A Density Functional Study on the Coordination of Aldehydes to *N*-Sulfonyl 1,3,2-Oxazaborolidin-5-one

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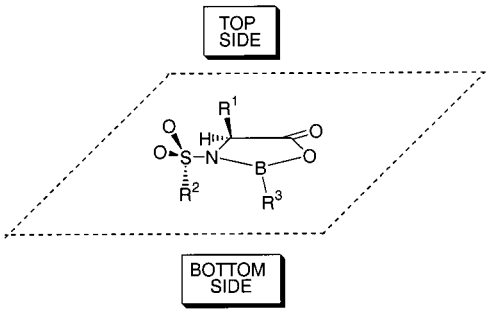
Abstract: The coordination of four aldehydes (formaldehyde, acetaldehyde, benzaldehyde, and *s-trans*-acrolein) to *N*-sulfonyl 1,3,2-oxazaborolidin-5-one has been studied by means of theoretical calculations. The effect of alkyl substituents on the ring has also been examined. Coordination can take place on each ring face, the energy minima presenting different types of interaction: hydrogen-bonds (S═O···H−C or B−O···H−C) or syn-periplanar H−B···O═C arrangements. In contrast with previous models, a preference for coordination on the top face has been found (by 2.0−2.3 kcal mol^{-1}). The largest interaction energies hold for complexation with benzaldehyde (∼7 kcal mol^{-1}). The configuration of the major products experimentally obtained in Diels−Alder and Mukaiyama-aldol reactions can be explained by means of two reaction models. Our results are consistent with available experimental data for enantiomeric excess. Thus, an enantiomeric excess of 99% is predicted for benzaldehyde reactions, in good agreement with the highest experimental values (98%). The only known case where the proposed models are not valid corresponds to reactions catalyzed by oxazaborolidinones bearing aromatic substituents, because of the stabilization of a structure presenting a B−O···H−C hydrogen-bond induced by the formation of a charge-transfer complex between the aromatic ring and the aldehyde.

Introduction

The use of chiral Lewis acids as catalysts of organic reactions has become one of the most effective methods of asymmetric synthesis.[1] In particular, a special interest has been paid to *N*-sulfonyl 1,3,2-oxazaborolidin-5-one (**1**) derivatives[2] (Scheme 1) because of the simplicity of their syntheses from α-amino acids as well as the high enantioselectivities induced. These catalysts have been mostly applied on Diels−Alder[3,4] and Mukaiyama-aldol reactions,[5] though good results have also been found for other processes.[6]

Because of the low Lewis acidity of oxazaborolidinones, only the most reactive substrates can be successfully used in the corresponding catalyzed reactions.[3] In particular, aldehydes are largely used in Mukaiyama-aldol reactions and Diels−Alder cycloadditions (conjugated enals, in the later case).

Scheme 1



1 R^1=H, R^2=H, R^3=H

Evidently, knowledge of the structure of the oxazaborolidinone−aldehyde complexes should be useful for a rational design of more efficient catalysts. Indeed, the aldehyde coordination can take place through either top or bottom heterocycle sides, according to Kiyooka's nomenclature[7] (Scheme 1). Since a relative rigidity of the donor−acceptor complex is necessary in order to explain satisfactorily the high enantioselectivities observed, a second interaction mechanism between the catalyst and the aldehyde should be present. Several interaction mechanisms have been proposed that include formation of hydrogen bonds with the aldehydic H-atom (S═O···H−C[8] or B−O···H−C[9]), H−B···O═C arrangements,[8a,10] and formation of a covalent

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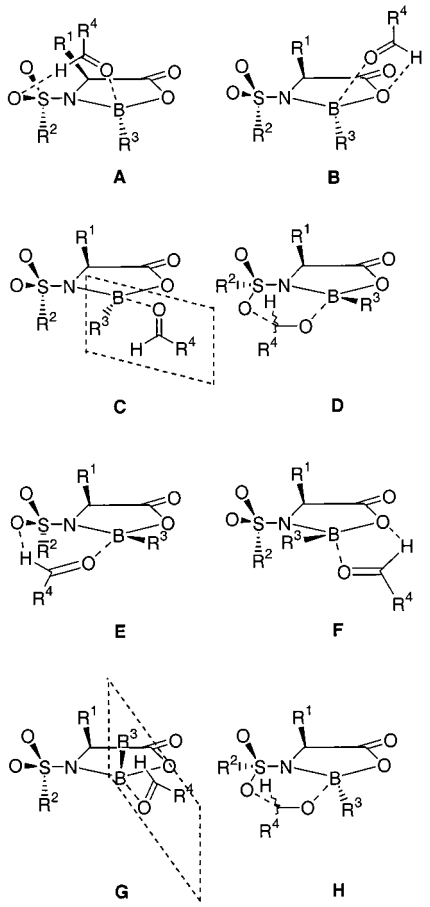

Figure 1. Possible anchoring ways for complexes between aldehydes and *N*-sulfonyl 1,3,2-oxazaborolidin-5-one (**1**).

bond between a sulfamide oxygen and the aldehydic carbon.[11] By combining the alternative coordination on both top and bottom sides and the four possible interaction mechanisms, a total of eight different anchoring ways can be considered (named as A−H in Figure 1).

