on each of the separate host chromophores, so that, using eq 37, 58, and 59, we have

$$\bar{R}(z) = -(2/r^3)R(A_h)/(\epsilon_h^2 - \epsilon_g^{z^2}) \qquad (70)$$

$$\bar{R}(xy) = +(2/r^3)R(A_h)/(\epsilon_h^2 - \epsilon_g^{xy^2}) \qquad (71)$$

where $R(A_h)$ is the exciton CD of the A_2 transition of the host system. Thus a z-polarized guest transition will have an ICD of sign *opposite* to that of the z-polarized host system transition, and an xy-polarized guest transition will similarly have a sign opposite to that of the CD of the host E_u transition. This is exactly opposite to the conclusion of the earlier paper, which stands corrected by eq 70 and 71 above.

If the polarizations of the guest transitions are known from an independent experiment (e.g., polarization studies in normal absorption), then the ICD may be used as a stereochemical probe, in that the absolute configuration may then be determined by the sign of the host exciton CD band corresponding to the A_2 transition. Similar conclusions are possible for saturated chelate systems, when the host parameter may be approximated by $\mathcal{H}(0)$. In this case, the host parameter is best determined parametrically for a complex in which all the other quantities are known, and then transferred to applications to other metal complexes with the same chelate systems.

Conclusions

Sign correlations or sector rules have enjoyed a wide populatiry in relating CD spectra to stereochemical factors. Many sector rules are empirically based, but suffer from an inability to predict when they will fail. The sign correlations developed in this paper in terms of a well-defined model will fail only when the well-defined restrictions or assumptions of the model are not relevant to the system under consideration. This failure immediately becomes a positive aspect of our approach, as it can be directly interpreted in terms of physical characteristics of the interacting systems and the intercalation process. It is not sufficient that a theoretical model predict a set of sector rules or sign correlations; it is crucial that it also (i) yield a quantitative description of the CD intensities observed experimentally, and (ii) be capable or predicting why and when the sign correlations or sector rules will fail.

Acknowledgment. The authors would like to thank Professor Bengt Nordên for the introduction to dye/DNA systems, and Dr. Tom Kurucsev for discussions on the cyclodextrin systems.

Registry No. I (A = OH), 108-95-2; I (A = NH_2), 62-53-3; II (A = OH), 120-80-9; II (A = NH_2), 95-54-5; III (A = OH), 108-46-3; III (A = NH_2), 108-45-2; IV (A = OH; B = OH), 123-31-9; IV (A = NH_2; B = NH_2), 106-50-3; IV (A = NO_2; B = NH_2), 100-01-6; IV (A = NO_2; B = OH), 100-02-7; β-cyclodextrin, 7585-39-9.

Conformational Mobility in the *trans*-Cycloheptene–Copper(I) Triflate Complex

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Abstract: The conformational properties of the copper(I) trifluoromethanesulfonate (CuOTf) complexes of (*E*)- and (*Z*)-cycloheptene and -cyclooctene have been studied by ^{13}C NMR. Both *cis*-cyclooctene·CuOTf and *trans*-cycloheptene·CuOTf show dynamic NMR behavior in the temperature range studied (30 to −117 °C) and yield values of $\Delta G^{\ddagger}_{173}$ = 7.8 kcal/mol and $\Delta G^{\ddagger}_{299}$ = 9.5 kcal/mol, respectively. The DNMR behavior of the *cis*- and *trans*-cyclooctene complexes as well as that of the *cis*-cycloheptene complex is very similar to that of the corresponding free olefins. It is now proposed that the seven nonequivalent ^{13}C NMR signals observed at low temperature for the *trans*-cycloheptene complex are due to an unsymmetrical chair conformation of the *trans*-cycloheptene ligand and that the dynamic process observed at higher temperatures involves a pseudorotation of the cycloheptene ring little affected by the complexed copper ion. Both molecular mechanics (MOLBD) and semiempirical quantum mechanical calculations (MNDO) on the free olefin find the unsymmetrical chair form to be an energy minimum and yield values for the free energy of activation which are in good agreement with the value experimentally determined for the complex.

