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Dianionic Tetraborates Do Exist as Stable Entities

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Abstract: To date, $B_6H_6^{2-}$ and some of its derivatives are the smallest members of the *closo*-borates that have been synthesized and analyzed in condensed phases. In contrast, no stable dianionic tetraborate has yet been observed, either in solution or solids or in the gas phase. In this work, the gas-phase stability of dianionic tetraborates $B_4X_4^{2-}$ (X = H, CN, NC, or BO) is investigated with ab initio methods. For this objective, the geometries of the dianions are optimized, the electronic stability is tested, and various fragmentation channels are studied. In agreement with previous examinations, tetrahedral isomers of all examined tetraborates have been found to represent geometrically stable isomers and to exhibit a triplet electronic ground state. However, these isomers are electronically unstable, i.e., their additional electrons are not bound. Furthermore, new D_{2d}-symmetric isomers of $B_4X_4^{2-}$ (X = H, CN, NC, or BO) have been identified that have a closed-shell singlet ground state and are lower in energy than their tetrahedral counterparts. Moreover, $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ represent stable gas-phase dianions and are predicted to be observable in suitable experiments. The electronic properties and geometries of these dianions are discussed in detail and explained in terms of the electrostatic repulsion of the excess electrons and the aromaticity of the dianions.

1. Introduction

Boron hydrides have attracted the interest of theoretical as well as experimental chemists since their first preparation by Stock.[1] Because of the electron deficiency of the boron hydrides, the description of their bonding was a problem in theoretical chemistry for many years. This led to the development of the concept of three-center two-electron bonds and the so-called styx code, which allows the description of the structure of the boron hydrides within a valence-bond framework.[2,3] Today, the structure of the boron hydrides is well understood within the generalized electron-counting scheme, known as Wade's rules.[4−6] In general, Wade's rules divide clusters into several groups with respect to the number of electron pairs associated with cage bonding. The designations are *hypercloso*, *closo*, *nido* and *arachno* for clusters with n, $n + 1$, $n + 2$, and $n + 3$ electron pairs, respectively, where n is the number of vertexes of the cluster.

The structurally most appealing boron hydrides are the borate dianions $B_nH_n^{2-}$ whose existence was predicted theoretically in 1954.[7−9] Because these dianions exhibit $n + 1$ cluster electron pairs, they have, in accordance with Wade's rules, regular polyhedral structures with triangular faces, sometimes called deltahedra.[10] Today, it is well-established and already textbook knowledge that, indeed, all borate dianions $B_nH_n^{2-}$ ($n \geq 5$) exhibit *closo*-structures.[11,12]

A famous exception to Wade's rules is $B_4H_4^{2-}$,[13] as it has, in contrast to all other dianionic *closo*-borates, an open-shell triplet ground state in the tetrahedral geometry. Hence, a rule based on the concept of electron pairs is no longer valid. Oxidation of the tetrahedral dianion leads to the neutral cluster B_4H_4 which is today well-known to also have a tetrahedral isomer that logically has a closed-shell singlet ground state.[14,15] In a recent publication, McKee pointed out that B_4H_4 exhibits several structurally stable isomers.[16] Altogether, five isomers of B_4H_4 have been identified, among which are two C_s-symmetric isomers, the above-mentioned tetrahedral structure,

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a D_{2d}-symmetric cluster, and a totally asymmetric species.[16,17] It has clearly been shown that the energetically lowest structure of B_4H_4 is not the tetrahedral cluster, but a classical planar C_s-symmetric arrangement. Therefore, one has to consider classical as well as nonclassical cluster structures when examining dianionic tetraborates in detail.

Some *closo*-borate dianions are known to exist in condensed phases, and the smallest synthesized and spectroscopically investigated system thus far is $B_6H_6^{2-}$ and several of its derivatives.[18] In contrast, the small members of the hydro-*closo*-borates $B_nH_n^{2-}$ (n < 12) are not stable in the gas phase but spontaneously emit one of their excess electrons.[19,20] The smallest hydro-*closo*-borate that is stable in the gas phase is $B_{12}H_{12}^{2-}$.[19] This is not surprising because it is well-known that most of the small multiply charged anions known from condensed phases, such as carbonate CO_3^{2-},[21−23] sulfate SO_4^{2-},[24−26] and phosphate PO_4^{3-},[24] are not stable in the gas phase owing to the strong electrostatic repulsion of the excess negative charges. For comprehensive reviews in this research field, the reader is referred to refs 27−32.

In a recent publication, the question was addressed whether exchange of the hydrogens of *closo*-$B_6H_6^{2-}$ with appropriate ligands, e.g., halogens or pseudohalogens, leads to stabilization of the excess negative charges and to the formation of stable gas-phase dianions.[20] Indeed, it could be shown by means of standard ab initio methods that the dianions $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$ and the tetra-substituted isomers represent stable gas-phase dianions and should thus be observable in mass spectrometric experiments.[20] Motivated by these findings, we reduced the size of the substituted *closo*-borates and studied the stability of the penta- and tetraborate dianions $B_5X_5^{2-}$ and $B_4X_4^{2-}$ (X = CN, NC, or BO).[33] All of these systems represent stable gas-phase dianions, although they are not yet known to exist either in solution or crystals or in the gas phase. The substituted pentaborates exhibit the typical trigonal bipyramidal *closo* structure predicted by Wade's rules. Although these species will be discussed elsewhere in detail, we present here the results of our ab initio study on the tetraborates $B_4(CN)_4^{2-}$, $B_4(NC)_4^{2-}$, and $B_4(BO)_4^{2-}$.

This paper is organized as follows. After a description of the computational details (section 2), the results of our calculations are presented (section 3). In the latter section, we first turn to the parent tetrahydrotetraborate $B_4H_4^{2-}$ (section 3.1) and then describe the results for the substituted tetraborate dianions $B_4X_4^{2-}$ (X = CN, NC, or BO) (section 3.2). In section 4, our results are discussed in detail. The paper is concluded by a brief summary of our major findings (section 5).

