

Probing Aromaticity of Borozene Through Optical and Dielectric Response: A Theoretical Study

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Abstract In this work, we report electronic structure calculations aimed at computing the linear optical absorption spectrum and static dipole polarizability of a newly proposed boron-based planar aromatic compound borozene ($B_{12}H_6$). For the purpose, we use the semiempirical INDO model Hamiltonian, accompanied by large-scale correlation calculations using the multi-reference singles-doubles configuration-interaction (MRSDCI) approach. We present detailed predictions about the energetics, polarization properties, and the nature of many-particle states contributing to various peaks in the linear absorption spectrum. Our results can be used to characterize this material in future optical absorption experiments. We also argue that one can deduce the aromaticity of the cluster from the optical absorption and static polarizability results.

Keywords Borozene · Optical properties · Aromaticity · Semi-empirical models

Introduction

Next to carbon-based chemistry, boron chemistry is surely one of the most active areas of research [1]. Boron exhibits a variety of polymorphisms which involve three-center two-electron (3c–2e) bonds [2], planar aromatic structures [3], nano-tubes [4], nano-ribbons [5], and fullerene-like cages

[6]. From the point of view of nano-technology, aromatic boron materials are of particular interest, because delocalized electron clouds in these materials will lead to large linear and non-linear optical susceptibilities, just like corresponding carbon-based structures. In order to achieve aromaticity, one needs to have a planar structure giving rise to π -orbitals. Indeed, aromaticity in boron-based clusters has been the subject of many recent investigations. Zhai et al. [7] in a recent joint theoretical and experiment study probed the issue of planarity and aromaticity of boron clusters. In another theory–experiment study, Zhai et al. [8] reported the discovery of planar boron clusters B_8 and B_9 clusters with “molecular wheel”-like structures and exhibiting both σ and π aromaticity. Aihara and coworkers [9] presented a theoretical investigation of aromaticity into several planar and quasi-planar boron clusters using the concept of “topological resonance energy”. Johansson [10] demonstrated theoretically the existence of strong magnetically induced ring currents in B_{20} and other toroidal clusters of boron, as an evidence of underlying aromaticity. Rincon et al. [11] theoretically demonstrated the σ aromaticity in several planar boron clusters performing an analysis of the electron-localization function (ELF). Similarly, Wu et al. [12] using an ab initio approach investigated the aromaticity of planar boron–carbon complex $C_6B_{12}^{-2}$. Another possible approach to achieve planarity, and, therefore, aromaticity in boron clusters is by hydrogenation of boron clusters. For example Alexandrova et al. [13] have demonstrated by means of theoretical calculations, that quasi-planar B_7^- cluster, upon hydrogenation, acquires a planar structure for $B_7H_2^-$. In a recent theoretical work, Szwacki et al. [14] proposed a novel planar aromatic cluster which can be obtained by hydrogenation of quasi-planar B_{12} cluster. They argued that the cluster is aromatic by performing a detailed analysis of its molecular orbitals and by examining magnetic

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properties such as nucleus-independent chemical shift (NICS), and anisotropy of magnetic susceptibility (AMS). Having thus demonstrated the similarities between the aromaticities of this cluster and benzene (including the number of π -electrons), they called it the boron analogue of benzene and named it borozene [14]. Encouraged by the work of Szwacki et al. [14], Forte et al. [15] performed *ab initio* calculations to predict larger aromatic compounds which can be constructed using borozene as formula unit. It is a well-known fact that the carbon-based aromatic materials including molecules such as benzene, naphthalene, anthracene, and longer π -conjugated polymers exhibit intense linear and non-linear optical response [16]. Therefore, it is of considerable interest to explore similar properties of aromatic materials consisting of elements other than carbon. With this aim in mind, here we present a systematic theoretical study, based upon a large-scale configuration-interaction (CI) methodology, of linear optical response of borozene. We believe our results will be useful in optical characterization experiments on this material, as also in exploring its possible application in nano-optics. Furthermore, we also perform calculations of static polarizability of this cluster, with the aim of exploring the signatures of aromaticity in its dielectric response. Aromaticity is an intuitive concept which essentially implies electron delocalization. Therefore, the consequences of this delocalization of electrons will be manifest in various properties of materials, including their magnetic as well as dielectric response. With the electrons delocalized along the plane of the molecule for conjugated systems as benzene, one would expect its “in-plane” dielectric response to be significantly more than its “perpendicular” response. Thus, this anisotropy in the static polarizability tensor α_{ij} can also be viewed as a signature of the aromaticity, in such systems. Indeed, this anisotropy in α has been verified theoretically by other authors in the past calculations on conjugated molecules [17–19] and has been used to formulate an “aromaticity scale” for such systems [17].