Introduction

Conformational processes in cyclic hydrocarbons have been extensively investigated with both experimental and theoretical techniques. Dynamic ^{13}C and ^{1}H NMR (DNMR) are probably the most widely used analytical methods and are capable of giving reliable activation parameters for the process under study, provided sufficient care is taken in the treatment of the spectral data.[2] Total line-shape analysis is the method of choice for evaluating such data and can be applied to systems ranging from simple two-site exchange through complex multispin systems.[3]

Computationally, cyclic hydrocarbons have been most throughly studied using molecular mechanics (force field) calculations, which enable one to determine stable ground-state structures and map potential surfaces in a routine manner.[4] Semiempirical quantum mechanical methods have also been applied to the conformational analysis of cycloalkenes.[5] complementing, rather than competing with, the aforementioned calculations.

For some time we have been interested in the structural characteristics of molecules possessing strained double bonds.[6] *trans*-Cyclooctene is the smallest *trans*-cycloalkene which has been

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[1] (a) Department of Chemistry. (b) Department of Chemical Engineering.

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Table I. Chemical Shifts for Free and Complexed Cycloalkenes

compound	$^{13}C^a$ olefinic	$^{13}C^a$ aliphatic	$^1H^a$ olefinic
High-Temperature Limit			
1 *cis*-cycloheptene^b	133.0	27.8, 29.8, 33.7	5.8
2 *c*-C_7H_{12}·CuOTf^c	109.0	30.0, 31.4, 32.4	5.6
3 *t*-C_7H_{12}·CuOTf^c	102.0	25.6, 30.0, 32.0	4.6
4 *cis*-cyclooctene^b	131.0	25.5, 26.2, 29.2	5.2
5 *c*-C_8H_{14}·CuOTf^c	106.4	26.8, 27.2, 30.4	5.6
6 *trans*-cyclooctene^b	134.8	35.7, 29.2	5.5
7 *t*-C_8H_{14}·CuOTf^c	106.0	28.2, 35.2, 35.8	4.9
8 (*t*-$C_8H_{14})_3$·CuOTf^c	123.6	29.1, 35.2, 35.8	5.4
Low-Temperature Limit			
3 *t*-C_7H_{12}·CuOTf^{c,d}	96.8, 99.6	23.6, 34.0, 24.4, 30.8, 31.2	
5 *c*-C_8H_{14}·CuOTf^{c,e}	101.4, 103.6	24.2, 24.6, 26.8 28.4, 28.6, 30.2	

^{a} In ppm, downfield from Me_4Si. ^{b} Acetone-d_6 solvent. ^{c} Diethyl ether solvent. ^{d} Chemical shifts reported at 179 K. ^{e} Chemical shifts reported at 156 K.

isolated and has been the subject of many investigations over the past 30 years.[7] *trans*-Cycloheptene has presumably been generated both thermally[8] and photochemically[9,10] and trapped. To date, however, it has not been isolated or characterized spectroscopically (conjugated derivatives of *trans*-cycloheptene such as 1-phenyl-*trans*-cycloheptene and *trans*-2-cycloheptenone have been observed[11]).

Recently, a stable copper(I) trifluoromethanesulfonate (triflate) complex of *trans*-cycloheptene has been prepared by irradiation of the copper(I) triflate complex of *cis*-cycloheptene.[12] The present paper reports DNMR studies of the cycloheptene and cyclooctene complexes of copper(I) triflate. We also report calculations of the conformational properties of the free *trans*-cycloheptene and relate them to the observed characteristics of the complexed olefin.

