Origin of Conformational Restriction in Complexes of Formyl Compounds with Boron Lewis Acids and Their Related Systems

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The conformational preference of the $RCHO\cdots BX_3$ complexes (R = H, CH_3, $CH_2{=}CH$, F, OH, NH_2, NMe_2; X = H, F, Cl) were studied. It was found that all of the $RCHO\cdots BH_3$ systems prefer the eclipsed conformation. Most, but not all, of the $RCHO\cdots BF_3$ systems prefer the eclipsed conformation. Most, but not all, of the $RCHO\cdots BCl_3$ systems prefer the staggered conformation. Three driving forces are responsible for the conformational preference of $RCHO\cdots BX_3$. The hyperconjugation interactions, including the σ^*(B−X)−Lp(O), σ^*(B−X)−π(C═O), π^*(C═O)−Lp(X), π^*(C═O)−σ(B−X), σ^*(formyl C−H)−Lp(X), and σ^*(C−R)−Lp(X) interactions, favor the eclipsed conformation. The steric effect favors the staggered conformation. Furthermore, the geometry relaxation effect favors the eclipsed conformation. A balance among the hyperconjugation interactions, steric effect, and geometry relaxation effect is present in both the eclipsed and staggered conformations. If the hyperconjugation interactions and the geometry relaxation effect dominate, as in $RCHO\cdots BH_3$ and most $RCHO\cdots BF_3$, the eclipsed conformation is preferred. If the steric effect dominates, as in most $RCHO\cdots BCl_3$, the staggered conformation is preferred. In addition, all of the $RCH{=}NH\cdots BX_3$ (R = H, CH_3, $CH{=}CH_2$; X = H, F, Cl) complexes are found to favor the eclipsed conformation because of the presence of the N−H bond. All of the $RCH{=}O\cdots AlX_3$ (R = H, CH_3, $CH{=}CH_2$, MeO, NH_2, Me_2N; X = H, F, Cl) complexes favor the eclipsed conformation because the O⋯Al distances are very long in these complexes, causing undersized steric effects.

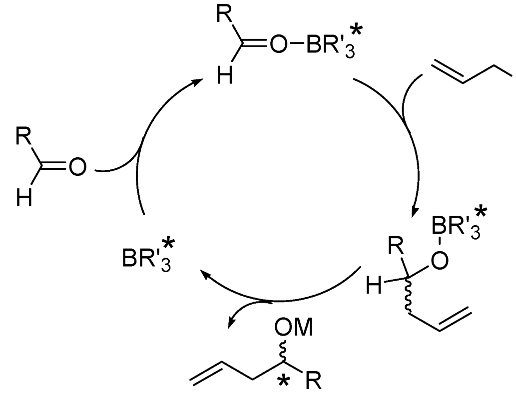
1. Introduction

Recently, there has been increasing interest in asymmetric organic reactions involving chiral Lewis acids, in which the chiral Lewis acids serve as both activators and the stereocontrolling agents.[1] One good example of chiral Lewis-acid-promoted enantioselective reactions is Yamamoto's aldehyde allylation reaction (see Scheme 1).[2] A key step in this reaction is the formation of the carbonyl−boron complex, which enhances the electrophilicity of the carbonyl carbon. Consequently, the stereochemistry of the allylation step is controlled by the chirality of the borane moiety. Another famous example is Corey's borane reduction reaction catalyzed by chiral oxazaborolidines.[3] Again, formation of the carbonyl−boron complex is the key step for chiral induction.

An interesting and important question associated with chiral Lewis acid catalysis is predicting the stereochemical course of the reaction. The answer to this question is obviously of enormous value for the design of novel and more efficient chiral Lewis acid catalysts. Before the answer can be obtained, it is crucial to understand the structure of the Lewis acid−substrate complex because the conformational preference of this complex ultimately determines the stereochemical course of the reaction. Unfortunately, little structural information on chiral Lewis acid−substrate complexes is currently available. The origins of the conformational preferences of many Lewis acid−substrate complexes are also poorly understood.

In 1986, Reetz et al. obtained X-ray structures of aldehyde−BF_3 complexes.[4] They found that one of the fluorine atoms in BF_3 eclipsed the formyl hydrogen (Scheme 2). This finding was in agreement with the early theoretical studies on aldehyde−BF_3 complexes using the HF/3-21G method.[5] It was proposed from these studies that the eclipsed orientation of fluoride was caused by a generalized anomeric effect in which electrons from the nonbonding lone pair on the aldehyde oxygen interacted with the antibonding orbital of the eclipsed B−F bond (Chart 1a).

SCHEME 1



SCHEME 2

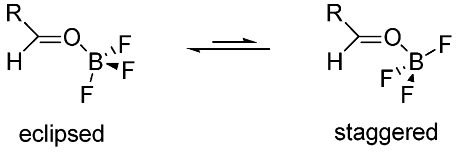


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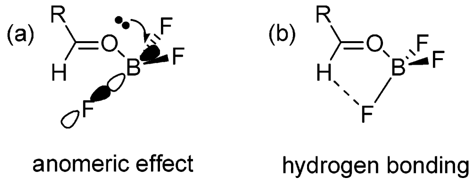
CHART 1



anomeric effect hydrogen bonding

In 1997, Corey et al. obtained crystal structures of complexes of dimethylformamide (DMF) with BF_3, BCl_3, BBr_3, and BI_3.[6] It was found that the BF_3 complex preferred the eclipsed structure but the BCl_3, BBr_3, and BI_3 complexes did not. It was proposed that C−H$\cdots$F hydrogen bonding could be the driving force for the eclipsed conformation (Chart 1b). This explanation appeared to be consistent with the observation that the BCl_3, BBr_3, and BI_3 complexes did not prefer the eclipsed conformation, because the C−H$\cdots$Cl, C−H$\cdots$Br, and C−H$\cdots$I interactions were usually much weaker than the C−H$\cdots$F interaction.

Corey et al. also pointed out[6] that the anomeric effect should decrease in the order B−I > B−Br > B−Cl > B−F because the energy of the antibonding orbital increases in the order B−I < B−Br < B−Cl < B−F [indeed, the energy of the σ^* antibonding orbitals for B−X in BX_3 increases in the order B−I (0.22889 au) < B−Br (0.30547 au) < B−Cl (0.38679 au) < B−F (0.77015 au) as calculated by us using the HF/6-311G* method]. Because the experimental finding was that the BF_3 complex preferred the eclipsed conformation whereas the BCl_3, BBr_3, and BI_3 complexes did not, the anomeric effect theory seemed to be incapable of explaining the experimental results.

Compared to the anomeric effect theory, Corey's C−H$\cdots$heteroatom hydrogen-bonding theory appears to be more successful in explaining the conformational preference of aldehydes complexed with Lewis acids. Corey and co-workers have also successfully utilized this theory as an organizational tool for formulating transition structure assemblies for many enantioselective reactions.[6] Despite these successes, a very recent computational study by Roush et al. showed that the contribution from the formyl H-bond to the conformation preference of boron complexes was negligible, if present at all.[7] Thus, the true origins of the conformational preferences of aldehyde−Lewis acid complexes still await further investigation.

