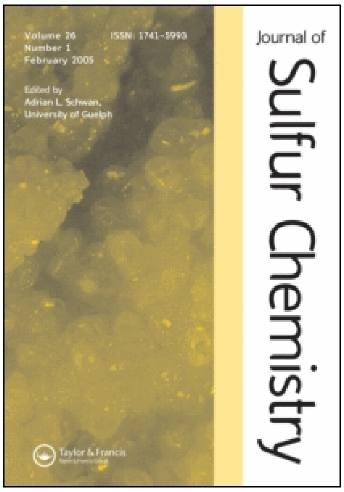

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Theoretical study of borthiin and its derivatives: structure and aromaticity

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RESEARCH ARTICLE

Theoretical study of borthiin and its derivatives: structure and aromaticity

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The electronic structure and properties of borthiin and 6 tri-substituted derivatives have been investigated using *ab initio* calculations. Basic measures of aromatic character derived from structure, and a variety of magnetic criteria (magnetic isotropic and anisotropic susceptibilities, magnetic susceptibilities exaltations, NICS are considered. Energetic criteria suggest that $\mathbf{B_3S_3Me_3}$ is the most aromatic of the species. However, by magnetic anisotropic susceptibilities, $\mathrm{NICS}_{zz}(2)$ $\mathbf{B_3S_3(CHO)_3}$ is the most aromatic of the family. $\mathrm{NICS}_{zz}(2)$ is found to be a reliable measure of the aromaticity for all species.

Keywords: Borthiin; Substituent Effect; Aromaticity; Magnetic Properties

1. Introduction

Benzene is the conventional example of a molecule that possesses notable physical properties arising from its delocalized π-electrons. In the past, chemists have searched for other molecules that are like benzene. Borazine ($B_3N_3H_6$) and boroxine ($B_3O_3H_3$) are examples that have been proposed: both are similar to benzene in geometry and in formal topology of the π-molecular orbitals. However, the question of whether their π-electrons are delocalized in the same sense as they are in benzene is less clear.

Aromaticity has many definitions. Bond-length equalization [1] extra energetic stabilization [2] with respect to an often hypothetical reference system, and the ability to sustain an induced diatropic ring current [3–6] have all been proposed as descriptors for aromaticity. Many studies have been devoted to the aromaticity of benzene analogues using concepts of aromatic stabilization energy (ASE), exaltation of diamagnetizability, Λ, and nucleus independent chemical shift (NICS7) [7–12]. On these criteria, 'inorganic benzenes' such as borazine ($B_3N_3H_6$), boroxine ($B_3O_3H_3$), and borthiin ($B_3S_3H_3$) are nonaromatic, whereas *s*-triphosphatriborin ($B_3P_3H_6$), hexaazabenzene (N_6), hexaphosphabenzene (P_6), and hexasilabenzene (Si_6H_6) are of modest aromatic character.

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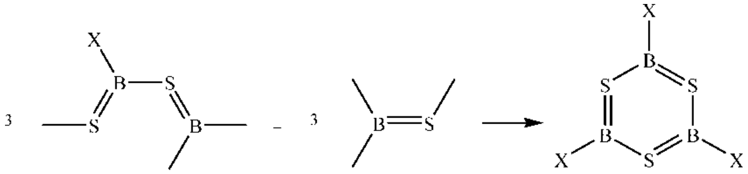
As an isoelectric compound with benzene, borthiin is an example of a six π- electron six-membered ring. Boron and sulfur combine to form an extensive series of molecular and solid state substances, but there is little resemblance to boron-oxygen chemistry. $B_3S_3(NMe_2)_3$has been synthesized by J. A. Forstner *et al.* [13].

The electronic structure of borthiin has raised many questions about the potential aromaticity of these compounds. In the present study, the structure, properties, and aromaticity of borthiin investigated. Also, substituent effects and the changes of the π-electron delocalization structure have been studied.