Despite some mechanistic studies, the exact role of each possible anchoring mode is not well-known. Thus, a reaction model for some Diels−Alder cycloadditions catalyzed by certain aromatic oxazaborolidinones (R^1 = 3-indolyl methyl, 3-indolyl 1-ethyl; R^2 = p-Tol; R^3 = H) has been proposed by Corey et al., although the structural details described cannot offer a general validity inasmuch as the opposite facial selectivity is experimentally observed when aliphatic amino acid derivatives are considered as catalysts or when acrolein (instead of methacrolein) is used as dienophile.[12] On the other hand, some oxazaborolidinone-aldehyde complexes have been studied by means of MNDO[7] and AM1[5,13] methods, though some caution should be taken with the results obtained because of the poor performance of these semiempirical techniques on hydrogen bonds.[14] Finally, studies based on high level calculations have also been published, though no systematic search of energy minima was apparently done.[8,11,15]

In this work, we present a density functional study on the role of the different anchoring ways in the complexation of **1** to different aldehydes R^4CHO: formaldehyde (R^4 = H, **2**), acetaldehyde (R^4 = Me, **3**), benzaldehyde (R^4 = Ph, **4**), and acrolein (R^4 = CH_2=CH-, **5**). The role of substituents has been examined in a few cases, namely R^3= CH_3 for complexes with **3** and R^1 = ^{i}Pr for complexes with **4**. An *S* configuration has been assumed for **1**-derivatives throughout this work (this determines the relative orientation of R^1 and R^2 as well as the definition of top and bottom sides according to Scheme 1). Evidently, the interpretation of the results described here can be applied to oxazaborolidinones derived from *R*-amino acids by considering the specular images of the structures involved.

Methods

Gaussian94 package[16] was used throughout this work. All calculations were carried out using the density functional theory (DFT) approach by means of the B3LYP hybrid functional.[17] This choice was based on two main reasons. First, recent investigations have demonstrated that the DFT-B3LYP method leads to excellent results for geometries and energies.[18] On the other hand, this approach is substantially less computer demanding than other methods (for instance, MP2), having a comparable accuracy. Therefore, considering the size and the number of systems studied, MP2 appeared to be less suitable than DFT-B3LYP (a typical geometry optimization for a complex took one week of CPU time in an IBM RISC 3BT workstation).

Full optimization of the structures of **1**, aldehydes, and the corresponding **1**−aldehyde complexes were achieved by means of the 6-31G** basis set, whereas single point energy calculations were carried out by using the 6-311+G(2d,2p) basis set, because of the good performance of this contraction pattern on intramolecular hydrogen bonds.[19] Unless otherwise stated, only energies computed by means of this triple-ζ basis set will be considered for discussion. Neither ZPE nor BSSE corrections were regarded in this work. Only the most stable conformer (*s-trans* conformation)[20] was considered for **5** in both isolated and **1**-coordinated forms.

Since aldehydes behave as electron-deficient compounds in aldol reactions and Diels−Alder reactions are usually controlled by HO-MO_{diene}−$LUMO_{dienophile}$ interactions, the comparison of LUMO energies for the complex structures obtained may be an indication of their relative reactivity, at least to some extent. Note that the energy of the LUMO has been found to be in all complexes studied substantially lower than the energy of the next nonoccupied molecular orbital, typically by about 0.1 hartrees. Thus, these values will be given for each complex using the triple-ζ basis set results.

Results and Discussion

1 and Aldehydes. The geometries obtained for **1** and the aldehydes studied are shown in Figure 2. The structure of **1** presents a nearly planar ring, whereas the oxygen atoms of

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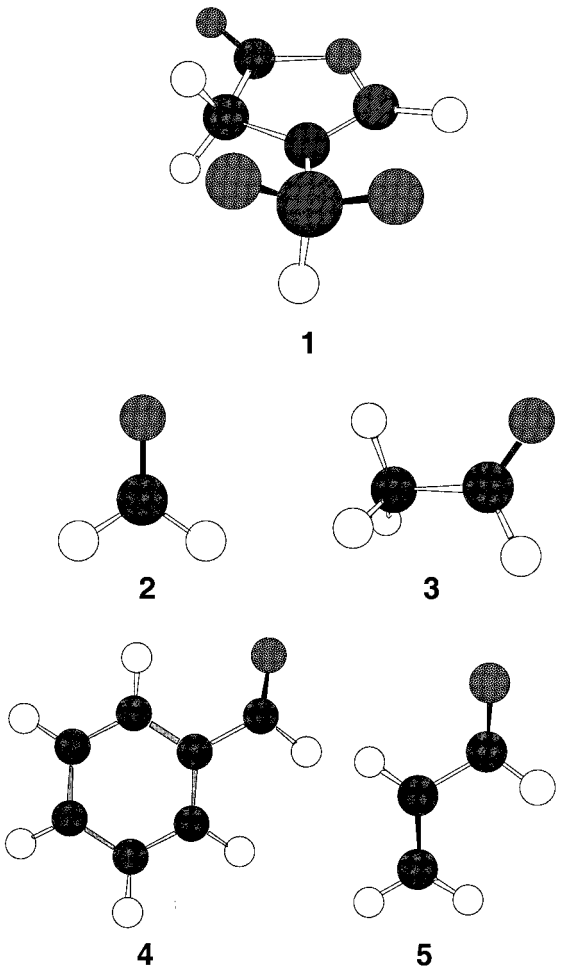

Figure 2. Structures of **1** and aldehydes.

sulfonyl group are close to the heterocycle plane and the hydrogen−sulfur bond is approximately perpendicular to the plane defined by the nitrogen-bonded atoms. This orientation of the *S*-substituent agrees with theoretical results on *N*-methyl methanesulfonamide[21] and experimental data on several arylsulfonamides.[22] This geometrical arrangement is also found in RHF/3-21G calculations on a substituted oxazaborolidinone ($R^1 = {}^{i}Pr$, $R^2 = Ph$, $R^3 = H$),[23] indicating that the replacement of such substituents by hydrogen atoms in the model system does not lead to substantial changes. As expected, the geometries obtained for aldehydes show planar frameworks in all cases.

1−2 Complexes. After a comprehensive investigation of the energy hypersurface of the **1−2** complex, only the energy minima corresponding to the anchoring ways A, C, and G could be localized. The corresponding geometries and binding energies are summarized in Figure 3 and Table 1, respectively. In contrast with previous results obtained at different theoretical levels (MP2/6-31G* [8b] and JMW/DNP[15] calculations as well as computations[8b,11] at ab initio RHF level by means of several basis sets) no energy minimum has been predicted for H complexes.

