Solid-State Borazine: Does it Deserve to be Entiteled "Inorganic Benzene"?

Roland Boese*, Andreas H. Maulitz, and Peter Stellberg

Institut für Anorganische Chemie der Universität-GH Essen,
Universitätsstraße 5–7, D-45117 Essen, Germany

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The molecular and solid-state structure of borazine has been determined at 115 and 160 K by single-crystal X-ray crystallography. The molecular structure has C_2 symmetry with small deviations from the expected D_{3h} symmetry. The mean value of the BN bond length is 1.429(1) Å and the interbond angles of the six-membered ring are 117.1(1)° at the boron atoms and 122.9(1)° at the nitrogen atoms (mean values). Similar to benzene an unambiguous assignment of the molecular symmetry is not possible. – The crystal packing is not comparable to any known phase of benzene, and surprisingly the molecules are not stacked having coplanar rings. Instead, the molecules are found in tilted layers. No significant intermolecular interaction could be detected. The generated difference electron density maps show the typical distribution pattern for polar bonds.

Borazine is generally introduced in textbooks as "inorganic benzene" under aspects of the isoelectronic relationship. This holds only for some physical and chemical properties. The prominent discrepancies in the reactivity are attributed to the significant difference between the electronegativities of boron and nitrogen atoms. Among the physical properties the density and boiling point are quite similar. However, the melting points differ by approximately 60°C. This suggests that the solid state of borazine must be quite different from that of benzene.

The crystal structures under various conditions of benzene are known for a long time[1], all of them exhibit the well-known herringbone pattern in the space groups *Pnma* and $P2_1/c$. A crystal structure determination of borazine has never been performed, obviously due to crystallization problems.

Moreover, even the molecular structures of both compounds are still debated. The vast amount of experimental data of benzene does not allow an unambiguous assignment of the symmetry of the equilibrium geometry[2]. However, the results from quantum-mechanical calculations favor D_{6h} symmetry[3].

The molecular structure of borazine has been determined by gas-phase electron diffraction[4]. In the latest electron diffraction study by Harshbarger et al.[4c] a planar D_{3h} and two nonplanar (C_2 and C_{3v}) models were discussed. The C_{3v} model was excluded because of inconsistency with a microwave investigation. A decision between a D_{3h} model with large vibrational amplitudes perpendicular to the ring plane and a nonplanar C_2 model was not possible. Thus, distinct assignments of the molecular geometry and symmetry by diffraction methods have not yet been made.

After many attempts we succeeded in growing a cylindrical single crystal by means of a miniature zone-melting procedure in a capillary directly on the diffractometer applying an infrared heat source[5]. The structure refinements in the tetragonal space group $P4_32_12$ from the diffraction data at 160 and 115 K give no evidence for solid-state phase transitions; the molecules behave like rigid bodies in the given temperature interval.

Results and Discussion

Borazine has crystallographic C_2 symmetry, the molecule deviates slightly from the expected D_{3h} symmetry (Figure 1). The BN distances are 1.429(1) Å (mean value) and comparable to those in bis(dimethylamino)methylborane[6] [1.434(1) and 1.427(1) Å], where likewise two nitrogen atoms act as π donors to one boron atom. The BN bonds are shorter than in tris(dimethylamino)borane[7] [1.441(1), 1.434(1) and 1.441(1) Å] and longer than in tetramethylaminoborane[8] [1.403(1) Å] where three and one nitrogen atom(s), respectively, exist for the back donation.

The bond angles in the six-membered ring are significantly different, 117.1(1)° at the boron atoms and 122.9(1)° at the nitrogen atoms (mean values). Similar findings have been mentioned for borazine derivatives[6a,9], but possible substituent effects or the accuracy of the results did not allow an unambiguous statement.

The phenomenon of the alternating angles in the six-membered ring can be understood by Bent's rule considering a rehybridization of the ring atoms[10]. The more electronegative nitrogen atoms prefer hybrid orbitals with lower s character. Therefore, the increased p character at the boron atoms results in decreasing bond angles, whereas the opposite behavior is observed at the nitrogen atoms.

