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Reference Values for the B-X Bond Lengths of BI_3 and BBr_3

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Abstract. High-resolution X-ray analysis of BI_3 and BBr_3 single crystals as well as high-level theoretical calculations agree on accurate but long B-X bond distances that should be used as future reference to account for their structure, bonding and reactivity.

Keywords: boron trihalides; high resolution X-ray crystallography; ab initio calculation; DFT calculation; Lewis acid

Introduction

It is well known that the BX_3 molecules do not obey the expected trend in Lewis acidity and, surprisingly, BF_3 is a much weaker Lewis acid than BI_3 [1]. The unexpected behavior of the boron trihalides may be explained in terms of σ- and π-bond donation [2], even though not everybody [3, 4] necessarily agrees with these findings. Experimentally, the extent of halogen-boron π-bonding has been investigated on the basis of core binding energies [5a], mass spectrometric analyses of trimethylamine adducts [5b] as well as IR and Raman studies of phosphine adducts [5c]. So far, many theoretical [2−4, 6] but very few experimental reports address the problem and there is a clear need for further experimental data on BX_3 (X = F-I) to finally resolve this long standing problem. One input for this discussion is an accurate determination of the B-X bond length. While these are known from gas phase studies on BF_3 [7a-c] and BCl_3 [7c], the available data for BBr_3 are only reasonable but those of BI_3 are less accurate and in part even lack the assignment of a standard deviation [8].

Experimental Section

All manipulations were carried out inside a glove box with inert gas atmosphere. Hexane was dried by distillation from Na and stored in a greaseless Schlenk vessel over molecular sieves (4 nm). Commercially available BBr_3 was distilled and stored in a greaseless Schlenk vessel containing some milligrams of Hg. BI_3 was prepared from $NaBH_4$ and I_2 in heptane according to reported procedures [9].

Crystal growth out of solution

BI_3: Sublimed BI_3 (10 g) was put into a previously dried Schlenk vessel equipped with a Young valve with glass stem. Hexane was condensed into the flask (ca. 20 ml). The flask was put inside a dewar vessel (5 l) containing ethanol. The dewar vessel was placed inside a 0 °C refrigerator. After 2 days at this temperature crystals suitable for X-ray diffraction were obtained.

BBr_3: Distilled BBr_3 (5 g) was condensed into a previously dried Schlenk vessel equipped with a J. Young valve with glass stem. Hexane was condensed into the flask (ca. 10 ml). The flask was put inside a dewar vessel containing 5 L ethanol. The dewar vessel was placed inside a −78 °C refrigerator. After 4 days at this temperature crystals suitable for X-ray diffraction were obtained.

Crystal growth inside a capillary

BBr_3: Distilled BBr_3 was condensed into a previously dried Lindemann glass capillary (outer diameter 0.2 mm) which was flamed sealed under vacuum. Using a procedure similar to the one reported in the literature [10] a single crystal was grown *in situ* on the diffractometer by slowly cycling the temperature of the *cryo*-stream between 227 K and 203 K. The crystallinity of the sample was checked every 3 seconds during the cycling procedure by the quality of the frames obtained. Close to the point where the sample started to give single crystal reflections, heating the sample with a green Laser (532 nm, 0.1 mA) for some seconds produced the desired homogeneity of the sample. After this point the sample was slowly (~ 30 K/h) cooled down to 100 K, the temperature at which the measurement was performed. With this procedure reproducibly single crystals of BBr_3 could be prepared.

Data collection

For both structures, data collection was performed at 100 K on a Nonius Kappa goniometer equipped with a Bruker APPEX II CCD detector and using Mo Kα (0.70173 Å) radiation.

A BI_3 single crystal was mounted at −70 °C on a specially designed device using a stream of cold gaseous N_2. Data collection was performed up to a limit of 80° in $2\theta_{max}$. $a = b = 6.9966$ Å, $c = 7.2615$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$. Z = 2, space group $P6_3/m$, $2\theta_{max} = 80°$, 24375 reflections collected (659 unique), R1 = 0.0156

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for 582 Fo > 4sig(Fo) and 0.0221 for all 659 data and 10 parameters, wR2 = 0.0273, GooF = S = 1.367. Crystal size = 0.02 x 0.02 x 0.02 mm. max/min larg. res. peak, 1.01/−0.95 e/Å^3. Absorption correction type: Spherical (r = 0.01). T_{min} = 0.7431, T_{max} = 0.7472.

BBr_3 inside the capillary was measured up to 72° in $2\theta_{max}$. $a = b$ = 6.4304 Å, c = 6.8466 Å, $\alpha = \beta = 90°$, $\gamma = 120°$. Z = 2, space group $P6_3/m$, $2\theta_{max} = 72°$, 15634 reflections collected (426 unique), R1 = 0.0261 for 372 Fo > 4sig(Fo) and 0.0339 for all 426 data, wR2 = 0.0628, GooF = S = 1.386. Crystal size (cylindrical): r = 0.099 mm, l = 0.3 mm. max/min larg. res. peak, 1.11/−0.69 e/Å^3. Cylindrical absorption correction (r = 0.08 mm). T_{min} = 0.0472, T_{max} = 0.0853.

