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# Quantum Chemical Modeling of Chiral Catalysis. Part 16. On the Isomerism of Dimers of Chiral Oxazaborolidines Used in the Catalytic Enantioselective Reduction of Ketones

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*Abstract:* - Relative stabilities of several dimeric isomers of oxazaborolidines were studied by means of *ab initio* MO (RHF) methods (1,3,2-oxazaborolidine 1' used as a model of oxazaborolidines). The most stable of the isomers found was 24 kJ mol$^{-1}$ (6-31G//6-31G) lower in energy than two separate monomeric oxazaborolidine (1') molecules. Formation of several other dimeric isomers was found to be energetically advantageous.

## INTRODUCTION

Chiral oxazaborolidines 1 are known to induce a highly enantioselective catalytic reduction of ketones when borane is used as a source of hydrogen (the CBS reduction). Two review articles summarize the present status of oxazaborolidines in the field of enantioselective synthesis.[1] Also the physical chemistry of oxazaborolidine derivatives and their borane adducts has been studied since Corey *et al.* reported that oxazaborolidines may dimerize.[2] Mathre *et al.* have identified several intermediates involved in the preparation of oxazaborolidines from the corresponding aminoalcohols and shown that some of those intermediates (e.g. water and methylboronic acid adducts of 1; R=Ph, R'=Me) can catalyze the enantioselective reduction of ketones in the presence of borane delivering agents.[3] Interestingly, Mathre *et al.* report that they were not able to prepare the parent oxazaborolidine (1; R=Ph, R'=H), instead they obtained its dimeric derivative (2; R=Ph).[3b] On the other hand, recent studies of Brunel *et al.* indicate that some derivatives of 2 (e.g. R=H) may lose hydrogen (H$_2$) giving rise to the formation of the corresponding oxazaborolidine 1 (R,R'=H) which would subsequently dimerize to give 3 (R=H).[4] Furthermore, recent reports of Brown *et al.* imply that oxazaborolidines derived from ephedrine may form dimers such as 4.[5] The formation of 4 was found to be sensitive to the nature of the substituents of the ring. Neither the oxazaborolidine with the 5-phenyl and 4-methyl *cis* about the ring nor the *N-i*-propyl derivative of the *trans* isomer dimerized to give analogs of 4.
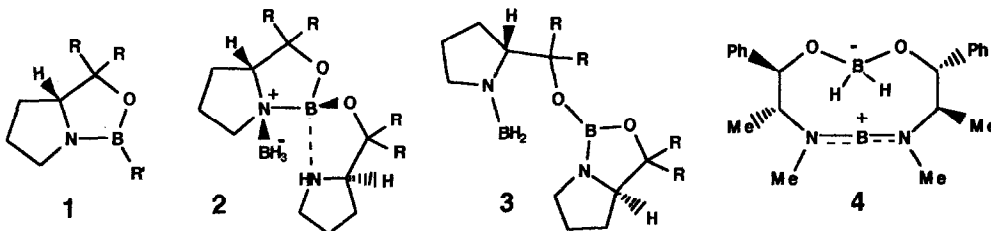


Formation of aggregates/dimers of 1 and its borane adducts has been studied also computationally.[6] Those studies cover the first intermediates which may form as oxazaborolidines aggregate (e.g. the formation of adducts 5 and 6)[6a] but plausible reactions of the aggregates have not been yet studied systematically. The cleavage A (Scheme I) of the 4-ring was predicted to be more probable than the other cleavage (B).[6a] However, the formation of 4 and related systems

could involve the latter cleavage (**B**, Scheme I). Scrambling of the hydrogens of borons of the cleavage product of **B** could lead to the formation of analogs of **3** and/or **4**.

