

Structures of Polyboron Fluorides

 The Surprising Structures of B_8F_{12} and $B_{10}F_{12}$ **

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Much is known about the structure of polyboron chlorides, bromides, and iodides^[1,2] and of cluster compounds of other Group 13 elements derived from their monohalides.^[3–5]

However, with the exception of B_2F_4 ,^[6] experimental structures of the polyboron fluorides are unknown. It is notable that no report of a theoretically predicted structure of B_8F_{12} has appeared since the molecule was first postulated to adopt a borane-like structure, $B_2(BF_2)_6$, in 1972.^[7] Herein we describe the experimentally determined structures of B_8F_{12} and of a completely new boron subhalide $B_{10}F_{12}$, both obtained by means of X-ray crystallography at low temperatures.

The yellow liquid B_8F_{12} was prepared, as earlier reported, by low-temperature decomposition of $(BF_2)_2BF$, which had been made by condensing gaseous BF with the vapor of B_2F_4 at 77 K.^[8] The colorless compound $B_{10}F_{12}$ was discovered by X-ray crystallography as a component of the mixture of the less volatile boron fluorides formed by the condensation of BF. The thermal stability of $B_{10}F_{12}$ seems comparable to or higher than that of B_8F_{12} , but both compounds decompose quite rapidly at 273 K. Samples of B_8F_{12} , and the fraction containing $B_{10}F_{12}$ were sealed in glass capillaries and crystals were grown at low temperatures on a diffractometer by using the laser technique employed by Boese and Nussbaumer.^[9] Structures were determined by X-ray crystallography for pure B_8F_{12} ,^[10] $B_8F_{12} \cdot 0.5 BF_3$, and $B_{10}F_{12}$.^[11] Molecular structures of B_8F_{12} and of $B_{10}F_{12}$ are shown in Figure 1 and Figure 2, respectively.

There are two crystallographically independent molecules of B_8F_{12} in the structure of $B_8F_{12} \cdot 0.5 BF_3$, and four in that of pure B_8F_{12} . However, the structures of all six of these molecules are essentially the same. It is interesting to view the structure of B_8F_{12} in relation to earlier attempts to understand the structure of diborane.^[12] It has both bridge

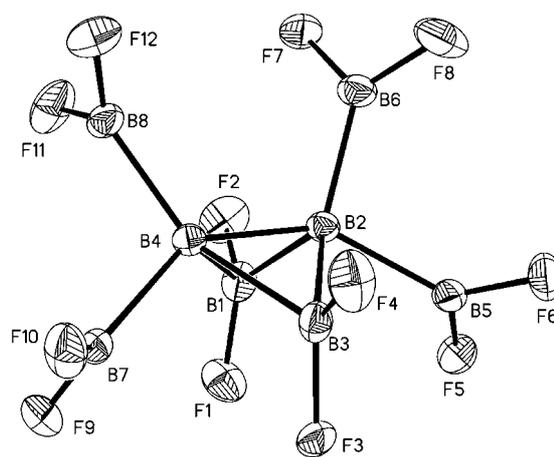


Figure 1. Structure of B_8F_{12} in the crystal. The numbering scheme shown was used for all molecules of B_8F_{12} observed in this study. In the supplemental data,^[10b] atoms in molecule 1 are labeled B11, B21 etc. Molecules 1–4 occur in B_8F_{12} , 5–6 in $B_8F_{12} \cdot 0.5 BF_3$. Average distances [in Å]: B1–F1 1.303(3), B1–F2 1.301(5), B3–F3 1.335(4), B3–F4 1.316(4), B5–F5 1.311(5), B5–F6 1.313(10), B6–B7 1.328(6), B6–F8 1.315(6), B7–F9 1.309(7), B7–F10 1.312(9), B8–F11 1.316(7), B8–F12 1.311(9), B1–B4 2.11(4), B1–B2 1.86(2), B2–B3 1.792(18), B3–B4 1.92(4), B2–B5 1.745(6), B2–B6 1.714(6), B4–B7 1.736(5), B4–B8 1.717(8), B2–B4 1.667(6). The errors quoted are unweighted sample standard deviations based on the dimensions of the six independent molecules observed crystallographically in B_8F_{12} and $B_8F_{12} \cdot 0.5 BF_3$; individual B–B and B–F distances in these structures had standard uncertainties of around 0.002 Å and 0.003 Å, respectively. Thermal ellipsoids are drawn at the 30% probability level.

