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**Polyhalogen Anions**

# Structural Evidence for Undecabromide $[Br_{11}]^-$**

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*Dedicated to Professor Werner Uhl on the occasion of his 60th birthday*

Among all known polyhalides, the chemistry of the iodine compounds has long been known and has been investigated extensively. Already in 1870 Jørgensen[1] discovered that triiodide was formed by mixing potassium iodide with iodine in an alcoholic solution. To date many examples of different mono-, di-, tri-, and tetraanions are known.[2] Focusing on the polyiodide monoanions, only compounds up to $[X_9]^-$ have to the best of our knowledge been structurally characterized. In 2011 Groessl et al. observed the first higher polyiodides $[I_{11}]^-$, $[I_{13}]^-$, and $[I_{15}]^-$ by mass spectrometry.[3] They mixed [PMIM]I (1-propyl-3-methylimidazolium) with the appropriate amount of iodine, diluted it in acetonitrile, and analyzed this mixture by ESI-MS. To confirm the observed fragmentation pathways, they calculated the stable structures for $[I_{2n+1}]^-$ ($n = 1$–7) at the DFT level. The observed compounds in this gas-phase experiment have the highest ratio of elements to charge of any previously studied polyhalides.

Regarding the lighter and more reactive homologue of the halogens, bromine, many fewer examples are known. Linear $[Br_4]^{2-}$,[4] Z-shaped $[Br_8]^{2-}$,[5] ring-shaped $[Br_{10}]^{2-}$,[6] and the recently found $[Br_{20}]^{2-}$ [7,8] are examples of known polybromide dianions.[9] Among the polybromide monoanions, only $[Br_3]^-$ has been known for a long time. Indeed, Chattaway and Hoyle[10] discussed already in 1923 the existence of higher polybromide monoanions but until 2010 there has been neither vibrational spectroscopy nor X-ray diffraction evidence for higher polybromides, such as $[Br_5]^-$, $[Br_7]^-$, and $[Br_9]^-$.[11] In 2011 our group reported the evidence for the structure of a higher polybromide monoanion $[NPr_4][Br_9]$.[12] Shortly thereafter Feldmann et al. synthesized and characterized $[P(Ph)_3Br][Br_7]$ in ionic liquids,[8] and very recently Himmel et al. reported on the structure of $[Br_5]^-$.[13] Beyond these polybromide anions also polychloride and fluoride anions have been characterized by IR and Raman spectroscopy. In the case of polychloride monoanions, $[Cl_3]^-$,[14] $[Cl_3\cdots Cl_2]^-$,[15] $[Cl_5]^-$,[16] and $[Cl_9]^-$[16] are known, whereby the latter exists only under cryogenic conditions. This holds also for the only example of a polyfluoride anion $[F_3]^-$, which was characterized by matrix-isolation spectroscopy in argon and neon matrices at 4 K.[17]

Herein, we report the largest structurally known polyhalide monoanion undecabromide $[Br_{11}]^-$, which was recently predicted to be thermochemically stable by 297.0 kJ mol$^{-1}$ against the elimination of five $Br_2$ molecules at SCS-MP2/def2-TZVPP level.[12] The reaction of bis(triphenylphosphine)iminium bromide (PPNBr) with an excess of bromine led to $[PPN][Br_{11}\cdot Br_2]$, which is the highest known ratio of elements to charge of any structural known polyhalide compound.

The single-crystal X-ray structure shows that the salt $[PPN][Br_{11}\cdot Br_2]$ crystallizes in the triclinic space group $P\bar{1}$. Similar to other polyhalides, $[Br_{11}\cdot Br_2]$ is built of the two building blocks $Br^-$ and $Br_2$. A central $Br^-$ is coordinating five $Br_2$ molecules (Figure 1). The charge of the central $Br^-$ is donated into the antibonding LUMOs of the end-on coordinated $Br_2$ molecules, thereby weakening and elongating their Br–Br bond by an average of 5.9 pm compared to molecular $Br_2$.[18]