## Scheme I



5   X,X'=NR; Y,Y'=O
6   X,Y'=O; X',Y=NR
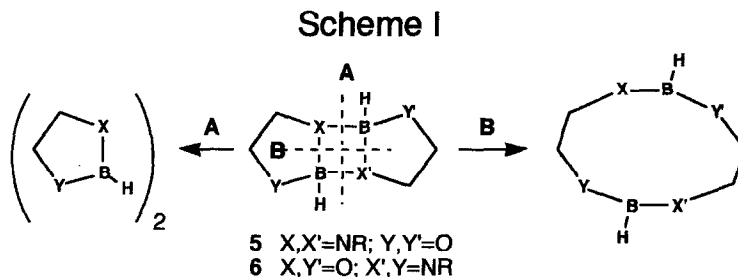
Altogether, as very little is know about these reactions the goal of the present work was to estimate relative energies of isomers one could generate in reactions related to the formation of analogs of **3** and **4** (**3'** - **4'**, Scheme II). As all the dimeric isomers of oxazaborolidines proposed so far[3-5] contain a boron bound to two oxygens these isomers (plausible reactions converting **6'** to **1'**, **3'**, **4'** and **7'** - **11'**, Scheme II) were studied before others. Properties of the isomers were investigated by means of *ab initio* MO (RHF) methods.
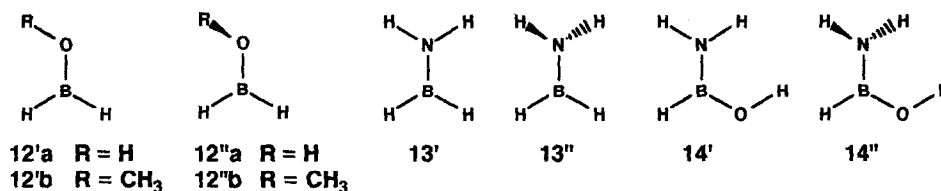
## Scheme II
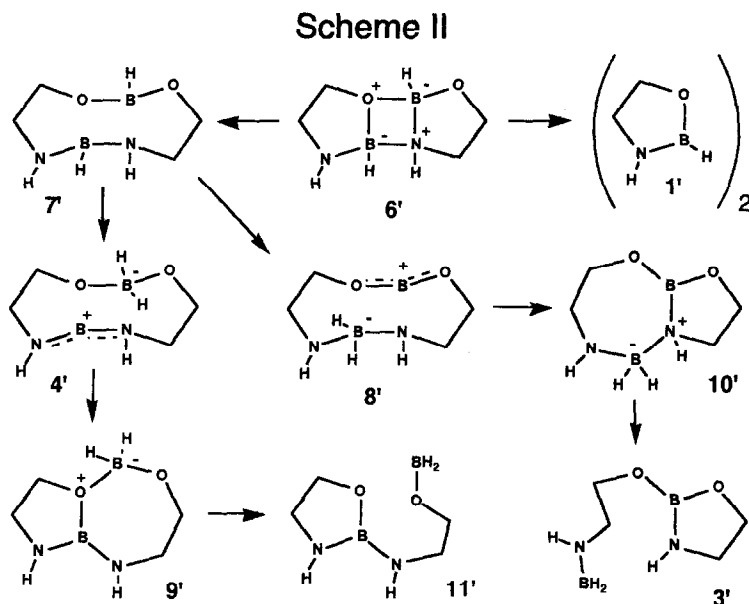


## MODELS AND COMPUTATIONAL METHODS

Standard *ab initio* MO calculations (RHF) were carried out by using the Gaussian 80 series of programs at the 3-21G, 4-31G and 6-31G levels.[7] Modeling techniques similar to those applied in previous reports of this series[6c] were employed. 1,3,2-Oxazaborolidine **1'** was used as a model of monomeric oxazaborolidines (**1**) and **3'** - **11'** (Scheme II) as models of the corresponding dimeric isomers. The models **1'** and **6'** have been described in the literature[6] whereas no other calculations on the models **3'**, **4'** or **7'** - **11'** appear to have been published.