Remainder of the paper is organized as follows. In “Introduction” section, we briefly describe the theoretical methodology employed for the present calculations and also discuss the geometry of the molecule. This is followed by the presentation and discussion of our results in “Results and Discussion”. Finally, in “Conclusions” section, we present our conclusions.

Theoretical Methodology

The basic structure of borozene is presented in Fig. 1, and it corresponds to point symmetry group D_{3h} [14]. Before proceeding with our calculations, for the purpose of verification, we decided to perform the geometry optimization

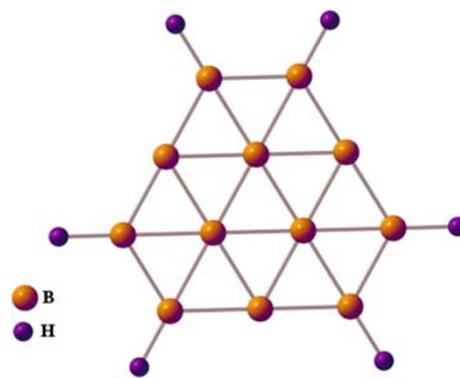


Fig. 1 (Color online) Structure of *S*-borozene considered in this work, assumed to lying in the *xy*-plane. Optimized bond lengths at INDO-HF level are B–B = 1.65 Å and B–H = 1.18 Å. Yellow dots indicate boron atoms and violet ones hydrogen atoms

on our own using the B3LYP-based hybrid DFT approach employing the 6-311++g(d) basis set as implemented in GAUSSIAN03 program [20]. The optimized structure thus obtained belonged to the D_{3h} point group symmetry with uniform value of B–H bond length 1.18 Å, and four distinct values of B–B bond lengths 1.63, 1.66, 1.81, and 1.86 Å. We, however, are interested in exploring an even more symmetric structure of borozene, so as to make the comparison with benzene more transparent. Therefore, we separately optimized a highly symmetric structure of borozene (*S*-borozene, henceforth) with identical B–B bond lengths, in addition to the B–H ones. For this purpose, as well as for the linear absorption spectrum calculations, we adopted an INDO model Hamiltonian [21] based approach implemented recently in a computer program developed by us [22]. INDO model is an effective valence-electron approach, employing a Slater-type minimal basis set, and some semi-empirical parameters [21]. The geometry optimization using our computer program, performed at the Hartree-Fock (HF) level (INDO-HF, henceforth), yielded bond lengths 1.65 Å for the B–B bond and 1.18 Å for the B–H bond. These values agree perfectly with 1.18 Å for the B–H bond length reported both by Szwacki et al. [14] and Forte et al. [15], and the average value of B–B bond length 1.649 Å reported by Forte et al. [15]. The total energy of the geometry-optimized *S*-borozene was higher than that of the borozene with distinct B–B bond lengths by ≈ 0.8 eV at the INDO-HF level.

