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On the Role of π-Stacking in Aldehyde Complexes of *N*-Sulphonylated Oxazaborolidinones Used as Chiral Catalysts

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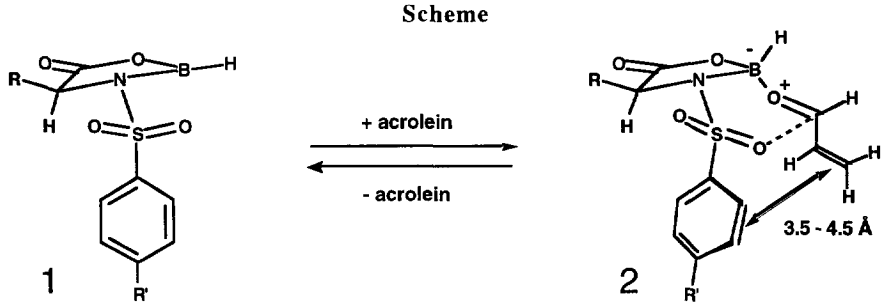
Abstract: - Aldehyde complexes of Lewis acidic chiral *N*-sulphonylated oxazaborolidinones (*e.g.* **1**) were studied by means of density functional methods at the JMW/DNP level. As a model of such complexes was chosen the acrolein *N*-phenylsulphonyl-1,3,2-oxazaborolidin-5-one adduct **2a**. Compared with the related adducts of the parent oxazaborolidinone (**2b**; the phenyl of **2a** replaced by hydrogen) the bidentate bonding of acrolein was found to be significantly dependent on the presence of the phenyl group. As the group was replaced by hydrogen the O_{SO_2} - $C_{C=O}$ bond lengthened substantially (by 0.225 Å) upon optimization. Distances between the vinyl and phenyl moieties were in the range of 3.7 - 4.0 Å in the complex **2a** suggest π-stacking. Almost equal energies of the formation of **2a** and **2b** imply the stacking to be passive in nature. Results of the Natural Bond Order analysis of **2a** support passive π-stacking; significant attractive interactions between the vinyl and phenyl groups of **2a** were not found.

INTRODUCTION

Chiral *N*-sulphonylated 1,3,2-oxazaborolidin-5-ones (*e.g.* **1**, the Scheme) have been shown to be efficient catalysts for asymmetric reactions (e.g. Diels-Alder).[1] On the basis of computational studies[2] on small models of the catalyst[2a] **1** and the related acrolein adducts[2b-c] **2**, aldehydes behaving as bidentate ligands[2c] has been proposed. In adducts **2** one face of the acrolein could be shielded[2b] (the Scheme) by the phenyl group.

Scheme



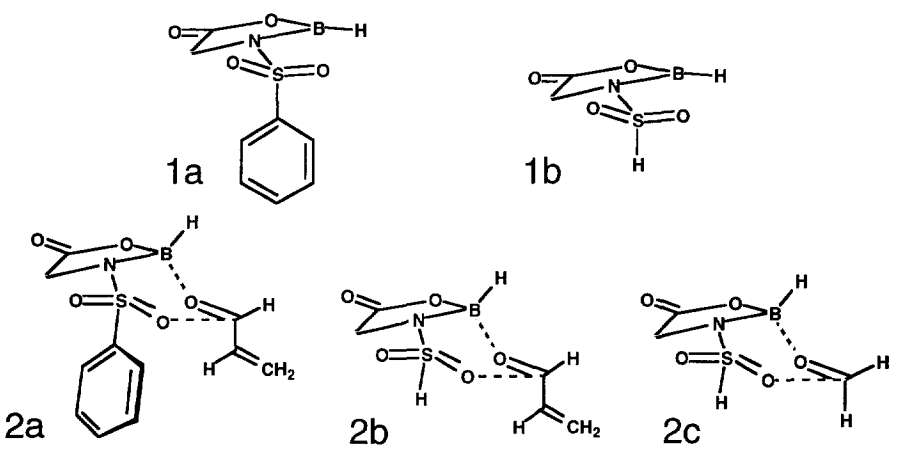
The phenyl group could direct the stereochemical outcome of the Diels-Alder reaction involving **2** in two ways. For instance, the phenyl group could just act as an inactive shield which covers one face of the acrolein moiety (passive π-stacking). On the other hand, the aromatic π-system (of the phenyl ring) could interact with that of the activated acrolein potentially donating electron density to the electron poor enal moiety bound to the

