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Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80302

Syntheses of New Phenylimido– and Sulfido–Tetraphosphorus Ring and Cage Compounds

CHUNG-CHENG CHANG,[1a] R. CURTIS HALTIWANGER, and ARLAN D. NORMAN*[1b]

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Two new tetraphosphorus cage compounds, α-$P_4S_3(NC_6H_5)$ and α-P_4S_4, have been obtained from the reaction of α-$P_4S_3I_2$ with aniline ($C_6H_5NH_2$). Infrared, ^1H NMR, and mass spectral evidence for the presence of $P_4S_3(NHC_6H_5)_2$ as a reaction intermediate has been obtained. On the basis of spectral data and chemical arguments, α-$P_4S_3(NC_6H_5)$ is assigned tentatively a cage structure in which the sulfur atoms maintain the sulfur atom arrangement and the phenylimido moiety (C_6H_5N) occupies what was the opened edge of α-$P_4S_3I_2$. The α-P_4S_4 structure has been established by a single-crystal x-ray study. Crystals of α-P_4S_4 are monoclinic (space group $C2/c$), with $a = 9.779$ (1) Å, $b = 9.055$ (1) Å, $c = 8.759$ (2) Å, $\beta = 102.65°$, $Z = 4$, $d_{calcd} = 2.213$ g cm^{-3}, and $d_{obsd} = 2.26$ g cm^{-3} (20 °C, Mo Kα). The crystal structure was solved by direct methods. The P_4S_4 model refined to $R_1 = 0.038$ and $R_2 = 0.048$ for 1680 independent observed reflections. Alternate refinement of an S_4P_4 model (atom positions reversed) and application of the Hamilton R-factor test, along with geometrical arguments, allow the S_4P_4 model to be rejected. α-P_4S_4 has approximate D_{2d} symmetry, a structure in which P atoms are pseudotetrahedral and S atoms are in a square plane. The mean P–S and P–P bond distances are 2.111 Å and 2.353 Å, respectively. The three cage bond angles are P–S–P = 98.92°, S–P–S = 95.18°, and S–P–P = 100.42°. Reaction of β-$P_4S_3I_2$ with $C_6H_5NH_2$ yields a diazadiphosphetidine [$P_2S_2(NC_6H_5)_2(NHC_6H_5)_2$], P_4S_3, and β-P_4S_4. Spectral data are presented which support β-P_4S_4 being the second of two possible isomers of an edge-substituted tetraphosphorus–tetrasulfide system. A new type of phosphorus–nitrogen ring compound, $P_4(NHC_6H_5)_4(NC_6H_5)_2$, a 1,4,2,3,5,6-diazatetraphosphorine, has been identified tentatively from the reaction of P_2I_4 with $C_6H_5NH_2$.

Introduction

Tetraphosphorus compounds of formula $P_4E_{0-6}A_{0-4}$, where E and A represent moieties in divalent edge or apical bonding positions on a P_4 tetrahedron (or distorted tetrahedron), comprise a general type of phosphorus cage system. In these, the P_4E_{0-6} unit constitutes a closo-type molecular cage and the A moieties can be regarded as cage substituents (Figure 1).[2] Well-characterized, selected examples of such compounds (classes in parentheses) are P_4S_3[3,4] (P_4E_3); $P_4S_3Mo(CO)_5$[5] (P_4E_3A); P_4S_5[6] (P_4E_4A); P_4S_7[7] ($P_4E_5A_2$); P_4O_6,[8] $P_4(NCH_3)_6$,[9] and $P_4[Ge(CH_3)_2]_6$[10] (P_4E_6); and $P_4O_6Ni(CO)_3$[11] (P_4E_6A). Noteworthy is the fact that all known cages, except perhaps that of the $P_4S_9N^-$ ion,[12] are homo edge-substituted, i.e., contain only one type of E substituent.

Recently, we have undertaken a study of syntheses of hetero edge-substituted $P_4E_xE'_{6-x}$ ($E \neq E'$) and new incompletely edge-substituted (P_4E_{1-5}) cage systems in order to extend our understanding of P_4-cage relative thermodynamic stabilities and chemical reactivities. Routes to phenylimido (>NC_6H_5) and sulfido (–S–) substituted P_4 cages, from reactions of α-$P_4S_3I_2$ (**1**),[13,14] β-$P_4S_3I_2$ (**2**),[15] and P_2I_4 with aniline have been examined. From these reactions, three new tetraphosphorus cage compounds, α-P_4S_4, α-$P_4S_3(NC_6H_5)$, and β-P_4S_4, and a new cyclic phosphorus–nitrogen compound, $P_4(NHC_6H_5)_4(NC_6H_5)_2$, have been obtained. A preliminary account of the independent synthesis and characterization of α- and β-P_4S_4 has appeared very recently, also.[16] The results of our work are described below.

Experimental Section

Apparatus and Materials. All operations were carried out in N_2-flushed glovebags or in evacuated systems.[17] Infrared, ^1H NMR (60.0 MHz), and mass spectra were obtained using Perkin-Elmer 337G, Varian A-60A, and Varian MAT CH-5 spectrometers, respectively. High-resolution mass spectra were obtained using an AEI MS-9 spectrometer. Phosphorus-31 NMR spectra were obtained on JEOL-PFT 100 and Varian HA-100 spectrometers equipped with standard-probe and radio-frequency unit accessories. ^1H and ^{31}P NMR chemical shifts were measured relative to internal $(CH_3)_4Si$ and external H_3PO_4, respectively. Chemical shifts downfield from the standards are given negative values. ^{31}P NMR chemical shifts are given to ±1 ppm. Single-crystal x-ray data were collected at ambient temperature using a Syntex $P\bar{1}$ automated diffractometer.

Tetraphosphorus trisulfide (K and K Laboratories) and aniline (Mallinckrodt Chemical Works) were purified routinely. Carbon disulfide, benzene, and chloroform were distilled from P_4O_{10} prior

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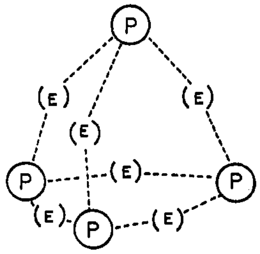


Figure 1. The fundamental P_4E_{0-6} cage system showing E moieties at cage edge positions. E substitution at a given edge results in P–E–P bond replacement of a P–P bond.

to use. Diphosphorus tetraiodide,[18] α-$P_4S_3I_2$,[14] and β-$P_4S_3I_2$[15] were prepared and purified as described previously. Purity of α- and β-$P_4S_3I_2$ samples was established by x-ray powder diffraction pattern data, in addition to melting point data.

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.

Reactions of α- and β-$P_4S_3I_2$ with Aniline. (A) α-$P_4S_3I_2$ (1). Typically, $C_6H_5NH_2$ (2.24 g, 24.1 mmol) was added to a frozen solution of α-$P_4S_3I_2$ (2.90 g, 6.1 mmol) in 100 mL of benzene at −78 °C under N_2. The reaction mixture, with occasional shaking, was warmed to 25 °C. White solid formed slowly as the solution turned yellow. After 3 h, the reaction mixture was filtered to remove solid. Extraction of the solid with water, followed by removal of water in vacuo, yielded $C_6H_5NH_3I$ (2.70 g, 12.2 mmol). The resulting yellow solution was worked up by two different methods, (i) and (ii), as described below.

