complex than recognized in the recent study by Trishin and co-workers.[12] They reported **1** as the exclusive product, isolated in 60% yield. The substantial quantity of **2** in the reaction mixture apparently was not recognized. We find that because **1** is less soluble than **2** in diethyl ether; the first fractions of crystals to precipitate from the solvent are mainly **1**. **1** obtained in this way has been characterized by single-crystal X-ray crystallography (below). However, typically we obtained no greater than 10–15% yields of pure **1**. Subsequent fractions of material to crystallize from the diethyl ether become enriched in **2**.

Characterization of **1** alone in solution, free of **2** and $C_6H_5NH_2$, was not possible because of the high lability of **1** and its tendency to undergo reaction according to eq 5. **1** when dissolved in nonprotic solvents such as benzene, toluene, or diethyl ether rapidly undergoes condensation to **2** with elimination of aniline. Although slow formation of condensation products subsequent to **2** occurs, making quantitative equilibrium data difficult to obtain, it is possible to establish that at equilibrium the reaction mixture contains **1** and **2** in an approximately equimolar ratio (Figure 1C). When pure **2** is dissolved in toluene, excess $C_6H_5NH_2$ added, and the reaction heated to 60 °C, cleavage of **2** occurs, **1** forms, and the equilibrium reaction shown in eq 5 is reestablished.

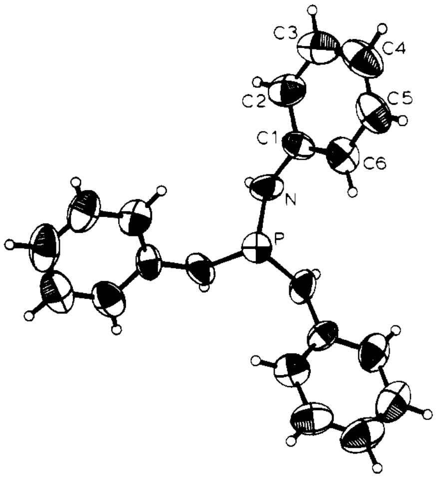
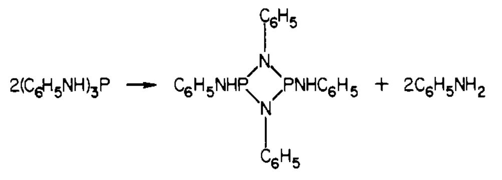


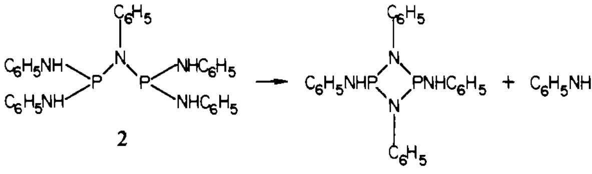
Figure 2. Structure of $(C_6H_5NH)_3P$ (**1**) (ORTEP diagram; thermal ellipsoids are drawn at the 50% probability level). Hydrogen atoms omitted for clarity.

It is reported that when $(C_6H_5NH)_3P$ is refluxed for 2.5 h in toluene, the reaction to produce the 1,3,2,4-diazadiphosphetidine, **3**, occurs[12] (eq 6). We have confirmed the formation of **3** as the reaction product under these conditions;[22] however, it seems likely that the diphosphine **2** is an intermediate between **1** and **3**, and that **3** may be formed from **2** according to eq 7. This may occur via the direct elimination of $C_6H_5NH_2$ from **2**; however, preliminary studies of the reaction shown in eq 7 indicate that one or more species may form as intermediates between **2** and **3**. Attempts to isolate and characterize these is in progress currently and will be reported later.