Lewis acidic boron of the catalyst (active π-stacking). The latter mechanism of stacking could be the less significant one (in the case of **2**) as the sulphonyl group should decrease the electron donating capability of the aromatic π-system.

In order to probe intramolecular interactions potentially playing a role in the asymmetric Diels-Alder reactions catalyzed by chiral *N*-sulphonylated oxazaborolidines, a series of models was studied using methods of computational chemistry. The models were particularly chosen to reveal the role of the phenyl (of the catalyst moiety) and vinyl (of the chelating enal) groups.

MODELS AND COMPUTATIONAL METHODS

The structures **1a-b** were used as models of the *N*-sulphonylated oxazaborolidines **1** whereas properties of aldehyde chelates **2** were studied using the models **2a-c**. Because we have shown earlier[3] that reliable results (compatible to those obtained using high level Hartree - Fock *ab initio* calculations; studies on the behaviour of ketones and aldehydes as bidentate ligands)[3] can be provided using DFT methods, the models **1a-b** and **2a-c** were optimized using DMol[4] (version 2.3 installed on a Convex C3840) at the JMW/DNP level (comparable with the MP2/6-31G** level in the Gaussian terminology[5]). In order to evaluate electronic effects related to the π-stacking Natural Bond Order (NBO)[6] analyses were performed using Gaussian 94 (installed on an SGI Power-Challenge) at the RHF/6-31G** level of theory.[5]



RESULTS AND DISCUSSION

The optimized structure of **1a** (compared with that of **1b**) is shown in Figure 1. The optimized structure of **2a** (compared with that of **2b**) accompanied with its dipole moment vector is shown in Figure 2. Energies and dipole moments of the models are shown in Table 1.

The energy of formation of **2c** (E_C, Table 1) is highly negative. This suggests that π-stacking would not be needed for the formation of bidentate chelates of aldehydes and *N*-sulphonylated oxazaborolidines. Interestingly, although the energies of formation of adducts **2a** and **2b** (E_C, Table 1) are considerably less negative than E_C of **2c**, the values of **2a** and **2b** are almost equal ($\Delta E_{2a,2b}$ = 0.2 kJ mol^{-1}, Table 1). This implies (together with the highly negative E_C of **2c**, Table 1) that π-stacking would not provide any significant contribution in the energy of formation of **2a**. Therefore, the aryl group of **2** would be predicted to behave only

as a passive shield (passive π-stacking) which is "forced" (by the topology and rigidity of the chelate system) to reside in the close neighborhood of the vinyl moiety (of the α,β-enal).

Table 1. Total energies,[a] dipole moments[a] and complexation energies.

Structure #	Total energy E_T [a.u.][a]	Dipole moment [D][a]	Complexation energy E_C [kJ mol^{-1}]
1a	-1081.853468	4.68	-
1b	-852.758954	2.50	-
2a	-1272.275995	6.18	-66.8
2b	-1043.181336	5.35	-66.4
2c	-966.454198	4.63	-107.8
H_2C=O	-113.654236	2.23	-
H_2C=CH-CHO	-190.397112	3.33	-

[a] Calculated with the DNP basis set using DMol.

