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The Synthesis of Tetraphenylarsonium Azide, $[Ph_4As]^+[N_3]^-$, and the Attempted Preparation of Tetraphenylarsonium Azidodithiocarbonate, $[Ph_4As]^+[SCSN_3]^-$

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ABSTRACT: *Tetraphenylarsonium azide was prepared from the reaction of tetraphenylarsonium chloride monohydrate and sodium azide in aqueous solution. $[Ph_4As]^+[N_3]^-$ crystallizes in the orthorhombic space group P_{nma} with $Z = 4$ and unit cell dimensions $a = 16.539(2)$, $b = 10.879(2)$, and $c = 12.671(2)$ Å. The preparation of the compound $[Ph_4As]^+[SCSN_3]^-$ was also attempted; however, it was found that at temperatures $\geq 0°C$, this compound always decomposed into the tetraphenylarsonium thiocyanate, $[Ph_4As]^+[SCN]^-$.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 325–329, 1999

INTRODUCTION

Recently, a large amount of work has been undertaken in an attempt to understand more fully the structures of the class of compounds known as the inorganic azides [1–8], a great deal of which has focused on the preparation of covalently bound azides. However, while the tetraphenylarsonium cation has been used in the preparation of many large transition metal-azide systems, the structure of the tetraphenylarsonium azide compound containing an ionic azide group has not been reported. In fact, as far as we are aware, prior to this study, Ph_4AsN_3 was unknown. With such an extensive amount of chemistry having been carried out with the $[Ph_4As]^+$ cation using large systems, we decided that it would be interesting to investigate the small azide system with this large cation to obtain a comparison with smaller ionic azide systems. Main group azide compounds tend generally to have often unpredictable explosive properties and crystal structures. Moreover, this explosivity and lack of stability often prevents the structure determination using X-ray diffraction techniques.

Though discovered in 1918, very little work has so far been carried out with the sodium pseudohalide $[Na]^+[CS_2N_3]^-$ [9], possibly due to its limited stability and tendency to form compounds that often have explosivity that is comparable with that of azides [10–21]. This pseudohalide has a thiatriazolethiolate structure. Therefore, we attempted the preparation of the compound $[Ph_4As]^+[SCSN_3]^-$ with the intention to investigate its stability and structure.

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EXPERIMENTAL

Materials and Methods

The vacuum lines and handling techniques used in this study have been described elsewhere [21–23]. The IR spectra were recorded on a Perkin-Elmer 983G spectrometer, the Raman spectra were recorded on a Perkin-Elmer R2000 spectrometer, and the NMR spectra on a Jeol 400 MHz NMR spectrometer. All ^{13}C and ^{14}N NMR spectra were measured in the proton decoupled mode. The X-ray diffraction analysis was carried out using a STOE IPDS image plate X-ray instrument. $[Na]^+[CS_2N_3]^-$ was prepared according to the literature [9]. All solvents were commercial materials and were used without further purification. NaN_3 (Fluka) and $[Ph_4As]^+[Cl]^-H_2O$ (Aldrich) were also used without further purification.

Preparation of $[Ph_4As]^+[N_3]^-$. In a typical reaction, 0.419 g (1.0 mmol) of $[Ph_4As]^+[Cl]^-$ was dissolved in 20 mL of water and was reacted with 0.065 g (1.0 mmol) of NaN_3 at room temperature for 30 minutes while stirring. After removal of water, $[Ph_4As]^+[N_3]^-$ was obtained in 75% yield as a white solid that could be recrystallized from H_2O overnight. The crystals obtained were mainly twins or conglomerates of crystallites that had multiply grown into each other; however, very small crystals suitable for single-crystal X-ray diffraction analysis were obtained, but due to the small size, an image plate X-ray instrument was used. We have tried also to collect data with a four-circle Rigaku AFC 7S instrument at low temperature; however, the data obtained were worse than those reported in this article. All attempts to grow better crystals under different conditions have failed.