bonds and a short central B–B bond, that is, it combines all the structural elements once considered diborane. Unlike the equivalent $B(\mu-H)_2B$ unit of diborane, however, the core $B(\mu-BF_2)_2B$ unit of B_8F_{12} is both nonplanar, with average angles between the B1–B2–B4 and B2–B3–B4 planes of 123.1° (range 121.6–125.7°), and markedly asymmetric, with the four B–B bridge bonds varying in length in all the six crystallographically independent molecules in the range of 1.79(2) to 2.11(4) Å in the sequence $B2-B3 < B2-B1 < B3-B4 \ll B1-B4$. Overall, these bond lengths are consistent with there being less electron density available for bridge bonding than in the classic three-center, two-electron bridge bonds of diborane, and with substantial electron density associated with the short, central B2–B4 bond (av 1.667(6) Å). The bond lengths and fold angles within the core B_4 unit might be expected to be easily deformed within a crystal, but all six independent molecules have very similar structures. The results of molecular orbital calculations at the MP2/6-31G* level^[13–15] show that this distorted and folded structure does indeed lie in an energy minimum in the gas phase. The optimized C_{2v} ($mm2$) structure with a nonplanar B_4 unit, in which the core B–B bond lengths are constrained to be equal, is not a potential energy minimum and is 8.77 kJ mol⁻¹ higher in energy than the distorted structure.

More detailed and extensive calculations (which will be the subject of a subsequent full paper) are needed to fully understand the origin of the observed unsymmetrical structure, but preliminary results indicate that intramolecular F...B interactions play a critical role. For example, for the

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compound B_8F_{12} a long bifurcated interaction between F3 and the boron atoms B5 and B7 in two of the terminal BF_2 groups pulls the B3 atom out of the plane of B1, B2, and B4 (Figure 1; observed experimental ranges 2.603(2)–2.675(2) Å for F3...B5 and 2.620(2)–2.693(2) Å for F3...B7; calculated ab initio values 2.572 and 2.587 Å, respectively). These interactions also affect the B3–F3 bond which, at an average of 1.335(4) Å (calcd 1.361 Å), is longer than other such bonds in the molecule. Furthermore, the atoms B2, B4, B5, B7, and B8 are coplanar, but B6 is displaced from this plane by an average of 0.43(7) Å to accommodate an interaction between F7 and B8. The longest B...F interaction (obs. 2.733(2)–2.942(2) Å; calcd 2.855 Å) is formed between F5 and B1. This contact may be responsible for the lengthening of the B1–B4 bridge bond. While the results of calculations at the MP2/6-31G* level point to some polarity in the B2–B4 bond (Mulliken charges; B2 –0.95, B4 –0.41), the very high volatility of B_8F_{12} indicates a compound with negligible intermolecular dipole–dipole interactions.

Calculations^[13–15] on the model compound $B_8H_4F_8$, in which the bridging BF_2 groups are replaced by bridging BH_2 groups, reveal a symmetrically bridged structure with a planar central B_4 unit and overall D_2 (222) symmetry. The calculations also indicate a twisting of the planes of the BH_2 groups with respect to the central B_4 unit, which can be attributed to intramolecular interactions between the highly electron-deficient bridging boron atoms and the fluorine atoms of terminal BF_2 groups. The π -donating ability of fluorine atoms means that BF_2 is less electron deficient than BH_2 . However, in B_8F_{12} the fluorine atoms of both the bridging and terminal BF_2 groups seem to be involved in long-range interactions with the boron atoms of other BF_2 groups. Clearly both the observed intramolecular interactions and the inherent electronic properties are critical in determining the precise structures adopted.

