4430 *Inorg. Chem.* **1981**, *20*, 4430-4432

Contribution from the Departments of Chemistry,
University of Calgary, Calgary, Alberta, Canada T2N 1N4, and
University of Arkansas, Fayetteville, Arkansas 72701

Variable Geometry of the S_4N^- Anion: Crystal and Molecular Structure of $Ph_4As^+S_4N^-$ and a Re-refinement of the Structure of $PPN^+S_4N^-$

N. Burford,[1a] T. Chivers,[1a] A. W. Cordes,*[1b] R. T. Oakley,[1a] W. T. Pennington,[1b] and P. N. Swepston[1b]

Received April 28, 1981

The sulfur-nitrogen anion S_4N^- is obtained by the deprotonation of heptasulfur imide[2] or by the thermal decomposition of salts of the $S_4N_5^-$ or $S_3N_3^-$ ions.[3] An X-ray structural determination of $PPN^+S_4N^-$ ($PPN^+ = (Ph_3P)_2N^+$) showed that the S_4N^- anion is an approximately planar cis-trans chain with nitrogen as the central atom.[4] A prominent feature of the anion structure was the pronounced asymmetry of the central S-N-S unit (d(S-N) = 1.667 (5) and 1.521 (5) Å). Subsequent ab initio Hartree-Fock-Slater SCF calculations of S_4N^- showed that the calculated statistical energy of the experimental conformation is comparable to that of the cis-trans or trans-cis conformations with equal S-N and S-S bond lengths.[4] Thus it might be expected that a change in the crystal environment could lead to a different geometry for the S_4N^- anion (cf. $S_4N_4^{2+}$ [5]). To test this idea, we have carried out an X-ray structural determination of $Ph_4As^+S_4N^-$. In this crystal the anion was found to be disordered; this has led to a re-refinement of the structure of $PPN^+S_4N^-$ using a disordered anion model.

Experimental Section

Synthesis of $Ph_4As^+S_4N^-$. $Ph_4As^+S_4N_5^-$ was prepared by the addition of $Ph_4As^+Cl^-$ (ROC/RIC) to an aqueous solution of $pip^+S_4N_5^-$, which was prepared from piperidine (pip) and S_4N_4.[6] The thermolysis of $Ph_4As^+S_4N_5^-$ was carried out in anhydrous acetonitrile under an atmosphere of N_2 according to the procedure described for $PPN^+S_4N_5^-$.[4] The dark blue crystals of $Ph_4As^+S_4N^-$ obtained from the thermolysis showed characteristic anion bands at 889 w, 711 w, 594 m, 573 vs, and 417 w cm^{-1} in the infrared spectrum (Nujol mull; CsI windows).[4]

X-ray Structural Determination of $Ph_4As^+S_4N^-$. Crystals of $C_{24}H_{20}AsNS_4$ (fw = 525.59) suitable for X-ray work were obtained by slow cooling of an acetonitrile solution. The crystal used for data collection was bounded by three pairs of parallel faces, parallel to the (011), (01$\bar{1}$), and (302) planes at face-to-center distances of 0.12, 0.16, and 0.32 mm, respectively. The crystal was mounted in a glass capillary under argon, with the a axis parallel to the capillary. The systematic extinctions ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely determine the space group as $P2_1/n$. Using the θ values of 15 reflections with $66 < 2\theta < 79°$ (λ(Cu Kα_1) = 1.5405 Å), a least-squares refinement gave a = 10.560 (2), b = 16.273 (8), and c = 13.994 (4) Å, β = 91.50 (2)°, V = 2404 Å^3, and d_{calcd} = 1.45 g cm^{-3} (for Z = 4).

Data were collected up to 100° in 2θ by using Cu Kα X-rays (λ = 1.5418 Å) on a GE XRD-5 manual diffractometer with θ-2θ scans of 2° at 2° min^{-1}. Stationary-crystal, stationary-background readings were taken for 10 s at each end of the scan. A total of 2473 reflections were scanned and, of these, 2180 had $I > 3\sigma(I)$. Analysis of the high-angle reflections indicated a low percentage of observed reflections at angles beyond 100°. The 2180 observed reflections (minus 9 reflections removed later because of extinction and obvious human errors in the manual data collection) were used for the solution and refinement of the structure. Three standard reflections were measured every 75 reflections. The standard reflections showed three abrupt changes in intensity of several percent, which were attributed to instrument instability rather than crystal decay and were treated by simple scaling factors. The μ for Cu Kα is 52.7 cm^{-1}; an analytical absorption correction gave correction factors that varied from 0.61 to 0.44.