Results

Copper(I) trifluoromethanesulfonate (CuOTf) complexes of stable cycloalkenes are readily prepared by reacting the olefin with the cuprous triflate–benzene complex.[13a] The 1:1 complexes of *cis*-cycloheptene (*c*-C_7H_{12}) and *cis*-cyclooctene (*c*-C_8H_{14}), as well as the tris(*trans*-cyclooctene) complex (*t*-$C_8H_{14})_3$·CuOTf, were prepared using this method. The cuprous triflate complexes of *trans*-cycloheptene (*t*-C_7H_{12}·CuOTf) and *trans*-cyclooctene (*t*-C_8H_{14}·CuOTf) were prepared by irradiating a solution of the corresponding cis isomer.[12] *t*-C_8H_{14}·CuOTf can also be prepared in the same manner as the (*t*-$C_8H_{14})_3$·CuOTf complex.[14]

DNMR. Table I lists the ^{13}C and ^1H chemical shifts for the five CuOTf complexes as well as the known NMR parameters for the free olefins. Note the large upfield shift for both the olefinic carbons and olefinic protons upon complexation. The origin of this shift has been discussed.[13b]

Even below −80 °C three of the complexes, *c*-C_7H_{12}·CuOTf, *t*-C_8H_{14}·CuOTf, and (*t*-$C_8H_{14})_3$·CuOTf, show only small changes in their ^{13}C chemical shifts. On the other hand, both *t*-C_7H_{12}·CuOTf and *c*-C_8H_{14}·CuOTf show dynamic behavior with the appearance of new signals as the temperature is lowered.

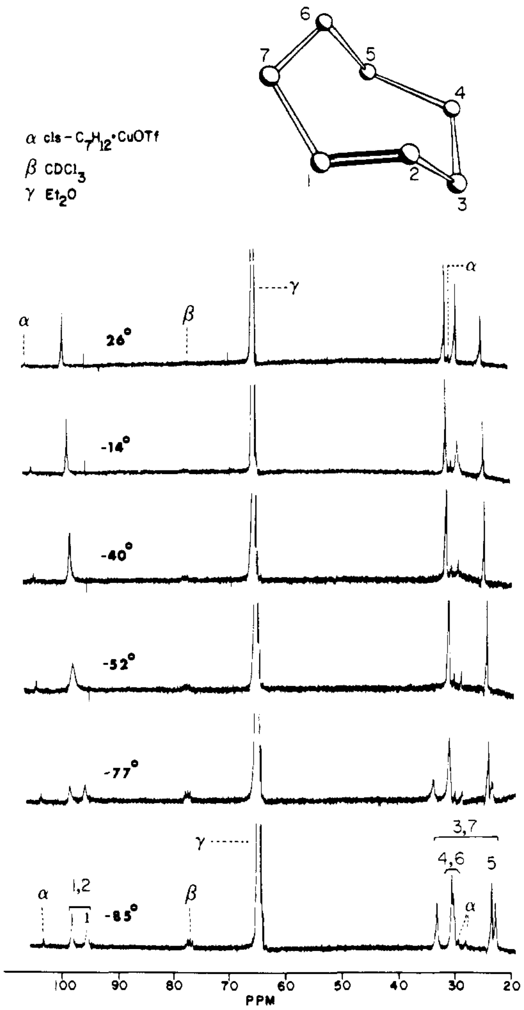

Figure 1. ^{13}C NMR spectra of *t*-C_7H_{12}·CuOTf in diethyl ether as a function of temperature.