As many of the models could be predicted to be flexible (e.g. the models contain 7- and 10-membered rings and also 5-rings with long sidechains) conformational properties of the models were assessed in the light of the rigidity of

the B-O, B-N and O-B-N (sub)structures (conformational constraints of the -$H_2$C-$CH_2$- counterpart can be easily rationalized). The rigidities were estimated by comparing energies of the simple models **12'a-b**, **13'** - **14'** ($\pi$-resonating B-N and B-O) with those of **12"a-b**, **13"** - **14"** ($\pi$-resonance not possible). The influence of the alkyl substituents was estimated by comparing the models **12'a-b** and **12"a-b**. Properties of the models **12'a-b**, **12"a-b**, **13'**, **13"** and **14'** computed at various levels of *ab initio* theory have been reported in the literature[6d-f,8] whereas no other calculations on the model **14"** appear to have been published. These small models (of which **12"a-b**, **13"** - **14"** are distorted systems) were studied also with inclusion of polarization functions.



| **12'a** R = H | **12"a** R = H | **13'** | **13"** | **14'** | **14"** |
| **12'b** R = $CH_3$ | **12"b** R = $CH_3$ | | | | |

## RESULTS AND DISCUSSION

Total energies, dipole moments and the relative energies of **1'** and the dimeric isomers (Scheme II) are presented in Table 1. The corresponding values of the models **12'a-b**, **13'** - **14'** and **12"a-b**, **13"** - **14"** are shown in Table 2. The zwitterionic systems **4'** and **8'** turned out to be unstable.[9] In the case of **7'** three different conformers (**7'a**, **7'b** and **7'c**, Figure 1) were identified (6-31G//6-31G).[10] Although the isomer **9'** (Figure 2) was found to be stable at all the levels of inspection **10'**, however, turned out to be stable[11] only at the 3-21G level (a more stable analog **10"** was studied instead,[10] Figure 2). The optimized (6-31G//6-31G) structures of isomeric 2-substituted oxazaborolidines (**3'** and **11'**) are shown in Figure 3.

**Table 1.** Total energies ($E_T$),[a] dipole moments (D)[b] and relative energies ($E_R$)[c] of the optimized structures of **1'**, **3'**, **6'**, **7'** and **9'** - **11'**.[d]

| Model[d] | 3-21G//3-21G | | | 4-31G//4-31G | | | 6-31G//6-31G | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E_T$[a] | D[b] | $E_R$[c] | $E_T$ | D | $E_R$ | $E_T$ | D | $E_R$ |
| 1' | -232.01452 | 3.16 | 0.0 | -232.95883 | 3.18 | 0.0 | -233.19703 | 3.21 | 0.0 |
| 3' | -464.03667 | 5.28 | -20 | -465.92577 | 5.23 | -21 | -466.40113 | 5.29 | -19 |
| 6' | -464.05069 | 3.12 | -57 | -465.91389 | 3.30 | +10 | -466.38775 | 3.36 | +17 |
| 7'a | -464.04125 | 1.43 | -32 | -465.92688 | 1.54 | -24 | -466.40197 | 1.57 | -21 |
| 7'b | -464.03810 | 2.92 | -24 | -465.92366 | 2.81 | -16 | -466.39868 | 2.82 | -12 |
| 7'c | -464.03896 | 3.43 | -26 | -465.92416 | 3.52 | -17 | -466.39885 | 3.59 | -13 |
| 9' | -464.04861 | 5.63 | -51 | -465.92575 | 5.13 | -21 | -466.40031 | 5.14 | -16 |
| 10' | -464.03195 | 3.94 | -8 | - | - | -[e] | - | - | - |
| 10" | -464.04098 | 4.17 | -31 | -465.92765 | 4.18 | -26 | -466.40327 | 4.30 | -24 |
| 11' | -464.02844 | 4.05 | +2 | -465.91795 | 4.04 | -1 | -466.39382 | 4.07 | +1 |

[a] Total energies ($E_T$) given in hartrees. [b] Dipole moments (D) given in debyes. [c] Relative energies ($E_R$) with respect to 2 eq. of **1'** (of which the energy is set zero). [d] See Scheme II. [e] The complex decomposed leading to **10"** (Figure 2).

