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Borane as a model of Lewis Acidic Activators of Chiral *N*-Sulphonylated Oxazaborolidinones Used to Catalyze Asymmetric Diels-Alder Reactions

Vesa Nevalainen

Laboratory of Organic Chemistry, P.O. Box 55, SF-00014 University of Helsinki, Finland

Abstract: - Lewis acids as activators of chiral *N*-sulphonylated oxazaborolidinones (*e.g.* **1**) were studied by means of *ab initio* MO methods at the MP2/6-31G* level. Small models [*N*-sulphonylated 1,3,2-oxazaborolidin-5-one **2** as a model of oxazaborolidinones and borane as a model of an activating Lewis acids] were used to probe preferred coordination sites of the Lewis acids. Acidity of the ring boron (of **2**) was predicted to increase as borane coordinates on any of the oxygens of **2**. Formation of the most stable one (*i.e.* **3**) of the $O_{c=o}$-adducts was favoured by about 15 ± 2 kJ mol^{-1} (MP2/6-31G*//MP2/6-31G*) over that of the related O_{SO_2}-adducts. The diborane type of hydride-bridged borane *N*-adduct **8** was the most stable [46 kJ mol^{-1} (MP2/6-31G*//MP2/6-31G*) below the level of **3**] one of all the adducts inspected. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Chiral *N*-sulphonylated oxazaborolidinones [*e.g.* **A** (R = *p*-H$_3$C-C$_6$H$_4$, the Scheme] have been shown to be efficient catalysts for asymmetric Diels-Alder reactions.[1] These catalysts can be prepared *in situ* by treating *N*-sulphonylated amino acids with borane (the Scheme).

Scheme

1449
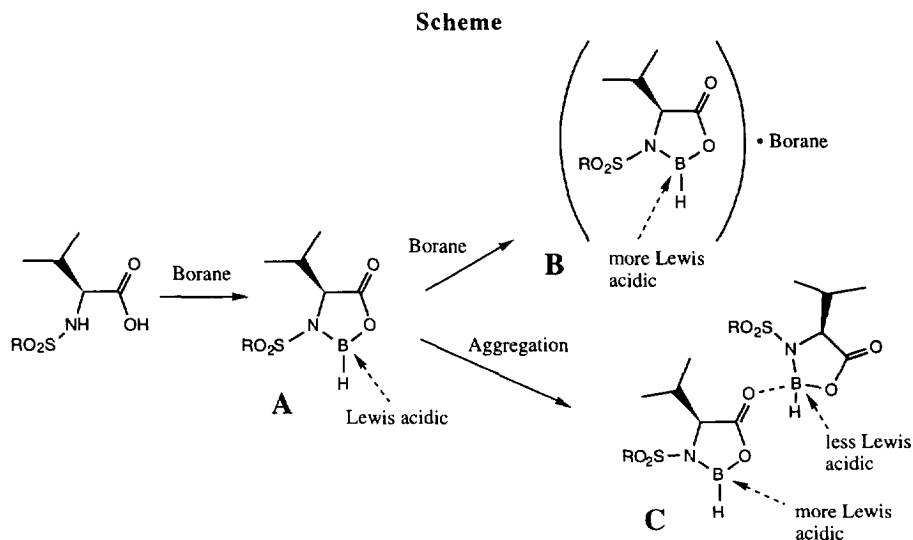
As hardly anything appears to be known about to role of aggregation and plausible activating role of Lewis acids [formation of adducts analogous to either **B** or **C** (as proposed by Sartor, Saffrich, Helmchen, Richards and Lambert),[18] the Scheme] the aims of this study were: 1) to determine whether the free electron pairs (Lewis basic centers) of *N*-sulphonylated oxazaborolidinones could bind borane; 2) to determine which one of the free electron pairs is the most Lewis basic one; 3) where the borane should coordinate in order to enhance Lewis acidity of the boron of the oxazaborolidinone ring as much as possible. The models used in this study were as follows: **1** - **2** as models of *N*-sulphonylated oxazaborolidinones, borane (H₃B) as a model of Lewis acids and **3-7** and **3'-5'** as models of the borane adducts of oxazaborolidinones. The bridged system **8** and the analog (*i.e.* **2'**) of **2** were included for purposes of comparisons.[2,3]
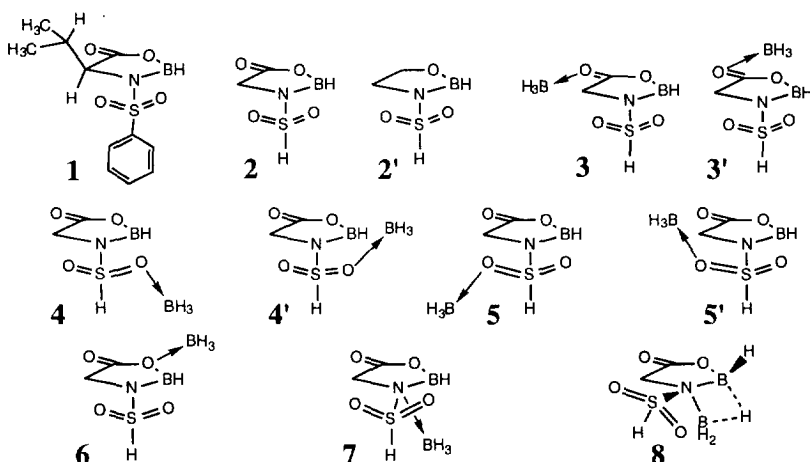
Standard *ab initio* MO calculations (RHF) were carried out using the Gaussian 92 series of programs.[4] The model **1** was studied using only the 3-21G basis whereas the models **2** - **8** were optimized (using the Gaussian 94 system) also with inclusion of electron correlation [at the level of second-order Møller-Plesset theory (MP2/6-31G*//MP2/6-31G*)].[4] No other calculations on **1** - **8** (except on **2'**)[2] appear to have been published.

