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Structural Characterization of *trans*-2,4-Dithio-2,4-dianilino-1,3-diphenyl-1,3,2,4-diazadiphosphetidine, $[(C_6H_5NH)P(S)NC_6H_5]_2$

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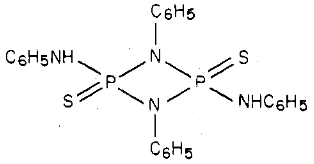
Reaction of β-$P_4S_3I_2$ with aniline results in formation of $[(C_6H_5NH)P(S)NC_6H_5]_2$, I, in moderate yield. The structure of I has been established by spectral data and a single-crystal X-ray analysis as *trans*-2,4-dithio-2,4-dianilino-1,3-diphenyl-1,3,2,4-diazadiphosphetidine. I forms monoclinic crystals in space group $P2_1/c$ with a = 15.287 (5) Å, b = 8.639 (2) Å, c = 18.728 (5) Å, β = 108.97 (2)°, Z = 4, d_{obsd} = 1.39 g cm^{-3}, d_{calcd} = 1.398 g cm^{-3} (20 °C, Mo Kα). The structure, solved by direct methods, refined to R_f = 0.062 and R_{wF} = 0.064 for 2127 independent observed reflections. The unit cell of I contains molecules of two slightly different conformational types, A and B, of C_i and approximate C_{2h} symmetries, respectively. The mean ring P—N, exocyclic P—N, and P=S distances are 1.688 (8), 1.670 (6), and 1.905 (4) Å, respectively. The mean ring P-N-P, ring N-P-N, and *exo*-S-P-N angles are 101.2 (3), 108.5 (4), and 102.3 (3)°, respectively. Comparison of $[(C_6H_5NH)P(S)NC_6H_5]_2$ from $(C_6H_5NH)_3PS$ thermolysis with I from the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction indicates that the two are identical. There is no evidence for cis isomeric product in either reaction system. From the reaction of α-$P_4S_3I_2$ with $C_6H_5NH_2$, traces of $[(C_6H_5NH)P(S)NC_6H_5]_2$ of a possibly different structural form than I are obtained.

Introduction

The reactions of aniline with α- or β-$P_4S_3I_2$ have been reported recently to yield compound(s) of formula $[(C_6H_5NH)P(S)NC_6H_5]_2$, in addition to a series of (phenylimido)- and sulfidotetraphosphorus ring and cage compounds.[2] The $[(C_6H_5NH)P(S)NC_6H_5]_2$ is a major recoverable product of the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction; however, it is present only as a trace product in the α-$P_4S_3I_2$–$C_6H_5NH_2$ system. Although spectral data indicated tentatively that the products are 2,4-dithio-1,3,2,4-diazadiphosphetidine(s)



in either or both of the cis and trans isomeric forms, structural characterization remained indefinite.

Single-crystal X-ray studies of dithiodiazadiphosphetidines of type $[RP(S)NR']_2$ ($R = C_6H_5$, $R' = CH_3$, C_2H_5, C_6H_5)[3-6] and correlation of their spectral data with cis and trans structural features have been reported.[6,7] Similar structural studies of the more interesting RNH-containing $[(RNH)P(S)NR]_2$ compounds have not appeared. Therefore, in order to establish unequivocally the structures of products from the β-$P_4S_3I_2$–aniline reactions and to establish structural bases for spectral correlation and for further syntheses, we carried out a single-crystal study of $[(C_6H_5NH)P(S)NC_6H_5]_2$ from the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction. In addition, a comparative study of this product with $[(C_6H_5NH)P(S)NC_6H_5]_2$ from $(C_6H_5NH)_3PS$ thermolysis,[8] which also has not been structurally characterized, has been effected.

Experimental Section

Apparatus and Materials. All inert-atmosphere manipulations were carried out in N_2-flushed glovebags and standard Schlenk-type glassware.[9] Infrared spectra (4000–400 cm^{-1}) were obtained by using Perkin-Elmer 337G and Beckman Model IR-12 spectrophotometers. High-resolution mass spectra were obtained by using an AEI MS-9 spectrometer at The Pennsylvania State University. Proton nuclear magnetic resonance spectra were collected at 90.0 Hz by using a Varian EM 390 spectrometer and at 100.0 MHz by using a JEOL-PFT 100 Fourier transform spectrometer. Both were equipped with standard variable-temperature probe accessories. Proton chemical shifts were measured relative to internal $(CH_3)_4Si$; chemical shifts downfield from the standard are given positive ($+\delta$) values. ^{31}P NMR spectra were obtained by using the JEOL-PFT 100 Fourier transform spectrometer equipped with standard 40.5-MHz probe accessories. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4. Chemical shifts downfield from the standard are given negative ($-\delta$) values. Spectral simulation and the calculation of spectral parameters for second-order spectra were accomplished by using a Nicolet 1080 Series NMR spectrum calculation program, NMRCAL NIC-801S-7117D, Nicolet Instrument Corp., Madison, Wis. Single-crystal X-ray data were collected at ambient temperature by using a Syntex $P\bar{1}$ automated diffractometer equipped with a graphite monochromator.

$(C_6H_5NH)_3PS$,[8] α-$P_4S_3I_2$,[10] and β-$P_4S_3I_2$[11,12] were prepared as reported earlier. Toluene was dried over $LiAlH_4$, CS_2 over P_4O_{10}, and $CHCl_3$ over P_4O_{10} before use. Ethanol (Mallinckrodt, absolute) was used as obtained.

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 spectra of samples prepared independently in our laboratories. Mass spectral data, in the sections below, refer to the major peak in the envelope in question.