Analytical Data of $[Ph_4As]^+[N_3]^-$. ^{14}N NMR (297 K, H_2O, $MeNO_2$, 28.904 MHz): −133.3 (1), −281.7 (2) (N_3^-). ^{13}C NMR (297 K, H_2O, TMS, 100.40 MHz): 134.4 (2), 133.3 (2), 130.63 (1), 109.91(1). IR (RT, KBr, nujol, ν/cm^{-1}): 672w, 689s, 739vs, 751s, 847w, 918w, 998s (C-H); 1023m, 1081s, 1164w, 1187m (δ ring); 1281w, 1314w, 1337w (O-H, H_2O); 1438vs, 1480s, 1580w, 1644m; 2037s (ν_{as} NNN); 3061m (C-H); 3410vs (O-H, H_2O). Raman (297 K, 1067 nm, solid, 200 mW, 300 scans, ν/cm^{-1}): 241 (7) (C-H); 612 (1) (C-H); 671 (2) (C-H); 1002 (10) (C-H); 1025 (6) (ν ring); 1083 (1) (ν ring); 1168 (1) (ν ring); 1189 (1); 1314 (1) (NNN, N_3^-); 1580 (7) (ring); 3061 (10) (C-H). Anal. calcd: C, 67.80; H, 4.70; N, 9.88; As, 17.62. Found: C, 67.95; H, 4.90; N, 9.73; As, 17.38.

Attempted Preparation of $[Ph_4As]^+[SCSN_3]^-$ (a) From $[Ph_4As]^+[Cl]^-$ *and* $[Na]^+[CS_2N_3]^-$. *In a typical reaction, 0.419 g (1.0 mmol) of* $[Ph_4As]^+[Cl]^-$ was dissolved in 20 mL water and was reacted with 0.213 g (1.0 mmol) of $[Na]^+[CS_2N_3]^-$ at room temperature for 30 minutes while stirring. On addition of the $[Na]^+[CS_2N_3]^-$, a pale green precipitate formed. After filtration, $[Ph_4As]^+[SCN]^-$ was obtained as a pale green solid that could be recrystallized from dichloromethane at room temperature over several days.

(b) From $[Ph_4As]^+[N_3]^-$ *and* CS_2. *A 0.425 g (1.0 mmol) amount was dissolved in 20 mL of water and reacted with an equimolar amount of* CS_2 (0.076 g, 1.0 mmol). The reaction mixture was heated to 40°C for 1 hour, stirred overnight, filtered, and the water evaporated. $[Ph_4As]^+[SCN]^-$ was obtained as a very light, pale green solid.

Analytica Data of $[Ph_4As]^+[SCN]^-$. ^{14}N NMR (297 K, H_2O, $MeNO_2$, 28.904 MHz): −71.7 (1) (N_2), −165.7 (4) (SCN^-). ^{13}C NMR (297 K, H_2O, TMS, 100.40 MHz): 134.4 (2), 133.3 (2), 130.6 (1), 120.5 (1) ($[Ph_4As]^+$). IR (RT, KBr, nujol, ν/cm^{-1}): 471m (δ NCS^-); 612m, 689s, 741vs, 751w (δ C-H); 897w, 918w, 996m (C-H); 1021w; 1050m; 1480m 1577w; 2052m (νCN, SCN^-). Raman (297 K 1067 nm, solid, 200 mW, 300 scans, ν/cm^{-1}): 471 (2) (NCS); 612 (1), 1002 (10) (C-H); 1024 (6), 1083 (1), 1161 (1), (ν ring, C_6H_5); 1186 (1), 1580 (7) (δ ring C_6H_5); 2056 (1) (ν CN, NCS); 3061 (8) (C-H).