2. Computational details

Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang and Parr (B3LYP) [14, 15] method in combination with 6-31G(d, p) basis set [15–20] for B, C, N, O, S) has been employed in searching for the most stable for all structures. Vibrational frequencies at the B3LYP method were calculated to characterize stationary points as minima. All calculations have been performed using the GAUSSIAN 98 quantum chemical package [21].

ASE and magnetic susceptibility exaltations (Λ) were calculated using the following homodesmotic reaction:



Cis-dienes were used in all cases in this study, because the dienes subsystems are in the *cis*-form in the six-membered aromatic [22].

The magnetic susceptibility and anisotropies were computed using the continuous set gauge transformations, CSGT [23] method and the B3LYP/6-31G(d, p) level.

The NICS was used as a descriptor of aromaticity from the magnetic point of view. The NICS values were computed using GIAO at the B3LYP/6-31G(d, p) level [24–27]. The index is defined as the negative value of the absolute magnetic shielding computed at ring centers or another interesting point of the system [28]. The NICS denoted as NICS(2) is calculated 2 Å above the center and is expected to better reflect the π-electron structure [29]. Another descriptor is the 'out-of-plane' component of the NICS tensor computed at 2 Å above the ring center [denoted here as NICS(2)zz], which was found to be a good measure for the characterization of the π system of the ring [30]. Rings with highly negative values of NICS are quantified as aromatic by definition, whereas those with positive values are anti-aromatic. Nonaromatic cyclic systems should therefore have NICS values around zero.

The natural bond orbital (NBO) analysis has been performed by using NBO as implemented in GAUSSIAN98 using B3LYP/6-31G(d, p) [31].

3. Results and discussion

3.1 *Energetics*

The optimized geometric structures for borthiin and its derivatives species are illustrated in figure 1 at the B3LYP level of theory.

