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The Molecular Structure of Boron Triiodide as Determined by Gas Electron Diffraction

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Synopsis. The B–I distance of BI_3 was determined to be 2.118 ± 0.005 Å. A modified Schomaker-Stevenson rule holds for the boron-halogen bond lengths of the boron trihalides except for the fluoride. The B–F distance is much shorter than the value predicted by the rule.

Previously one of the present authors (S.K.) and co-workers reported the molecular structures of BF_3,[1] BCl_3,[2] and BBr_3[3] as determined by gas-phase electron diffraction. The present note will report on the molecular structure of BI_3 as determined by the same method, aiming at a comparison of the boron–halogen bond distances.

The sample was obtained commercially and was purified by sublimation before use. Diffraction photographs were taken with a high-temperature nozzle under the following experimental conditions: camera length, 123.9 mm; accelerating voltage, about 42 kV; beam current, 0.06 μA; exposure time, 240 s; nozzle temperature, about 60 °C. The scale factor was determined by using the diffraction pattern of carbon disulfide. The data covered the $6<s<26$ Å^{-1} range.[4] The measurement of the scattering intensities and the reduction of the molecular intensities were carried out by our usual procedure.[5] Three plates were selected for analysis. The dots in Fig. 1 typify the observed molecular intensities.

The structure was determined by the least-squares method.[5] In the analysis, a planar equilibrium structure with D_{3h} symmetry was assumed. The B–I bond distance, which contributes little to the total intensity,

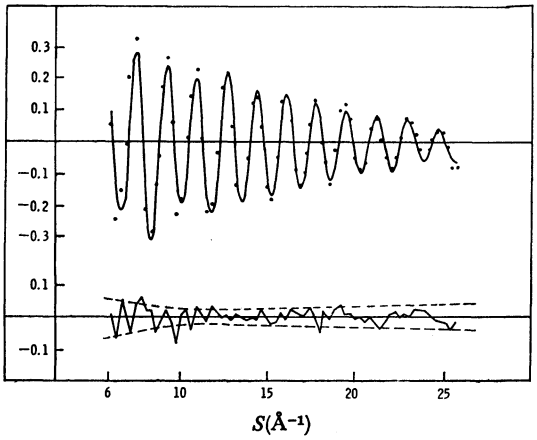

Fig. 1. The observed (dots) and theoretical (solid curve) molecular intensities and the differences. The broken line shows the estimated uncertainty in the intensity measurement.

Table 1. The structure of BI_3 (in Å units)[a]

	B–I	I···I
r_g	2.118 ± 0.005	3.662 ± 0.008

a) The B–I distance was calculated from the observed I···I distance. The errors represent the limits of error.

was constrained to have an r_a distance calculated from the I···I distance by taking the shrinkage effect into account.[6] The B–I mean-amplitude was fixed at the value evaluated at 60 °C, 0.059 Å, using the force filed proposed by Cyvin.[7] The Hartree-Fock and the Thomas-Fermi-Dirac elastic scattering factors for B and I respectively,[8] and the Thomas-Fermi inelastic scattering factors,[9] were used.[10] The interatomic distances thus derived are shown in Table 1. The I···I mean amplitude and the index of resolution were determined to be 0.078 ± 0.006 Å and 0.63 ± 0.05 respectively. The errors indicate the limits of error, which include both the random error and the systematic error due to the uncertainty in the scale factor. The corresponding theoretical intensity curve and the differences from the observed intensities are shown in Fig. 1. The observed index of resolution, 0.63, is unexpectedly small in our ordinary experimental experience,[11] and the I···I mean amplitude is smaller than the calculated value, 0.089 Å. One of the most probable causes of these discrepancies seems to be the extraneous background due to scattering from impurities produced by reactions with moisture, nozzle materials, and grease, and also by thermal decomposition during the loading and heating of the sample in the high-temperature nozzle. At a nozzle temperature of about 60 °C, HI and I_2 are thought to be the main impurities contributing to the background scattering. In order to examine the influence of these impurities on the results, the data were analyzed by assuming mixtures in various ratios of BI_3 and HI or I_2 by the use of known structures for the latter molecules.[12,13] In the cases of mixtures of BI_3 and I_2, the index of resolution increased with an increase in the amount of mixed I_2, becoming about unity in the case of a mixture of 50% I_2 in mole fraction. On the other hand, the standard deviations for the I···I distance and its mean amplitude increased approximately proportionally to the amount of mixed I_2 and became, for a 50% mixture, about three times as large as those in the case of pure BI_3. Those results indicate that no significant amount of I_2 is present in the sample gas. For mixtures of BI_3 and HI, the index of resolution increased linearly with an increase in the amount of HI, for instance, from 0.63 in the case of pure BI_3 to 0.96 in the case of a mixture containing 60% HI, while the other parameters and their standard deviations remained practically the same

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as the quoted results. The amount of HI mixing in the sample gas is not known. However, the injected gas can hardly be considered to contain 50% or more impurities. There seems to be another unknown background spreading over the inner scattering region. In any case, this extraneous scattering has no influence on the resulting I···I distance and its mean amplitude. The discrepancy between the experimental and calculated I···I mean amplitudes remains unexplained.

TABLE 2. COMPARISON OF THE OBSERVED AND CALCULATED BOND LENGTHS (in Å units).

Molecules	Obsd.[a] r_g(B−X)	Sum of covalent radii[b] r_B+r_X	$(r_B+r_X)-r_g$(B−X)	Electronegativity correction $0.06\lvert\chi_B-\chi_X\rvert$
BF_3[c]	1.313 (1)	1.53	0.22	0.12
BCl_3[d]	1.742 (4)	1.80	0.06	0.06
BBr_3[e]	1.893 (5)	1.95	0.06	0.05
BI_3[f]	2.118 (5)	2.14	0.02	0.03

a) The numbers in parentheses represent the limits of error to the last significant figures.
b) Ref. 15. c) Ref. 1. d) Ref. 2. e) Ref. 3.
f) The present study.

Table 2 compares the observed bond lengths, r_g, the sums of the covalent radii, r_B+r_X, the differences, $(r_B+r_X)-r_g$, and modified Schomaker-Stevenson correction terms proportional to the differences in electronegativity, $0.06|\chi_B-\chi_X|$, for boron trihalide molecules.[14] The observed B–X bond lengths, except for the fluoride, can be reproduced by this equation with a correction term for bond ionicity, while the B–F bond length is much shorter than the value predicted by the equation. This extra shortening of the B–F bond seems to reflect a larger amount of double-bond character in the B–F bond.[15]

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4) The original intensity data were deposited with the Chemical Society of Japan (Document No. 7420).
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6) r_a(B−I)=$(1/\sqrt{3})r_a$(I···I)+0.0035 Å.
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