(6)

3



(7)

2

3

$(C_6H_5NH)_3P$ (1) Structure. The structure of **1** is shown in Figure 2, and a stereoview of the packing within the unit cell is shown in Figure 3. Bond distances and angles are given in Table III. The molecules are oriented around threefold rotation triads with the phosphorus atoms on the triads at $^1/_3$, $^2/_3$, 0.87 and $^2/_3$, $^1/_3$, 1.37. There are no significant intramolecular contacts between anilino groups in the crystal. The

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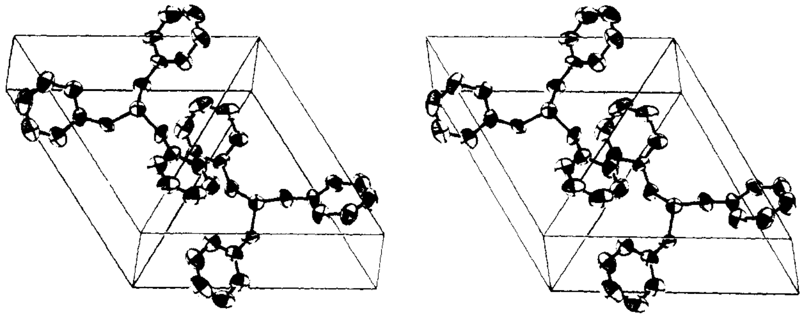

Figure 3. Unit cell of **1**, along the *c* axis.

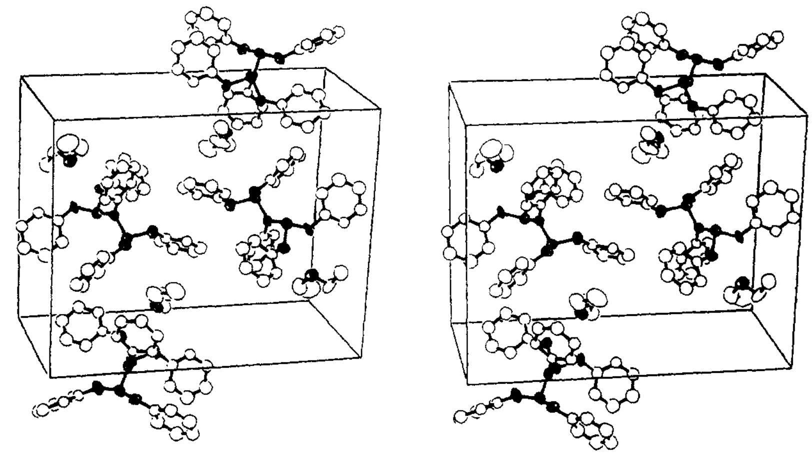

Figure 4. Unit cell of $[(C_6H_5NH)_2P]_2NC_6H_5{\cdot}O(C_2H_5)_2$ viewed along the *a* axis.

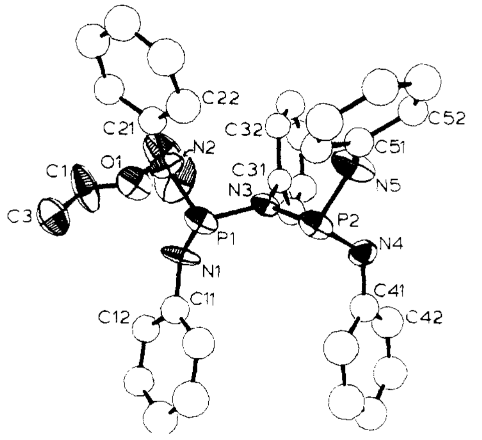

Figure 5. Structure of **2**$\cdot O(C_2H_5)_2$ (ORTEP diagram; thermal ellipsoids are drawn at the 50% probability level). Hydrogen atoms omitted for clarity.

