

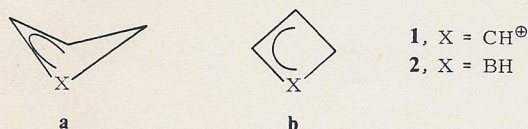
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1,2-Dihydroborete: Structure of a Potential Homoaromatic System**

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Experimental and theoretical studies of cyclobutenyl cations **1** indicate that, due to relatively strong 1,3-interactions, the nonplanar form **1a** is more favorable than the planar form **1b**^[1-3]. On the basis of quantum chemical model calculations, we now show that similar structural behavior is expected for 1,2-dihydroboretes **2**, which are isoelectronic to **1**.



Complete optimization of the geometry of **2** using the MINDO/3 method^[4] leads to the nonplanar form **2a**, which is 6.1 (5.3) kcal/mol more stable than **2b**^[5]. The corresponding value for **1** is 9.8 kcal/mol^[3] (experimental value: 8.4 kcal/mol^[1]).

Reinvestigation of the equilibrium structure determined for **2a** using ab initio calculations of the Hartree-Fock (HF) type with an extended 6-31G* basis set^[6] led to the structural data summarized in Figure 1. Hence, the fold angle α in **2a** (152°, cf. Figure 1) is only slightly different from the calculated value of 148° for **1a** (HF/6-31G*^[3]; exp.: 148.5°^[2]). The 1,3-distance of 1.90 Å is somewhat longer than that in **1a** (HF/6-31G*^[3]: 1.79 Å^[3]; exp.:

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1.78 Å^[2]). The relatively long B1C4 bond and the relatively short C3C4 bond indicate that delocalization of the two π electrons in the B1C4C3 region is not fully established^[7].

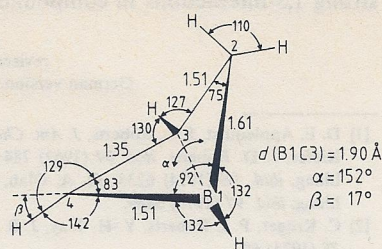


Fig. 1. Calculated structural parameters for the 1,2-dihydroborete **2a** (all values obtained from 6-31G* calculations; bond lengths [Å], bond angles [°]). The fold angle α is the angle between planes B1C2C3 and C3C4B1. Angle β measures the deviation of the bond vector C4H from the plane B1C4C3. Further parameters: B1H = 1.19, C4H = 1.07, C3H = 1.07, C2H = 1.08 Å, \angle C2C3C4 = 103°.

The degree of 1,3-interaction can be determined by analysis of the one electron density distribution $\rho(r)$ ^[8]. In proceeding from **2b** to **2a**, $\rho(r)$ between B1 and C3 increases by 20%; at the same time, the gross electron population at B1 and C3 grows, while that at C4 decreases. Although accumulation of $\rho(r)$ in the X1C3 region (X = B) is substantial, it is less than in **1a** (X = C⁺). This result, together with the inversion barrier calculated for **2a**, is an index for the 1,3-interaction, which is weaker than in **1**. In contrast to the homotropylium ion^[8], accumulation of $\rho(r)$ between the interacting atoms in **1** and **2** does not lead to a saddle point in the electron density distribution^[9].

In terms of an exactly defined model for homoconjugation based on the properties of $\rho(r)$, neither **1** nor **2** involve completely extended homoaromatic 1,3-bonding^[8]; however, if the term *homoaromaticity* is used merely qualitatively to signify a change in structural and spectroscopic properties relative to those of a given reference state, without intending to specify quantitatively the difference between bonding and nonbonding 1,3-interactions, then both **1** and **2** can be described as homoaromatic^[10].

Preliminary calculations with a minimal basis set (HF/STO-3G^[11]) on the spirocyclic 1,2-dihydroborete **3**, several derivatives of which have recently been synthesized^[12], also indicate a nonplanar structure for the dihydroborete ring (Fig. 2).

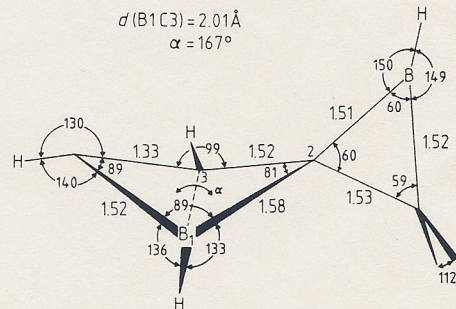


Fig. 2. HF/STO-3G parameters for the spirocyclic 1,2-dihydroborete **3** (bond lengths [Å], bond angles [°]). The fold angle α is the angle between the planes B1C2C3 and C3C4B1. Further parameters: B1H = 1.16, C3H = 1.09, C4H = 1.08, B5H = 1.15, C6H = 1.08 Å, \angle C2C3H = 128, \angle C4C3H = 132, \angle B1C2B5 = 134, \angle C3C2B5 = 131, \angle B1C2C6 = 131, \angle C3C2C6 = 129°.

Since the endocyclic angle at C2 in **3** is strongly compressed, forcing the B1C2C3 angle to widen, the nonplanarity of **3** represents further evidence for the presence of strong 1,3-interactions in compounds of type **2**.

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