The Syntheses and Structures of Ph_4EN_3 (E = P, As, Sb), an Example for the Transition from Ionic to Covalent Azides within the Same Main Group

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Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. The compounds Ph_4EN_3 (E = P, As, Sb) were prepared from the corresponding halides by ion exchange in aqueous solution. [Ph₄P]N₃ crystallizes in the triclinic space group $P\overline{l}$, while [Ph₄As]N₃·H₂O and Ph₄SbN₃ crystallize in the monoclinic space group $P2_1/n$. In contrast to ionic [Ph₄P]⁺[N₃]⁻ and [Ph₄As]⁺[N₃]⁻, the antimony atom in Ph₄SbN₃ is pentacoordinated and contains a covalently bound azide ligand. This family of compounds serves

Introduction

There has been much recent interest in polyazido chemistry [1-13]. The azido group is highly energetic and adds about 70 kcal·mol⁻¹ to the energy content of a molecule. Polyazides are, therefore, highly endothermic compounds, whose energy content increases with an increasing number of azido ligands. The relatively stable azide anion possesses two double bonds, but covalent azides are polarized towards structures containing a single and a triple bond, which greatly facilitates the elimination of dinitrogen and enhances their sensitivity. The synthesis of molecules with a high number of azido groups is a useful but challenging way to synthesize high energy-density materials (HEDM). Neutral covalent polyazides are extremely shock-sensitive compounds. The danger can be reduced, at least in part, by anion formation due to reaction of the neutral compound with ionic azides [Eq. (1)].

$$M(N_3)_x + A^+ N_3^- \to A^+ [M(N_3)_{x+1}]^-$$
(1)

The resulting $A^+[M(N_3)_{x+1}]^-$ salts are stabilized by their crystal lattice enthalpies and the increased formal negative charges of the anions. These negative charges reside largely on the terminal N_{γ} atoms, reducing the N_{β} - N_{γ} triple-bond character and the ease of N_2 elimination. In addition, the detonation velocity is greatly reduced or propagation of decomposition is completely eliminated by separation of the

* Dr. R. Haiges, Dr. T. Schroer, M. Yousufuddin, Prof. Dr. K. O. Christe Loker Research Institute and Department of Chemistry University of Southern California Los Angeles, CA 90089-1661 /USA Fax: (+1) 213-740-6679 E-mail: haiges@usc.edu, kchriste@usc.edu as an example for the transition from ionic to covalent azides with increasing size of the central atom within the same group of the periodic table.

Keywords: Azides; Phosphorus; Arsenic; Antimony; Crystal structures; Ion exchange

polyazido anions by large counter-ions (e.g. $[EPh_4]^+$, E = P, As). Therefore, ionic azides with large counter-ions, such as $[Ph_4P]^+N_3^-$ and $[Ph_4As]^+N_3^-$, are frequently used reagents in polyazide chemistry.

Phosphonium-, arsonium- and stibonium azides are generally prepared by metathesis between the corresponding chloride and an excess of sodium azide [Eq. (2), E = P, As, Sb] [14].

$$Ph_4ECl + NaN_3 \rightarrow Ph_4EN_3 + NaCl$$
 (2)

Another method is the reaction of the bromide or iodide compound with silver azide, respectively, [Eq. (3), X = Br, I] [2, 15, 16].

$$Ph_4EX + AgN_3 \rightarrow Ph_4EN_3 + AgX$$
 (3)

However, azides obtained from reaction (2) may contain impurities of chloride which often cannot be removed. Furthermore, reaction (3) involves the handling of shock sensitive silver azide and is not a convenient general method. It was therefore desirable to find a convenient method for converting halide salts into the corresponding azide salts in high yield and purity. In addition, only the structure of the arsenic compound in the series Ph₄EN₃ (E = P, As, Sb) has previously been determined by X-ray diffraction techniques [14]. Furthermore, the detailed X-ray data files deposited under the given number with the FIZ, Karlsruhe, are for N(C₂H₅)₄⁺N₃⁻ and not for [Ph₄As]N₃.

