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Polybromides

Structural Proof for a Higher Polybromide Monoanion: Investigation of $[N(C_3H_7)_4][Br_9]$**

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The chemistry of polyhalides, especially of polyiodides, has long been known.[1,2] The first systematic investigation of these anions goes back to Jörgensen[3] in 1870. Since these pioneering years, a great variety, mainly of polyiodides, have been investigated.[4–6] The lighter and more reactive halogens, bromine, chlorine, and fluorine, have been less explored which is probably due to the relative ease of handling iodine. However, in the past year, the investigation of lighter polyhalides has once again come into the focus of the scientific community. Feldmann et al. have reported the preparation of a 3D polybromide network $[C_4MPyr]_2[Br_{20}]$[7] in ionic liquids. A series of tetraethylammonium polybromides[8] was also investigated by Raman spectroscopy.[8] Moreover, the first free trifluoride monoanion was characterized by matrix-isolation spectroscopy under cryogenic conditions in argon and neon matrices.[9] All these recent reports indicate that our knowledge of polyhalides is still relatively limited and provides room for new discoveries.

The chemistry of polybromides is especially limited compared to the extensive chemistry of polyiodides.[1] Among the polybromide monoanions, only the $[Br_3]^-$ anion was fully characterized, including single-crystal X-ray diffraction.[10–12] All other known polybromide monoanions (penta, hepta, and nona) were only characterized by IR and/or Raman spectroscopy. Based on these data, their structures were only tentatively assigned. High level quantum-chemical calculations, which could support the structure assignment based on vibrational data for the nonabromide have not been performed. Only calculations at the HF level have been carried out but these do not provide definitive information because of the lack of electron correlation. By far the most prominent polybromides are dianions, such as $[Br_8]^{2-}$,[10] $[Br_{10}]^{2-}$,[13] and $[Br_{20}]^{2-}$[7] or polybromide networks[7,14–16] $[\{Br_3\}^-\cdot\frac{1}{2}Br_2]$, and $[(Br^-)_2\cdot 3Br_2]$. These compounds are not only of academic interest, they can be used for many practical applications such as zinc–bromine batteries,[17,18] water treatment,[19] or selective bromination reactions.[20] Furthermore, an application as redox couple in dye-sensitized solar cells (DSSC) is promising, a field which is a more and more important in energy generation.

Herein, we report the first synthesis of the nonabromide salt $[NPr_4][Br_9]$. The reaction of tetrapropylammonium bromide and excess bromine leads to the formation of brownish red crystals. These crystals are relatively stable and can even be handled briefly in air.

The single-crystal X-ray structure determination shows that the salt $[NPr_4][Br_9]$, crystallizes in the tetragonal space group $I\bar{4}$, Figure 1. Similar to other known polyhalides, the $[Br_9]^-$ structure is based on a central bromide anion Br^-, which is the donor of charge to end-on coordinated Br_2 Lewis acceptor molecules (Figure 2). The charge is donated into the antibonding LUMOs, thereby weakening the Br–Br bond of the coordinated Br_2 molecules. Indeed the bond length of the terminal Br_2 ligands is increased by 6.9 pm (235.0 pm) over molecular Br_2 (228.1 pm).[21] It is however still shorter than the calculated $[Br_2]^-$ bond of 286.2 pm at the CCSD(T)/aug-cc-pVTZ level. This $[Br_9]^-$ configuration differs from the known heavier homologues of the nonaiodides $[I_9]^-$ where three configurations were characterized $[\{I_3^-\}\cdot 3I_2]$, $[\{I_5^-\}\cdot 2I_2]$, or $[\{I_7^-\}\cdot I_2]$.[1] In addition to these distances, there are longer bonds of 339.5 pm between the $[Br_9]^-$ units. These bonds are also shorter than twice the bromine van der Waals radius of 370 pm. These longer contacts link the $[Br_9]^-$ units to a three-dimensional network (Figure 1).