Standard Patterson and Fourier techniques led to the position of all atoms except the anion nitrogen atom. The location of two possible nitrogen sites on a difference map indicated the S_4N^- anion possesses a 2-fold disorder; the sulfur atoms from the two orientations are nearly superimposed. The disorder was unraveled by a utilization of difference Fourier techniques and isotropic temperature factors for the anion atoms included at unresolved atom positions. The occupancy factor ratio for the two orientations (0.6:0.4) is based on the relative heights of the nitrogen Fourier peaks. The final S-S separations between resolved S atom pairs S(1)/S(6), (S(2)/S(7), S(4)/S(10), and S(5)/S(9) are 0.28 (2), 0.772 (9), 0.879 (9), and 1.04 (1) Å, respectively.

In the final full-matrix least-squares refinement, all nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the phenyl rings were maintained at calculated positions (C-H = 0.95 Å) with isotropic thermal parameters of 5.0 Å^2. For the final refinement there were 2171 reflections and 316 parameters; no parameter shifted by more than 0.11σ, R = 0.040, R_w = 0.056, and the standard deviation of the observation of unit weight was 0.62. The weighting scheme used was $w = 1/2F_{min} + F_o + 2F_o^2/F_{max}$). The $\Delta F/\sigma(F)$ residues showed no dependence on either F or θ for the weighting scheme. The largest peak in the final difference map was 0.4 e/Å^3 and was located 1.25 Å from the As atom.

Re-refinement of $PPN^+S_4N^-$. Details of crystal data, structural determination, and refinement with an ordered anion model can be found in ref 4. Atomic positional and thermal parameters and a tape of structure factors and their σ's were obtained from Molecular Structure Corp. (College Station, Texas).

A difference Fourier map calculated for the best plane defined by the atoms of the S_4N^- anion revealed several centers of electron density that were suggestive of the type of disorder just described in the Ph_4As^+ structure. After a least-squares refinement in which the anion was refined with isotropic temperature factors, a difference map revealed all four sulfur atoms for the second orientation of the disordered anion. The positional parameters of the sulfur atoms of the second orientation were refined along with the positional and anisotropic thermal parameters of the original orientation. Refinement of the sulfur population parameters indicated an occupancy factor ratio of 0.9:0.1 for the two orientations. The population parameters of the anion atoms were fixed at these values thereafter. During the last stages of refinement, the nitrogen atom of the minor component was included in a calculated position and all five atoms of this orientation were assigned isotropic temperature factors of 6.0 Å^2.

In the final cycle of full-matrix least-squares refinement (409 variable parameters; 2987 observed reflections) the largest parameter shift was 0.09σ and the standard deviation of an observation of unit weight was 1.74. The final residuals were R = 0.052 and R_w = 0.063, where $w = 1/(\sigma(F))^2$ (in the original refinement R = 0.064 and R_w = 0.083). The largest peak in the final difference map was 0.39 e/Å^3 and was located 0.89 Å from the nitrogen atom of the major orientation at a position that was chemically uninterpretable. There was no unusual dependence of $\Delta F/\sigma(F)$ on the magnitudes of the observed structure factors or on θ. The final S-S separations between resolved S atom pairs S(1)/S(6), S(2)/S(7), S(4)/S(10), and S(5)/S(9) are 0.48 (3), 0.69 (3), 1.01 (3), and 1.31 (2) Å, respectively.

Results

Fractional coordinates for the nonhydrogen atoms of the two crystals are given in Table I. Tables II and III give the derived bond distance, bond angle, and planarity data for the anions. The structure factor tables, the thermal parameters, and the bond distances and bond angles for the cations for both structures have been deposited; see the paragraph at the end of this paper regarding supplementary material. Figure 1 gives the atom numbering for the disordered anions, and Figure 2 is a stereoview of the crystal packing.