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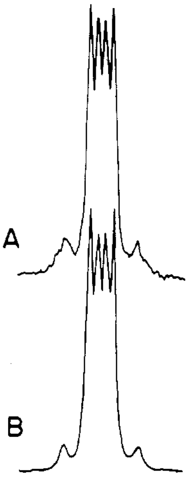

Figure 1. Observed (A) and simulated (B) ^{31}P NMR spectra of $[(C_6H_5NH)P(S)NC_6H_5]_2$, I.

$[(C_6H_5NH)P(S)NC_6H_5]_2$ (I) from β-$P_4S_3I_2$ and $C_6H_5NH_2$. To β-$P_4S_3I_2$ (3.8 g, 8.0 mmol) in 150 mL of benzene frozen to −30 °C, was added $C_6H_5NH_2$ (2.9 g, 32 mmol) under N_2. The reaction mixture was warmed slowly to room temperature with constant stirring. Rapid reaction and $C_6H_5NH_3I$ precipitation occurred as soon as the reaction mixture melted and neared room temperature. After 10 min, the reaction solution was reduced to one-half volume, $C_6H_5NH_3I$ was removed by filtration, and the benzene solution was evaporated to dryness in vacuo. Heating the residual solid in a horizontal sublimation tube at 130–150 °C removed P_4S_3 and β-P_4S_4.[2] Further heating to 200–220 °C resulted in sublimation of *trans*-$[(C_6H_5NH)P(S)NC_6H_5]_2$, I, as colorless crystals (mp 242–244 °C; typical yield 0.55–0.72 g). Anal. Calcd for $C_{24}H_{22}N_4P_2S_2$: C, 58.54; H, 4.5; N, 11.38; P, 12.58; S, 12.02; mol wt 492.0760. Found: C, 58.72; H, 4.51; N, 11.36; P, 12.49; S, 12.76; mol wt 492.0805. Recrystallization of I from ethanol resulted in a crystalline product which melts at 240–242 °C.

In several experiments, β-$P_4S_3I_2$ and $C_6H_5NH_2$ were allowed to react in benzene or toluene solvent at 25 °C. After $C_6H_5NH_3I$ formation appeared to be complete, the reaction mixture was refluxed under N_2 for periods ranging from 6 to 48 h. Periodically during the reaction, samples were withdrawn and subjected to ^{31}P NMR and mass spectral analysis. ^{31}P NMR analysis was accomplished, after filtration of $C_6H_5NH_3I$, by concentrating the reaction solution directly, or in some cases by evaporation of solvent and redissolution of the resulting solid in CS_2 solvent.

I from $(C_6H_5NH)_3PS$ Thermolysis. Under conditions described by Buck et al.,[8] I was prepared from the thermolysis at 220–225 °C of $(C_6H_5NH)_3PS$. Extraction with hot C_2H_5OH followed by repeated recrystallization from C_2H_5OH and drying in vacuo yielded product which melted at 235–237 °C (lit.[8] mp 235–237 °C). Sublimation of the crystalline material at 220 °C results in sample which melts at 236–242 °C.

Spectral Data for I. Infrared, ^1H and ^{31}P NMR, and mass spectra of I from $(C_6H_5NH)_3PS$ thermolysis or the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction, after sublimation or after recrystallization from C_2H_5OH, were obtained. Spectra of I obtained from either reaction or by either method of purification were essentially superimposable, except that traces of C_2H_5OH were seen in spectra of samples obtained from C_2H_5OH recrystallizations. The seven most intense mass spectral envelopes occur at *m/e* (relative intensity) 492 (63.8), 399 (100.0), 213 (42.7), 154 (27.4), 122 (79.5), 93 (79.5), and 77 (21.6). Infrared absorptions occur at (KBr pellet) 3330 (m), 3015 (w), 1592 (vs), 1490 (vs), 1376 (s), 1330 (m), 1263 (vs), 1230 (m), 1105 (w), 1078 (s), 1033 (s), 1012 (w), 963 (vs), 937 (vs), 768 (sh), 754 (vs), 685 (vs), 588 (w), 516 (m), 482 (s), and 447 (s) cm^{-1}. The ^1H NMR spectrum exhibits a complex resonance at δ 7.13–7.58 (relative area 20, phenyl) and a complex six-line AA′XX′ multiplet[13] at δ 5.65 (relative area 2, NH). The ^{31}P NMR spectrum (Figure 1A) is a six-line AA′XX′ multiplet at δ −39.5, which from spectral simulation (Figure 1B) yields $^2J_{PH}$ = 15.4 Hz, $^2J_{PP}$ = 21.1 Hz, and $^4J_{PH}$ = 0.2 Hz.