(i) The solution was evaporated to dryness in vacuo. The resulting yellow solid was transferred to a 40-cm, gradient-heated sublimation tube. At 90–100 °C, P_4S_3, **3** (0.45 g, 2.0 mmol), sublimed from the solid. Repeated sublimation of the remaining solid at 190–200 °C yielded two additional low-volatility fractions, α-P_4S_4, **4**, and trace quantities of a white solid, **5**. The nonvolatile residue which remained in the sublimation tube was not analyzed further.

Compound **3** is a bright yellow solid. It shows infrared absorptions (KBr pellet) at 738 (w), 680 (w), 478 (m), 469 (m), 433 (s), and 417 (sh) cm^{-1}. The ^{31}P NMR (CS_2) and mass spectra of **3** agree closely with those of β-P_4S_3. No mass spectral envelopes occur above *m/e* 220. Compound **3** undergoes greater than 40% oxidation to oxyphosphorus sulfides during a 2-h exposure to ambient air. After several days in vacuo at 25 °C, the bright yellow **3** becomes pale yellow, characteristic of the known P_4S_3 isomer.[3,4]

Pure **4** was obtained by its repeated sublimation at 190–200 °C. Compound **4** is pale yellow and decomposes without clear melting at ca. 230 °C. Anal. Calcd for P_4S_4: P, 49.14; S, 50.86; mol wt 251.7832. Found: P, 49.22; S, 50.77; mol wt 251.7822. Infrared absorptions (KBr pellet) occur at 445 (s), 423 (vs), and 415 (m) cm^{-1}. The seven most intense mass spectral envelopes occur at *m/e* (relative intensity) 252 (57.6), 220 (22.4), 189 (44.4), 157 (18.4), 125 (27.5), 94 (12.0), and 63 (100.0). The ^{31}P NMR spectrum (CS_2) shows a singlet resonance at δ −201 ppm. Compound **4** shows no appreciable decomposition after 20 days at 25 °C. X-ray characterization data are given below.

Compound **5** appears moderately unreactive to ambient air. Anal. Calcd for $C_{24}H_{22}N_4P_2S_2$: mol wt 492.0760. Found: mol wt 492.0805. The eight most intense mass spectral envelopes occur at *m/e* (relative intensity) 492 (50.0), 400 (34.8), 246 (28.0), 213 (100.0), 154 (23.6), 122 (23.6), 93 (32.0), and 77 (53.0). Because yields of pure **5** were very low, attempts to characterize it further were judged not feasible.

(ii) The alternative workup to (i) consisted of evaporating the yellow reaction solution slowly to half volume, during which time precipitation of a mixture of **4** and α-$P_4S_3(NC_6H_5)$, **6**, occurred. The yellow solution contains only **4** and **6** (within our detection limits). Repeated precipitation of **6** from benzene solution, by slow evaporation of the benzene, yields nearly pure **6** (estimated at >95%). Compound **6** decomposes slowly above 50 °C. Owing to this thermal instability, attempts to obtain it completely free of **4** were unsuccessful.

Compound **6** shows a phenyl resonance at δ −7.17 ppm in the ^1H NMR spectrum. Infrared absorptions (KBr pellet) occur at 2990 (w), 1592 (vs), 1490 (vs), 1460 (sh), 1362 (s), 1270 (s), 1260 (sh), 1218 (m), 1068 (w), 1028 (m), 900 (s), 885 (sh), 757 (s), 750 (sh), 690 (s), 607 (w), 520 (w), 496 (m), 470 (s), 447 (m), and 425 (m) cm^{-1}. The six most intense mass spectral envelopes occur at *m/e* (relative intensity) 311 (26.9), 248 (27.8), 122 (100.0), 94 (61.1), 77 (55.6), and 63 (43.9). The low solubility of **6** in solvents with which it did not react precluded obtaining ^{31}P NMR spectral data.

Reactions of α-$P_4S_3I_2$ with $C_6H_5NH_2$ in benzene at 25 °C, but for reaction periods just long enough to allow complete precipitation of $C_6H_5NH_3I$ (20–30 min), were carried out under conditions as described above. Upon completion of reaction, $C_6H_5NH_2I$ was filtered and the reaction solution evaporated slowly to one-half to one-third volume. The resulting precipitate was a mixture of **6**, a thermally unstable species, **7**, and in some cases traces of **4**. Compound **7** was too unstable to be separated from **6** (or **6** and **4**); however, it exhibited a mass spectral parent envelope at *m/e* 404, a NH resonance at δ −0.10 ppm in the ^1H NMR spectrum, and an NH absorption at 3290 cm^{-1} in the infrared spectrum. These spectral features were clearly evident, in addition to those expected from **6**.

In several cases, reactions of α-$P_4S_3I_2$ and $C_6H_5NH_2$ were allowed to occur in carbon disulfide solvent. In each case, reaction products as obtained in benzene solvent were obtained, in addition to large amounts of $(C_6H_5NH)_2CS$. The presence of the latter product complicated product isolation and made further studies impractical.

(B) β-$P_4S_3I_2$ (2) Reactions. Typically, β-$P_4S_3I_2$ (3.79 g, 8.0 mmol) in 150 mL of benzene was allowed to react with $C_6H_5NH_2$ (2.9 g, 32 mmol) as in the α system, above. Rapid reaction, as evidenced by $C_6H_5NH_3I$ precipitation, occurred as soon as the reaction mixture melted, mixed, and warmed near room temperature. The $C_6H_5NH_3I$ (3.19 g, 14.5 mmol) was removed by filtration. The supernatant solution contained considerable P_4S_3 along with lesser quantities of other imido–sulfido–phosphorus products. Evaporation of solvent, followed by sublimation of the resulting yellow solid at 90–100 °C in a gradient-heated tube, removed P_4S_3 (1.36 g, 6.2 mmol). Further heating to 150–160 °C and finally 200–210 °C yielded fractions containing mainly β-P_4S_4, **8**, and $P_2S_2(NC_6H_5)_2(NHC_6H_5)_2$, **9**, respectively.

Repeated attempts to obtain pure **8** were unsuccessful, due to its slow decomposition in solution and upon sublimation. Repeated sublimation of the β-P_4S_4 fraction resulted, in each case, in samples of **8** (0.08 g, 0.3 mmol) contaminated with small quantities (estimated at ca. 10% α-P_4S_4, P_4S_3, and P_4S_5). Higher purity samples of **8** were obtained by its repeated crystallization from cold CS_2. Compound **8** is pale yellow. Anal. Calcd for P_4S_4: mol wt 251.7832. Found: mol wt 251.7822. Infrared absorptions (KBr pellet) occur at 783 (w), 680 (w), 478 (m), 469 (m), 431 (s), and 415 (s) cm^{-1}. The seven most intense mass spectral envelopes occur at *m/e* (relative intensity) 272 (8.1), 220 (65.4), 189 (5.8), 157 (25.0), 125 (58.7), 94 (17.3), and 63 (100.0). Owing to the low solubility of **8**, an adequate ^{31}P NMR spectrum was not obtained.