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Table I. Fractional Coordinates for $Ph_4As^+S_4N^-$ and $PPN^+S_4N^-$

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
			a. $Ph_4As^+S_4N^-$				
S(1)	0.1558 (10)	0.1096 (6)	0.4296 (6)	C(19)	0.7503 (4)	0.4359 (3)	0.5001 (4)
S(2)	0.1116 (4)	0.1991 (3)	0.3408 (3)	C(20)	0.8462 (5)	0.4774 (3)	0.5507 (5)
N(3)	0.0149 (10)	0.2638 (8)	0.3878 (8)	C(21)	0.9000 (5)	0.4441 (4)	0.6314 (5)
S(4)	−0.0312 (4)	0.3406 (2)	0.3312 (3)	C(22)	0.8616 (5)	0.3691 (4)	0.6637 (4)
S(5)	0.0407 (6)	0.3509 (3)	0.2065 (3)	C(23)	0.7668 (5)	0.3258 (3)	0.6161 (3)
S(6)	0.1357 (19)	0.1161 (12)	0.4191 (13)	C(24)	0.5306 (4)	0.3535 (3)	0.3535 (3)
S(7)	0.0537 (7)	0.2109 (5)	0.3705 (5)	C(25)	0.6066 (5)	0.3324 (3)	0.2782 (4)
N(8)	0.1488 (13)	0.2662 (9)	0.3065 (10)	C(26)	0.5831 (6)	0.3658 (4)	0.1895 (4)
S(9)	0.0963 (6)	0.3446 (4)	0.2537 (5)	C(27)	0.4824 (7)	0.4178 (4)	0.1750 (4)
S(10)	−0.0798 (6)	0.3648 (4)	0.2721 (7)	C(28)	0.4056 (6)	0.4375 (4)	0.2490 (5)
As(11)	0.56845 (4)	0.30748 (3)	0.47633 (3)	C(29)	0.4313 (5)	0.4060 (3)	0.3396 (3)
C(12)	0.6045 (5)	0.1942 (3)	0.4568 (3)	C(30)	0.4279 (4)	0.3288 (3)	0.5565 (3)
C(13)	0.5078 (5)	0.1421 (3)	0.4286 (3)	C(31)	0.3093 (5)	0.3011 (3)	0.5333 (4)
C(14)	0.5345 (6)	0.0606 (3)	0.4063 (4)	C(32)	0.2095 (5)	0.3197 (3)	0.5913 (4)
C(15)	0.6568 (6)	0.0327 (3)	0.4127 (4)	C(33)	0.2297 (5)	0.3670 (3)	0.6712 (4)
C(16)	0.7532 (6)	0.0849 (3)	0.4401 (4)	C(34)	0.3475 (5)	0.3958 (3)	0.6945 (3)
C(17)	0.7288 (5)	0.1661 (3)	0.4625 (3)	C(35)	0.4484 (4)	0.3765 (3)	0.6363 (3)
C(18)	0.7118 (4)	0.3614 (3)	0.5338 (3)				
			b. $PPN^+S_4N^-$				
S(1)	0.4098 (2)	0.8483 (2)	0.0794 (3)	C(26)	0.9338 (5)	0.3306 (3)	0.4767 (5)
S(2)	0.5685 (2)	0.7699 (1)	0.0279 (2)	C(27)	1.0273 (5)	0.2928 (4)	0.5732 (6)