Next, large-scale correlation calculations were performed on the ground and the excited states of *S*-borozene, using the multi-reference singles-doubles configuration-interaction (MRSDCI) approach as implemented in the MELD package [23] but employing the one- and two-electron matrix elements of the INDO Hamiltonian supplied by our program [22]. Thus, these correlated calculations were entirely within the INDO model and will be called

INDO-MRSDCI calculations, henceforth. During these calculations, point symmetry group C_{2v} was utilized, as against the D_{3h} symmetry group, because the MELD [23] package is restricted to D_{2h} and its sub-groups. Therefore, we classify the many-electron states of the system in terms of the irreducible representations (irreps) of C_{2v} group. The optical absorption spectra were calculated under the electric-dipole approximation employing the Lorentzian line shape. For both the ground and the excited states, these calculations were performed in an iterative manner, until the optical absorption spectra computed from them converged. We have extensively used this approach in our earlier calculations on conjugated polymers [24–27] as well as on B_{12} icosahedral and quasi-planar clusters reported recently [28].

Results and Discussion

Symmetry group C_{2v} consists of four irreps labeled a_1 , a_2 , b_1 , and b_2 . Assuming that the Cartesian xy -plane lies in the plane of the molecule (*cf.* Fig. 1), the symmetry adapted electronic structure of the HF ground state obtained from our code is $1a_1^2 2a_1^2 1b_1^2 3a_1^2 2b_1^2 4a_1^2 1b_2^2 3b_1^2 5a_1^2 4b_1^2 6a_1^2 7a_1^2 8a_1^2 5b_1^2 2b_2^2 1a_2^2 9a_1^2 6b_1^2 7b_1^2 10a_1^2 8b_1^2$, leading to 1A_1 many-particle configuration. Some of the lowest unoccupied orbitals in the ascending order of energy are $3b_2$, $2a_2$, $4b_2$, $11a_1$, $9b_1$ etc. Of all the orbitals, the ones belonging to a_2 and b_2 irreps are π orbitals and a_1 and b_1 are of σ type. Thus, we note that the highest occupied molecular orbital (HOMO) is a σ orbital, while the lowest unoccupied molecular orbital (LUMO) is a π orbital. For the sake of visualization, some of the orbitals are given in Fig. 2.

While our LUMO orbital matches perfectly with that reported by Szwacki et al. [14], however, we have a disagreement on the nature of the HOMO orbital which was

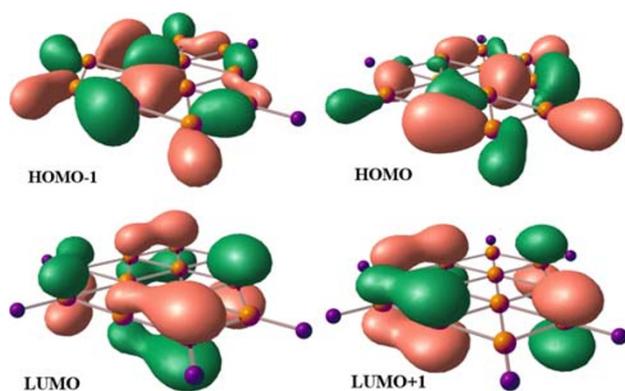


Fig. 2 (Color online) Molecular orbitals (iso plots) of *S*-borazene from HOMO–1 to LUMO+1, obtained from the INDO-HF calculations

reported to be of π -type by them [14], but we obtain it to be of σ -type within the INDO model. In order to rule out the possibility that this disagreement could be due to the use of the INDO model, or due to the *S*-borazene geometry, we studied the nature of the HOMO obtained using the 6-311++g(d) basis set both at RHF and DFT-B3LYP levels of *ab initio* theory [20] at various geometries. In all such DFT calculations, it turned out to be a σ -type orbital, but for the RHF calculations, the nature of HOMO was highly geometry sensitive with some geometries yielding it to be σ -type, while others of π -type. This, in our opinion, is a significant difference between the electronic structures of benzene (whose HOMO and LUMO both are π type) and borazene. Thus, borazene, in our opinion is an example of both σ and π conjugation because, close to the Fermi level, occupied orbitals are mainly of σ type, while the unoccupied ones (*LUMO*, *LUMO* + 1, *LUMO* + 2) are of π type. Before presenting the results of our calculations of linear optical absorption spectrum of *S*-borazene, we would like to discuss the influence of geometry on the optical properties of borazene, considering the fact that our calculations were performed on a highly symmetric conformer *S*-borazene. For the purpose, we performed the optical absorption calculations at the singles-CI (SCI) calculations both on the lowest energy structure of borazene with unequal B–B bond lengths and *S*-borazene. We found that qualitatively, at the SCI level, spectra were very similar for both the geometries, except that for *S*-borazene it was slightly red-shifted compared to borazene. The first peak for borazene in this SCI calculation was obtained at 2.6 eV in perfect agreement with excitation energy of the first excited reported by Szwacki et al. [14], while that for *S*-borazene was located at 2.4 eV.