X-ray Structure Determination of $[Ph_4As]^+[N_3]^-$ Crystal Data. Tetraphenylarsonium azide, $C_{24}H_{20}AsN_3$, M = 425.36, orthorhombic, a = 16.539(2), b = 10.879(2), c = 12.671(2), A; U = 2279.8(9) Å^3, space group P_{nma}, Z = 4, D_c = 1.244 g cm^{-1}. Crystal dimensions 0.14 × 0.16 × 0.80 mm, yellow. $\mu(\text{Mo-K}_\alpha) = 1.5\ \text{mm}^{-1}$, λ = 0.71073 Å, $F(000)$ = 872.0. Alternatively, we tried to solve the structure in the acentric space group $Pna2_1$ ($Pn2_1a \rightarrow Pna2_1$), which was shown not to be appropriate.

Data Collection and Processing. STOE IPDS diffractometer, 20°C, $2\theta_{max.}$ = 48.4°, φ_{total} = 200.0°, $\Delta\varphi$ = 1.0°, t_{total} = 21 hours, Δt = 3 minutes. Graphite monochromated Mo-K_α radiation, 50 kV, 50 mA, 0.8 mm collimator, D = 80 mm, 14,059 total measured reflections, 1860 independent measured reflections, 1330 reflections used for structure solution [$F_0 > 4\sigma F_0$]. No absorption correction was made.

Structure Analysis and Refinement. The structure was solved using direct methods, and all nonhydrogen atoms were refined anisotropically. Refinement was by block-cascade full-matrix least squares to $R_1 = 0.1310$ for 1330 ($F_0 > 4\sigma F_0$), $R_1 = 0.1527$ for all 1860 independent measured reflections. Computations were carried out using the SHELXS-86 and SHELXL-93 program systems and published scattering factors [24–26].

Further details of the crystal structure determination are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number 406973, the names of the authors, and the journal citation.

RESULTS AND DISCUSSION

The synthesis of the novel ionic arsonium azide, tetraphenylarsonium azide, $[Ph_4As]^+[N_3]^-$ was achieved by the reaction of tetraphenylarsonium chloride monohydrate with sodium azide:

$$[Ph_4As]^+[Cl]^- + NaN_3 \rightarrow [Ph_4As]^+[N_3]^- + NaCl \qquad (1)$$

The ionic nature of $[Ph_4As]^+[N_3]^-$ was established in solution using ^{14}N NMR spectroscopy. The spectrum clearly shows two nitrogen resonances in the rough intensity ratio of 1:2 corresponding to the two equivalent terminal and the central nitrogen atom. Furthermore, the ionic nature in the solid state was established by Raman spectroscopy (for details, see Experimental). The new compound, $[Ph_4As]^+[N_3]^-$, shows two characteristic azide bands in the IR spectrum: the very strong asymmetric stretching mode (IR, 2037 cm^{-1}) and also a weak band at 1314 cm^{-1}, which can be attributed to the symmetric N_3 stretching mode (Figure 1). Several crystals of $[Ph_4As]^+[N_3]^-$ were recrystallized from water, and, despite several attempts to obtain higher quality crystals, the R_1 value could not be improved over 13% (15%) for all reflection. The structure of $[Ph_4As]^+[N_3]^-$ was determined by X-ray diffraction analysis to be that of the structure predicted for the tetraphenylarsonium cation and a linear azide group as is shown in Figure 2 [27]. The most important structural parameters are shown in Table 1, and all agree nicely with previous studies concerning the linear azide anion. The average As–C bond in the cation of 1.89 Å corresponds to an As–C single bond but which is slightly shorter than the sum of the covalent radii (1.21 + 0.77 = 1.98 Å) [27], but this is expected due to the cationic nature of the tetraphenylarsonium cation, $[Ph_4As]^+$. The analogous reaction with the $[Na]^+[SCSN_3]^-$ salt (Equation 2) was predicted to form a compound with the same structure for the $[Ph_4As]^+$ cation, but instead for the linear azide unit to have a five-membered anionic ring structure. However, the decomposition of the $[SCSN_3]^-$ ring occurs readily to form thiocyanate, which is the observed product of this reaction (Equation 3).

