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Structure, Bonding, and Chemistry of *closo*-Tetraphosphorus Hexakis(methylimide), P4(NCH3)6, and Its Derivatives. 3. Structures of the Dithio and Trithio Derivatives

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The crystal and molecular structures of the title compounds, $S_2P_4(NMe)_6$ and $S_3P_4(NMe)_6$, have been determined. The former gives monoclinic crystals belonging to the space group $P2_1/n$ with unit cell dimensions $a = 12.582$ (3) Å, $b = 13.110$ (3) Å, $c = 9.747$ (2) Å, $\beta = 95.00$ (2)°, $V = 1602$ (1) Å^3, $d_{calcd} = 1.502$ g/cm^3 for $Z = 4$, and $M_r = 362.27$. The latter crystallizes in the orthorhombic space group $Pbca$ with $a = 9.839$ (4) Å, $b = 13.383$ (7) Å, $c = 25.839$ (10) Å, $V = 3402$ (3) Å^3, $d_{calcd} = 1.540$ g/cm^3 for $Z = 8$, and $M_r = 394.23$. The results presented here together with those reported earlier for $P_4(NCH_3)_6$, $SP_4(NCH_3)_6$, and $S_4P_4(NCH_3)_6$ allow a search for, and analysis of, systematic trends in N–P bond lengths. Because of scatter in the data for each compound, error bars on average values are fairly large. The following are the averages: P–NP, 1.70 (1) Å; P–NPS, 1.73 (2) Å; SP–NP, 1.65 (2) Å; SP–NPS, 1.68 (2) Å. The $S_2P_4(NCH_3)_6$ structure is the most precise of those determined, and the four types of P–N distances therein have higher precision than the overall averages for all compounds. The coplanarity of the bonds about all the nitrogen atoms and the significant shortening, by 0.07–0.10 Å, of the P–N bonds with respect to P(III)–N(sp^2) and P(V)–N(sp^2) standards are interpreted as resulting from N(pπ)→(P(dπ) contributions, with total bond orders of ca. 1.2–1.3. Some transmission of electronic effects is also seen in the SP–N–P pattern and is attributed to the N pπ electrons being more attracted to the SP–N side at the expense of the N–P side.

Introduction

In previous publications we have reported the molecular and crystal structures of $P_4(NMe)_6$,[2,3] $O_4P_4(NMe)_6$,[3] $S_4P_4(NMe)_6$,[3] and $SP_4(NMe)_6$[4] and commented on the structure parameters and how they are affected by attachment of O or S atoms to the phosphorus atoms. With this paper we complete the structural information on the $S_nP_4(NMe)_6$ ($n = 0$–4) series by reporting the structures of the compounds with $n = 2$ or 3. In $SP_4(NMe)_6$ an interesting pattern of variation in the N–P distances was observed and the present structures afford the opportunity to see if such a pattern is a consistent one for molecules containing an incomplete set of sulfur atoms.

Procedure

The compounds were prepared by methods previously described.[5] Crystals were grown by sublimation. Freshly sublimed $P_4(NCH_3)_6S_2$ (120 °C, 2 mmHg), or $P_4(NCH_3)_6S_3$ (150 °C, 2 mm Hg), was transferred under dry argon to one end of a 20 cm long, 2 cm diameter glass tube, which was evacuated and sealed. The tube was then heated in a horizontal tubular furnace having a regular temperature gradient from 65 to 25 °C. Transparent well-formed crystals were collected at the coldest end after 4–5 days. The crystals appear to be very deformable and fragile and must be transported and handled gently.

The general crystallographic procedures have already been described[3,4] and referenced.

$S_2P_4(NCH_3)_6$. **Data Collection.** The crystal chosen was an approximate sphere (diameter ~ 0.4 mm); it was lightly coated with epoxy cement and mounted on a glass fiber. Data were collected at 21 ± 1 °C on a Syntex P$\bar{1}$ automated diffractometer using Mo Kα radiation monochromatized with a graphite crystal in the incident beam, and the usual automatic centering and indexing procedures[3,4] were followed. Preliminary photographs revealed monoclinic symmetry. The systematic absences ($0k0$, $k \neq 2n$; $h0l$, $h + l \neq 2n$) uniquely established the space group as $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14). The principal crystallographic data are as follows: $a = 12.582$ (3) Å, $b = 13.110$ (3) Å, $c = 9.747$ (2) Å, $\beta = 95.00$ (2)°, $V = 1602$ (1) Å^3, $d_{calcd} = 1.502$ g/cm^3 for $Z = 4$, and a molecular weight of 362.27.

