



A computational study on the activation of chiral *N*-sulphonylated oxazaborolidinones by Lewis acids

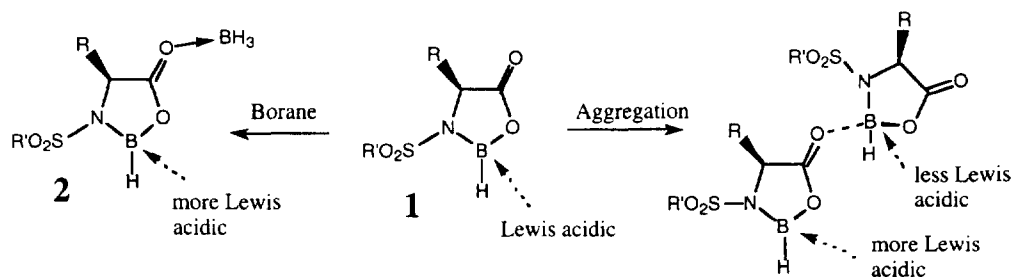
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Abstract: Activation of *N*-sulphonylated oxazaborolidin-5-ones as Lewis acids capable of binding aldehydes was studied computationally by means of *ab initio* methods. Formaldehyde was used as a model of aldehydes and *N*-sulphonyl-1,3,2-oxazaborolidin-5-one **1'** as a model of the oxazaborolidinones. Energies (RHF/MP2/6-31G**//RHF/MP2/6-31G*) of the coordination of H₂C=O to **1'** were -42 kJ mol^{-1} (H₂C=O as a monodentate ligand) and -25 kJ mol^{-1} (H₂C=O as a bidentate ligand) when **1'** was activated (by coordination of borane to O_{5C=O} of the oxazaborolidin-5-one moiety). The corresponding energies were -23 and -4 kJ mol^{-1} in the case of non-activated **1'**. Results of this study support the existence of novel C–H...O hydrogen bonds proposed by Corey et al. but indicate that the bonds can be based on electrostatic interactions only. Energies of the novel bonds were estimated to be about 10 kJ mol^{-1} (as calculated in CH₂Cl₂). © 1997 Elsevier Science Ltd

Introduction

Chiral *N*-sulphonylated 1,3,2-oxazaborolidin-5-ones (e.g. **1**, Scheme 1) have been shown to be efficient catalysts for asymmetric Diels–Alder,¹ Mukaiyama aldol,^{1c,2} and 1,3-dipolar cycloaddition³ reactions of nitrones to ketene acetals. Deactivation of the oxazaborolidinone system by self-aggregation (Scheme 1) has been proposed by Sartor *et al.*¹ⁱ On the other hand, recent *ab initio* studies⁴ on borane^{4a} and aldehyde^{4b} adducts of **1** (borane as a model of an activating Lewis acid) indicate that self-aggregation could have an activating influence.⁴



Scheme 1.

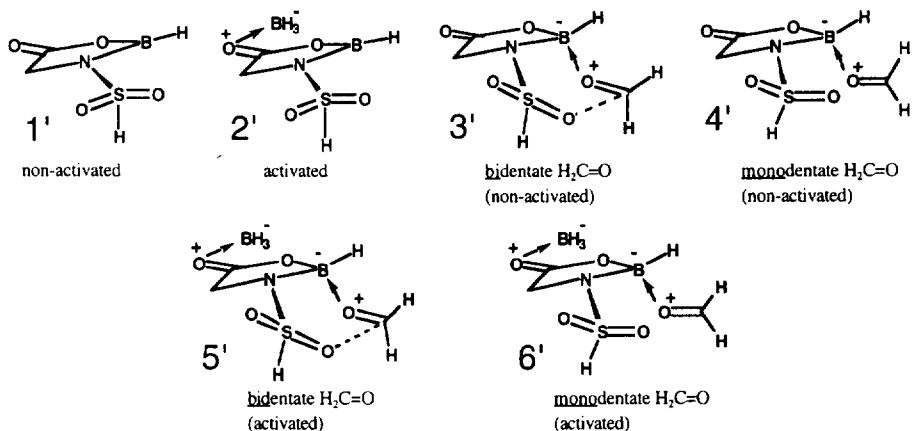
In order to study R-CHO–Lewis acid interactions,^{5,6} single X-ray crystal structures of (C₆F₅)₃B-complex of benzaldehyde,⁵ dimethylformamide (DMF) complexes of BX₃ (X=F, Cl, Br, I),^{6a} *B*-bromocatecholborane^{6b} and 2-(*N,N*-dimethylamino)phenoxyboron diiodide have been determined. On the basis of those studies,⁶ Corey et al.⁷ have proposed a novel C–H...X (X=F, O) hydrogen bond to be involved (as one of several structural elements) when aldehydes coordinate to fluoroboranes and alkoxyboranes.⁷ Nevertheless, no experimental studies clearly and directly revealing the role of (de)activation (Scheme 1) appear to have been published so far. Therefore, the aim of this study was to