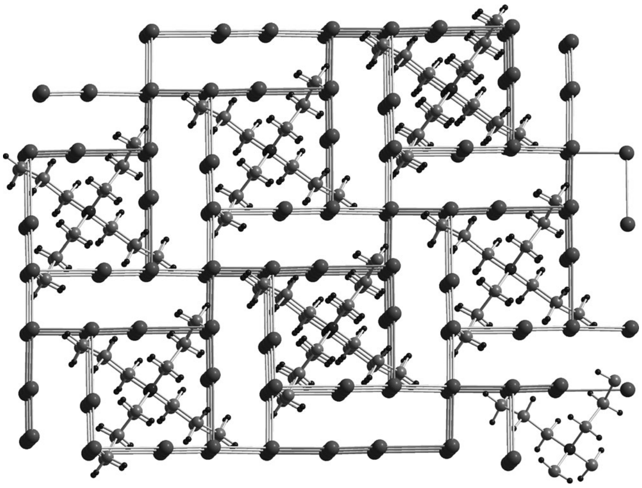

Figure 1. Three-dimensional network of the $[NPr_4][Br_9]$ complex in the tetragonal space group $I\bar{4}$.

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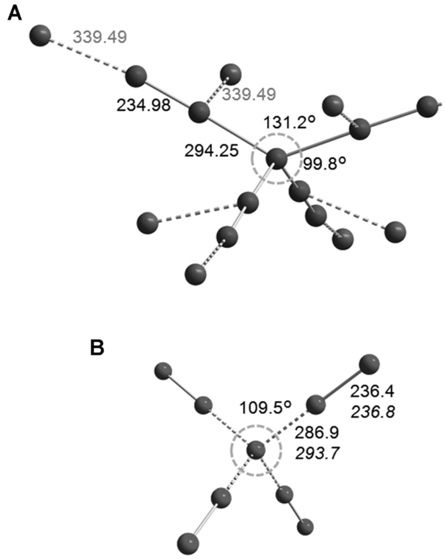

Figure 2. A) Crystal structure of the $[Br_9]^-$ unit. B) Optimized structure of $[Br_9]^-$ (T_d symmetry), MP2/def2-TZVPP (regular font), SCS-MP2/def2-TZVPP (*italic font*).

The investigation of the molecular units of $[Br_9]^-$ by quantum-chemical calculations gives more insights into the chemistry of this anion. Hence, all possible isomers were calculated at MP2 and HF level identifying the tetrahedral arrangement (T_d symmetry) of four Br_2 molecules around the bromide anion as the most stable isomer. This is in agreement with a previous investigation at HF level.[8] However, the former study has determined that the other isomer structures of **B** (C_{2v}), **E** (D_{3h}), and **F** (D_{4h}) are transition states or higher order saddle points (Figure 3). Furthermore, it was reported that no closed-ring structure was computed to be stable.[8] This is in contradiction to our calculations at MP2 level, where these isomers were computed as true minima on the hypersurface, using the same symmetry restrictions (Figure 3). This is also the case for the ring structures, for which we have computed the minimum structure **C** (C_{2v} symmetry) to be stable towards the elimination of one Br_2 by 29.4 kJ mol^{-1} at the MP2/def2-TZVPP level.

This discrepancy is mainly due to the lack of electron correlation in the HF method, while DFT methods have reproduced our MP2 results. Nevertheless, the $[Br_9]^-$ structure in the crystal, can in principle, be interpreted as a distorted tetrahedral structure. This observed deformation between the crystal and the gas-phase structure is mainly due to crystal packing effects. Indeed, successive scanning of the angle opening at different levels of theory has shown a very flat energy profile for a wide range of the bonding angle α allowing a broad range of configurations (Figure 4).