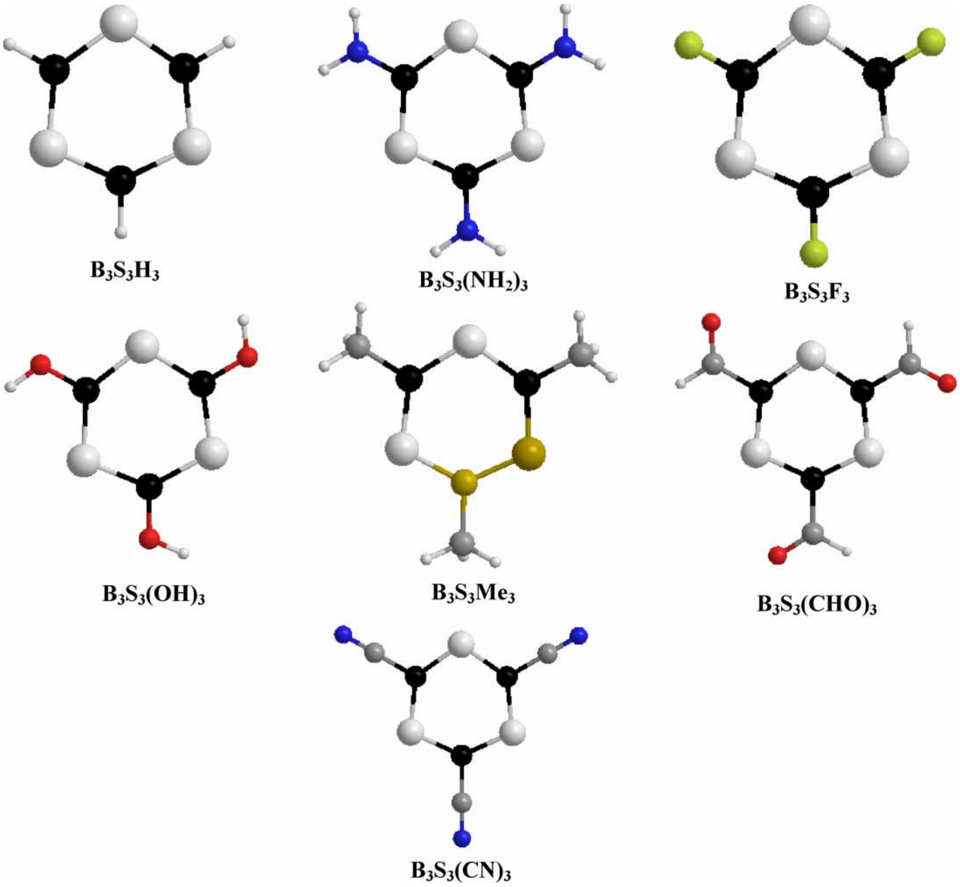


Figure 1. The geometric structure of borthiin and its derivatives.

The aromatic stabilization energies (ASE) for all structures were obtained at the B3LYP/6-31G(d, p) level. The ASE values are listed in table 1. These values show that $\mathbf{B_3S_3Me_3}$ is the most aromatic species. Also, the ASE values predict meta-directing groups have less aromaticity and aromaticity in substituted species is less than $\mathbf{B_3S_3H_3}$.

Table 1. Calculated (ASE, kcal/mol), Magnetic susceptibility exaltation (Λ, ppm), magnetic susceptibility anisotropies (χ aniso, ppm), NICS(2) and NICSzz(2) of borthiin and its derivatives at B3LYP/6-31G(d, p) level of theory.

Structure	ASE	Λ	χ aniso	NICS(2)	NICSzz(2)
benzene	−33.35	−12.97	−69.33	−11.31	−29.16
$B_3S_3H_3$	−7.92	−8.10	−56.64	−2.27	−8.08
$B_3S_3(NH_2)_3$	−7.35	−0.36	−28.20	−1.08	−5.37
$B_3S_3(OH)_3$	−5.50	−2.35	−28.24	−1.51	−5.84
$B_3S_3Me_3$	8.10	−5.74	−50.96	−1.94	−7.00
$B_3S_3F_3$	−5.92	−5.22	−28.12	−1.55	−6.17
$B_3S_3(CN)_3$	−2.44	−7.40	−36.25	−2.49	−7.94
$B_3S_3(CHO)_3$	1.14	−1.66	−56.13	−2.84	−9.06

Table 2. The selected of geometric structural parameters of borthiin and its derivatives (bond length are given Å, bond angles in degree).

Structure	r(B-S, Å)	∠B-S-B(degree)	∠S-B-S(degree)
$B_3S_3H_3$	1.810	109.9	130.1
$B_3S_3(NH_2)_3$	1.838	110.9	129.1
$B_3S_3(OH)_3$	1.836, 1.830	110.3	129.7
$B_3S_3Me_3$	1.824	112.5	127.5
$B_3S_3F_3$	1.823	108.4	131.5
$B_3S_3(CN)_3$	1.813	108.9	131.1
$B_3S_3(CHO)_3$	1.816, 1.804	109.3	130.6

Table 3. Frontier orbital energies (ε_{HOMO}, and ε_{LUMO}), HOMO-LUMO gap ($\Delta\varepsilon$) for borthiin and its derivatives at B3LYP/6-31G(d, p) level of theory (1 eV = 27.2116 Hartree).

Structure	ε(HOMO)	ε(LUMO)	$\Delta\varepsilon$ (eV)
$B_3S_3H_3$	−0.301	−0.077	6.10
$B_3S_3(NH_2)_3$	−0.239	0.017	6.96
$B_3S_3(OH)_3$	−0.272	−0.018	6.93
$B_3S_3Me_3$	−0.279	−0.051	6.19
$B_3S_3F_3$	−0.304	−0.055	6.78
$B_3S_3(CN)_3$	−0.338	−0.144	5.29
$B_3S_3(CHO)_3$	−0.266	−0.134	3.58

3.2 *Molecular geometries*

The lengths of the B-S bonds (in Å), B-S-B and S-B-S angles of borthiin and its derivatives are listed in table 2. As shown in table 2, the variation of B-S bond length with meta-directing groups is minor (±0.06 Å). The deactivating groups tend to decrease the ∠B-S-B angle while increasing the ∠S-B-S angle.