2. Computational Details

The computer programs used for our calculations stem from the Aces2[34,35] packages of programs. Our calculations comprise the optimization of the geometry of the tetraborate dianions and the determination of the binding energies of the excess electrons as well as the determination of possible fragmentation channels at various levels of theory.

The data at the independent-particle level were obtained using the standard self-consistent field (SCF) restricted Hartree−Fock (RHF) method for the closed-shell *closo*-tetraborate dianions and the restricted open-shell Hartree−Fock (ROHF) technique for the corresponding open-shell monoanions and the tetrahedral dianionic isomers with a triplet ground state.

To explore the influence of the size of the basis set on the results of our calculations, we performed a basis set study on the D_{2d} isomer of $B_4(CN)_4^{2-}$ at the theoretical level of RHF. We restricted ourselves to the use of basis sets with double-ζ quality comprising Dunning's contractions[36,37] of Huzinaga's primitive sets.[38] The use of larger basis sets of triple-ζ quality is prohibitive because of the large size of the examined dianions and the need for high-quality methods such as CCSD and OVGF. The basis set study showed that the use of the standard DZP basis set augmented with an additional p-type diffuse function localized at each atomic center is sufficient to describe the properties of the examined dianions. The coefficients of the diffuse p-type functions are 0.016 63 for boron, 0.039 24 for nitrogen, 0.027 19 for carbon, and 0.050 70 for oxygen. Henceforth, this basis set is denoted as DZP+p. For hydrogen, the standard DZP basis set without diffuse functions was used. Moreover, the use of diffuse function always favors the dianion over the monoanion as the orbitals of a dianion are significantly more diffuse than the orbitals of the corresponding monoanion. Consequently, it is sufficient to use a moderately diffuse basis set to establish electronic stability, because the stability increases when more diffuse basis sets are used. In summary, the DZP+p basis set seems to be an ideal compromise between basis size and calculation time, and hence, we use this basis set as the standard in our calculations, unless the use of different basis sets is explicitly mentioned.

The geometries of the examined dianions were optimized at the SCF and MP2 levels of theory. In the case of the $B_4(CN)_4$ dianion, we also optimized the structure at the CCSD level of theory, which is known to give very reasonable geometries,[39,40] to check the reliability of the MP2-optimized geometries. The deviations between the MP2- and CCSD-optimized geometries turned out to be only marginal (see also section 3.2.2), and therefore we optimized the geometries of all other isomers only at the SCF and MP2 levels of theory.

The electron detachment energy (EDE) of the dianionic tetraborates can be obtained in two principally different ways. On one hand are the so-called "direct" methods, of which we have used Koopman's theorem

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(KT) and the outer-valence Green's function (OVGF) approach.[41,42] Whereas KT relates the orbital energy obtained in a closed-shell RHF calculation directly to the electron detachment energy, OVGF considers electron correlation and orbital relaxation effects. Thus, this method yields an improved electron detachment energy compared with KT. On the other hand, one can compute the EDE "indirectly" by subtracting the total energies of the monoanion and dianion. These methods are also referred to as Δ methods. We have employed ΔSCF, ΔMP2, and ΔCCSD. Note that a positive EDE indicates that energy has to be applied to detach an electron, i.e., the system is stable with respect to electron autodetachment.

Furthermore, the dianions were investigated with respect to fragmentation into two monoanionic fragments. For this objective, the geometries of possible fragmentation products were optimized at the CCSD level of theory, and the difference between the sum of the total energies of the fragments and the total energy of the dianion was calculated. This energy difference corresponds to the reaction energy of the corresponding fragmentation channel. If the total energy of the dianion is lower than the sum of the total energies of the fragmentation products, the reaction energy has a positive sign, and the dianion is thermodynamically stable with respect to fragmentation. If the reaction energy is negative, the dissociation pathway must be calculated explicitly to estimate the lifetime of the dianion with respect to this decay channel.

3. Dianionic Tetraborates

The theoretical investigation of multiply charged anions, in this work dianions, is generally more involved than the investigation of cationic or neutral systems. This is due to the strong electrostatic repulsion of the excess negative charges of dianions, which strongly supports the emission of one of the additional electrons. Consequently, whenever a dianion is examined, the electronic stability of the system has to be thoroughly studied. Only when the electronic stability is given, or the dianion represents a long-lived resonance, can meaningful quantitative predictions be made by means of standard bound-state quantum chemical methods.[43,44] Furthermore, fragmentation of the nuclear framework has to be considered, because the additional charges also favor the fragmentation of the dianion into monoanionic fragments. This phenomenon is well-known for multiply charged cations under the term Coulomb explosion and is due only to the dominating electrostatic repulsion of the additional charges.

In principle, a theoretical investigation of an unknown species always starts with the search for equilibrium structures corresponding to isomers of the given species. In the case of the tetraborates, we started the geometry optimizations with the five isomers of B_4H_4 discussed by McKee,[16] replaced the hydrogen atoms by the appropriate ligands, added two additional electrons, and reoptimized the structures at various levels of theory. Whereas the assumption of classical C_s- and C_1-symmetric structures for $B_4H_4^{2-}$ did not lead to stationary points on the corresponding potential energy surface (PES), a tetrahedral and D_{2d}-symmetric structure yielded minima on the PES of the $B_4X_4^{2-}$ (X = H, CN, NC, BO) dianions, and consequently, those minima represent isomers of the respective dianions.

In the following, we present our results for the dianionic tetraborates $B_4X_4^{2-}$ (X = H, CN, NC, BO). First, we present our results for the tetrahydrotetraborate $B_4H_4^{2-}$ in section 3.1. In section 3.2, we turn to the substituted species $B_4X_4^{2-}$ (X = CN, NC, BO), where we first briefly outline our results for the tetrahedral isomers (section 3.2.1) and then give a detailed description of our results for the D_{2d}-symmetric isomers (section 3.2.2).