A total of 2833 unique reflections with $0 < 2\theta \leq 50°$ were collected with use of the θ–2θ scan technique, variable scan rates from 4.0 to 24.0°/min, and a scan range from 2θ(Mo Kα_1) – 0.8° to 2θ(Mo Kα_2) + 0.8°. The intensities of 3 standard reflections monitored after every 100 reflections showed a gradual decrease of about 10% during data collection, so a decay correction was applied. Data were also corrected for Lorentz and polarization effects, but an absorption correction was not necessary (linear absorption coefficient $\mu = 7.13$ cm^{-1}).

$S_2P_4(NMe)_6$. **Solution and Refinement of the Structure.** The positions of all phosphorus, sulfur, and nitrogen atoms were obtained from an E map. This map was generated by using as a starting phase set the one with the highest figure of merit produced by the program MULTAN operating on an input of the 315 reflections with E values greater than 1.60. These positions were used to phase a Fourier difference map, from which all the carbon atoms were located. Three cyles of least-squares refinement of a scale factor, all positional parameters, and isotropic temperature factors gave the discrepancy indices

$$R_1 = \sum ||F_o| - |F_c||/|F_o| = 0.123$$
$$R_2 = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2} = 0.193$$

Only those 2213 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were included in the refinement. Atomic scattering factors were those for neutral atoms with anomalous scattering terms included for all atoms. The function minimized during all least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor is $w = 4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for p in the calculation of σ.

Three least-squares cycles refining the scale factor, positional parameters, and anisotropic temperature factors reduced R_1 to 0.053 and R_2 to 0.091. The largest parameter shift on the last cycle was less than 0.10 times the estimated standard deviation. The esd of an observation of unit weight was 2.102. A final Fourier difference map contained only peaks due to hydrogen atoms.

$S_3P_4(NMe)_6$. **Data Collection.** A crystal was ground to a sphere ~ 0.35 mm in diameter and mounted, in a sealed capillary, on the Syntex P$\bar{1}$ diffractometer. Proceeding as above for the dithio compound, we found the space group to be Pbca and the following unit cell dimensions were measured: $a = 9.839$ (4) Å, $b = 13.383$ (7) Å, $c = 25.839$ (10) Å, $V = 1602$ (1) Å^3, $d_{calcd} = 1.54$ g/cm^3 for $Z = 8$, and a molecular weight of 394.26. Absorption corrections were omitted since $\mu = 7.9$ cm^{-1} for Mo Kα radiation and the crystal was spherical. Three standard reflections measured after every 150 data points fluctuated randomly by ±4%. Of 3255 reflections measured

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Table I. Positional Parameters for $S_2P_4(NMe)_6$ [a]

atom	x	y	z
S(1)	0.6605 (1)	0.0970 (1)	0.2313 (1)
S(2)	0.4302 (1)	0.3312 (1)	0.2609 (2)
P(1)	0.66751 (9)	0.16962 (9)	0.0612 (1)
P(2)	0.29880 (11)	0.29479 (10)	0.3331 (1)
P(3)	0.06333 (11)	0.29791 (11)	0.2811 (1)
P(4)	0.17358 (11)	0.12445 (10)	0.4363 (2)
N(1)	0.2770 (3)	0.3584 (3)	0.4786 (4)
N(2)	0.0686 (3)	0.3573 (3)	0.4403 (4)
N(3)	0.6676 (3)	0.2952 (3)	0.0776 (4)
N(4)	0.1885 (4)	0.3227 (3)	0.2318 (4)
N(5)	0.2867 (3)	0.1720 (3)	0.3685 (5)
N(6)	0.0757 (3)	0.1721 (3)	0.3245 (5)
C(1)	0.8032 (4)	0.0297 (4)	0.9753 (6)
C(2)	0.9594 (4)	0.3713 (4)	0.4860 (5)
C(3)	0.7150 (5)	0.3409 (4)	0.2083 (6)
C(4)	0.1909 (6)	0.3001 (6)	0.0797 (5)
C(5)	0.3841 (5)	0.1072 (5)	0.4021 (8)
C(6)	0.9781 (5)	0.1096 (5)	0.3112 (10)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table II. Positional Parameters for $S_3P_4(NMe)_6$ [a]