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estimate computationally how a Lewis acid coordinating on $O_{5C=O}$ of the oxazaborolidin-5-one ring of aldehyde-1 adducts activates the aldehyde moiety.

Models and computational methods

Oxazaborolidinone **1'** was used as a model of **1** whereas activation of **1** was studied using **2'**. Coordination of aldehydes to **1** and **2** was studied using **3'**–**6'** as models. The models were optimized at the RHF/6-31G* (using Gaussian 92),⁸ RHF/MP2/6-31G* and RHF/MP2/6-31G** (using Gaussian 94)⁹ levels. Models **1'**–**3'** have been studied with methods capable of describing electron correlation (RHF/MP2 or DFT/JMW)⁴ whereas computational studies on **4'**–**6'** appear not to have been published. Bonds of **3'**–**6'** were inspected also on the basis of Natural Bond Orbital (NBO)¹⁰ analyses performed using Gaussian 94.



Results and discussion

The optimized (RHF/MP2/6-31G**/RHF/MP2/6-31G*) structures of **3'** and **4'** are shown in Figure 1. The corresponding structures of **5'** and **6'** (along with selected values of **6'** optimized at the RHF/MP2/6-31G** level) are depicted in Figure 2. Total energies, energies of coordination of H₂C=O to **1'** and **2'**, dipole moments and selected charges of the optimized structures are shown in Table 1.

Bond lengths (Figs 1 and 2) and energies (Table 1) obtained at the RHF/MP2/6-31G* level indicate that correlation effects are important for the description of **3'**–**6'** [whereas inclusion of polarization functions for hydrogen atoms hardly causes changes at all (the most significant change in the structure of **6'** is shortening of the $O_{5C=O}-B_{BH_3}$ bond by 0.005 Å, Figure 1)]. Lengths of the polar B–N bonds of the adducts shorten (as do the $B-O_{H_2C=O}$ bonds of **5'** and **6'**; Figure 2) although all other bonds lengthen while moving to the RHF/MP2/6-31G* level (from the RHF/6-31G* one). Furthermore, no stationary point of **4'** (Figure 1) was found at the RHF/6-31G* level; interactions between the formaldehyde and oxazaborolidinone moieties were repulsive. That could be related to the positive energies of formation [E_C (RHF), Table 1] of the adducts [only the value of **6'** was negative (*i.e.* –16.1 kJ mol⁻¹; Table 1) without correlation effects]. Despite of these differences, the charges (Q_C and Q_L , Table 1) of **3'**–**6'** calculated at both RHF/MP2/6-31G* and RHF/6-31G* levels are closely similar. Also the relative order of stabilities of **3'**, **5'** and **6'** is similar at both levels.