In contrast to the expected D_{3h} symmetry it is noteworthy that our results are in line with the mentioned C_2 model of Harshbarger. Although two structure determinations in different states have been carried out it is still impossible to attribute D_{3h} symmetry to borazine. Even several ab initio calculations, which have been performed up to now, do not

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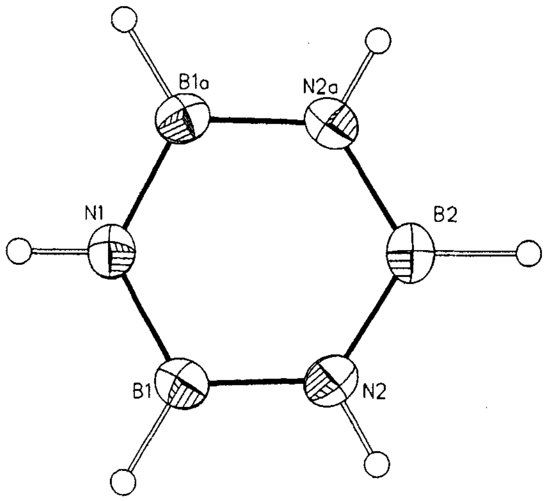

Figure 1. Crystal structure of borazine at 115 K. The ellipsoids corresponds to 50% probability of electron distribution, distances [Å], angles and torsion angles [°] (standard deviations in brackets): N1–B1 1.429(1), B1–N2 1.431(1), N2–B2 1.431(1); B1–N1–B1a 122.9(1), N1–B1–N2 117.1(1), B1–N2–B2 123.1(1), N2–B2–N2a 116.8(1), B1a–N1–B1–N2 0.7(1), B2–N2–B1–N1 −1.5(1), B1–N2–B2–N2a 0.8(1)

allow to decide which symmetry corresponds to the global minimum[11].

We suppose that the free borazine has D_{3h} symmetry with an extremely flat potential energy surface. Like the discussion on benzene, the symmetry of this six-membered ring is not unambiguous.

The crystal packing (Figure 2) is not comparable to any of the known phases of benzene[1,12]. Also, the molecules are not stacked with the boron atoms situated directly above nitrogen atoms with coplanar rings. Instead, the stacks are tilted, and the layers have interplanar angles of 65.2°. The coplanar molecules have a minimum distance of one of the shorter cell axis [5.463(1) Å]. The molecular planes and the short cell axes include an angle of 49.6°, which results in an approach of the boron and nitrogen atoms up to 3.57 Å. It is noteworthy that the shortest intermolecular distances between ring atoms are B···B or N···N distances and not, as expected from electrostatic interaction, between boron and nitrogen atoms. Intermolecular contacts between atoms shorter than the sum of the van der Waals radii are not present[13], the shortest intermolecular H···H distance is 2.49 Å.

The precision of the measured data was sufficient for the calculation of X–X difference electron density maps (Figure 3). As expected, the electron density appears to be increased at the nitrogen atoms and in countermove decreased at the boron atoms. The difference electron density maps and a careful analysis of the molecular packing reveal no evidence of an intermolecular perturbation of the molecular geometry.

From these results we elucidate that in the solid state, as it is known for the chemical behavior, borazine and benzene are incomparable. However, the molecular symmetry of both borazine and benzene cannot be assigned unambiguously.

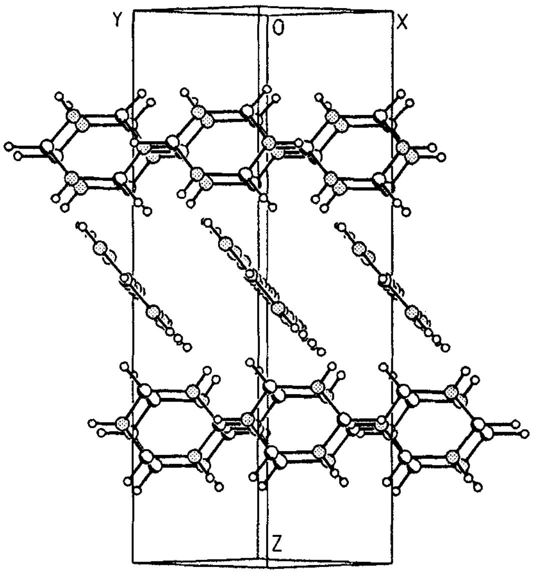

Figure 2. Unit cell of the crystal structure of borazine in viewing along the 110 direction