3.3 *Frontier orbital energies*

The frontier orbital energies of all structure are given in table 3. This table shows that, *ortho-para* directing groups cause increasing $\Delta\varepsilon$ values. An increase in the HOMO energy level indicates better donors and increasing of nucleophilicity (except $B_3S_3F_3$, $B_3S_3(CN)_3$). On the other hand, an increase in the LUMO energy level in the *ortho-para* directors causes decreasing electron accepting nature of compounds.

Ortho-para directors have the most $\Delta\varepsilon$ values. The decrease in the $\Delta\varepsilon$ values of *meta*directors indicates the lowering of kinetic stability of these species.

4. Relative aromaticity of borthiin and its derivatives from global magnetic aromaticity indices

4.1 *Relative aromaticities of borthiin and its derivatives from magnetics anisotropies*

Aromaticity of the borthiin and its derivatives also was assessed with global magnetic aromaticity indicators, such as anisotropy [32]. This is defined in Scheme 1 as the difference between the out-of-plane and the average in-plane diamagnetic susceptibilities ($\Delta\chi$) for a ring lying in the (xy) plane.

$$\Delta\chi = \chi_{zz} - \left(\frac{1}{2}\right)[\chi_{xx} + \chi_{yy}]$$

SCHEME 1

An advantage of this index is independence from a reference system.

Magnetic properties including magnetic shielding, magnetic susceptibilities, χ_{iso}, and magnetic susceptibility anisotropies, χ_{aniso}, have been computed for the set of borthiin and its derivatives are summarized in table 1.

Anisotropic values, χ_{aniso}, predict that substitution causes decreasing aromaticity. $\mathbf{B_3S_3(CHO)_3}$ is predicted to be the most aromaticity.

4.2 *Relative aromaticity of borthiin and its derivatives from magnetic susceptibility exaltation (Λ)*

The relative aromaticity of the borthiin and its derivatives was derived from the magnetic susceptibility exaltation [33]. The magnetic susceptibility exaltation Λ is the difference between the magnetic susceptibility of the system χ and that of a reference value derived for atom or bond increments:

$$\Lambda = \chi - \chi'$$

Estimates of the magnetic susceptibility exaltation can be found in table 1. The aromaticity decreases in substituted species also listed in table 1. Λ values predict $B_3S_3(CN)_3$ to be the most aromatic molecule.

4.3 *Relative aromaticity of borthiin and its derivatives from NICS*

The relative aromaticity of the borthiin and its derivatives was derived from the nucleus-independent chemical shifts. The GIAO NICS values for the all species (B3LYP/6-31G(d, p) level) are given in table 1. For a point located at the geometrical ring center and at point located above these rings center, equally spaced by 1.0 and 2.0 Å. The data in table 1 confirm that the aromaticity of borthiin and its derivatives are smaller than benzene, because they possess small negative NICS values. Also, NICS values show that the *meta*-director groups have the most negative NICS value in the ring planes.

NICSzz(2) calculated as the NICS tensor component corresponding to the principal axis perpendicular to the ring plane at the 2 Å above the ring center, has advantage over other criteria (ASE, MSE), in not requiring reference molecule, increment schemes, or calibration of equations. Furthermore, it avoids introduction spurious effect arising from the electron flow perpendicular to the ring plane, since it corresponds directly to the induced current densities in the molecular ring system when a magnetic field is applied perpendicular to the ring plane. NICSzz(2) values have been shown to work satisfactory in the estimation of the aromaticity of borazine derivatives [34]. Thereby, NICSzz(2) is taken as the major aromaticity criterion in this study. As listed in table 1, NICSzz(2) predicts that *meta*-directors, are the most aromatic species.