Bidentate vs. monodentate ligand

For purposes of a comparison of effects (RMP2) related to the role of H₂C=O as a bi- or monodentate ligand, the following five observations were made: 1) energies (E_C ; Table 1) of **4'** and **6'** (monodentate H₂C=O) are more negative (by about 20 kJ mol⁻¹) than those of **3'** and **5'** (bidentate H₂C=O); 2) the positive charges (Q_C ; Table 1) of $C_{H_2C=O}$ of **4'** and **6'** (monodentate) are lower than those of the corresponding bidentate analogs (**3'** and **5'**); 3) the positive charges (Q_L ; Table 1) of the formaldehyde

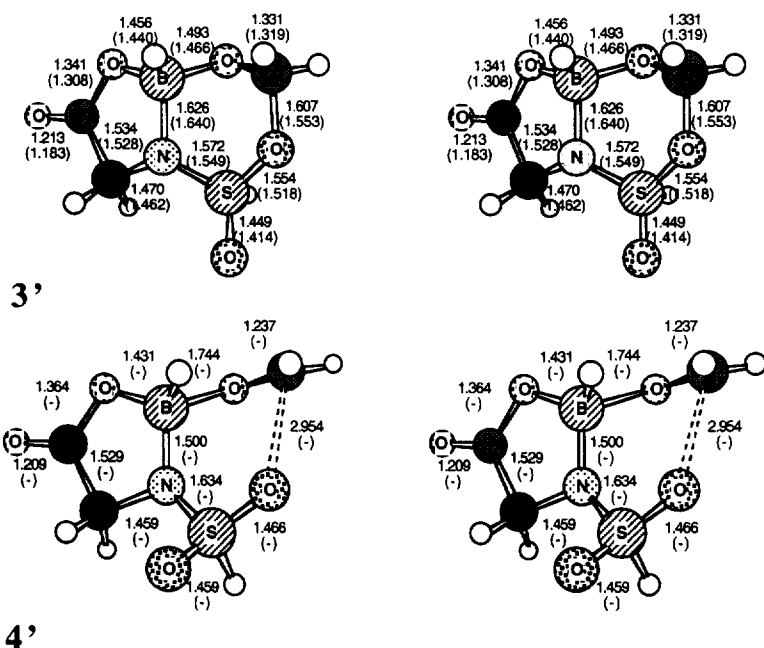


Figure 1. Stereoscopic presentation of the optimized (RHF/MP2/6-31G**//RHF/MP2/6-31G*) structures of 3' and 4'. Selected bond lengths [in Å] are shown (the corresponding RHF/6-31G**//RHF/6-31G* values in parentheses; values of 4' missing because 4' was found to be unstable at the 6-31G**//6-31G* level).

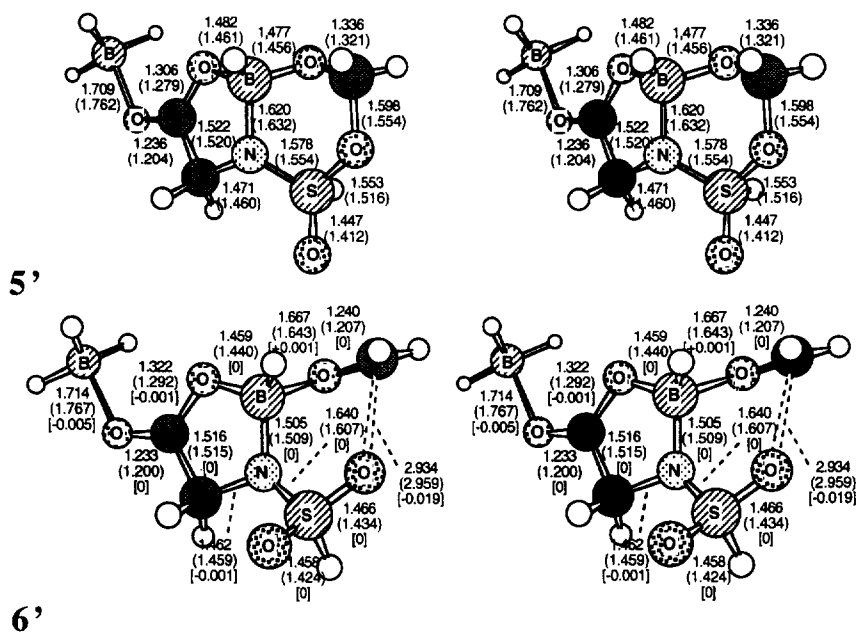


Figure 2. Stereoscopic presentation of the optimized (RHF/MP2/6-31G**//RHF/MP2/6-31G*) structures of 5' and 6'. Selected bond lengths [in Å] are shown (the corresponding RHF/6-31G**//RHF/6-31G* values in parentheses). Changes of bond lengths observed when 6' (RHF/MP2/6-31G**//RHF/MP2/6-31G*) was reoptimized at the RHF/MP2/6-31G** level are shown in brackets (positive/negative values indicate lengthening/shortening of the related bonds).

