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INORGANIC POLYMER

SILICATES -

In chemistry, a **silicate** is any member of a family of <u>anions</u> consisting of <u>silicon</u> and <u>oxygen</u>, usually with the general formula $[SiO^{(4-2x)-}_{4-x}]_n$, where $0 \le x < 2$. The family includes

<u>orthosilicate</u> SiO^{4–}₄ (x = 0),

<u>metasilicate</u> SiO^{2–}₃ (x = 1), and

pyrosilicate Si₂O^{6–}₇ (x = 0.5, n = 2).

The name is also used for any <u>salt</u> of such anions, such as <u>sodium metasilicate</u>; or any <u>ester</u> containing the corresponding <u>chemical group</u>, such as <u>tetramethyl</u> <u>orthosilicate</u>.^[1]

Silicate anions are often large <u>polymeric</u> molecules with an extense variety of structures, including chains and rings as in polymeric

<u>metasilicate</u> $[SiO^{2-}_3]_n$),

double chains (as in $[Si_2O^{2-}_5]_n$, and sheets (as in $[Si_2O^{2-}_5]_n$.

Silicates are extremely important materials, both natural (such as <u>granite</u>, <u>gravel</u>, and <u>garnet</u>) and artificial (such as <u>Portland cement</u>, <u>ceramics</u>, <u>glass</u>, and <u>waterglass</u>), for all sorts of technological and artistic activities.

BORAZINE-

Borazine is a polar <u>inorganic compound</u> with the <u>chemical formula</u> $B_3H_6N_3$. In this <u>cyclic compound</u>, the three BH units and three NH units alternate. The compound is <u>isoelectronic</u> and <u>isostructural</u> with <u>benzene</u>. For this reason borazine is sometimes referred to as "inorganic benzene". Like benzene, borazine is a colourless <u>liquid</u>.

Synthesis

The compound was reported in 1926 by the chemists <u>Alfred Stock</u> and Erich Pohland by a reaction of <u>diborane</u> with <u>ammonia</u>.^[3]

Borazine is synthesized from <u>diborane</u> and <u>ammonia</u> in a 1:2 ratio at 250–300 °C with a <u>conversion</u> of 50%.

 $3 \text{ } \text{B}_2\text{H}_6 + 6 \text{ } \text{NH}_3 \rightarrow 2 \text{ } \text{B}_3\text{H}_6\text{N}_3 + 12 \text{ } \text{H}_2$

An alternative more efficient route begins with <u>lithium borohydride</u> and <u>ammonium chloride</u>:

3 LiBH₄ + 3 NH₄Cl \rightarrow B₃H₆N₃ + 3 LiCl + 9 H₂

In a two-step process to borazine, <u>boron trichloride</u> is first converted to trichloroborazine:

 $3 \text{ BCl}_3 + 3 \text{ NH}_4\text{Cl} \rightarrow \text{Cl}_3\text{B}_3\text{H}_3\text{N}_3 + 9 \text{ HCl}$

The B-Cl bonds are subsequently converted to B-H bonds:

 $2 \text{ Cl}_3\text{B}_3\text{H}_3\text{N}_3 + 6 \text{ NaBH}_4 \rightarrow 2 \text{ B}_3\text{H}_6\text{N}_3 + 3 \text{ B}_2\text{H}_6 + 6 \text{ NaCl}$

Structure

Borazine is isoelectronic with benzene and has similar connectivity, so it is sometimes referred to as "inorganic benzene". This comparison is not rigorously valid due to the <u>electronegativity</u> difference between boron and nitrogen. <u>X-ray</u> <u>crystallographic</u> structural determinations show that the bond lengths within the borazine ring are all equivalent at 1.429 Å, a property shared by benzene.^[4] However, the borazine ring does not form a perfect hexagon. The bond angle is

 117.1° at the boron atoms and 122.9° at the nitrogens, giving the molecule distinct symmetry.

The <u>electronegativity</u> of boron (2.04 on the <u>Pauling scale</u>) compared to that of nitrogen (3.04) and also the electron deficiency on the boron <u>atom</u> and the lone pair on nitrogen favor alternative <u>mesomer</u> structures for borazine.

Boron behaves as a Lewis acid and nitrogen behaves as a Lewis base.

Aromaticity

Due to its similarities to benzene, there have been a number of computational and experimental analyses of borazine's aromaticity. The number of pi electrons in borazine obeys the 4n + 2 rule, and the B-N bond lengths are equal, which suggests the compound may be aromatic. The electronegativity difference between boron and nitrogen, however, creates an unequal sharing of charge which results in bonds with greater ionic character, and thus it is expected to have poorer delocalization of electrons than the all-carbon analog.

Electron Localization Function

Topological analysis of bonding in borazine by the <u>Electron Localization Function</u> (ELF) indicates that borazine can be described as a π aromatic compound. However, the bonding in borazine is less delocalized than in benzene based on a difference in bifurcation values of the electron basins. Larger bifurcation values indicate better electron delocalization, and it is argued that when this bifurcation value is greater than 0.70, the delocalization is sufficient to designate a compound aromatic.^[6] For benzene, this value is 0.91, but the borazine π system bifurcates at the ELF value 0.682.^[7] This is caused by the difference in electronegativity between B and N, which produces a weaker bond interaction than the C-C interaction in benzene, leading to increased localization of electrons on the B-H and N-H units. The bifurcation value is slightly below the limit of 0.70 which suggests moderate aromaticity.