In the present study, we performed some detailed investigations of the conformational restriction in the complexes between formyl compounds and boron Lewis acids. We analyzed the contributions of various hyperconjugation interactions to the conformational preference. We also investigated the importance of the steric effect and C−H$\cdots$X hydrogen bonding in the conformational preference. In addition, we studied a number of related systems for which the conformational preferences had not been reported. By comparing these related systems to the aldehyde−boron complexes, we tried to verify that the conclusions drawn for the aldehyde−boron systems were generally applicable.

2. Method

All calculations were performed using the Gaussian 03 suite of programs[8] and NBO 5.0 programs.[9] The structures of the compounds were optimized using the MP2/6-311++G(2d,p) method with varying restrictions as mentioned below. The energy of each optimized conformer was calculated using the MP2/6-311++G(2d,p) method. Higher-level theoretical methods such as CCSD/6-311++G(d,p) and MP2/6-311++G(3df,2p) were also used in some cases to confirm the conformational preferences predicted by the MP2/6-311++G(2d,p) method. The HF/6-311++G(2d,p) method was utilized for all of the NBO analyses. We chose the HF method, instead of the MP2 method, for the NBO analysis because currently the NBO method cannot provide the hypercojugation energies estimated by the second-order perturbation approach (see ref 17 for further explanation). Previous studies also showed that the HF NBO analysis is at least qualitatively valid.[17]

It is worthwhile to note that the NBO program was used to evaluate the hyperconjugation interactions and steric effects. The NBO analysis transforms the canonical delocalized Hartree−Fock MOs into localized orbitals that are closely tied to chemical bonding concepts.[10] This process involves sequential transformation of nonorthogonal atomic orbitals to the sets of "natural" atomic orbitals, hybrid orbitals, and bond orbitals (NBOs). Each of these localized basis sets is complete and orthonormal. Filled NBOs describe the hypothetical, strictly localized Lewis structure.

The interactions between filled and vacant orbitals represent the deviation of the molecule from the Lewis structure and can be used as a measure of delocalization.[10] This method gives energies of hyperconjugation interactions both by deletion of the off-diagonal Fock matrix elements between the interacting orbitals and by the second-order perturbation approach

$$E(2) = q_i \frac{< i|F|j >^2}{\epsilon_j - \epsilon_i} = q_i \frac{{F_{ij}}^2}{\epsilon_j - \epsilon_i} \qquad (1)$$

where $< i|F|j >$, or F_{ij}, is the Fock matrix element between the ith and jth NB orbitals, ϵ_i and ϵ_j are the energies of ith and jth NBOs, and q_i is the population of the donor orbital.

Exchange repulsion arises as a consequence of the Pauli-principle requirement that the N-electron wave function be antisymmetric with respect to interchange of pairs of electrons.[11] In effect, wave function antisymmetry provides the quantum pressure that resists crowding too many electrons into the same spatial region. The principal energetic consequence of antisymmetrization is implicit orbital orthogonalization. One can exclude the exchange repulsion in a system by calculating the energetic cost of orthogonalization of nonorthogonal NBOs.

3. Results and Discussion

3.1. $CH_3CHO\cdots BF_3$ vs $CH_3CHO\cdots BCl_3$. *3.1.1. Fully Optimized Structures.* Figure 1 shows the optimized structures [MP2/6-311++G(2d,p)] for CH_3CHO, eclipsed and staggered $CH_3CHO\cdots BF_3$, and eclipsed and staggered $CH_3CHO\cdots BCl_3$. The eclipsed $CH_3CHO\cdots BF_3$ structure is more stable than the staggered $CH_3CHO\cdots BF_3$ structure by 1.58 kJ/mol. Staggered $CH_3CHO\cdots BCl_3$ is more stable than eclipsed $CH_3CHO\cdots BCl_3$ by 1.96 kJ/mol. These conformational preferences are consistent with the previous experimental and theoretical results.[4,5] Furthermore, the MP2/6-311++G(2d,p) results are in qualitative agreement with higher-level calculation results. At the CCSD/6-311++G(d,p) level, eclipsed $CH_3CHO\cdots BF_3$ is more stable than staggered $CH_3CHO\cdots BF_3$ by 1.00 kJ/mol. Staggered $CH_3CHO\cdots BCl_3$ is more stable than eclipsed $CH_3CHO\cdots BCl_3$ by 1.29 kJ/mol.

There are some interesting issues regarding the structures of the above species. First, the acetaldehyde moiety always prefers the eclipsed conformation over the bisected conformation. π^*(C=O)−π(CH_3) and π(C=O)−π^*(CH_3) hyperconjugation interactions are known to be important for this conformational preference.[12] We recently demonstrated that the σ(C_{methyl}−H)−σ^*($C_{carbonyl}$−H) hyperconjugation interaction is also essential for the same conformational preference.[13]

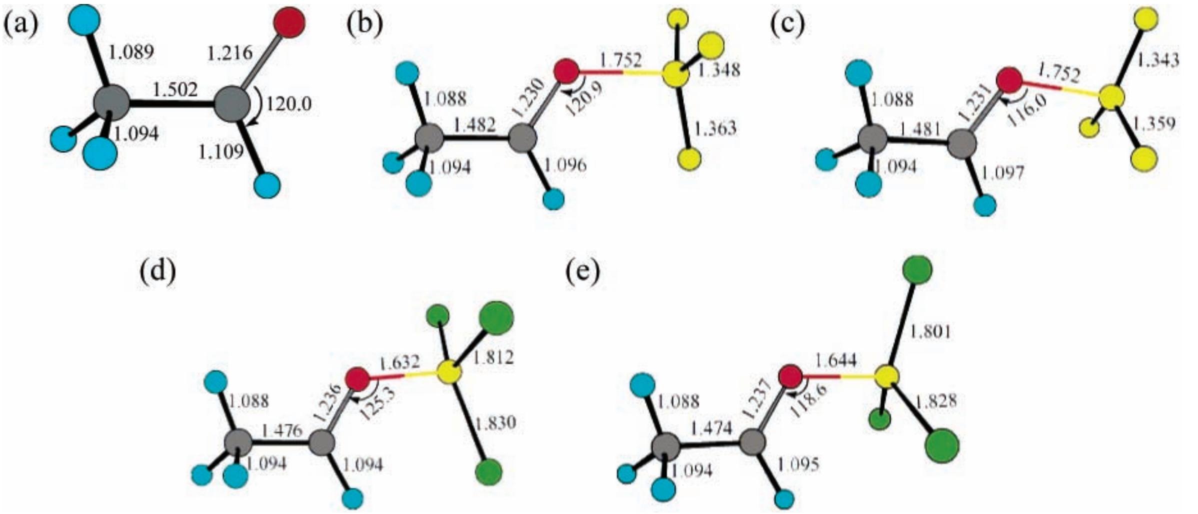


Figure 1. MP2/6-311++G(2d,p)-optimized structures for (a) CH_3CHO, (b) eclipsed $CH_3CHO\cdots BF_3$, (c) staggered $CH_3CHO\cdots BF_3$, (d) eclipsed $CH_3CHO\cdots BCl_3$, and (e) staggered $CH_3CHO\cdots BCl_3$.