Next, we present and discuss the results of our INDO-MRSDCI-based optical absorption calculations on *S*-borazene. Comparisons are also made with the absorption spectra of quasi-planar B_{12} bare cluster, and also with that of benzene. As the ground state of the system is 1A_1 , as per electric-dipole selection rules, it can make linear optical transitions to excited states belonging to symmetry manifolds 1A_1 , 1B_1 , and 1B_2 through photons polarized along the y -axis, x -axis, and z -axis, respectively. Thus, transitions to 1A_1 and 1B_1 are through photons polarized in the plane of the molecule (xy -plane in the present case), while those to 1B_2 will be through perpendicularly polarized photons. The INDO-MRSDCI calculations presented here involved construction and diagonalization of very large CI matrices running into millions of configurations, because simultaneously several states were targeted. For example, for the 1A_1 symmetry manifold, the total number of configurations was more than 2.1 millions, while those for 1B_1 and 1B_2 manifolds were in excess of 2.5, and 3 millions, respectively. Because of the large-scale nature of

these calculations, we believe that the results account for electron correlation effects properly.

In Fig. 3, we present the combined optical absorption spectrum of *S*-borozene, obtained from our INDO-MRSDCI calculations. As is obvious from the figures that the first absorption feature is a small peak located at 2.25 eV, corresponding to a *z*-polarized transition into a B_2 state. The many-particle wave function of this peak consists mainly of two single excitations $H \rightarrow L + 1$ and $H - 1 \rightarrow L$ ($H \equiv HOMO$; $L \equiv LUMO$), both of which are of $\sigma \rightarrow \pi^*$ type. After this feature at 2.25 eV, the next peak follows after a large gap of ≈ 5 eV and is due to two closely placed states at 7.38 eV (B_1 -type) and 7.55 eV (A_1 -type). Thus, this intense peak can be reached through photons which are polarized in the molecular plane, but not through the *z*-polarized ones. The many-particle wave functions of both these states are dominated by singly excited configurations, with the main configurations being $|H \rightarrow L + 3\rangle$ for the B_1 state, and $|H - 1 \rightarrow L + 3\rangle$ for the A_1 state. Thus, both these states correspond to $\sigma \rightarrow \sigma^*$ transitions.

Peak III of the spectrum, which is a weaker feature located at 8.44 eV, corresponds to a B_2 state and can be reached through a *z*-polarized photon. Many-particle wave function of this state is a mixture of several singly excited configurations which include $|H - 4 \rightarrow L\rangle$, $|H - 3 \rightarrow L + 1\rangle$, and $|H \rightarrow L + 8\rangle$, all of which are $\sigma \rightarrow \pi^*$ type excitations. Finally, feature IV near 9.1 eV draws its oscillator strength from the transition of the ground state to three closely spaced excited states of symmetries A_1 , B_1 , and B_2 located at 9.03, 9.01, and 9.19 eV, respectively. The peak has mixed polarization features, out of which *x*- and *y*-polarized transitions are more intense when compared to the *z*-polarized one. The many-particle wave function of the A_1