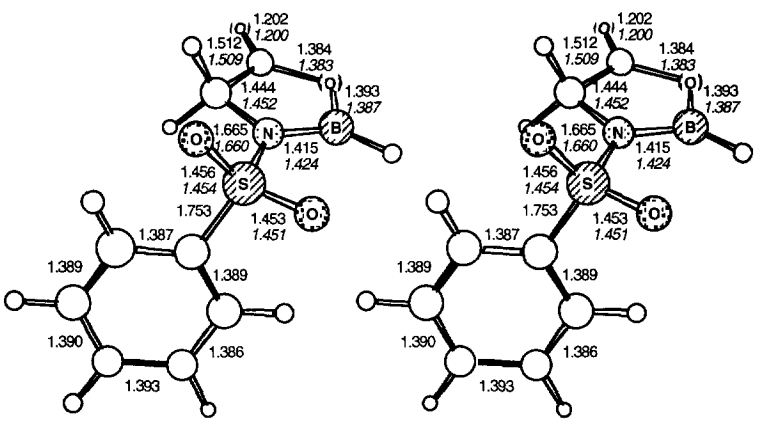


Figure 1. The optimized (JMW/DNP) structure of **1a**. Selected bond lengths [in Å] are shown [values of **1b** *in Italics*].

Structural parameters of **1a** (Fig. 1) are very similar to those of **1b** [e.g. the maximum difference of bond lengths between **1a** and **1b** is 0.009 Å (the *B-N* bond), Fig. 1]. Therefore, it looks as if bonding in the oxazaborolidine moiety would not be affected by the nature of the *S*-substituent of the sulphonyl group. This implies that **1b**, despite of its simplicity, would be a good model of **1a** (and **1**). The overall shape (*e.g.* the conformation of the *N*-sulphonyl group) of the structure of **1b** is also very similar to that of the 4-*i*-propyl substituted analog of **1a** studied earlier[2a] using *ab initio* methods (at the RHF/3-21G level).

Structural changes related to the formation of the cyclic chelate system of **2a-b** are similar to those of **2c** reported earlier[2b] on the basis of low level (*i.e.* RHF/6-31G) *ab initio* studies. The *S-O*, *B-N* and *C=O* bonds (participating in the formation of the 6-ring) lengthen whereas the *N-S* bond shortens.[2b] Bonding in the phenyl group appears to be only slightly affected by the chelation process [*e.g.* lengths of the bonds of the aromatic system of **1a** (Fig. 1) are almost equal to those of **2a** (Fig. 2)].

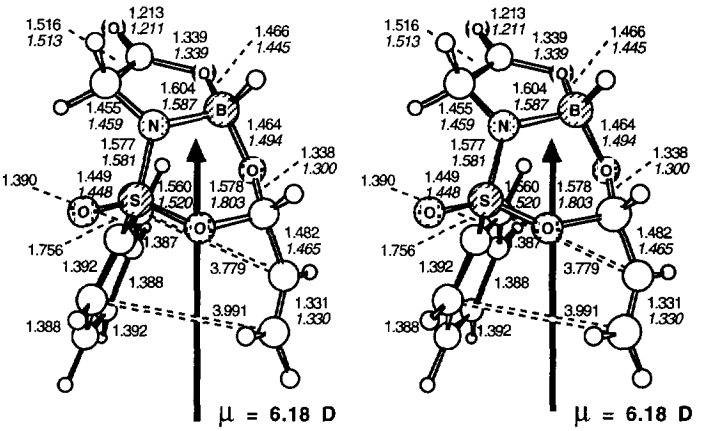


Figure 2. The optimized (JMW/DNP) structure of **2a**. Selected bond lengths [in Å] are shown [values of **2b** *in Italics*].

As proposed earlier on the basis of low level (*i.e.* RHF/6-31G) *ab initio* studies on simple models of **2c**, structural parameters of the optimized structure of **2a** (Fig. 2) indicate that the vinyl moiety of acrolein would indeed be efficiently shielded by the phenyl group. Interestingly, when the phenyl group of **2a** is replaced by a hydrogen (π-stacking not possible) the donor - acceptor system between the sulphonyl group and $C_{C=O}$ of acrolein weakens substantially (the O_{SO_2} - $C_{C=O}$ bond lengthens by 0.225 Å). A comparison of the most dissimilar bonds of **2a-c** is shown in Figure 3.