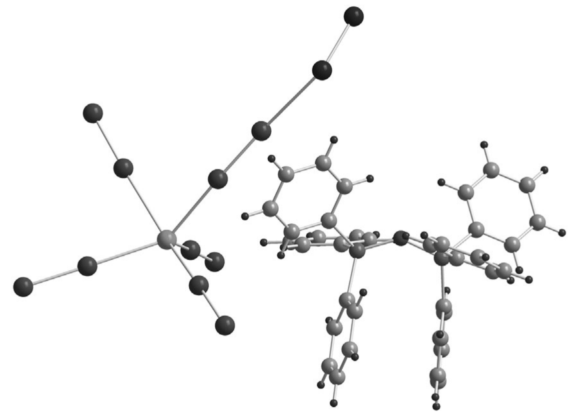

***Figure 1.*** Molecular structure of $[PPN][Br_{11}\cdot Br_2]$ in the solid state. Five bromine molecules are coordinated to a central $Br^-$ to form the polybromide anion $[Br_{11}]^-$.

The $[Br_{11}]^-$ units are linked to form chains in which a sixth bromine molecule is embedded. These chain-linking Br–Br contacts are much longer than the contacts in the $[Br_{11}]^-$ units but nevertheless shorter than twice the bromine van der Waals radius of 370 pm. The contacts between the $[Br_{11}]^-$ units and the embedded bromine molecule is also shorter than 370 pm, but the embedded $Br_2$ molecule is not linked to a $Br^-$ anion and the Br-Br distance (0.31 pm) is practically not elongated (Table 1, Figure 2). Therefore this $Br_2$ molecule is not attributed to the polyhalide monoanion.

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*Table 1:* Measured and computed distances [pm] of $[Br_{11}{\cdot}Br_2]^-$.[a]

| Distance | Exp. | SCS-MP2[b] | BP86 | PBE0[b] | BHLYP[b] |
|---|---|---|---|---|---|
| Br1–Br2 | 294.55(3) | 296.2/*301.4* | 292.0 | 293.1/*295.0* | 303.6/*304.7* |
| Br2–Br3 | 233.31(3) | 234.0/*238.6* | 241.7 | 234.5/*236.4* | 233.6/*235.7* |
| Br1–Br4 | 308.09(3) | 299.1/*305.1* | 298.2 | 298.2/*299.8* | 307.4/*309.0* |
| Br4–Br5 | 232.02(3) | 233.3/*237.7* | 239.8 | 233.2/*235.1* | 232.8/*234.8* |
| Br1–Br6 | 290.71(3) | | | | |
| Br6–Br7 | 233.52(3) | | | | |
| Br1–Br8 | 303.97(3) | | | | |
| Br8–Br9 | 232.76(3) | | | | |
| Br1–Br10 | 295.27(3) | | | | |
| Br10–Br11 | 233.02(3) | | | | |
| Br11–Br12 | 328.84(3) | | | | |
| Br12–Br13 | 227.31(5)[c] | | | | |
| Br3–Br12 | 366.86(4) | | | | |
| Br5–Br7 | 334.88(3) | | | | |

[a] For atom numbering, see Figure 2. [b] Square-pyramidal structures computed at DFT-D3 and ab initio level using the def2-TZVPP and *def-SV(P)* basis set. [c] Br13 is disordered; only the values for the major domain are discussed.

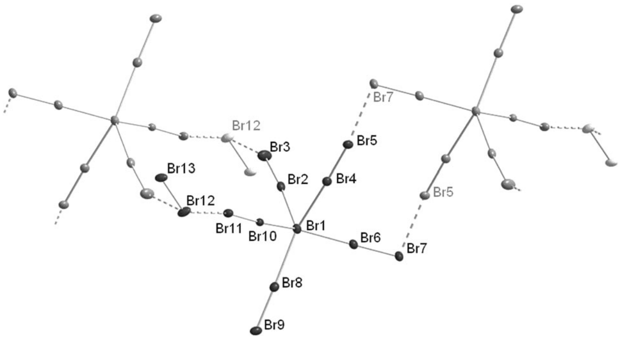

***Figure 2.*** Chain-like structure of $[PPN][Br_{11}{\cdot}Br_2]$ in which the $[Br_{11}]^-$ units are connected by embedded $Br_2$ molecules. Ellipsoids are set at 50% probability and cations are omitted for clarity.