Attempts to isolate minor reaction products, or to isolate and characterize intermediate reaction materials from the β-$P_4S_3I_2$–$C_6H_5NH_2$ reactions, using a variety of solvent extraction, recrystallization, and sublimation techniques were unsuccessful.

Reactions of P_2I_4 with $C_6H_5NH_2$. A solution of $C_6H_5NH_2$ (2.2 g, 23 mmol) in benzene was added dropwise to a stirred solution of P_2I_4 (2.15 g, 3.8 mmol) in 30 mL of benzene at 25 °C. The reaction mixture was heated slowly during 2 h to 60 °C, during which time the reaction mixture changed from deep red to light orange and precipitation of solids occurred. Upon completion of the reaction, the reaction mixture at 60 °C was evaporated to dryness in vacuo, washed with petroleum ether, and extracted three times with 50-mL portions of hot carbon disulfide. Evaporation of carbon disulfide and repeated precipitation of the solid from carbon disulfide by titration of the solution with benzene yielded pure $P_4(NHC_6H_5)_4(NC_6H_5)_2$, **10** (16% yield).

Compound **10** is a colorless solid (decomposition at 150 °C without melting). Anal. Calcd for $C_{36}H_{34}P_4N_6$: C, 63.53; H, 5.04. Found: C, 63.41; H, 4.9. The ^1H NMR spectrum (CS_2) shows a broad resonance at δ −7.02 ppm (relative area 7.5, phenyl) and a singlet at δ −0.16 ppm (relative area 1.0, N–H). The ^{31}P NMR spectrum (CS_2) consists of a singlet at δ −136 ppm. Infrared absorptions (KBr pellet) occur at 3300 (w), 3000 (w), 1595 (vs), 1485 (vs), 1375 (w), 1272 (s), 1228 (m), 1082 (m), 1035 (m), 910 (m), 878 (w), 845 (m), 767 (vs), 690 (vs), 615 (w), 557 (m), 522 (w), and 495 (w) cm^{-1}. The parent and six most intense mass spectral envelopes occur at *m/e* (relative intensity) 674 (2.0), 580 (26.9), 457 (37.5), 366 (12.6), 122

Table I. Crystal Data for α-P_4S_4

Crystal system: monoclinic	$T = 24$ °C
Space group: $C2/c$	$Z = 4$
$a = 9.779$ (1) Å[a,b]	Mol wt 252.152
$b = 9.055$ (1) Å	d_{obsd}[c] = 2.23 g cm^{-3}
$c = 8.759$ (2) Å	d_{calcd} = 2.213 g cm^{-3}
$\beta = 102.65$ (1)°	μ(Mo Kα) = 19.33 cm^{-1}
$F(000) = 496$ e	λ(Mo Kα) = 0.710 69 Å
$V = 756.8$ (2) Å^3	

[a] Cell dimensions determined and refined by least-squares fit of the cell parameters to 15 reflections centered on the diffractometer. [b] Estimated standard deviations shown in parentheses in this and subsequent tables are of the least significant digits of the preceding number. [c] Measured using the flotation (CH_2I_2 + CCl_4) method.

(100), 92 (33.3), and 77 (19.2). Compound **10** is soluble in carbon disulfide and to a lesser extent in benzene and chloroform.

Hydrogen bromide gas was bubbled slowly through a sample of **10** (0.53 g) in benzene during 30 min at 25 °C. At the end of this time, mass spectral analysis of the reaction mixture indicated that all $P_4(NHC_6H_5)_4(NC_6H_5)_2$ had reacted. The precipitate which formed was filtered, washed with benzene, and characterized as $C_6H_5NH_3Br$ (0.84 g).

In several experiments, reactions between P_2I_4 and $C_6H_5NH_2$ were carried out at temperatures up to 90 °C, for times up to 4 h, and with different reactant P_2I_4:$C_6H_5NH_2$ ratios. In every case, lower yields of **10** were obtained. The CS_2 solution which remained after **10** had been precipitated, from a reaction carried out at 90 °C, was subjected to mass spectral analysis. Envelopes due to **10** were still clearly evident. In addition, the envelopes at m/e 580 and 488 had increased in intensity relative to the parent molecular envelope of **10** at m/e 674. However, attempts to separate additional products from **10** by sublimation or fractional crystallization were unsuccessful.

A reaction between n-$C_4H_9NH_2$ and P_2I_4 was carried out under conditions analogous to those used in the $C_6H_5NH_2$–P_2I_4 reactions. A reddish brown solid formed, which contained n-$C_4H_9NH_3I$. No other tractable products could be isolated or characterized.

Single-Crystal X-Ray Data. A crystalline sample of α-P_4S_4, (**4**), obtained by sublimation, of dimensions 0.26 × 0.28 × 0.33 mm with facial planes $[001]$, $[00\bar{1}]$, $[111]$, $[11\bar{1}]$, $[1\bar{1}1]$, $[1\bar{1}\bar{1}]$, $[\bar{1}11]$, $[\bar{1}1\bar{1}]$, $[\bar{1}\bar{1}1]$, and $[\bar{1}\bar{1}\bar{1}]$ was mounted and aligned on a Syntex $P\bar{1}$ diffractometer. Crystal parameters for **4** are given in Table I. The space group was determined from the systematic absences (hkl, $h + k = 2n + 1$; $00l$, $l = 2n + 1$) observed in the diffractometer data. Intensity measurements were made at room temperature using the θ–2θ scan technique as programmed by Syntex. The scan rate was varied from 24.0°/min for reflections with more than 1500 counts in a 2-s scan to 2.0°/min for reflections with less than 150 counts in an equivalent scan. The scan range was calculated to start 1.0° below 2θ for Kα_1 and end 1.0° above 2θ for Kα_2. Background measurements were made at the beginning and end of each scan for a total period equal to half the scan time. The background, collected using the stationary-crystal, stationary-counter technique, was assumed to be linear between the two measured points. Some 3500 reciprocal lattice points were surveyed within a single quadrant (hkl and $hk\bar{l}$) to 2θ of 90.0°. The data collection was monitored every 100 measurement cycles by 4 reference reflections. Their variation over the course of the data collection was less than 3% in I_{obsd}. No correction was applied. Data were processed in the usual way with the values of I_{obsd} and $\sigma(I_{\text{obsd}})$ corrected for Lorentz and polarization effects.[19] The data were corrected for absorption using an analytical method based on the work of de Menlenaer and Tompa.[20] The average transmission coefficient was 0.6277 with the maximum correction 0.679 and the minimum correction 0.576. Of the 3400 independent points measured, 1615 were determined to have intensity significantly above background[21] $[(F_o^2) > 3.0\,\sigma(F_o^2)]$ and were used in the refinement.