Second, from free acetaldehyde to the acetaldehyde complexes, the C−H bond in the CHO moiety is always shortened. The eclipsed $CH_3CHO\cdots BX_3$ structure has a shorter C−H bond in the CHO moiety than the staggered $CH_3CHO\cdots BX_3$ structure. This seems to be contradictory to Corey's $C-H\cdots X$ hydrogen-bonding theory, because ordinary hydrogen bonds should exhibit C−H elongation (i.e., red shift).[14] It is worth noting that blue-shifted (i.e., shortened) hydrogen bonds also do exist.[15] Therefore, the $C-H\cdots X$ interaction in $CH_3CHO\cdots BX_3$ systems is possibly a blue-shifted hydrogen-bonding interaction.

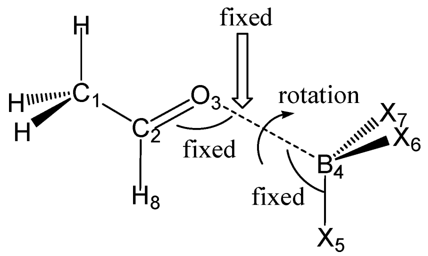
Finally, the C−O−B angle is significantly smaller in the staggered conformation (116.0° for $CH_3CHO\cdots BF_3$ and 118.6° for $CH_3CHO\cdots BCl_3$) than in the eclipsed conformation (120.9° for $CH_3CHO\cdots BF_3$ and 125.3° for $CH_3CHO\cdots BCl_3$). The eclipsed conformation has a larger C−O−B angle to minimize the steric repulsion between the H and X atoms in the same plane. The staggered conformation has a smaller C−O−B angle to bring the aldehyde and BX_3 moieties closer to each other, thereby maximizing the hyperconjugation interactions.

3.1.2. Rigidified Models. It is clear from the above analysis that the eclipsed and staggered $CH_3CHO\cdots BX_3$ complexes differ not only in conformation, but also in bond lengths and bond angles. The difference in bond lengths and angles can significantly change the hyperconjugation interactions and steric repulsions involved in a system. Therefore, when we compare the hyperconjugation and steric effects in the fully optimized systems, we need pay attention not only to the conformational difference, but also to the change of bond lengths and angles. This brings about unnecessary complications.

Herein, we wish to study only those alternations of hyperconjugation and steric effects caused by conformational changes, but not those caused by changes of any bond length or angle. Thus, we need to develop more well-defined systems in which all of the bond lengths and angles are fixed. Ideally, the systems should also have a certain symmetry with respect to the rotational axis. At this point we construct rigidified systems as shown in Table 1.

Our rigidified systems were constructed using the fully optimized CH_3CHO molecule (see Figure 1a) and rigidified BX_3. The C2−O3−B4 angle was fixed at 120°. The O_3−B4 distance, B4−X5 bond length, and three O3−B4−X angles were also fixed using the parameters shown in Table 1. These parameters were chosen to equal the average values in the fully optimized systems so that the rigidified systems were sufficiently close to the fully optimized ones. The whole rigidified $CH_3CHO\cdots BX_3$ complex was allowed to change only its C2−O3−B4−X5 dihedral angle. It is worth noting that the (O3, B4, X5, X6, X7) subsystem has C_{3v} symmetry, which is ideal for the study of conformational effects on hyperconjugation interactions and steric repulsions.

TABLE 1. Rigidified $CH_3CHO\cdots BX_3$ Complexes[a]



parameter	$CH_3CHO\cdots BF_3$	$CH_3CHO\cdots BCl_3$
O3−B4 (Å)	1.752	1.640
B4-X (Å)	1.350	1.815
C2−O3−B4 (deg)	120.0	120.0
O3−B4−X (deg)	101.0	104.0

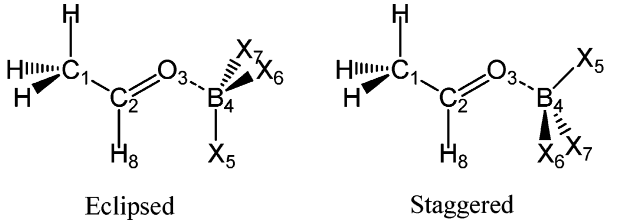
[a] The structure of the CH_3CHO moiety is the same as the fully optimized free acetaldehyde (see Figure 1a for details).

Single-point energy calculations suggest that the rigidified eclipsed $CH_3CHO\cdots BF_3$ is more stable than the rigidified staggered $CH_3CHO\cdots BF_3$ by 0.03 kJ/mol. (More precisely, we should say that these two conformers are nearly equal in energy because the energy difference is so tiny.) The rigidified staggered $CH_3CHO\cdots BCl_3$ structure is more stable than the rigidified eclipsed $CH_3CHO\cdots BCl_3$ structure by 19.77 kJ/mol. These conformational preferences are the same as those for the fully optimized systems.

3.1.3. Hyperconjugation Interactions. Using the rigidified models, we can study the effect of hyperconjugation interactions on the conformational preference without worrying about the difference in bond lengths and angles. We need focus only on the hyperconjugation interactions that can change the conformational preference, which always involve one bonding orbital on one side of the complex and one antibonding orbital on the other. These hyperconjugation interactions were calculated using eq 1 (see Table 2).

From Table 2, it is clear that the hyperconjugation interaction between the σ^*(B−X) antibond and the lone-pair electrons of