Results and Discussion

Tetraphenylphosphonium, tetraphenylarsonium, and tetraphenylstibonium azide were prepared in quantitative yields from the corresponding chlorides, bromides or iodides, respectively, by ion exchange in aqueous solution [Eq. (4), X = halogen].

 $\operatorname{Resin-NR_3^+N_3^-} + \operatorname{Ph_4EX} \to \operatorname{Ph_4EN_3} + \operatorname{Resin-NR_3^+X^-}$ (4)

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	CUND		C II N Sh
empirical formula	$C_{24}H_{20}N_{3}P$	$C_{24}H_{22}AsN_3O$	$C_{24}H_{20}N_{3}SD$
formula weight	381.40	441.35	4/2.18
Temperature, K	110(2)	133(2)	143(2)
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Á	9.671(2)	10.778(3)	12.3975(14)
<i>b</i> , Å	10.208(2)	16.040(5)	10.5524(12)
<i>c</i> , Å	11.237(2)	12.853(4)	16.3295(19)
α, °	72.397(4)	90	90
β,°	69.412(3)	90.545(4)	107.132(2)
γ, °	80.509(4)	90	90
<i>V</i> , Å ³	987.6(4)	2222.1(11)	2041.5(4)
Ζ	2	4	4
ρ _{calc} g/cm ³	1.283	1.319	1.536
F(000)	400	904	944
Index ranges	$-10 \le h \le 10$,	$-13 \le h \le 13$,	$-12 \le h \le 16$,
	$-11 \le k \le 7$,	$-16 \le k \le 16$,	$-12 \le k \le 13$,
	$-12 \le l \le 12$	$-20 \le 1 \le 12$	$-21 \le 1 \le 20$
μ , mm ⁻¹	0.153	1.548	1.365
crystal size, mm	0.12 x 0.16 x 0.08	0.22 x 0.15 x 0.04	0.67 x 0.12 x 0.02
λ, Å	0.71073	0.71073	0.71073
no. of rflns. collect.	4309	13294	12097
no. of indep. rflns.	2807	4958	4576
R _{int}	0.0414	0.0411	0.0432
no. of params.	254	285	253
<i>R</i> 1, $w\hat{R}2$ [I>2 σ (I)]	0.0438, 0.0730	0.0482, 0.1308	0.0351, 0.0687
R1, $wR2$ (all data)	0.0780, 0.0793	0.0584, 0.1354	0.0523, 0.0733
$(\Delta/\rho)_{\rm min/max}$, e Å ⁻³	0.248/-0.263	1.492/-0.402	0.866/-0.560

Table 1 Structure refinement data for $[Ph_4P]N_3$, $[Ph_4As]N_3$ ·H₂O, and Ph_4SbN_3

Table 3 Atomic coordinates $(x10^4)$ and isotropic displacement factors U_{eq} /Å²x10³ for [P(C₆H₅)₄]N₃. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

у

х

P(1)	640(1)	3440(1)	2672(1)	23(1)
N(1)	4126(3)	8761(3)	3343(3)	48(1)
N(2)	4802(3)	9757(3)	2866(2)	30(1)
N(3)	5480(3)	10767(3)	2394(2)	38(1)
C(1)	-1261(3)	4106(3)	2983(3)	24(1)
C(2)	-1630(3)	5518(3)	2813(3)	32(1)
C(3)	-3105(4)	6017(3)	3037(3)	39(1)
C(4)	-4201(4)	5116(4)	3432(3)	41(1)
C(5)	-3839(3)	3709(4)	3620(3)	41(1)
C(6)	-2382(3)	3192(3)	3404(3)	32(1)
C(7)	1068(3)	2382(3)	1547(3)	22(1)
C(8)	140(3)	2392(3)	832(3)	27(1)
C(9)	554(3)	1617(3)	-75(3)	34(1)
C(10)	1892(3)	833(3)	-285(3)	35(1)
C(11)	2821(3)	834(3)	409(3)	34(1)
C(12)	2417(3)	1592(3)	1324(3)	30(1)
C(13)	975(3)	2455(3)	4184(3)	22(1)
C(14)	-189(3)	1892(3)	5313(3)	29(1)
C(15)	140(3)	1046(3)	6417(3)	34(1)
C(16)	1591(4)	732(3)	6414(3)	33(1)
C(17)	2752(3)	1291(3)	5297(3)	31(1)
C(18)	2443(3)	2155(3)	4192(3)	29(1)
C(19)	1855(3)	4834(3)	1887(3)	22(1)
C(20)	2054(3)	5628(3)	2629(3)	27(1)
C(21)	2930(3)	6743(3)	2013(3)	30(1)
C(22)	3604(3)	7078(3)	656(3)	32(1)
C(23)	3418(3)	6301(3)	-92(3)	30(1)
C(24)	2546(3)	5183(3)	518(3)	26(1)