Solution and Refinement of the Structure. Normalized structure factors, $E(hkl)$, were calculated using the program FAME. The phase problem was solved routinely using the program MULTAN.[22] A starting set of two origin-defining reflections ([152] and [243]) and four other unknown reflections ([2,12,6], [2,6,–1], [8,6,–1], and [3,1,–5]) applied to the highest 254 E's ($E > 1.9$) and using 1999 phase relationships resulted in 16 solutions. The solution with the second best figures of merit resulted in an E map which revealed the positions of all atoms.

Table II. Final Structural Parameters in α-P_4S_4

(A) Atomic Positional Parameters

Atom	x/a[a]	y/b	z/c	X[b]	Y	Z
S(1)	0 (0)	5 053 (7)	25 000 (0)	−0.480	0.458	2.137
S(2)	0 (0)	53 792 (7)	25 000 (0)	−0.480	4.871	2.137
S(3)	19 616 (5)	29 449 (6)	16 573 (6)	1.600	2.667	1.416
P(1)	−176 (5)	20 228 (5)	6 683 (5)	−0.145	1.832	0.571
P(2)	15 012 (5)	38 611 (6)	36 981 (6)	0.759	3.496	3.161

(B) Atomic Thermal Parameters

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	1094 (8)	651 (7)	1093 (8)	0 (0)	201 (6)	0 (0)
S(2)	897 (7)	634 (7)	1559 (11)	0 (0)	45 (7)	0 (0)
S(3)	650 (4)	1272 (7)	1190 (6)	−56 (4)	341 (4)	−116 (5)
P(1)	867 (5)	938 (6)	729 (5)	−102 (4)	168 (4)	−121 (4)
P(2)	606 (4)	916 (6)	1019 (6)	−15 (4)	−11 (4)	−190 (4)

[a] Fractional cell coordinates (×10^5). [b] Cartesian coordinates (Å), where $X = x + z\cos\beta$, $Y = y$, and $Z = z\sin\beta$. [c] Anisotropic thermal parameters (×10^5) are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table III. Root-Mean-Square Amplitudes of Vibration (×10^4)

Atom	Min, Å	Intermed, Å	Max, Å
S(1)	1644 (8)	2010 (8)	2264 (8)
S(2)	1623 (8)	1975 (8)	2534 (9)
S(3)	1614 (6)	2072 (6)	2348 (6)
P(1)	1592 (6)	1916 (6)	2099 (6)
P(2)	1552 (6)	1862 (6)	2202 (6)

Five cycles of isotropic refinement on the complete P_4S_4 structure converged with $R_1 = 0.1300$ and $R_2 = 0.1954$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ with weights calculated by the equation $w = 4F_o^2/\sigma^2(F_c^2)$. Atomic scattering factors used were those of Cromer and Waber.[23] Corrections for anomalous dispersion of the atoms were made with the values of $\Delta f'$ and $\Delta f''$ taken from Cromer and Liberman.[24] Four cycles of further refinement with all atoms anisotropic converged at $R_1 = 0.0380$ and $R_2 = 0.0480$. The final value for the standard deviation of an observation of unit weight was 1.494. A final three-dimensional difference map was featureless.[25] Final positional and thermal parameters and their errors are listed in Table II. Table III gives root-mean-square amplitudes of vibration.

Refinement of an S_4P_4 model (P and S atom positions reversed from that of P_4S_4) was carried out also. Upon isotropic refinement, the R_2 value converged at 0.199; anisotropic refinement resulted in $R_2 = 0.0683$.

Results and Discussion

α-$P_4S_3I_2$–$C_6H_5NH_2$ Reactions. Aniline and α-$P_4S_3I_2$ (**1**, Figure 2a) react at 25 °C in benzene over a 2-h period to form $C_6H_5NH_3I$ and a series of products, the nature of which depends on the method of product isolation. If the reaction product mixture is heated under sublimation conditions, the initial product obtained is P_4S_3, **3**, followed by considerable quantities of α-P_4S_4, **4**, and finally a trace product, **5**, of apparent composition $P_2S_2(NHC_6H_5)_2(NC_6H_5)_2$. Nonvolatile, uncharacterized solid remains after the sublimation; however, if products are isolated from the original reaction solution by the milder technique of crystallization, α-$P_4S_3(NC_6H_5)$, **6**, along with lesser quantities of **4**, is the principal product. Compound **6** could be obtained only under the latter conditions. In no case, could evidence be obtained for its presence among the products obtained on sublimation.

α-$P_4S_3(NC_6H_5)$ (**6**) (Figure 2c) and α-P_4S_4 (**4**) (Figures 2e and 3) are characterized structurally as new *closo*-tetraphosphorus compounds, based on spectral data and an x-ray single-crystal study, respectively. Characterization of **6** was complicated by its tendency to undergo thermal decomposition above 50 °C. Samples of **6** invariably contained small quantities (<5%) of **4** as a contaminant. However, because

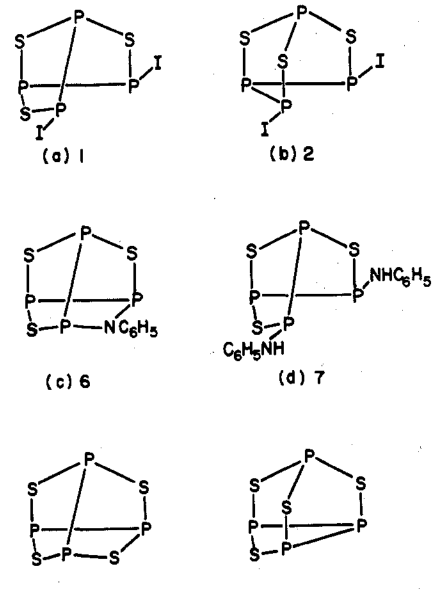


Figure 2. Molecular structures: (a) α-$P_4S_3I_2$, **1**; (b) β-$P_4S_3I_2$, **2**; (c) α-$P_4S_3(NC_6H_5)$, **6**; (d) $P_4S_3(NHC_6H_5)_2$, **7**; (e) α-P_4S_4, **4**; (f) β-P_4S_4, **8**.

spectral features of **4** are both simple and highly characteristic, minor contributions from **4** to spectra of **6** could be recognized and accounted for. Mass spectral data establish its molecular composition, molecular weight, and general structural features. Especially characteristic fragmentation ions occur at *m/e* (assignment in parentheses) 248 ($C_6H_5NP_3S_2^+$), 216 ($C_6H_5NP_3S^3$), 185 ($C_6H_5NP_2S^+$), 122 ($C_6H_5NP^+$), and 77 ($C_6H_5^+$). The ^1H NMR spectrum exhibits only a phenyl resonance at δ -7.17 ppm, in the region typical of C_6H_5NP moieties.[26] Although the infrared spectrum is complex, absorptions at 900 (P–N–P asymmetric stretch), 496 (P–S–P asymmetric stretch), 470 (P–S–P symmetric stretch), and 425 cm^{-1} (P–P) stretch can be assigned tentatively.[27] Absorptions due to N—H (3100–3300 cm^{-1}), P=S (645–680 cm^{-1}), and P=N (1360–1380 cm^{-1}) bonds are not evident, precluding these bond types in the structure of **6**. Owing to the low solubility and thermal stability of **6**, satisfactory ^{31}P NMR spectral data could not be obtained. The spectral data are consistent with the cage being of the edge-substituted P_4E_3E' ($E \neq E'$) type. No apical substitution is indicated. Consequently, because **6** forms from α-$P_4S_3I_2$ (**1**) under conditions sufficiently mild that rearrangement of the α sulfur arrangement might not be expected and because thermolysis of **6** subsequently yields α-P_4S_4 (**4**), the structure for **6** shown in Figure 2c is preferred. In this structure, the phenylimido moiety ($C_6H_5N<$) occupies the bonding positions of the iodine atoms in α-$P_4S_3I_2$ and in doing so converts the bicyclic tetraphosphorus system to a *closo*-tetraphosphorus cage.

