# Preparation and Crystal Structure of Tetraphenylphosphonium Triiodotetrabromide $[PPh_4][I_3Br_4]$

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*Received March 7, 2000*

Tetraphenylphosphonium triiodotetrabromide $[PPh_4][I_3Br_4]$ is obtained by the reaction of tetraphenylphosphonium bromide with iodine monobromide. It is the first example of an iodine rich, seven-membered polybromide. $[PPh_4][I_3Br_4]$ crystallizes triclinic in the space group $P\bar{1}$ with $a = 10.947(1)$ Å, $b = 11.945(1)$ Å, $c = 12.896(1)$ Å, $\alpha = 66.80(1)°$, $\beta = 77.21(1)°$, $\gamma = 85.73(1)°$, and two formula units per unit cell. The final $R$ indices $[I > 4\sigma(I)]$ are R1 = 0.0362 and wR2 = 0.0944.

## Introduction

In opposition to the group of polyiodides, polybromides are a still not well-explored field of research. Many crystal structures of salts are known, which contain anions such as $I_x^-$ ($x = 3, 5, 7$).[1−4] These anions show a great variety of geometry, depending on the structure and bulkiness of the cations. In general, polyiodide anions that contain five or more atoms are stabilized by cations such as $R_4N^+$ or $R_4P^+$, where R is a bulky organic group. In 1985, Parlow and Hartl reported the synthesis and crystal structure of $[BPH][I_2Br_3]$ ([BPH]: 2,2′-bipyridylium), the first known crystal structure of a five-membered polybromide.[5] The anion is V-shaped like $I_5^-$ or $I_2Cl_3^-$.[6] Robertson et al. showed by ab initio calculations that the total electronic 6-311G* energy for a V-shaped $Br_5^-$ is just slightly lower than that found for the linear one.[7] They reported that, for $Br_7^-$, the trihedral structure ($C_{3v}$ symmetry) has a minimum in energy. Furthermore, they obtained the crystal structure of $Br_8^{2-}$, a nearly Z-shaped anion.[7] It shows similarity to $I_8^{2-}$ and yields hope to synthesize further polybromides in analogy to polyiodides.

Since no crystal structure of a seven-membered polybromide anion existed, we tried to obtain $Br_7^-$ or mixed anions like $I_nBr_{7-n}^-$ ($n = 1−6$). In this work, we report the synthesis and crystal structure of $[PPh_4][I_3Br_4]$.

## Experimental Section

**CAUTION!** IBr is sensitive to moisture. Skin contact should be avoided because hydrolysis leads to HBr, which causes burns.

All synthetic work and sample handling was performed using standard Schlenck techniques and a standard glass vacuum line. Nonvolatile materials were handled under dry nitrogen. Infrared spectra were recorded on a Bruker IFS 113v spectrophotometer. Spectra of dry powders were obtained in an IR cell with CsBr plates coated with the pure sample.[8] Raman spectra were recorded on a Jobin Yvon T64000 spectrometer by using an $Kr^+$ laser (647.1 nm, Spectra Physics). The spectra were recorded in glass cells at room temperature.[9] Single crystals were placed in Lindemann capillaries in a stream of dry nitrogen, and an X-ray diffraction study was carried out by using a Nonius Kappa CCD diffractometer.

**Preparation of $[PPh_4][I_3Br_4]$. (a) Reaction between IBr and $[PPh_4][Br]$.** $[PPh_4][Br]$ (0.84 g, 2 mmol) was brought into a dry glass vessel with greaseless stopcocks (Young) and diluted in 20 mL of $CH_2Cl_2$. Then IBr (1.30 g, 6 mmol) was added and the mixture held at room temperature over a period of 24 h. After removal of the volatile materials under vacuum at −5 °C the formation of a dark red solid was observed. $[PPh_4][I_3Br_4]$ is sensitive to moisture and decomposes at 78 °C. For crystallization it was diluted in $CH_2Cl_2$, and the resulting single crystals were stored under dry nitrogen at 20 °C.