$[(C_6H_5NH)P(S)NC_6H_5]_2$ (II) from α-$P_4S_3I_2$ and $C_6H_5NH_2$. Under conditions analogous to those used in β-$P_4S_3I_2$–$C_6H_5NH_2$ reactions, α-$P_4S_3I_2$ (2.9 g, 6.1 mmol) and $C_6H_5NH_2$ (2.2 g, 24.1 mmol) in benzene were allowed to react. The $C_6H_5NH_3I$ was removed and the reaction solution was evaporated to dryness in vacuo. The remaining reaction solids were heated in a sublimation tube at 90–100 °C to remove P_4S_3 and α-P_4S_4. Repeated sublimation of the remaining material at 190–200 °C yields traces (typically 5–20 mg) of microcrystalline solid of composition $[(C_6H_5NH)P(S)NC_6H_5]_2$, II (mp 224–226 °C). Molecular weight: calcd for $C_{24}H_{22}N_4P_2S_2$, 492.0760; found, 492.0807. The eight most intense mass spectral envelopes occur at *m/e* (relative intensity) 492 (50.0), 399 (34.8), 246 (28.0), 213 (100), 154 (23.6), 122 (23.6), 93 (32.0), and 77 (53.0). Infrared absorptions occur at (KBr pellet) 3330 (m), 3015 (w), 1928 (w), 1756 (w), 1592 (vs), 1490 (vs), 1450 (sh), 1376 (s), 1330 (m), 1263 (vs), 1220 (m), 1105 (w), 1078 (s), 1033 (s), 963 (vs), 937 (vs), 754 (vs), 685 (vs), 617 (w), 582 (w), 519 (s), 473 (m), and 455 (m) cm^{-1}. Samples large enough for adequate ^1H or ^{31}P NMR spectral analysis were not obtained. Crystals suitable for X-ray analysis could not be obtained.

Crystal Data for I. A crystal of I of dimensions 0.3 × 0.2 × 0.4 mm, obtained from the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction by sublimation, was mounted with epoxy resin. The complete X-ray diffraction analysis was done on this crystal. The cell parameters, determined by precession photography and refined by least-squares fit of the parameters to 15 reflections carefully centered on the diffractometer for the monoclinic crystal, are a = 15.287 (5) Å, b = 8.639 (2) Å, c = 18.728 (5) Å, and β = 108.97 (2)°. With V = 2339 (1) Å^3 and M_r = 492.544, assuming Z = 4, the calculated density is 1.398 g cm^{-3}, in good agreement with the measured density of 1.39 g cm^{-3}. The space group, $P2_1/c$, was determined from the systematic absences[14] observed in the preliminary precession photographs and during data collection. $F(000)$ is 1024. The absorption coefficient (Mo Kα) is 3.71 cm^{-1}.

In several cases, crystals of I from $(C_6H_5NH)_3PS$ thermolysis obtained by sublimation (mp 239–242 °C) or recrystallization from C_2H_5OH (mp 235–237 °C) or from the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction by recrystallization from C_2H_5OH (mp 240–242 °C) were examined. In every case, the crystals were found to be monoclinic, space group $P2_1/c$, with cell dimensions within experimental error equal to those of the crystal described above which was analyzed completely.

Intensity Measurements. The θ–2θ scanning technique as programmed by Syntex was used at room temperature for the data collection. The scan rate was 2.0°/min with scan ranges calculated to start 1.0° below 2θ for Mo Kα (λ 0.709 26 Å) and end 1.0° above 2θ for Mo Kα_2 (λ 0.713 54 Å). Background measurements, collected using the stationary-crystal, stationary-counter technique, were made at the beginning and end of each scan for total period equal to the scan time. The sphere of reflection was surveyed within a single quadrant such that $2.0° \leq 2\theta < 50.0°$. The data set, monitored every 100 measurement cycles, showed a decline of approximately 10% over the course of the experiment. Data were corrected for this decline and for Lorentz and polarization effects.[15] No corrections were made for absorption, the maximum error based on the crystal dimensions being less than 4% in F_o. Of the 4513 independent reflections measured, 2127 were determined to have intensity significantly above background[16] and were used in the refinement.

Solution and Refinement of the Structure. The structure was solved by direct methods using the program MULTAN.[17] The solution with the highest figure of merit, 1.290, and the lowest Karle residual, 14.2, gave phases for all 250 reflections with $E \geq 1.85$. An E map based on this solution revealed clearly the positions of the phosphorus, sulfur, and ring nitrogen atoms. The remaining atoms were located by normal Fourier methods. By use of full-matrix least-squares procedures, the model was refined by assuming isotropic thermal parameters to conventional unweighted and weighted residuals[18] of R = 0.090 and R_w = 0.098. With the assumption of anisotropic thermal parameters, for phosphorus, sulfur, and nitrogen atoms only, further refinement converged with R = 0.078 and R_w = 0.087. The positions of all hydrogen atoms were determined from a three-dimensional difference map. Further refinement with the hydrogen atoms included with fixed isotropic thermal parameters converged with R = 0.062 and R_w = 0.064. The standard deviation of an observation of unit weight was 1.63. The ratio of observation to parameters was 9:1. The maximum shift over error on the last cycle was 0.11 for the z coordinate of $H(1C5)_A$. For nonhydrogen atoms the highest value was 0.04. A final difference map was featureless except for some signs of anisotropic vibration in the vicinity of carbon atoms. Final positional and thermal parameters and their errors are listed in Tables I and II. The scattering factors used are contained in ref 19. The weighting scheme was based on counting statistics such that the weight was w =

Table I. Atomic Positional and Thermal Parameters for $[(C_6H_5NH)P(S)NC_6H_5]_2$, I