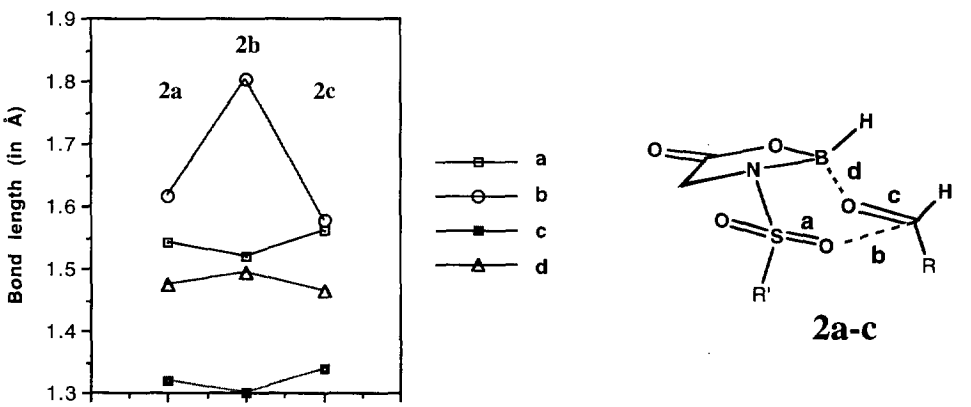


Figure 3. A comparison of lengths of the most dissimilar bonds of the optimized (JMW/DNP) structures of **2a-c**.

The comparison of bond lengths shown in Figure 3 indicates that lengths of the bonds of these chelates are not dependent on the nature of the O_{SO_2} - $C_{C=O}$ interaction. The large change in the O_{SO_2} - $C_{C=O}$ distance hardly causes any changes (of bond lengths) in the rest of the structure. Nevertheless, the charge distribution and hybridization of $C_{C=O}$ of the α,β-enal moiety are affected.

The acrolein moiety of **2a** is slightly positively charged [$Q_{acrolein}$(**2a**) = +0.087][7] indicating that reactivity (with systems capable of donating electrons, *e.g.* dienes) of acrolein is enhanced in consequence of the

formation of a chelate such as **2a**. However, the positive charge (in contrast to the hybridization of $C_{C=O}$)[8] of the acrolein moiety of **2b** (hybridization[8] of $C_{C=O}$ = $sp^{2.39}$) turned out to be substantially higher [$Q_{acrolein}$(**2b**) = +0.133][7] than that of **2a** (hybridization[8] of $C_{C=O}$ = $sp^{2.68}$). This implies that the reactivity (unfortunately not necessarily the selectivity) of these adducts (of α,β-enals to **1**) towards electron rich systems (*e.g.* dienes) could increase with the decreasing amount of O_{SO_2} - $C_{C=O}$ interaction.

As the structural differences between **2a** and **2b** appear to be related to the steric demand of the phenyl group in **2a** (*i.e.* if the volume of the phenyl group could be as small as that of a hydrogen atom the structure of **2a** would probably resemble more that of **2b** than the structure shown in Figure 2 does) the relative difference of the structures of **2b** and **2c** remains to be explained. In the case of **2b** and **2c** the structural differences can hardly originate from properties of the catalyst (in both systems the aldehyde is bound to **1b**) but from those of the coordinating aldehyde. However, in the case of **2b** the partial positive charge induced by the electron withdrawing oxazaborolidinone could be resonance stabilized as shown in Figure 4. In the case of **2b** (resonance stabilization by **A** <-> **B** <-> **C**, Fig. 4) stabilization available through the O_{SO_2} and $C_{C=O}$ interaction is needed less than in the case of **2c** (resonance stabilization only by **A** <-> **B**, Fig. 4). Consequenly, the O_{SO_2} and $C_{C=O}$ distance can be longer in **2b** than in **2c**.