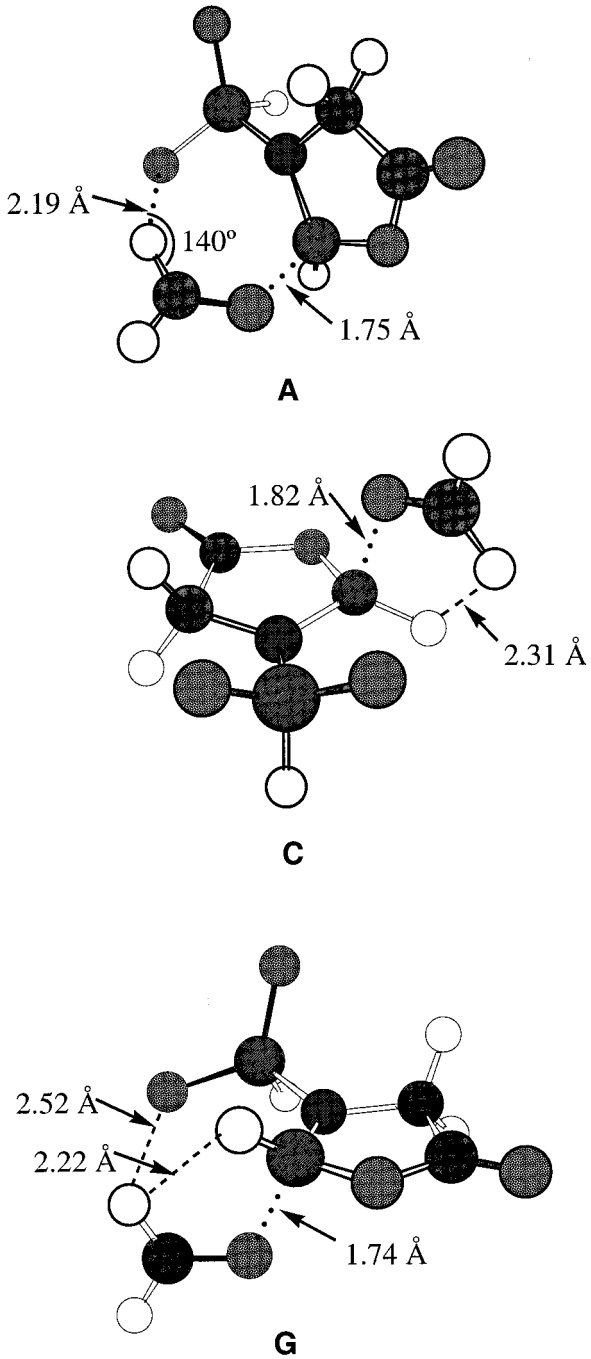

Figure 3. Structures of **1−2** complexes.

Table 1. Binding Energies (kcal mol^{-1}) of the 1−2 Complexes after B3LYP/6-31G** and B3LYP/6-311+G(2d,2p) Calculations

structure	B3LYP/6-31G**	B3LYP/6-311+G(2d,2p)[a]
A	−4.6	−0.9
C	−5.2	−2.0
G	−3.0	+0.3

[a] B3LYP/6-31G** geometries.

Preference for structure H has been reported in the literature through RHF[8b,11] or DFT-LDA[15] (local density approximation) calculations. It may be attributed to an artifact of these methods which is probably related to an overestimation of the net charge on the sulfamide oxygen atoms. Indeed, poor results are obtained for S=O bond-containing molecules with such techniques (exaggeration of dipole moments in RHF calculations,[24] over-

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estimation of the S−O length by LDA methods[25]). MP2/6-31G* calculations also predict a minimum energy for structure H, though this form is substantially less stable than G (by 4.7 kcal mol^{-1}).[8b] The latter computations are certainly more reliable than either RHF or LDA. Differences with respect to our values may be ascribed in part to basis set effects due to the lack of polarization function on H-atoms. MP2/6-31G** calculations[8a] have also been done but they were mainly devoted to the study of the of B−O···H−C and H−B···O═C interactions in complex **1**−**2** showing that no-minima exist for the former arrangement at that computational level. It is interesting to note that such a conclusion is reached here too, although we show below that structures of type B or F may indeed be obtained for other aldehydes.

Structural data for the complexes considered can be used to interpret the origin of their relative energies (see Figure 3). For structure A, the geometrical features of the S═O···H−C interaction agree with the existence of a hydrogen bond. Thus, the C−H···O angle (140°) agrees with typical experimental values found for this type of bonds (110−180°),[26] whereas the short oxygen−hydrogen distance (2.19 Å) indicates a relatively strong interaction.[26] Previous theoretical studies have shown that S═O···H−C interactions can lead to significant stabilizations.[27]

For structures C and G, approximately planar dispositions are found for the atom connections H−B···O═C−H in such a way that the hydrogen atoms involved are placed at distances of 2.31 Å (structure C) and 2.22 Å (structure G). The existence of form G had been predicted by MP2/6-31G* calculations, although its stability had been explained in terms of a S═O···H−C hydrogen bond.[8] However, we think that this interaction cannot be present in G since the computed O···H distance is rather large (e.g., 2.52 Å for the MP2/6-31G* geometry[8] and 2.54 Å for the B3LYP/6-31G** calculation).

The triple-ζ single point calculations (see Table 1) lead to binding energies which are substantially smaller than those derived using the double-ζ basis set (note that form G has now a positive value). This result agrees with theoretical computations for other formaldehyde-Lewis acid complexes showing that the increase of the flexibility of the basis set leads to a decrease of the binding energy calculated.[28] Because of the magnitude reduction of the basis set superposition error by increasing the basis set flexibility, the binding energy decrease could be due in part to such an effect.