Table IV. Structural Parameters for $[(C_6H_5NH)_2P]_2P]_2NC_6H_5{\cdot}O(C_2H_5)_2$ (**2**)

	Bond Lengths, Å		
P(1)-N(3)	1.67 (1)	P(2)-N(3)	1.71 (1)
P(1)-N(1)	1.70 (1)	P(2)-N(4)	1.66 (1)
P(1)-N(2)	1.70 (1)	P(2)-N(5)	1.71 (1)
O(1)-C(1)	1.40 (2)	O(1)-C(2)	1.44 (2)
C(1)-C(3)	1.51 (2)	C(2)-C(4)	1.46 (2)
N(1)-C(11)	1.39 (1)	N(4)-C(41)	1.42 (1)
N(2)-C(21)	1.37 (1)	N(5)-C(51)	1.39 (1)
N(3)-C(31)	1.47 (1)		
C-C(phenyl)	1.39[a]		
	Bond Angles, Deg		
N(1)-P(1)-N(2)	94.0 (5)	N(4)-P(2)-N(5)	95.7 (6)
N(1)-P(1)-N(3)	105.7 (5)	N(3)-P(2)-N(5)	105.2 (5)
N(2)-P(1)-N(3)	104.4 (5)	N(3)-P(2)-N(4)	105.9 (5)
P(1)-N(3)-P(2)	117.7 (5)	P(2)-N(4)-C(41)	126.4 (9)
P(1)-N(1)-C(11)	124.8 (9)	P(2)-N(5)-C(51)	121.8 (9)
P(1)-N(2)-C(21)	126.7 (8)	P(2)-N(3)-C(31)	120.0 (8)
P(1)-N(3)-C(31)	122.1 (8)	O(1)-C(1)-C(3)	112.6 (1.3)
C(1)-O(1)-C(2)	113.6 (1.2)	O(1)-C(2)-C(4)	115.6 (1.7)
C-C-C(phenyl)	120.1[b]		

[a] Minimum and maximum deviation from average of −0.05 and +0.05. [b] Minimum and maximum deviation from average of −3.5 and +3.9.

shortest intermolecular contact is 3.52 (2) Å between C(3) and C(6) at symmetry position *y*, 1.0 − *x* + *y*, −0.5 + *z*. C(4) is 3.65 (1) and 3.64 (2) Å from N and C(1), respectively, both at symmetry position *y*, 1.0 − *x* + *y*, 0.5 + *z*.

The structure of **1** consists of a trigonal arrangement of anilino groups around a central phosphorus, in a C_3 molecular symmetry arrangement. The atoms of the anilino groups are, within experimental limits, coplanar. The equation for the plane is $6.78x - 4.16y - 6.01z = -5.06$, and the atoms and deviations are C(1) −0.01 (1), C(2) 0.00 (1), C(3) 0.03 (2), C(4) −0.01 (1), C(5) −0.00 (1), C(6) 0.01(1), and N 0.00 (0). The dihedral angle between the anilino group planes and the plane formed by the three nitrogen atoms (*x*, *y* plane) is 143°. The paucity of inter- and intramolecular contacts in the crystal leads to the suggestion that the conformation assumed is the preferred orientation for the molecule. This result is particularly interesting, if it is general for triaminophosphines, since photoelectron spectral data for $[(CH_3)_2N]_3P$ has been interpreted in terms of conformations other than of the C_3 molecular[23,24] symmetry type.

The structural and bonding parameters for **1** (Table III) are consistent with those expected for anilinophosphine systems. The P–N distance of 1.70 Å is close to distances of 1.69, 1.63, and 1.67 Å, observed for the $C_6H_5(H)N$–P distances in $[(C_6H_5NH)P_2(NC_6H_5)_2]_2NC_6H_5$,[25] $(C_6H_5NH)_2P(O)H$,[26] and

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Table V

Least-Squares Planes and Deviations (Å) of Atoms from Planes for $[(C_6H_5NH)_2P]_2NC_6H_5$