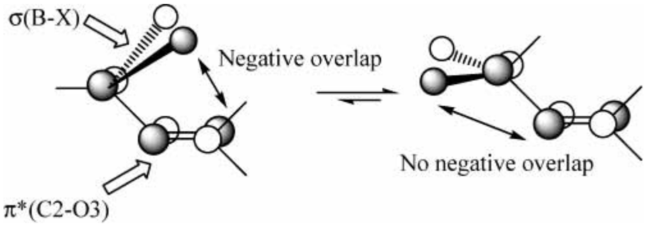
TABLE 2. Strength of Each Hyperconjugation Interaction in the Rigidified $CH_3CHO\cdots BX_3$ Complexes (kJ/mol)



hyperconjugation interaction	$CH_3CHO\cdots BF_3$		$CH_3CHO\cdots BCl_3$	
	eclipsed	staggered	eclipsed	staggered
σ*(B−X)−Lp(O3)[a]	7.74	7.11	15.31	14.18
σ*(B−X)−π(C2−O3)	10.29	9.96	23.85	21.59
σ*(B−X)−σ(C2−O3)	0.00	0.50	0.00	0.00
σ*(B−X)−σ(C2−H8)	0.00	0.00	1.51	3.84
total for σ*(B−X)	19.74	17.57	40.67	39.61
$\Delta\Delta E$ for σ*(B−X)[b]	+2.17		+1.06	
π*(C2−O3)−Lp(X)	3.47	0.00	7.11	3.60
π*(C2−O3)−σ(B−X)	0.92	0.00	5.44	1.51
total for π*(C2−O3)	4.39	0.00	12.55	5.11
$\Delta\Delta E$ for π*(C2−O3)	+4.39		+7.44	
σ*(C2−O3)−Lp(X)	2.55	2.59	0.63	0.82
σ*(C2−O3)−σ(B−X)	2.64	2.71	4.39	5.56
total for σ*(C2−O3)	5.19	5.30	5.02	6.38
$\Delta\Delta E$ for σ*(C2−O3)	−0.11		−1.36	
σ*(C2−H8)−Lp(X)	2.13	0.00	34.02	0.00
σ*(C2−H8)−σ(B−X)	0.00	0.00	1.42	0.54
total for σ*(C2−H8)	2.13	0.00	35.44	0.54
$\Delta\Delta E$ for σ*(C2−H8)	+2.13		+34.90	
σ*(C1−C2)−Lp(X)	3.10	0.00	5.48	1.17
σ*(C1−C2)−σ(B−X)	0.67	0.00	1.72	0.00
total for σ*(C1−C2)	3.77	0.00	7.20	1.17
$\Delta\Delta E$ for σ*(C1−C2)	+3.77		+6.03	
total $\Delta\Delta E$	+12.35		+48.07	

[a] Lp means lone-pair electrons. [b] $\Delta\Delta E$ = hyperconjugation energy (eclipsed) − hyperconjugation energy (staggered).

SCHEME 3



O3 is stronger in the eclipsed conformation than in the staggered conformation. This observation is consistent with the anomeric effect theory (see Chart 1a).[5] As demonstrated before,[17] the antiperiplanar arrangement is better than the synperiplanar arrangement for $\sigma \leftrightarrow \sigma^*$ and lone pair $\leftrightarrow \sigma^*$-type hyperconjugation because of the better orbital overlap in the antiperiplanar arrangement.

Table 2 also show that the σ*(B−X)−π(C2−O3), π*(C2−O3)−Lp(X), and π*(C2−O3)−σ(B−X) hyperconjugation interactions are stronger in the eclipsed conformation than in the staggered conformation. The reason for this observation is possibly the negative overlap effect proposed by Hehre et al.,[18] which can exist only in the staggered conformation (see Scheme 3). Further NBO analysis supports this explanation. As seen in Figure 2, the blue part of the σ(B−F) bonding orbital is far from the yellow part of the π*(C−O) antibond in the eclipsed conformation. The opposite is true in the staggered conformation, which gives negative overlap.

The σ*(C2−H8)−Lp(X) hyperconjugation interactions also favor the eclipsed conformation. This is consistent with Corey's hydrogen-bonding theory.[6] As shown in Figure 3, two of the three pairs of lone pair electrons can interact with the σ*(C2−H8) antibond in the eclipsed conformation. On the other hand, there is no orbital overlap between σ*(C2−H8) and Lp(X) in the staggered conformation. Interestingly, we find that the σ*(C2−H8)−Lp(Cl) interaction (34.02 kJ/mol) is much stronger than the σ*(C2−H8)−Lp(F) interaction (2.13 kJ/mol). However, this does not mean that the C−H···Cl interaction is stronger than the C−H···F interaction because the Cl atom should cause much stronger steric repulsion than F.

In addition to σ*(C2−H8), the σ*(C1−C2) antibond can also interact with Lp(X) (see Figure 4). For geometric reasons similar to those shown in Figure 3, σ*(C1−C2)−Lp(X) hyperconjugation favors the eclipsed conformation over the staggered conformation. Moreover, the σ*(C2−H8) and σ*(C1−C2) antibonds can interact with the σ(B−X) orbitals. These interactions favor the eclipsed conformation for the same reason as the σ*(C2−H8)−Lp(X) and σ*(C1−C2)−Lp(X) interactions. It should be noted that the σ*(C2−H8)−σ(B−X) and σ*(C1−C2)−σ(B−X) interactions are much weaker than the σ*(C2−H8)−Lp(X) and σ*(C1−C2)−Lp(X) interactions because the energy of σ(B−X) is much lower than that of Lp(X).

The above results suggest that the hyperconjugation interactions involving the σ*(B−X), π*(C2−O3), σ*(C2−H8), and σ*(C1−C2) should all favor the eclipsed conformation in the rigidified $CH_3CHO\cdots BX_3$ complexes. There is only one antibond that favors the staggered conformation, which is σ*(C2−C3). It prefers to the antiperiplanar arrangement when interacting with σ(B−X) or Lp(X).[19] Nonetheless, because the energy of σ*(C2−C3) is much higher than that of π*(C2−C3), neither the σ*(C2−O3)−σ(B−X) nor the σ*(C2−O3)−Lp(X) interaction is significant for the conformational preference of the whole system (see Table 2 for the $\Delta\Delta E$ values).

To summarize, the hyperconjugation interactions favor the eclipsed conformation. Six types of hyperconjugation interactions are the most important for the conformation preference, including σ*(B−X)−Lp(O3), σ*(B−X)−π(C2−O3), π*(C2−O3)−Lp(X), π*(C2−O3)−σ(B−X), σ*(C2−H8)−Lp(X), and σ*(C1−C2)−Lp(X). Because the bonding orbitals of BCl_3 are higher in energy than those of BF_3 while the antibonding orbitals of BCl_3 are lower in energy than those of BF_3, these hyperconjugation interactions are usually stronger in $CH_3CHO\cdots BCl_3$ than in $CH_3CHO\cdots BF_3$. The total $\Delta\Delta E$ value for the hyperconjugation interaction energy between eclipsed and staggered $CH_3CHO\cdots BF_3$ is +12.35 kJ/mol. The total $\Delta\Delta E$ value for $CH_3CHO\cdots BCl_3$ is +48.07 kJ/mol.

3.1.4. Steric Effects. The steric exchange repulsions in rigidified $CH_3CHO\cdots BX_3$ systems can be calculated as the energetic cost of orthogonalization of nonorthogonal NBOs.[20] For $CH_3CHO\cdots BF_3$, the total steric exchange energy is calculated to be 611.12 kJ/mol for the rigidified eclipsed conformation and 599.45 kJ/mol for the rigidified staggered conformation. For $CH_3CHO\cdots BCl_3$, the total steric exchange energy is calculated to be 680.05 kJ/mol for the rigidified eclipsed conformation and 616.38 kJ/mol for the rigidified staggered conformation. Thus, the eclipsed conformation has a larger steric repulsion than the staggered conformation. It is also clear that the Cl atom gives a larger steric repulsion than the F atom in the eclipsed conformation.