N(3)	0.5556 (5)	0.7319 (4)	−0.1278 (6)	C(28)	1.0604 (7)	0.3412 (6)	0.6923 (7)
S(4)	0.6734 (2)	0.6596 (1)	−0.1949 (2)	C(29)	1.0008 (9)	0.4249 (7)	0.7124 (8)
S(5)	0.8182 (2)	0.6345 (1)	−0.0628 (2)	C(30)	0.9096 (9)	0.4631 (4)	0.6176 (8)
S(6)	0.371 (3)	0.849 (2)	0.050 (3)	C(31)	0.8747 (6)	0.4167 (4)	0.4984 (6)
S(7)	0.523 (2)	0.769 (1)	−0.026 (3)	C(32)	0.8438 (4)	0.1752 (3)	0.6268 (5)
N(8)	0.6509	0.7819	0.0419	C(33)	0.9545 (5)	0.1111 (3)	0.6011 (5)
S(9)	0.774 (2)	0.714 (1)	−0.012 (2)	C(34)	1.0518 (5)	0.0917 (3)	0.7030 (6)
S(10)	0.755 (2)	0.622 (1)	−0.153 (2)	C(35)	1.0396 (6)	0.1360 (4)	0.8323 (6)
P(11)	0.8771 (1)	0.2683 (1)	0.3326 (1)	C(36)	0.9302 (7)	0.1982 (4)	0.8587 (6)
P(12)	0.7268 (1)	0.2012 (1)	0.4850 (1)	C(37)	0.8313 (5)	0.2177 (3)	0.7590 (5)
N(13)	0.7757 (3)	0.2296 (2)	0.3654 (4)	C(38)	0.6821 (4)	0.1078 (3)	0.4214 (5)
C(14)	0.8081 (4)	0.3348 (3)	0.1998 (5)	C(39)	0.6858 (5)	0.0504 (4)	0.5092 (6)
C(15)	0.8756 (5)	0.3788 (3)	0.1508 (5)	C(40)	0.6487 (6)	−0.0201 (4)	0.4591 (7)
C(16)	0.8231 (7)	0.4269 (3)	0.0463 (6)	C(41)	0.6073 (6)	−0.0328 (4)	0.3218 (8)
C(17)	0.7021 (7)	0.4334 (4)	−0.0116 (6)	C(42)	0.6040 (5)	0.0235 (4)	0.2342 (6)
C(18)	0.6349 (6)	0.3898 (4)	0.0358 (7)	C(43)	0.6410 (5)	0.0945 (4)	0.2829 (6)
C(19)	0.6873 (5)	0.3407 (3)	0.1400 (6)	C(44)	0.5918 (5)	0.2807 (4)	0.5495 (6)
C(20)	1.0132 (4)	0.1874 (3)	0.2701 (5)	C(45)	0.4978 (7)	0.2611 (5)	0.5930 (9)
C(21)	1.1261 (5)	0.2044 (3)	0.2678 (6)	C(46)	0.3998 (8)	0.3245 (7)	0.653 (1)
C(22)	1.2288 (5)	0.1427 (4)	0.2177 (7)	C(47)	0.3943 (9)	0.4044 (7)	0.6651 (9)
C(23)	1.2191 (6)	0.0636 (4)	0.1693 (7)	C(48)	0.487 (1)	0.4246 (5)	0.623 (1)
C(24)	1.1084 (7)	0.0466 (3)	0.1707 (6)	C(49)	0.5871 (7)	0.3628 (4)	0.5653 (9)
C(25)	1.0045 (5)	0.1081 (3)	0.2205 (5)				