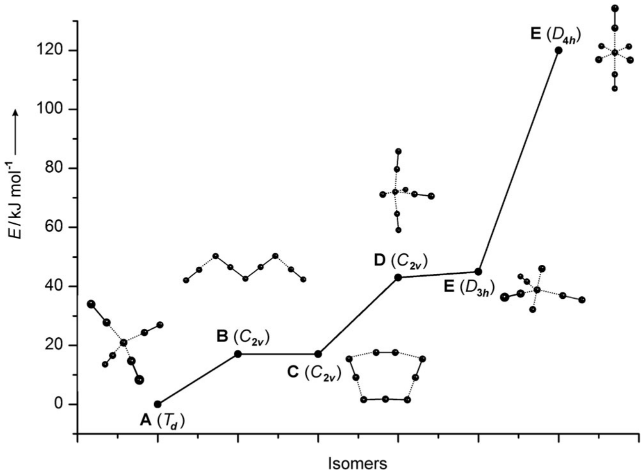

Figure 3. Computed potential energy diagram of $[Br_9]^-$ isomers at the RI-MP2/def2-TZVPP level. Values are energies in kJ mol^{-1} relative to the most stable isomer A; **A** 0, **B** 17, **C** 17, **D** 43, **E** 45, **F** 120 kJ mol^{-1}.

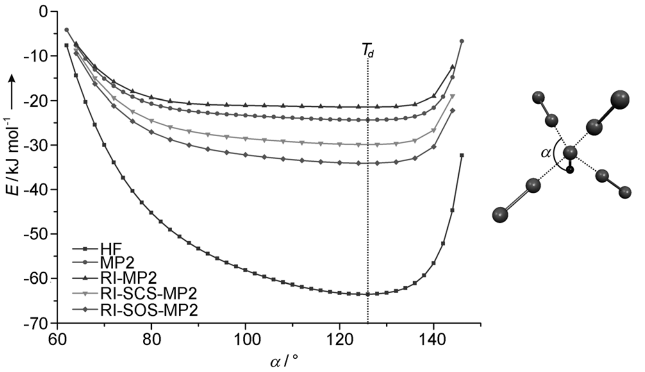

Figure 4. Energy profile of the $[Br_9]^-$ α-angle opening.

In any case, this relatively large crystal packing effect has almost no influence on the vibrational spectra of $[NPr_4][Br_9]$. Our polybromide sample has shown strong Raman scattering, indicating that Raman spectroscopy is the method of choice. The experimental and calculated ($[Br_9]^-$ in T_d symmetry) Raman spectra are in excellent agreement (Figure 5). Furthermore, owing to the electronic charge donation into the LUMO of the coordinated Br_2 unit and the subsequent

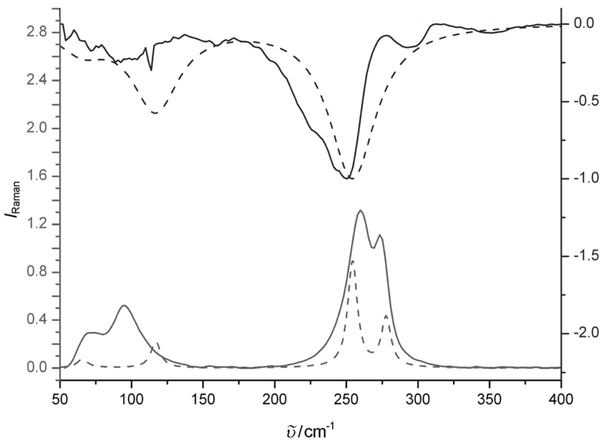

Figure 5. Comparison of experimental vibrational spectra (Raman continuous line, bottom; IR continuous line, top) and calculated spectra at RI-MP2/def2-TZVPP (Raman intensities at HF level) dashed lines (A_1 Raman 274 cm^{-1}, calcd 277 cm^{-1}; T_2 Raman exp. 259 cm^{-1}, calcd 255 cm^{-1}; IR exp. 250 cm and 113 cm^{-1} and calcd 254 and 116 cm^{-1}).

weakening of the Br–Br bond, we observe a red shift of coordinated Br_2 with respect to free Br_2 of 45 cm^{-1}.