Both structures were solved (SHELX 6.14) by the Patterson heavy atom method and successive interpretation of the difference Fourier maps, followed by least-square refinement. All atoms were refined anisotropically.

Calculations

DFT (BP86), *ab initio* (MP2) and hybrid (PBE0) computations were done with the program TURBOMOLE [11a]. The geometries of all species were optimized with the spilt valence polarization SVP, the TZVP, or the TZVPP basis sets respectively, as implemented in the program [11b]. Frequency calculations were performed at the BP86/SVP level, and all structures represent true minima without imaginary frequencies on the respective hyper surface. Hybrid HF-DFT (PBE1PBE = PBE0 from Turbomole) and CCSD(T) calculations using (SDB)-Aug-cc-pVTZ and (SDB)-Aug-cc-pVQZ as basis set were performed with the program GAUSSIAN 03 Revision C.02 [12]. In all cases the core electrons of Br (10 e) and I (28 e) were replaced by a scalar relativistic ECP. The basis sets and ECP's were downloaded from **http://emsl.pnl.gov/forms/basisform.html**, references to these basis sets are quoted there.

Results and Discussion

We report here high resolution single crystal X-ray data for BI_3 and BBr_3. BI_3 single crystals were grown either by sublimation or from a hexane solution; the later provided the best crystallographic data sets. Single crystals were grown by slowly cooling a saturated hexane solution from room temperature to 0 °C. As in previous powder experiments [13]. BI_3 crystallizes in the space group $P6_3/m$ and the molecules are trigonal planar (see figure 1a). Our best data set ($2\theta_{max} = 80°$, R1 = 1.56 %, wR2 = 2.73 %) gave a B-I bond length of 212.51(3) pm, which is longer than the spectroscopic value provided by *Binbrek* et al. (212 pm, no standard deviation given) [8] or the x-ray powder data [13] report which concluded a value of 211.2(8) pm. Correction for libration by a riding model [14] did not change our B-I distance. We note here that according to our experience the B-I bond length depends critically on the quality of the crystal, apparently with lower crystal quality leading to shorter B-I distances. The new data set presented here emerged as the last of a series of continuous improvements and was measured from a very small crystal of 0.02x0.02x0.02 mm to minimize absorption effects. The refinement has higher accuracy than previously reported values and should be used as a basis for further discussions of the bonding in BI_3 (σ- and π-contributions, Coulomb interaction).

The intramolecular I-I distances (409 pm) from molecules within the same plane are longer than the sum of the van der Waals radii (r_B = 200 pm, r_I = 198 pm) [15] see figure 1. All I-I and B-I intramolecular contacts to molecules in the upper and lower planes are above 409 pm. From this, it is evident that the B-I bond is not affected by weak intermolecular interactions in the unit cell and its length relies almost exclusively on the nature of the interaction between the boron and iodine atoms composing the molecule.

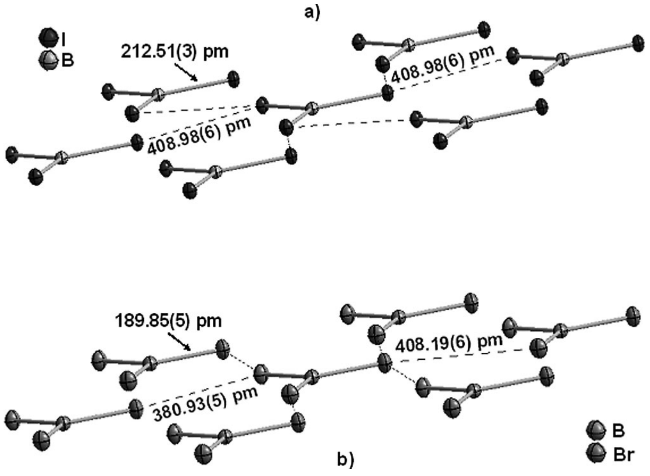

Fig. 1 In plane packing of the BX_3 molecules showing the intermolecular B-X and the shortest intramolecular X-X distances. a) BI_3, b) BBr_3. Thermal ellipsoids are drawn at 50 % probability level.

As a cross check we performed a series of quantum chemical calculations. As a quantum chemical reference the BI_3 distance was assessed at the highly correlated CCSD(T) level using the very flexible (SDB)-Aug-cc-pVQZ basis set. This calculation essentially reproduced the experimental value within 0.1 pm, i.e. $B\text{-}I_{CCSD(T)}$ = 212.6 pm (see table 1). By contrast, standard DFT calculations (BP86) overestimate the B-I bond length, while *ab initio* calculations (MP2) and hybrid HF-DFT methods with very flexible QZ basis sets predict shorter B-I bonds (211.3 to 211.8 pm). It is noteworthy that the B-I bonds shrink for MP2/HF-DFT from values larger than the experiment to a distance shorter than the experimental bond length if going from a DZ to a TZ and QZ basis. Only the highly correlated CCSD(T) method with a scalar relativistic effective core potential and a flexible valence basis for I reproduced the experimental B-I distance. This shows the necessity to employ highly accurate experimental and theoretical methods to understand the true nature of the B-X bond in the simple but delicate boron trihalides.

