

A Density Functional Theoretical Studies on the Boroles Dianion: Structure, Properties and Aromaticity

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Received: Junio 10, 2012; Accepted: Septiembre 28, 2012

Abstract. The electronic structures and properties of the substituted boroles ($C_4H_4BX^{2-}$; X=H, BH₂, CH₃, NH₂, OH) have been investigated using hybrid density functional B3LYP theory. Basic measures of aromatic character are derived from structure, chemical shift, and Nucleus-independent chemical shift (NICS). Energetic criteria suggest that X=OH enjoys conspicuous stabilization. Apart from aromatic stabilization energies the other descriptors of aromaticity vary to very similar trend. Electronic delocalization index (DI), and quantum atoms in molecules analysis (QAIM) have been investigated in all compounds.

Key words: Aromaticity, Borole dianion, substituted boroles dianion, Density function Theory, electronic delocalization index (DI), quantum atoms in molecules analysis (QAIM).

Resumen. The electronic structures and properties of the substituted boroles ($C_4H_4BX^{2-}$; X=H, BH₂, CH₃, NH₂, OH) have been investigated using hybrid density functional B3LYP theory. Basic measures of aromatic character are derived from structure, chemical shift, and Nucleus-independent chemical shift (NICS). Energetic criteria suggest that X=OH enjoys conspicuous stabilization. Apart from aromatic stabilization energies the other descriptors of aromaticity vary to very similar trend. Electronic delocalization index (DI), and quantum atoms in molecules analysis (QAIM) have been investigated in all compounds.

Palabras clave: Aromaticity, Borole dianion, substituted boroles dianion, Density function Theory, electronic delocalization index (DI), quantum atoms in molecules analysis (QAIM).

Introduction

The close resemblance between cyclopentadienyl anion ($C_5H_5^-$) and borole dianion in terms of structure demonstrated that replacement of one methine group of cyclopentadienyl anion by an isoelectronic group does not disrupt aromaticity and is mainly responsible for the formulation of the concept of aromaticity. Borole dianion results from the replacement of the methine group by BH⁻ fragment [1].

Many studies have been devoted to the aromaticity of benzene analogues using concepts of aromatic stabilization energy, exaltation of diamagnetizability, Λ , and nucleus independent chemical shift (NICS) [2-5]. 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*-triphosphatiborin ($B_3P_3H_6$), hexaazabenzene (N_6), hexaphosphabenzene (P_6), and hexasilabenzene (Si_6H_6) are of modest aromatic character. As well as, aromaticity of the others inorganic and organometallic rings has been studied [6-21].

The present study investigated the family of borole dianion compounds in light of several of established criteria of aromaticity, using computational methodology.

Computational Methods

All calculations were carried out with the Gaussian 98 suite of program [22] using the 6-311G(d, p) basis set for all elements (C, H, N, B, O) [23, 24]. Geometry optimization was performed utilizing Becke's hybrid three-parameter exchange functional

and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP)[25]. A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum. Optimized geometries, energies of all the molecules discussed in this paper.

Calculations of nucleus-dependent and -independent chemical shifts were carried out using the gauge-invariant atomic orbital (GIAO) approach [26, 27] with the 6-311G(d, P) basis sets. The magnetic susceptibility exaltation was computed using continues set gauge transformations, CSGT [28], methods also using the 6-311G(d, P) basis set.

The degree of π -electron delocalization can be quantified on the basis of Bader's “atoms in molecules” (AIM) theory by using the delocalization index (DI), $\delta(A,B)$, that is obtained by double integration of the exchange-correlation density over the basins of atoms A and B[29,30]:

$$\delta(A, B) = - \int \int_{A B} \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 -$$

$$\int \int_{B A} \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = -2 \int \int_{A B} \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

The basin of an atom in the AIM theory is defined as the region in real space bound by Zero-flux gradient surfaces in the one electron density, $\rho(r)$, or by infinity. Quantitatively, δ provides an idea of the number of electrons delocalized (or shared) between A and B[30].

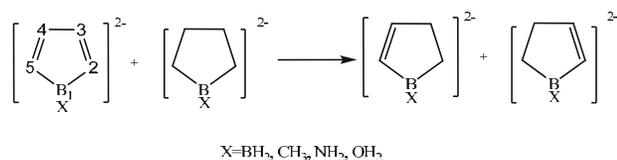
The AIM2000 program[31] was used for topological analysis of electron density and calculation of delocalization index. The following characteristics of ring critical points (RCPs) are

taken into account: density at RCP ($\rho(\text{rc})$), and its Laplacian ($\nabla^2(r_c)$). These calculations were at B3LYP/6-311G(d,p) level of theory.