3.1. Tetrahydrotetraborate $B_4H_4^{2-}$. As a starting point and for reference, we studied the tetrahydrotetraborate $B_4H_4^{2-}$, even though it is well-known that this dianion does not represent a stable gas-phase dianion. Searching the potential energy surface for stationary points, we found two structures that correspond to minima, because their harmonic frequencies exhibit only real values. The first isomer exhibits a tetrahedral geometry and a triplet $^3A_1$ ground state. This is in agreement with previous findings for $B_4H_4^{2-}$, which is known to exhibit a doubly degenerate HOMO (highest-occupied molecular orbital).[13,14] We optimized its geometry at the ROHF, MP2, and CCSD levels of theory using the DZP+p basis set for boron and the DZP basis set for hydrogen and calculated the vertical electron detachment energies (EDEs). At the CCSD level of theory, we found a B−B bond length of 1.779 Å and a B−H distance of 1.214 Å. For the vertical electron detachment energy, we obtained values of −9.30, −8.49, and −8.48 eV at the ΔSCF, ΔMP2, and ΔCCSD levels, respectively. Consequently, the tetrahedral $B_4H_4^{2-}$ is electronically very unstable in the gas phase.

The second isomer of $B_4H_4^{2-}$ that we identified has D_{2d} symmetry and a singlet $^1A_1$ ground state. To the best of our knowledge, this is the first time that this structural isomer has been reported in the literature. The geometry optimization of this isomer at the CCSD level of theory gave values of 1.662 and 1.235 Å for the B−B and B−H bond lengths, respectively. The B−B−B angle was found to be 82.0°, the B−B−H angle 139°, and the B−B−B−B dihedral angle 41°. Compared to the tetrahedral isomer, the D_{2d}-symmetric $B_4H_4^{2-}$ is significantly more stable with respect to electron emission, because the vertical EDE has values of −4.19, −2.88, and −3.17 eV at the theoretical levels of ΔSCF, ΔMP2, and ΔCCSD, respectively. Nevertheless, it is electronically very unstable.

In summary, our calculations confirm the high electronic instability of the tetrahydrotetraborate dianion $B_4H_4^{2-}$ and indicate the existence of a closed-shell D_{2d}-symmetric isomer for this class of dianions. Here, we emphasize again that the results of the calculations presented so far were obtained with bound-state methods for highly unbound species. This calls into question the quantitative values of the bond lengths and electron detachment energies. Especially the EDEs have no quantitative meaning, except that the dianion is unstable with respect to electron emission. To obtain reliable values, resonance-state calculations need to be performed, as typically done by Sommerfeld.[43]

3.2. Substituted Tetraborates $B_4X_4^{2-}$ (X = CN, NC, BO). The preliminary investigation of $B_4H_4^{2-}$ has already indicated that two different isomers exist for this class of dianions: a tetrahedral isomer with a triplet ground state and a D_{2d}-symmetric isomer with a singlet ground state. Substitution of the hydrogen atoms by the pseudohalogen ligands CN, NC, and BO does not change this situation. In analogy, only these two different isomers could be identified for the dianions $B_4(CN)_4^{2-}$, $B_4(NC)_4^{2-}$, and $B_4(BO)_4^{2-}$. In the following sections, we briefly

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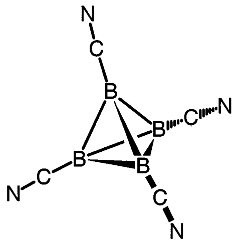

Figure 1. Geometry of the T_d-symmetric isomer of $B_4(CN)_4^{2-}$.

Table 1. Geometrical Parameters and Vertical Electron Detachment Energies of the Tetrahedral Isomers of $B_4(CN)_4^{2-}$, $B_4(NC)_4^{2-}$, and $B_4(BO)_4^{2-}$ for the ROHF- and MP2-Optimized Geometries[a]

	$B_4(CN)_4^{2-}$		$B_4(NC)_4^{2-}$		$B_4(BO)_4^{2-}$	
	ROHF	MP2	ROHF	MP2	ROHF	MP2
			geometrical parameters			
r(B−B)	1.686	1.687	1.691	1.683	1.698	1.697
r(B−L$_i$)	1.555	1.519	1.482	1.448	1.652	1.626
r(L$_i$−L$_o$)	1.150	1.201	1.156	1.204	1.217	1.247
			EDE			
ΔSCF	−2.062	−1.668	−2.973	−3.147		−1.365
ΔMP2	−1.610	−1.492	−1.951	−1.944		−1.314
ΔCCSD	−1.652	−1.519	−2.210	−2.290		−1.317

[a] L$_i$ and L$_o$ refer to the inner and outer atoms, respectively, of the diatomic ligands. The bond lengths are given in angstroms, and the energies are in electronvolts.

describe our findings for the tetrahedral isomers (section 3.2.2) and then turn to the D_{2d}-symmetric ones (section 3.2.2).

3.2.1. Tetrahedral Isomers. Substitution of the hydrogen atoms of the tetrahedral isomer of $B_4H_4^{2-}$ by CN, NC, and BO gives rise to tetrahedral isomers of $B_4(CN)_4^{2-}$, $B_4(NC)_4^{2-}$, and $B_4(BO)_4^{2-}$, each of which exhibits a triplet $^3A_1$ ground state. The geometry optimizations of these dianions at the ROHF and MP2 levels of theory converged quickly to stationary states, which all represent minima on the respective PESs. As an example, the tetrahedral structure of $B_4(CN)_4^{2-}$ is shown in Figure 1. The B−B distance within the B_4 tetrahedron in all isomers has a value of around 1.69 Å (Table 1), which is slightly shorter than the values found for the B−B bond in $B_6(CN)_6^{2-}$ (1.72 Å).[20] The cage ligand bonds are clearly single bonds with typical values for the three examined dianions. The C−N bond of $B_4(CN)_4^{2-}$ and the N−C bond of $B_4(NC)_4^{2-}$ have lengths typical for triple bonds, whereas the B−O bond of $B_4(BO)_4^{2-}$ has more double bond character.