Table 1. Total energies (E_T), dipole moments (M_D), atomic charges of $C_{H_2C=O}$ (Q_C), partial charges of $H_2C=O$ (Q_L) moieties and energies (E_C) of coordination of $H_2C=O$ to **1'** and **2'**

Struct.	E_T [a.u.]		M_D [D]		Q_C [e]		Q_L [e]		E_C [kJ mol ⁻¹]		
	#	RMP2 ^a	RHF ^b	RMP2	RHF	RMP2	RHF	RMP2	RHF	RMP2	RHF
1'		-855.497986	-854.166252	3.22	2.97	-	-	-	-	-	-
2'		-881.978360	-880.562036	5.95	3.66	-	-	-	-	-	-
3'		-969.667126	-968.020918	5.52	5.43	+0.268	+0.281	+0.086	+0.094	-3.7	+30.7
4'		-969.674640	^c	6.76	^c	+0.169	^c	+0.158	^c	-23.4	^c
5'		-996.155550	-994.422611	9.57	9.32	+0.266	+0.278	+0.106	+0.115	-24.8	+15.1
6'		-996.162192	-994.434487	10.08	9.44	+0.175	+0.171	+0.206	+0.214	-42.3	-16.1
$H_2C=O$		-114.167748	-113.86633	2.84	2.67	+0.135	+0.134	±0.000	±0.000	-	-

^a RMP2 values are based on the RHF/MP2/6-31G**//RHF/MP2/6-31G* calculations. ^b RHF values are based on the calculations carried out at the RHF/6-31G* level. ^c Found to be unstable at the RHF/6-31G* level.

moieties of **4'** and **6'** (monodentate) are higher than those of the corresponding bidentate analogs (**3'** and **5'**); 4) the dipole moments (M_D ; Table 1) of **4'** and **6'** (monodentate) are higher than those of the corresponding bidentate analogs (**3'** and **5'**); 5) faces of the formaldehyde moieties of **4'** and **6'** (monodentate) are less selectively shielded (Figs 1 and 2) than those of the corresponding bidentate analogs **3'** and **5'** (the face being completely blocked in **3'** and **5'** is partially open in **4'** and **6'**). These five observations, except the positive charges (Q_C ; Table 1) of $C_{H_2C=O}$ of **3'/4'** and **5'/6'**, indicate that, when an aldehyde behaves as a monodentate ligand, it would be activated more than that behaving as a bidentate ligand. On the other hand, the enhanced activity could be predicted to be accompanied with a diminished face selectivity. Nevertheless, the less shielded face of the activated aldehyde would be the same one in the case of both types of chelates.

As both of the chelation modes appear to be energetically advantageous and reactions of both types of chelates (with electron rich compounds) should have the same stereochemical outcome, involvement of neither one of the types could be neglected while considering mechanistic aspects of reactions catalyzed by **1** (Scheme 1). In the case of the simple models **3'**–**6'** interactions between the $H_2C=O$ and oxazaborolidin-5-one moieties are not affected by substituents (binding of $H_2C=O$ should be so tight as it can be at best). In the case of substituted derivatives of **1**, steric bulk and secondary electronic effects (*e.g.* π -stacking) related to interactions between the substituents (**R** and **R'**; Scheme 1) of the oxazaborolidin-5-one and the aldehyde (to be activated by **1**) would determine which one of the binding modes would be involved.