RESULTS AND DISCUSSION

Total and relative energies, dipole moments and some selected properties related to bond lengths and charges of the optimized structures are shown in Table 1. The optimized (MP2/6-31G*//MP2/6-31G*) structure of **2** (compared with that of **2'**) is shown in Figure 1. The optimized (3-21G/3-21G) structure of **1** is depicted in Figure 2. The optimized structures (MP2/6-31G*//MP2/6-31G*) of H₃B adducts are shown in Figures 3-5.

Catalyst models

The structural parameters of **2** compared with those of **2'** indicate that in 5-oxo derivatives (*e.g.* **2**) the oxygen of the oxazaborolidinone ring does not interact with the adjacent boron as much as in the related 5,5-dihydro analogs [the B-O bond of **2** is longer (and the B-N bond shorter) than that of **2'**; Fig. 1]. That implies that **2** should be a stronger Lewis acid than **2'**. The same conclusion could be drawn also by comparing the LUMO energies of **2** and **2'**. The LUMO of **2** is 3.23 eV whereas that of **2'** is considerably higher (4.46 eV; Table 1). A comparison of atomic charges of **2** and **2'** reflecting Lewis acidity / basicity reveals that the carbonyl

group polarizes the oxazaborolidine ring by drawing electron density from Lewis basic centers (oxygens) while leaving acidic ones almost intact (*e.g.* boron and sulphur). Nevertheless, the dipole moment of **2** is 1.62 D lower than that of **2'** (4.84 D; MP2/6-31G*//MP2/6-31G*, Table 1).

The high similarity of the structures of **1** and **2** (Fig. 2) indicates that the latter could be used as a model of the former. Lengths of the polar bonds playing a role in reactions catalyzed by **1** are almost equal (within ± 0.004 Å; 3-21G//3-21G) to those of **2**. Although only one conformer of **1** was fully optimized for this work preliminary results imply that methyls of the *i*-propyl group would be oriented away from the sulphonyl oxygen residing out of the plane of the oxazaborolidinone ring (the other oxygen resides almost in the plane of the ring, Fig. 2). In this conformation one face of the oxazaborolidinone ring of **1** would be efficiently blocked. In that case coordination of a Lewis base (e.g. an aldehyde) should preferably occur on the face *syn* to the phenyl of the sulphonyl group (as has been proposed[2] earlier).