*On the conformational constraints of the dimeric isomers of oxazaborolidines*

The relative energies ($E_R$) of rotamers **12'a-b**, **13'** - **14'** and **12"a-b**, **13"** - **14"** (Table 2) imply the rotational barriers of the B-O and B-N bonds to be high; clearly higher than the relative energies of the dimeric isomers (Table 1). Furthermore, the ($E_R$) values (Table 2) indicate that rotating the B-N bond of aminoboranes (e.g. **13'/13"**, disturbs the B-N <-> $B^-$=$N^+$ $\pi$-resonance) would be much more energy demanding than the corresponding action in the case of analogous hydroxy- or alkoxyboranes (e.g. **13'a/13"**, influences the B-O <-> $B^-$=$O^+$ $\pi$-resonance). The ($E_R$)

value of **14''** is significantly lower than that of **13''** because in **14''** the loss of the B-N $\pi$-resonance is partially compensated by the enhanced importance of the remaining B-O $\pi$-resonance. The influence of alkyl substituents to the $E_R$ values appears to be insignificant (the $E_R$ values of **12''a** and **12''b** are closely similar). These results imply that in the case of **3'**, **7'**, **9'- 11'** rather high amounts of energy would be required for bending an atom adjacent to O or N out of the plane of the neighboring $sp^2$ hybridized boron. Consequently, the 10-membered ring system of **7'** would be rigid. Actually, the model **7'** could be considered to consist of two asymmetric "plates" connected by two C-C bonds (conformationally analogous to cyclophanes). The asymmetry is related to the relative orientation of the two B-H bonds. The bonds could point either to the same direction or to the opposite ones. The conformer **7'b** could be assigned to the former class of systems and **7'a** and **7'c** to the latter one (Figure 1). Attempts to optimize the other conformer (the B-H bonds oriented to the same direction; plates eclipsed) of **7'b** lead to **7'b**. Also attempts to find a conformation of **7'** in which the orientation of the plane of one boron center had been perpendicular to that of the other all failed. All these observations indicate that the ring system of **7'** would be rigid and that the number of conformers of **7'** would be much more limited than expected. Results of calculations performed with inclusion of polarization functions (6-31G*//6-31G, Table 2) do not change this conclusion.

**Table 2.**  Total energies ($E_T$),[a] dipole moments (D)[b] and relative energies ($E_R$)[c] of the optimized rotamers **12'a-b**,  **13' - 14'** and **12''a-b**, **13'' - 14''**.

| Model[d] | 3-21G//3-21G | | | 6-31G//6-31G | | | 6-31G*//6-31G* | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E_T{}^a$ | $D^b$ | $E_R{}^c$ | $E_T$ | D | $E_R$ | $E_T$ | D | $E_R$ |
| 12'a  | -100.76196 | 1.91 | 0 | -101.27793 | 1.89 | 0 | -101.32139 | 1.68 | 0 |
| 12''a | -100.74288 | 1.96 | +50 | -101.26049 | 1.76 | +46 | -101.29856 | 1.70 | +60 |
| 12'b  | -139.57090 | 2.16 | 0 | -140.28052 | 2.06 | 0 | -140.34556 | 1.71 | 0 |
| 12''b | -139.55445 | 2.21 | +43 | -140.26356 | 2.03 | +45 | -140.32498 | 1.66 | +54 |
| 13'   | -81.04343 | 2.01 | 0 | -81.46276 | 1.76 | 0 | -81.48910 | 1.82 | 0 |
| 13''  | -80.98979 | 1.36 | +141 | -81.40964 | 1.10 | +140 | -81.43518 | 1.19 | +142 |
| 14'   | -155.55682 | 3.27 | 0 | -156.35434 | 3.23 | 0 | -156.40862 | 2.96 | 0 |
| 14''  | -155.52878 | 2.37 | +74 | -156.32407 | 2.49 | +80 | -156.38474 | 1.83 | +63 |

[a] Total energies ($E_T$) given in hartrees.  [b] Dipole moments given in debyes.  [c] Energy ($E_R$) relative to the energy of the corresponding planar conformer.