Table 2 Selected bond length /Å and angles /° for $[Ph_4P]N_3$ and Ph_4SbN_3

	$[Ph_4P]N_3$	Ph_4SbN_3
N1-N2	1.179(3)	1.198(4)
N2-N3	1.193(3)	1.150(4)
M-C1	1.800(3)	2.102(3)
M-C7	1.801(3)	2.121(3)
M-C13	1.803(3)	2.153(3)
M-C19	1.801(3)	2.102(3)
M-N1	_	2.373(3)
N1-N2-N3	179.4(3)	178.2(4)
C1-M-C7	109.27(13)	119.49(12)
C1-M-C13	110.93(13)	94.81(11)
C1-M-C19	110.15(13)	115.26(12)
C7-M-C13	110.18(12)	95.40(12)
C7-M-C19	107.07(13)	115.26(12)
C13-M-C19	109.16(13)	97.15(12)
N1-M-C1	_	82.47(11)
N1-M-C7	_	84.13(11)
N1-M-C13	_	176.54(10)
N1-M-C19	_	86.14(11)
M-N1-N2	_	124.8(2)

The ion-exchange resin was prepared from Amberjet 4200 quaternary ammonium chloride resin by exchange with azide ions and proper washing. The corresponding azides were isolated as colorless solids, and were characterized by their crystal structure and vibrational spectroscopy.

Tetraphenylphosphonium azide crystallizes in the triclinic space group $P\overline{1}$. The crystallographic data, bond distances, and atomic coordinates are listed in Tables 1-3. As expected for tetraphenylphosphonium compounds [17-20], and shown in Figure 1, the cations and anions are well separated. The closest P···N contact between neighbor-

Table 4 Atomic coordinates $(x10^4)$ and isotropic displacement factors U_{eq} (Å²x10³ for Sb(C₆H₅)₄N₃. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	х	У	Z	U_{eq}
Sb(1)	7705(1)	3056(1)	248(1)	25(1)
N(1)	8393(2)	2525(3)	-920(2)	35(1)
N(2)	8675(2)	3278(3)	-1366(2)	33(1)
N(3)	8948(3)	3976(3)	-1808(2)	56(1)
C(1)	9206(3)	2143(3)	961(2)	28(1)
C(2)	9915(3)	2752(3)	1670(2)	36(1)
C(3)	10892(3)	2150(4)	2150(2)	44(1)
C(4)	11135(3)	938(4)	1941(2)	38(1)
C(5)	10426(3)	329(3)	1253(2)	32(1)
C(6)	9458(3)	934(3)	749(2)	29(1)
C(7)	6290(3)	1950(3)	-416(2)	29(1)
C(8)	6360(3)	971(3)	-963(2)	32(1)
C(9)	5396(3)	314(3)	-1392(2)	39(1)
C(10)	4369(3)	639(4)	-1290(2)	43(1)
C(11)	4301(3)	1601(4)	-748(2)	45(1)
C(12)	5263(3)	2256(3)	-298(2)	36(1)
C(13)	7118(3)	3429(3)	1341(2)	27(1)
C(14)	7152(3)	2428(3)	1910(2)	34(1)
C(15)	6693(3)	2539(4)	2577(2)	40(1)
C(16)	6208(3)	3659(4)	2712(2)	46(1)
C(17)	6177(3)	4677(4)	2167(2)	41(1)
C(18)	6619(3)	4561(3)	1485(2)	34(1)
C(19)	7688(3)	4941(3)	-172(2)	29(1)
C(20)	8552(3)	5769(3)	204(2)	39(1)
C(21)	8479(3)	7019(3)	-42(2)	41(1)
C(22)	7554(3)	7454(4)	-664(3)	45(1)
C(23)	6693(3)	6629(4)	-1053(2)	50(1)
C(24)	6755(3)	5373(3)	-814(2)	41(1)