**(b) Reaction between IBr and $[PPh_4][Cl]$.** $[PPh_4][Cl]$ (0.75 g, 2 mmol) was brought into a dry glass vessel with greaseless stopcocks (Young) and diluted in 20 mL of $CH_2Cl_2$. Then IBr (2.10 g, 10 mmol) was added and the mixture held at room temperature over a period of 24 h. After removal of the volatile materials under vacuum at −5 °C the formation of two different solids, a dark red and a yellow one, was observed. The resulting dark red crystals were identified as $[PPh_4][I_3Br_4]$ and stored under dry nitrogen at 25 °C. A structure elucidation of the yellow crystals characterized them as $[PPh_4][ICl_2]$, which crystal structure will be described elsewhere.[10]

## Results and Discussion

**Formation of $[PPh_4][I_3Br_4]$.** $[PPh_4][I_3Br_4]$ is obtained by the reaction of IBr with $[PPh_4][Br]$ (eq 4) or $[PPh_4][Cl]$, respectively. The synthesis using $[PPh_4][Cl]$ is, in our opinion, a three-step reaction. The first step is the formation of $[PPh_4][ClIBr]$. It seems that the tetraphenylphosphonium cation is not suitable to stabilize $ClIBr^-$ under these conditions, and therefore it decomposes to $[PPh_4][Br]$ and ICl. At first sight this reaction is unusual and $ClIBr^-$ would be expected to decompose into the starting materials IBr and $Cl^-$.[11] A comparison of the bond energies of I−Cl (210 kJ mol$^{-1}$) and I−Br (178 kJ mol$^{-1}$) shows that the formation of I−Cl is favored. It is likely that removing ICl by reaction with $Cl^-$ to give $ICl_2^-$ (eq 3) shifts equilibrium 2 to the right side. Finally, $[PPh_4][Br]$ reacts with IBr to $[PPh_4][I_3Br_4]$ (eq 4).[12]

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10.1021/ic000257y CCC: $20.00

**Table 1.** X-ray Diffraction Data of $[PPh_4][I_3Br_4]$

| | | | |
|---|---|---|---|
| space group | $P\bar{1}$ | $Z$ | 2 |
| $a$, Å | 10.947(1) | fw, g mol$^{-1}$ | 1039.71 |
| $b$, Å | 11.945(1) | $\mu$, cm$^{-1}$ | 84.55 |
| $c$, Å | 12.896(1) | $T$, °C | 25(2) |
| α, deg | 68.80(1) | $\lambda$, Å | 0.71069 |
| $\beta$, deg | 77.21(1) | $R^a$ $[I > 2\sigma(I)]$ | R1 = 0.0362, wR2 = 0.0944 |
| $\gamma$, deg | 85.73(1) | | |
| vol, Å$^3$ | 1511.3(2) | $R^a$ (all data) | R1 = 0.0779, wR2 = 0.1207 |
| $\rho_{calcd}$, g cm$^{-3}$ | 2.285 | | |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. Refinement method: full-matrix least-squares calculations based on $F^2$.