As shown in Table 1, relative energies predict a slight preference for structure C which is 1.1 kcal mol^{-1} below A and 2.3 kcal mol^{-1} below G. Thus, these results indicate predilection for coordination on the top face. Such a preference has been attributed to a directing effect of the R^2SO_2 group.[10] Curiously, the small size of the *S*-substituent considered in this model (R^2 = H) shows that this effect presents a noticeable nonsteric component. This result can be considered as a new example of diastereofacial selectivity induced by stereoelectronic effects.[29]

Table 2. Binding Energies (kcal mol^{-1}) of the 1−3 Complexes after B3LYP/6-31G** and B3LYP/6-311+G(2d,2p) Calculations

structure	B3LYP/6-31G**	B3LYP/6-311+G(2d,2p)[a]
A	−7.9	−4.2
B	−5.2	−2.2
C	−8.7	−5.2
G	−6.4	−2.9

[a] B3LYP/6-31G** geometries.

The LUMO energies for A and C structures are, respectively, −0.132 and −0.119 hartrees. Therefore, these values suggest a larger reactivity for complex A.

1−3 Complexes. The investigation of the potential energy hypersurface of the **1**−**3** complex allowed to localize four different anchoring ways (corresponding to structures A, B, C, and G), shown in Figure 4, whereas the corresponding binding energies are gathered in Table 2.

Energy values show that the complex formation is exothermic for all four anchoring ways. When analogous structures are compared, one can observe that complexes of **3** are ∼3 kcal mol^{-1} more stable than those corresponding to **2**, in agreement with the greater Lewis basicity of the former.[30] A preference for coordination to the top face can be noticed, that on the bottom side being disfavored by 2.3 kcal mol^{-1}. As found for **1**−**2** complexes, the most favorable anchoring way corresponds to form C. Structure A energy is 1 kcal mol^{-1} higher, and the other structures are less stable than C by more than 2 kcal mol^{-1}. Interestingly, the preference for structure C had already been predicted by MNDO calculations for a related system (R^1 = ^{i}Pr, R^2 = Ph, R^3 = H, R^4 = ^{i}Pr).[7]

These results can be used to model the behavior of aliphatic aldehydes on Mukaiyama-aldol reactions catalyzed by oxazaborolidinones. Thus, we propose two different reaction models (named as I and II in Figure 5), which are based, respectively, on structures A and C. We assume in both cases steric hindrance of R^1 forces R^2 to be placed on the opposite ring side (shown as top and bottom face, respectively), as proposed by Helmchen and co-workers.[10] Furthermore, the origin of diastereoselectivity is attributed to the steric repulsion in the transition state between the incoming reactant and different groups of the catalyst (R^1 for model I and the sulfamide oxygen atoms for model II). As one can remark, both reaction models predict the attack on the Si face of the aldehyde. Although calculations suggest a preference for model II, the low energy difference involved does not allow ruling out a significant role for model I.

The experimental results on the configuration of the major products obtained in Mukaiyama-aldol reactions show a complex pattern (Scheme 2). The stereochemistries of the compounds obtained in a number of these reactions by using aliphatic aldehydes agree with the attack to the Si face of the aldehyde,[31−36]

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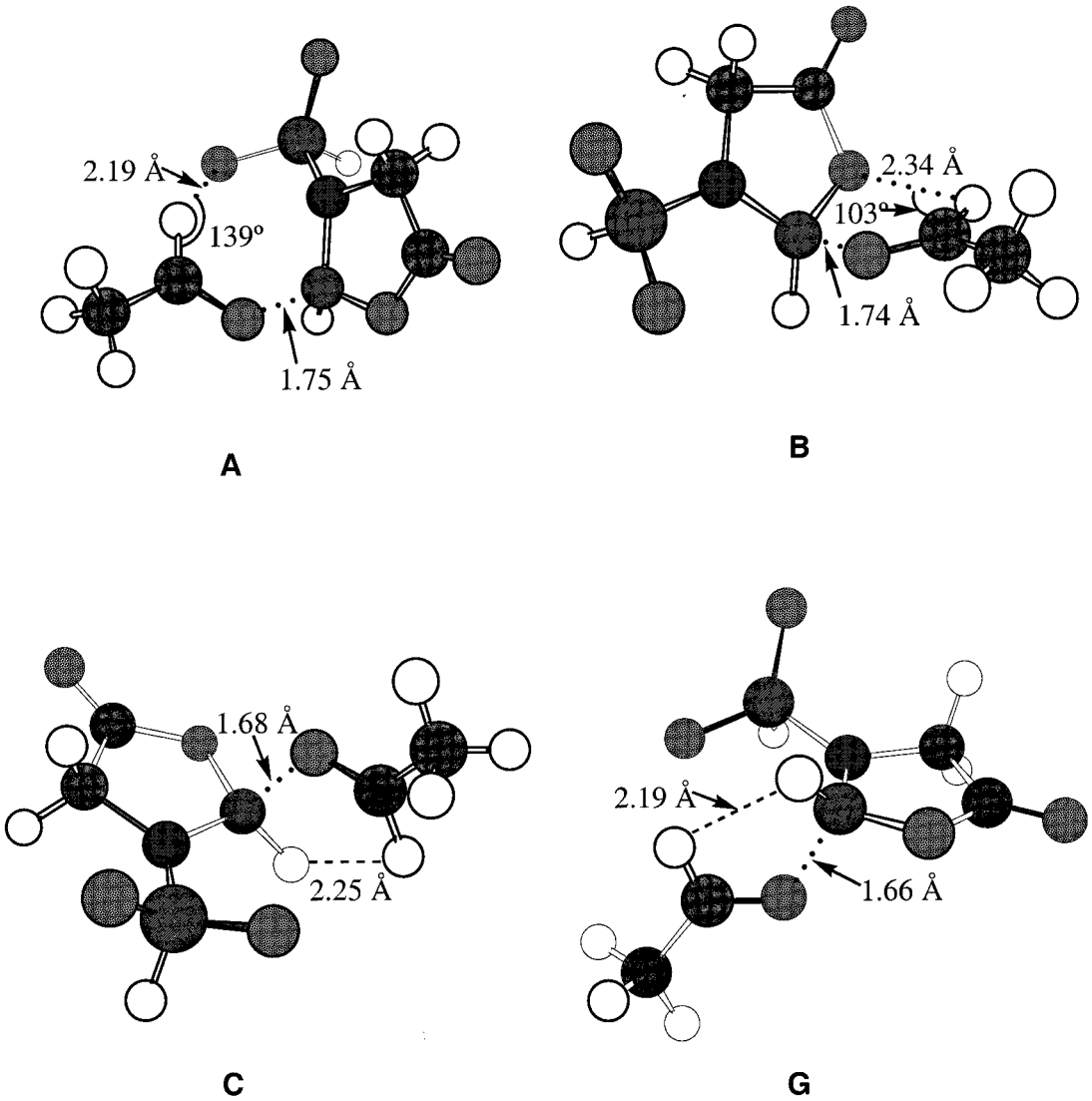