ing ions of 4.973 Å is considerably longer than the sum of van der Waals radii (1.55 + 1.80 = 3.35 Å) [21]. The azide anion is symmetric and linear.

Tetraphenylarsonium azide monohydrate crystallizes in the monoclinic space group $P2_1/n$. The crystallographic data are listed in Table 1. Although the refined structure (Fig. 2) had a low R factor of 4.8 %, the anion part was



Fig. 1 ORTEP drawing of $[P(C_6H_5)_4]N_3$. Thermal ellipsoids are shown at the 50 % probability level



Fig. 2 ORTEP drawing of the disordered $[As(C_6H_5)_4]N_3 \cdot H_2O$ structure. Thermal ellipsoids are shown at the 50% probability level, and the water molecule has been omitted

disordered. The structure clearly showes an isolated $[Ph_4As]^+$ cation with the expected tetrahedral structure around the arsenic atom. This structure is not discussed in further detail because that for anhydrous $[Ph_4As]^+N_3^-$ has already been reported previously [14].

Tetraphenylstibonium azide also crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell. The crystallographic data, bond distances, and atomic coordinates are listed in Tables 1, 2, and 4, respectively. The mo-



Fig. 3 ORTEP drawing of $Sb(C_6H_5)_4N_3$. Thermal ellipsoids are shown at the 50 % probability level



Fig. 4 IR (top) and Raman (bottom) spectra of $[P(C_6H_5)_4]N_3$

lecular structure (Fig. 3) is that of a trigonal bipyramid with the azido and one phenyl-group occupying the axial positions. The angle N-Sb-C13 of 176.54(10)° is nearly linear. The atoms Sb, C1, C7, and C19 are approximately coplanar. These findings are in excellent agreement with infrared and electrical conductance studies on Ph_4SbN_3 [15] and previously reported structures of other tetraphenyl-stibonium compounds [22–27].

The observed vibrational frequencies of $[Ph_4P]N_3$, $[Ph_4As]N_3$, and Ph_4SbN_3 and their tentative assignment are listed in the Experimental Part. The vibrational spectra of $[Ph_4P]N_3$ (Fig. 4) and $[Ph_4As]N_3 \cdot H_2O$ confirm their ionic nature in the solid state, while that of Ph_4SbN_3 (Fig. 5) lends further support for its covalent structure. The IR spectra of the compounds show the two characteristic azide bands: the very intense antisymmetric stretching mode at about 2000 cm⁻¹ and the weak symmetric stretching mode at



Fig. 5 IR (top) and Raman (bottom) spectra of $Sb(C_6H_5)_4N_3$

about 1300 cm⁻¹. The absence of the antisymmetric stretching mode in the Raman spectra of $[Ph_4P]N_3$ and $[Ph_4As]N_3$ demonstrates the presence of ionic azides. As expected for a compound with a covalently bonded azido ligand, the antisymmetric N₃ stretching mode is observed in the Raman spectrum of Ph₄SbN₃. The infrared spectrum of $[Ph_4P]N_3$ is in excellent agreement with a previous report by *Mueller*, *Duebgen* and *Dehnicke* [28].

In summary, the crystal structures and vibrational spectra of the series Ph_4EN_3 (E = P, As, Sb) demonstrate the ionic characters of the phosphorus and arsenic compounds and the covalent nature of the antimony analogue. It exemplifies that, with increasing size and coordination number of the central atom, the energy gained by the formation of an additional covalent bond outweighs the Coulomb energy gained by the formation of an ionic compound with lower coordination number.