Our sample shows relatively low bromine volatility, determined by visual inspection of the gas phase above the substance compared with elemental bromine. To investigate its thermal decomposition we applied thermogravimetric analysis (TGA) of $[NPr_4][Br_9]$. The melting point was measured to be only 37.5 °C (see Supporting Information). Thereafter we observe a continuous evaporation of bromine until 233.3 °C with the characteristic decomposition of $[NPr_4]Br$ at 264.3 °C (literature 265 °C). This low vapor pressure of Br_2 with its low melting point gives some evidence that it can be characterized as ionic liquid.

To put this observation of the bromine volatility of the nonabromide into perspective, we have investigated the thermochemical stability of several polybromide monoanions by quantum-chemical calculations (Table 1). The preferred decomposition channel of $[Br_3]^-$ is the elimination of Br_2 (127.4 $kJ\,mol^{-1}$) instead of $[Br_2]^-$ (207.4 $kJ\,mol^{-1}$), calculated at single-point CCSD(T)/def2-TZVPP level. The elimination energy of Br_2 decreases with the size of the polybromide monoanion from $[Br_3]^-$ to $[Br_{11}]^-$. The largest shift is computed between $[Br_3]^-$ and $[Br_5]^-$ from 127.4 to 56.3 $kJ\,mol^{-1}$, respectively. Further elimination of Br_2 from $[Br_7]$ or $[Br_9]$ was computed to be 43.0 and 36.7 $kJ\,mol^{-1}$ at SCS-MP2 level, respectively.

Table 1: Computed reaction energies ($kJ\,mol^{-1}$) of polybromide monoanions at various levels of theory based on RI-MP2/def2-TZVPP optimized structures.

Reaction[a]	MP2	SCS-MP2	SOS-MP2	CCSD	CCSD(T)
a) $[Br_3]^- \rightarrow Br_2 + Br^-$	138.5	126.9	121.1	114.3	127.4
b) $[Br_3]^- \rightarrow [Br_2]^- + Br$	229.1	214.8	207.6	186.7	207.4
c) $[Br_5]^- \rightarrow [Br_3]^- + Br_2$	66.1	55.6	50.4	47.0	56.3
d) $[Br_7]^- \rightarrow [Br_5]^- + Br_2$	51.1	43.0	39.0	38.5	43.6
e) $[Br_9]^- \rightarrow [Br_7]^- + Br_2$	43.8	36.7	33.2		
f) $[Br_{11}]^- \rightarrow [Br_9]^- + Br_2$	43.0	34.7	30.6		
g) $[Br_5]^- \rightarrow 2\,Br_2 + Br^-$	204.6	182.5	171.5	161.4	183.7
h) $[Br_7]^- \rightarrow 3\,Br_2 + Br^-$	255.8	225.6	210.5		
i) $[Br_9]^- \rightarrow 4\,Br_2 + Br^-$	299.6	262.3	243.7		
j) $[Br_{11}]^- \rightarrow 5\,Br_2 + Br^-$	342.6	297.0	274.2		

[a] Dissociation energies: a) DFT LSD-NL level 135.1 $kJ\,mol^{-1}$,[23] MP2 120.6 $kJ\,mol^{-1}$,[24] 159.2 $kJ\,mol^{-1}$;[25] b) DFT LSD-NL 200.7 $kJ\,mol^{-1}$,[23] 221.9 $kJ\,mol^{-1}$;[25] c) DFT LSD-NL 59.8 $kJ\,mol^{-1}$.[23]

Even the, to date, experimentally unknown $[Br_{11}]^-$ was calculated to be stable with respect to Br_2 elimination. This species shows two minimum configurations, which differ energetically by less than 1 $kJ\,mol^{-1}$. One configuration shows a square-pyramidal arrangement (C_{4v} symmetry) of five Br_2 molecules around one bromine anion and the second is computed to be trigonal bipyramidal with D_{3h} symmetry (see Supporting Information). It can also seen that further addition of bromine reaches an energetic plateau at $[Br_9]^-$ because extra coordination of bromine accounts for only approximately 35 $kJ\,mol^{-1}$ at the SCS-MP2 level, whereas earlier coordination of Br_2 stabilizes the polybromide monoanions far more (Table 1).