For BBr_3, a liquid with a melting point of −46 °C, the crystallization process in hexane at −78 °C is as straightforward as for BI_3. However, the mounting of single crystals has been problematic due to the reactivity of the material. We have been able to mount and measure single crystals of BBr_3 grown from a hexane solution, but the quality of these data sets was only average. Nevertheless, we reproducibly have been able to obtain good data sets ($2\theta_{max} = 72°$, $R1 = 0.0261$, $wR2 = 0.0628$) of BBr_3 single crystals grown *in situ* on the cryo-stream of the diffractometer (see figure 1b), using a procedure similar to the one reported in the literature [10]. BBr_3 crystallizes in the same space group as BI_3, namely $P6_3/m$. To the best of our knowledge, there is no literature value available for the B-Br bond length in the condensed phase [16]. Gas electron diffraction of BBr_3 suggested $d(\text{B-Br})_{GED} = 190.0(4)$ pm [17]. This is in very good agreement with the value that we have obtained for the condensed phase, namely $d(\text{B-Br})_{x\text{-ray}} = 189.85(5)$ pm. It should be noted that the standard deviation in our structure is by about one order of magnitude smaller. However, correction for libration [14] according to a riding model gives a corrected $d(\text{B-Br})_{x\text{-ray,libr}}$ of 190.3 pm indicating that some residual libration may be present at the temperature of the measurement (100 K).

In BBr_3, the shortest intermolecular B-Br and Br-Br distances are as long as the sum of the van der Waals radi ($r_B = 200$ pm, $r_{Br} = 185$ pm) [15], again providing evidence that the crystal structure provides direct information on the nature of the undistorted B-Br bond.

As in the case of BI_3, the DFT calculations overestimate the B-Br bond length. The MP2 and the hybrid HF-DFT calculations gave shorter bond lengths even with a very flexible QZ basis set (189.3 to 189.6 pm). Again, only a highly correlated method like CCSD(T) gives a converged distance close to the experimental x-ray value corrected for libration, i.e. $d(\text{B-Br})_{CCSD(T)} = 190.2$ pm, see table 1.

Table 1 Comparison of the B-X bond lengths in BX_3 ($X = I, Br$) molecules based on experimental work and theoretical calculations. Values in [ ] were taken from the literature. All values in pm.

		DZ	**TZ(d)**	**TZ(2d,f)**	**QZ(3d,2f,1g)**	
	BP86 b)	191.5	191.6	191.2	191.2	**Experimental**
BBr_3	**PBE0** b)	189.9	189.9	189.7	189.6	[190.0(4)] a)
	MP2 b)	190.5	190.4	189.8	189.3	**189.85(5)**
	CCSD(T) c)	–	–	190.2	**190.2**	**190.3** d)
		DZ	**TZ(d)**	**TZ(2d,f)**	**QZ(3d,2f,1g)**	
	BP86 b)	214.6	214.0	213.4	213.3	
BI_3	**PBE0** b)	213.0	212.5	212.0	211.8	**Experimental**
	MP2 b)	213.4	212.6	211.4	211.3	[212] e)
	CCSD(T) c)	–	–	212.7	**212.6**	**212.51(3)**

a) See ref.[17]. *b)* DZ = def-SV(P), TZ(d) = def-TZVP, TZ(2d,f) = def-TZVPP, QZ(3d,2f,1g) = (SDB)-Aug-cc-pVQZ. *c)* TZ(2d,f) = (SDB)-Aug-cc-pVTZ, QZ(3d,2f,1g) = (SDB)-Aug-cc-pVQZ. *d)* Corrected for libration by a riding model, see ref. [14]. *e)* See ref. [8].

Agreements to experimental values from previously reported calculations (e.g Ref's [2−4, 6]) using any other method with lower quality basis sets as the one we have used were in part fortuitous, due to the inferior quality of the experimental B-X distance to which they were compared. Future analysis of structure and bonding of the heavier BX_3 molecules should be done with reference to the values reported here.

In conclusion we note that according to high quality x-ray crystal structures as well as highly correlated *ab initio* calculations with very flexible basis sets the B-X bond lengths of the heavier BX_3 molecules are rather long. Of course that does not answer the question about the bonding in BI_3 and BBr_3, but gives an insight that π−back donation might be of minor importance. With this work we have shown that it is possible to obtain very good experimental crystallographic data sets for both BI_3 and BBr_3 which are in very good agreement with high level theoretical calculations. However, we failed to obtain data sets sufficient to be used for a multipole refinement [18] in order to determine as accurate as possible the electron distribution in such delicate systems. This would indeed give more insight on the real bonding in BI_3 and BBr_3.

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