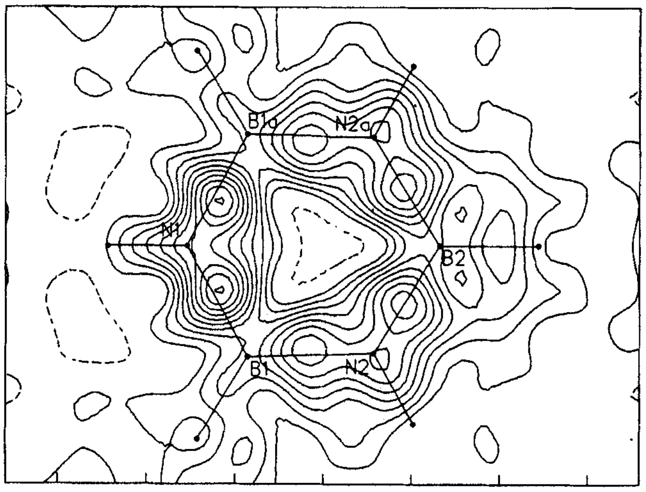

Figure 3. Difference electron density map of borazine in the ring plane at 115 K. Contour lines at intervals of 0.05 eÅ^{-3}, negative electron density dotted, intervals 0.1 eÅ^{-3}. The difference electron density map from the measurement at 160 K is similar to the shown figure

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Experimental

X-Ray Single-Crystal Structure Determination of Borazine: Chemical formula: $B_3N_3H_6$ Molecular weight 80.5 gmol^{-1}. A cylindric crystal of 0.3 mm diameter was measured with a Nicolet R3m/V four-circle diffractometer with Mo-K_α radiation (graphite monochromator). The crystal system is tetragonal, and the cell dimensions were refined from the diffractometer angles of 50 centered reflections in the 2Θ range of 15–25°, $a = b = 5.463(1)$, $c = 16.315(4)$ Å, $V = 486.9(2)$ Å^3 (160 K), $a = b = 5.428(1)$, $c = 16.279(8)$ Å, $V = 479.5(4)$ Å^3 (115 K), space group $P4_32_12$ (No. 96), $Z = 4$, $\rho_{calc.} = 1.089$ gcm^{-3} (160 K), 1.115 gcm^{-3} (115 K), $\mu = 0.07$ mm^{-1}. Correction for a cylindric single crystal has been performed. The maximum scan angle in 2Θ is 90°, which leads to 1390 unique intensities (160 K, $R_{merg} = 0.037$) and 1149 observed ones $[F_o \geq 4\sigma(F)]$. At 115 K the maximum scan angle in 2Θ was 60° with 701 unique intensities ($R_{merg} = 0.026$) and 665 observed $[F_o \geq 4\sigma(F)]$. The structure solution with direct methods and the refinement with full matrix least squares were performed with the SHELXTL-Plus program package (Vers. 4.11/V). 41 parameter were refined with anisotropic displacement parameters for B and N, hydrogen atoms with isotropic displacement parameters. $R = 0.052$, $R_w = 0.057$ $w^{-1} = [\sigma^2(F_o) + 0.0025 \cdot F_o^2)$ (160 K), $R = 0.036$, $R_w = 0.039$, $w^{-1} = [\sigma^2(F_o) + 0.0015 \cdot F_o^2)$ (115 K). The maximum residual electron density is 0.44 eÅ^{-3} (160 K) and 0.39 eÅ^{-3} (115 K). The refinement of the X–X difference electron density maps was performed with a weighting scheme of $1 - \exp[-10(\sin\Theta/\lambda)^2]$.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401085 (160 K) and CSD-401086 (115 K), the names of the authors, and the journal citation.

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[13] For the estimation of the intermolecular contacts the BH bond distances were shifted to 1.189 Å and the NH bond distances to 1.008 Å. These distances were taken from an ab initio calculation optimization in D_{3h} symmetry on MP2(fu)/6–31 + G**).

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