Results and Discussion

1. Relative energetic

Aromatic stabilization energy (ASE) and magnetic susceptibility exaltations (Λ) were calculated using the following homodesmotic reaction[32]:



The calculated ASE values are given in Table 1. It was observed that the order of the aromaticity calculated with ASE measurements show that aromaticity increases in the following order: $\text{X}=\text{OH} > \text{NH}_2 > \text{CH}_3 > \text{BH}_2$.

2. Relative aromaticity from magnetic susceptibility exaltation (Λ)

The relative aromaticity of the borole dianion and its substituted borole dianion 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:

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

The estimates of the magnetic susceptibility exaltation can be found in Table 1. Also listed in Table 1 the most aromaticity is $\text{X}=\text{OH}$. This variation is compatible with ASE and NICS(0.0) values.

3. Nucleus-independent chemical shift analysis (NICS)

The nucleus-independent chemical shift (NICS) method has been widely employed to characterize the aromaticity[34]. As an effort to discuss the use of NICS as a measure of aromaticity

for five-membered, we have calculated NICS values along the z-axis to the ring plane beginning on the center of the ring up to 2.0 Å. These calculations show that the shape of NICS profile with respect to the distance from the ring center is similar. In addition, for all species, we have localized the NICS maxima and minima and determined the distances to the center of the ring at which they occur (Table 1). For all molecules, the highest absolute value of NICS is close to the center of the ring. It is possible that induced magnetic fields generated by the σ aromaticity are particularly large in the center of the ring, but systems having π aromaticity indicate a minimum NICS at the certain distance from the center of the ring. From Table 1, it can be seen that all five-membered ring compounds have large negative NICS values, indicating their enhanced aromatic properties. All these NICS values are mainly attributed to the delocalized π electrons current. The NICS (0.0) calculations indicated that the aromaticity of molecules generally increases from $\text{X} = \text{BH}_2$ to $\text{X} = \text{OH}$. The NICS (0.0) calculations results for aromatic character were in agreement with the isodesmic reactions results (Figure 1).

4. QTAIM analysis

QTAIM analysis provides a delocalization index for each bond between vicinal atoms. The delocalization index is a measure of the number of electrons that are shared or exchanged between two atoms or basins. Integration of the Fermi hole density leads to the localization index (LI) and delocalization index (DI). The Delocalization Index as an electronic aromaticity

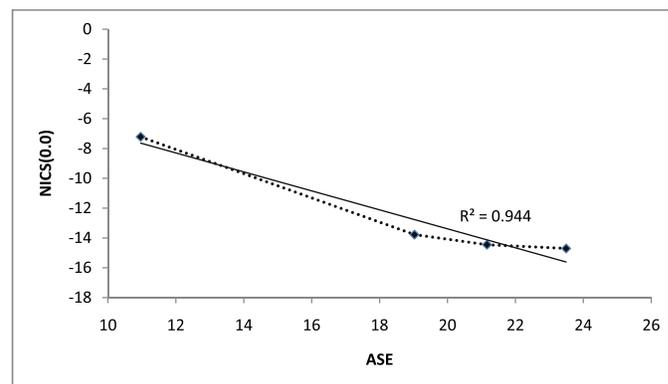


Fig. 1. Dependence of NICS(0.0) vs ASE for substituted boroles dianion ($\text{C}_4\text{H}_4\text{BX}^{2-}$; $\text{X}=\text{BH}_2, \text{CH}_3, \text{NH}_2, \text{OH}$).

Table 1. Aromatic stabilization energy (ASE, kcal/mol), magnetic susceptibility exaltation (Λ), NICS(0.0), NICS(0.5), NICS(1.0), NICS(1.5), and NICS(2.0) (ppm) values for borole dianion and substituted borole dianion.