Activated vs. non-activated catalyst

For purposes of a comparison of effects (RMP2) related to the activating role of Lewis acids coordinating to the lone electron pair of $O_{5C=O}$ of the oxazaborolidinone ring the following five observations were made: 1) energies (E_C ; Table 1) of **3'** and **4'** (non-activated) are less negative (by about 20 kJ mol⁻¹) than those of **5'** and **6'** (activated); 2) the positive charge (Q_C ; Table 1) of $C_{H_2C=O}$ of **3'** (non-activated) is 0.002 units higher than that of **5'** (activated) whereas, in contrast to that, Q_C of **6'** (activated) is 0.006 units higher than that of **4'** (non-activated); 3) the positive charge (Q_L ; Table 1) of the formaldehyde moiety of **5'** (activated) is 0.020 units higher than that of **3'** (non-activated); a similar (but higher) difference (*i.e.* 0.048) can be seen in the case of **4'/6'**; 4) the dipole moments (M_D ; Table 1) of **5'** and **6'** (activated) are significantly higher than those of the corresponding non-activated analogs (**3'** and **4'**); 5) the relative difference of shielding of faces of the formaldehyde moiety does not change in consequence of the activation (Figs 1 and 2). These five observations indicate, for instance, that both (mono- and bidentate) types of adducts could be activated. Furthermore, it looks as

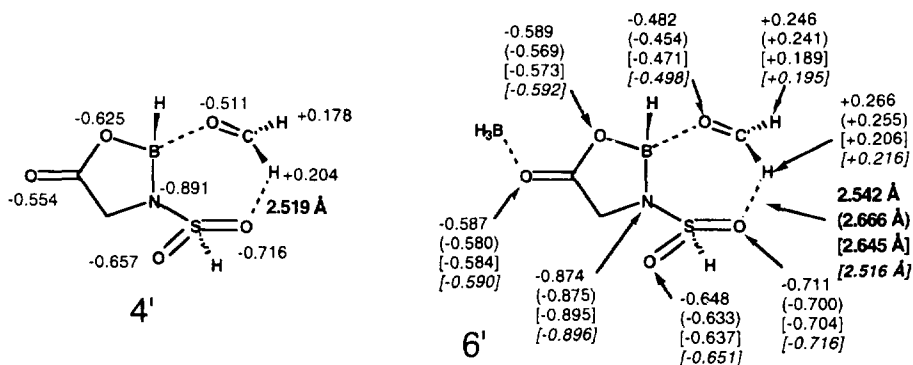


Figure 3. Total atomic charges of the oxygen, nitrogen and formyl hydrogen atoms of the optimized structures of 4' and 6' (RHF/MP2/6-31G**/RHF/MP2/6-31G*). The distance between the formyl hydrogen (the more positive one) and the sulphonyl oxygen (the more negative one) is also included. The corresponding values of 6' optimized at the RHF/6-31G*, RHF/6-31G** and RHF/MP2/6-31G** levels (values of 4' are not given, see Figure 1) are shown in parentheses (6-31G*), in brackets [6-31G**] and in italics in brackets [MP2/6-31G**].

if adducts, in which an aldehyde behaves as a monodentate ligand (e.g. 4'), would be activated more than the corresponding bidentate analogs. Interestingly, the Lewis acid activating the catalyst appears not to affect the orientation of the aldehyde moiety (Figs 1 and 2).

Novel C–H–O hydrogen bonds

Corey et al.^{6,7} have proposed a novel C–H–O hydrogen bond to be involved (as one of several structural elements) when aldehydes coordinate to alkoxyboranes.^{6,7} Because the oxygen involved in that type of hydrogen bond must be Lewis basic, inspection of the atomic charges of the interacting counterparts could be useful. Prior studies^{4a} on 1' indicate that negative atomic charges of *N* and *O*_{SO2} atoms of 1' are higher than those of the other atoms (of 1'). Results of the present calculations (Figure 3) indicate that the coordination of borane, H₂C=O, or both borane and H₂C=O to 1' does not change this relative order of the charges (Figure 3).

The influence of basis set size on the charges of monodentate complexes (4' and 6') was studied in the case of 6' (4' was unstable at the 6-31G* level). A comparison of the charges of 6' determined at the RHF/MP2/6-31G*, RHF/MP2/6-31G**, RHF/6-31G* and RHF/6-31G** levels (Figure 3) indicates that, although the charges are slightly different at each level of inspection, the relative order of the values does not change. Therefore, one can safely compare the charges of 4' and 6' (Figure 3).