	molecule A				molecule B			
atom	x^a	y	z	B,^{b} Å^2	x	y	z	B, Å^2
S(1)	−0.18603 (12)	0.43195 (24)	0.39709 (10)	3.71	−0.36941 (13)	0.23129 (23)	−0.01731 (11)	3.88
P(1)	−0.06093 (11)	0.40536 (20)	0.46053 (9)	2.32	−0.41769 (12)	0.04391 (21)	0.00818 (9)	2.47
N(1)	0.0259 (3)	0.5173 (6)	0.4513 (3)	2.6	−0.4935 (3)	0.0456 (6)	0.0572 (3)	2.5
N(2)	−0.0289 (4)	0.2253 (6)	0.4639 (3)	2.9	−0.3309 (4)	−0.0740 (7)	0.0473 (3)	3.0
C(1)	0.0526 (4)	0.5519 (8)	0.3877 (3)	2.4 (1)	−0.4860 (4)	0.1104 (8)	0.1289 (4)	2.7 (1)
C(2)	0.0102 (5)	0.4802 (9)	0.3197 (4)	3.4 (2)	−0.5640 (6)	0.1619 (10)	0.1413 (5)	4.6 (2)
C(3)	0.0383 (5)	0.5200 (9)	0.2575 (4)	4.1 (2)	−0.5554 (6)	0.2260 (12)	0.2139 (6)	6.0 (2)
C(4)	0.1061 (5)	0.6251 (9)	0.2637 (5)	4.1 (2)	−0.4716 (6)	0.2376 (11)	0.2668 (5)	5.3 (2)
C(5)	0.1480 (5)	0.6952 (9)	0.3315 (4)	3.9 (2)	−0.3951 (6)	0.1860 (10)	0.2537 (5)	4.4 (2)
C(6)	0.1230 (5)	0.6595 (8)	0.3951 (4)	3.0 (1)	−0.4009 (5)	0.1193 (9)	0.1841 (4)	3.7 (2)
C(7)	0.0627 (4)	0.1664 (7)	0.5046 (4)	2.5 (1)	−0.3259 (5)	−0.2066 (8)	0.0934 (4)	3.1 (1)
C(8)	0.1160 (5)	0.1176 (9)	0.4588 (4)	3.5 (2)	−0.3918 (5)	−0.3198 (9)	0.0755 (4)	3.8 (2)
C(9)	0.2028 (6)	0.0569 (10)	0.4936 (4)	4.2 (2)	−0.3831 (6)	−0.4492 (10)	0.1237 (5)	4.8 (2)
C(10)	0.2381 (5)	0.0480 (9)	0.5710 (4)	4.1 (2)	−0.3065 (6)	−0.4637 (11)	0.1863 (5)	4.8 (2)
C(11)	0.1854 (5)	0.0954 (10)	0.6142 (5)	4.3 (2)	−0.2399 (6)	−0.3544 (10)	0.2027 (5)	4.5 (2)
C(12)	0.0973 (5)	0.1567 (9)	0.5785 (4)	3.5 (2)	−0.2480 (5)	−0.2250 (9)	0.1564 (4)	3.8 (2)
H(1N2)	−0.070 (5)	0.157 (9)	0.443 (4)	3.0	−0.281 (5)	−0.034 (9)	0.049 (4)	2.9
H(1C2)	−0.035 (5)	0.411 (9)	0.318 (4)	3.5	−0.624 (6)	0.163 (9)	0.104 (5)	4.6
H(1C3)	0.004 (5)	0.459 (9)	0.207 (4)	4.2	−0.605 (6)	0.256 (11)	0.204 (5)	5.8
H(1C4)	0.123 (5)	0.659 (9)	0.218 (4)	4.2	−0.469 (5)	0.274 (10)	0.321 (5)	5.3
H(1C5)	0.189 (5)	0.768 (9)	0.344 (4)	3.9	−0.331 (6)	0.180 (9)	0.285 (5)	4.7
H(1C6)	0.160 (5)	0.710 (8)	0.446 (4)	3.0	−0.349 (5)	0.082 (9)	0.177 (4)	3.7
H(1C8)	0.089 (5)	0.123 (9)	0.405 (4)	3.5	−0.440 (5)	−0.321 (9)	0.032 (4)	3.8
H(1C9)	0.229 (5)	0.031 (10)	0.466 (4)	4.1	−0.433 (6)	−0.509 (10)	0.107 (4)	4.8
H(1C10)	0.302 (5)	0.014 (9)	0.597 (4)	4.2	−0.299 (5)	−0.562 (10)	0.226 (4)	4.7
H(1C11)	0.205 (5)	0.104 (9)	0.668 (5)	4.1	−0.180 (6)	−0.362 (9)	0.251 (5)	4.5
H(1C12)	0.061 (5)	0.178 (9)	0.605 (4)	3.4	−0.201 (5)	−0.160 (9)	0.162 (4)	3.7

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] Isotropic thermal parameters for the hydrogen atoms were set equal to the isotropic thermal parameter of the atom to which they are attached. "Equivalent isotropic" thermal parameters are given for the atoms refined anisotropically.

Table II. Anisotropic Thermal Parameters (Å^2) and Root-Mean-Square Amplitudes of Vibration (Å) for $[(C_6H_5NH)P(S)NC_6H_5]_2$, I

atom	$B_{11}{}^a$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^b$		
				Molecule A					
S(1)	2.91 (8)	4.30 (11)	3.93 (9)	−0.31 (8)	0.14 (7)	0.54 (8)	0.171 (3)	0.219 (3)	0.261 (3)
P(1)	2.32 (7)	2.31 (8)	2.35 (7)	−0.26 (7)	0.63 (6)	0.20 (7)	0.160 (3)	0.169 (3)	0.190 (3)
N(1)	2.5 (2)	2.3 (2)	2.1 (2)	−0.2 (2)	1.0 (2)	−0.1 (2)	0.152 (9)	0.167 (9)	0.185 (8)
N(2)	3.0 (3)	2.3 (3)	3.3 (3)	−0.6 (2)	0.4 (2)	−0.3 (2)	0.152 (11)	0.199 (9)	0.227 (9)
				Molecule B					
S(1)	3.41 (9)	3.68 (10)	4.54 (10)	−0.53 (8)	1.11 (8)	0.90 (8)	0.184 (3)	0.215 (3)	0.263 (3)
P(1)	2.40 (7)	2.66 (9)	2.36 (8)	−0.25 (7)	0.61 (6)	0.13 (7)	0.168 (3)	0.172 (3)	0.194 (3)
N(1)	2.3 (2)	3.2 (3)	2.1 (2)	−0.6 (2)	0.5 (2)	−0.3 (2)	0.154 (9)	0.175 (9)	0.210 (9)
N(2B)	2.4 (2)	3.2 (3)	3.4 (3)	−0.1 (2)	0.6 (2)	0.5 (2)	0.173 (9)	0.188 (10)	0.227 (9)

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter. They enter into the expression for the structure factor in the form $\exp[-{}^1/_4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. Relative orientations can be seen in the figures.