As pointed out by a referee, unsymmetrical bridging is well-known in carbocation chemistry, where there is a continuum of hyperconjugation, asymmetric bridging, and symmetric bridging, depending on the strength of interaction between a σ donor and a center of electron deficiency. To quote the referee, “ B_8F_{12} would seem to belong to the world between pure classical and pure nonclassical structures”. The detailed calculations referred to above should shed light on these structural issues (as well as the reasons for the intense yellow color of the compound) and we are currently trying to refine gas-phase electron-diffraction data for the molecule.

The structure of $B_{10}F_{12}$ (Figure 2) has crystallographic S_4 symmetry and is based on a central distorted tetrahedron of boron atoms (B1 and its symmetry equivalents B1A, B1B, and B1C) each with a terminal BF_2 substituent, similar to the known B_4X_4 tetrahedra,^[1] but with BF_2 bridges across the B1–B1B and B1A–B1C edges. If each BF_2 group is replaced by an H atom, this structure equates to $B_4H_4(\mu-H)_2$. Organic derivatives of $B_4H_4(\mu-H)_2$ of type $B_4R_4(\mu-H)_2$ have been reported^[16,17] and while the structures were not established by X-ray crystallography, there seems little doubt that they have a similar B_4 core to $B_{10}F_{12}$ but with bridging H atoms across opposite edges of the tetrahedron. Nevertheless, such organo-boron compounds and related derivatives of tetrabor-

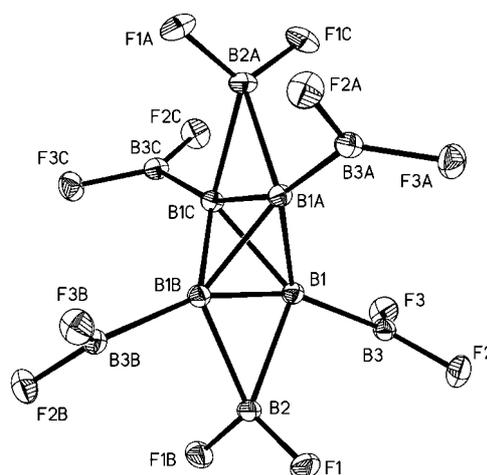


Figure 2. Structure of $B_{10}F_{12}$ in the crystal. Bond lengths [Å]: B1–B1A 1.7583(14), B1–B1B 1.6053(18), B1–B2 1.8070(15), B1–B3 1.7037(13), B2–F1 1.3266(9), B3–F2 1.3052(11), B3–F3 1.3191(11). Thermal ellipsoids are drawn at the 30% probability level.

ane (6)^[18,19] are much more electron rich and thus more stable than $B_{10}F_{12}$, which depends on relatively weak F–B π -bonding to compensate for its electron deficiency.

Exchange reactions of BCl_3 with B_8F_{12} and $B_{10}F_{12}$ were studied, and are a route to the formation of new polyboron chlorides.^[20] Polyboron fluorides less volatile than $B_{10}F_{12}$ are also formed by the condensation of BF, and efforts are being made to determine their molecular structures by X-ray crystallography.