Figure 4. Structures of **1**−**3** complexes.

as predicted by our models. Although a model based on structure F also allows to predict the same major product,[32] such an anchoring way is disfavored by our calculations since it does not correspond to an energy minimum. On the other hand, experimental data on reactions carried out by means of catalysts derived from (*S*)-tryptophan show the opposite facial selectivity.[37] This discrepancy can be attributed to the preference for a reaction mechanism based on structure B induced by the formation of charge-transfer complexes between the indole ring and the aldehyde, as proposed by Corey.[12] The interaction energy necessary to reverse the relative stabilities of structures B and C (more than 3 kcal mol^{-1}) is consistent with typical binding energies of charge-transfer complexes (6−10 kcal mol^{-1}).[38]

Although oxazaborolidinones bearing B−H bonds (i.e., R^3 = H) are usually preferred in Mukaiyama-aldol reactions because of their greater reactivity,[5] the analogous *B*-alkylated heterocycles have been used in some occasions.[33] The possible modification of the relative energies for the different anchoring ways in these catalysts has been analyzed by means of B3LYP/6-311+G(2d,2p)//B3LYP/6-31G** calculations for the complexes formed between **3** and the *B*-methyl derivative of **1**. Only A, C, and G structures were computed. As for **1**−**3**, our results indicate a preference for structure C, that is more stable than A by 0.6 kcal mol^{-1}. A in turn is more stable than G by 1.9 kcal mol^{-1}. One may note that the methyl-group effect is to decrease the C−A energy difference and to increase the A−G one, which can be attributed to the steric repulsion between the methyl group bound to boron and the aldehyde hydrogen in C and G structures.

The energy of the LUMO predicted for A and C complexes are respectively: −0.115 and −0.106 hartrees in the case of nonmethylated derivatives, and −0.102 and −0.097 hartrees for the methylated ones. Note that the complexation energies are slightly greater for the methylated derivatives (−0.106 vs −0.097 hartrees for C, for instance).

1−**4 Complexes.** In addition to the four structures localized for the **1**−**3** complex, form F has also been found for the **1**−**4** one, all five structures being shown in Figure 6. It can be observed that the formation of a B−O···H−C hydrogen bond as well as the syn-periplanar conformation of the H−B···O═C connection allow the coordination on both sides of **1**, whereas the formation of a S═O···H−C hydrogen bond is only possible for the association on the top side. The lack of an energy

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(38) (a) Willner, I.; Eichen, Y.; Doron, A.; Marx, S. *Isr. J. Chem.* **1992**, *32*, 53−59. (b) Stynes, D. V. *Inorg. Chem.* **1994**, *33*, 5022−5029. (c) Odani, A.; Sekiguchi, T.; Okada, H.; Ishiguro, S.-i.; Yamauchi, O. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2093-2102. (d) Klemm, L. H.; Solomon, W. C.; Tamiz, A. P. *J. Org. Chem.* **1998**, *63*, 6503−6510.

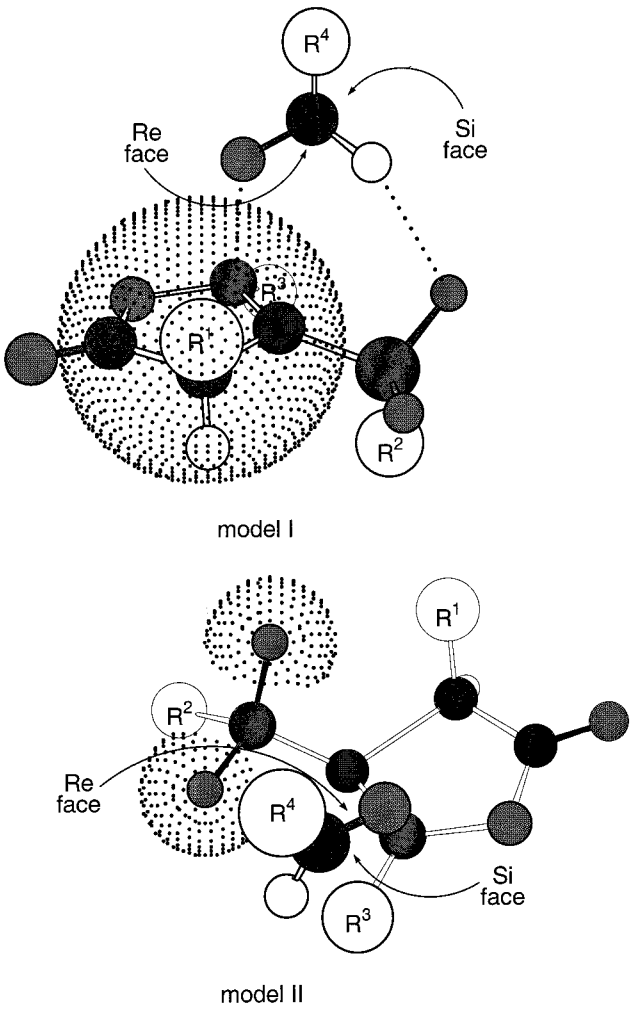
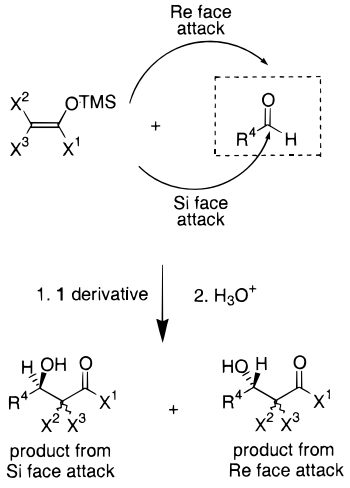


Figure 5. Reaction models I and II.