According to the procedure described by Addison et al.,[19] the coordination of the five ligand $Br_2$ molecules around the central $Br^-$ is almost square pyramidal in the present compound (Figure 1). The geometric parameter $\tau = (\beta - \alpha)/60°$, where $\beta$ and $\alpha$ are the largest angles in the coordination sphere, is determined to be 0.18 (for square pyramidal geometries ($C_{4v}$) $\tau = 0$; for trigonal pyramidal geometries ($D_{3h}$) $\tau = 1$). For more structural details, such as angles, see Table S7 in the Supporting Information.

Based on the previous gas-phase investigation of polyiodides, we compare our observed crystal structure of the $[Br_{11}]^-$ with the computed structure of $[I_{11}]^-$. It was found at the B3LYP level that the undecaiodide structure has $C_s$ symmetry (Figure 3, **A**). This is in contrast to our obtained crystal structure, which shows an almost square-pyramidal arrangement of the $Br_2$ units around the central $Br^-$, which is also in agreement with the quantum-chemical results of Pichierri.[20] Indeed if we optimize the most probable structures in $C_s$, $D_{3h}$, or $C_{4v}$ symmetry by DFT at the B3LYP level, we observe that the previously found structure of the $[I_{11}]^-$ in $C_s$ symmetry is the lowest in energy for both undecahalides of iodine and bromine (Figure 3).

However, if we apply an ab initio method, such as SCS-MP2, which performed very well in previous investigations of polyhalides, including $[Br_{11}]^-$, we observe the $D_{3h}$ and $C_{4v}$ structures to be lower in energy (see the Supporting Information for reference [12]). This discrepancy is based on two facts: the lack of dispersion in the DFT treatment of polyhalogens, and the direct Hartree–Fock (HF) exchange in the DFT treatment (Figure 4). It is also seen that there is almost no energetic preference between the trigonal-bipyramidal and square-pyramidal structure, which is in accordance with other known five-coordinate complexes. However, the intermolecular exchange between these two isomers by Berry pseudo rotation is hindered in the solid. In this case the crystal packing effects force the molecular structure of the $[Br_{11}]^-$ anion to be nearly square-pyramidal (see above). This is in line with the systematic investigation of the influence of the cation size to the crystal structure of the polybromide anion.[11]

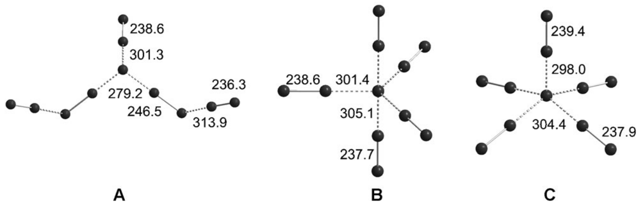

***Figure 3.*** Computed $[Br_{11}]^-$ structures at the SCS-MP2/def2-SV(P) level. **A**: $C_s$ symmetry, **B**: $D_{3h}$ symmetry, and **C**: $C_{4v}$ symmetry.

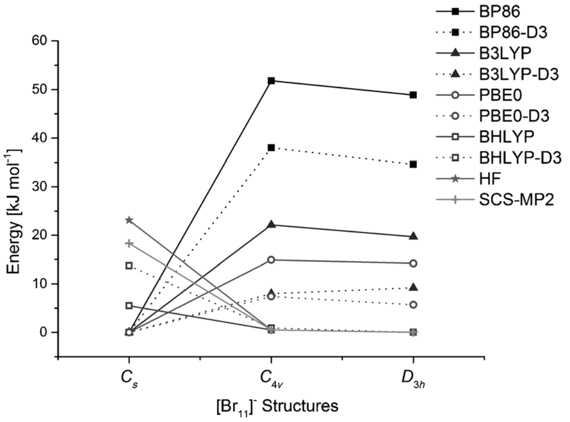

***Figure 4.*** Energy diagram of different quantum-chemical methods applied to the three minima for the structures of $[Br_{11}]^-$ in $C_s$, $C_{4v}$, and $D_{3h}$ symmetry.