atom	x	y	z
S(1)	0.6581 (5)	0.3868 (3)	0.1431 (2)
S(2)	0.2831 (5)	0.0946 (4)	0.2487 (1)
S(3)	0.1102 (4)	0.2955 (3)	0.0492 (2)
P(1)	0.5241 (3)	0.2837 (2)	0.1322 (1)
P(2)	0.3422 (3)	0.1436 (3)	0.1831 (1)
P(3)	0.2594 (3)	0.2398 (2)	0.0867 (1)
P(4)	0.4737 (3)	0.0865 (2)	0.0846 (1)
N(1)	0.4535 (8)	0.2380 (6)	0.1865 (3)
N(2)	0.2193 (8)	0.1941 (7)	0.1456 (3)
N(3)	0.3818 (10)	0.3204 (6)	0.0989 (3)
N(4)	0.5765 (8)	0.1843 (6)	0.0992 (3)
N(5)	0.4127 (9)	0.0597 (6)	0.1462 (3)
N(6)	0.3374 (9)	0.1443 (7)	0.0581 (3)
C(1)	0.429 (1)	0.3169 (11)	0.2287 (5)
C(2)	0.082 (1)	0.1413 (15)	0.1506 (6)
C(3)	0.413 (2)	0.3991 (11)	0.0545 (6)
C(4)	0.726 (1)	0.1567 (10)	0.1003 (5)
C(5)	0.475 (1)	-0.0325 (9)	0.1712 (5)
C(6)	0.301 (1)	0.1117 (8)	0.0038 (4)

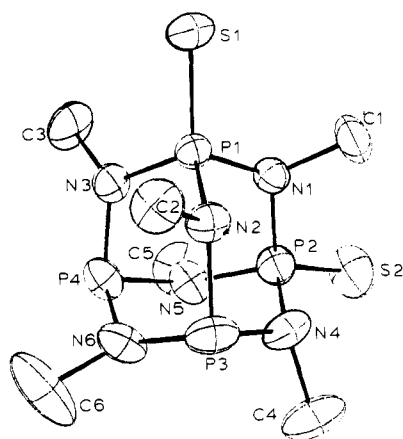[a] Figures in parentheses are the estimated standard deviations in the least significant figures.

Figure 1. The $S_2P_4(NMe)_6$ molecule, showing the atom numbering scheme. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density.
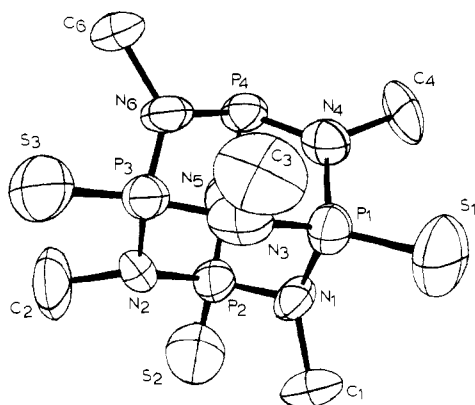

Figure 2. The $S_3P_4(NMe)_6$ molecule, showing the atom numbering scheme. The methyl carbon atom C(5) lies below (and is bonded to) N(5), but it is covered by other atoms. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density.

Table III. Selected Bond Distances (Å) and Angles (Deg) in $S_2P_4(NCH_3)_6$

S(1)–P(1)	1.920 (1)	P(1)–N(2)	1.676 (3)
S(2)–P(2)	1.913 (1)	P(1)–N(3)	1.654 (3)
S–P (av)	1.916 (5)	P(2)–N(4)	1.673 (3)
		P(2)–N(5)	1.657 (3)
P(3)–N(6)	1.706 (3)	SP–NP (av)	1.665 (11)
P(4)–N(6)	1.691 (3)		
P–NP (av)	1.699 (10)	P(1)–N(1)	1.695 (3)
		P(2)–N(10)	1.689 (3)
P(3)–N(2)	1.732 (3)	SP–NPS (av)	1.692 (4)
P(3)–N(4)	1.717 (3)		
P(4)–N(3)	1.741 (3)	P(3)–P(4)	3.003 (1)
P(4)–N(5)	1.736 (3)	P–P (av)	3.003 (1)
P–NPS (av)	1.732 (10)		
		P(1)–P(3)	2.955 (1)
N(1)–C(1)	1.504 (4)	P(1)–P(4)	2.966 (1)
N(2)–C(2)	1.493 (4)	P(2)–P(3)	2.962 (1)
N(3)–C(3)	1.485 (4)	P(2)–P(4)	2.959 (1)
N(4)–C(4)	1.514 (4)	SP–P (av)	2.961 (5)
N(5)–C(5)	1.503 (4)		
N(6)–C(6)	1.472 (4)	P(1)–P(2)	2.921 (1)
N–C (av)	1.495 (15)	SP–PS (av)	2.921 (1)