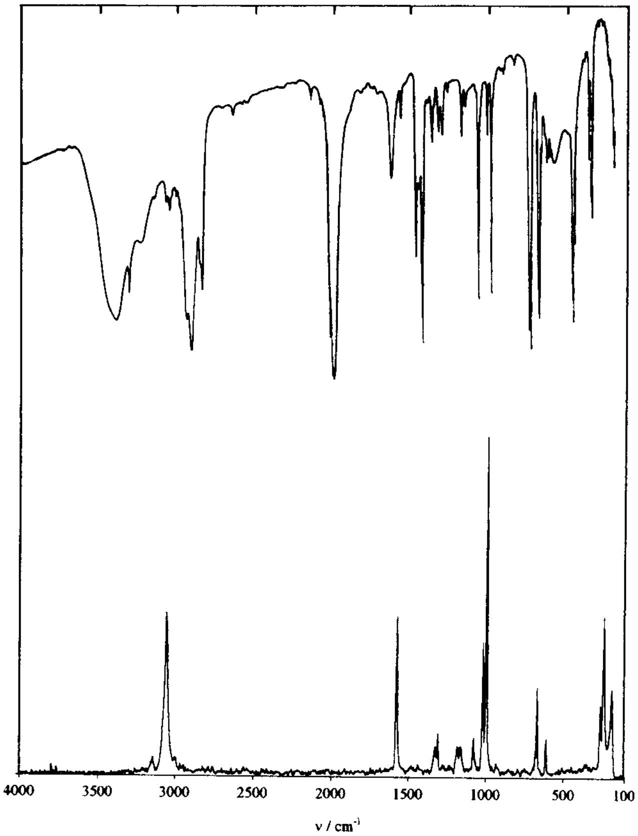

FIGURE 1 IR (*top*) and Raman spectra (*bottom*) of tetraphenylarsonium azide, $[Ph_4As]^+[N_3]^-$

$$[Na]^+[SCSN_3]^- + [Ph_4As]^+[Cl]^- \rightarrow \{[Ph_4As]^+[SCSN_3]^-\} + Na^+Cl^- \qquad (2)$$

$$\{[Ph_4As]^+[SCSN_3]^-\} \rightarrow [Ph_4As]^+[SCN]^- + 1/8\ S_8 + N_2 \qquad (3)$$

The decomposition does follow that for $[Na]^+[SCSN_3]^-$ [9–21]. It is, however, surprising that $[Na]^+[SCSN_3]^-$ (prepared from NaN_3 and CS_2) can be stored for some time in the freezer, whereas we have been unable to isolate the corresponding $[Ph_4As]^+[SCSN_3]^-$ salt. In order to investigate this phenomenon in more detail, we attempted the preparation of $[Ph_4As]^+[SCSN_3]^-$ in analogy to that of the sodium salt according to Equation 4.

$$[Ph_4As]^+[N_3]^- + CS_2 \xrightarrow{water,\ 40°C} [Ph_4As]^+[SCSN_3]^- \qquad (4)$$