As we have shown before, Raman spectroscopy is the method of choice for the investigation of such polyhalides.[12,16,22] Our experimental spectrum shows four Raman bands above 200 cm$^{-1}$, of which three bands agree well with our quantum-chemical calculations at SCS-MP2 level (Table 2 and Figure 6). The fifth band ($\nu_1$) is not found in our computed spectrum, it is assigned to the stretching mode of the embedded bromine molecule (Br12–Br13), which was not considered in our quantum-chemical description. The wavenumber of 297 cm$^{-1}$ is in fair agreement with experimentally observed solid bromine (308 cm$^{-1}$; Table 2). The vibrational modes $\nu_{2-4}$ in the range 286–264 cm$^{-1}$ correspond to the stretching modes of the coordinated $Br_2$ units. Both modes $\nu_3$ and $\nu_4$ are close to each other, so that we only observe a shoulder for $\nu_4$ on $\nu_3$ in the experimental spectra. The $\nu_5$ band is the deformation mode of $Br^-\cdots Br_2$ (Figure 5).

***Table 2:*** Measured and computed Raman frequencies [cm$^{-1}$] of $[Br_{11}\cdot Br_2]$ and molecular $Br_2$.

| Vibration | Exp. | SCS-MP2/ def2-TZVPP Structure C | SCS-MP2/ def-SV(P) Structure B |
|---|---|---|---|
| $\nu$ ($Br_{2g}$) | 325[21] | 334 | 310 |
| $\nu$ ($Br_{2s}$) | 308 | | |
| $\nu_1$ ($Br_2$) | 297 | | |
| $\nu_2$ | 286 | 295 | 277 |
| $\nu_3$ | 269 | 278 | 259 |
| $\nu_4$ | 264 | 271 | 255 |
| $\nu_5$ | | 95 | 108 |

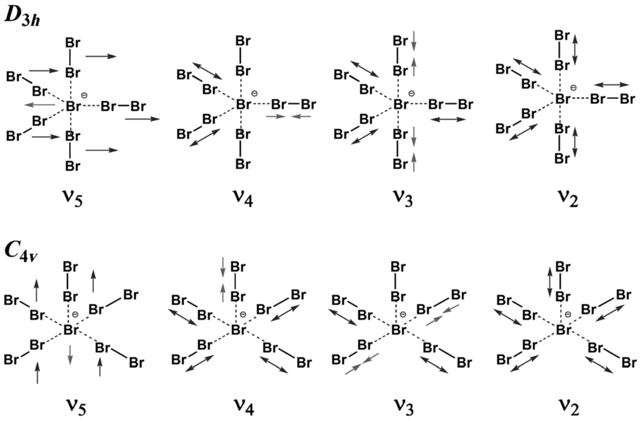

***Figure 5.*** The most intense Raman modes of the $[Br_{11}]^-$ anion at $D_{3h}$ and $C_{4v}$ symmetry.

These modes have been computed to be almost 170 cm$^{-1}$ below the $Br_2$ stretching modes of which the $\nu_5$ mode is by far the most intense. This $\nu_5$ band in the experimental spectrum is overlaid by the longitudinal and transversal vibrations of the solid, which usually appear below 150 cm$^{-1}$. In any case, our experimental and computed spectra show good agreement in the 300–200 cm$^{-1}$ region and support our experimental findings (Figure 6).

In conclusion, we reported herein the first structural evidence of a undecabromide $[Br_{11}]^-$ stabilized by a bis(triphenylphosphine)iminium cation. It shows an almost square-pyramidal arrangment in the crystal structure. This outcome is supported by quantum-chemical calculations at ab-initio SCS-MP2 level, where the trigonal-pyramidal and also the square-pyramidal structure were shown to be the lowest in energy, indicating a very shallow potential energy surface. Furthermore, we have shown that the description of polyhalides by DFT methods is problematic, which is most likely due to the lack of dispersion and direct HF exchange in the DFT treatment.