For comparison we have also investigated the thermochemistry of the corresponding polyiodide monoanions from $[I_3]^-$ to $[I_9]^-$. Although the structures of the higher polyiodides $[I_7]^-$ and $[I_9]^-$ in C_{3v} and T_d symmetry have not been observed experimentally, they are minima on the potential energy surface. Our calculations show that the polyiodide monoanions are marginally more stabilized by 5–10 $kJ\,mol^{-1}$ at SCS-MP2 level. The significance of dispersion interaction has been evaluated as well using the DFT-D3 dispersion correction of Grimme.[22] It is shown that the dispersion correction is for both halogens on the same level where it becomes more important for the larger compounds (Table SI3 in the Supporting Information). Furthermore, the importance of spin-orbit coupling on the thermochemical stability was evaluated by two-component BP86 calculations. It was found that this relativistic effect makes no significant contribution and can be neglected (Table SI3 in the Supporting Information). Note, the thermochemical data computed at the SCS-MP2 level is in excellent agreement with the CCSD(T) values, which allows a reliable thermochemical estimation even for larger polybromide networks (Table 1).

Such larger polybromide networks have been assumed to play an important role in the unusually high electrolytic conductivity of Br^-/Br_2 mixtures.[26] In these conductivity investigations of elemental bromine and iodine doped with corresponding anions in the solid and liquid phase, a Grotthuss-type mechanism has been supposed.[26–29] Based on these previous findings we have measured the conductivity of $[NPr_4][Br_9]$ at different temperatures ranging from 20 to 65 °C, (see Supporting Information). Even at 25.7 °C, where the measurement of the nonabromide is performed in its undercooled melt, we observed a surprisingly high value of 22.8 $mS\,cm^{-1}$. At 52 °C we reached an extreme value of 52.6 $mS\,cm^{-1}$, indicating that this high conductivity is based on a hopping mechanism of the Grotthuss-type where the charge is transferred by the $[Br_9]^-$ units [Eq. (1)].

$$[Br_9]^- + Br^- \rightarrow Br^-\text{-}Br_8 \cdots Br^- \rightarrow Br^- \cdots Br_8\text{-}Br^- \rightarrow Br^- + [Br_9]^- \qquad (1)$$

In conclusion, we report herein the first crystal structure and state-of-the-art quantum-chemical calculations of a higher polybromide monoanion. The structural deformation of $[NPr_4][Br_9]$ from the ideal tetrahedral arrangement (gas-phase structure) is due to crystal packing effects and was investigated by potential-energy scans around the bonding angle, indicating a very flat hypersurface. Raman and IR spectra of tetrapropylammonium nonabromide have been recorded, indicating that it was prepared in essentially quantitative yield.

Its facile preparation and handling at room temperature and in air could make this complex an ideal reagent for bromination reactions. Moreover based on its very high conductivity it could be used as liquid electrolyte in batteries or in DSSC applications; one essential part in DSSC applications is the usage of liquid electrolytes to reduce the dye cation. The most common electrolyte is iodide/triiodide (I^-/I_3^-) dissolved in, for example, acetonitrile or in ionic liquids.[30–32] This new redox couple (Br^-/Br_9^-) would open a larger potential window without the use of any extra solvent. Further investigations on polyhalides and their applications are continuing in our group.