An investigation of the electronic stability of the tetrahedral tetraborates clearly shows that none of these isomers represent electronically stable dianions. For the MP2-optimized geometries, a vertical EDE of −1.519 eV was found for $B_4(CN)_4^{2-}$, of −2.290 eV for $B_4(NC)_4^{2-}$, and of −1.317 eV for $B_4(BO)_4^{2-}$. The substantially negative values for the vertical EDEs for all of these dianions rule out the existence of these species in the gas phase, but it might be possible to observe them in the condensed phases, e.g., in matrix isolation experiments. As has been pointed out previously, unstable dianions such as carbonate CO_3^{2-} and sulfate SO_4^{2-} experience a significant stabilization of several electronvolts by the neighboring atoms and molecules in condensed phases, e.g., water.[45]

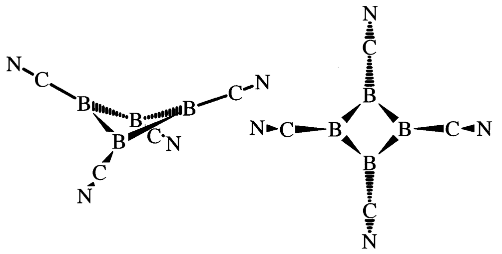

Figure 2. Structure of the D_{2d}-symmetric dianion $B_4(CN)_4^{2-}$ in side (left) and top (right) views.

3.2.2. *D$_{2d}$*-Symmetric Isomers. The geometries of the D_{2d}-symmetric isomers of the tetrasubstituted tetraborates $B_4X_4^{2-}$ (X = CN, NC, or BO) derived from the analogous $B_4H_4^{2-}$ isomer were optimized at the theoretical levels of SCF and MP2, with the CN-substituted system also optimized at the theoretical level of CCSD. Analyses of the harmonic frequencies of these geometries show only real values at all levels of theory; hence, the D_{2d}-symmetric structures do indeed represent minima on the corresponding PESs. The electronic ground state of each of these isomers is a closed-shell $^1A_1$ state.

The B−B bond length of $B_4(CN)_4^{2-}$ has values of 1.624, 1.621, and 1.618 Å at the levels of SCF, MP2, and CCSD, respectively, which indicates shortened B−B single bonds (see Figure 2 and Table 2). The values found for the B−C bond length of 1.576 (SCF), 1.542 (MP2), and 1.555 (CCSD) Å are typical values for B−C single bonds,[11] while the C−N bond lengths of 1.149, 1.199, and 1.184 at the SCF, MP2, and CCSD levels, respectively, clearly indicate triple-bond character. The B−B−B angle decreases by about 3° from 83.8° to 80.7° when going from the SCF to the MP2 level of theory and slightly increases again when the geometry is optimized at the CCSD level to give 81.7°. Whereas the B−B−C angle remains more or less unchanged at 139° through all levels of theory, the B−B−B−B dihedral angle increases from 37° at the RHF level to 44° at the MP2 level and decreases again to 42° at the CCSD level. Because the geometrical parameters do not change significantly from the MP2 to the costly CCSD level, it is sufficient to optimize the geometries of the other dianions at the SCF and MP2 levels to obtain reliable results.

In the D_{2d}-symmetric isomer of $B_4(NC)_4^{2-}$, the B−B, B−N, and N−C bonds exhibit lengths of 1.641 (1.621), 1.508 (1.479), and 1.154 (1.198) Å at the SCF (MP2) level of theory, respectively (Table 2). According to these values, the B−B bond is again a shortened B−B single bond, the B−N bond is a single bond, and the N−C bond clearly corresponds to a triple bond. When going from the RHF level to the MP2 level, one observes a bending of the $B_4(NC)_4^{2-}$ dianion, which results in a decrease of the B−B−B angle from 87° to 83° and a significantly enlarged B−B−B−B dihedral angle from 23° to 36°.

The geometrical parameters of the $B_4(BO)_4^{2-}$ isomer exhibit similar characteristics (Table 2). The cluster B−B bond, the ligand B−B bond, and the B−O bond have values of 1.631 (1.626), 1.669 (1.640), and 1.216 (1.247) Å at the level of SCF (MP2). These lengths correspond to a shortened B−B single bond within the B_4 frame, a typical B−B single bond between the frame and the BO ligand, and a B−O double bond, respectively. Also, the $B_4(BO)_4^{2-}$ isomer bends slightly when going from the SCF to the MP2 level of theory, which can be seen best in the decrease from 81.4° to 79° of the B−B−B angle and the increase from 42.2° to 47.3° of the B−B−B−B dihedral angle.

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Table 2. Geometrical Parameters for the D_{2d}-Symmetric Equilibrium Structures of $B_4(CN)_4^{2-}$, $B_4(NC)_4^{2-}$, and $B_4(BO)_4^{2-}$ [a]

	$B_4(CN)_4^{2-}$			$B_4(NC)_4^{2-}$		$B_4(BO)_4^{2-}$	
	RHF	MP2	CCSD	RHF	MP2	RHF	MP2
r(B−B)	1.624	1.621	1.618	1.641	1.621	1.631	1.626
r(B−L_i)	1.576	1.542	1.555	1.508	1.479	1.669	1.640
r(L_i−L_o)	1.149	1.199	1.184	1.154	1.198	1.216	1.247
∠(B−B−B)	83.79	80.77	81.65	87.43	83.70	81.44	78.94
∠(B−B−L_i)	138.10	139.62	139.18	136.29	138.15	139.28	140.53
∠(B−B−B−B)	36.40	43.66	41.73	23.94	36.67	42.19	47.30

[a] Geometries of the dianions were optimized at the levels of SCF and MP2 and also at the CCSD level for $B_4(CN)_4^{2-}$ using the DZP+p basis set. The bond lengths are given in angstroms, and the angles are in degrees.