$$[PPh_4][Cl] + IBr \xrightarrow{25\ °C} [PPh_4][ClIBr] \qquad (1)$$

$$[PPh_4][ClIBr] \xrightarrow{25\ °C} [PPh_4][Br] + ICl \qquad (2)$$

$$[PPh_4][Cl] + ICl \xrightarrow{25\ °C} [PPh_4][ICl_2] \qquad (3)$$

$$[PPh_4][Br] + 3\ IBr \xrightarrow{25\ °C} [PPh_4][I_3Br_4] \qquad (4)$$

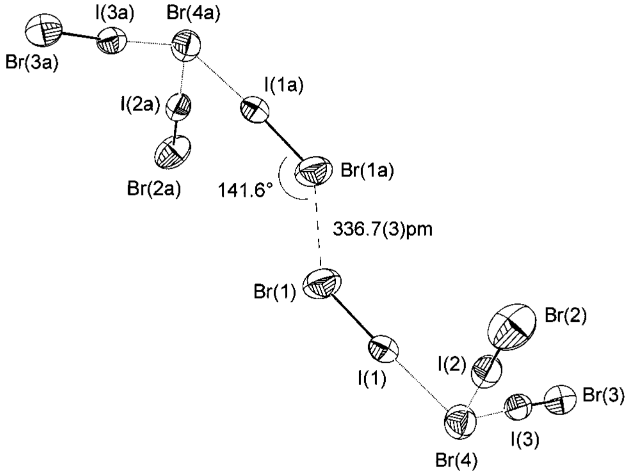

**Figure 1.** Projection of two $I_3Br_4^-$ anions. The anions are linked to dimers by an interionic Br−Br contact. Symmetry transformation is a = −$x$ + 2, −$y$ + 1, −$z$ + 2. Thermal ellipsoids are drawn at the 50% probability level.

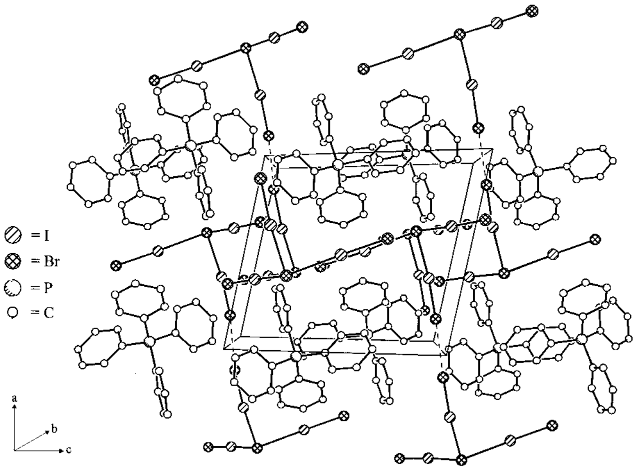

**Figure 2.** View of the unit cell of $[PPh_4][I_3Br_4]$ in $b$-orientation. The ions are arranged in alternating layers parallel to the $b$−$c$ plane. The anions layers are linked by interionic Br−Br contacts with a length of 3.367(3) Å.

The formation of $[PPh_4][I_3Br_4]$ under these conditions is an example of an uncommon but reasonable halogen exchange. Future studies will have to show whether the synthesis of a seven-membered interhalogen anion with chloride at the central position is possible.

**Crystal Structure of $[PPh_4][I_3Br_4]$.** $[PPh_4][I_3Br_4]$ crystallizes triclinic in the space group $P\bar{1}$ with $a$ = 10.947(1) Å, $b$ = 11.945(1) Å, $c$ = 12.896(1) Å, α = 66.80(1)°, $\beta$ = 77.21(1)°, $\gamma$ = 85.73(1)°, and two formula units per unit cell. The crystal structure was solved by direct methods, and the program X-PREP indicated no higher symmetry. A final refinement with anisotropic thermal parameters gave values of R1 = 0.0362 and wR2 = 0.0944. For the data reduction, structure solution, and refinement, programs in the SHELXTL package and PARST were used.[13−15] The crystal data are summarized in Table 1.

The anion has a distorted pyramidal structure with nearly $C_{3v}$ symmetry. It can be described as three IBr units linked by a bromide ion over the iodine atoms. Bond lengths and selected angles for $[PPh_4][I_3Br_4]$ are listed in Table 2. The central I−Br bond lengths with values of 2.936(1), 2.968(1), and 2.993(1) Å are significantly longer than the terminal ones of nearly 2.54 Å. The resulting Br−I−Br units are nearly linear with angles of 176°, and the three atoms are bonded by unsymmetrical 3-center-4-electron semi-ionic bonds. A similar linkage is found in $[PPh_4][I_7]$ and $[BPH][I_2Br_3]$.[4,5] The $I_2Br_3^-$ anion is V-shaped with a bromide ion in the central position.[5] The central I−Br bonds are significantly shorter and the terminal bonds longer than in $[PPh_4][I_3Br_4]$. In the Z-shaped $Br_5^+$ cation the terminal bonds are observed to be about 10% shorter than the central ones.[16,17] The symmetrical, linear $IBr_2^-$ anion has bond lengths of 2.695(2) Å.[18] This comparison shows a general tendency. The influence of the central ion toward the terminal units decreases with increasing number.