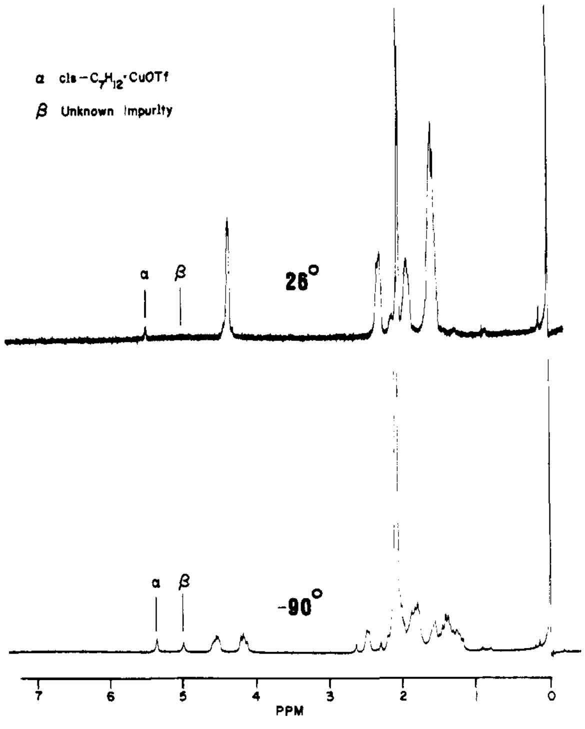

Figure 2. ^1H NMR spectra of *t*-C_7H_{12}·CuOTf in acetone-d_6 in the high- and low-temperature limits: Acetone-d_6 solvent; Me_4Si internal reference.

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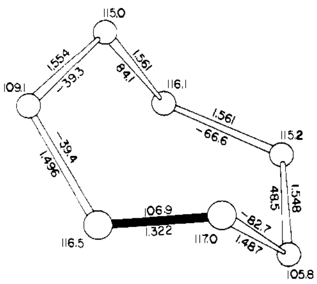
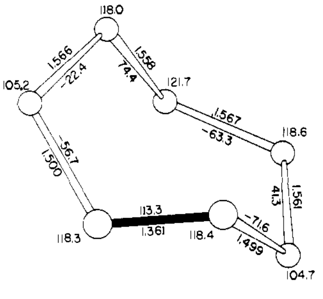
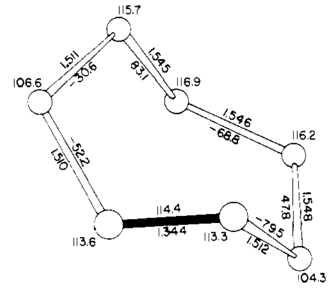


MOLBD ΔH_f = 29.3 kcal/mol

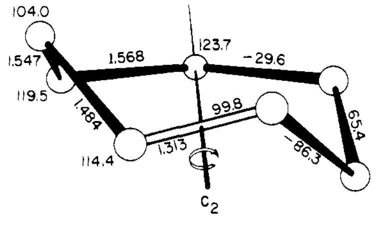


MNDO ΔH_f = 23.3 kcal/mol

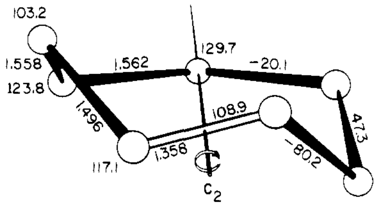


VFF(Ermer) ΔH_f = 27.7 kcal/mol

Figure 3. Calculated equilibrium geometries of uncomplexed t-C_7H_{12}. Bond length in angstroms and torsion angle given for each C–C bond, CCC valence angle for each C atom.



MOLBD $\Delta H^{\ddagger}$ = 9.4 kcal/mol



MNDO $\Delta H^{\ddagger}$ = 8.1 kcal/mol

Figure 4. Calculated transition-state geometries for the pseudorotation of t-C_7H_{12}. See caption to Figure 3.

At 26 °C t-C_7H_{12}·CuOTf gives four proton-decoupled ^{13}C resonances as shown in Figure 1. As the temperature is lowered, three of these signals broaden and split until at temperatures below −80 °C seven different signals can be observed. Furthermore, the ^1H NMR spectra show two nonequivalent olefinic protons when the sample is cooled to −90 °C as seen in Figure 2. Similarly, the four ^{13}C signals observed in the proton-decoupled room-temperature spectrum of c-C_8H_{14}·CuOTf broaden and then split into eight signals at −117 °C, indicating that all of the carbons are then nonequivalent.