The same planarity / rigidity constraints (as in the case of **7'** discussed above) apply also in the case of the isomers **3'** and **9'-11'**. The conformational freedom of these isomers arises from rotations in the O-CH$_2$-CH$_2$-N segment of the 2-substituent of the oxazaborolidine ring. Because energies of conformers of **3'** and **9'-11'** would be dependent on the nature and strength of interactions between their Lewis acidic and basic centers a full conformational analysis of these isomers would be a highly demanding task and was not attempted. Nevertheless, a rough comparison of properties of two "ultimate" classes of the conformers turned out to be achievable. One class consists of systems in which interactions between distinct Lewis acidic and basic centers would be in minimum (distances between the centers so high as possible). The other class would cover those conformers in which the centers interact without restrictions (the centers so close together as possible). The models **3'** and **11'** represent the former class of conformers and the models **9'** and **10'** the latter one. Therefore, whenever the energies/dipole moments shown in Table 1 are inspected one should remember that this work does not cover all the possible conformers.

*On the relative stabilities of the dimeric isomers*

On the basis of the relative energies ($E_R$) shown in Table 1 one can conclude that dimeric isomers of **1'** can be more stable (e.g. **7'a-c**, **9'-10'** and **10''**) than two monomeric molecules of **1'** (set at an infinite distance). The isomer **6'** is clearly less stable than the others [e.g. $E_R$ of **6'** is +17 kJ mol$^{-1}$ (6-31G //6-31G) whereas $E_R$ of **7'a** is -21 kJ mol$^{-1}$; Table 1]. Nevertheless, as the $E_R$ of **6'** is rather low, it should not be surprising if some oxazaborolidines dimerize and isomerize to systems such as those shown in Scheme II. What isomers would be produced would depend on the substitution of the reacting oxazaborolidines and factors related to the kinetics of hydride scrambling.

Relative energies of two pairs of isomers (9' / 10' and 3' / 11') are worth of a further inspection. Namely, the isomer 9' (stable) is a derivative of 4' whereas 10' (unstable, less stable than 9') is a derivative of 8'. Brown et al.[5] report NMR and IR studies related to 4' but do not mention the other isomer (8'). However, the results of this work indicate that the observations of Brown et al.[5] could be explained by involving an equilibrium depicted in Scheme III. If A and C (Scheme III) would be in a rapid equilibrium spectroscopic measurements would allow one to draw a conclusion that B (an average structure) would be present. On the other hand, although the results of this work indicate that B (Scheme III) would not represent an optimum of the energy hypersurface of A/B (no optimum was found for 4') the intermediate B could be a transition state structure interconnecting A and C.
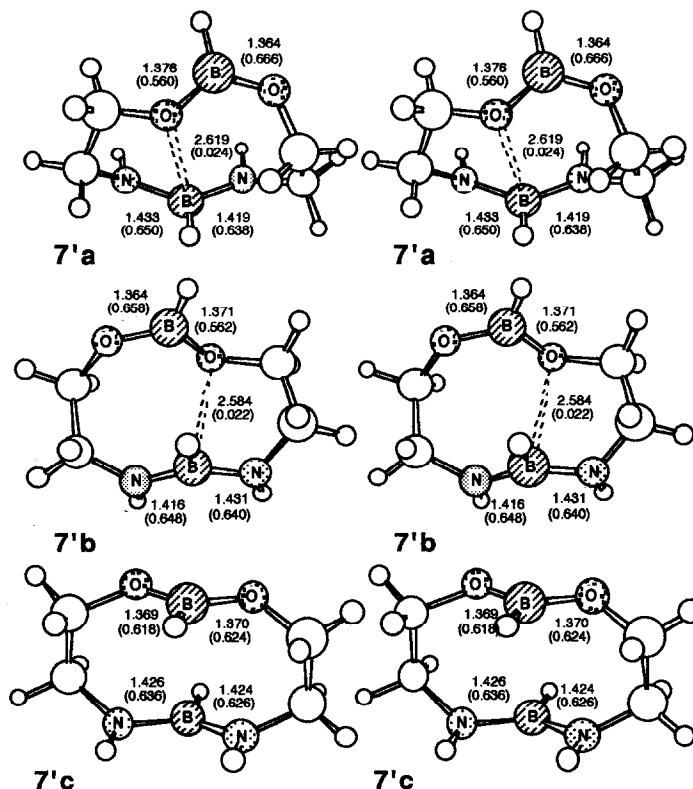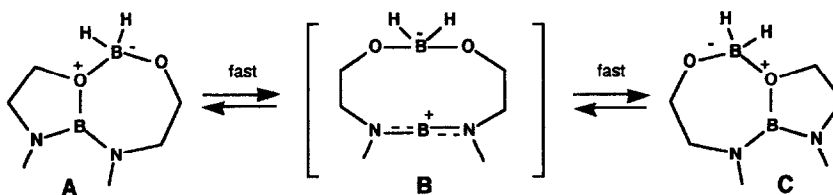