Table 1. Energies, dipole moments, selected bond lengths and selected charges of the models.[a-g]

	3-21G//3-21G				MP2/6-31G*//MP2/6-31G*						
#	E^a	D^b	E_R^c	R_{AB}^d	E	D	E_R	R_{AB}	L_{MO}^e	O_Q^f	Q_{H3B}^g
1	-1194.29647	6.03	-	-	-	-	-	-	-	-	-
2	-849.51987	3.96	-	-	-855.49799	3.22	-	-3.23	3.23	0.605	-
2'	-776.22526	5.13	-	-	-781.61355	4.84	-	-4.46	4.46	0.601	-
3	-875.77882	5.51	0.0	1.751	-881.98341	4.83	0.0	1.718	2.26	0.610	-0.167
3'	-875.77538	6.48	9.0	1.812	-881.97836	5.95	13.3	1.774	2.27	0.617	-0.146
4	-875.79102	4.40	-32.1	1.672	-881.97702	3.89	16.8	1.724	2.97	0.625	-0.160
4'	-875.78906	6.62	-26.9	1.698	-881.97707	5.66	16.7	1.778	3.03	0.637	-0.130
5	-875.79157	3.70	-33.5	1.699	-881.97834	2.95	13.3	1.796	2.84	0.608	-0.129
5'	-875.78712	6.93	-21.8	1.713	-881.97836	5.61	14.2	1.801	2.96	0.617	-0.120
6	-875.77505	5.96	9.9	1.798	-881.97426	5.04	24.1	1.853	2.73	0.632	-0.092
7	-875.77548	2.31	8.8	1.758	- h	-	-	-	-	- -	-
8	-875.76837	4.89	27.5	1.624	-882.00101	4.53	-46.3	1.585	3.51	0.482	+0.078
H₃B	-26.23730	0	-	-	-26.46424	0	-	-	2.41	0.123	0.000

[a] Total energies (**E**) given in hartrees. [b] Dipole moments (**D**) given in debyes. [c] Energies (E_R) relative to **3** given in kJ mol⁻¹. [d] The H₃B-X (X=O or N of **4**) distances given in ångströms. [e] LMO energies given in electron volts. [f] The charge (Q_B) of the boron of the oxazaborolidinone ring. [g] The charge (Q_{H3B}) of the H₃B moiety. [h] All attempts to optimize **7** led to **8**.
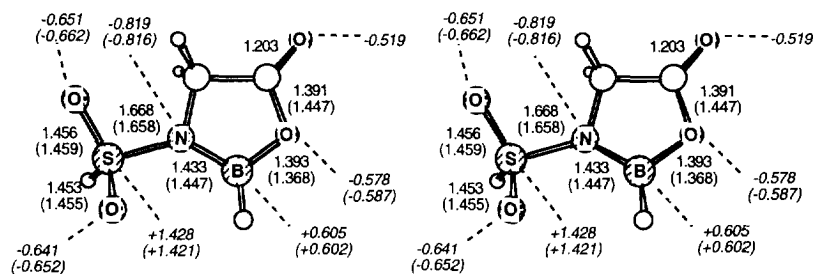
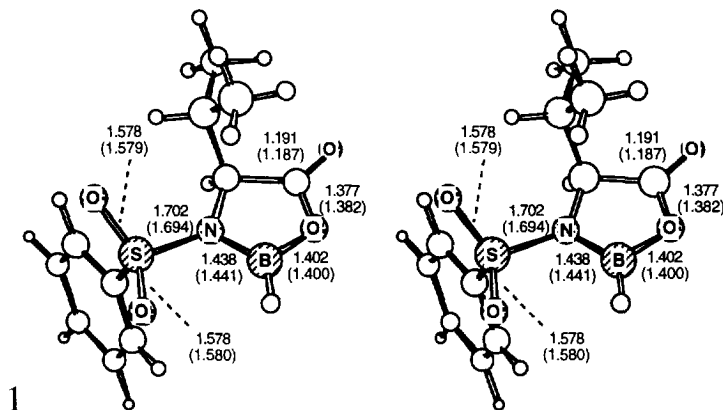

Figure 1. Optimized (MP2/6-31G*//MP2/6-31G*) structure of **2**. Selected bond lengths [in Å] and net atomic charges (*in Italics*) are shown (values of **2'** in parentheses).