$1.0/\sigma^2(F_o) = 4.0F_o{}^2/\sigma^2(F_o{}^2)$. All programs used were contained in or derived from the Northwestern University Crystallographic Computing Library of Dr. J. A. Ibers. The data reduction program, based in part on routines supplied by Syntex and Dr. Ibers, was written in this laboratory.

Results and Discussion

Single-crystal X-ray analysis of crystalline samples of $[(C_6H_5NH)P(S)NC_6H_5]_2$, I, obtained from $(C_6H_5NH)_3PS$ thermolysis or the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction, indicates that the products obtained from the two different sources are structurally identical. The unit cell of I contains four molecules of two types (molecules A and B) which have different orientations and are not mutually related by symmetry. Molecules IA and IB are located on centers of inversion symmetry at $(-{}^1/_2, 0, 0)$ and $(0, {}^1/_2, {}^1/_2)$. Owing to this inversion symmetry, only half of each molecule is crystallographically independent.

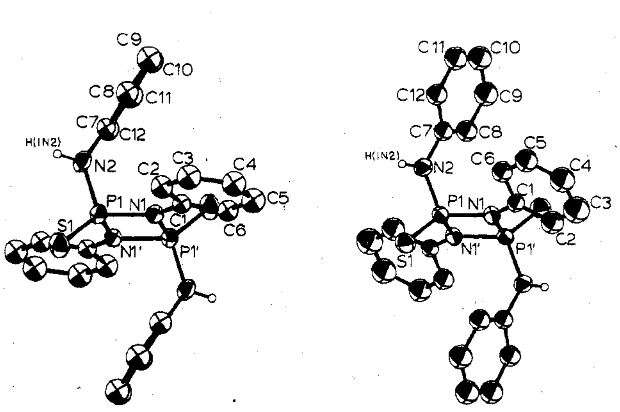

Figure 2. Structure of the A and B molecules of $[(C_6H_5NH)P(S)NC_6H_5]_2$, I (ORTEP diagram; 70% probability).

The structure of I (molecules A and B) shown in Figure 2 consists of a planar four-membered P_2N_2 1,3,2,4-diazadiphosphetidine ring. Phenyl rings are attached at nitrogen atoms N(1) and N(1)′. Anilino and sulfido moieties are attached at phosphorus atoms P(1) and P(1)′ above and below

Table III. Intramolecular Distances and Angles in $[(C_6H_5NH)P(S)NC_6H_5]_2$

	molecule A	molecule B		molecule A	molecule B
		(a) Bond Lengths, Å			
P(1)-S(1)	1.912 (2)	1.905 (3)	C(3)-C(4)	1.356 (10)	1.345 (11)
P(1)-N(1)	1.698 (5)	1.699 (5)	C(4)-C(5)	1.366 (10)	1.348 (10)
P(1)-N(1)′[a]	1.701 (5)	1.693 (5)	C(5)-C(6)	1.400 (9)	1.404 (10)
P(1)-N(2)	1.627 (6)	1.646 (6)	C(7)-C(8)	1.384 (9)	1.367 (9)
N(1)-C(1)	1.414 (7)	1.427 (7)	C(7)-C(12)	1.368 (9)	1.388 (9)
N(2)-C(7)	1.442 (8)	1.422 (8)	C(8)-C(9)	1.380 (10)	1.416 (11)
C(1)-C(2)	1.376 (9)	1.365 (9)	C(9)-C(10)	1.376 (10)	1.369 (11)
C(1)-C(6)	1.396 (9)	1.378 (9)	C(10)-C(11)	1.380 (10)	1.351 (11)
C(2)-C(3)	1.411 (10)	1.436 (12)	C(11)-C(12)	1.399 (10)	1.397 (10)
		(b) Bond Angles, Deg			
S(1)-P(1)-N(1)	121.8 (2)	121.2 (2)	C(1)-C(2)-C(3)	118.5 (7)	118.1 (8)
S(1)-P(1)-N(1)′	119.5 (2)	119.5 (2)	C(2)-C(3)-C(4)	121.6 (8)	120.0 (9)
S(1)-P(1)-N(2)	111.6 (2)	108.4 (2)	C(3)-C(4)-C(5)	119.5 (8)	121.2 (9)
N(1)-P(1)-N(1)′	82.3 (2)	82.3 (3)	C(4)-C(5)-C(6)	121.3 (7)	120.7 (8)
N(1)-P(1)-N(2)	108.2 (3)	111.0 (3)	C(5)-C(6)-C(1)	118.6 (7)	118.7 (7)
N(1)′-P(1)-N(2)	110.0 (3)	112.4 (3)	N(2)-C(7)-C(8)	119.1 (6)	122.6 (6)
P(1)-N(1)-P(1)′	97.7 (2)	97.7 (2)	N(2)-C(7)-C(12)	121.3 (6)	118.1 (6)
P(1)-N(1)-C(1)	131.2 (4)	130.8 (4)	C(8)-C(7)-C(12)	119.6 (6)	119.2 (7)
P(1)′-N(1)-C(1)	130.6 (4)	131.5 (4)	C(7)-C(8)-C(9)	120.0 (7)	120.0 (7)
P(1)-N(2)-C(7)	126.2 (4)	130.3 (5)	C(8)-C(9)-C(10)	120.6 (7)	119.8 (8)
N(1)-C(1)-C(2)	120.5 (6)	118.8 (6)	C(9)-C(10)-C(11)	119.9 (8)	120.2 (9)
N(1)-C(1)-C(6)	118.9 (5)	119.8 (6)	C(10)-C(11)-C(12)	119.3 (8)	120.7 (8)
C(2)-C(1)-C(6)	120.5 (6)	121.4 (7)	C(11)-C(12)-C(7)	120.6 (7)	119.9 (7)