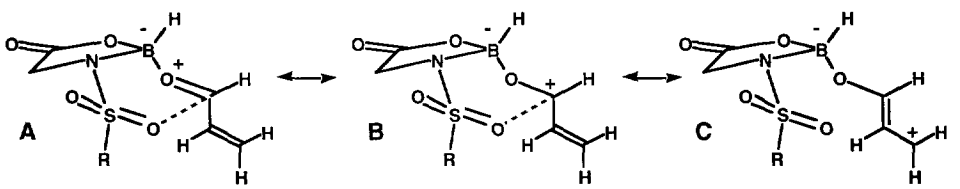


Figure 4. Resonance stabilization in aldehyde adducts of oxazaborolidines.

Natural Bond Orbital (NBO) analyses of 2a and 2b: Results of the NBO analyses of **2a** and **2b** are summarized in Table 2. The analyses (Table 2) imply that all of the bonds of the 6-membered chelate ring (as those of the oxazaborolidine ring) can be described as normal σ-bonds. Clear π-bonds can be recognized in the vinyl and 5-carbonyl groups (of the oxazaborolidinone ring) of both **2a** and **2b**. The highest occupied natural bonding orbital (HONBO-1; being not a part of the aromatic ring of **2a**) is related to the π-bond of the vinyl group in the case of both **2a** and **2b** (NBO energies -10.86 and -11.59 eV, Table 2). The HONBO-2 (being not a part of the aromatic ring of **2a**) can be located in the C=O π-bond of the oxazaborolidinone ring (NBO energies -14.12 and -14.29 eV, Table 2).

Results of the NBO analyses (Table 2) indicate also that the bond between $C_{C=O}$ of acrolein and the chelating oxygen O_{SO_2} weakens considerably (NBO energy increasing by 5.20 eV; Table 2) when the phenyl group of **2a** is replaced by hydrogen. While the $C_{C=O}$ - O_{SO_2} bond weakens, the adjacent $C_{C=O}$ - $O_{acrolein}$, S - $O_{chelating}$ bonds strengthen together with the $C_{C=O}$ - C_α and C_α - C_β bonds of the acrolein moiety (the corresponding NBO energies decrease by 2.31, 1.20, 1.25 and 1.71 eV, Table 2). The $C_{C=O}$ - O_{SO2} bond is (together with the B - O bonds) one of the most ionic bonds of **2b** (in the case of all these bonds more than 80 % of the bonding electrons originates from the oxygen). The $C_{C=O}$ - O_{SO_2} bond of **2a** (75.8 % of the bonding density from O_{SO_2} and 23.0 % from $C_{C=O}$) is, however, somewhat less ionic than that of **2b** (82.6 % of the bonding density from O_{SO_2} and 14.9 % from $C_{C=O}$). In addition to the features related to normal σ- and π-bonding, the NBO analysis of **2a** reveals that there are no significant (*i.e.* higher than 2.1 kJ mol^{-1}) bonding interactions between the vinyl and phenyl groups of **2a**. This result is consistent with the conclusions drawn on the basis of the energies of formation of **2a** and **2b** (E_C, Table 1); conformational changes related to the

formation of the chelate system simply force the vinyl and phenyl groups to form a stack type of arrangement in which, nevertheless, one face of the vinyl group is shielded efficiently by the phenyl ring.

Table 2. Energies of selected natural bond orbitals[a] of the chelates (**2a** and **2b**)[b] as determined on the basis of NBO[c] analysis.