Examination of the P_4S_3 (**3**), formed during sublimation of the α-$P_4S_3I_2$–$C_6H_5NH_2$ reaction products, indicates that it may contain material of isomeric composition other than that of the known sublimed P_4S_3.[28] This is particularly interesting because a reaction which in effect results in closure of α-$P_4S_3I_2$ (**1**, Figure 2) could yield a new isomer of P_4S_3. Compound **3** exhibits ^{31}P NMR[29] and mass spectra which are characteristic of known P_4S_3;[3,4] however, the infrared spectrum is clearly different. It shows unique absorptions at 738 and 680 cm^{-1}, in addition to absorptions at 478, 469, and 433 cm^{-1} which are close to but not identical in shape with those of sublimed P_4S_3 at 485, 440, and 423 cm^{-1}.[28] Thus, **3** could be a new tetraphosphorus trisulfide isomer(s), or a mixture of new isomers, along with the known P_4S_3. The IR spectral absorptions at 738 and 680 cm^{-1} may be due to P=S bond absorptions, indicating that the new P_4S_3 isomer(s) are not edge substituted only and possibly are of P_4E_2A and/or P_4EA_2 structural classes. Why the ^{31}P NMR and mass spectra of **3** are like those of known P_4S_3, whereas the infrared spectrum is different, is still unclear. However, it may be that in solution or at the elevated temperatures of the mass spectrometer inlet, rapid isomerization of **3** to known P_4S_3 occurs. Attempts are being made currently to obtain crystals of **3** sufficiently pure to allow a single-crystal x-ray study.

Evidence for the presence of a bis(phenylamido)tetraphosphorus trisulfide intermediate prior to formation of α-$P_4S_3(NC_6H_5)$ (**6**) has been obtained by analyzing the composition of the reaction mixture after short reaction times. The reaction was allowed to proceed only until $C_6H_5NH_3I$ precipitation was complete (15–20 min). Then $C_6H_5NH_3I$ was filtered from the benzene solution and the benzene removed quickly in vacuo. Analysis of the benzene-soluble products revealed the presence of a thermally unstable compound, $P_4S_3(NHC_6H_5)_2$ (**7**), along with **6** and in some cases traces of **4**. Spectral characterization of **7** was complicated by the unavoidable presence of **6** and **4**, particularly since **6** has many spectral features in common with **7**; however, in the ^1H NMR, infrared, and mass spectra, features unique to **7** could be identified satisfactorily. There is a mass spectral parent-ion envelope with a distinct cutoff at *m/e* 404 which can be assigned readily to an ion of composition $P_4S_3(NC_6H_5)H_2^+$. A ^1H NMR spectral resonance at δ 0.10 ppm and an infrared spectral absorption at 3290 cm^{-1} confirm the presence of N–H bond units in the molecule.[27] Thus, we propose that the structure of **7** may be as shown in Figure 2d, a bis(phenylamido) derivative of α-$P_4S_3I_2$ (**1**).

Sufficient evidence has been obtained to provide some indication of the sequence of reactions by which products **3**, **4**, **6**, and **7**, in addition to $C_6H_5NH_3I$, are formed in the α-$P_4S_3I_2$–$C_6H_5NH_2$ reaction. Compound **5** must be characterized completely before its origin can be discussed. The iodine atoms of α-$P_4S_3I_2$ are eliminated quantitatively as iodide to form $C_6H_5NH_3I$ in a reaction whose α-$P_4S_3I_2$ reactant: $C_6H_5NH_3I$ product ratio is 1:2. An overall reaction consistent with this which yields **6** is

$$3C_6H_5NH_2 + \underset{1}{\alpha\text{-}P_4S_3I_2} \rightarrow 2C_6H_5NH_3I + \underset{6}{\alpha\text{-}P_4S_3(NC_6H_5)} \tag{1}$$

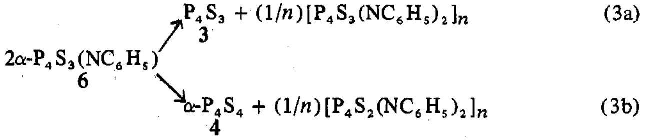
Our data indicate that **7** is an intermediate in this reaction, possibly formed in the first step of a two-step process (eq 2).

$$4C_6H_5NH_2 + \underset{1}{\alpha\text{-}P_4S_3I_2} \rightarrow 2C_6H_5NH_3I + \underset{7}{P_4S_3(NHC_6H_5)_2} \tag{2a}$$

$$7 \rightarrow C_6H_5NH_2 + \underset{6}{\alpha\text{-}P_4S_3(NC_6H_5)} \tag{2b}$$

Condensation of aniline with the phosphorus–iodine bonds of **1** results in phosphorus–nitrogen bond formation in eq 2a. Cage closure to **6** could then occur via elimination of $C_6H_5NH_2$ from **7** (eq 2b).

Compounds **3** and **4**, which apparently result from thermolysis of **6** (or **6** and **7**), may form in cage disproportionation (eq 3a) and cage-moiety exchange (eq 3b) reactions, respectively.



$$\underset{6}{2\alpha\text{-}P_4S_3(NC_6H_5)} \nearrow \underset{3}{P_4S_3} + (1/n)[P_4S_3(NC_6H_5)_2]_n \tag{3a}$$

$$\underset{6}{2\alpha\text{-}P_4S_3(NC_6H_5)} \searrow \underset{4}{\alpha\text{-}P_4S_4} + (1/n)[P_4S_2(NC_6H_5)_2]_n \tag{3b}$$

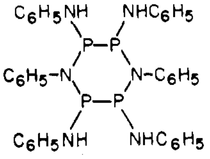
The $[P_4S_3(NC_6H_5)_2]_n$ and $[P_4S_2(NC_6H_5)_2]_n$ products may be contained in the intractable solids left after sublimation. Cage disproportionation, e.g., P_4S_5 to P_4S_3 and P_4S_7,[30] has been reported previously; however, since no other hetero-edge-substituted P_4 cages have been studied, no precedent exists for the cage-moiety exchange reaction.