Borane adducts of N-sulphonylated oxazaborolidin-5-ones

The relative energies of isomeric borane adducts **3** - **8** (E_R, MP2/6-31G*//MP2/6-31G*, Table 1) indicate that formation of the hydride-bridged adduct (**8**, Fig. 5) would be much more advantageous than that of the

others. Analogous formation of a hydride-bridged adduct of the parent oxazaborolidine has been reported earlier.[3]

Figure 2. Optimized (HF/3-21G//3-21G) structure of **1**. Selected bond lengths [in Å] are shown. The corresponding values of **2** are shown in parentheses.
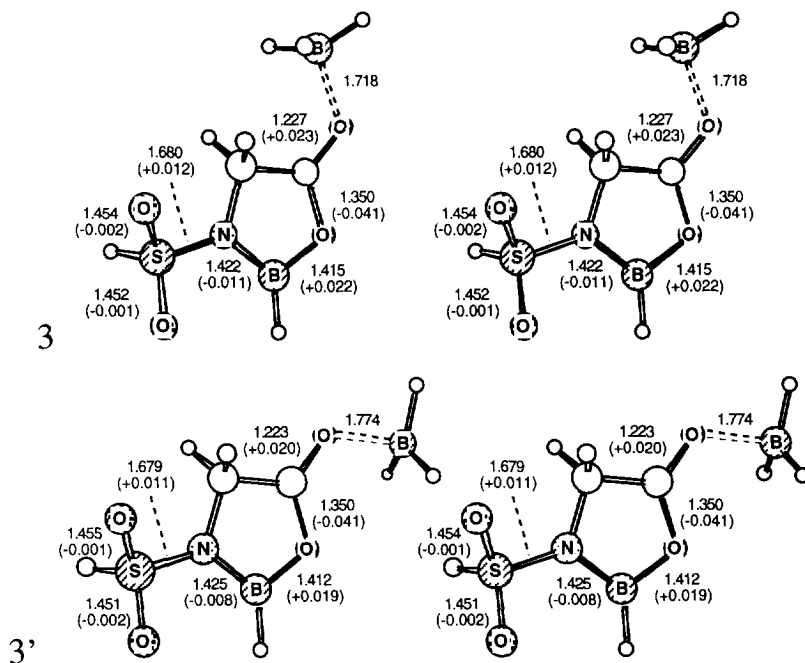