P(1)–N(1)–P(2)	119.35 (16)	P(4)–N(5)–C(5)	113.2 (3)
P(1)–N(2)–P(3)	120.25 (15)	P(3)–N(6)–C(6)	117.3 (3)
P(1)–N(3)–P(4)	121.71 (16)	P(4)–N(6)–C(6)	114.0 (3)
P(2)–N(4)–P(3)	121.85 (17)	P–N–C (av)	115.0 (25)
P(2)–N(5)–P(4)	121.46 (17)		
P(3)–N(6)–P(4)	124.23 (18)	P(2)–P(1)–P(3)	60.54 (3)
P–N–P (av)	121.5 (16)	–P(4)	60.35 (3)
		P(3)–P(1)–P(4)	60.95 (3)
P(1)–N(1)–C(1)	114.3 (2)	P(1)–P(2)–P(3)	60.30 (3)
P(2)–N(1)–C(1)	114.3 (2)	–P(4)	60.57 (3)
P(1)–N(2)–C(2)	117.5 (2)	P(3)–P(2)–P(4)	60.95 (3)
P(3)–N(2)–C(2)	111.0 (2)	P(1)–P(3)–P(2)	59.16 (3)
P(1)–N(3)–C(3)	118.8 (2)	P(1)–P(3)–P(4)	59.69 (3)
P(4)–N(3)–C(3)	113.1 (2)	P(2)–P(3)–P(4)	59.48 (3)
P(2)–N(4)–C(4)	116.6 (3)	P(1)–P(4)–P(2)	59.07 (3)
P(3)–N(4)–C(4)	109.5 (3)	–P(3)	59.35 (3)
P(2)–N(5)–C(5)	120.4 (3)	P(2)–P(4)–P(3)	59.57 (3)
		P–P–P (av)	60.0 (6)

in the range $0 < 2\theta \leq 50°$ with graphite-monochromated Mo Kα radiation 1379 had $I > 3\sigma(I)$ and were retained and used.

$S_3P_4(NMe)_6$. **Solution and Refinement of the Structure.** Positional parameters for two of the three sulfur atoms and the four phosphorus atoms were derived from an E map, on the basis of the phase set derived from the 250 highest E's and having the highest figure of merit, and computed from an adapted version of MULTAN. A difference electron density map following least-squares refinement of the positional and isotropic thermal parameters for these six atoms revealed the positions of the remaining non-hydrogen atoms of the asymmetric unit. All atoms were first refined by employing isotropic thermal parameters and then using anisotropic thermal parameters (using p = 0.06 in assigning weights) to give the final residuals R_1 = 0.074 and R_2 = 0.105, with no parameter shift exceeding 5% of its esd in the final cycle. Attempts to locate hydrogen atoms following the anisotropic refinement were unsuccessful, owing most likely to rotational disorder of the methyl groups. The final difference map was devoid of chemically significant features.

Table IV. Bond Distances (Å) and Bond Angles (Deg) in $S_3P_4(NMe)_6$[a-c]

S(1)–P(1)	1.929 (3)	P(1)–P(2)	2.907 (3)
S(2)–P(2)	1.909 (3)	–P(3)	2.916 (3)
S(3)–P(3)	1.912 (3)	P(2)–P(3)	2.919 (3)
S–P (av)	1.916 (11)	SP–PS (av)	2.914 (6)
P(4)–N(4)	1.697 (7)	P(4)–P(1)	2.954 (3)
–N(5)	1.740 (6)	–P(2)	2.957 (3)
–N(6)	1.693 (6)	–P(3)	2.943 (3)
P–NPS (av)	1.710 (26)	SP–P (av)	2.951 (7)
P(1)–N(4)	1.662 (6)	N(1)–C(1)	1.538 (10)
P(2)–N(5)	1.627 (7)	N(2)–C(2)	1.531 (11)
P(3)–N(6)	1.665 (6)	N(3)–C(3)	1.588 (11)*
SP–NP (av)	1.651 (21)	N(4)–C(4)	1.520 (9)
P(1)–N(1)	1.681 (7)	N(5)–C(5)	1.522 (10)
–N(3)	1.713 (7)	N(6)–C(6)	1.514 (9)
P(2)–N(1)	1.674 (6)	N–C (av)	1.525 (10)
–N(2)	1.690 (6)		
P(3)–N(2)	1.687 (6)		
–N(3)	1.647 (7)		
SP–NPS (av)	1.682 (21)		