atom	dev	atom	dev	atom	dev	atom	dev
Plane 1: $8.67x + 1.69y + 3.53z = 0.833$[a]							
C(11)*[b]	0.00 (1)	C(13)*	−0.00 (1)	C(15)*	0.00 (1)	N(1)	0.00
C(12)*	−0.00 (1)	C(14)*	0.00 (1)	C(16)*	−0.00 (1)	P(1)	0.42
Plane 2: $5.36x - 7.92y + 10.79z = 2.81$							
C(21)*	−0.00 (1)	C(23)*	−0.01 (1)	C(25)*	0.00 (1)	N(2)	−0.01
C(22)*	0.01 (1)	C(24)*	−0.00 (1)	C(26)*	−0.00 (1)	P(1)	−0.51
Plane 3: $7.23x - 11.45y - 6.42z = 3.17$							
C(31)*	0.01 (1)	C(33)*	0.01 (1)	C(35)*	−0.00 (1)	N(3)	−0.19
C(32)*	−0.01 (1)	C(34)*	0.00 (1)	C(36)*	−0.00 (1)	P(1)	−1.46
						P(2)	−1.43
Plane 4: $5.78x - 12.14y - 9.88z = 1.23$							
C(41)*	−0.00 (1)	C(43)*	−0.01 (1)	C(45)*	0.01 (2)	N(4)	0.04
C(42)*	0.01 (1)	C(44)*	0.00 (1)	C(46)*	−0.00 (1)	P(2)	−0.52
Plane 5: $4.64x + 6.63y - 14.25z = -1.74$							
C(51)*	−0.00 (1)	C(53)*	−0.01 (1)	C(55)*	0.01 (1)	N(5)	0.04
C(52)*	0.01 (1)	C(54)*	−0.00 (1)	C(56)*	−0.01 (1)	P(2)	0.76
Plane 6: $3.54x + 0.52y + 14.50z = -0.06$							
N(1)*	−0.10 (1)	N(4)*	0.11 (1)	N(3)	0.22	P(2)	−0.65
N(2)*	0.11 (1)	N(5)*	0.10 (1)	P(1)	−0.67		
Plane 7: $-3.27x - 3.01y - 14.57z = -0.90$							
N(1)*	0.00	N(3)*	0.00	N(5)	0.61	P(2)	0.97
N(2)*	0.00	N(4)	0.19	P(1)	0.76		
Plane 8: $3.83x - 1.84y + 14.15z = -0.32$							
N(3)*	0.00	N(5)*	0.00	N(2)	−0.23	P(2)	−0.74
N(4)*	0.00	N(1)	−0.62	P(1)	−1.00		
Plane 9: $-7.36x + 5.09y - 7.53z = -2.91$							
P(1)	0.00	N(2)*	0.00	N(3)	−1.55	P(2)	−1.72
N(1)*	0.00						
Plane 10: $1.75x - 5.37y - 16.02z = 0.12$							
P(2)*	0.00	N(5)*	0.00	N(3)	−1.57	P(1)	−1.69
N(4)*	0.00						
Plane 11: $4.23x + 18.52y - 3.33z = -4.38$							
P(1)*	0.00	N(3)*	0.00	N(1)	1.40	N(4)	1.19
P(2)*	0.00	C(3)	0.12	N(2)	−1.06	N(5)	−1.30

Selected Dihedral Angles (Deg) between Planes

planes	angle	planes	angle	planes	angle	planes	angle
1–6	48	8–10	140	7–8	166	6–9	144
2–6	28	1–7	130	8–11	91	7–9	41
4–6	105	2–7	145	1–9	156	9–11	94
5–6	123	4–8	99	2–9	162	3–11	94
3–6	89	5–8	123	4–10	40	6–10	144
6–7	173	3–7	86	5–10	39	7–11	99
6–11	86	6–8	7	3–8	84	10–11	90

[a] The planes are calculated according to: Hamilton, W. C. *Acta Crystallogr.* 1961, *14*, 185. The parameters x, y, and z are fractional monoclinic coordinates. [b] Atoms marked with an asterisk define the plane and were used to calculate the plane.

2 (below), respectively. The N–P–N′ angle is closely similar to those of 96.5 and 97.5° observed for the tris(dialkylamino)phosphines, $[(CH_3)_2N]_3P$ and $[(CH_2)_2N]_3P$.[27]

$[(C_6H_5NH)_2]_2NC_6H_5$ (2) Structure. Compound **2** crystallizes as a diethyl ether monosolvate. The packing of **2**·$O(C_2H_5)_2$ in the unit cell and the structural arrangement of the **2**·$O(C_2H_5)_2$ unit are shown in Figures 4 and 5, respectively. Bond distances and angles are given in Table IV. Least-squares planes and deviations of atoms from these planes are given in Table V.