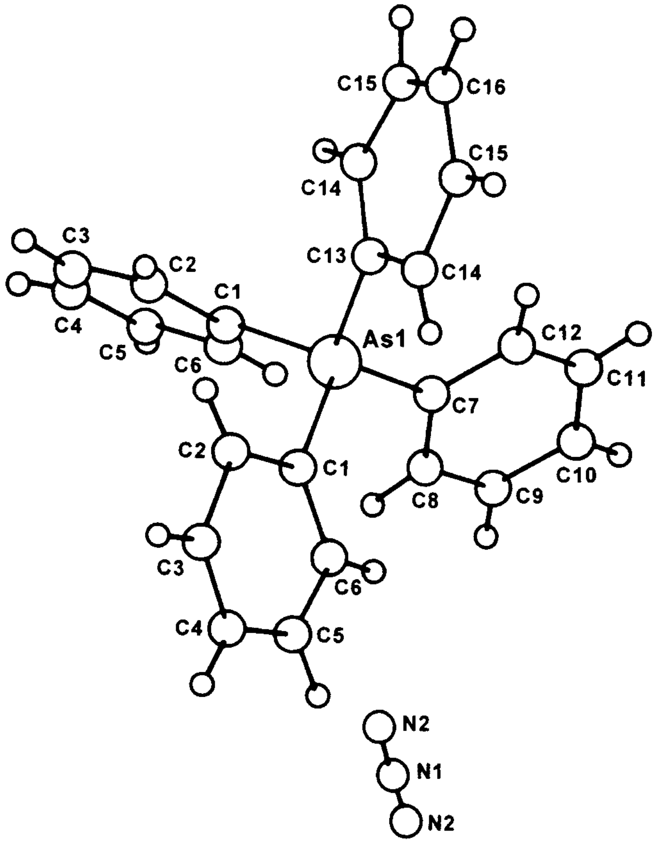

FIGURE 2 Structure of a tetraphenylarsonium azide formula unit, $[Ph_4As]^+[N_3]^-$, in the crystal.

TABLE 1 Selected Bond Lengths [Å] and Angles [°] of Tetraphenylarsonium Azide, $[Ph_4As]^+[N_3]^-$ (for atomic labeling, see Figure 2)

As1-C13	1.86 (2)	C13-As1-C7	109.0 (8)
As1-C7	1.87 (2)	C13-As1-C1	198.5 (6)
As1-C1	1.91 (1)	C7-As1-C1	111.1 (6)
N1-N2	1.18 (7)	C1-As1-C1	108.6 (8)
C7-C12	1.42 (3)	N2-N1-N2	180.0
C7-C8	1.42 (2)	C8-C7-C12	116 (2)
C8-C9	1.40 (4)	C9-C10-C11	116 (2)
C9-C10	1.40 (3)	C7-C12-C11	122 (1)
C11-C12	1.40 (3)	C7-C8-C9	120 (2)
C10-C11	1.34 (4)	C8-C9-C10	123 (2)
		C10-C11-C12	123 (2)

However, also from this reaction, we could not isolate the desired $[Ph_4As]^+[SCSN_3]^-$ but identified $[Ph_4As]^+[SCN]^-$ as the reaction product instead (*cf.* Equation 3).

The fact that $[Na]^+[SCSN_3]^-$ is stable in aqueous solution at least for a short time whereas $[Ph_4As]^+[SCSN_3]^-$ always seems to decompose immediately may be due to the different solubility of both compounds in water. Whereas $[Na]^+[SCSN_3]^-$ has pronounced solubility in water, the tetraphenylarsonium salt will dissolve only very sparingly in water and always immediately precipitates. This behavior can easily be understood from the very different ionic radii of the $[Na]^+$ and the $[Ph_4As]^+$ cation. While the lattice energy is inversely proportional to the sum of the ionic radii (of cation and anion), the solvation enthalpy is proportional to the sum of the reciprocal radii. Therefore, for salts with equally large ions ($r_+ \approx r_-$; e.g., $[Ph_4As]^+[SCSN_3]^-$), the lattice energy dominates (i.e., low solubility), whereas for salts with $r_+ \gg r_-$ or $r_+ \ll r_-$ ($[Na]^+[SCSN_3]^-$), the solvation enthalpy dominates (i.e., better solubility). For a detailled discussion of this effect, see References 28–30.

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REFERENCES

[1] Klapötke, T. M.; Tornieporth-Oetting, I. C. Angew Chem Int Ed Engl 1995, 34, 511–520.

[2] Klapötke, T. M. Chem Ber 1997, 130, 443–451.

[3] Klapötke, T. M., Tornieporth-Oetting, I. C., Nichtmetallchemie; VCH: Weinheim, 1994.