β-$P_4S_3I_2$–$C_6H_5NH_2$ Reactions. Aniline reacts rapidly with β-$P_4S_3I_2$ (**2**, Figure 2b), as evidenced by immediate $C_6H_5NH_3I$ precipitation upon reagent mixing, yielding P_4S_3, a second isomeric tetraphosphorus tetrasulfide β-P_4S_4, **8**, and traces of P_4S_5. The P_4S_3 is a major reaction product. A mass spectral examination of the reaction mixture immediately after $C_6H_5NH_3I$ precipitation was complete showed no conclusive evidence for the presence of intermediate phenylamido– or phenylimido–tetraphosphorus trisulfides, i.e., β-$P_4S_3(NHC_6H_5)_2$ or β-$P_4S_3(NC_6H_5)$, analogous to what was observed in the α-$P_4S_3I_2$–$C_6H_5NH_2$ reactions.

Characterization of β-P_4S_4 (**8**) as an edge-substituted tetraphosphorus tetrasulfide is based on spectral data, since a crystalline sample suitable for x-ray analysis could not be obtained. Infrared spectral absorptions at 480 (P–S–P asymmetric stretch) and 430 cm^{-1} (P–S–P symmetric stretch) indicate the presence of sulfur atoms in cage edge positions.[27] No absorptions indicative of tetraphosphorus apical substitution (P=S) are evident. The mass spectrum exhibits characteristic, readily assigned ions at *m/e* (assignment in parentheses) 252 ($P_4S_4^+$), 220 ($P_4S_3^+$), 189 ($P_3S_3^+$), 157 ($P_3S_2^+$), 125 (P_3S^+), 94 ($P_2S_2^+$), and 63 (PS^+). The fragmentation pattern is analogous to that observed for α-P_4S_4 (**4**) but with significant differences in relative peak intensities. This is illustrated by examining the $P_4S_4^+$(*m/e* 252):$P_4S_3^+$ (*m/e* 220) relative intensity ratios which are 58:22 and 6:65 for α-P_4S_4 and β-P_4S_4, respectively. A relatively low stability for the $P_4S_4^+$ ion of β-P_4S_4 relative to that of α-P_4S_4 is indicated. Because of the low solubility of **8** and its tendency to decompose slowly in solution, satisfactory ^{31}P NMR spectral data could not be obtained. However, since there are only two isomeric possibilities for an edge-substituted P_4E_4 cage system, the structure of **8** must be that shown in Figure 2f. In this structure, the characteristic β arrangement of three sulfur atoms of β-$P_4S_3I_2$ (**2**) is retained. The fourth sulfur atom bonds into a cage edge to the phosphorus atoms previously bonded to iodine atoms.

Less evidence is available for how products are formed in the β-$P_4S_3I_2$–$C_6H_5NH_2$ reaction than in the α-$P_4S_3I_2$–$C_6H_5NH_2$ system. No evidence for the formation of phenylimido– or phenylamido–tetraphosphorus trisulfide molecule species has been obtained, although by analogy with what occurs in the α system, their formation as intermediates seems reasonable. Possibly, the β-$P_4S_3(NHC_6H_5)_2$ and/or β-$P_4S_3(NHC_6H_5)$ species are much more reactive than the α analogues and as a result proceed rapidly to the observed rearrangement and degradation products (**8**, **9**,[31] P_4S_3, and P_4S_5). Until additional information about reaction intermediates can be obtained, further speculation seems unwarranted.

P_2I_4–$C_6H_5NH_2$ Reactions. Aniline reacts with P_2I_4 to form a mixture of phenylimido– and phenylamido–tetraphosphorus products. The only product isolated and characterized so far is a new cyclic compound characterized tentatively as a 1,4,2,3,5,6-diazatetraphosphorine, $P_4(NHC_6H_5)_4(NC_6H_5)_2$, **10**.



10

The reaction which results in **10** can be written as

$$14C_6H_5NH_2 + 2P_2I_4 \rightarrow P_4(NHC_6H_5)_4(NC_6H_5)_2 + 8C_6H_5NH_3I \quad (4)$$

The mass spectrum of **10** shows the distinct cutoff at *m/e* 674 expected for the $P_4(NHC_6H_5)_4(NC_6H_5)_2^+$ ion. Although its infrared spectrum is complex, it is entirely consistent with the diazatetraphosphorine formulation. The presence of C_6H_5NH moieties and P–N–P and P–P bond units is supported by the presence of characteristic absorptions at 3300, 900, and 495 cm^{-1}, respectively.[27] The absence of an absorption in the 1350–1385-cm^{-1} range precludes the presence of phenylimino (C_6H_5N=P) groups. The ^{31}P NMR singlet resonance at δ −136 ppm indicates that all phosphorus atoms are equivalent and trigonally bonded.[32,33] The ^1H NMR spectrum shows phenyl and N–H resonances at δ −7.02 and −0.16 ppm, respectively, in the positions and relative area ratio (7.5:1) expected for **10**. Final conformation of compound stoichiometry is obtained from the reaction of **10** with excess HBr. Phosphorus–nitrogen bond cleavage occurs, 6 mol of $C_6H_5NH_3Br$/mol of **10** is formed, and **10** is consumed entirely. Because of the recognized tendency for P–P bond disproportionation and/or cleavage to occur in such a reaction,[26,34] no attempt was made to characterize the phosphorus bromide products.

Compound **10** is of particular interest because it is the first member of a new class of P–P bond containing phosphorus(III)–nitrogen ring compounds. Moreover, the reaction between P_2I_4 and aniline is the first involving a primary amine to yield a P–P bond containing product. Reactions of alkylamines with diphosphorus tetrahalides have previously resulted only in intractable polymeric products, apparently the result of P–P bond rupture.[34] These observations have been confirmed in our laboratory, where reactions of *n*-$C_4H_9NH_2$ with P_2I_4 have been found to yield only *n*-$C_4H_9NH_3I$ along with intractable products.

The formation of **10** from reaction of P_2I_4 with $C_6H_5NH_2$ may be analogous to the previously reported formation of α-$P_4S_3I_2$ from reaction of P_2I_4 with H_2S.[35] The latter reaction differs primarily in that it yields a bicyclic product. In addition, we have obtained evidence recently for P_4S_4 as a minor product of the H_2S–P_2I_4 reaction if it is carried out under more vigorous conditions.[36] It is possible that this reaction proceeds via the stepwise formation of monocyclic (so far unobserved), bicyclic (α-$P_4S_3I_2$), and cage (P_4S_4) tetraphosphorus products. Similarly, the stepwise loss of one or two molecules of $C_6H_5NH_2$ between pairs of C_6H_5NH moieties in trans positions of **10** could yield bicyclic $P_4(NHC_6H_5)_2(NC_6H_5)_3$ and cage $P_4(NC_6H_5)_4$ molecules. In order to test this hypothesis, the products of $P_4(NHC_6H_5)_4(NC_6H_5)_2$ thermolyses and of P_2I_4–$C_6H_5NH_2$ reactions carried out for up to 4 h at 90 °C were studied. Mass spectral evidence for species of formulas $P_4(NC_6H_5)_5H_x$ and $P_4(NC_6H_5)_4H_x$ was obtained. However, the low product(s) yield and complexity of the product mixture precluded isolation and characterization of the potentially new tetraphosphorus systems of interest.