Figure 3. Optimized (MP2/6-31G*//MP2/6-31G*) structures of **3** and **3'**. Selected bond lengths [in Å] are shown. Changes (relative to **2**) of bond lengths are shown in parentheses ("+" indicates lengthening and "-" shortening of the related bonds).
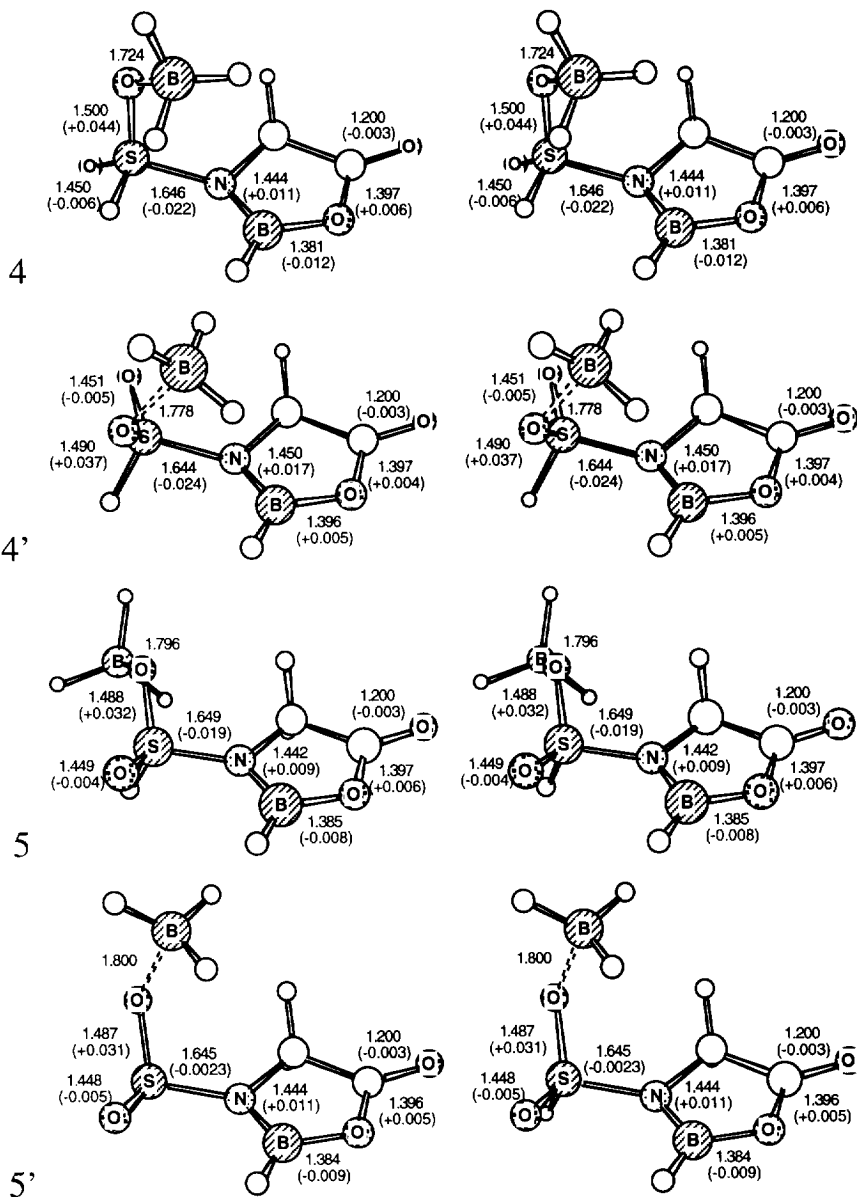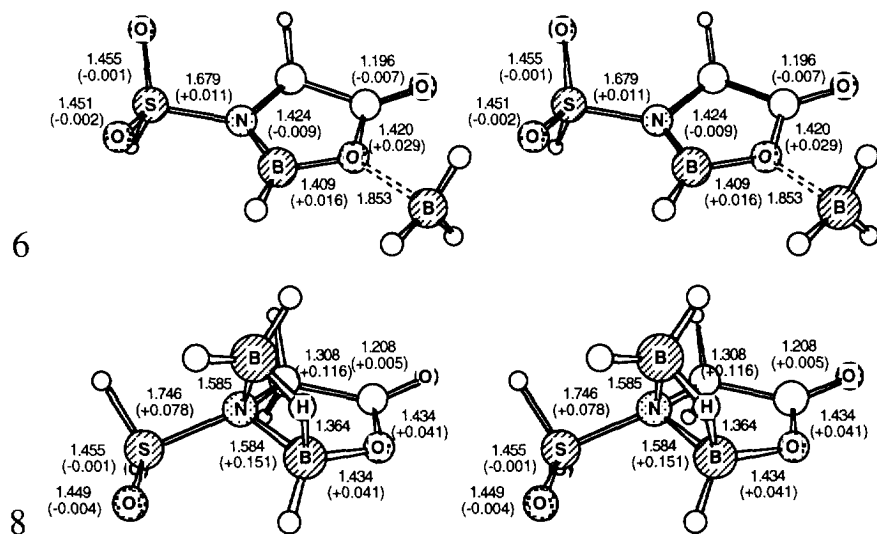
Figure 4. Optimized (MP2/6-31G*//MP2/6-31G*) structures of **4**, **4'**, **5** and **5'**. Selected bond lengths [in Å] are shown. Changes (relative to **2**) of bond lengths are shown in parentheses ("+" indicates lengthening and "-" shortening of the related bonds).