The proton-decoupled 300-MHz ^{13}C NMR spectra of the above complexes were analyzed using the total line-shape method with a two-site exchange program employing visual fitting of the experimental and calculated curves. Rate constants for the dynamic processes were determined at 11 temperatures for t-C_7H_{12}·CuOTf and at a single temperature for c-C_8H_{14}·CuOTf. In the case of t-C_7H_{12}·CuOTf, both the olefinic and the allylic carbon signals were fitted, where possible, while in the case of c-C_8H_{14}·CuOTf only the olefinic resonances were used in the determination of the rate constant. The free energies of activation for these processes were calculated using the Eyring equation. The value of $\Delta G^{\ddagger}$ for t-C_7H_{12}·CuOTf varied between 9.47 and 9.66 kcal/mol over the temperature range 299–179 K. $\Delta G^{\ddagger}_{299}$ for t-C_7H_{12}·CuOTf was 9.47 ± 0.20 kcal/mol while the value for c-C_8H_{14}·CuOTf was 7.80 ±0.06 kcal/mol at 173 K. The low-temperature ^{13}C chemical shift data for both complexes are shown in Table I. We hoped originally that we would be able to determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ separately for these processes, since we were able to observe several pairs of exchanging nuclei with different coalescence temperatures. Unfortunately, we were unable to determine the rate constants in the fast and slow exchange regions with sufficient accuracy to allow us to obtain reliable values.[15]

Calculations. Molecular mechanics calculations of the ground-state geometry and of the proposed conformational isomerization for uncomplexed t-C_7H_{12} were done using a slightly modified version of Boyd's MOLBD III program.[16] Semiempirical quantum mechanical calculations were done using the MNDO[17] method. The resulting equilibrium geometries as well as that recently published as a result of another force field calculation[4b] are shown in Figure 3.

Preliminary potential energy profiles were calculated for the pseudorotation of the t-C_7H_{12} ring by the MOLBD III and MNDO techniques, by varying the 4567 torsion angle (Figure 1) in stepwise increments from its initial geometry to that found in the pseudorotated final state. Neither technique gave a profile which was a true minimum energy path. The transition state on the MOLBD energy path was then determined by choosing the geometry corresponding to the peak of the preliminary potential energy profile and using its coordinates as input for an unconstrained search for a stationary state by the Newton–Raphson procedure.[4a] The transition state on the MNDO surface was determined by minimizing the norm of the gradient using the highest energy conformation on the preliminary potential energy profile as the initial geometry. In both cases, the stationary point obtained had a C_2 axis of symmetry (Figure 4) and the force constant matrix had the requisite single negative eigenvalue. The energy of the transition state was 9.4 (MOLBD III) or 8.1 (MNDO) kcal/mol above that of the equilibrium geometry (both methods are parameterized so as to incorporate zero-point energies in an approximate way; these are therefore not considered explicitly). In both calculations the entropies of activation were determined from the calculated vibrational frequencies of the ground and transition states. The $T\Delta S^{\ddagger}$ values at 299 K are 1.1 kcal/mol from MOLBD and 0.50 kcal/mol from MNDO. This yields $\Delta G^{\ddagger}_{299}$ values of 10.5 and 8.6 kcal/mol from MOLBD and MNDO, respectively.

Discussion

DNMR. Dynamic processes in organometallic compounds are well documented.[2] Olefin rotation, ligand exchange, and olefin isomerization are some of the mechanisms which give rise to ^{13}C

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[15] See ref 3 for a discussion of the sources of error present in the calculation of activation parameters.

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DNMR effects in metal–olefin complexes. In the present case we propose that the last named mechanism is operating and, specifically, that the DNMR effects observed are due to the conformational isomerization of the cycloalkene.