3.1.5. Relaxation Effects. The rigidified eclipsed $CH_3CHO\cdots BF_3$ conformation is more stable than the rigidified staggered $CH_3CHO\cdots BF_3$ conformation by 0.03 kJ/mol, whereas

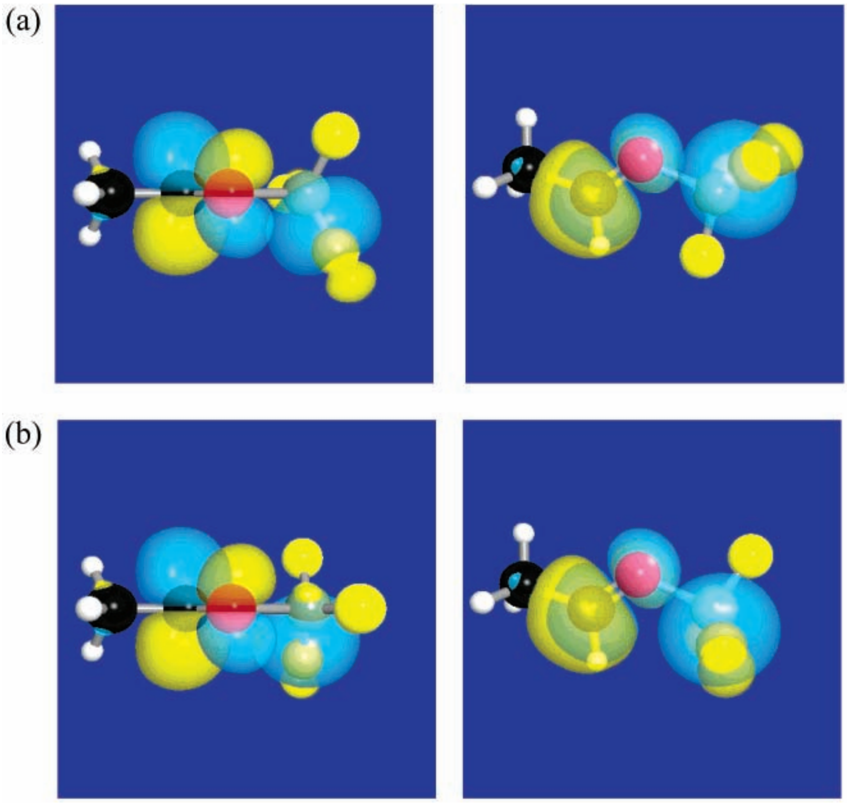


Figure 2. Orbital overlap between σ(B−F) and π*(C−O) in eclipsed and staggered $CH_3CHO\cdots BF_3$.

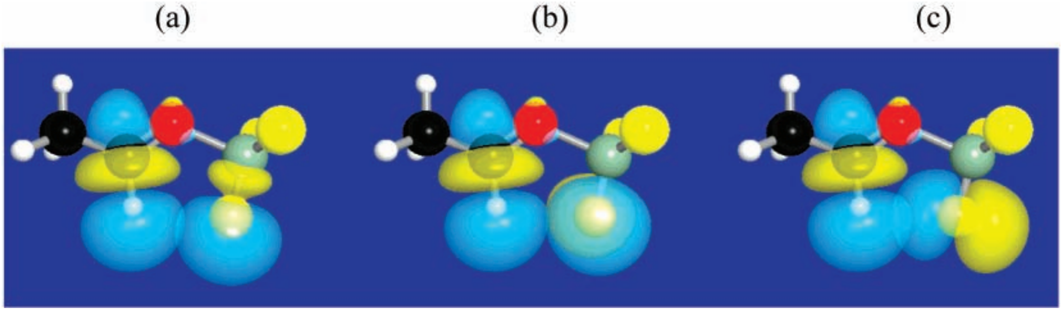


Figure 3. σ*(C2−H8)−Lp(X) interactions in eclipsed $CH_3CHO\cdots BF_3$.

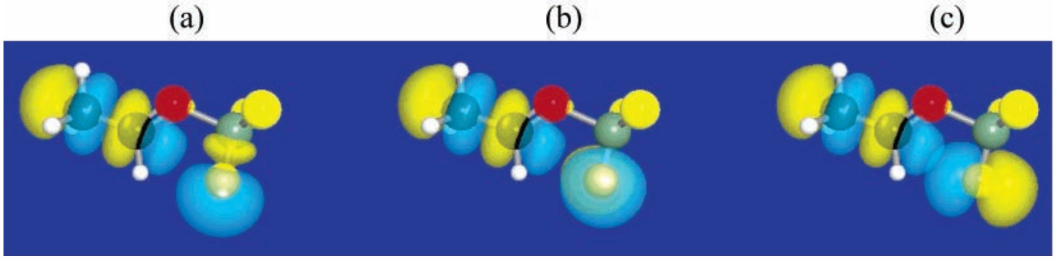


Figure 4. σ*(C1−C2)−Lp(X) interactions in eclipsed $CH_3CHO\cdots BF_3$.

the fully optimized eclipsed $CH_3CHO\cdots BF_3$ conformation is more stable than the fully optimized staggered $CH_3CHO\cdots BF_3$ conformation by 1.58 kJ/mol. The reason for this should be the geometry relaxation effect, whose purpose is to reach the highest stability either by enhancing the hyperconjugation interactions or by decreasing the steric exchange repulsions. For $CH_3CHO\cdots BF_3$, it is clear that a stronger relaxation effect occurs in the eclipsed conformation. Thus, the preference for the eclipsed conformation is enhanced by the relaxation effect.

For $CH_3CHO\cdots BCl_3$, a stronger geometry relaxation effect also occurs in the eclipsed conformation. This should weaken the preference for the staggered conformation. Indeed, although the rigidified staggered $CH_3CHO\cdots BCl_3$ conformation is more stable than the rigidified eclipsed $CH_3CHO\cdots BCl_3$ conformation by 19.77 kJ/mol, the fully optimized staggered $CH_3CHO\cdots BCl_3$ conformation is more stable than the fully optimized eclipsed $CH_3CHO\cdots BCl_3$ conformation by only 1.96 kJ/mol.

3.1.6. Summary for $CH_3CHO\cdots BF_3$ vs $CH_3CHO\cdots BCl_3$. Three effects have been discussed for the conformational preferences of the $CH_3CHO\cdots BF_3$ and $CH_3CHO\cdots BCl_3$ systems. The hyperconjugation effect and the geometry relaxation effect favor the eclipsed conformation, whereas the steric repulsion effect favors the staggered conformation. For $CH_3CHO\cdots BF_3$ the steric repulsion effect is not large, and therefore, the eclipsed conformation is the optimal. For $CH_3CHO\cdots BCl_3$, the steric repulsion is so large that the staggered conformation is the most favorable.