Experimental Section

The volatile products, obtained from the condensation of gaseous BF (1.5 g, 50 mmol) with excess gaseous B_2F_4 at 77 K, were fractionated on a low-temperature distillation column^[21] to yield $(F_2B)_2BF$ (ca. 0.35 g, 2.7 mmol), which came off the column at about 200 K, and a fraction (ca. 0.2 g) that was partly liquid, partly crystalline on the column, which came off slowly at about 235 K. The $(F_2B)_2BF$ was held at 250 K to allow it to disproportionate to B_8F_{12} (ca. 0.17 g, 0.54 mmol) and B_2F_4 , which were easily separated. Both B_8F_{12} and the 235 K fraction were sealed in Pyrex capillaries (ca. 0.3 mm bore) on a vacuum line. Crystals of the compounds were grown in these capillaries, which were mounted on a Bruker AXS Smart Apex diffractometer equipped with an Oxford Cryosystems Cryostream and an OHCD IR laser-assisted crystallization device. Crystal growth of B_8F_{12} was hampered by glass formation, but crystals were grown from a sample that had been annealed into a polycrystalline powder at 160 K, by moving the point of focus along the capillary over a period of 13 h, then ramping down the laser power from 1.9 W to zero over 1 h. Prior to this study, crystallization of B_8F_{12} had never been observed to occur; when it was handled at low temperature on a vacuum line, it always formed a glassy solid.

A crystal of $B_{10}F_{12}$ was grown without difficulty by establishing a stable solid–liquid equilibrium at 200 K with a laser power of 2.5 W at one end of the sample. The position of the phase boundary was moved along the length of the sample over the course of 5 min, then the laser power was ramped down to zero over another 5 min.