A propeller-like rotation of the olefin is known to render the olefinic carbons pairwise equivalent in some systems containing an unsymmetrically substituted metal.[2b] This unsymmetrical environment is absent in the copper(I) triflate complexes. Although the analogous copper halide olefin complexes often exist as polynuclear aggregates because of bridging by halide, this is not the case when triflate is the counterion.[13a] Moreover, this process of olefin rotation should be occurring in all of the cycloalkene complexes, albeit at various rates, and would be expected to show DNMR effects in $c\text{-}C_7H_{12}\cdot CuOTf$, $t\text{-}C_8H_{14}\cdot CuOTf$, and $(t\text{-}C_8H_{14})_3\cdot CuOTf$ as well as in $t\text{-}C_7H_{12}\cdot CuOTf$ and $c\text{-}C_8H_{14}\cdot CuOTf$.

While some CuOTf complexes are known to undergo ligand exchange,[13a] this process clearly cannot be occurring in the solutions of $t\text{-}C_7H_{12}\cdot CuOTf$, since the free olefin is not stable at room temperature[8-10] while the solutions of the complex are. For $c\text{-}C_8H_{14}\cdot CuOTf$ in the fast exchange limit, intermolecular olefin exchange would give a single ^{13}C peak (olefinic carbons) at the weighted average of the chemical shifts of $c\text{-}C_8H_{14}\cdot CuOTf$ and free $c\text{-}C_8H_{14}$. In the slow exchange limit, it would give resolved peaks corresponding to these species. The two equivalent intensity peaks observed at low temperature have chemical shifts of 101.4 and 103.6 ppm (Table I), very different from the value of 131 ppm for $c\text{-}C_8H_{14}$, ruling out olefin exchange in this case as well. This leaves us with dynamic processes involving conformational change in the cycloalkenes as the most likely explanation of the observed spectral changes. In the following, we interpret the DNMR results observed for $c\text{-}C_7H_{12}\cdot CuOTf$, $c\text{-}C_8H_{14}\cdot CuOTf$, $t\text{-}C_8H_{14}\cdot CuOTf$, and $(t\text{-}C_8H_{14})_3\cdot CuOTf$ in terms of the conformational behavior of the stable free olefins. Conversely, we propose that the conformational behavior of the seven-membered ring in $t\text{-}C_7H_{12}\cdot CuOTf$ provides a useful guide to that of the so far unreported free $t\text{-}C_7H_{12}$.

***cis*-Cycloheptene and Its Complexes.** As stated previously, $c\text{-}C_7H_{12}\cdot CuOTf$ does not show any dynamic behavior in the temperature range studied. On the basis of ^1H DNMR[18] as well as a number of force field[19] and quantum mechanical[5] calculations, $c\text{-}C_7H_{12}$ is believed to adopt a symmetrical chair conformation **9** as shown in Figure 5. The ring inversion process observed in the ^1H NMR spectrum of the free olefin ($\Delta G^{\ddagger} = 5.4$ kcal/mol) would be unobservable by ^{13}C NMR. If this symmetrical chair conformation is preserved in $c\text{-}C_7H_{12}\cdot CuOTf$ with CuOTf in the symmetry plane of the molecule, the number of carbon resonances at low temperature should be the same as that observed for the free olefin. In this view, the coordinated copper ion would have little effect on the rapid ring inversion of $c\text{-}C_7H_{12}$. An alternative explanation which cannot be ruled out is that the presence of the CuOTf moiety freezes out the ring inversion at room temperature and that only one conformer is present, most likely the structure with the copper ion and C5 anti with respect to the remainder of the ring.