P(1)–N(1)–P(2)	120.1 (4)	S(1)–P(1)–N(1)	114.9 (3)
P(2)–N(2)–P(3)	119.6 (3)	–N(3)	115.3 (3)
P(1)–N(3)–P(3)	120.4 (4)	–N(4)	115.8 (3)
P(1)–N(4)–P(4)	123.2 (4)	S(2)–P(2)–N(1)	114.4 (3)
P(2)–N(5)–P(4)	123.8 (4)	–N(2)	115.4 (3)
P(3)–N(6)–P(4)	122.5 (4)	–N(5)	114.4 (3)
P–N–P (av)	121.6 (1.8)	S(3)–P(3)–N(2)	114.8 (2)
C(1)–N(1)–P(1)	117.1 (6)	N(1)–P(1)–N(3)	100.7 (3)
–P(2)	116.7 (6)	–N(4)	105.3 (3)
C(2)–N(2)–P(2)	113.6 (6)	N(3)–P(1)–N(4)	103.0 (3)
–P(3)	116.7 (6)	N(1)–P(2)–N(2)	101.3 (3)
C(3)–N(3)–P(1)	113.2 (7)	–N(5)	105.8 (3)
–P(3)	116.0 (7)	N(2)–P(2)–N(5)	104.2 (3)
C(4)–N(4)–P(1)	119.1 (6)	N(2)–P(3)–N(3)	103.7 (3)
–P(4)	113.2 (5)	–N(6)	103.3 (3)
C(5)–N(5)–P(2)	118.9 (6)	N(3)–P(3)–N(6)	104.5 (3)
–P(4)	114.5 (6)	N(4)–P(4)–N(5)	99.3 (3)
C(6)–N(6)–P(3)	121.6 (5)*	–N(6)	102.1 (3)
–P(4)	115.6 (5)	N(5)–P(4)–N(6)	101.0 (3)
C–N–P (av)	115.8 (21)	N–P–N (av)	102.9 (20)

[a] Numbers in parentheses are esd's occurring in the last significant figures. [b] Numbers marked with an asterisk were omitted in computing averages and their esd's. [c] All angles have esd's of 1°.

Table V. Average Values of P–N Distances (Å) of Various Types

	P–NP	P–NPS	SP–NP	SP–NPS
$P_4(NMe)_6$	1.695 (12)			
$SP_4(NMe)_6$	1.70 (1)	1.73 (2)	1.63 (2)	
$S_2P_4(NMe)_6$	1.698 (10)	1.732 (10)	1.665 (10)	1.692 (4)
$S_3P_4(NMe)_6$		1.710 (26)	1.651 (21)	1.682 (21)
$S_4P_4(NMe)_6$				1.656 (14)
averages	1.70 (1)	1.73 (2)	1.65 (2)	1.68 (2)[a]

[a] OP–NPO (av) = 1.67 (2) Å in $O_4P_4(NMe)_6$.

Tables of thermal vibration parameters and observed and calculated structure factors are available as supplementary material.

Results

Tables I and II report the atomic positional parameters for $S_2P_4(NMe)_6$ and $S_3P_4(NMe)_6$, respectively, and Figures 1 and 2 illustrate the molecular structures and define the atomic numbering schemes. In each case the crystallographic asymmetric unit is one entire molecule and no symmetry is required crystallographically. Tables III and IV report the individual bond lengths and bond angles as well as the average values which are computed with the assumption of C_{2v} and C_{3v} symmetry for $S_2P_4(NMe)_6$ and $S_3P_4(NMe)_6$, respectively.