[4] Klapötke, T. M.; Geissler, P. J Chem Soc Dalton Trans 1995, 20, 3365–3366.

[5] Geissler, P.; Klapötke, T. M.; Kroth, H. J. Spectrochim Acta 1995, 51, 1075–1078.

[6] Hargattai, M.; Molnar, J.; Klapötke, T. M.; Tornieporth-Oetting, I. C.; Kolonits, M.; Hargattai, I. J Phys Chem 1994, 98, 10095–10097.

[7] Hargattai, M.; Tornieporth-Oetting, I. C.; Klapötke, T. M.; Kolonits, M.; Hargattai, I. Angew Chem Int Ed Engl 1993, 32, 759–761.

[8] Buzek, P.; Klapötke, T. M.; Schleyer, P. v. R.; Tornieporth-Oetting, I. C.; White, P. S. Angew Chem Int Ed Engl 1993, 32, 275–277.

[9] Sommer, F. Ber Dtsch Chem Ges 1915, 48, 1833–1844.

[10] Browne, A.; Hobl, A. J Am Chem Soc 1922, 44, 2106–2116.

[11] Browne, A.; Hobl, A. J Am Chem Soc 1922, 44, 2315–2320.

[12] Currier, A.; Browne, A. J Am Chem Soc 1922, 44, 2849–2854.

[13] Browne, A.; Audrieth, L. J Am Chem Soc 1927, 49, 917–925.

[14] Audrieth, L.; Smith, G.; Browne, A. J Am Chem Soc 1927, 49, 2129–2133.

[15] Leite Manzano, M. F.; Tfouni, E.; Franco, D. W. Polyhedron 1986, 5, 2119–2120.

[16] Conti, M.; Franco, D. W.; Trisic, M. Inorg Chim Acta 1986, 113, 71–74.

[17] Neves, E. A.; Franco, D. W. J Inorg Nucl Chem 1974, 36, 3851–3854.

[18] Neves, E. A.; Franco, D. W. J Inorg Nucl Chem 1975, 37, 277–281.
[19] Neves, E. A.; Milcken, N.; Franco, D. W. J Inorg Nucl Chem 1981, 43, 2081–2086.
[20] Smith, G.; Warttman, P.; Browne, A. J Am Chem Soc 1923, 45, 2604–2613.
[21] Perman, C. A.; Gleason, W. B. Acta Crystallogr Sect C 1991, 47, 1018–1021.
[22] Klapötke, T. M.; White, P. S., Heteroatom Chem 1997, 8, 267–271.
[23] Tornieporth-Oetting, I. C.; Klapötke, T. M. In Inorganic Experiments; Woolins, J. D., Ed.; VCH Verlagsgesellschaft: Weinheim, 1994; p S 217.
[24] (a) Sheldrick, G. M. SHELXS-86, Structure Solving Program for Crystal Structure Determination; University of Göttingen: Göottingen, Germany, 1986; (b) Sheldrick, G. M. SHELXS-93, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1993.
[25] Hahn, T., Ed. International Tables for X-ray Crystallography; Kynoch: Birmingham, England, 1974; Vol. IV.
[26] Motherwell, S. Pluto Plotting; University Chemical Laboratory: Cambridge, England, 1978.
[27] Klapötke, T. M., Tornieporth-Oetting, I. C., Nichtmetallchemie; VCH: Weinheim, 1994; Appendix C1.
[28] Johnson, D. A. Some Thermodynamic Aspects of Inorganic Chemistry, 2nd ed.; Cambridge University Press: Cambridge, England, 1982.
[29] (a) Morris, D. F. C. Struct Bonding 1968, 4, 63; (b) Morris, D. F. C. Struct Bonding 1969, 6, 157.
[30] Klapötke, T. M., Tornieporth-Oetting, I. C., Nichtmetallchemie; VCH: Weinheim, 1994; 99–100.