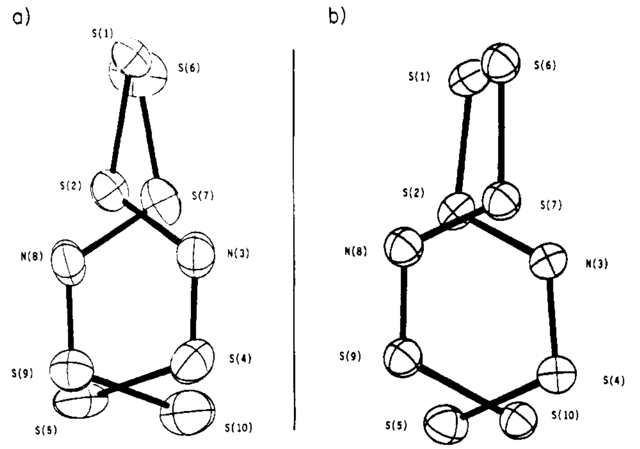

Figure 1. Thermal ellipsoids for the disordered anion models in (a) $Ph_4As^+S_4N^-$ and (b) $PPN^+S_4N^-$. The ellipsoids shown are at the 50% probability level. In each case the anion containing S(1) has the highest occupancy factor.

Table II. Selected Distances (Å) and Angles (Deg) in the S_4N^- Anion

a. $Ph_4As^+S_4N^-$

orientation A (mult = 0.6)		orientation B (mult = 0.4)	
S(1)-S(2)	1.96 (1)	S(6)-S(7)	1.89 (2)
S(2)-N(3)	1.62 (1)	S(7)-N(8)	1.63 (2)
N(3)-S(4)	1.55 (1)	N(8)-S(9)	1.57 (2)
S(4)-S(5)	1.928 (6)	S(9)-S(10)	1.913 (9)
S(1)-N(3)	2.97 (2)	S(6)-N(8)	2.91 (2)
S(2)-S(4)	2.753 (6)	S(7)-S(9)	2.77 (1)
S(2)-S(5)	3.181 (6)	S(7)-S(10)	3.17 (1)
S(1)-S(2)-N(3)	111.6 (5)	S(6)-S(7)-N(8)	111.4 (9)
S(2)-N(3)-S(4)	120.6 (8)	S(7)-N(8)-S(9)	119.5 (9)
N(3)-S(4)-S(5)	114.0 (5)	N(8)-S(9)-S(10)	114.1 (7)

b. $PPN^+S_4N^-$

orientation A (mult = 0.9)		orientation B (mult = 0.1)	
S(1)-S(2)	1.930 (3)	S(6)-S(7)	1.97 (4)
S(2)-N(3)	1.572 (6)	S(7)-N(8)	1.57 (2)
N(3)-S(4)	1.625 (5)	N(8)-S(9)	1.59 (2)
S(4)-S(5)	1.914 (3)	S(9)-S(10)	1.95 (2)
S(1)-N(3)	2.885 (6)	S(6)-N(8)	2.99 (4)
S(2)-S(4)	2.777 (3)	S(7)-S(9)	2.67 (3)
S(2)-S(5)	3.141 (3)	S(7)-S(10)	3.21 (3)
S(1)-S(2)-N(3)	110.5 (3)	S(6)-S(7)-N(8)	115 (2)
S(2)-N(3)-S(4)	120.5 (4)	S(7)-N(8)-S(9)	115 (1)
N(3)-S(4)-S(5)	111.0 (3)	N(8)-S(9)-S(10)	119 (1)

The crystal structure of $Ph_4As^+S_4N^-$ consists of discrete cations and anions. There are no interionic contacts shorter than van der Waals contacts. In the tetraphenylarsonium cation the C–As–C bond angles range from 106.7 (2) to 114.9

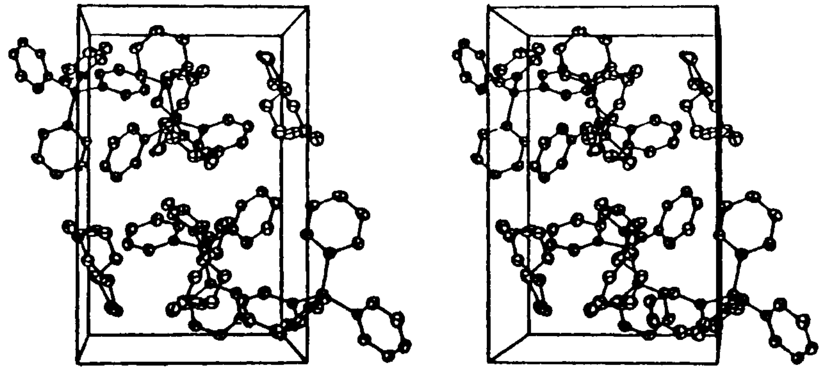

Figure 2. Crystal packing of $Ph_4As^+S_4N^-$. The unit cell origin is in the lower, front, right corner, with *a* horizontal, *b* vertical, and *c* perpendicular to the paper.

Table III. Atomic Displacement from Anionic Best Planes[a]

a. $Ph_4As^+S_4N^-$

plane 1-a		plane 2-a	
atom	dev, Å	atom	dev, Å
S(1)	−0.04 (1)	S(6)	−0.09 (2)
S(2)	0.01 (5)	S(7)	0.023 (8)
N(3)	−0.01 (1)	N(8)	0.01 (1)
S(4)	0.001 (4)	S(9)	−0.002 (7)
S(5)	−0.008 (5)	S(10)	−0.010 (8)

b. $PPN^+S_4N^-$

plane 1-b		plane 2-b	
atom	dev, Å	atom	dev, Å
S(1)	0.044 (4)	S(6)	0.05 (4)
S(2)	−0.025 (3)	S(7)	−0.04 (3)
N(3)	−0.036 (7)	N(8)[b]	−0.02
S(4)	−0.038 (3)	S(9)	0.01 (2)
S(5)	0.011 (3)	S(10)	0.01 (2)

[a] Each atom included in the calculation for a plane was weighted by $1/\sigma^2$, where σ is the positional uncertainty component perpendicular to the plane. [b] This atom was not included in the calculation of the plane because its positional parameters were not refined.