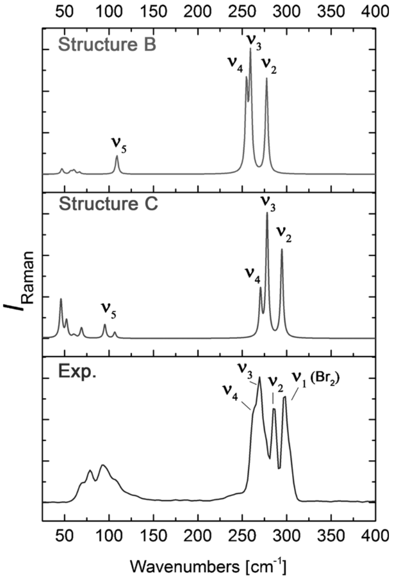

***Figure 6.*** Experimental and computed (SCS-MP2) Raman spectra for $[PPN][Br_{11}\cdot Br_2]$ and $[Br_{11}]^-$, respectively.

This novel anion is the highest known ratio of elements to charge of any structurally known polyhalide compound and is therefore an ideal benchmark molecule for the investigation of weak interactions.

## *Experimental Section*

[PPN]Br was synthesized as previously described.[23,24] The synthesis of $[PPN]^+[Br_{11}\cdot Br_2]^-$ was carried out in pure elemental bromine by adding or condensing bromine (Merck) to [PPN]Br in a 1:6 ratio, forming a red-brown liquid. After maintaining the reaction mixture at room temperature for several days, red-brown clusters of crystals of $[PPN][Br_{11}\cdot Br_2]$ were obtained. At room temperature, the crystals are only stable in the reaction mixture.

The FT-Raman spectra were recorded on a Bruker Vertex 70 spectrometer equipped with a RAM II module using a Ge detector cooled with liquid nitrogen. Raman spectra were recorded (back-scattering mode) at room temperature and also cooled with liquid nitrogen in flame-sealed glass capillaries (1064 nm, 10 mW power, resolution 4 cm$^{-1}$).

Crystal data for $[PPN]^+[Br_{11}\cdot Br_2]^-$: $C_{36}H_{30}Br_{13}N_1P_2$, $M_w = 1577.38$, triclinic, space group $P\bar{1}$, $a = 12.5230(2)$, $b = 12.6557(2)$; $c = 16.1176(3)$ Å, $\alpha = 104.5740(10)$, $\beta = 106.0260(10)$, $\gamma = 96.4340(10)°$, $V = 2330.48(7)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 2.248$ Mg m$^{-3}$, F(000) = 1476, $\lambda = 0.71073$ Å, $T = 100(2)$ K, absorption coefficient = 11.266 mm$^{-1}$, absorption correction: multi-scan, $T_{min} = 0.5003$, $T_{max} = 0.7469$. Data for the structure were collected on a Bruker SMART APEX2 CCD area-detector diffractometer with Mo$K_\alpha$ radiation. A single crystal has been taken directly from the reaction mixture coated at 0 °C with perfluoroether oil and mounted on a 0.1 mm Micromount. The structure was solved by direct methods in SHELXTL[25] and OLEX2[26] and refined by least squares on weighted $F^2$ values for all reflections. The final refinements converged at GooF = 1.024, $R1 = 0.0312$, and $wR2 = 0.0621$ for reflections ($I > 2\sigma(I)$), $R1 = 0.0506$, and $wR2 = 0.0667$ for all reflections. The hydrogen atoms were included in the refinement in calculated positions by a riding model. The graphical representations were prepared with Diamond.[27] CCDC 906333 ($[PPN]^+[Br_{11}\cdot Br_2]^-$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum-chemical calculations were performed at various levels of density functional theory (DFT) and at ab initio HF, SCS-MP2 level. The gradient-corrected BP86[28–32] functional, the hybrid functionals B3LYP,[28–31,33,34] PBE0,[28,29,35–37] and BHLYP[28,29,31,33,38] with 25 % and 50 % HF exchange admixture were used. The def-SV(P) and def2-TZVPP basis sets were used for bromine and iodine. All calculations were carried out with the Turbomole V6.3[39] program and the analytical gradient methods implemented therein. Structures have been fully optimized at DFT, HF, and SCS-MP2[40] level. The Grimme dispersion correction D3 as implemented in Turbomole was used.[41] Minima on the potential energy surface were characterized by harmonic vibrational frequency analyses, using numerical second derivatives based on energies and analytical gradients. We provide relative energies without zero-point vibrational corrections, as these do not alter the thermochemistry significantly.

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