[a] Prime marks indicate atoms related by an inversion center of symmetry in this and succeeding tables.

the P_2N_2 ring in a trans configuration. In both IA and IB, the anilino groups are in a conformation such that one anilino phenyl ring is folded back approximately over and one anilino phenyl ring is folded under the P_2N_2 ring. Molecules IA and IB differ mainly with respect to the orientation of the phenyl ring of the anilino moieties and the phenyl groups on the P_2N_2 rings. The approximate molecular symmetries of IA and IB conform to symmetry point groups C_{2h} (approximate) and C_i, respectively.

The structural and bonding parameters for IA and IB are given in Tables III–V. Small differences between IA and IB in interatomic distances are seen, but they appear to be too small to be chemically significant. The mean distances and angles agree favorably, insofar as they can be compared, with those obtained for *trans*-2,4-dithio-1,3,2,4-diazadiphosphetidines of type $[RP(S)NR']_2$ ($R = C_6H_5$, $R' = CH_3$, C_2H_5, C_6H_5).[4-7] The mean P(1)–N(1), P(1)–N(1)′, and P(1)–S(1) distances of 1.698 (5), 1.697 (5), and 1.908 (3) Å, are consistent with the previously observed values of 1.680–1.696, 1.690–1.695, and 1.910–1.938 Å, respectively. The angles P(1)–N(1)–P(1)′ and N(1)–P(1)–N(1)′ of 97.7 (2) and 82.3 (2)° agree well (literature ranges 96.8–98.1 and 81.9–83.7°) as do the nonbonded intramolecular P(1)–P(1)′ and N(1)–N(1)′ distances of 2.556 (4) and 2.234 (10) Å (literature ranges 2.550–2.580 and 2.330–2.360 Å). The mean P(1)–N(2) distance of 1.635 (2) Å and the P–N ring distances are considerably shorter than the normal P–N single-bond distance of 1.76 Å.[20] This bond shortening may suggest the existence of $\pi_{p\text{-}d}$ bonding in the ring and external P–N bonds.[4]

An interesting structural feature of IA and IB is the apparent tendencies of the phenyl rings which are bonded to the P_2N_2 rings to approach coplanarity with the P_2N_2 ring (Table IV). In IA, the plane of the phenyl rings (plane 4) is twisted by only 6.0° from the P_2N_2 plane (plane 1). In IB the interplane dihedral angle is 28.5°. These angles are somewhat larger than those of 5.8 and 9.7° observed for the A and B type molecules of $[C_6H_5P(S)NC_6H_5]_2$, reported previously,[3] but suggest that as in the latter system there may be a tendency toward π-electron delocalization between the phenyl and P_2N_2 ring system. The packing arrangement which exists between A and B type molecules in the unit cell (Figure 3) results in short intramolecular contact distances (3.52 and 3.67 Å) between C(7) and C(12) of a B molecule and C(8) and C(9) of an A molecule compared to other intermolecular carbon–carbon distances in the system (Table V). These contacts may provide an explanation for the larger torsional angle (28.5°) observed between planes 1 and 4 in molecule B than in molecule A.

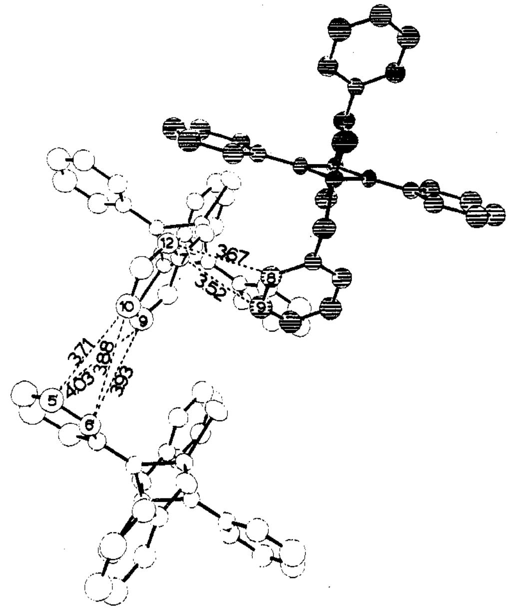

Figure 3. View of molecule B–molecule B and molecule A–molecule B intermolecular interactions in a unit cell of $[(C_6H_5NH)P(S)NC_6H_5]_2$, I. Open spheres represent molecules B; shaded spheres represent molecule A.

Atoms C(7), P(1), N(2), and H(1N2) form a plane (plane 3) in IA and are close to planar in IB, indicating that trigonal-planar coordination occurs at N(2). Clearly, there is an apparent tendency toward sp^2 hybridization at N(2). Further examination of the structures of other *trans*-$[R_2NP(S)NR']_2$ type diazaphosphetidines seems warranted in order to test the generality of this structural phenomenon.