The structure of **2**·$O(C_2H_5)_2$ is such that the ether oxygen is hydrogen bonded to **2** at nitrogen atoms N(1) and N(2), with N–H···O bond angles of 154 and 155°, respectively. The N_2P–N–PN_2 skeleton of **2** (Figure 6) consists of an approximately planar arrangement of nitrogen atoms (plane 6) with phosphorus atoms uniformly displaced from the plane by a mean distance of 0.66 Å. The phosphorus atoms are pyramidal, and the phenylimido nitrogen, N(3), is planar. The dihedral angle betwen planes 7 and 8, which is equivalent to the "twist" angle between lone pair electrons on phosphorus if phosphorus is assumed to be sp^3 hybridized, is 24°. Thus

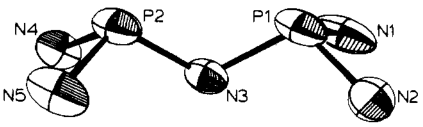

Figure 6. N_2P–N–PN_2 skeleton of **2**.

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Table VI. Selected Inter- and Intramolecular Nonbonding and Hydrogen-Bonding Contacts (Å) for $[(C_6H_5NH)_2P]_2NC_6H_5$ (**2**)

(a) Intermolecular Contacts			
C(3)–C(13)	3.60 (2)	C(12)–C(14)	3.46 (2)
C(3)–C(14)	3.67 (2)	C(13)–C(12)	3.41 (2)
C(11)–C(13)	3.57 (2)	C(13)–C(11)	3.57 (2)
C(11)–C(43)	3.74 (2)	C(13)–C(13)	3.59 (2)
C(12)–C(13)	3.41 (2)	C(14)–C(12)	3.46 (2)
(b) Intramolecular Contacts			
P(1)–P(2)	2.897 (6)	N(5)–C(31)	3.23 (2)
N(1)–C(31)	3.20 (2)	N(5)–C(32)	3.50 (2)
N(1)–C(36)	3.40 (2)	P(1)–C(2)	3.54 (1)
N(2)–C(31)	3.11 (2)	P(1)–C(6)	3.58 (1)
N(2)–C(32)	3.26 (2)	P(2)–C(2)	3.53 (1)
N(4)–C(31)	3.10 (2)	P(2)–C(6)	
N(4)–C(36)	3.25 (2)		
(c) Hydrogen Bonding Contacts			
O(1)–N(1)	3.04 (1)	O(1)–H(1N1)	2.13 (1)
O(1)–N(2)	3.03 (1)	O(2)–H(2N2)	2.09 (1)

the skeleton conformation is twisted slightly from a pure cisoid, C_{2v}, molecular symmetry pattern. This general conformation has been reported previously for $[(C_6H_5NH)_2P_2(NC_6H_5)_2]_2NC_6H_5$[26] and $[(C_6H_5)_2PN(CH_3)PN(t\text{-}C_4H_9)]_2$[28] in the solid and postulated, based on nuclear magnetic resonance coupling constant data, for bisphosphinoamines in solution.[29]

The structural and bonding parameters for **2** (Table IV) as with **1** are consistent with those of previously studied phenylamido- and/or phenylimidophosphines.[25,26] The anilino groups are planar (planes 1–5) within experimental error. Mean C_6H_5N–P distances of 1.69 Å are identical with the mean exo-$C_6H_5N(H)$–P distances of 1.69 Å. The N–P–N angles in the molecule vary somewhat; mean $C_6H_5N(H)$–P–$N(H)C_6H_5$ angles are 94.8° and mean $C_6H_5N(H)$–P–NC_6H_5 angles are 105.3°. However, the mean of all N–P–N angles is 101.8°, only slightly greater than that of 99.5° observed for the structurally less complex **1**. Comparison of the bond lengths and angles involving N(1) and N(2) with these around N(4) and N(5) suggests that hydrogen bonding has little effect on the conformation of **2**.