The anomeric theory[5] is clearly not complete for the conformational preferences of the $CH_3CHO\cdots BX_3$ systems. Although σ*(B−X)−Lp(O3) hyperconjugation does contribute to the preference of the eclipsed conformation, its importance is not as great as those of the π-type hyperconjugations [i.e., σ*(B−X)−π(C2−O3), π*(C2−O3)−Lp(X), and π*(C2−O3)−σ(B−X)] and the σ*(C2−H8)−Lp(X) and σ*(C1−C2)−Lp(X) hyperconjugations (see Table 2).

Corey's C−H···X hydrogen-bonding theory[6] is consistent with the σ*(C2−H8)−Lp(X) hyperconjugation effect. This hyperconjugation effect is truly important for the preference of the eclipsed conformation. Nevertheless, the importance of other hyperconjugations should not be ignored. In particular, the σ*(C1−C2)−Lp(X) and π*(C2−O3)−Lp(X) hyperconjugations strongly favor the eclipsed conformation.

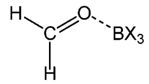
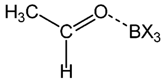
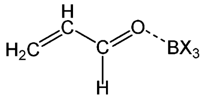
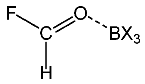
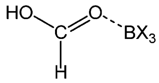
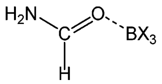
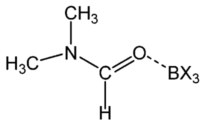
At this point, we need to provide some explanation for the contraction of the C2−H8 bond in the $CH_3CHO\cdots BX_3$ complexes because this contraction appears inconsistent with the C−H···X hydrogen-bonding theory. We find that the driving force for the C2−H8 contraction is the weakening of the σ*(C2−H8)−Lp(O3) hyperconjugation in aldehyde−BX_3 complexation. For free CH_3CHO, the energy of the σ*(C2−H8)−Lp(O3) hyperconjugation is 95.16 kJ/mol. In the $CH_3CHO\cdots BF_3$ complex, the energy of the σ*(C2−H8)−Lp(O3) hyperconjugation is 37.03 (eclipsed) or 35.03 (staggered) kJ/mol. In the $CH_3CHO\cdots BCl_3$ complex, the energy of the σ*(C2−H8)−Lp(O3) hyperconjugation is 45.84 (eclipsed) or 44.04 (staggered) kJ/mol. The reason for the weakening of the σ*(C2−H8)−Lp(O3) hyperconjugation is the charge transfer from Lp(O3) to the B−X antibond. This lowers the energy of Lp(O3) and, consequently, weakens the σ*(C2−H8)−Lp(O3) hyperconjugation. Therefore, the C−H···X hydrogen bonding is real, and the blue shift is also legitimate. Because of the particular mechanism for the blue shift that has not been noticed before, the C−H···X hydrogen bond in the $CH_3CHO\cdots BX_3$ systems actually represents a novel type of blue-shifted hydrogen bond.[22]

3.2. Related Systems. *3.2.1. R−CHO···BX_3.* We have explained the conformational preferences of the $CH_3CHO\cdots BF_3$ and $CH_3CHO\cdots BCl_3$ systems. At this point, we wish to determine whether the same theory can be applied to the conformational preferences of related systems. Thus, we calculated the energy differences between the eclipsed and staggered conformers of the BX_3 complexes with various substituted formyl compounds (i.e., R−CHO). For X, we considered F, Cl, and H. For R, we considered H, CH_3, $CH{=}CH_2$, F, OH, NH_2, and NMe_2. The results are summarized in Table 3.

From Table 3, it can be seen that all of the BH_3 complexes favor the eclipsed conformation. This is easy to rationalize, because H can cause only a very small steric effect. Only the hyperconjugation and geometry relaxation effects are important for the conformational preference of a $RCHO\cdots BH_3$ complex. These two effects both favor the eclipsed conformation.

Most of the BF_3 complexes favor the eclipsed conformation. This can also be attributed to the relatively small steric effect caused by F, as demonstrated in section 3.1. Nevertheless, for $NH_2CHO\cdots BF_3$, the preference for the eclipsed conformation over the staggered conformation is very small (by only 0.01 kJ/mol). For $Me_2NCHO\cdots BF_3$, the staggered conformation is favored over the eclipsed one by 0.90 kJ/mol.

TABLE 3. Energy Differences between the Eclipsed and Staggered Conformers of the BX_3 Complexes with Various Substituted Formyl Compounds (kJ/mol)[a]

Complex	ΔE^a		
	X = H	X = F	X = Cl
	−4.98	−1.54	−1.02
	−4.44	−0.65	+1.22
	−4.46	−0.77	+1.39
	−2.98	−1.14	+0.19
	−3.33	−1.08	+2.16
	−3.16	−0.01	+4.33
	−2.47	+0.90	+6.31

[a] ΔE = energy (eclipsed) − energy (staggered). A negative ΔE value means that the eclipsed conformation is more stable. Otherwise, the staggered conformation is more stable. All geometries were fully optimized using the MP2/6-311++G(2d,p) method. The ΔE values are also calculated using the MP2/6-311++G(2d,p) method.

TABLE 4. Energy Differences between the Eclipsed and Staggered Conformers of the $Me_2NCHO\cdots BF_3$ Complex Calculated by Various Theoretical Methods (kJ/mol)[a]

optimization method	method for single-point energy calculation	ΔE^a
MP2/6-311++G(2d,p)	MP2/6-311++G(2d,p)	+0.90
MP2/6-311++G(2d,p)	CCSD/6-31+G(d)	+1.56
MP2/6-311++G(2d,p)	MP4/6-31+G(d)	+1.50
MP2/6-311++G(3df,2p)	MP2/6-311++G(3df,2p)	+0.67
MP2/aug-cc-pvdz	MP2/aug-cc-pvdz	+1.12

[a] ΔE = energy (eclipsed) − energy (staggered). A negative ΔE value means that the eclipsed conformation is more stable. Otherwise, the staggered conformation is more stable.

It is worth noting that Corey actually observed the eclipsed conformation in the crystal structure of the $Me_2NCHO\cdots BF_3$ complex.[6] This questions whether our computational result about $Me_2NCHO\cdots BF_3$ is correct. Thus, we utilized a number of ab initio methods to calculate the conformational preference of the $Me_2NCHO\cdots BF_3$ (see Table 4). Surprisingly, all of these methods predicted that the staggered conformation is more stable than the eclipsed one.