Scheme 2



minimum for E can be attributed to the geometrical requirements necessary for the formation of such a hydrogen bond (the corresponding hydrogen and oxygen atoms being too far because of the orientation of the S═O bonds toward the top face).

The energies calculated for **1**−**4** complexes, gathered in Table 3, indicate that binding interactions present larger absolute values than those corresponding to **1**−**3** structures, in agreement with a previous theoretical study showing a larger BF_3 affinity of **4** relative to that of **3**.[39] This result can be attributed to the greater ability of phenyl group to delocalize the positive charge induced by the complex formation. Relative energies show a preference for structure C, although form A presents a value only 0.3 kcal mol^{-1} higher. Instead, all other structures correspond to significantly higher energies (at least 2 kcal mol^{-1}). The preference for structure C contrasts with AM1 results for a related system (R^1 = ^{i}Pr, R^2 = p-Tol, R^3 = H, R^4 = Ph), indicating a global minimum for A.[5,13]

Table 3. Binding Energies (kcal mol^{-1}) of the 1−4 Complexes after B3LYP/6-31G** and B3LYP/6-311+G(2d,2p) Calculations

structure	B3LYP/6-31G**	B3LYP/6-311+G(2d,2p)[a]
A	−10.3	−6.7
B	−7.8	−4.9
C	−10.0	−7.0
F	−6.5	−3.4
G	−8.1	−4.9

[a] B3LYP/6-31G** geometries.

The results obtained for the **1**−**4** complex indicate again a preference in ∼2 kcal mol^{-1} for the coordination the top face, in disagreement with the reaction models for related systems proposed by Corey (R^1 = ^{i}Pr, R^2 = p-Tol, R^3 = H, R^4 = Ph)[40] and Kiyooka (R^1 = ^{i}Pr, R^2 = *p*-$NO_2C_6H_4$, R^3 = H, R^4 = Ph).[34]

The experimental results on the major products obtained from the Mukaiyama-aldol reactions of benzaldehyde show the same behavior pattern observed for aliphatic aldehydes. For this reason, the application of reaction models I and II allows to predict correctly the major products obtained in the Mukaiyama-aldol reactions of benzaldehyde catalyzed by oxazaborolidinones bearing an aliphatic R^1 group,[35] whereas tryptophan-derived oxazaborolidinones induce the opposite configuration.[37] This later result can be explained by means of the particular stability of structure B because of the charge transfer between the indole ring and the aldehyde.[12]

An upper limit for the chiral induction achieved by oxazaborolidinones in benzaldehyde reactions can be roughly estimated by assuming a total shielding for all structures regarded (A, C, and F forms leading to the opposite enantiomer than B and G). For a temperature of −78 °C (typical condition for Mukaiyama-aldol reactions), an enantiomeric excess of 99% is predicted, in good agreement with the highest experimental values found (98% ee).[33,36,41]

It could be argued that the presence of a substituent on C4 (R^1) could affect the relative stability of structures A and C because of the possibility for different steric interactions with the aldehyde group. However, B3LYP/6-311+G(2d,2p)//B3LYP/6-31G** calculations carried out for the complexes formed between **4** and the valine-derivated oxazaborolidinone (R^1 = ^{i}Pr) have shown again a slight preference for structure A (form C being 0.3 kcal mol^{-1} higher) for the most stable conformation of isopropyl group (which has been previously described[15] for a noncoordinated catalyst).

The values of LUMO energies for forms A (−0.136 hartrees) and C (−0.131 hartrees) indicate, as before, a greater reactivity for structure A in aldol reactions, although the difference is no much smaller.

1−**5 Complexes.** All five structures found for the **1**−**4** complex have also been localized for the **1**−**5** one and are shown in Figure 7, whereas the corresponding energies are gathered in Table 4. Relative energies show a preference for structure

(39) Gung, B. W. *Tetrahedron Lett.* **1991**, *32*, 2867−2870.
(40) Corey, E. J.; Barnes-Seeman, D.; Lee, T. W. *Tetrahedron Lett.* **1997**, *38*, 4351−4354.
(41) Kiyooka, S.-i.; Kaneko, Y.; Komura, M.; Matsuo, H.; Nakano, M. *J. Org. Chem.* **1991**, *56*, 2276−2278.