***cis*-Cyclooctene and Its Complexes.** $c\text{-}C_8H_{14}$ is believed to have an unsymmetrical structure **10** similar to that shown in Figure 5 based on DNMR,[20] force field,[21] and semiempirical quantum-mechanical[22] calculations. Two dynamic processes have been identified for the olefin by ^1H NMR: a ring inversion ($\Delta G^{\ddagger} = 8.2$ kcal/mol) with a time average plane of symmetry and a faster process ($\Delta G^{\ddagger} = 5.8$ kcal/mol) which results in a time average twofold axis of symmetry through the double bond.[20] Only the faster process would be seen in ^{13}C NMR since both processes must be frozen out before all eight carbon atoms in the free olefin become nonequivalent. A recent ^{13}C NMR study found the value of 6.3 kcal/mol as the free energy of activation in free $c\text{-}C_8H_{14}$ for a process which removes the low-temperature nonequivalence of all eight cycloalkene carbons.[23] The authors proposed that this process corresponds to the faster process with $\Delta G^{\ddagger} = 5.8$ kcal/mol reported in ref 20. For the $Fe(CO)_4$ complex of $c\text{-}C_8H_{14}$, the same authors found a free energy of activation of 7.8 kcal/mol for a process that removes the low-temperature inequivalence of all eight carbon atoms.[23] The lower symmetry of the complex removes the possibility of having a time-average effective C_2 axis of symmetry even if the process responsible for its presence in the free olefin goes on as before. Thus, in the complex, freezing out the ring inversion is sufficient to render all eight carbon atoms nonequivalent. The good agreement between the $\Delta G^{\ddagger}$ value of 7.8 kcal/mol found for the $Fe(CO)_4$ complex and the value 8.2 kcal/mol reported for the high-energy conformational process[20] led the authors of ref 23 to the conclusion that the unsymmetrical conformation of the complexed olefin was probably very similar to that found in the free olefin.

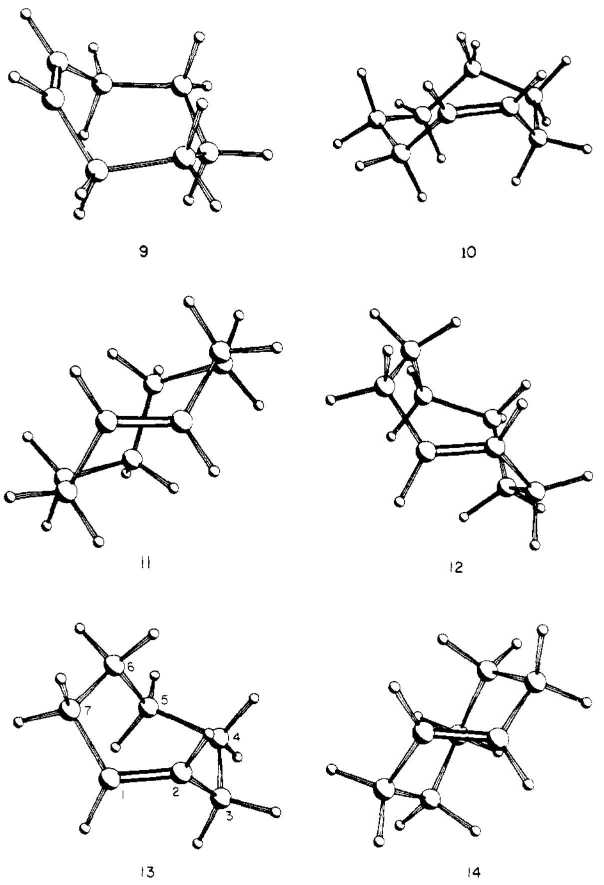

Figure 5. Possible minimum energy conformations for (*E*)-and (*Z*)-cycloheptene and -cyclooctene.

The value of $\Delta G^{\ddagger}$ which we find for $c\text{-}C_8H_{14}\cdot CuOTf$ is identical with that reported[22] for $c\text{-}C_8H_{14}\cdot Fe(CO)_4$, and this suggests that the conformational isomerization processes in the two complexes are similar to each other and to that in the free olefin.