The atomic charges of 4' and 6' (Figure 3) imply, that a Lewis acid coordinating to the lone electron pair of *O*_{5C=O} of an oxazaborolidin-5-one ring decreases negative charges of the atoms adjacent to the ring boron. The charge of *O*_{5C=O} (Figure 3) decreases more than charges of the other atoms whereas the charge of *O*_{5O2} (the more negative one) can be predicted to be affected less (than the others). On this basis one could predict that the novel hydrogen bonds similar to those proposed by Corey et al.^{6,7} should be seen (if they exist in 4' or 6') between the *O*_{5O2} (the more negative one) and *H*_{H2C=O} (the more positive one) atoms. Indeed, the *O*_{5O2}–*H*_{H2C=O} distances of 4' and 6' (2.52 and 2.54 Å; Figure 3) are well in the range (2.41–2.59 Å)^{6a} of the novel hydrogen bonds proposed^{6a} by Corey et al. Furthermore, a comparison of the charges and *O*_{5O2}–*H*_{H2C=O} distances of 4' and 6' reveals that the novel hydrogen bonds should be stronger in the case of activated complexes.

NBO-analysis of bonding in 3'–6'

Results of the NBO analyses are summarized in Figure 4. Energies of the lone electron pairs of 4' (Figure 4) suggest that the most Lewis basic site in 4' is the lone pair of *O*_{5C=O} [4'(LP2) = -11.66 eV, i.e. the least negative one of the lone pairs of 4'; Figure 4] whereas the most Lewis acidic site is the π*-orbital (+3.43 eV; Figure 4) of the aldehyde moiety. The least Lewis basic site of 4' appears to

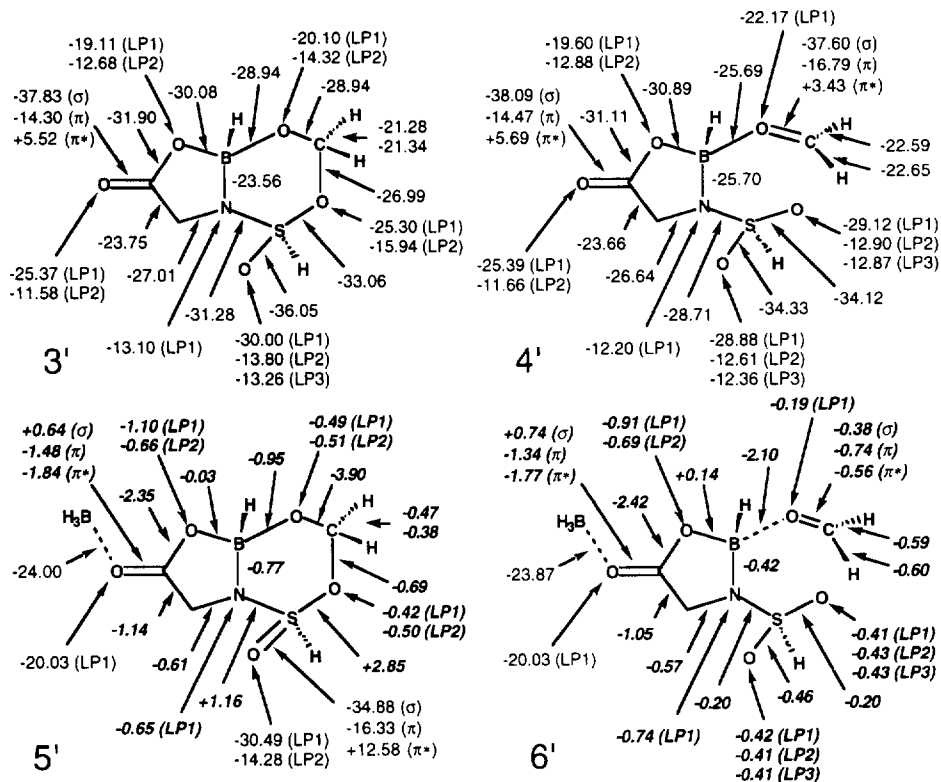


Figure 4. Absolute and relative energies (in eV) of selected natural localized bond orbitals (including lone electron pairs) of 3'–6' (RHF/MP2/6-31G**//RHF/MP2/6-31G*) as determined on the basis of NBO analysis carried out at the RHF/6-31G* level. Some of the values of 5' and 6' are relative (shown in *bold italics*) to those of 3' (in the case of 5') and 4' (in the case of 6').