Although the formation of bridged adducts similar to **8** appears to be highly favorable in the case of borane as a Lewis acid other Lewis acids may not react in the same way (because of sterical hinderance). Furthermore, in consequence of the formation of adducts analogous to **8** the active center of the catalyst would be shielded and Lewis acidity of the catalyst should substantially decrease. Indeed, the LUMO energy (L_{MO}, Table 1) of **8** is higher [and the positive charge of the boron of the oxazaborolidinone ring lower (Q_B, Table 1)]

than that of any other of the isomeric adducts. Furthermore, the charge of the borane moiety (Q_{H3B}, Table 1) of **8** is reverse (in the case of formation **8** borane donates electron density to the oxazaborolidinone) to that of the other adducts (in the case of formation **3** - **7** borane receives electron density from the oxazaborolidinone).

The relative energies (E_R, MP2/6-31G*//MP2/6-31G*, Table 1) of borane adducts **3** - **8** imply that the borane $O_{C=O}$-adducts could be more stable than the related O_{SO2}- or O_{ring}-adducts. In **3** *the B-O=C-O* torsion angle is 178.5° (an *anti* adduct; Fig. 3). In this orientation the borane appears to draw more electron density from the oxazaborolidinone moiety than in the case of any other orientation inspected (the Q_{H3B} value of **3** is more negative than that of any other of the adducts, Table 1). The related *syn* adduct (*i.e.* **3'**) is less stable (by 13.3 kJ mol⁻¹ at the MP2/6-31G*//MP2/6-31G* level; Table 1). Nevertheless, Lewis acidity of the adduct **3'** [coordination of the activating Lewis acid in a manner analogous to that (**C**, the Scheme) proposed by Sartor *et al.*,[18]] could be predicted to be similar to that of **3** [although the dipole moment of **3'** is 1.12 D higher than that of **3**, the LUMO energies (L_{MO}) of **3** and **3'** are almost equal, the boron of the oxazaborolidinone ring is only slightly more positive (Q_B) than that of **3**, and the oxazaborolidinone moiety of **3** is more positively polarized than that of **3'** (Q_{H3B} of **3** more negative than that of **3'**), Table 1].

Figure 5. Optimized (MP2/6-31G*//MP2/6-31G*) structures of **6** and **8**. Selected bond lengths [in Å] are shown. Changes (relative to **2**) of bond lengths are shown in parentheses ("+" indicates lengthening and "-" shortening of the related bonds).

Structural parameters of **3** and **3'** (Fig. 3) are closely similar. Except the lengths of H_3B-$O_{C=O}$ bonds (R_{AB}, Table 1) which differ by 0.056 Å, bonds of **3** and **3'** are almost equally long. This indicates that the structure of the active center of *N*-sulphonylated oxazaborolidin-5-ones is neither sensitive to the orientation at which the activating Lewis acid approaches the carbonyl group nor to the distance at which the acid finally resides. Conclusions not much different from these could be drawn in the case of the H_3B-O_{SO2} adducts **4**, **4'**, **5** and **5'** (Fig. 4).

The relative energies of the H_3B-O_{SO2} adducts **4**, **4'**, **5** and **5'** (Fig. 4) are closely similar (E_R values of **4**, **4'**, **5** and **5'** are all within the range of +15.1 ± 3.5 kJ mol⁻¹, Table 1), as are (except the H_3B-O_{SO2} bonds)

the bond lengths (the C=O bonds 1.200 Å, $C-O_{ring}$ bonds 1.397 ± 0.001 Å, $B-O_{ring}$ bonds 1.383 ± 0.002 Å, $B-N_{ring}$ bonds 1.446 ± 0.004 Å, $S-N_{ring}$ bonds 1.647 ± 0.003 Å, $S-O_{BH3}$ bonds 1.494 ± 0.007 Å and the S-O bonds 1.450 ± 0.002 Å long, Fig. 4). Therefore, as in the case of **3'** and **3**, neither the orientation of the borane nor the H_3B-O_{SO2} distance (varying within the range 1.762 ± 0.038 Å) appears to correlate with the energies of formation (E, Table 1) or the structural changes (Fig. 4).