Table 3. Vertical and Adiabatic Electron Detachment Energies (EDEs) at Various Levels of Theory for the RHF-, MP2-, and CCSD-Optimized Geometries of the Dianions[a]

	$B_4(CN)_4^{2-}$			$B_4(NC)_4^{2-}$		$B_4(BO)_4^{2-}$	
geometry	RHF	MP2	CCSD	RHF	MP2	RHF	MP2
			vertical EDE				
KT	0.657	0.834	0.796	−0.250	−0.248	0.545	0.790
ΔSCF	−0.743	−0.611	−0.324	−1.302	−1.394	−0.512	−0.31
ΔMP2	0.415	0.474	0.692	0.439	0.439	0.467	0.592
ΔCCSD	0.096	0.158	0.397	−0.033	−0.095	0.196	0.340
OVGF	0.289	0.301	0.414	0.278	0.297	0.323	0.465
			adiabatic EDE				
ΔSCF	−0.883					−0.778	
ΔMP2		0.392					0.531

[a] Most reliable values are those at the DCCSD and OVGF levels of theory. The energies are given in electronvolts.

An investigation of the electronic stability of the dianionic tetraborates reveals that $B_4(CN)_4^{2-}$ has a vertical electron detachment energy (EDE) of +0.796 eV at the theoretical level of KT and of −0.324 eV at the ΔSCF level using the CCSD-optimized geometry. This decrease of the EDE is easily understood by the fact that KT does not contain orbital relaxation effects but describes the EDE in terms of a static orbital approximation. ΔSCF considers orbital relaxation and thus favors the monoanion and leads to a decrease of the EDE. Turning to correlated methods, the vertical EDE of $B_4(CN)_4^{2-}$ increases to 0.692, 0.397, and 0.414 eV at the theoretical levels of ΔMP2, ΔCCSD, and OVGF, respectively. This increase of the EDE when correlation is included is simply due to the fact that one electron more is correlated in the dianion than in the monoanion. The adiabatic EDE, which is calculated with respect to a separately geometry-optimized monoanion, has values of −0.883 and 0.392 eV at the ΔSCF and ΔMP2 levels, respectively. In conclusion, the D_{2d}-symmetric isomer of $B_4(CN)_4^{2-}$ is stable with respect to electron loss.

Upon closer examination of the computed values for the EDE of the D_{2d}-symmetric isomer of $B_4(NC)_4^{2-}$ (Table 3), it turns out that this system is a borderline case. At both the RHF- and the MP2-optimized geometries, the vertical EDE has negative values of about −0.25 eV at the theoretical level of KT and about −1.35 eV at the ΔSCF level. Turning to correlated methods, the obtained values for the vertical EDE are +0.439 eV at the ΔMP2 level, +0.297 eV using the OVGF approach, and −0.095 eV for ΔCCSD at the MP2 geometry. Judging from these results, it is hardly possible to make a reliable prediction concerning the electronic stability of this isomer of $B_4(NC)_4^{2-}$. In view of these results, $B_4(NC)_4^{2-}$ is a borderline case, and we can consider this species to be either stable or at least long-lived with respect to electron emission. If the true EDE is slightly negative, the species is unstable, but the emission of one of the excess electrons is hindered by the repulsive Coulomb barrier. The repulsive Coulomb barrier is a general phenomenon in multiply charged anions and has been discussed in detail.[32,44,46−50] Nevertheless, it is clear that $B_4(NC)_4^{2-}$ is substantially more stable than the tetrahedral isomer but also significantly less stable than the D_{2d}-symmetric isomer of the $B_4(CN)_4^{2-}$ isomer.

The third investigated system, the D_{2d} isomer of $B_4(BO)_4^{2-}$, is again clearly an electronically stable dianion. The vertical EDE has positive values throughout all correlated levels of theory (Table 3). At the ΔMP2 level, the vertical EDE has a value of 0.592 eV (0.467 eV); at the OVGF level, 0.340 eV (0.196 eV); and at the ΔCCSD level, 0.465 eV (0.323 eV) using the MP2 (RHF)-optimized geometry within the calculation.

Summarizing the investigation of the electronic stability of the D_{2d}-symmetric isomers of the substituted tetraborates, we have established the stability of $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ and the possible longevity of $B_4(NC)_4^{2-}$ with respect to electron emission. As already mentioned, a stable gas-phase dianion must exhibit a second major property, which is stability with respect to fragmentation of the nuclear framework. Only fragmentations into two monoanionic fragments are relevant in this context, because these channels are, in general, energetically strongly favored because of the electrostatic repulsion of the excess negative charges.

A study of various fragmentation channels of $B_4(CN)_4^{2-}$ showed that the most relevant fragmentation channels for this dianion are the following three

$$B_4(CN)_4^{2-} \rightarrow CN^- + B_4(CN)_3^- \qquad (I)$$

$$B_4(CN)_4^{2-} \rightarrow BCN^- + B_3(CN)_3^- \qquad (II)$$

$$B_4(CN)_4^{2-} \rightarrow 2\ B_2(CN)_2^- \qquad (III)$$

Our investigation of these fragmentation channels comprised the geometry optimization of the fragments at the CCSD level using the DZP+p basis set and the calculation of the sum of the total energies of the fragments at the SCF, MP2, and CCSD levels of theory. The difference between the sum of the fragments and the total energy of the dianion corresponds to the reaction energy. If the reaction energy has a positive sign, energy must be applied to break up the dianion, i.e., $B_4(CN)_4^{2-}$ is thermodynamically stable with respect to fragmentation.