The conformation of groups around the P(1)–N(2) bond seems surprising, since it results in the near-eclipsing of the

Table IV

Least-Squares Planes and Deviations (Å) of Atoms from Planes

	molecule A				molecule B			
plane	atom	dev	atom	dev	atom	dev	atom	dev
1	$8.683x - 6.546y + 2.293z = -2.127$[a]				$3.522x - 7.666y + 5.715z = -1.761$			
	P(1)*	0.000 (2)[b]	S(1)	−1.406	P(1)*	0.000 (2)	S(1)	−1.412
	P(1)′*	0.000 (2)	N(2)	1.465	P(1)*	0.000 (2)	N(2)	1.433
	N(1)*	0.000 (5)	C(1)	−0.141	N(1)*	0.000 (5)	C(1)	−0.061
	N(1)′*	0.000 (5)			N(1)*	0.000 (5)		
2	$9.199x + 1.307y - 17.59z = -8.173$				$-3.422x + 3.238y + 17.33z = 1.713$			
	P(1)*	0.000 (2)			P(1)*	0.000 (2)		
	S(1)*	0.000 (2)			S(1)*	0.000 (2)		
	N(2)*	0.000 (6)			N(2)*	0.000 (6)		
3	$8.152x + 1.110y - 18.09z = -8.378$				$0.2308x + 4.980y + 14.41z = 0.2400$			
	P(1)*	0.000 (2)	S(1)	0.158	P(1)*	0.000 (2)	S(1)	0.577
	C(7)*	−0.000 (6)	N(1)	1.000	C(7)*	0.001 (7)	N(1)	0.697
	N(2)*	−0.000 (6)	N(1)′	1.224	N(2)*	−0.003 (6)	N(1)′	−1.407
	H(1N2)*	−0.03 (8)			H(1N2)*	0.22 (8)		
4	$9.720x - 6.328y + 0.5205z = -2.782$				$3.947x + 7.830y - 7.551z = -2.026$			
	N(1)*	−0.005 (5)	P(1)	−0.136	N(1)*	0.003 (5)	P(1)	0.659
	C(1)*	0.003 (6)	H(1C2)	0.01	C(1)*	−0.001 (7)	H(1C2)	0.06
	C(2)*	0.009 (7)	H(1C3)	0.03	C(2)*	0.000 (9)	H(1C3)	0.10
	C(3)*	−0.003 (8)	H(1C4)	−0.08	C(3)*	−0.012 (10)	H(1C4)	−0.10
	C(4)*	−0.006 (8)	H(1C5)	−0.06	C(4)*	0.010 (10)	H(1C5)	−0.02
	C(5)*	−0.006 (8)	H(1C6)	0.07	C(5)*	0.007 (9)	H(1C6)	−0.05
	C(6)*	0.010 (7)			C(6)*	−0.012 (8)		
5	$5.980x + 7.952y - 1.66z = 0.8546$				$10.47x - 4.236y - 13.76z = -3.805$			
	N(2)*	−0.008 (6)	P(1)	1.237	N(2)*	0.002 (6)	P(1)	−0.868
	C(7)*	0.008 (6)	H(1N2)	−0.76	C(7)*	0.018 (8)	H(1N2)	0.33
	C(8)*	0.010 (7)	H(1C8)	−0.02	C(8)*	0.017 (9)	H(1C8)	0.12
	C(9)*	−0.011 (8)	H(1C9)	−0.02	C(9)*	−0.006 (9)	H(1C9)	−0.05
	C(10)*	0.000 (8)	H(1C10)	0.07	C(10)*	−0.005 (8)	H(1C10)	−0.06
	C(11)*	−0.010 (8)	H(1C11)	0.09	C(11)*	0.005 (8)	H(1C11)	−0.01
	C(12)*	0.010 (8)	H(1C12)	−0.08	C(12)*	0.009 (8)	H(1C12)	0.14

Dihedral Angles between Planes

	angle, deg			angle, deg			angle, deg	
planes	A	B	planes	A	B	planes	A	B
1-2	91.6	91.3	2-3	5.1	18.6	3-4	87.9	75.5
1-3	93.8	100.3	2-4	85.6	91.3	3-5	73.0	135.5
1-4	6.0	28.5	2-5	70.0	145.4	4-5	114.5	94.9
1-5	117.5	68.0						

[a] The planes are calculated according to W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961). 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.

Table V. Selected Intra- and Intermolecular Contacts (Å)

(a) Intramolecular Contacts

	molecule A	molecule B
P(1)-P(1)′	2.560 (3)	2.553 (4)
N(1)-N(1)′	2.237 (9)	2.232 (10)
S(1)-H(1N2)	2.92 (8)	2.74 (8)

(b) Intermolecular Contacts

$C(7)_B$[a]$-C(9)_A$	$-x, -0.5 + y, 0.5 - z$	3.52 (1)
$C(10)_B-C(5)_B$	$x, -1.0 + y, z$	3.71 (1)
$C(12)_B-C(8)_A$	$-x, -0.5 + y, 0.5 - z$	3.67 (1)
$S(1)_A-H(1C10)_B$	$x, 1.0 + y, z$	3.12 (8)
$S(1)_B-H(1C4)_B$	$x, 0.5 - y, -0.5 + z$	2.92 (9)

[a] Subscripts A and B refer to molecules A and B in the unit cell.