Properties related to Lewis acidity (L_{MO} and Q_B, Table 1) indicate that the adducts **4**, **4'**, **5** and **5'** (Fig. 4) could be predicted to be weaker Lewis acids than borane or the $H_3B-O_{C=O}$ adduct **3**. On the other hand, as the former adducts could be predicted (on the same basis) to be stronger Lewis acids than **2** or **2'** one could draw a conclusion that coordination of a Lewis acid (either on $O_{C=O}$ or O_{SO2}) could activate the catalyst as a Lewis acid. The least Lewis basic free electron pairs of **2** appear to be those of the oxygen of the oxazaborolidin-5-one ring. This conclusion could be drawn on the basis of a comparison of the E_R, R_{AB} and Q_{H3B} values (Table 1). The relative energy ($E_R = +24.1$ kJ mol^{-1}, Table 1) of **6** (Fig. 5) is higher, the H_3B-O_{ring} bond longer ($R_{AB} = 1.853$ Å, MP2/6-31G*//MP2/6-31G*, Table 1) and the Q_{H3B} value less negative than the related values of the other adducts. Interestingly, the H_3B-O_{ring} adduct **6** (Fig. 5) could be predicted to be a stronger Lewis acid than the related H_3B-O_{SO2} adducts **4 - 5**, **4' - 5'**. The LUMO energy of **6** (2.73 eV, Table 1) is lower [and the positive charge of the boron of the oxazaborolidin-5-one ring (Q_B) higher, Table 1] than the corresponding values of the H_3B-O_{SO2} adducts. The high energy of formation of **6** could be rationalized also on the basis of π-resonances of **2** (coordination of a Lewis acid to O_{ring} disturbs the $B-O_{ring}$ <-> $B^-=O_{ring}^+$ resonance). Furthermore, in consequence of the formation of **6** the oxygen atom (O_{ring}) which resides between two positively charged atoms (B and $C_{C=O}$) would be required to donate electrons (making electron poor atoms even poorer). In this light it is not surprising that the negative charge (Q_{H3B}, Table 1) received by H_3B is lower in the case of **6** than in the case of the other adducts [e.g. the charge (Q_{H3B}) received by H_3B is -0.167 in the case of **3** whereas that of **6** is only -0.092, Table 1].

In contrast to the other isomers, the borane *N*-adduct **7**, of which the relative HF/3-21G energy (Table 1) was almost equal to that of **6** (Fig. 5), turned out to be unstable when optimized at the MP2/6-31G* level (Table 1). One of the hydrides of the borane moiety formed a hydride bridge (formation of **8**, Fig. 5). Adducts analogous to **7** could, however, be predicted to play a minor role in reactions catalyzed by most known *N*-sulphonylated oxazaborolidin-5-ones. Other (less reactive and/or more bulky) Lewis acids may not react in the same way (*e.g.* self-aggregation of **1**) as borane.

On the performance of the computational methods

The structures of borane *O*-adducts **3 - 6** and **3' - 5'** optimized at the HF/3-21G level resemble those obtained at the MP2/6-31G* level [*e.g.* the H_3B-O distances (R_{AB}, Table 1) obtained at the HF/3-21G and MP2/6-31G* levels are within 1.742 ± 0.070 Å and 1.786 ± 0.068 Å, respectively]. Nevertheless, the relative stabilities calculated at the HF/3-21G level differ from those obtained at the MP2/6-31G* level. Furthermore, the high stability of the hydride-bridged system **8** was severely underestimated at the HF/3-21G level. Therefore, although relative energies of isomeric systems can often be reliably determined at the HF/3-21G level, it looks as if in the case of these borane adducts the relative energies determined at the HF/3-21G level (E_R, Table 1) would be all wrong. Even less reliable results were obtained when structures of the adducts **3 - 8** and **3' - 5'** were optimized at the HF/6-31G* level. Due to the nature of the results (*e.g.* H_3B-O_{SO2} bonds of the adducts

optimized at the 6-31G* level were 0.4 - 0.7 Å longer than those of the adducts inspected at the HF/3-21G or MP2/6-31G* levels) those calculations are not reported here.

CONCLUSIONS

On the basis of the above inspection one could draw a conclusion that N-sulphonylated oxazaborolidin-5-ones bind borane. The free electron pair (*anti* to the ring oxygen about the C=O bond) of the carbonyl group would be the most basic site for borane type of Lewis acids (except the parent borane H_3B capable of forming hydride bridges) to coordinate on. Coordination on the oxygens (O_{SO2}) of the N-sulphonyl group would be slightly [and on the oxygen (O_{ring}) of the oxazaborolidin-5-one ring clearly] less favorable than that on $O_{C=O}$. All these borane O-adducts could be predicted to be stronger Lewis acids than the parent N-sulphonylated oxazaborolidin-5-one. In this light it looks as if coordination of Lewis acids (including self-aggregation) on the oxygen of either carbonyl or sulphonyl group of **1** and related analogs could lead to the activation of the catalyst as a Lewis acid. Further studies on the binding propensities of these (activated) catalysts are in progress.

ACKNOWLEDGEMENTS

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