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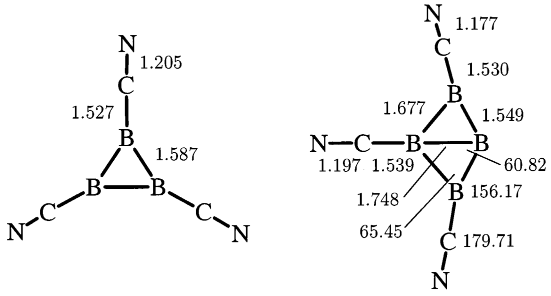

Figure 3. Structures and geometrical parameters of the D_{3h}-symmetric fragmentation product $B_3(CN)_3^-$ emerging from channel II and of the C_{2v}-symmetric fragmentation product $B_4(CN)_3^-$ of channel I. The geometries have been optimized at the CCSD level of theory using the DZP+p basis set. Lengths are given in angstroms; angles in degrees.

Table 4. Reaction Energies for the Fragmentation Pathways I, II, and III (see text) of $B_4(CN)_4^{2-}$ [a]

	fragmentation pathway		
	I	II	III
SCF	259.6	247.6	208.6
MP2	344.6	383.9	296.6
CCSD	318.7	371.6	265.6

[a] Energies (kJ/mol) calculated at the SCF, MP2, and CCSD levels of theory using the CCSD-optimized geometries of the dianion and the fragments.

Geometry optimization of the dissociation products of channel I at the CCSD level of theory yields a bond length of 1.199 Å for the CN^- anion and a C_{2v} geometry for the $B_4(CN)_3^-$ fragment, which is analogous to the C_{2v}-symmetric structure that has been found for $B_4H_3^-$.[16] The structure is displayed in Figure 3, together with the optimized geometrical parameters. Calculation of the reaction energy for fragmentation channel I shows clearly positive values, e.g., 318 kJ/mol at the CCSD level (Table 4), and consequently, $B_4(CN)_4^{2-}$ is stable with respect to the departure of a CN^- anion.

A second possible fragmentation path is given by channel II, which is fragmentation into BCN^- and a $B_3(CN)_3^-$ fragment. At the CCSD level of theory, the BCN^- anion is linear, with B−C and C−N bond lengths of 1.413 and 1.182 Å, respectively. The structural parameters of the D_{3h}-symmetric $B_3(CN)_3^-$ anion are given in Figure 3. In analogy to channel I, only clearly positive values of the reaction energy were found for fragmentation pathway II (Table 4), with a value of 371 kJ/mol at the CCSD level of theory.

A separate geometry optimization of the $B_2(CN)_2^-$ anion, which is the fragmentation product of channel III, revealed that this anion exhibits a linear $D_{\infty h}$ symmetry (NCBBCN). The B−B, B−C, and C−N bonds have lengths of 1.480, 1.511, and 1.182 Å, respectively. $B_4(CN)_4^{2-}$ is also thermodynamically stable with respect to this fragmentation channel, because the reaction energy again has only positive values at all applied levels of theory (Table 4). Consequently, $B_4(CN)_4^{2-}$ is clearly thermodynamically stable with respect to fragmentation of the nuclear framework, which can be attributed to the mainly covalent character of the involved bonds. Because the bonding situations of $B_4(NC)_4^{2-}$ and $B_4(BO)_4^{2-}$ are very similar to that of $B_4(CN)_4^{2-}$, as was pointed out in section 3.1, stability with respect to dissociation can be expected for those dianions as well. According to these results, the stability with respect to fragmentations of the whole family of dianionic borates $B_nX_n^{2-}$ ($n \geq 4$) can be taken for granted.

Summarizing the investigation of the dianionic tetraborates $B_4(CN)_4^{2-}$, $B_4(NC)_4^{2-}$, and $B_4(BO)_4^{2-}$, the tetrahedral isomers of all of these species are not stable gas-phase dianions, but rather, they spontaneously emit one of their excess electrons. In contrast, the D_{2d}-symmetric isomers of $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ are stable with respect to electron emission as well as fragmentations and do, therefore, represent stable gas-phase dianions. The corresponding $B_4(NC)_4^{2-}$ isomer is a borderline case, but it is at least long-lived with respect to electron loss. Judging from our findings, we predict the D_{2d}-symmetric isomers to be observable in the gas phase in mass spectrometric experiments as typically performed by Wang et al.[48] These systems might also be observable in rare gas matrix environments, where reactions with solvent or other molecules can be excluded.

4. Discussion

In the previous section, we established the gas-phase stability of the D_{2d}-symmetric isomers of $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ and the longevity of the corresponding $B_4(NC)_4^{2-}$ isomer. To the best of our knowledge, this is the first time that the existence of D_{2d}-symmetric isomers of dianionic tetraborates has been reported. In this section, we want to shed some light onto the nature of the structure of this new isomer and explain why the pseudohalogen-substituted species are electronically stable entities. We also outline the difference between the CN- and NC-substituted species.