α-P_4S_4 (4) Structure. The molecular structure of **4** is shown in Figure 2e and Figure 3, along with the numbering scheme used in the x-ray data analysis. The molecule is oriented around a crystallographic twofold symmetry axis along the *b* axis of the unit cell, which passes through S(1) and S(2). Thus P(1) is symmetry related to P(1)′, P(2) to P(2)′, and S(3) to S(3)′. Interatomic bond distances and angles are listed in Table IV.

The **4** in the crystal exhibits slightly distorted D_{2d} symmetry, containing phosphorus and sulfur atoms in bisphenoidal and square-planar arrangements, respectively. Since the ^{31}P NMR spectrum of **4** exhibits a sharp singlet in solution, it seems likely that the distortion from D_{2d} symmetry seen in the crystal is the result of crystal packing forces. The weighted average[37] P–S bond distance is 2.1109 (4) Å, within the 2.08–2.14-Å range observed previously for P–S bonds in *closo*-tetraphosphorus sulfide cages.[38] Intramolecular bond angles are somewhat less than those observed in other symmetrical

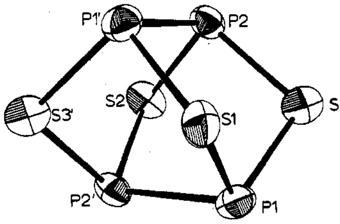


Figure 3. Molecular structure of α-P_4S_4 showing the numbering system used in this paper.

Table IV. Distances (Å) and Angles (deg) in α-P_4S_4

	A. Bond Lengths		
P(1)–S(1)	2.1095 (7)	P(2)–S(2)	2.1145 (7)
P(1)–S(3)	2.1117 (7)	P(2)–S(3)	2.1068 (8)
P(1)–P(2)′	2.3530 (8)		
	B. Bond Angles		
P(1)–S(1)–P(1)′	98.71 (4)	S(2)–P(2)–P(1)′	100.37 (3)
P(1)–S(3)–P(2)	99.02 (3)	S(1)–P(1)–P(2)′	100.61 (3)
P(2)–S(2)–P(2)′	98.91 (4)	S(3)–P(1)–P(2)′	100.40 (3)
S(1)–P(1)–S(3)	95.25 (3)	S(3)–P(2)–P(1)′	100.30 (3)
S(2)–P(2)–S(3)	95.11 (3)		
	C. Intramolecular Contacts Less Than 3.9 Å		
S(1)–S(3)	3.1184 (7)	S(3)′–P(2)	3.4337 (8)
S(1)–P(2)	3.4373 (8)	P(1)–P(1)′	3.2013 (11)
S(2)–S(3)	3.1150 (7)	P(1)–P(2)	3.2083 (8)
S(2)–P(1)	3.4350 (8)	P(2)–P(2)′	3.2135 (9)
S(3)–P(1)	3.4276 (8)		
	D. Intermolecular Contacts Less Than 3.9 Å		
S(1)–P(1)$^{\mathrm{I,II}}$ [a]	3.6004 (8)	S(2)–P(1)$^{\mathrm{VII,VIII}}$	3.6410 (8)
S(1)–S(3)$^{\mathrm{IV,V}}$	3.7132 (7)	P(1)–P(2)$^{\mathrm{IX}}$	3.5545 (8)
S(3)–S(3)$^{\mathrm{III}}$	3.3950 (11)	P(1)–P(1)$^{\mathrm{I}}$	3.8482 (11)
S(3)–S(2)$^{\mathrm{XI}}$	3.7162 (7)	P(2)–P(2)$^{\mathrm{X}}$	3.6252 (10)
S(3)–P(2)$^{\mathrm{VI}}$	3.8438 (8)		

[a] Contacts are between the first atom at x, y, z and the second atom at the symmetry-related position denoted by the Roman numeral superscript. Where there are two superscripts, there are two symmetry-related contacts of equal length. Positions: I $(-x, -y, -z)$; II $(x, -y, 0.5 + z)$; III $(0.5 - x, 0.5 - y, -z)$; IV $(-0.5 + x, -0.5 + y, z)$; V $(0.5 - x, -0.5 + y, 0.5 - z)$; VI $(x, 1.0 - y, -0.5 + z)$; VII $(-x, 1.0 - y, -z)$; VIII $(x, 1.0 - y, 0.5 + z)$; IX $(-0.5 + x, 0.5 - y, -0.5 + z)$; X $(0.5 - x, 0.5 - y, 1.0 - z)$; XI $(0.5 + x, -0.5 + y, z)$.

closo-tetraphosphorus sulfide cages (P_4S_3,[3] P_4S_7,[7] and P_4S_{10};[39] range in parentheses): P–S–P, 98.92 (2)° (103–109.5°); S–P–S, 95.18 (2)° (100–109.5°); S–P–P, 100.42 (2)° (102–103°). Of particular interest is the unusually long P–P bond distance of 2.3530 (8) Å. Generally, P–P bond distances vary only slightly (2.13–2.25 Å) and appear to be relatively insensitive to phosphorus oxidation state and/or type of substitution.[38] Only in the P_4S_7 cage has a P–P bond distance of 2.35 Å been reported.[7] This bond elongation may indicate a weakened P–P bond which could give rise to interesting P–P bond reaction chemistry in these systems.

Four molecules of α-P_4S_4 are packed in the unit cell as shown in Figure 4. The shortest intermolecular atom contacts are P(1)–P(2) = 3.5545 (8) Å, P(1)–S(1) = 3.6004 (8) Å, and S(3)–S(3) = 3.3950 (11) Å. The P–P and P–S distances are only slightly less than the van der Waals distances of 3.80 and 3.75 Å[40] and no special significance is given to the differences. However, the intramoleculr S–S distance is appreciably less than the 3.75-Å van der Waals distance[40] suggesting the presence of weak intermolecular bonding interactions in the α-P_4S_4 crystal. These close S–S interactions between α-P_4S_4 molecules in the approximately vertically arranged chains is evident in Figure 4.