(2)° and the average As–C bond distance is 1.909 (9) Å; these values are typical of those found for this cation.[7] The phenyl C–C distances have a range of 1.361 (8)–1.402 (6) Å. Both orientations A and B of the S_4N^- anion are nearly planar and possess a "sickle-shaped" cis–trans conformation. The largest deviation from the best plane of orientation A is 0.04 Å for atom S(1) and from the best plane of orientation B is 0.09 Å for atom S(6) (Table IV). The two cis S–S distances are 1.927 (6) and 1.913 (9) Å, the two short S–N bonds are 1.55 (1) and 1.57 (2) Å, the two long S–N bonds are 1.62 (1) and 1.63 (2) Å, and the two trans S–S bonds are 1.96 (1) and 1.89 (2) Å. The difference in the trans S–S distances may very likely arise from limitations of the refinement. The S(1)···S(6) separation is only 0.28 (2) Å, and differences in the S(1) and S(6) thermal ellipsoids and in their deviations from the anion best planes support this conclusion. Inclusion of a small amount of anion disorder in the re-refinement of $PPN^+S_4N^-$ resulted in several significant changes of structural parameters for the anion. The biggest change is the diminished difference in the S–N bond lengths: the 1.667 (5) and 1.521 (5) Å values obtained previously from the ordered refinement have become 1.625 (5) and 1.572 (6) Å in the present model. The short S–S bond length of 1.879 (3) Å has changed to a more typical value of 1.914 (3) Å in the present work. The re-refinement had very little effect on the PPN^+ cation; no cation positional parameter changed by more than 2σ.

The anion disorder in $PPN^+S_4N^-$ is similar to that found in $Ph_4As^+S_4N^-$ (Figure 1). The dihedral angle between the planes of the two disordered anions in PPN^+ is 148 (1)°, and the corresponding value in the Ph_4As^+ structure is 147 (1)°.

Discussion

The discovery of different geometries for the acyclic S_4N^- anion, which was predicted by molecular orbital calculations,[4] is established by the crystal structures of $Ph_4As^+S_4N^-$ and $PPN^+S_4N^-$. The structural uncertainties introduced by the crystal disorders cannot alter this conclusion. The "long–short" S–N bond sequence in the anion of the Ph_4As^+ salt is 1.62 (2) and 1.56 (2) Å, found by using the averages of the two disordered anion components; the opposite sense "short–long" S–N bonds of the anion in the PPN^+ salt are 1.572 (6) and 1.625 (5) Å, found by using the parameters of the major component of the disordered anion pair. The ratio of the two anion components in the disordered PPN^+ salt could not be determined accurately because of the small separation of the sulfur atoms and the small percentage of the minor component, but a variety of Fourier and least-squares refinements have shown (a) the anion ratio of 9:1 is a good approximation, (b) the structural parameters of the major component are much more reasonable when the minor component is included, and (c) no reasonable model of disorder can change the "short–long" S–N bond sequence to the "long–short" sequence found in $Ph_4As^+S_4N^-$.

It is fortuitous that the first two crystal structures containing the S_4N^- anion provide experimental verification of the low-energy barriers between various geometries for the anion. Structures containing the trans–trans form or forms with equal S–N bond distances are also predicted and will be of interest in future studies. The small anion appears to form stable crystals only when separated by bulky cations. This has the positive feature of giving minimal ionic packing effects on the anion, but it also has the negative feature of increasing the likelihood of disorder as observed in the structures of this report.

Acknowledgment. Financial supports in the form of a fellowship to P.N.S. from Phillips Petroleum Co. and computing grant moneys from the University of Arkansas Research Committee are gratefully acknowledged.

Registry No. $Ph_4As^+S_4N^-$, 79233-89-9; $Ph_4As^+S_4N_5^-$, 79233-90-2; $PPN^+S_4H_5^-$, 74273-18-0.

Supplementary Material Available: Anisotropic thermal parameters for both crystals (Tables IV and V), distances and angles for Ph_4As^+ (Table VI), distances and angles for PPN^+ (Table VII), and listings of structure factor amplitudes for both crystals (22 pages). Ordering information is given on any current masthead page.

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(7) For example see: Cotton, F. A.; Lippard, S. J. *Inorg. Chem.* **1966**, *5*, 416.