**Figure 1.** Stereo representations of the optimized (6-31G//6-31G) structures of conformers 7'a, 7'b and 7'c. Some of the most important bond lengths [in Å] and the corresponding Mulliken overlap populations (values in parentheses below the bond lengths) are shown.

## Scheme III



The other pair of isomers (3'/11') is interesting in the light of the properties of 9' and 10'. Namely, Brunel et

*al.*[4] have discussed the formation of **3** (analog of **3'**) but have not mentioned other plausible isomers (e.g. **11'**). On this basis one could draw a conclusion that the formation of dimers analogous to **3'** could be more advantageous than that of those analogous to **11'**. This conclusion is reasonable also in the light of the relative energies of **3'** and **11'**. The isomer **3'** is 20 kJ mol$^{-1}$ more stable than **11'** (6-31G//6-31G; Table 1).
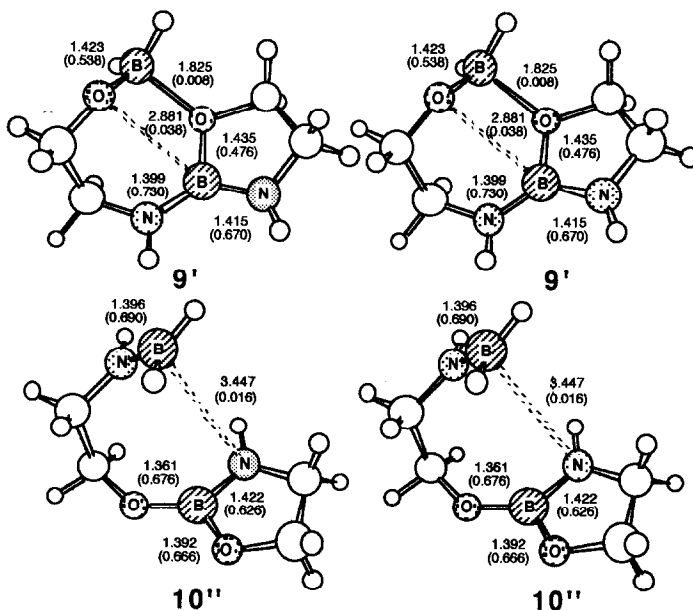


**Figure 2.** Stereo representations of the optimized (6-31G//6-31G) structures of isomers **9'** and **10''**. Some of the most important bond lengths [in Å] and the corresponding Mulliken overlap populations (values in parentheses below the bond lengths) are shown.

*Structure and bonding*

The optimized structures of three conformers of **7'** (i.e. **7'a-c**) are shown in Figure 1. Structural parameters of **7'a-c** are closely similar to those of oxazaborolidines. Lengths of the B-N and B-O bonds of **7'a-c** are 1.424 ± 0.009 and 1.370 ± 0.006 Å (Figure 1) whereas the B-N and B-O bonds of **1'**[6a] are 1.406 and 1.390 Å long. The corresponding Mulliken overlaps are less similar [e.g. B-N and B-O overlaps of **7'a-c** are 0.638 ± 0.012 and 0.613 ± 0.053 (Figure 1) whereas the corresponding overlaps of **1'** are 0.692 and 0.650[6b]].