It is possible that all of the above methods failed to predict the conformational preference for the $Me_2NCHO\cdots BF_3$ complex. However, we do not believe that this could be true, because we obtained the same conformational preference by using much larger basis set [i.e., 6-311++G(3df,2p)] and higher-level correlation methods (i.e., MP4 and CCSD). At this point, a possible explanation for the contradiction between theory and experiment is the crystal packing effect. This effect is probably present in the experiment, changing the conformational preference, but it has was not considered in our theoretical methods. Regardless, more studies are needed before one can fully clarify the contradiction. This is beyond the scope of the present work.

What needs to be explained in the present work is why the $Me_2NCHO\cdots BF_3$ complex prefers the staggered conformation *in the gas phase*, even though most other $RCHO\cdots BF_3$ complexes favor the eclipsed conformation. A possible reason is that the $Me_2NCHO\cdots BF_3$ complex has a much stronger interaction energy than the other $RCHO\cdots BF_3$ complexes. In fact, at the MP2/6-311++G(2d,p) level, the interaction energies between RCHO and BF_3 using the eclipsed conformation were calculated to be 36.0 (R = H), 47.7 (R = CH_3), 49.7 (R = $CH{=}CH_2$), 23.9 (R = F), 34.6 (R = OH), 63.9 (R = NH_2), and 78.6 (R = NMe_2) kJ/mol. The strong interaction in the $Me_2NCHO\cdots BF_3$ complex is readily explained by the strong electron-donating effect of the NMe_2 group. This strong interaction forces the Me_2NCHO and BF_3 moieties to be too close to each other,[23] which results in a strong steric effect. The strong steric effect then leads to the staggered conformation of the $Me_2NCHO\cdots BF_3$ complex.

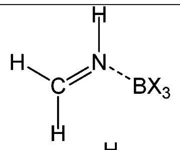
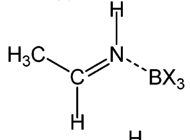
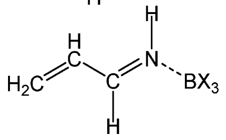
Finally, for most $RCHO\cdots BCl_3$ complexes, the staggered conformation is favored. This is readily explained by the large steric effect caused by the Cl atom, as demonstrated in section 3.1. Nevertheless, it is surprising to see that the $HCHO\cdots BCl_3$ complex actually favors the eclipsed conformation. This is in contradiction to the generally accepted conception that all of the $RCHO\cdots BCl_3$ complexes should favor the staggered conformation.

We attribute the preference $HCHO\cdots BCl_3$ for the eclipsed conformation by to its much lower interaction energy (31.0 kJ/mol) compared to those of $CH_3CHO\cdots BCl_3$ (48.4 kJ/mol) and $CH_2{=}CHCHO\cdots BCl_3$ (53.3 kJ/mol). Therefore, compared to other saturated or unsaturated aldehydes, the $HCHO\cdots BCl_3$ moiety is less tightly bound. This leads to a smaller steric effect in $HCHO\cdots BCl_3$, which then leads to a preference for the eclipsed conformation.

In agreement with the above explanation, the $NH_2CHO\cdots BCl_3$ and $Me_2NCHO\cdots BCl_3$ complexes show much stronger preferences for the staggered conformation than the corresponding $CH_3CHO\cdots BCl_3$ and $CH_2{=}CHCHO\cdots BCl_3$ complexes, because the very strong interaction in the $NH_2CHO\cdots BCl_3$ (68.8 kJ/mol) and $Me_2NCHO\cdots BCl_3$ (90.0 kJ/mol) complexes must cause a very significant steric effect. As shown in Table 3, the $NH_2CHO\cdots BCl_3$ and $Me_2NCHO\cdots BCl_3$ complexes favor the staggered conformation by 4.33 and 6.31 kJ/mol, respectively, whereas the $CH_3CHO\cdots BCl_3$ and $CH_2{=}CHCHO\cdots BCl_3$ complexes favor the staggered conformation by only 1.22 and 1.39 kJ/mol, respectively.

The above explanation, however, cannot be used for the $FCHO\cdots BCl_3$ complex. The interaction energy of this complex (15.6 kJ/mol) is even lower than that of $HCHO\cdots BCl_3$, but this complex still favors the staggered conformation over the eclipsed conformation by 0.19 kJ/mol. We consider the reason for the preference of staggered conformation by $FCHO\cdots BCl_3$ to be its relatively weak hyperconjugation interactions compared to $HCHO\cdots BCl_3$. As a highly electronegative atom, F significantly lowers the energies of the Lp(O) and π(C=O) orbitals.[24] Therefore, the hyperconjugation interactions involving the Lp(O) and π(C=O) orbitals are not as strong as the corresponding interactions in $HCHO\cdots BCl_3$. Admittedly, at the same time, F also decreases the energies of the σ^*(C−H) and σ^*(R−C) orbitals. However, the much longer $O\cdots B$ distance in $FCHO\cdots BCl_3$ (2.103 Å) compared to that in $HCHO\cdots BCl_3$ (1.677 Å) makes the hyperconjugation interactions involving the σ^*(C−H) and σ^*(R−C) orbitals less important.

TABLE 5. Energy Differences between the Eclipsed and Staggered Conformers of the trans BX_3 Complexes with Imines (kJ/mol)[a]

Complex	X = H	X = F	X = Cl
	−9.84	−5.77	−8.67
	−9.04	−5.02	−6.55
	−8.88	−5.04	−6.31

[a] ΔE = energy (eclipsed) − energy (staggered). A negative ΔE value means that the eclipsed conformation is more stable. Otherwise, the staggered conformation is more stable. All geometries were fully optimized using the MP2/6-311++G(2d,p) method. The ΔE values are also calculated using the MP2/6-311++G(2d,p) method.

3.2.2. R−CH=NH$\cdots$BX$_3$. In addition to the formyl compounds, imines can also be activated by boron-based Lewis acids.[25] Therefore, it is interesting to compare the conformational preferences for the imine−BX_3 complexes with those for the formyl−BX_3 complexes. For this purpose, we calculated the energy differences between the eclipsed and staggered conformers of the trans BX_3 complexes with some representative imines (see Table 5).

The results suggest that all of the $RCH{=}NH\cdots BX_3$ complexes strongly favor the eclipsed conformation in which one B−X group is eclipsed relative to the C−H bond. Analysis reveals that the reason for this strong preference is the presence of the N−H bond. The eclipsed conformation actually has two B−X groups staggered with respect to the N−H bond, whereas the staggered conformation has one B−X group eclipsed with respect to the N−H bond. Because the $N{-}H\cdots B{-}X$ steric effect is more significant than the $C{-}H\cdots B{-}X$ steric effect, we now have an $RCH{=}NH\cdots BX_3$ system in which both hyperconjugation and steric effects favor the eclipsed conformation. Thus, the preference for the eclipsed conformation by the $RCH{=}NH\cdots BX_3$ complexes is inevitable.