The Bond	Type of bond	NBO-E[a] in **2a**	NBO-E[a] in **2b**	ΔE[a]	Type of bond	NBO-E[a] in **2a**	NBO-E[a] in **2b**	ΔE[a]
C5 - $O_{C=O}$	π	-14.12	-14.29	-0.16	π*	+5.71	+5.77	+0.05
C5 - $O_{5\text{-ring}}$	σ	-31.73	-31.86	-0.13	σ*	+18.53	+18.48	-0.05
B - $O_{5\text{-ring}}$	σ	-29.66	-30.29	-0.63	σ*	+16.68	+17.01	+0.33
B - N	σ	-23.32	-23.95	-0.63	σ*	+14.50	+14.64	+0.14
B - $O_{Acrolein}$	σ	-29.50	-29.20	+0.30	σ*	+16.52	+15.29	-1.22
C_{CO}-$O_{Acrolein}$	σ	-32.22	-34.53	-2.31	σ*	+17.71	+18.50	+0.79
N-S	σ	-30.59	-30.53	+0.05	σ*	+12.44	+12.03	-0.41
S-$O_{Chelating}$	σ	-32.38	-33.58	-1.20	σ*	+9.88	+11.27	+1.39
S-$O_{Non\text{-}chelating}$	σ	-35.84	-35.70	+0.13	σ*	+14.37	+14.20	-0.16
$C_{CO\text{-}Acrolein}$-$O_{Chelating}$	σ	-27.18	-21.99	+5.20	σ*	+8.63	+3.51	-5.12
$(C_{CO}\text{-}C_{\alpha})_{Acrolein}$	σ	-24.65	-25.91	-1.25	σ*	+18.67	+18.69	+0.03
$(C_{\alpha}\text{-}C_{\beta})_{Acrolein}$	π	-10.86	-11.59	-1.71	π*	+6.07	+5.80	-0.27

[a] Energies in electron volts. [b] Optimized with the DNP basis set using DMol. [c] Carried out at the RHF/6-31G** level.

On the basis of the inspection of charge distributions and hybridizations of C_{CO} of the acrolein moieties of **2a** and **2b** (discussed above) we concluded, that the reactivity of the vinyl system (towards electron rich molecules such as dienes) would increase with the decreasing amount of $C_{C=O}$ - O_{SO_2} bonding. This conclusion is supported also by the results of NBO analyses (Table 2). The NBO energy of the π*-orbital located to the C_a=C_b of **2a** decreases while the $C_{C=O}$ - O_{SO_2} interaction weakens [NBO of π* $(C_a\text{-}C_b)_{acrolein}$ of **2b** is 0.27 eV lower than that of **2a**, Table 2] in consequence of the replacement of the phenyl group (**2a** -> **2b**). In the case of **2b** the lowest natural unoccupied orbital (LNUO) can be clearly located in the $C_{C=O}$ - O_{SO_2} bond (NBO energy +3.51 eV, Table 2) whereas in the case of **2a** the LNUO locates on the 5-carbonyl group of the oxazaborolidinone moiety [NBO energy of π* (*C5* - O_{CO}) = +5.71 eV, Table 2]. These results indicate that nucleophiles encountering **2a** or **2b** could attach either to the carbonyl group of the oxazaborolidinone ring, to the C=C double bond of the vinyl group, or to the carbonyl carbon of the acrolein moiety. Which one of these sites would react, depends on the properties of the nucleophile as a Lewis base.

On the basis of the LNUO-1, LNUO-2 and LNUO-3 energies of **2a** (+5.71, +8.63 and +6.07 eV, Table 2) one could predict, that hard nucleophiles (*e.g.* hydride, some carbanions) could prefer an attach to the empty σ* ($C_{C=O}$ - O_{SO_2}) orbital (a reaction which immediately leads to the opening of the 6-membered ring of the chelate) whereas soft nucleophiles could favour interacting with the adjacent empty π* $(C_a\text{-}C_b)_{acrolein}$ or with the π* (*C5* - O_{CO}) orbital of the oxazaborolidinone ring. The known Diels - Alder reactions belong to the latter group. Only a few examples of the former reactions are known, but the addition of ketene silyl acetals to aldehydes reported (by Masamune *et al.*)[9] to be catalyzed by chiral *N*-sulphonylated oxazaborolidinones could belong to the former group. To summarize, the results of the NBO analyses confirm the proposals made on the

basis of the above comparisons of bonds lengths, charges and hybridizations and prove that the $C_{C=O}$ - O_{SO_2} bonds (of the chelate rings of **2a** and **2b**) are normal σ-bonds.