be, however, the oxygen of the oxazaborolidin-5-one ring (as proposed on the basis of the analysis of charges of 4' and 6' discussed above). Interestingly, the nitrogen of the oxazaborolidin-5-one ring of 4' appears to be slightly more Lewis basic than the oxygens of the sulphonyl group (Figure 4). A comparison of values of 4' and 6' (Figure 4) implies that a Lewis acid coordinating to the lone pair of $O_{SC=O}$ of an oxazaborolidin-5-one ring stabilizes the oxazaborolidin-5-one–aldehyde complex and activates its aldehyde moiety. Namely, energies of almost all of the localized natural bond orbitals, lone pairs and π^* -orbitals (Figure 4) decrease as borane coordinates to 4' (formation of 6'). Although the decrease of the π^* -energy of C=O of the oxazaborolidin-5-one ring is larger than that of the aldehyde moiety, the π^* -orbital of the latter (+2.87 eV, Figure 4) is clearly more Lewis acidic than that of the former one (+3.92 eV) in 6' (Figure 4). Similar conclusions can be drawn when the values of 3' and 5' (Figure 4) are compared. Energies of the localized natural bond orbitals [except those related to the N–S and (one of the) S–O bonds] and lone pairs decrease as borane coordinates to 3' (formation of 5'; Figure 4). Interestingly, the NBO-analysis of 5' (Figure 4) revealed a sulphur–oxygen π -bond (all other oxygens of the sulphonyl groups of 3'–6' were found to be sp^3 -hybridized; Figure 4). The NBO analysis of 3' and 5' (Figure 4) suggests, that a Lewis acid coordinating to the lone electron pair of $O_{SC=O}$ of an aldehyde–oxazaborolidin-5-one complex (aldehyde as a bidentate ligand) strengthens the O_{SO_2} – $C_{aldehyde}$ and $C_{aldehyde}$ – $O_{aldehyde}$ bonds. Similar conclusions were drawn on the basis of the inspection of 3' (Figure 1) and 5' (Figure 2) discussed above.

As regarding to the novel hydrogen bonds, the NBO analysis (of 4' and 6', Figure 4) gives a few answers. Namely, none of the Lewis donor–acceptor interactions found in 4' and 6' was related

to these hydrogen bonds [*i.e.* if interactions $\text{LP}(\text{O})_{\text{SO}_2} \rightarrow \sigma^*(\text{C}-\text{H})_{\text{H}_2\text{C}=\text{O}}$ were there in **4'** or **6'** their significance must be less than 2 kJ mol^{-1}]. More hints related to the nature of the novel hydrogen bond(s) were found when hybridizations of the natural localized bonds (NBO analysis) and Mulliken populations of **4'** and **6'** were inspected. In the case of **4'** (MP2/6-31G*/MP2/6-31G*) a very low but attractive $\text{O}_{\text{SO}_2}-\text{H}_{\text{H}_2\text{C}=\text{O}}$ interaction (of which the Mulliken population was 0.0011) was detected. Also in the case of **6'**, a similar low attractive $\text{O}_{\text{SO}_2}-\text{H}_{\text{H}_2\text{C}=\text{O}}$ interaction (of which the Mulliken population was 0.0014) was detected. Furthermore, the *s*-orbital of $\text{H}_{\text{H}_2\text{C}=\text{O}}$ appeared to contaminate one of the lone pairs of O_{SO_2} by 0.013% (NBO hybridization analysis of **6'**). These results imply, that the novel hydrogen bonds^{6,7} are possible but in the case of adducts analogous to **4'** and **6'** the bonds can be based on electrostatic interactions only (*i.e.* the role of covalent binding is negligible). The charges and distances of O_{SO_2} and $\text{H}_{\text{H}_2\text{C}=\text{O}}$ of **4'** and **6'** (RHF/MP2/6-31G*; Figure 3) correspond (as calculated in CH_2Cl_2)¹¹ to the electrostatic energies¹¹ of -9.1 and $-11.6 \text{ kJ mol}^{-1}$ which can be considered as energies of formation of the $\text{O}_{\text{SO}_2}-\text{H}_{\text{H}_2\text{C}=\text{O}}$ bonds (of **4'** and **6'**). The corresponding energies¹¹ calculated in *vacuum* are -81.3 and $-103.4 \text{ kJ mol}^{-1}$ (maxima of the energies of the $\text{O}_{\text{SO}_2}-\text{H}_{\text{H}_2\text{C}=\text{O}}$ bonds of **4'** and **6'**; energies of hydrogen bonds normally vary within the range of $50\text{--}125 \text{ kJ mol}^{-1}$).