Discussion

With this paper we complete our reports on the structures

Figure 3. Schematic display of significant average structural data for the $S_2P_4(NCH_3)_6$ molecule (bond lengths in Å).

of the $X_nP_4(NMe)_6$ compounds with X = O, n = 4, and X = S, n = 0–4. Our purpose has been to accumulate enough data to determine whether consistent trends in the N–P distances, and perhaps other structural parameters, could be observed as a function of the number and positions of the attached X atoms. Table V collects all of the available information on N–P distances.

As in each of the two previous studies, we find here again that there is considerable variation among bond lengths that should be equal under the presumed idealized symmetry of the molecule, i.e., C_{2v} for $S_2P_4(NMe)_6$ and C_{3v} for $S_3P_4(NMe)_6$. When the various "chemically equivalent" values are averaged and the esd's of these averages, computed as $[\sum(\Delta_i)^2/(N-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value in a set of N values from the arithmetic mean, are taken into account, the precision with which any given type of bone length (or bond angle) can be stated becomes 0.01–0.02 Å. As we shall see, these esd's are sometimes large enough, compared to the differences between the various average values, that it becomes uncertain whether the differences are real.

There are in principle four chemically distinct kinds of P–N distances: (1) those in P–N–P groups; (2) those in SP–N–PS groups; (3) the SP–NP type; (4) the SPN–P type. All P–N (average) distances are so classified in Table V. It is likely that there may be a second-nearest-neighbor effect, since those of type 3 seem to be slightly shorter than those of type 2 and those of type 4 slightly longer than those of type 1. The esd's are such that this is not certain, but the observation of the same trend throughout the series is suggestive. The one thing that is certain is that P–N distances of types 3 and 4 are consistently and significantly different, by about 0.08 (3) Å.

Of all the compounds studied, only one, $S_2P_4(NCH_3)_4$, contains all four types of P–N bond. Moreover, for each type the mean value in this compound is statistically equal to the average for that type over all the compounds in which it occurs, but the uncertainty interval is smaller. To put it another way, the structure of $S_2P_4(NCH_3)_6$ seems to be the most regular structure available and at the same time it provides an example of each type of structural feature to be found in the entire series of compounds. We may thus take this molecule as a paradigm for the structural manifestation of electronic effects in the entire class of compounds. The pertinent features of this structure are schematically displayed in Figure 3.

Two other structural features pertaining to the P–N bonding may be examined with the $S_2P_4(NCH_3)_6$ paradigm. There are three different classes of nitrogen atoms: (1) the one in the SP–N–PS group; (2) the four in SP–N–P groups; (3) the one in the P–N–P group. In all cases the P–N–P angle is significantly larger than the P–N–C angles, the former averaging 121.5 ± 1.6° and the latter 115.0 ± 2.5°. The P–N–P angle at N(6), 124.2°, is much larger than the other five. For nitrogen atoms of type 1 and 3, that is, those in symmetrical

environments, the two P–N–C angles are equal or differ but little. For the four nitrogen atoms of type 2, however, the two P–N–C angles are markedly and consistently unequal, those of the SP–N–C type each being on average 6.6 ± 0.5° larger than the associated P–N–C type. This is probabbly an intramolecular steric effect, resulting from the nonbonded repulsions between the S atoms and the CH_3 groups. A further consequence of this would be increased crowding at the tricoordinated phosphorus atoms, which may explain the much lower reactivity observed for the residual tricoordinated phosphorus atom in $S_3P_4(NCH_3)_6$, compared to that in P_4-$(NCH_3)_6$, under the action of CH_3I, PhN_3, B_2H_6, or $Ni(CO)_4$, and the lower stability of the $S_3P_4(NCH_3)_6M$ adducts, where M = BH_3 or $Ni(CO)_3$.[6]

The deviations from strict planarity of the bonds about each nitrogen atom are in the range 5.5–12.0° but show little or no correlation with the type of nitrogen atom. For N(1), the SP–N–PS type, the sum of the three angles about the atom is 348.0°, while for N(6), the P–N–P type, the sum is 355.5°. The difference is in the sense expected if steric factors in the former would be tending to force the C(1) methyl group out of the S(1)–P(1)–N(1)–P(2)–S(2) plane. However, the validity of this apparent correlation is called into question by the wide variation of the angle sums at the other nitrogen atoms, which are 348.8, 353.6, 348.0, and 355.1° for N(2)–N(5), respectively.