P(1)–S(1) and N(2)–H(1N2) bonds. The dihedral angles between the P(1), C(7), N(2), and H(1N2) plane (plane 3) and the P(1), S(1), and N(2) plane (plane 2) are 5.1 and 18.6° for A and B, respectively. It is interesting to speculate that this conformational preference is the result of intramolecular forces other than those of the crystal-packing type. The mean S(1)–H(1N2) distance of 2.78 (8) Å is shorter than the 3.05 Å minimum van der Waals distance,[21] which may indicate the existence of weak hydrogen bonding between the anilino hydrogen and sulfur atoms in the molecule.

Our studies indicate that crystalline I, from either the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction or the $(C_6H_5NH)_3PS$ thermolysis, obtained either by sublimation or ethanol recrystallization, are structurally identical. Although there is variation in melting points between samples from different sources, this appears not to indicate the presence of isomeric compounds. The infrared, ^1H and ^{31}P NMR, and mass spectral data of sublimed and recrystallized material are also essentially superimposable, with the exception that traces of ethanol can be detected in samples of I obtained by recrystallization from ethanol. The ^{31}P NMR spectrum upon ^1H decoupling collapses to a singlet peak. Likewise, only one NH resonance is seen in the ^1H NMR spectrum. Within the limits of detection, only one isomer seems present in solution. Further, since the $[(C_6H_5NH)P(S)NC_6H_5]_2$ samples obtained from the sulfurization of $[(C_6H_5NH)PNC_6H_5]_2$[22] or the $C_6H_5NH_2$–$P(S)Cl_3$ reaction,[23] after recrystallization from ethanol, both melt at 235–237 °C, it seems reasonable to suggest that the product from these sources is also the trans isomer.

Very low yields of a $[(C_6H_5NH)P(S)NC_6H_5]_2$, II, which may be a different isomer from I, are obtained from the thermolysis products of the α-$P_4S_3I_2$–$C_6H_5NH_2$ reaction. Because the compound appears less stable than I and only low yields were obtained, adequate crystals for X-ray analysis or sufficiently large samples for NMR spectral analysis were not obtained.

The formation of I in the β-$P_4S_3I_2$–aniline reaction represents a novel source of it. I undoubtedly forms as a result of a complex series of reactions. However, by examination of ^{31}P NMR and mass spectra of samples collected from β-$P_4S_3I_2$–$C_6H_5NH_2$ reactions in toluene solvent, which were carried out for varying time and temperature conditions, some information about the sequence of events that occurs can be obtained. β-$P_4S_3I_2$ and $C_6H_5NH_2$ react immediately upon combination, below room temperature. Precipitation of $C_6H_5NH_3I$ occurs, and P_4S_3 forms along with a complex mixture of (phenylamino)- and/or (phenylimido)phosphorus sulfide materials. After the reaction mixture was heated at 80–90 °C for 3–4 h, small quantities of what can be characterized tentatively in the mixture as $(C_6H_5NH)_3PS$, along with traces of I and β-P_4S_4, are evident. Further heating results in increased formation of I and traces of P_4S_5. Attempts to identify other materials have so far been unsuccessful. However, studies of the reaction products and the mechanism of formation of I are being pursued, currently.

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Registry No. I, 70160-66-6; II, 55935-79-0; β-$P_4S_3I_2$, 34330-76-2; $C_6H_5NH_2$, 62-53-3; α-$P_4S_3I_2$, 19257-89-7; $(C_6H_5NH)_3PS$, 4743-38-8.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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

(16) A reflection was taken as significant when $F_o^2 > 3.0\sigma(F_o^2)$. $\sigma(F_o^2) = \mathrm{RLP}\{\mathrm{TSC} + \mathrm{BACK} + [P(\mathrm{TSC} - \mathrm{BACK})]^2\}^{1/2}$, 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, a damping factor, was given a value of 0.04 [W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957); P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967)].

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Synthesis and Structure of Diiododicarbonyltris(*tert*-butyl isocyanide)tungsten(II), an Example of the 4:3 Piano Stool Seven-Coordinate Geometry[1]

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The synthesis of diiododicarbonyltris(*tert*-butyl isocyanide)tungsten(II) from $(t\text{-}C_4H_9NC)_3W(CO)_3$ and elemental iodine is described. The compound crystallizes in polymorphic forms, depending upon the choice of solvent. The structure of an orthorhombic modification, space group *Pbca*, was revealed in a single-crystal X-ray diffraction study. The crystal parameters are $a = 18.297$ (5) Å, $b = 20.632$ (6) Å, and $c = 13.550$ (4) Å. With eight molecules per unit cell the calculated density is 1.930 g/cm^3, comparable to the observed value of 1.92 (3) g/cm^3. The structure was solved and refined on F to a final value of 0.045 for the discrepancy index R_1 by using 2832 unique observed reflections. The tungsten atom is coordinated to two iodine atoms with W–I bond lengths of 2.863 (1) and 2.865 (1) Å, two carbonyl groups, W–C = 1.997 (13) and 1.959 (15) Å, and three isocyanide ligands, W–C = 2.093 (13), 2.100 (13), and 2.145 (13) Å. A detailed analysis of the geometry reveals the coordination polyhedron of the tungsten to be that of a 4:3 square base–trigonal cap piano stool. Criteria for choosing this structure are discussed.

Introduction

The geometries of most seven-coordinate complexes can be described in terms of one of three idealized structures, the 1:5:1 D_{5h} pentagonal bipyramid, the 1:4:2 C_{2v} capped trigonal prism, and the 1:3:3 C_{3v} capped octahedron.[3-9] It was therefore unexpected when the structure of $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$, prepared in the course of studies of the chemistry of higher coordinate isocyanide complexes,[2] could not clearly be assigned

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