Experimental Part

Materials and Apparatus

Infrared spectra were recorded in the range $4000-400 \text{ cm}^{-1}$ on a Midac FT-IR model 1720 at a resolution of 1 cm^{-1} using KBr pellets. The pellets were prepared in the dry argon atmosphere of a glove box using an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range $3600-80 \text{ cm}^{-1}$ on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd-YAG laser at 1064 nm with power levels of less than 100 mW. Pyrex melting point tubes that were baked out at 300 °C for 48 h at 10 mTorr vacuum were used as sample containers. AgNO₃, NaN₃, NaOH, [(C₆H₅)₄P]Cl, [(C₆H₅)₄As]Cl·H₂O, (C₆H₅)₄SbCl, and Amberjet 4200(Cl) (all Aldrich) were used without further purification.

Preparation of azide loaded ion-exchange resin

50 g (185 meq) Amberjet 4200(Cl) quaternary ammonium resin was loaded into a 5 cm o.d. glass column which was equipped with a grease-free Teflon valve. The resin was washed with 10 % NaOH solution, until the eluents gave no precipitate with AgNO₃. Then

it was washed with de-ionized water, until the eluents were neutral (pH 7). After that, the resin was washed with 150 ml of 10 % NaN₃ solution and then with de-ionized water, until the eluents gave no precipitate with AgNO₃.

Preparations of $(C_6H_5)_4EN_3$ (E = P, As, Sb)

20 mmol of $(C_6H_5)_4EX$ (X = Cl, Br, I) were dissolved in 100 ml of de-ionized water and 50 ml ethanol. This solution was passed through the azide loaded Amberjet 4200 resin column and then washed with de-ionized water, until the eluents gave no precipitate with AgNO₃. The eluents were combined, and the water was pumped off, leaving behind colorless solids. Single crystals were obtained from ethanol/water solutions by slow evaporation of the solvent with a stream of nitrogen.

[(C₆H₅)₄P]N₃: yield: 98 %.

IR (20 °C, KBr) $\tilde{\nu}$ = 3447w (OH, H₂O); 3282mw (v_{as} + v_s N₃⁻); 3081w, 3048mw, 3018w, 2992w (vC-H), 2036m, 1998vs (v_{as}N₃⁻); 1585m, 1481m, 1439s, 1434s, 1342w (ring); 1314mw (v_sN₃⁻); 1184mw, 1158mw, 1107s, 1025w (ring); 997m, 859w, 764m, 750m, 722s, 693s, 668w, 634w (C-H); 616w (\deltaN₃⁻); 528vs, 460w (C-H) cm⁻¹. Raman (20 °C, 50 mW) $\tilde{\nu}$ = 3067 (4.9) (vC-H); 1586 (4.4), 1575 (1.1), 1482 (0.1), 1436 (0.2) (ring); 1314 (2.0) (v_sN₃⁻); 1241 (0.3), 1187 (0.6), 1163 (0.5), 1108 (0.9), 1098 (1.7), 1028 (2.5) (ring); 1001 (6.6), 727 (0.3), 679 (1.4), 614 (1.1), 283 (1.0), 266 (1.2), 257 (2.2) (C-H); 208 (1.1), 198 (1.4), 107 (10.0) cm⁻¹.

[(C₆H₅)₄As]N₃: yield: 95 %.

IR (20 °C, KBr) $\tilde{\nu}$ = 3442ms (OH, H₂O); 3076w, 3049w, 3015w (vC-H); 2037s, 2000vs (v_{as}N₃⁻); 1635w, 1580w, 1482m, 1440s, 1339vw (ring); 1311w (v_sN₃⁻); 1183w, 1162vw, 1083s, 1025w (ring); 997s, 757s, 693s (C-H); 616w (8N₃⁻); 481s, 469s, 454w (8C₆H₃) cm⁻¹. Raman (20 °C, 50 mW) $\tilde{\nu}$ = 3063 (6.2) (vC-H); 1579 (3.7), 1481 (0.3), 1436 (0.3) (ring); 1314 (2.4) (v_sN₃⁻); 1242 (0.5), 1182 (0.8), 1172 (0.4), 1161 (0.6), 1082 (1.1), 1024 (2.7) (ring); 1002 (9.1), 681 (0.6), 670 (2.6), 612 (1.1), 362 (0.4), 351 (0.4), 265 (1.5), 261 (1.5), 242 (3.5) (C-H); 193 (1.7), 184 (2.3), 98 (10.0) cm⁻¹.