The I−Br−I angles in $I_3Br_4^-$ show large deviations from the ideal value of about 109°. This is probably caused by repulsive interactions of the lone pairs at the iodine atoms. There is only one interionic contact, between Br(1) and Br(1a), with a length of 3.367(3) Å, 9% below the sum of the van der Waals radii of 3.80 Å.[19] These contacts result in the formation of anion dimers (Figure 1). The same arrangement is found for $[PPh_4][I_7]$.[4]

The $PPh_4^+$ cation is tetrahedral with P−C bond lengths of overall 1.799(5) Å and shows no interionic interactions below the sum of the van der Waals radii.

As shown in Figure 2 the ions are arranged in alternating layers parallel to the $b$−$c$ plane. The anion layers are linked by interionic Br−Br contacts with lengths of 3.367(3) Å.

**Vibrational Spectra.** As shown by its crystal structure, $I_3Br_4^-$ has nearly $C_{3v}$ symmetry with 15 fundamental vibrations and the $PPh_4^+$ cation is tetrahedral. The assignment for the cation

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(15) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150988 ($PPh_4^+I_3Br_4^-$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax, +44-1223/336-033; E-mail, deposit@ccdc.cam.ac.uk).

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**Table 2.** Comparison of Calculated Bond Lengths (Å) and Selected Angles (deg) for $[PPh_4][I_3Br_4]$ with the Experimentally Observed Ones

| | expt | B3LYP/LANL2DZ | | expt | B3LYP/LANL2DZ |
|---|---|---|---|---|---|
| I(1)−Br(1) | 2.537(1) | 2.778 | Br(1)−I(1)−Br(4) | 174.82(3) | 178.10 |
| I(1)−Br(4) | 2.936(1) | 3.106 | Br(2)−I(2)−Br(4) | 177.9(3) | 178.09 |
| I(2)−Br(2) | 2.541(1) | 2.778 | Br(3)−I(3)−Br(4) | 176.28(3) | 178.06 |
| I(2)−Br(4) | 2.993(1) | 3.106 | I(1)−Br(4)−I(2) | 87.1(3) | 111.15 |
| I(3)−Br(3) | 2.539(1) | 2.778 | I(1)−Br(4)−I(3) | 103.26(3) | 111.81 |
| I(3)−Br(4) | 2.968(1) | 3.106 | I(2)−Br(4)−I(3) | 121.2(3) | 111.82 |
| Ø P−C | 1.799(5) | *a* | Ø C−P−C | 109.5(3) | *a* |
| Ø C−C | 1.378(8) | *a* | Ø C−C−C | 120.0(6) | *a* |

[a] Structural parameters of the cation were not calculated.