As the electrostatic effects discussed above, also analyses of the energies of intramolecular Lewis donor–acceptor interactions and hybridizations of the natural localized bonds of **4'** and **6'** suggest that $\text{O}_{\text{SO}_2}-\text{C}_{\text{H}_2\text{C}=\text{O}}$ interactions should be more significant than the $\text{O}_{\text{SO}_2}-\text{H}_{\text{H}_2\text{C}=\text{O}}$ ones (the novel hydrogen bonds^{6,7}). Energies of the $\text{LP}(\text{O})_{\text{SO}_2} \rightarrow \pi^*(\text{C}=\text{O})_{\text{H}_2\text{C}=\text{O}}$ interaction were found to be 4.6 kJ mol^{-1} in the case of both **4'** and **6'** (NBO analyses of the structures optimized at the RHF/MP2/6-31G* level). Furthermore, orbitals of $\text{C}_{\text{H}_2\text{C}=\text{O}}$ appeared to contaminate (NBO-analysis) three of the lone pairs of O_{SO_2} (contributions of the contaminant were 0.051, 0.018 and 0.114% whereas the related contamination was only 0.013% in the case of $\text{H}_{\text{H}_2\text{C}=\text{O}}$).

To summarize, results of the computational inspection of **1'–6'** indicate that a Lewis acid coordinating to $\text{O}_{\text{C}=\text{O}}$ of an oxazaborolidin-5-one could change (*i.e.* enhance) the activity of the oxazaborolidin-5-one as a Lewis acid but not change stereochemistry related to the coordination of an aldehyde to the catalyst. If the formaldehyde moiety of **3'–6'** is replaced by an α,β -enal, an attack of a diene to that complex would lead to the formation of the product which also has been observed experimentally.¹ Interestingly, stabilities of activated bidentate complexes (*e.g.* **5**) could be predicted to be similar to those of the corresponding non-activated monodentate ones. This suggest that an aggregated catalyst could form bidentate complexes with aldehydes (particularly, if steric bulk of the aggregate hampers the formation of the corresponding monodentate complex) equally well as the monomeric non-activated catalyst forms monodentate complexes.

Conclusions

Results of this study imply, that both bi- and monodentate chelation of aldehydes to *N*-sulphonylated oxazaborolidin-5-ones would be energetically advantageous. In the latter case, activation of the aldehyde can be predicted to be higher. Coordination of a Lewis acid to one of the lone pairs of $\text{O}_{\text{C}=\text{O}}$ of an oxazaborolidin-5-one can be predicted to tighten the $\text{O}_{\text{SO}_2}-\text{C}_{\text{C}=\text{O}}$ interaction (in bidentate system) and activate the aldehyde bound to the catalyst (particularly in monodentate systems). Results of this study support the existence of novel C–H–O hydrogen bonds proposed by Corey et al.^{6,7} but indicate that, in the case of aldehyde–oxazaborolidin-5-one complexes analogous to those of this study, the bonds can be based on electrostatic interactions only.

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