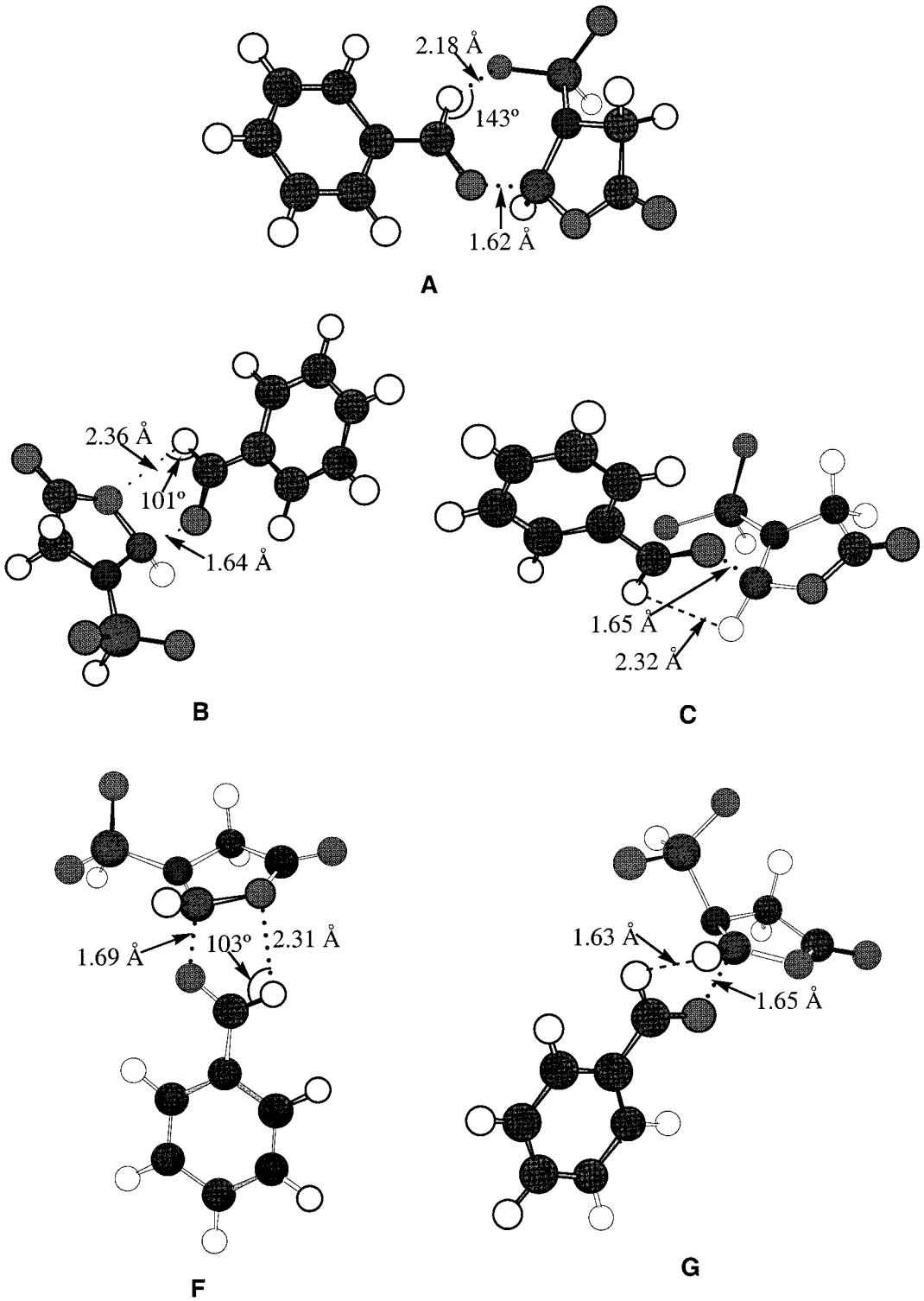


Figure 6. Structures of **1**−**4** complexes.

Table 4. Binding Energies (kcal mol^{-1}) of the 1−5 Complexes after B3LYP/6-31G** and B3LYP/6-311+G(2d,2p) Calculations

structure	B3LYP/6-31G**	B3LYP/6-311+G(2d,2p)[a]
A	−9.5	−5.5
B	−6.5	−3.4
C	−9.3	−5.8
F	−5.6	−2.4
G	−7.4	−3.8

[a] B3LYP/6-31G** geometries.

C, although the difference with form A is only 0.3 kcal mol^{-1}, the other structures being disfavored by at least 2 kcal mol^{-1}. The binding energies for **1**−**5** complexes present intermediate values between those obtained for **1**−**3** and **1**−**4** structures.

The possibility of conformational equilibrium in α,β-unsaturated aldehydes produces a higher degree of complexity on the system studied because of the opposite topicity of both conformers. Thus, although the common aldehydes (such as acrolein[20] or methacrolein)[42] show a preference for the *s-trans*

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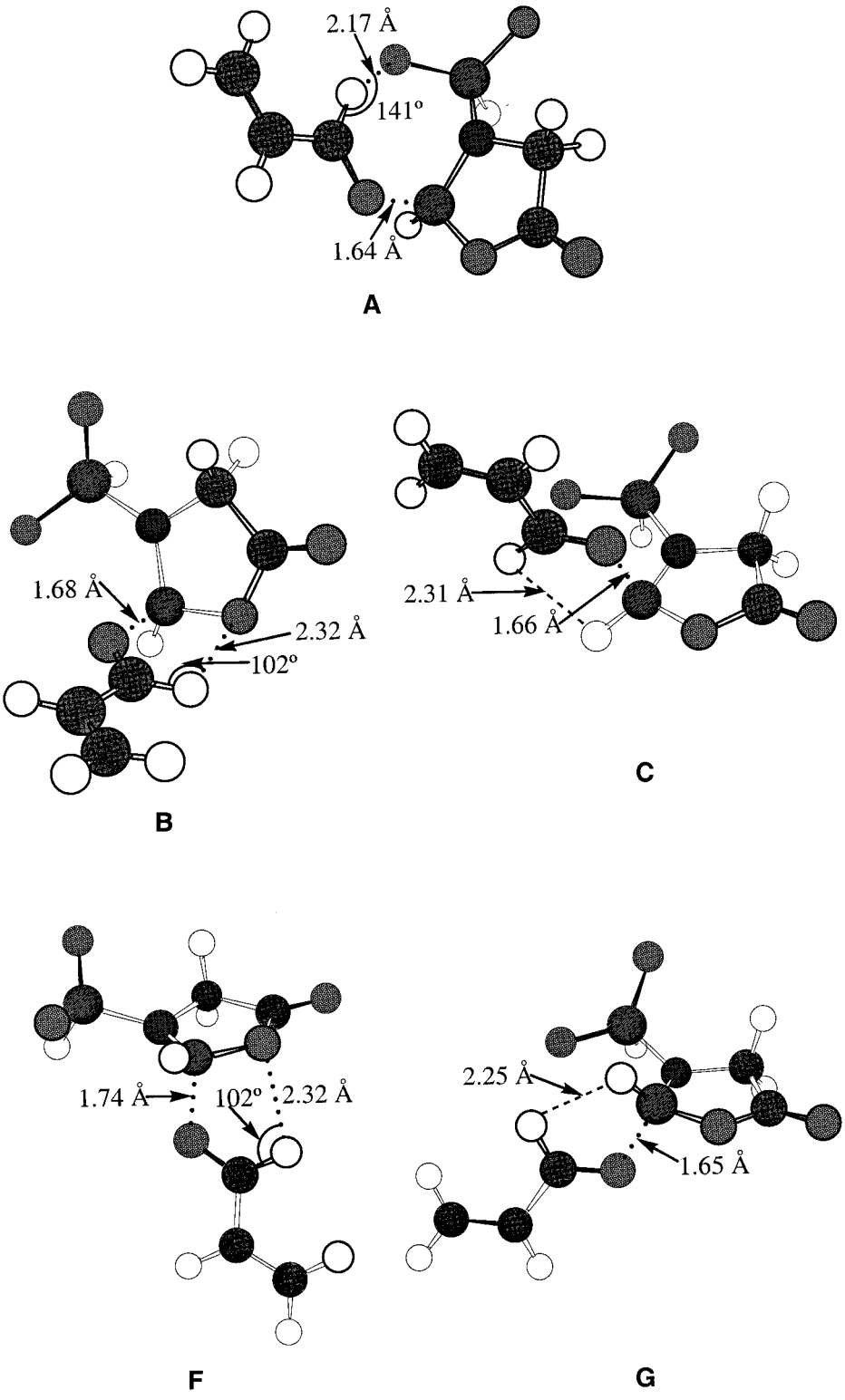


