An MNDO Investigation of the Complexes of Carbonyl Compounds with Lewis Acids

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Carbonyl complexes of several cations and uncharged Lewis acids have been studied by using MNDO molecular orbital calculations. The geometries of the bent and the linear conformations of the carbonyl complexes of beryllium, boron, and aluminum derivatives were calculated, and partial searches of the potential energy surfaces were carried out. In the complexes with the uncharged species the bent conformations are more stable. The conformation of each cation complex is dependent upon the electronegativity of the metal atom in the cation; a lower electronegativity favors a linear geometry. The fact that most of the experimental data pertaining to the conformation of carbonyl complexes with NMR shift reagents indicate bent geometries supports our deduction that uncharged Lewis acids are better NMR shift reagent models than cations.

The energies and geometries of carbonyl complexes with cations and with uncharged Lewis acids are of great moment in diverse areas of chemistry including biochemistry,[1] catalysis,[2] and polymer chemistry.[3] Theoretical calculations on the cation complexes[4] predict that they have linear (C=O—Met angle = 180°) rather than bent structures. However, the results of the cation complex calculations are being extrapolated to the structures of carbonyl–lanthanide shift reagent (LSR) complexes.[4] This inference does not necessarily follow, since the shift reagents are not formally charged. The propriety of this deduction is important because it leads indirectly to a theoretical justification of the application of ketone–NMR shift reagent complex data to considerations of carbonyl–cation geometries and reactivities. While it is obvious that there must be some similarities, a total extrapolation may not be justified and merits further investigation.

NMR shift reagents have become important in the determination and refinement of structures of carbonyl compounds. Numerous studies have been made of the structures of ketone–lanthanide shift reagent complexes in order to increase the understanding and utility of these reagents.[4,5] Recently, boron trihalides[6,7] and aluminum trihalides[7,8] have been used as NMR shift reagents in structural and site activity studies of carbonyl compounds. The nature of the alkyl-transfer step in organoaluminum addition to ketones was probed by using trimethylaluminum as an NMR shift reagent.[9] Also, various theoretical calculations upon carbonyl complexes have been carried out in order to elucidate the nature of the interactions in ketone–LSR complexes.[4,5]

Table I. Calculated (MNDO) Heats of Formation for Bent and Linear C=O—X Conformations of Dimethylcyclopropanone–X Complexes

	C=O—X configurations			
	bent		linear	
X	angle, deg	ΔH_f, kcal/mol	angle, deg	ΔH_f, kcal/mol
BeH^+	150.0[a,c]	138.7	180.0	137.1
$BeMe^+$	150.0[a,c]	110.1	178.4	108.7
BF_2^+	133.5	−11.27	180.0[a,b]	−6.85
			(perp)[a,b,e]	−6.87
BMe_2^+[d]	139.4	135.9	180.0[a,b]	138.3
			(perp)[a,b,e]	138.2
AlF_2^+	157.2	−61.8	179.6	−61.7
$AlMe_2^+$[d]	136.0[a,c]	111.7	179.5	108.8
BeH_2	149.8	−27.04	179.9	−26.63
$BeMe_2$	149.2	−74.12	179.3	−73.78
BF_3	133.4	−270.8	180.0[a,b]	−265.6
BMe_3[d]	131.6	−28.85	180.0[a,b]	−20.03
AlF_3	143.5	−322.0	180.0[a,b]	−320.8
$AlMe_3$[d]	138.8	−52.24	180.0[a,b]	−49.49

[a] A fixed C=O—X angle was imposed. [b] The structure optimizes to the bent form when the geometrical constraint is removed. [c] The structure optimizes to the linear form when the geometrical constraint is removed. [d] Cyclopropanone is used as the model ketone. [e] The boron–fluorine or boron–carbon bonds are twisted 90° out of the plane formed by the carbonyl compound.

In most of the investigations of carbonyl–NMR shift reagent complexes,[5,6,8,9] evidence for the complex existing predominantly in a bent, rather than linear, conformation was obtained. There was also reported theoretical and experimental evidence for the greater stability of the linear conformation.[4] In that study, using an ab initio method, various cations were employed to model the shift reagent.[4] However, since shift reagents are uncharged species, it seems that uncharged Lewis acids, rather than cations, should best model these compounds. While relatively small Lewis acids have been used as models for LSR's, it must be noted that steric effects in the ketone–LSR complexes may predominate, and extrapolation of calculations by any method using small Lewis acids, charged or uncharged, may be invalid. However, no such problems

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should exist with boron and aluminum shift reagents, since these are comparable in size to the models used. Because of the interest in elucidating the structures of and interactions within these carbonyl complexes and in order to identify the most suitable shift reagent models, we have studied the complexation of dimethylcyclopropanone with derivatives of three metals, beryllium, boron, and aluminum, via MNDO molecular orbital calculations.[10]

Results and Discussion

Using the MNDO method, we calculated the minimum energy geometries of complexes of *trans*-dimethylcyclopropanone with a series of NMR shift reagents and LSR models. Complexes with cations and with uncharged Lewis acids were calculated for comparison. *trans*-Dimethylcyclopropanone was chosen as the model ketone in order to investigate the effects of steric interactions in the complexes. Since shift reagents are often employed with highly branched ketones we avoided selecting carbonyl models such as formaldehyde or acetone when possible. Thus, the incorporation of the two methyl substituents in the model ketone increased the generality of our results and guaranteed that we did not artificially sterically favor the bent conformation.