As *N*-sulphonylated oxazaborolidin-5-ones have been predicted (by Sartor *et al.*[1h]) to aggregate and the capability of oxazaborolidin-5-ones to bind Lewis acids such as borane has been lately demonstrated (on the basis of computational studies[2a] on isomeric borane adducts of **1b**), it could be interesting to compare the lone electron pairs of oxygen and nitrogen atoms of **2a** and **2b** in order to detect the location which another (activating) Lewis acid could most favorably interact with. Results of the NBO analysis of the lone pairs of **2a** and **2b** are summarized in Table 3.

Table 3. Energies of the natural bond orbitals[a] of the lone pairs of oxygen and nitrogen atoms of **2a** and **2b**[b] as determined on the basis of NBO[c] analysis.[d]

The atom	NBO-E[a] in **2a**	NBO-E[a] in **2b**	ΔE[a] [eV]
$O_{C=O\text{-}5\text{-ring}}$	-11.40	-11.46	-0.06
$O_{5\text{-ring}}$	-12.49	-12.57	-0.08
N	-12.65	-12.93	-0.27
$O_{Acrolein}$	-13.96	-14.37	-0.41
$O_{SO2\text{-Chelating}}$	-15.35	-15.02	+0.33
$O_{SO2\text{-Non-chelating}}$	-12.71	-12.95	-0.24

[a] Energies in electron volts. [b] Optimized with the DNP basis set using DMol. [c] Carried out at the RHF/6-31G** level. [d] The energy of the most Lewis basic pair of each atom is shown.

NBO analysis of the lone pairs (Table 3) reveals that the most Lewis basic location of **2a** and **2b** is one of the lone pairs of $O_{C=O}$ of the oxazaborolidin-5-one system (NBO energy -11.40 eV, Table 3) and that the weakening of the $C_{C=O}$ - O_{SO_2} bond does not change the relative basicity order of the pairs. Relative changes (ΔE, Table 3) of the values of **2a** and **2b** indicate that weakening of the $C_{C=O}$ - O_{SO_2} bond decreases the basicity of all of the lone pairs, except, not surprisingly, that of the chelating O_{SO_2} atom. The change of basicity of $O_{Acrolein}$ is larger than that of the others. This, however, indicates that coordination of a second Lewis acid to the lone pair of α,β-enal (*e.g.* coordination of a Lewis acid to the lone pair of the acrolein moiety of **2a**) could tighten the adjacent $C_{C=O}$ - O_{SO_2} bond of the related chelate. Further studies on the properties of aldehyde adducts of *N*-sulphonylated oxazaborolidin-5-ones are in progress.

CONCLUSIONS

Results of this study imply, that bidentate chelation of aldehydes to *N*-sulphonylated oxazaborolidinones would be energetically advantageous. The O_{SO_2} - $C_{C=O}$ interaction in the chelates can be predicted to play less important role in the case of (adducts of) aldehydes capable of delocalizing the positive charge (created in consequence of the coordination of the Lewis acidic oxazaborolidin-5-one to the Lewis basic lone pair of the aldehyde). Coordination of another Lewis acid to one of the lone pairs (particularly that of the aldehyde moiety of the chelate) could tighten the O_{SO_2} - $C_{C=O}$ interaction in the chelate.

The nature of π-stacking proposed to play a role in the asymmetric reactions catalyzed by **1** cannot be active; no attractive interactions between the stacking counterparts were found. The observed π-stacking could better originate from the topological constraints of the chelate system (*i.e.* the π-stack is not self-organizing but created in consequence of the other structural changes related to the formation of the 6-membered ring of the chelate system).

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