The higher variation of the Mulliken overlap populations related to the B-O interactions in **7'a-c** imply that binding of some of the oxygens could be different from that of the others. If the structures (**7'a-c**) are inspected more thoroughly, it turns out that in the case of **7'a-b** one of the oxygens is interacting with the boron adjacent to the nitrogens. Although the corresponding B-O distances are rather long (2.619 Å in the case of **7'a** and 2.584 Å in **7'b**) the related overlaps are positive (0.024 in the case of **7'a** and 0.022 in **7'b**). However, these modest long distance interactions have rather significant consequences in the O-B-O system. The overlap between the non-interacting oxygen and its adjacent boron is almost 20% higher than that of the oxygen interacting with the boron adjacent to the nitrogens (Figure 1). On the N-B-N site the consequences of this long distance B-O interactions are less significant. All the B-N overlap populations are closely similar (Figure 1). Interestingly, the dipole moment of **7'a** [Table 1, B-H bonds oriented to the opposite directions (Figure 1)] is lower than that of any other of the dimeric isomers studied. The second most low moment is that of **7'b** [the B-H bonds point to the same direction (Figure 1)]. The dipole moment of the isomer **7'c** is, however, considerably higher [although the B-H bonds of **7'c** are oriented to opposite directions as those of **7'a** (Figure 1)].

By comparing the structural parameters of **9'** (Figure 2) and **11'** (Figure 3) it can be seen that the B-N bonds shorten and the corresponding overlap populations increase (i.e. the B-N bonds strengthen) in consequence of the reaction **11'** -> **9'**. The same observations have been made earlier in the case of the formation of borane O-adduct of **1'**.[6c] Also other bonding interactions of **9'** resemble those of the borane O-adduct of oxazaborolidine **1'**.[6c] On the other hand, there are more stabilizing interactions in **9'** than in the borane O-adduct[6c] of **1'**. For example, the boron of the oxazaborolidine moiety of **9'** has two adjacent nitrogens (the borane O-adduct of **1'** has only one). As the π-resonance [B-N <-> B⁻=N⁺] enhances the stability of amino/alkoxyboranes more than the resonance [B-O <-> B⁻=O⁺] would do (e.g. the $E_R$ value of aminoborane is much higher than that of hydroxy- or alkoxyborane, Table 2) the boron of the oxazaborolidine ring of **9'** is not significantly less resonance-stabilized than that of **11'** [in consequence of the reaction **11'** -> **9'** the ring boron will lose only one B-O resonance].
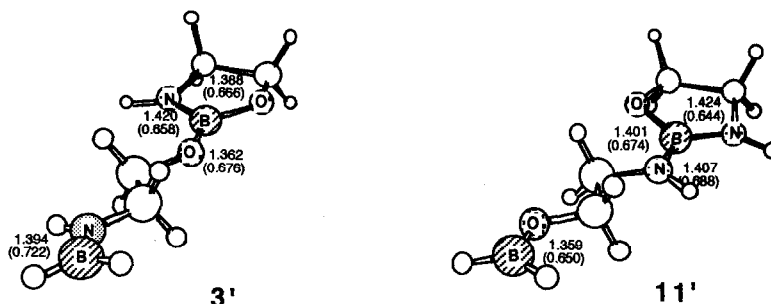


**Figure 3.** The optimized (6-31G//6-31G) structures of isomers **3'** and **11'**. Some of the most important bond lengths [in Å] and the corresponding Mulliken overlap populations (values in parentheses below the bond lengths) are shown.