3.2.3. R−CH=O$\cdots$AlX$_3$. Another interesting system that is related to formyl−BX_3 is the complex between a formyl complex and an aluminum-based Lewis acid. It has been known for quite a long time that aluminum-based Lewis acid can promote the reactions of formyl compounds.[26] However, the conformational preferences of the formyl−AlX_3 systems remain largely unclear.

Our calculation results for the conformational preference of the formyl−AlX_3 systems are reported in Table 6. The results suggest that all of the $RCHO\cdots AlX_3$ (X = H, F, Cl) complexes favor the eclipsed conformation. This is different from the $RCHO\cdots BX_3$ cases simply because the $O\cdots Al$ distances (ca. 1.95 Å) in $RCHO\cdots AlX_3$ are much longer than the $O\cdots B$ distances (ca. 1.7 Å) in $RCHO\cdots BX_3$ (see Figures 5 and 1). As a result, the steric effect in the $RCHO\cdots AlX_3$ complexes is not as significant as that in the $RCHO\cdots BX_3$ complexes. Because of the hyperconjugation and geometry relaxation effects, the $RCHO\cdots AlX_3$ systems favor the eclipsed conformation.

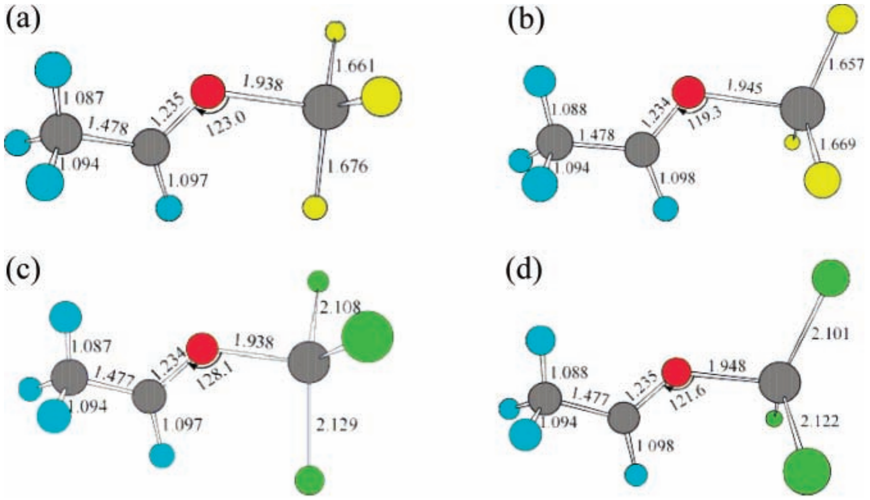
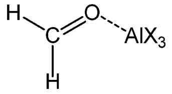
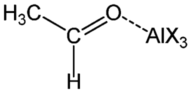
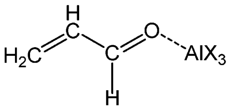
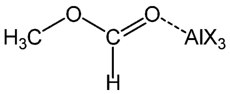
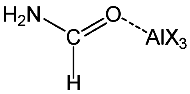
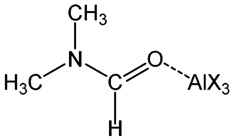


Figure 5. MP2/6-311++G(2d,p)-optimized structures for (a) eclipsed $CH_3CHO\cdots AlF_3$, (b) staggered $CH_3CHO\cdots AlF_3$, (c) eclipsed $CH_3CHO\cdots AlCl_3$, and (d) staggered $CH_3CHO\cdots AlCl_3$.

TABLE 6. Energy Differences between the Eclipsed and Staggered Conformers of the AlX$_3$ Complexes with Formyl Compounds (kJ/mol)[a]

Complex	X = H	X = F	X = Cl
	−4.16	−4.37	−1.93
	−3.67	−3.73	−1.09
	−3.94	−4.22	−1.40
	−3.90	−4.73	−1.78
	−4.23	−5.05	−1.21
	−3.63	−4.52	−0.56

[a] ΔE = energy (eclipsed) − energy (staggered). A negative ΔE value means that the eclipsed conformation is more stable. Otherwise, the staggered conformation is more stable. All geometries were fully optimized using the MP2/6-311++G(2d,p) method. The ΔE values are also calculated using the MP2/6-311++G(2d,p) method.

4. Conclusions

In the present work, we studied the conformational preferences of RCHO···BX$_3$ complexes (R = H, CH$_3$, CH$_2$=CH, F, OH, NH$_2$, NMe$_2$; X = H, F, Cl) and their related systems. We report the following major, new findings:

(1) All of the RCHO···BH$_3$ systems prefer the eclipsed conformation. Most, but not all, of the RCHO···BF$_3$ systems prefer the eclipsed conformation. Most, but not all, of the RCHO···BCl$_3$ systems prefer the staggered conformation. Me$_2$NCHO···BF$_3$ prefers the staggered conformation in the gas phase. HCHO···BCl$_3$ prefers the eclipsed conformation in the gas phase.

(2) Three driving forces are responsible for the conformational preferences of the RCHO···BX$_3$ systems. The hyperconjugation interactions favor the eclipsed conformation. The steric effect favors the staggered conformation. The geometry relaxation effect favors the eclipsed conformation.

(3) Six types of hyperconjugation interactions are important, including σ^*(B−X)−Lp(O), σ^*(B−X)−π(C=O), π^*(C=O)−Lp(X), π^*(C=O)−σ(B−X), σ^*(formyl C−H)−Lp(X), and σ^*(C−R)−Lp(X) interactions. The σ^*(B−X)−Lp(O) interaction was proposed previously as the anomeric effect. The σ^*(formyl C−H)−Lp(X) interaction was proposed previously as the C−H···X hydrogen-bonding effect. The anomeric effect and the C−H···X hydrogen-bonding effect are definitely crucial in determining conformational preferences, but the importance of the other four hyperconjugation interactions should not be neglected.

(4) A balance among the hyperconjugation interactions, steric effect, and geometry relaxation effect is present in both the eclipsed and staggered conformations. If the hyperconjugation interactions and the geometry relaxation effect dominate, as for RCHO···BH$_3$ and most RCHO···BF$_3$, the eclipsed conformation is preferred. If the steric effect dominates, as for most RCHO···BCl$_3$, the staggered conformation is preferred.

(5) All of the RCH=NH···BX$_3$ (R = H, CH$_3$, CH=CH$_2$; X = H, F, Cl) complexes favor the eclipsed conformation because of the presence of the N−H bond. All of the RCH=O···AlX$_3$ (R = H, CH$_3$, CH=CH$_2$, MeO, NH$_2$, Me$_2$N; X = H, F, Cl) complexes favor the eclipsed conformation because the O···Al distances are long in these complexes, causing a small steric effect.

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Supporting Information Available: Detailed three-dimensional structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The energies of the Lp(O) and π(C=O) orbitals in HCHO are −0.471 and −0.535 au, respectively. These values are less negative than the corresponding values in FCHO, which are −0.482 [Lp(O)] and −0.587 [π(C=O)] au, respectively.

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