**Table 3.** Raman and IR Frequencies of $[PPh_4][I_3Br_4]$

| Raman ($T = 20$ °C) | IR ($T = 20$ °C) | assignment |
|---|---|---|
| 3060 (3) | | $\nu$ CH |
| 3054 (3) | | $\nu$ CH |
| 1587 (3) | 1586 (w) | $\nu$ CC |
| | 1485 (w) | |
| | 1435 (m) | |
| | 1339 (vw) | |
| 1303 (3) | 1313 (vw) | |
| 1269 (2) | | $\delta$ CH |
| 1192 (1) | 1183 (vw) | |
| 1165 (2) | 1157 (vw) | |
| 1111 (1) | 1108 (m) | $\delta$ CC |
| 1097 (2) | | $\delta$ CH |
| | 1070 (vw, sh) | |
| 1027 (3) | 1025 (vw) | |
| 1001 (6) | 996 (m) | ring breathing |
| 926 (1) | 924 (w) | $\delta$ CH |
| 850 (1) | 848 (vw) | $\delta$ CH |
| | 759 (m) | $\nu_{as}$ $C_4P$ |
| 750 (1) | 752 (m) | $\delta$ CH |
| 724 (1) | 722 (s) | $\delta$ CC |
| 681 (1) | 686 (s) | $\delta$ CC |
| 617 (1) | 618 (w) | $\nu_s$ $C_4P$ |
| | 527 (vs) | $\delta$ CC |
| | 453 (m) | $\delta$ CC |
| 308 (5) | | 2× $\nu_{as}$ $I_3Br$ |
| | 293 (w) | |
| 254 (6) | 250 (vw) | $\delta$ $C_4P$ |
| 228 (89) | 231 (vs) | $\nu$ IBr (terminal) |
| 215 (100) | 218 (s, sh) | $\nu$ IBr (terminal) |
| 190 (17) | 197 (vw) | 2× $\nu_s$ $I_3Br$ |
| 161 (28) | 165 (vs) | $\nu_{\alpha s}$ $I_3Br$ |
| | 116 (m) | |
| 101 (27) | 106 (m) | $\nu_s$ $I_3Br$ |
| | 97 (vw) | $\delta$ $IBr_2$ |
| | 90 (m) | $\delta$ $IBr_2$ |
| 72 (27) | | $\delta$ $I_3Br$ |
| 61 (35) | | lattice mode |
| 51 (45) | | lattice mode |

was made on the basis of other reports on salts containing $PPh_4^+$.[20,21] Frequencies and assignments are listed in Table 3.

For $I_3Br_4^-$, the $I_3Br$ symmetric and antisymmetric stretching modes are observed at around 103 and 163 $cm^{-1}$, respectively. The I−Br stretching modes of the terminal units are assigned to the strong IR and Raman bands between 215 and 231 $cm^{-1}$. Considering that the I−Br bonds are slightly elongated, this is in good accordance with the value of 268 $cm^{-1}$ reported for IBr.[22] The bending modes, $\delta$ $IBr_2$ and $\delta$ $I_3Br$, are observed between 72 and 97 $cm^{-1}$. Since these vibrations are expected to exhibit similar frequencies and intensities, a reverse assignment is also possible.

**Table 4.** NBO Delocalization Energies (kcal $mol^{-1}$) for the B3LYP/LANL2DZ Optimized $I_3B_4^-$ Anion[a]

| | $n_1$, Br(4) | $n_2$, Br(4) | $n_3$, Br(4) | $n_4$, Br(4) | $\Sigma$ |
|---|---|---|---|---|---|
| $\sigma^*_{I(1)-Br(1)}$ | 1.87 | 5.94 | 18.20 | 5.63 | 31.64 |
| $\sigma^*_{I(2)-Br(2)}$ | 1.87 | 5.94 | 17.35 | 6.50 | 31.66 |
| $\sigma^*_{I(3)-Br(3)}$ | 1.87 | 5.99 | *b* | 23.73 | 31.59 |
| $\Sigma$ | 5.61 | 17.87 | 35.55 | 35.86 | |

[a] The numbers give the second-order perturbation estimate of the $n_{Br} \rightarrow \sigma^*_{I-Br}$ delocalization energies $E^{(2)}_{n\rightarrow\sigma^*}$ from four Br(4) lone pairs into three I−Br antibonds. [b] The interaction energy falls short of the default threshold of 0.5 kcal $mol^{-1}$.