First, we compared the geometries of the complexes of dimethylcyclopropanone with BeR^+ and with BeR_2 (R = H, Me). Our calculations using BeR^+ as a model for the shift reagent favor the linear geometry (Table I). In these charged systems, we found no energy minimum corresponding to a bent structure. However, if BeH_2 or $BeMe_2$ is used as the NMR shift reagent model, the bent structure is more stable. The complexes of dimethylcyclopropanone with BeH_2 or with $BeMe_2$ are calculated to be only slightly more stable with the C=O—Be angle bent at about 150° than in a linear arrangement (Table I). In each case, the most stable conformation is with beryllium lying in the nodal plane of the carbonyl π bond and associated with the nonbonding electrons on oxygen. The potential energy difference between the two conformations is very small (0.4 kcal/mol), indicating that such a complex could exist in a rapid equilibrium. Thus, in this system, the calculations could support either the bent structure or the linear structure depending upon whether a charged or an uncharged Lewis acid is chosen as the NMR shift reagent model. As mentioned above, these and earlier[4] calculations may not be applicable to ketone–LSR complexes because of larger steric requirements which would tend to favor the linear conformation.

In many studies of unsymmetrical ketone–BCl_3 or –$AlCl_3$ adducts, there is evidence that each complex exists predominantly in the two bent conformations, which undergo a rapid syn–anti exchange.[6] In the investigation of the nature of the alkyl-transfer step in organoaluminum addition to ketones,[9] the results indicate that the major conformation of the trimethylaluminum–ketone complex is the bent one. The interest in these complexes prompted us to carry out MNDO calculations upon the complexes of dimethylcyclopropanone with BF_3, with AlF_3, and with their cationic derivatives. Unsubstituted cyclopropanone was used in the calculations with the methyl analogues, BMe_3, BMe_2^+, $AlMe_3$, and $AlMe_2^+$, in order to reduce the size of the computation.

In each complex with a neutral boron or aluminum compound, the bent form is calculated to be more stable (1.2–8.8 kcal/mol) than the linear form (Table I). Thus, our calculations support the interpretation of the experimental results that the bent conformation is the more stable one. The C=O—Met angles in the optimized structures were slightly smaller in the complexes with the boron compounds (~132°) than in those with the aluminum analogues (~141°). This is probably in part due to the boryl groups being smaller than their aluminum analogues. The heats of formation for the linear complexes (Table I) were obtained by holding the C=O—Met angle at 180° and allowing the other geometrical parameters to optimize. Thus, the linear conformations of the complexes of BMe_3, BF_3, $AlMe_3$, and AlF_3 are not at energy minima, and each optimizes to the bent analogue for which data is given in Table I if the C=O—Met angle is allowed to vary too.

Except for $AlMe_2^+$, each complex with a boron or an aluminum cation is more stable in the bent conformation than in the linear conformation. Thus, our results using MNDO are similar to those using ab initio calculations[4] in that the complexes with cations having less electronegative elements (Be or Al) favor linear geometries. However, the tendency is less when MNDO is used; the linear form of the perpendicular boryl cation complex was predicted by using ab initio calculations to be more stable than the bent one, but with MNDO, neither of the linear forms of the boryl cation complexes were more stable than the bent conformations. MNDO also predicts less stabilization from overlap between the oxygen lone pair p orbital and the boron empty p orbital, since the perpendicular form is only ≤0.1 kcal more stable than the planar form. In the case of BF_2^+, the planar and perpendicular conformations have essentially equal heats of formation. This presumably can be attributed to the fact that the formally empty p orbital on boron is partially occupied due to conjugation with fluorine, and there is less conjugation with oxygen.

Conclusion

MNDO molecular orbital calculations upon several ketone complexes indicate that, in general, the bent conformations are more stable than linear ones in complexes with uncharged Lewis acids. However, the linear structure is favored in complexes with cations having less electronegative elements. Since NMR shift reagents are uncharged Lewis acids and not cations having highly electropositive metals, the best models should be uncharged molecules.

Methods Section

Theoretical Procedure. The calculations were carried out on an IBM 3081 computer using the MNDO molecular orbital approximation.[10] The MNDO program was obtained through *QCPE*,[11] converted to VS FORTRAN 77, and adapted to run on the IBM 3081 computer. The geometries of stable species were found by minimizing the total energy using the standard Davidon–Fletcher–Powell[12] optimization procedure. Except where noted otherwise, all geometrical variables were allowed to optimize.

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