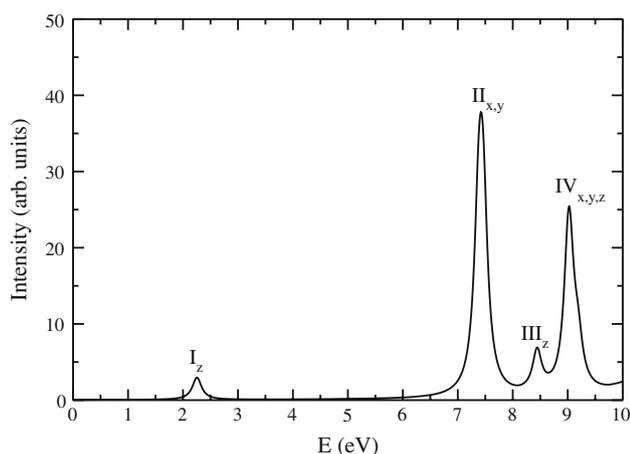


Fig. 3 Linear optical absorption spectrum of *S*-borozene, computed using the INDO-MRSDCI approach. Important peaks, along with their polarization characteristics, are labeled. A line width of 0.1 eV was used to compute the spectrum

state is dominated by configurations $|H - 1 \rightarrow L + 5\rangle$ and $|H \rightarrow L + 4\rangle$, while that of B_1 state consists mainly of $|H - 1 \rightarrow L + 4\rangle$ and $|H \rightarrow L + 5\rangle$, all of which are of $\sigma \rightarrow \sigma^*$ type. The dominant configurations in the wave function of the B_2 state are $|H \rightarrow L + 8\rangle$ and $|H - 1 \rightarrow L + 7\rangle$, which are of $\sigma \rightarrow \pi^*$ type. The absorption spectrum of *S*-borozene consists of several very intense features beyond 10 eV as well, but we are not discussing them here, given the fact that the ionization potential of this material is estimated close to 9 eV [14].

As Szwacki et al. [14] called borozene the boron analogue of benzene, it is interesting to compare the optical absorption spectra of the two materials. It is a well-known fact that the first dipole allowed transition in benzene is from the $^1A_{1g}$ ground state to the $^1E_{1u}$ excited state with the peak around 6.99 eV, through photons polarized in the plane of the molecule (*xy*-plane in our case) [29]. This compares very well with peak II (*cf.* Fig. 3) of *S*-borozene which is also caused by photons polarized in the the *xy*-plane and is located around 7.5 eV. The only difference being that for the the $^1E_{1u}$ state in benzene corresponds to a $\pi \rightarrow \pi^*$ transition, while the peak II of borozene corresponds to $\sigma \rightarrow \sigma^*$ transitions. This supports the hypothesis that borozene is both π and σ conjugated [14]. The difference between the optics of the two materials is the presence of low energy feature (peak I) in *S*-borozene corresponding to a *z*-polarized transition, whose counterpart in benzene does not exist.

Recently, we studied the linear optical absorption in quasi-planar B_{12} cluster which has a convex shape with symmetry group C_{3v} [28] and can be seen as a precursor of borozene [14]. Therefore, a comparison of the optical properties of quasi-planar B_{12} and borozene can help us understand the influence of hydrogen passivation on the optical properties of B_{12} . In Fig. 4, the linear optical absorption spectra of the two clusters are presented, and it is obvious that the first few peaks of *S*-borozene occur at lower energies when compared to the quasi-planar B_{12} . Moreover, the $H \rightarrow L$ transition is symmetry forbidden in *S*-borozene, which is not the case for quasi-planar B_{12} , and indeed contributes to the wave function of the first peak in its spectrum. Thus, the main contribution of hydrogen passivation on the optical properties is that it makes the structure completely planar (as against quasi-planar) leading to conjugation and higher symmetry. Lower energy gap of *S*-borozene is most certainly a consequence of conjugated nature of electrons in the system.