Short intramolecular contacts are present between carbon atoms C(31), C(32), and C(36) and nitrogen atoms N(1), N(2), N(4), and N(5) (Table VI). These are consistent with the approximately perpendicular orientation of phenyl ring 3 (plane 3) with respect to the P(1), N(3), P(2) plane (plane 11); dihedral angle = 94°. Examination of intermolecular contacts shows, except for the oxygen atom, C(3) is the only atom in the ether with possibly significant contacts with **2**, i.e., C(3)···C(13) and C(3)···C(14). Phenyl ring 1 is related to itself through the inversion center at 0, $^1/_2$, 0. C(11), C(12), C(13), and C(14) are related by this symmetry operator such that the contacts between them vary from 3.4 to 3.6 Å. These are in the range reported for phenyl stacking interactions.[30] It seems likely that the phenyl stacking has more influence on the configuration of compound **2** than the contacts involving C(3).

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Registry No. 1, 15159-51-0; **2**·$O(C_2H_5)_2$, 80953-59-9; $C_6H_5NH_2$, 62-53-3; $[(C_2H_5)_2N]_3P$, 2283-11-6.

Supplementary Material Available: Listings of structure factor amplitudes, calculated hydrogen positions and thermal parameters, and thermal parameters for nonhydrogen atoms (12 pages). Ordering information is given on any current masthead page.

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Molecular Structure of Gaseous Vanadium Pentafluoride, VF_5

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The molecular structure of VF_5 has been investigated at 30 °C by electron diffraction from the gas. Two models were tested, one based upon an assumed D_{3h} symmetry and one in which all distances were refined as independent parameters without regard for geometrical consistency. The purpose was to explore possible deviations from D_{3h} symmetry implicit in the existence of low-lying polar states discovered from electric field deflection experiments. The results are inconclusive. Although the D_{3h} model gives a slightly poorer fit than does the other, the difference is not statistically significant. At the same time, there are indications in the values of the vibrational amplitudes and in the nonbond distance defects ("shrinkages") that some aspects of the molecular motion are not properly accounted for by either of the models. Such indications are consistent with small deviations from D_{3h} symmetry, e.g., not more than a few degrees in any bond angle. Our distance (r_a) and amplitude (l) values in angstroms with estimated 2σ uncertainties for the D_{3h} model followed by those of the free-distance model are as follows: $r(V\text{–}F_{eq}) = 1.708$ (5), 1.701 (7); $r(V\text{–}F_{ax}) = 1.734$ (7), 1.747 (13); $r(F_{eq}\cdots F_{ax}) = 2.432$ (3), 2.428 (4); $r(F_{eq}\cdots F_{eq}) = 2.950$ (8), 2.947 (12); $r(F_{ax}\cdots F_{ax}) = 3.463$ (14), 3.471 (17); $l(V\text{–}F_{eq}) = l(V\text{–}F_{ax}) = 0.051$ (3), 0.047 (2); $l(F_{eq}\cdots F_{ax}) = 0.093$ (5), 0.093 (5); $l(F_{eq}\cdots F_{eq}) = 0.114$ (10), 0.115 (10); $l(F_{ax}\cdots F_{ax}) = 0.068$ (14), 0.067 (14). Results also include the symmetrized quadratic force field used to calculate corrections for the effects of vibrational averaging.

Introduction

Two types of structures have been observed for inorganic pentafluoride molecules in the gas phase, tetragonal pyramidal (C_{4v} symmetry) and trigonal bipyramidal (D_{3h} symmetry). The halogen pentafluorides are of the first type and pentafluorides of atoms from groups 5A and 5B are of the second. From among the latter the structures of PF_5,[1] AsF_5,[2] VF_5,[3] NbF_5,[3a,4] and TaF_5[3a,4] have been measured by electron diffraction. Other structurally related measurements include NMR (for PF_5[5,6] and AsF_5[7]), infrared and Raman spectra (for

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