Table 4. Hybrids of natural bond orbitals π (B-S) calculated by NBO analysis of borthiin and its derivatives at B3LYP level of theory using 6-31G(d, p) basis set.

Structure	Occupancy	π (B-S)
$B_3S_3H_3$	1.8052	0.3641 (p 1.00)$_B$ + 0.9314 (p 1.00)$_S$
	1.8052	0.9314 (p 1.00)$_S$ + 0.3641 (p 1.00)$_B$
	1.8052	0.3641 (p 1.00)$_B$ + 0.9314 (p 1.00)$_S$
$B_3S_3(NH_2)_3$	–	–
$B_3S_3(OH)_3$	–	–
$B_3S_3Me_3$	1.8175	0.3492 (p 1.00)$_B$ + 0.9370 (p 1.00)$_S$
	1.8178	0.9370 (p 1.00)$_S$ + 0.3493 (p 1.00)$_B$
	1.8178	0.3492 (p 1.00)$_B$ + 0.9371*S (p 1.00)$_S$
$B_3S_3F_3$	1.8444	0.3301 (p 1.00)$_B$ + 0.9439 (p 1.00)$_S$
	1.8444	0.9439 (p 1.00)$_S$ + 0.3301 (p 1.00)$_B$
	1.8444	0.3301 (p 1.00)$_B$ + 0.9439 (p 1.00)$_S$
$B_3S_3(CN)_3$	1.7834	0.3843 (sp 1.00)$_B$ + 0.9232 (p 1.00)$_S$
	1.7834	0.9232 (p 1.00)$_S$ + 0.3843 (p 1.00)$_B$
	1.7834	0.3843 (p 1.00)$_B$ + 0.9232 (p 1.00)$_S$
$B_3S_3(CHO)_3$	1.7901	0.3936 (p 1.00)$_B$ + 0.9193 (p 1.00)$_S$
	1.7901	0.9193 (p 1.00)$_S$ + 0.3936 (p 1.00)$_B$
	1.7901	0.3936 (p 1.00)$_B$ + 0.9193 (p 1.00)$_S$

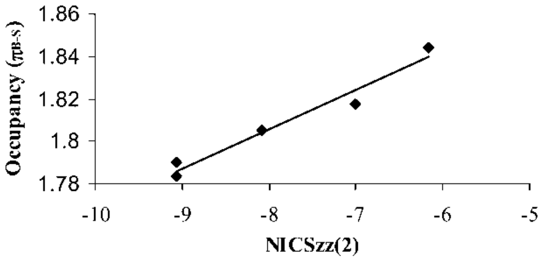


Figure 2. The variation of occupancy ($\pi_{\mathrm{B-S}}$) with NICszz(2) in borthiin and its derivatives.

5. NBO analysis

Occupancies of π(B-S) bonds are listed in table 4. The trends of variation in occupancies of π(B-S) bond are in good agreement with those of variation in the aromaticity predicted by NICSzz(2). This correlation relationship is graphed in figure 2.

$$\mathrm{NICSzz(2)} = 0.0186\ \mathrm{Occupancy}\ (\pi_{B-S}) + 1.9546;\ R^2 = 0.9625$$

These values show that the *meta*-director groups decrease the occupancy of borthiin, namely, decrease the π-bond order of B-S bonds.

6. Conclusion

In this paper, the structure and aromaticity of borthiin and its derivatives has been studied and the effects of substituent on the molecular structure, properties and aromaticity have been presented using energetic and magnetic criteria. Calculations show that deactivating susbtituents have a tendency to decrease the ∠B-S-B angle and increase the ∠S-B-S angle.

NICSzz(2) has been taken as the major criterion and to correlate well with the occupancy of B-S π-bond.

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