Turning to the geometry of the D_{2d}-symmetric isomers, we have found a length for the B−B bond of the B_4 frame of about 1.62 Å, which corresponds to a shortened single bond. A B−B single bond has a typical length of about 1.7 Å.[11] This suggests that another factor is contributing to the strength of these bonds. Indeed, the HOMO (Figure 4) has substantial π character and makes a binding contribution to the B−B bonds. Consequently, the bond order of the B−B bond is increased, and its length decreased compared to a typical B−B single bond. The shape of the HOMO is strongly reminiscent of the π orbital of aromatic hydrocarbons that arises through the all-binding combination of the atomic p orbitals. Thus, a question to be asked is whether the D_{2d}-symmetric isomers of the tetraborates exhibit aromatic character as well. The bond equivalence of the four B−B bonds gives a first positive hint, but a reliable and today well-established method for checking for aromaticity is the calculation of the so-called NICS (nuclear-independent chemical shift) value.[19,51−53] The NICS value is defined as the negative isotropic shielding in the ring center, and aromaticity is indicated when the NICS value is negative. For the $B_4(CN)_4^{2-}$ dianion, we obtained a NICS value of −22.8 using the gauge-independent atomic orbital method at the RHF level of theory. Judging from this result, $B_4(CN)_4^{2-}$ and also the corresponding isomers of $B_4(NC)_4^{2-}$ and $B_4(BO)_4^{2-}$ clearly have aromatic character. For instance, benzene has a NICS value of about −10.[54]

A second effect that influences the structure of the D_{2d}-symmetric isomers is the strong electrostatic repulsion of the

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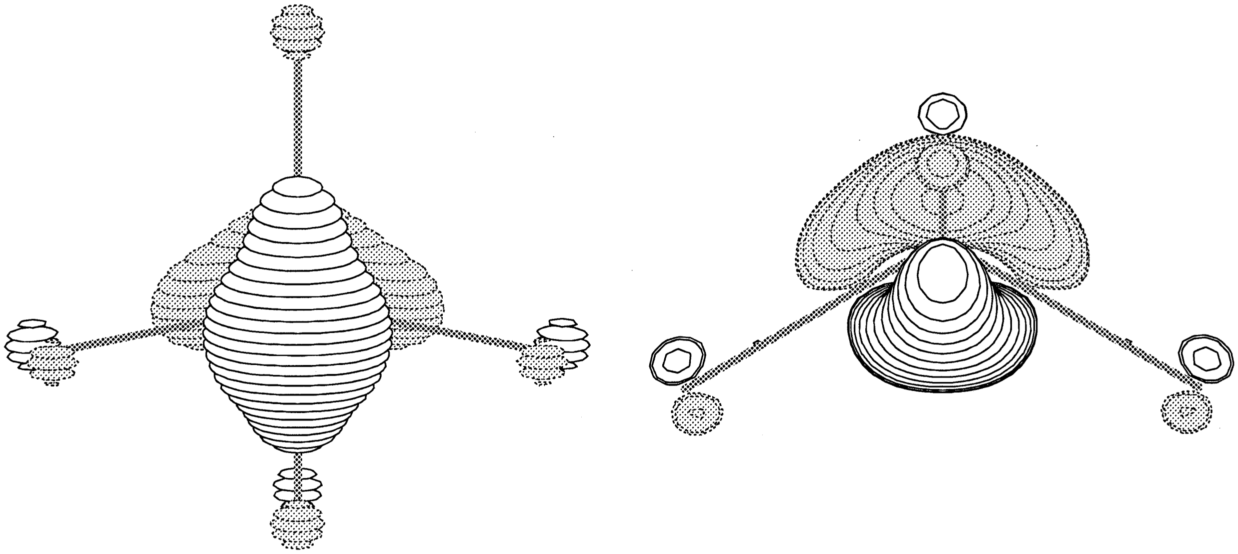

Figure 4. Highest-occupied molecular orbital of $B_4(CN)_4^{2-}$ in top view (left) and side view (right). Its appearance is similar to that of the orbital of aromatic hydrocarbons that arises through an all-binding combination of the 2p orbitals of the carbons.

Table 5. Mulliken Charge Distribution for the D_{2d}-Symmetric Tetraborates Calculated at the MP2-Optimized Geometries with the DZP+p Basis Set[a]

	B	L_i	L_o
$B_4(CN)_4^{2-}$	−0.09	−0.01	−0.40
$B_4(NC)_4^{2-}$	0.00	−0.38	−0.12
$B_4(BO)_4^{2-}$	−0.24	0.32	−0.58

[a] Note that the negative charge is located at the outer ligand (L_o) in $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$, whereas in $B_4(NC)_4^{2-}$, it is mostly located at the inner nitrogen atom (L_i).

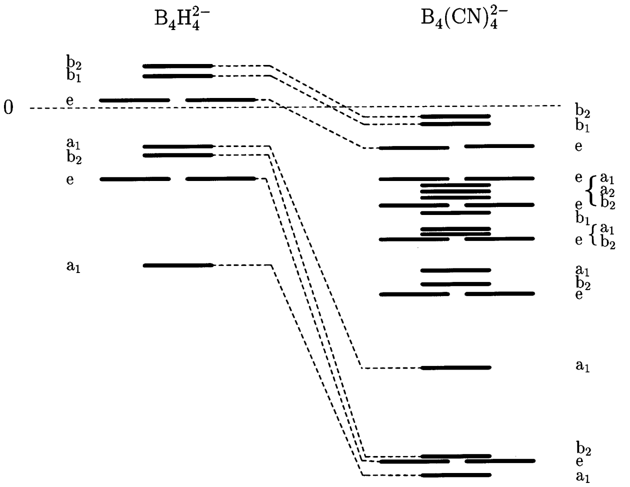

Figure 5. Comparison of the orbital energies of the D_{2d}-symmetric isomers of $B_4H_4^{2-}$ and $B_4(CN)_4^{2-}$. The related orbitals are connected and drop in energy because of the decreased electrostatic repulsion of the excess electrons in the spatially larger $B_4(CN)_4^{2-}$ dianion.

excess negative charges. A Mulliken charge analysis indicates that the charges are strongly localized on the pseudohalogen ligands (Table 5). Consequently, the ligands strongly repel each other, and to minimize this repulsion, the distance between the ligands has to be maximized. The D_{2d}-symmetric structure can, therefore, be understood as an ideal compromise between maximum aromaticity, which favors a planar geometry, and maximum distance between the ligands, which favors a tetrahedral geometry.