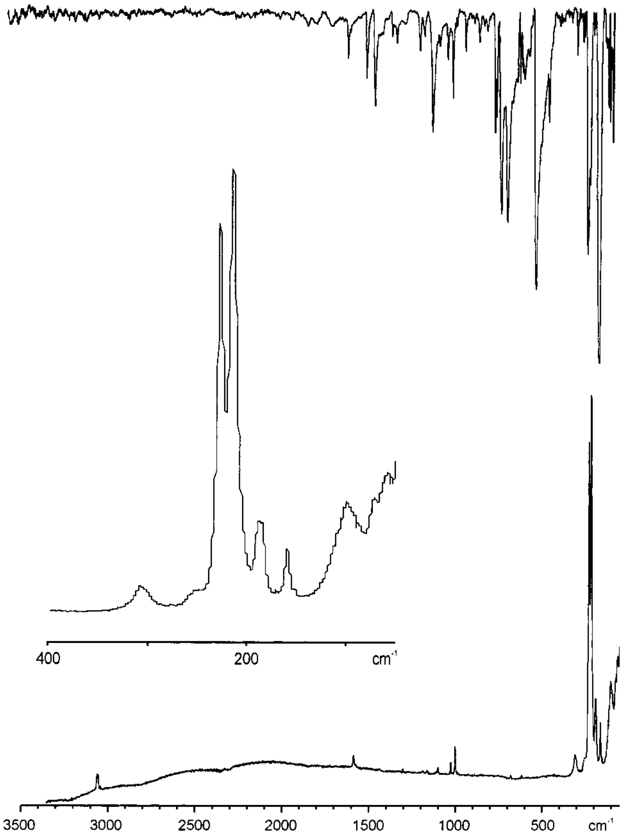

**Figure 3.** For $[PPh_4][I_3Br_4]$: (top) Raman and (bottom) IR spectra. Inset: part of the Raman spectrum on an enlarged scale.

**Quantum Mechanical Calculations.** The quantum mechanical calculations for the $I_3Br_4^-$ anion were performed at the B3LYP density functional level of theory using the Gaussian 94 program.[23] The calculations were carried out with a LANL2DZ basis set.[24] The B3LYP structure of the anion is nearly tetrahedral ($C_{3v}$) with I−Br−I angles of about 111°. The Br(4)−I bond lengths show nearly identical values of about 3.107 Å, and for the terminal I−Br bonds a length of 2.778 Å is calculated. A comparison to the experimentally observed bond lengths is given in Table 2. The calculated terminal and central

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bond lengths are about 9% and 5% longer than those found in the crystal structure. For the optimized B3LYP/LANL2DZ molecular structure, the wave functions were analyzed by the natural bond orbital (NBO) method, a standard program option of Gaussian 94.[25−27] The charge delocalization from a filled lone pair $n_{Br}$ of the donor Br(4) into an adjacent unfilled antibonding orbital $\sigma^*_{I-Br}$ of the acceptor I−Br leads to an energy stabilization that can be estimated from simple perturbation theory considerations.[27] The stabilization energies $\Delta E^{(2)}$ $(n_{Br} \rightarrow \sigma^*_{I-Br})$ are given in Table 4. The four bromide lone pairs ($n_{Br}$) donate charge into the I−Br antibonding orbitals ($\sigma^*_{I-Br}$), thus weakening all terminal I−Br bonds and resulting in three unsymmetrical 3-center-4-electron, semi-ionic bonds. The four lone pairs of Br(4) have different overlaps with the antibonding orbitals caused by their orientation as shown in Figure 4. Lone pair $n_1$, Br(4) donates only trace amounts, $n_2$, Br(4) a little, and the other two lone pairs large amounts of charge into the respective antibonds, contributing in different ways to the weakening of the terminal I−Br bonds. The total charge transfer into each antibond coming from different lone pairs is similar, resulting in three nearly equivalent Br(4)−I−Br units.

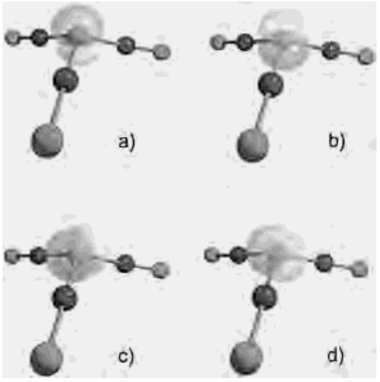

**Figure 4.** Projection of the four electron pairs of the central bromine Br(4): (a) LP1 Br(4); (b) LP2 Br(4); (c) LP3 Br(4); (d) LP4 Br(4).

**Acknowledgment.** This work was supported by the Fonds der Chemischen Industrie.

**Supporting Information Available:** One X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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