(C₆H₅)₄SbN₃: yield: 94 %.

IR (20 °C, KBr) $\tilde{\nu}$ = 3442mw (OH, H₂O); 3340w; 3062w, 3056w, 3040w (vC-H); 2038vs (v_{as}N₃⁻); 1636w, 1576mw, 1479m, 1457vw, 1434ms, 1430ms, 1419vw, 1334w, 1325m (ring); 1307w (v_sN₃⁻); 1262w, 1183w, 1162w, 1068m, 1066m, 1062m, 1020m (ring); 996mw, 745ms, 698ms, 692s, 655w, 634w (C-H); 613w, 605w (\deltaN₃); 464ms, 456ms, 445m (\deltaC₆H₃) cm⁻¹. Raman (20 °C, 50 mW) $\tilde{\nu}$ = 3070 (3.6), 3063 (3.1), 3056 (6.1), 3048 (6.9), 3041 (5.9) (vC-H); 2040 (0.6), 2034 (0.5), 2027 (0.2) (v_{as}N₃); 1576 (2.8), 1570 (1.4), 1478 (0.5), 1438 (0.3), 1434 (0.3) (ring); 1333 (0.8) (ring); 1325 (1.5) (v_sN₃); 1266 (0.3), 1186 (1.0), 1166 (0.4), 1161 (0.5), 1156 (0.6), 1067 (0.5), 1021 (2.8) (ring); 1002 (8.4), 997 (5.1), 985 (0.4) (C-H); 736 (0.1) 730 (0.1), 655 (3.5) (C-H); (35 (0.2) (\deltaN₃); 613 (0.8), 467 (0.3), 448 (0.3), 295 (0.4), 261 (1.5), 251 (1.2), 239 (1.4), 225 (4.3), 215 (2.9) (C-H); 193 (1.4), 180 (1.8), 168 (2.1), 95 (10.0) cm⁻¹.

Crystal structure determination

The single crystal X-ray diffraction data of $[(C_6H_5)_4P]N_3$, $[Ph_4As]N_3 \cdot H_2O$, and $(C_6H_5)_4SbN_3$ were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (APEX) detector with the χ -axis fixed at 54.74° and using Mo K_{α} radiation (Graphite monochromator) from a fine-focus tube. This diffractometer was equipped with an LT-3 apparatus for low-tem perature data collection using controlled liquid nitrogen boil off. A few reasonably well-formed single crystals were selected in a glovebox with a microscope. The crystals were coated with epoxy grease and then mounted on a magnetic goniometer head. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of 30second per frame at a detector resolution of 512 x 512 pixels using the SMART software package [29]. A total of 1271 frames were collected in three sets and a final set of 50 frames, identical to the first 50 frames, was also collected to determine any crystal decay. The frames were then processed on a PC, running Windows 2000 software, by using the SAINT software package [30] to give the hkl files corrected for Lp/decay. The absorption correction was performed using the SADABS program [31]. The structures were solved by the direct method using the SHELX-90 program and refined by the least squares method on F^2 , SHELXL-97 incorporated in SHELXTL Suite 6.12 for Windows NT/2000 [32]. All nonhydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. ORTEP drawings were prepared using the ORTEP-3 for Windows V1.076 program [33]. Further details of the crystal structure investigations reported in this paper may be obtained from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ (UK) (fax: +44 (1223)336-033 or email: deposit@ccdc.cam.ac.uk) by quoting the depository numbers CCDC 263415 ($(C_6H_5)_4SbN_3$), CCDC 269384 ($[(C_6H_5)_4A_8]N_3 \cdot H_2O$), and CCDC 263416 $([(C_6H_5)_4P]N_3).$

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