The Electronic Structure of Borazine as seen by ^{10}B, ^{11}B, and ^{14}N Nuclear Quadrupole Double Resonance*

A. Lötz and J. Voitländer
Institut für Physikalische Chemie, Universität München

J. A. S. Smith
King's College (Kensington Campus), Campden Hill Road, London W8 7AH, Great Britain

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The nitrogen nuclear quadrupole coupling in borazine is reported and interpreted in combination with the previously measured boron coupling. A novel Townes-Dailey type of analysis was employed to obtain the electron distribution in borazine. A calculated π-donation of ~ 0.5 e from the nitrogen atom to the vacant π-orbital of boron is accompanied by a strong polarisation of the σ-skeleton, imparting a negative charge to nitrogen and a positive charge to boron.

Introduction

Borazine, $B_3N_3H_6$, has attracted the attention of chemists since its discovery in 1926 [1]. It is isoelectronic and isosteric with benzene. Its thermodynamic data show a striking similarity to benzene so that it is not surprising that borazine has been called "inorganic benzene" [2]. Yet, in spite of its close relationship with benzene, there are also profound differences, especially the reactivity of borazine which is a consequence of the polarity of the B–N bond.

This polarity is connected with several interesting questions about the nature of this compound. The first is, whether and to what extent the nitrogen atom donates π-electron density into the vacant π-orbital of boron, thus establishing a partial double bond character of the B–N bond. The second question is, whether or not the boron atom, having gained charge by π-donation from nitrogen carries a net negative charge as the classical valence bond structure suggests. Thirdly, one may ask whether the π-charge transfer from nitrogen to boron is confined to three distinct double bonds in the ring or whether there is a delocalisation of electron density over the whole π-system of the ring as in benzene, that means, in a broad sense, can borazine be regarded as being "aromatic"?

Electron diffraction [3] shows that all B–N bond distances in borazine are equally long and just midway between the distances for a single and a double bond thus seemingly answering questions 1 and 3. The direction of the polarity of the B–N bond is apparently revealed by the addition reaction of HCl with borazine, with chlorine always binding to boron [4]. This polarity is in the reverse sense than that of VB theory.

Despite the facts, there has been much argument about these questions. In spite of its D_{3h} symmetry, which may be regarded as an indicator of its aromaticity, borazine does not react like an aromatic ring. Furthermore, it may be features of the transition state which determine the direction of HCl addition, not the atomic charge in the molecular ground state. Hence, a quantitative assessment of the electron distribution in borazine is clearly desirable, and this has been attempted on many occasions by quantum chemical calculations and also by some physical methods, notably vibrational spectroscopy, nuclear magnetic resonance, and measurement of the diamagnetic susceptibility and magnetorotation [5, 6].

Nuclear quadrupole resonance (n.q.r.) differs from these methods insofar as it combines the advantages of providing a local probe of the electron distribution in the ground state in the vicinity of the nuclei under study with an easy and quantitative interpretation in terms of the electronic struc-

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Reprint requests to Prof. Dr. J. Voitländer, Institut für Physikalische Chemie, Universität München, Sophienstraße 11, D-8000 München 2.

ture of the molecule. Furthermore, this method is ideally suited for borazine, and B−N bonds in general, because both nuclei, boron and nitrogen, possess a nuclear quadrupole moment.

Experimental

Most of the lines of the nuclear quadrupole double resonance spectrum can be assigned to ^{10}B transitions because they fit the ^{10}B multi-level system. The intensity of one of the lines is much stronger than expected from theory [7]. This line is in that range (0.7 − 1.9 MHz) in which the ν_+ line of nitrogen should lie according to an earlier measurement of the quadrupolar relaxation of nitrogen in solution via its influence on the proton NMR spectrum [8]. The comparison of the spectra of $B_3{}^{14}N_3H_6$ and $B_3{}^{15}N_3H_6$ now firmly establishes this line to be the ν_+ transition of nitrogen. Higher resolution also allows for detection of the ν_- line which was hidden under the low frequency wing of the ν_+ line in earlier spectra. The ν_0 line of nitrogen at 65 kHz and two unresolved, low-frequency ^{10}B transitions around 200 kHz are now likewise assigned. The boron and nitrogen coupling constants are

$$e^2qQ/h\,(^{11}\mathrm{B}) = 3249\,(3)\ \mathrm{kHz}\,, \quad \eta\,(^{11}\mathrm{B}) = 0.133\,(4)\,,$$
$$e^2qQ/h\,(^{14}\mathrm{N}) = 1440\,(10)\ \mathrm{kHz}\,, \quad \eta\,(^{14}\mathrm{N}) = 0.10\,(2)\,.$$

Interpretation

A combined Townes-Dailey analysis at both nuclei with six linear equations for the six unknown orbital population numbers is not feasible, because the determinant of the system of equations vanishes regardless of the assignment of the principal axes.

An extended model is adopted in which the reference field gradient q_c (formerly q_0) changes according to the charge c residing on the respective atom. The well established formula [9]

$$q_c = q_0\,(1+\varepsilon)^c \quad (c = \text{charge on atom},\ q_0 = \text{field gradient of neutral atom})$$

is used in the truncated form

$$q_c = q_0\,(1 + c \ln (1+\varepsilon)) \qquad (\varepsilon < 0.5,\ c \sim 1)\,.$$

A system of quadratic equations within the framework of the Townes-Dailey model can then be set up which is solvable by numerical methods. Physical restrictions on the magnitude of the figures for the population numbers eliminate most of the multitude of solutions of this system of equations. The π-electron distribution in borazine thus obtained is in accord with results of other physical methods [10, 11] and quantum chemical calculations [12−14]. There is a π-density transfer of ~ 0.5 e from nitrogen to boron, together with a strong polarisation of the σ-skeleton, especially the B−N bond from boron to nitrogen which leaves nitrogen negatively charged. On account of the approximations made, this σ-polarisation is however overestimated.

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