Experimental Section

All experiments were performed using standard Schlenk techniques. By adding or condensing bromine (Merck) to tetrapropylammonium bromide (Acros Organics, 98 %) at 1:8 ratio, a red-brown liquid was obtained. After keeping the reaction mixture at room temperature for several days under an argon atmosphere, red-brown clusters of crystals of $[N(C_3H_7)_4][Br_9]$ were obtained.

The FT-Raman spectra were recorded on a Bruker Vertex 70 spectrometer equipped with a RAM II module using a liquid-nitrogen cooled Ge detector. Raman spectra were recorded (backscattering mode) at room temperature as well as cooled with liquid nitrogen in flame-sealed glass capillaries (1064 nm, 10 mW power, resolution 4 cm^{-1}). IR spectra were recorded on a Nicolet Magna-IR 760 spectrometer using a diamond Orbit ATR (Attenuated Total Reflection) unit. The spectra were corrected because of the penetration of depth and refractive index dependence of intensities and frequencies with standard techniques implemented in the OMNIC software package.

Simultaneous measurement of the thermogravimetry (TG) and differential thermoanalysis (DTA) was performed with a STA 429 (Netzsch company). The sample was heated in a corundum crucible from room temperature to 550 °C in synthetic dry air (200 $mL\,min^{-1}$) with a rate of heating of 5 $°C\,min^{-1}$. As DTA reference we used Al_2O_3. Minor amounts of black carbon remain inside the crucible.

Conductivity measurements have been performed with a S30 SevenEasy (Mettler Toledo) using a platinum electrode InLab710 with a cell constant of 0.8096 cm^{-1} in a cell filled with 3.5 mL of the sample.

Crystal data for $[N(C_3H_7)_4]^+[Br_9]^-$: $C_{12}H_{28}NBr_9$, $M_w = 905.50\,g\,mol^{-1}$, tetragonal, space group $I\bar{4}$, $a = b = 12.112(3)$; $c = 8.666(2)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 1271.2(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.365\,Mg\,m^{-3}$, $F(000) = 844$, $\lambda = 0.71073$ Å, $T = 100(2)$ K, absorption coefficient $= 14.188\,mm^{-1}$, absorption correction: multi-scan, $T_{min} = 0.3156$, $T_{max} = 0.7469$. Data for the structure were collected on a Bruker SMART APEX2 CCD area detector diffractometer with Mo-K_α radiation. A single crystal was coated at room temperature with perfluoroether oil and mounted on a 0.1 mm Micromount. The structure was solved by direct methods in SHELXTL[33] and OLEX2[34] and refined by least squares on weighted F^2 values for all reflections. The final refinements converged at $GooF = 1.014$, $R1 = 0.0357$ and $wR2 = 0.0824$ for all reflections ($I > 2\sigma(I)$). The hydrogen atoms were included in the refinement in calculated positions by a riding model. All attempts to find the positions of the hydrogen atoms in the difference Fourier maps failed. The graphical representations were prepared with Diamond.[35] CCDC 835811 ($[N(C_3H_7)_4]^+[Br_9]^-$) 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: Calculations were performed at various levels of density functional theory (DFT) and at ab initio HF, MP2, SCS-MP2, SOS-MP2, CCSD, CCSD(T) level. The gradient-corrected BP86[36–40] functional, the hybrid functionals PBE0[36,37,41–43] with 25 % HF exchange admixture were used together with the def-SV(P) and def2-TZVPP basis set for bromine and iodine. Quasirelativistic energy-adjusted, small-core pseudopotentials (effective-core potentials, ECP) of the Stuttgart/Cologne group were used for iodine.[45]

All calculations were done with the Turbomole V6.2[44] program and the analytical gradient methods implemented therein. Structures have been fully optimized at DFT, HF and MP2 level. Data on spin-scaled MP2 (SCS[45] or SOS,[46] see Supporting information) as well as coupled-cluster values have been performed on optimized RI-MP2/def2-TZVPP structures. 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. Spin-orbit effects have not been considered for bromine only for iodine.

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