The P–S distances in all four compounds, $S_nP_4(NCH_3)_6$, n = 1–4, are invariant, namely, 1.92 (1), 1.916 (5), 1.92 (1), and 1.91 (2) Å for n = 1 to n = 4, respectively. The grand average, 1.92 Å, is not significantly different from the sum of Pauling double-bond radii for P and S, namely, 1.94 Å. Again, the mean value for $S_2P_4(NMe)_6$ is the most precise and does not differ significantly from the grand average.

Correlation of Structural Data with P–N Bonding. We come now to the crucial question: What, if anything, can we conclude about the P–N bonding in this class of compounds from the now complete set of structural data for $P_4(NCH_3)_6$, $O_4P_4(NMe)_6$, and the $S_nP_4(NCH_3)_6$ series?

We may begin by observing that the arrangement of the bonds around all of the nitrogen atoms is close to planarity; $N(p\pi) \rightarrow P(d\pi)$ interactions are most likely to be the cause of this. Then we observe that all P–N bonds in these compounds are shorter than both the so-called "standard P–N single-bond length" of 1.77 Å found[7] in H_3N–PO_3^- and the sum of Pauling single-bond radii, 1.80 Å. It has been customary in other classes of compounds such as the phosphonitrilic compounds,[8] to regard decreases in P–N bond lengths relative to these values as evidence for multiple bonding. However, this is a relatively crude argument if the decreases are small and it is particularly defective in that if fails to take account of the effect of changes in hybridization at the nitrogen atom and changes in the formal oxidation number of the phosphorus atom.

As for the first of these factors, we think it would be reasonable to allow a decrease of about 0.03 Å in the radius of the nitrogen atom for the change from sp^3 hybridization to sp^2 hybridization. This would place the standard for a single bond from P^V to sp^2 N in the range 1.74–1.77 Å. The change to be expected in the radius of a phosphorus atom on changing

from P^{III} to P^V in the present compounds should be well modeled by the following changes[9] in the P–C bond lengths:
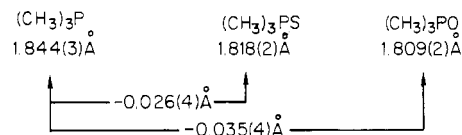
These data lead us to expect that a standard $N(sp^2)$–P^{III} single-bond length should be ca. 0.03 Å greater than the $N(sp^2)$–P^V bond length, namely, 1.77–1.80 Å.

After having thus considered more carefully what the P–N single-bond length standards should be, we still conclude that in the compounds we are considering the bonds are significantly shorter than single bonds. The P–NP bonds in all compounds have an average length of 1.70 (1) Å, which is some 0.07–0.10 Å shorter than expected for single bonds. On the basis of Cruickshank's demonstration[10] that for P–O, S–O, and P–N type bonds with orders between 1.0 and 2.0, we have $2.5 \leq d(BO)/d(BL) \leq 3.0$, where BO and BL represent bond order and bond length in Å, respectively, this means that the P^{III}–NP^{III} bond orders lie between 1.18 and 1.30.

When we turn to the P^V–NP^V type bonds, the results seem somewhat inconsistent with the P^{III}–NP^{III} results and among themselves. The average SP–NPS distance, 1.68 (2) Å, is not significantly different from the average P–NP distance, whereas we would have expected a smaller value simply because of the change in the standard on going from N–P^{III} to N–P^V. On top of this, the greater electron-attracting power of P^V compared to that of P^{III} might have been expected to increase the $N(p\pi) \rightarrow P(d\pi)$ bonding and shorten the bond even more. However, part of the bond-length shortening that would normally result from a given π contribution in an open system is probably absorbed here in counteracting increased van der Waals repulsions between nonbonded atoms in the closed, constrained, polycyclic system. It might also be expected that OP–NPO bonds would be about 0.02 Å shorter than SP–NPS bonds, but the two observed average values, 1.67 (2) and 1.68 (2) Å, have such large uncertainties that, again, no information is provided on this point.

The average values for SP–NP and P–NPS bond lengths, 1.65 (2) and 1.73 (2) Å, as well as those in the $S_2P_4(NCH_3)_6$ molecule, 1.67 (1) and 1.73 (1) Å, are significantly different and appear to be consistent with the idea that, in a P–N–PS unit, the N pπ electrons are attracted to the PS side, thus reducing the P–NPS bond order and lengthening that bond by about 0.03 Å and increasing the PN–PS bond order enough to shorten that bond by about 0.03 Å.

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