In order to explore the aromaticity of borozene, Szwacki et al. [14] computed and discussed its NICS plots and anisotropy of magnetic susceptibility (AMS). With a similar aim, we computed the three diagonal Cartesian components of the static polarizability tensor, α_{xx} , α_{yy} , and α_{zz} of borozene both at the INDO-HF and INDO-SDCI levels.

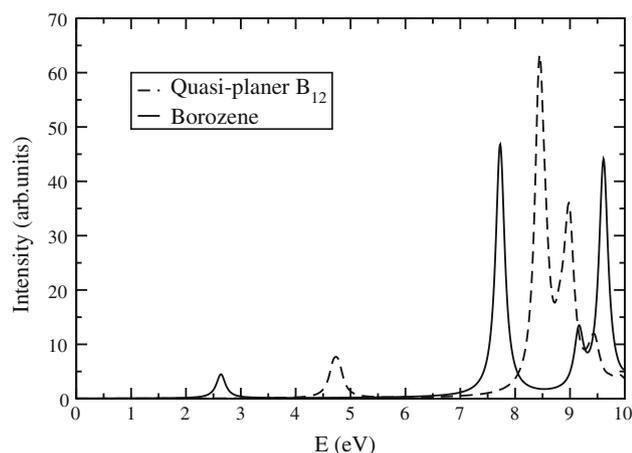


Fig. 4 A comparison of the linear optical absorption spectra between *S*-borazene (solid line) quasi-planer B₁₂ (broken line). The spectrum of *S*-borazene is significantly red-shifted when compared to that of B₁₂. A line width of 0.1 eV was used to compute the spectrum

For the purpose, we adopted a finite-field approach and computed the second derivative of the total energy of the system numerically, with respect to the three Cartesian components of the external electric field, whose values were taken to be 0.005 atomic units. The numerical values obtained in our calculations correspond to valence-electron contribution to the polarizability because of the nature of the INDO Hamiltonian. However, our aim here is not to obtain exact numerical values of the polarizability tensor, rather to compare the values of its various components. It is obvious from the results of our calculations presented in Table 1 that: (a) inclusion of correlation effects does not change the values of α_{ii} very much, and (b) the values of in-plane components (α_{xx} and α_{yy}) are significantly larger than the perpendicular component α_{zz} . *Ab initio* calculations performed on conjugated molecules like benzene, [17, 19] anthracene [18], and ethane [19] exhibit similar anisotropy in the components of the polarizability tensor. And, indeed, based upon the magnitude of this “in-plane” vs. “perpendicular” anisotropy, Lazzarretti and Tossell [17] argued for an “aromaticity scale” to characterize π -conjugated systems. Using the same logic, the same anisotropy found in our calculations clearly implies the aromaticity in borazene, but as a consequence of both π and σ conjugation in the plane of the molecule. This fact is also obvious from

Table 1 Values of the components of static dipole polarizability tensor of borazene computed using the INDO-HF and INDO-SDCI methods (in atomic units)

Method	$\alpha_{xx} = \alpha_{yy}$	α_{zz}
INDO-HF	34.273	21.833
INDO-SDCI	33.705	22.119

the optical absorption spectrum of the material in which intensities of the *z*-polarized peaks are much smaller than those of *x*- and *y*-polarized ones.

Conclusions

In conclusion, a correlated study on electronic structure and optical properties of a recently proposed boron-hydrogen cluster, borazene, was presented using the semi-empirical MRSDCI-INDO method. Our calculations of the linear optical absorption spectrum can be used to characterize this substance in future optical absorption experiments. We also calculated the diagonal components of the static polarizability tensor α_{ij} of the cluster and found significant larger values for the components along the plane of the molecule, when compared to the one perpendicular to it. This anisotropy in the components of the polarizability tensor implies that the electrons are quite delocalized along the plane of the molecule leading to a considerably larger response to an electric field directed along the plane, when compared to that perpendicular to the plane. Therefore, we argue that this anisotropy in the static dielectric polarizability of the cluster is an evidence of its aromaticity, [17] caused both by σ and π conjugation along the plane of the molecule.

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