To provide further evidence on the relative importance of the [B-N <-> B⁻=N⁺] and [B-O <-> B⁻=O⁺] π-resonances an isomer of **9'** (Figure 4) forming as the BH₂ group coordinates to one of the nitrogens of **9'** was studied. In consequence of the coordination one B-N resonance of the oxazaborolidine boron is lost; the B-N and B-O bonds of the oxazaborolidine moiety shorten and the corresponding overlap populations increase (these bonds are still capable of π-resonating). The B-N bond of which the nitrogen end interacts with the BH₂ group (Figure 4) lengthens and the corresponding overlap population decreases substantially. This isomer (Figure 4) of **9'** turned out to be significantly less stable than **9'** (Figure 2); 44 kJ mol⁻¹ at the 6-31G level (that corresponds to an $E_R$ of +27 kJ mol⁻¹). Consequently, it is the least stable one among the dimeric isomers studied in this work. However, the corresponding relations of **3'** and **10'** are different from those of **11'** and **9'**.
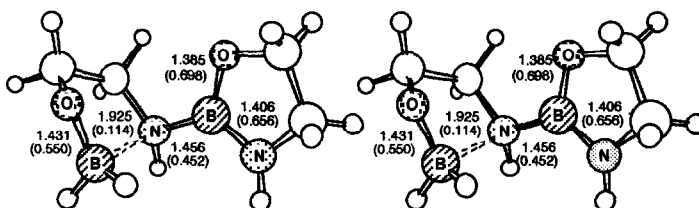


**Figure 4.** A stereo representation of an optimized (6-31G//6-31G) structure of an isomer of **9'** (the BH₂ group interacting with a nitrogen instead of the oxygen). Some of the most important bond lengths [in Å] and the corresponding Mulliken overlap populations (values in parentheses below the bond lengths) are shown.

In consequence of the coordination of the BH₂ group to the ring nitrogen in the isomer **3'** (corresponding to the reaction **3'** -> **10'**) the ring boron would lose its only B-N π-resonance as would do the coordinating aminoborane end (i.e. total of two B-N π-resonances would be lost). Apparently the remaining two B-O resonances would not

compensate the loss of the B-N resonances as **10'** was found to be unstable[11] [calculated at the 3-21G level (which strongly overestimates binding interactions in the case of these systems) $E_R$ of **10'** (-8 kJ mol$^{-1}$; Table 1) was less advantageous than that of **3'** (-20 kJ mol$^{-1}$; Table 1)]. Results of this work indicate that the boron of the $BH_2$ group (of **3'**) may approach the ring nitrogen until the corresponding B-N distance is 3.447 (6-31G//6-31G); thereafter the oxazaborolidine moiety starts to repel the approaching $BH_2$ group. The complex (**10"**) shown in Figure 2 corresponds to that borderline structure. Interestingly, the complex **10"** was the most stable ($E_R$ of **10"** is -24 kJ mol$^{-1}$; Table 1) of the dimeric isomers inspected. Computational studies on the properties of oxazaborolidine catalysts continue.

## CONCLUSIONS

Results of this work indicate that several isomeric structures could form in consequence of hydride scrambling reactions taking place in dimeric aggregates of oxazaborolidines (most of the dimeric isomers were more stable than two separate monomers). What isomers would be produced would depend on the substitution of the reacting oxazaborolidines and factors related to the kinetics of hydride scrambling.

## ACKNOWLEDGEMENTS

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9.  Also water adducts of **4'** (the oxygen of water coordinated to the boron of the -N-B=N$^+$- moiety) and **8'** (the oxygen of water coordinated to the boron of the -O-B=O$^+$- moiety) were studied. Both of these adducts were found to be unstable.

10. As electron correlation has not been taken into account in this work energies of all complexes which have long bonds between Lewis acidic and basic centers must be treated with caution.

11. All attempts to optimize the structure of **10'** lead (except that performed at the 3-21G level) to **10"**. Reasons behind this behaviour would require a study on the transition state structures and involvement of electron correlation. That was not undertaken as conclusions satisfactory for the purposes of understanding the most important properties of dimeric isomers of oxazaborolidines can be drawn on the basis of the present work already.