Figure 7. Structures of **1**−**5** complexes.

conformation, these reactants participate in the Diels−Alder reactions mainly through the *s-cis* conformer.[43]

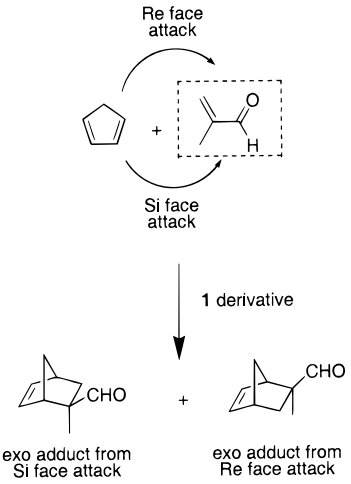
Experimental data on the configuration of the major adducts from Diels−Alder reactions show again a complex pattern of behavior. Thus, the cyclopentadiene + methacrolein reaction catalyzed by an oxazaborolidinone derived from (*S*)-tryptophan yields the exo *S*-cycloadduct with high enantiomeric purity,[12] whereas the analogous reaction induced by the corresponding (*S*)-valine derivative leads mainly to the exo *R*-adduct (Scheme 3).[44]

If *s-cis* conformation is assumed for the enal in the transition state, one can deduce that adduct configuration is determined by the face attacked by the diene. Thus, the configuration of the major adducts obtained in Diels−Alder reactions catalyzed by oxazaborolidinones derived from aliphatic amino acids agrees

(43) (a) García, J. I.; Martínez-Merino, V.; Mayoral, J. A.; Salvatella, L. *J. Am. Chem. Soc.* **1998**, *120*, 2415−2420. (b) Salvatella, L.; Mokrane, A.; Cartier, A.; Ruiz-López, M. F. *J. Org. Chem.* **1998**, *63*, 4664−4670.

(44) Sartor, D.; Saffrich, J.; Helmchen, G.; Richards, C. J.; Lambert, H. *Tetrahedron: Asymmetry* **1991**, *2*, 639−642.

Scheme 3



with that predicted by our models,[44,45] whereas the opposite configuration is found when charge-transfer interactions between R^1 and the aldehyde are possible.[12,37,46]

Again, a lower LUMO energy is found for form A (−0.144 hartrees) in comparison with C (−0.139 hartrees), indicating a greater reactivity for the former structure.

Conclusions

Among the eight anchoring ways considered for the coordination between **1** and four different aldehydes, only three to five energy minima could be localized, depending on the carbonyl compound considered. Despite the different number of possible conformational minima, some trends have been detected for all **1**−aldehyde complexes studied.

No structure presenting a covalent bond between a sulfamide oxygen and the aldehydic carbon could be localized. Precedents of such structures described in the literature must be attributed to artifactual stabilizations inherent to the methods used, arising from the exaggeration of the charge excess on sulfamide oxygen atoms.

Only some types of interaction favor the occurrence of conformational minima: hydrogen bond formation (both S═O···H−C and B−O···H−C are possible) and syn-periplanar H−B···O═C arrangements. Due to geometrical requirements, the occurrence of structures presenting a S═O···H−C hydrogen bond when the aldehyde is coordinated on the bottom side of **1** is not allowed.

Preference for coordination on the top side of the ring has been found, this fact being due to the stereoelectronic effects induced by the orientation of the sulfonyl group. In all cases, two structures (A and C) are favored, the latter presenting a slightly lower energy, although the analysis of LUMO energies indicates a greater reactivity for the former. All other structures present higher energies (in at least 2 kcal mol^{-1}). Two reaction models (corresponding to structures A and C) have been proposed. In general, these models allow correctly predicting experimental results for the configuration of the major products in Mukaiyama-aldol and Diels−Alder reactions (by assuming in the latter an *s-cis* conformation for the conjugated enal). The only exception corresponds to the case of oxazaborolidinones bearing aromatic substituents. This fact may be explained by stabilization of structure B due to the formation of charge-transfer interactions between the aromatic rings and the aldehyde.

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Supporting Information Available: Tables of total energies for all the structures described in this work (ASCII and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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