Turning to the electronic stability of the tetraborate dianions, the exchange of the hydrogen atoms of $B_4H_4^{2-}$ by the pseudohalogen ligands CN, NC, and BO, leads to a dramatic stabilization of the additional electrons. This effect is simply due to the increased system size and molecular space of the substituted species compared to that of the parent $B_4H_4^{2-}$ dianion, which leads to a substantial decrease of the electrostatic repulsion between the excess negative charges of the dianions. This reduction manifests itself in the orbital energies of the corresponding species. Comparing the orbital energies of $B_4H_4^{2-}$ with those of $B_4(CN)_4^{2-}$ (Figure 5), a tremendous drop in energy becomes evident. Whereas the first three orbitals are unbound in $B_4H_4^{2-}$, the decrease of electrostatic repulsion in $B_4(CN)_4^{2-}$ results in an energetic drop of the previously unbound orbitals below zero, i.e., these orbitals are now bound. For the energetically low-lying orbitals of $B_4H_4^{2-}$, the drop is even more pronounced because they are localized in the inner region of the dianion and, thus, experience a stronger repulsion through the excess negative charges. In Figure 5, the related orbitals of $B_4H_4^{2-}$ and $B_4(CN)_4^{2-}$ are connected by dashed lines. The additional orbitals of $B_4(CN)_4^{2-}$ are strictly localized at the CN ligands and correspond to the CN triple bonds and the lone pairs at the nitrogen atom.

The investigation of the electronic stability of the tetraborates showed that the D_{2d}-symmetric isomers of $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ are clearly stable with respect to electron loss. The corresponding isomer of $B_4(NC)_4^{2-}$ is probably electronically unstable but long-lived. The instability of the latter system can be explained within the framework of the involved elements and their electronegativities. As mentioned previously, the excess negative charges repel each other strongly and, thus, tend to localize on the ligands or, more specifically, at the terminal ends of the ligands. In the case of the $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ dianions, the terminal atoms of the ligands correspond to the elements with the highest electronegativities. In other words, in these systems, the trend in electronegativity supports the localization of the excess electrons at the terminal ends of the ligands and, hence, contributes to the minimization of their electrostatic repulsion. This is not the case in the $B_4(NC)_4^{2-}$ isomer. Here, the element with the highest electronegativity, the nitrogen, is directly bound to the B_4 frame, and the carbon is in the terminal ligand position. Because of the electronegativities, the electrons tend to localize on the nitrogen atoms, which opposes the minimization of the electrostatic repulsion between the additional electrons and, therefore, leads to a decreased stability. A Mulliken charge analysis strongly supports this picture (Table 5). In the $B_4(CN)_4^{2-}$ dianion, the boron atoms have a partial charge of -0.09, the carbon atom has a charge of -0.01, and the terminal nitrogen has a charge of -0.4, i.e., the excess negative charges are mainly localized at the terminal nitrogen. In contrast, in the $B_4(NC)_4^{2-}$ dianion, the boron atoms carry no charge, the nitrogen -0.38, and the terminal carbon -0.12, i.e., the negative charge is now more localized on the inner nitrogen atom and not on the terminal positions. This leads to destabilization of the dianion, which, in the D_{2d}-symmetric isomer of $B_4(NC)_4^{2-}$, is sufficient to result in electronic instability. A similar effect has been observed for $B_6(NC)_6^{2-}$,[20] as well as for different isomers of SiC_6^{2-}.[55,56]

A glance at the total energies of the tetrahedral and D_{2d}-symmetric isomers of the tetraborates $B_4X_4^{2-}$ (X = H, CN, NC, or BO) indicates that the latter closed-shell isomers are clearly lower in energy than the tetrahedral isomers with triplet electronic ground state.s The D_{2d} isomers of $B_4(CN)_4^{2-}$, $B_4(NC)_4^{2-}$, and $B_4(BO)_4^{2-}$ are 1.55 eV (149.4 kJ/mol), 1.79 eV (172.1 kJ/mol), and 1.265 eV (122.1 kJ/mol), respectively, lower in energy than the corresponding tetrahedral isomers. According to these results, decay of the singlet D_{2d} isomers into the triplet isomers followed by electron loss is excluded.

5. Brief Summary

Using high-level ab initio methods, a new isomer of the tetraborate dianion $B_4H_4^{2-}$, that exhibits a D_{2d}-symmetric geometry and a closed-shell electronic ground state has been identified. Although its electronic stability is increased compared to that of the tetrahedral isomer, it still is a very unstable species and spontaneously emits an electron in the gas phase.

An investigation of substituted tetraborates $B_4X_4^{2-}$ (X = CN, NC, or BO) has shown that these species also exhibit tetrahedral and D_{2d}-symmetric isomers, of which the first have triplet and the latter singlet electronic ground states. Whereas the tetrahedral isomers are unstable with respect to electron emission, the D_{2d}-symmetric isomers of $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ are electronically clearly stable. The corresponding isomer of $B_4(NC)_4^{2-}$ is a borderline case and is probably unstable, but it might be long-lived because of the repulsive Coulomb barrier. The instability of $B_4(NC)_4^{2-}$ is due to the difference of the electronegativities of carbon and nitrogen, which opposes the trend of the excess electrons to localize at the outermost atoms of the ligands.

The calculation of possible fragmentation paths has shown that these dianions are thermodynamically stable with respect to dissociation of the nuclear framework. This property can be assigned to the covalent nature of the involved bonds and can thus be taken for granted for all borate dianions. The D_{2d} isomers are clearly lower in energy than their tetrahedral counterparts; because they obey Hückel's $4n + 2$ electron rule, they exhibit aromatic character, which is confirmed by their computed NICS values. Their structure is explained as a compromise between aromaticity, which favors a planar geometry, and the electrostatic repulsion of the partially negatively charged ligands. Judging from our findings, we predict that the D_{2d}-symmetric isomers of $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ exist as stable entities in the gas phase and should be observable in suitable experiments.

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