The structure of α-P_4S_4 is analogous to that reported for As_4S_4.[41] However, a structure in which the phosphorus and sulfur atoms are transposed to an S_4P_4 structure analogous to that of S_4N_4[42] must be considered, since sulfur and phosphorus atom positions are practically indistinguishable from x-ray data. Examination of isotropic temperature factors was inconclusive. Assignment of atom positions as an S_4P_4 structure would result in an S–S bond distance of 2.353 Å, mean P–S–P angles of 95.18°, and mean S–P–S angles of 98.92°. A 2.353-Å S–S bond distance would be in the normal S–S bond range of 2.00–2.40 Å.[43] The P–S–P and S–P–S angles for P_4S_4 vs. S_4P_4 are not sufficiently different to allow their use as criteria for atom position assignment. However, there are arguments against the S_4P_4 model. First, the S_4P_4 model would require trigonal and digonal covalencies for sulfur (–S<) and phosphorus (–P–), respectively, or the involvement of alternating multiple phosphorus–sulfur bonds in a ring as occurs in S_4N_4. Precedent for either of these in phosphorus sulfide cage systems is lacking. Second, the S_4P_4 model can be refined both isotropically and anisotropically and the Hamilton R-factor test applied, hypothesizing that S_4P_4 is a better model than P_4S_4.[44] The ratios of $R_2(S_4P_4){:}R_2(P_4S_4)$ (isotropic) and $R_2(S_4P_4){:}R_2(P_4S_4)$ (anisotropic) are 1.230 and 1.422, respectively, considerably higher than the expected ratios of 1.0133 and 1.0222. Thus, the hypothesis that S_4P_4 is correct can be rejected at the 99.5% confidence level. For the above reasons and the existence of structural precedents of the other tetraphosphorus sulfides, the phosphorus–sulfur atom arrangement for α-P_4S_4 shown in Figure 3 appears well justified.

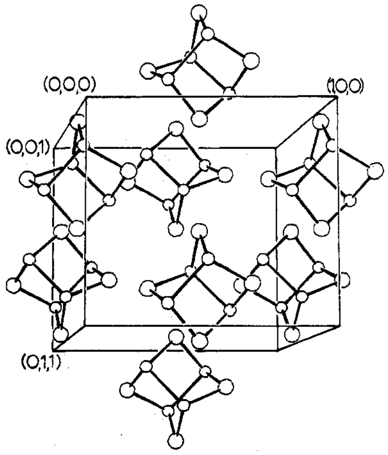


Figure 4. View of the unit cell of crystalline α-P_4S_4. Small spheres represent P atoms and the larger spheres represent S atoms.

A preliminary report of the preparation and characterization of α- and β-P_4S_4 has appeared recently. Sheldrick et al.[16] obtained α- and β-P_4S_4 from reactions of $[(CH_3)_3Sn]_2S$ with α- and β-$P_4S_3I_2$, respectively, in what appear to be high-yield reactions. The chemical properties and structural parameters determined by them are in close agreement with what we observe, although an assessment of the relative desirability of their synthetic route as compared to ours cannot be made until a detailed report of their work appears.

α-P_4S_4 (**4**) and β-P_4S_4 (**8**) represent the only two isomeric possibilities that exist for an edge-substituted tetraphosphorus tetrasulfide system. These compounds are the first well-characterized examples of tetraphosphorus sulfides containing an even number of sulfur atoms (excepting P_4S_{10}) and may indicate that under the right conditions an entire series of new tetraphosphorus sulfides can be obtained. Tentative evidence has been reported for the preparation of a P_4S_4 from the slow cooling of a P_4S_{10}–red phosphorus melt.[45] However, the infrared spectrum of this compound was noted to be identical with that of P_4S_5, raising the possibility that the P_4S_4 is an isomer of the P_4E_3A type or perhaps a P_4S_5–P_4S_3 mixture. Attempts to obtain this P_4S_4 material and to compare its thermodynamic and chemical properties with those of α-P_4S_4

(**4**) and β-P_4S_4 (**8**) are being pursued currently in our laboratories.

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Registry No. **1**, 19257-89-7; **2**, 34330-76-2; **3**, 1314-85-8; **4**, 39350-99-7; **5**, 65995-90-6; **6**, 65815-60-3; **7**, 65815-59-0; **8**, 20419-03-8; **10**, 65815-62-5; $C_6H_5NH_2$, 62-53-3; P_2I_4, 13455-00-0.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Taken in part from the Ph.D. Thesis of C.-C. Chang, University of Colorado, Boulder, Colo., 1977. (b) Alfred P. Sloan Fellow, 1973–1975.

(2) The $P_4E_{0-6}A_{0-4}$ cages can be viewed as closo cages, which derive 12 bonding electrons from the P_4 atom unit. $P_4E_{0-6}A_{0-4}$ cages are to be differentiated from $P_4F_4A_{0-4}$ cages in which F and A represent moieties in facial and apical bonding positions, respectively, on a tetrahedral P_4 atom unit, e.g., $P_4(\pi\text{-}C_5H_5CO)_4$: G. L. Simon and L. F. Dahl, *J. Am. Chem. Soc.*, **95**, 2175 (1973.

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$$\frac{2.0 + \sin\theta\cos\theta}{0.5\dfrac{\cos^2 2\theta_{\mathbf{mono}} + \cos^2 2\theta}{1.0 + \cos^2 2\theta_{\mathbf{mono}}} + 0.5\dfrac{\cos^2 2\theta_{\mathbf{mono}} + \cos^2 2\theta}{1.0 + \cos^2 2\theta_{\mathbf{mono}}}}$$

where 2θ is the calculated Bragg angle and $2\theta_{\mathrm{mono}}$ is the monochromator angle.

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Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80302

Oxidative Cleavage of Dimethylstannaundecaborane: Preparation and Structural Characterization of 5,10-Dibromodecaborane(14)

TIMOTHY J. DUPONT, ROBERT E. LOFFREDO,[1] R. CURTIS HALTIWANGER, CHARLES A. TURNER, and ARLAN D. NORMAN*[2]

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Reaction of $(CH_3)_2SnB_{10}H_{12}$ with halogens ($X_2 = Br_2, I_2$) yields $(CH_3)_2SnX_2$ and $B_{10}H_{12}X_2$ as products. The principal dibromodecaborane product has been characterized, based on spectral data and a single-crystal x-ray analysis, as 5,10-$B_{10}H_{12}Br_2$. Crystals of 5,10-$B_{10}H_{12}Br_2$ are monoclinic (space group $P2_1/c$), a = 13.323 (3) Å, b = 7.416 (3) Å, c = 24.890 (8) Å, β = 153.61 (1)°, Z = 4, and d = 1.701 g cm^{-3}. The structure was solved by the heavy-atom method and was refined by block-diagonal least squares to R_1 = 0.051 and R_2 = 0.053 for 1440 independent reflections. The 5,10-$B_{10}H_{12}Br_2$ has approximate C_s molecular symmetry in the crystal. The mean B–Br distance is 1.941 (8) Å. The B_{10}-cage unit shows only slight distortions from the cage structure seen in $B_{10}H_{14}$. The $B_{10}H_{12}I_2$ obtained is thermally unstable and consequently was not characterized structurally. Reaction of $(CH_3)_2SnB_{10}H_{12}$ with a deficiency of Br_2 yields traces of product identified as $(CH_3)_2SnBrB_{10}H_{12}Br$, providing evidence that Br_2 cleavage of $(CH_3)_2SnB_{10}H_{12}$ occurs via the stepwise cleavage of B–Sn–B three-center bonds in an oxidative cleavage reaction process.

Introduction

Dialkylstannaundecaboranes,[3] $R_2SnB_{10}H_{12}$, are a potentially useful series of *nido*-borane derivatives upon which to base syntheses of other substituted decaboranes. An x-ray structural analysis shows the R_2Sn moiety is bonded to the decaborane cage at edge boron atoms B(5)–B(6) and B(9)–B(10) by what

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