X	ASE	Λ	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
H	14.76	-23.55	-14.09	-12.46	-9.29	-6.64	-4.49
BH_2	10.96	-15.11	-7.22	-7.21	-6.38	-5.07	-3.64
CH_3	19.03	-23.43	-13.78	-11.77	-8.56	-6.07	-4.08
NH_2	21.16	-23.25	-14.46	-12.11	-8.44	-5.69	-3.69
OH	23.49	-28.46	-14.70	-12.63	-8.74	-5.77	-3.68

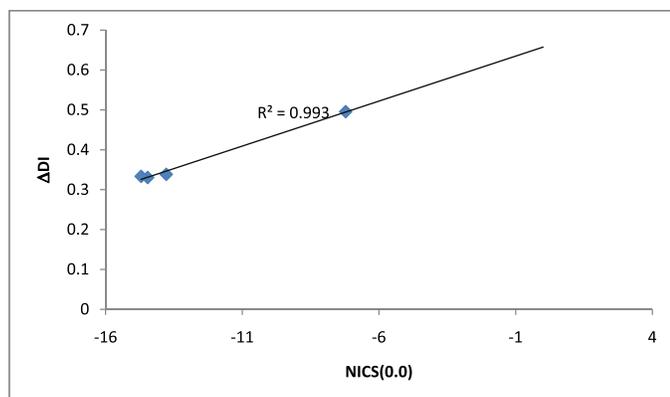


Fig. 2. Dependence of Δ DI vs NICS(0.0) for substituted borole dianion ($C_4H_4BX^{2-}$; X=BH₂, CH₃, NH₂, OH).

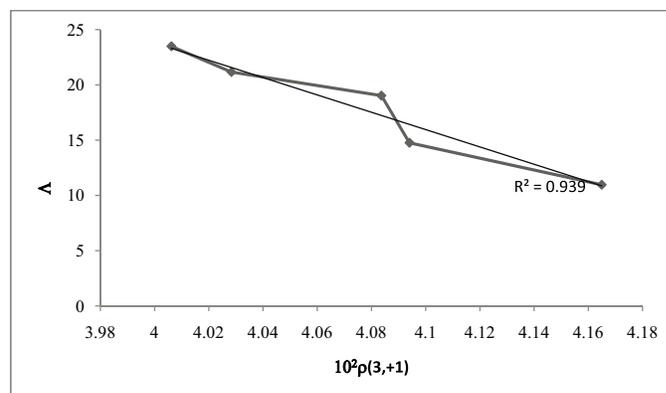


Fig. 3. Dependence of Λ vs $\rho(3,+1)$ for borole and substituted borole dianion ($C_4H_4BX^{2-}$; X=BH₂, CH₃, NH₂, OH).

criterion to a series of planar polycyclic aromatic hydrocarbons has been studied[35]. The mean of delocalization index has been defined as a new aromaticity criterion based on electron delocalization. The delocalization index for CC and CB bonds, average and sum of these values in a ring for the considered systems are collected in Table 2. On the other hand, Δ DI as the difference between $[DI(C2/C3)+DI(C4C5)/2]$ and $DI(C3C4)$ delocalization indices has been defined. These values indicate the more aromatic rings have the larger DI (C2C3), the smaller DI (C4C5) and DI (C3C4). There is a good linear correlation between NICS(0.0) and Δ DI (Figure 2).

Also, analysis of electron density by means of the Bader's methodology (AIM) provides useful tools to provide the $\rho(3,+1)$ (electron density) and $\nabla^2\rho(3,+1)$ (electron density laplacian) in ring center. Figure 3 presents a good correlation between magnetic susceptibility exaltation (Λ) and $\rho(3,+1)$ ($R^2 = 0.939$).

Conclusion

The electronic structure and properties of borole dianion and substituted borole dianion ($C_4H_4BX^{2-}$; X=BH₂, CH₃, NH₂, OH) have been investigated using ab initio calculations. Basic measurement of aromatic character derived from ASE, magnetic susceptibilities exaltations, and NICS suggest that the most aromaticity is for X=OH. Calculation of delocalization indices indicated the more negative the NICS values, the larger DI (C2C3) and the smaller DI (C4C5) and DI (C3C4).

Table 2. Electronic delocalization index (DI), sum and average of DI, Δ DI, electron density (e/a_0^3) and laplacian of electron density (e/a_0^5) in ring critical point for borole dianion and substituted borole dianion.

X	B1C2	C2C3	C3C4	C4C5	C5B1	Σ DI	\langle DI \rangle	Δ DI	$\rho(3,+1)$	$\nabla^2\rho(3,+1)$
H	1.370	1.385	1.371	0.785	0.785	5.697	1.139	0.3300	0.0409	0.2346
BH ₂	1.541	1.220	1.541	0.689	0.689	5.681	1.136	0.4955	0.0416	0.2366
CH ₃	1.360	1.396	1.360	0.755	0.755	5.625	1.125	0.3385	0.0408	0.2344
NH ₂	1.335	1.424	1.335	0.731	0.730	5.555	1.111	0.3305	0.0403	0.2316
OH	1.338	1.427	1.329	0.722	0.722	5.539	1.108	0.3335	0.0401	0.2306

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