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- [1] J. A. Morrison, *Chem. Rev.* **1991**, *91*, 35.
- [2] W. Hönlle, Y. Grin, A. Burkhardt, U. Wedig, M. Schultheiss, H. G. von Schnering, *J. Solid State Chem.* **1997**, *133*, 59.
- [3] C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chem.* **1996**, *108*, 141; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 129.
- [4] A. Rodig, G. Linti, *Angew. Chem.* **2000**, *112*, 3076; *Angew. Chem. Int. Ed.* **2000**, *39*, 2952.
- [5] A. Schnepf, H. Schnöckel, *Angew. Chem.* **2001**, *113*, 734; *Angew. Chem. Int. Ed.* **2001**, *40*, 712.
- [6] L. Trefonas, W. N. Lipsomb, *J. Chem. Phys.* **1958**, *28*, 54.
- [7] R. W. Kirk, D. L. Smith, W. Airey, P. L. Timms, *J. Chem. Soc. Dalton Trans.* **1972**, 1392.
- [8] P. L. Timms, *J. Am. Chem. Soc.* **1967**, *89*, 1629.
- [9] R. Boese, M. Nussbaumer in *Correlations, Transformations and Interactions in Organic Crystal Chemistry*, IUCr Crystallographic Symposia, Vol. 7 (Eds.: D. W. Jones, A. Katrusiak), Oxford University Press, Oxford, UK, **1994**, pp. 20–37.
- [10] a) Crystal structure analysis of B_8F_{12} : $M_r = 1257.86$, monoclinic $P2_1/c$, $a = 24.577(3)$, $b = 7.3341(8)$, $c = 24.493(3)$ Å, $\beta = 106.708(2)^\circ$, $V = 4401.1(9)$ Å³, $T = 120$ K, $\rho_{\text{calc}} = 1.898$ g cm⁻³, $\lambda = 0.71073$ Å. Yellow cylinder, $0.30 \times 0.30 \times 1.0$ mm, $\mu(\text{Mo}_{K\alpha}) = 0.244$ mm⁻¹. An absorption correction was performed by the multiscan method using the program SADABS ($0.76 < T < 0.93$). Data were collected to $2\theta_{\text{max}} = 57.6^\circ$ comprising 39515 measured and 10721 unique data, of which 7462 with $F > 4\sigma(F)$ were used for refinement. The structure was solved by direct methods using SHELXTL^[22] and refined by full-matrix least-squares against F , with anisotropic displacement parameters on all atoms and a Chebychev three-term polynomial weighting scheme (CRYSTALS).^[23] The final R factor was 0.0298, $R_w = 0.0334$, for 721 parameters. The final difference map max. and min were $+0.36$ and -0.19 e Å⁻³, respectively. Further analyses were performed with PLATON.^[24] b) Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; email: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-412616 (B_8F_{12}), CSD-412617 ($B_{17}F_{27}$), and CSD-412618 ($B_{10}F_{12}$).
- [11] Crystal structure analysis of $B_{10}F_{12}$: $M = 336.08$, tetragonal $I4_1/a$, $a = 6.4118(8)$, $c = 25.551(5)$ Å, $V = 1132.6(3)$ Å³, $T = 150$ K, $\rho_{\text{calc}} = 1.971$ g cm⁻³, $\lambda = 0.71073$ Å. Colorless cylinder, o. d. 0.36 mm, $\mu(\text{Mo}_{K\alpha}) = 0.242$ mm⁻¹. An absorption correction was performed by the multiscan method using the program SADABS ($0.762 < T < 1$). Data were collected to $2\theta_{\text{max}} = 58^\circ$ comprising 3613 measured and 728 unique data, of which 685 with $F > 4\sigma(F)$ were used for refinement. The structure was solved by direct methods and refined as a merohedral twin using a twofold axis about [110] as the twin law by full-matrix least-squares against F , with anisotropic displacement parameters on all atoms and a Chebychev three-term polynomial weighting scheme. The final R factor was 0.0219, $R_w = 0.0252$, for 52 parameters. The final difference map max. and min. were $+0.22$ and -0.15 e Å⁻³, respectively, and the twin-component scale factors were 0.5841 and 0.4186(16).^[10b] The programs used were the same as those in reference [10a].
- [12] P. Laszlo, *Angew. Chem.* **2000**, *112*, 2151; *Angew. Chem. Int. Ed.* **2000**, *39*, 2071.
- [13] All calculations were performed by using the GAUSSIAN98 computer program^[14] using resources of the UK Computational Chemistry Facility, on a DEC 8400 superscalar cluster equipped with 10 fast processors, 6 GB of memory, and 150 GB disc. Calculations were performed at the MP2/6-31G* level of theory.^[14] Calculations were carried out starting with the crystal coordinates of B_8F_{12} , and a similar structure, whereby the central four B–B distances were constrained to be equal. Calculations were also carried out on the structure of $(F_2B)_2B(\mu-BH_2)_2(BF_2)_2$ to determine how removing fluorine atoms from the bridging groups affects the structural symmetry in B_8F_{12} . Frequency calculations allowed the nature of any stationary points to be determined, which confirms the structures as either local minima, transition states, or saddle points on the potential energy surfaces.
- [14] GAUSSIAN98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [15] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618; P. Hohenberg, W. Kohn, *Phys. Rev. B* **1964**, *136*, 864.
- [16] A. Neu, T. Mannekes, U. Englert, P. Paetzold, M. Hoffman, P. von Schleyer, *Angew. Chem.* **1997**, *109*, 2211; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2117.
- [17] A. Neu, T. Mannekes, U. Englert, P. Paetzold, M. Hoffman, P. von Schleyer, *Inorg. Chim. Acta* **1999**, *289*, 58.
- [18] C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2002**, *114*, 1597; *Angew. Chem. Int. Ed.* **2002**, *41*, 1526.
- [19] A. Maier, M. Hofmann, H. Pritzkow, W. Siebert, *Angew. Chem.* **2002**, *114*, 1600; *Angew. Chem. Int. Ed.* **2002**, *41*, 1529.
- [20] J. A. J. Pardoe, N. C. Norman, P. L. Timms, *Polyhedron* **2002**, *21*, 543.
- [21] See: D. F. Shriver, *Manipulation of Air Sensitive Compounds*, McGraw-Hill, New York, **1969**, p. 91.
- [22] G. M. Sheldrick, SHELXTL version 5, Bruker-AXS, Madison, Wisconsin, **1995**.
- [23] D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, R. I. Cooper, CRYSTALS Issue 11. Chemical Crystallography Laboratory, Oxford, UK, **2001**.
- [24] A. L. Spek, PLATON, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **2002**. PC version part of the WINGX suite: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.