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Journal of Molecular Structure: THEOCHEM 728 (2005) 197–202

THEO CHEM

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Substituent effect on molecular geometry and aromaticity of symmetric B-trisubstituted borazine

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Received 24 March 2005; revised 21 May 2005; accepted 23 May 2005

Abstract

Theoretical calculations have been performed to investigate the substituent effect on molecular geometry and aromaticity of the symmetric B-trisubstituted borazine. Deactivating (electron-withdrawing) substituents tend to shorten the B–N bond, decrease the ∠B–N–B angle and increase the ∠N–B–N angle; while activating (electron-donating) substituents induce the contrary geometric variations. Energetic and magnetic criteria have been used to investigate the molecular aromaticity of the symmetric B-trisubstituted derivatives of borazine. $\mathrm{NICS}_{zz}(2)$ is found to be a reliable measure of the aromaticity for derivatives of borazine and taken as the major criterion in the present study. Meta directing and deactivating substituents tend to enhance the molecular aromaticity; while *ortho–para* directing and deactivating substituents as well as *ortho–para* directing and activating substituents tend to decrease it.

Keywords: Borazine; Substituent effect; Molecular geometry; Aromaticity; Aromatic stabilization energy; Magnetic susceptibility exaltation; Nucleus independent chemical shift; NICS_{zz}; AIM

1. Introduction

Inorganic cyclic ring systems that are isoelectronic with benzene have been known for many years, of which borazine is a textbook, example [1]. Many derivatives of borazine have been synthesized and well characterized [2]. Planarity, equal bond lengths, and the similarity in physical properties to benzene gave the name 'inorganic benzene' to borazine. However, when compared to benzene, the cyclic delocalization of electrons in the borazine ring is reduced due to the large electronegativity difference between boron and nitrogen. The polarity of the B–N bond causes borazine to show a reactivity pattern different from that of benzene [1,3]. Borazine readily undergoes several polar addition reactions that are difficult with benzene. It still remains a controversy whether borazine is aromatic or non-aromatic [4–6], but it is well accepted that borazine is considerably less aromatic in comparison with benzene.

It is intuitively understandable that replacing hydrogen atoms bonded to boron with more electronegative substituents will draw more electrons from nitrogen to boron, thereby enhancing the molecular aromaticity [7]. Parker et al. [8] investigated the aromaticity of a series of fluoroderivaties of borazine by performing vibrational analysis and claimed that fluorination on boron increases the molecular aromaticity. Nevertheless, as reported in our previous study [9], both energetic (aromatic stabilization energy, ASE [10]) and magnetic (magnetic susceptibility exaltation, MSE [11] and nucleus independent chemical shift tensor component, NICS_{zz} [12,13]) criteria concluded that fluorination on boron decreased the molecular aromaticity. This was further confirmed by separation of π component from the overall B–N bonding, which revealed that fluorination on boron weakened π bonding while strengthened σ bonding. Strengthening of σ bonding is a consequence of strong σ-electron withdrawing ability of fluorine; weakening of π bonding is considered to result from the fact that its π-electron donating ability actually cause the π-electrons transfer toward nitrogen [9].

Therefore, the substituents that strongly withdraw both σ- and π-electrons, e.g. nitro group, should be expected to strengthen both σ- and π-electron sharing of B–N bond and consequently increasing molecular aromaticity; while those electron-donating substituents, e.g. amino group, may be expected to cause the contrary variations in the aromaticity.

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0166-1280/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2005.05.020

Boron nitride fibers prepared from borazine and its substituted derivatives have been found to have promising practical application in ceramic material; and tempering the electronic structure of borazine by substitution in order to control the spinnability of the derived polymers and the mechanical properties of the final boron-containing ceramic fibers is an active research area in advanced material technologies [14]. The theoretical study of the substituent effect on the molecular geometry and aromaticity may help guide experimentalists in efforts to design borazine-based ceramic materials.

With the intention to obtain more general trend of substituent effect on the molecular geometry and aromaticity of the substituted derivatives of borazine, we extend our study to take a diversity of typical substituents into investigation. The substituents considered in this study are classified into three groups: meta directing and deactivating substituents, nitro group (–NO_2), cyano group (–CN), formyl group (–CHO); *ortho–para* directing and deactivating substituents, fluoro group (–F); *ortho–para* directing and activating substituents, hydroxyl group (–OH), amino group (–NH_2), methyl group (–CH_3). The terms (meta, *ortho–para* directing and activating, deactivating substituents) are widely used in hydrocarbon aromatics; we presume to use them here considering the similarity between borazine and benzene, and this also facilitates our classification and discussion, as shown in the following text.

The objective of the present study is twofold. Firstly, the variations in the geometric parameters induced by different substituents are investigated; the second objective is to estimate the substituent effect on the molecular aromaticity of borazine derivatives using energetic (ASE) and magnetic (MSE, NICS, $NICS_{zz}$) criteria. The general trend of substituent effect is also studied and discussed.

2. Theoretical methods

The geometry of all studied molecules was fully optimized at B3LYP level using 6-311+G** basis set, and confirmed to be energy-minimum by frequency analysis (having no imaginary frequency). DFT method (B3LYP) has been proved to be able to accurately predict structural properties and vibrational frequencies of borazine and its derivatives, in good agreement with the experimental values [8]. All calculations were performed using the GAUSSIAN 98 program suite [15].

Aromatic stabilization energies (ASE) and magnetic susceptibility exaltations (MSE) were calculated using homodesmotic reaction (**I**). Cis-dienes were used in all cases in this study, since the dienes subsystems are in *cis*-form in six-membered aromatics [16]. The magnetic susceptibilities and anisotropies were computed using CSGT [17]—B3LYP/6-311+G**//B3LYP/6-311+G**, and the NICS values were computed with GIAO [18]—HF/6-311+G**//B3LYP/6-311+G**. NICS(0) was calculated at the geometrical center of the ring, and NICS(1) were calculated at points 1.0 Å above the geometric ring center. As pointed out in our previous study [9], the NICS values could not correctly estimate the aromaticity of borazine derivatives. This probably results from the fact that NICS merely gives the information of shielding constant (i.e. the isotropic values, 1/3 of the trace of the shielding tensors), thus may cause loss of information on diatropic character of aromatic molecules and introduce spurious effects arising from electron flow perpendicular to the molecular plane [19]. It has been found that the NICS tensor component corresponding to the principal axis perpendicular to the ring plane, $NICS_{zz}$ could serve as a good measure for the characterization of the π system of the ring, since it corresponds more directly to the induced current densities in the molecular ring system when a magnetic field is applied perpendicular to the ring plane, and it has been concluded that the $NICS_{zz}$ calculated at large distances away from the ring center, i.e. 2 Å ($NICS_{zz}(2)$) or larger, where the $NICS_{zz}$ value is dominated by contributions from the π system, characterize NICS well [13]. $NICS_{zz}(2)$ values have been demonstrated to be a reliable measure of the aromaticity for borazine derivatives in our previous report [9]. Thus we only consider $NICS_{zz}(2)$ in the present study and NICS(0), NICS(1) values will not be discussed as aromaticity criteria but will be listed for comparison purpose.

Topological parameters of the bond critical point (BCP) of B–N bond were determined using Bader's theory of AIM [20,21]. The electronic density analysis was performed using B3LYP/6-311+G** level wavefunction by means of AIMPAC program [22].

All computations were performed on SGI3800 workstation and Dawning workstation in Nanjing University Supercomputer Center.