***trans*-Cyclooctene and Its Complexes.** The conformation of $t\text{-}C_8H_{14}$ was, until recently, a matter of some dispute. Electron diffraction results[24] now have shown that the free olefin exists in the twist or crown conformation **11** as shown in Figure 5. Furthermore, X-ray structures of both *trans*-dichloro[(−)-$t\text{-}C_8H_{14}$][(+)-α-methylbenzylamine]Pt[25] and $[Cu_2Cl_2(t\text{-}C_8H_{14})_3]$[26]

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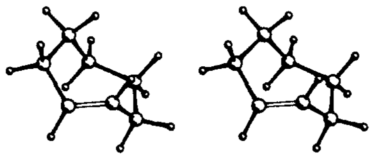

Figure 6. Stereoscopic view of the calculated (MOLBD III) equilibrium geometry of *t*-C_7H_{12}.

show the twist conformation to be present in the complexed olefin as well.[27] The distorted chair form originally proposed for *t*-C_8H_{14}[28] (**12**, Figure 5) has been calculated to be only 3.5 kcal/mol higher in energy than the twist structure,[4] and recently a bicyclic *t*-C_8H_{14} analogue has been prepared in this chair conformation.[29] The twist conformation possesses a C_2 axis of symmetry and, if it is preserved in the CuOTf complex as expected, the CuOTf moiety would have to lie on this axis of symmetry. A symmetric chair form would also possess a C_2 axis of symmetry. Either of these possibilities is compatible with the observed absence of DNMR effects for both *t*-C_8H_{14}·CuOTf and (*t*-C_8H_{14})$_3$·CuOTf since each complex would have four different pairs of isochronous carbons, as is the case for the free olefin.

In summary, the dynamic characteristics of the complexes *c*-C_7H_{14}·CuOTf, *c*-C_8H_{14}·CuOTf, *t*-C_8H_{14}·CuOTf, and (*t*-C_8H_{14})$_3$·CuOTf can be explained adequately in terms of the conformational characteristics of the corresponding free olefins. In these cases, coordination to CuOTf or Fe(CO)$_4$ appears not to perturb the motions of the hydrocarbon skeleton to a large extent. The maximum distortion expected would be at the double bond, but even so, in the CuCl complex of *t*-C_8H_{14} the double bond torsion angle differs by only 2° from the value found in the free olefin.[7]

***trans*-Cycloheptene Complex.** The seven carbon resonances observed at low temperature for *t*-C_7H_{12}·CuOTf suggest an unsymmetrical conformation for the olefin. The calculated chair form of *t*-C_7H_{12} (**13**, Figure 5) is presented in a stereoscopic view in Figure 6 (cf. Figure 3). It lacks any symmetry elements, but a rapid pseudorotation would average C(1) with C(2), C(3) with C(7), and C(4) with C(6), giving four ^{13}C signals in the fast exchange limit. The experimental $\Delta G^{\ddagger}_{299}$ for the proposed automerization is 9.5 kcal/mol. The nature of the motion involved in the pseudorotation is discussed in the following.

Calculations. Our goal in performing these calculations was, first, to determine whether or not the proposed chair conformation was a reasonable ground-state minimum energy structure and, second, to see if the energy profile for the proposed pseudorotation could be calculated and a transition state identified using molecular mechanics and semiempirical quantum mechanical methods. The merits and shortcomings of the two techniques of calculation have been discussed.[30]

Equilibrium Geometry. A number of force fields have been developed to calculate ground-state structures and to simulate conformational processes in cycloalkenes. A very extensive recent collection of results of molecular mechanics calculations by the method of Ermer on molecules with strained double bonds,[4b] including *t*-C_7H_{12}, contains a conformation for *t*-C_8H_{14} which is in excellent agreement with electron diffraction data.[24] Prior calculations[31] by the method of Boyd determined a ground-state twist conformation for *t*-C_8H_{14} with a value of 135.4° for the ring torsional angle of the double bond. The latter is a measure of the twist of the double bond and is in agreement with the experimental value of 136.0°. Quantum mechanical calculations, while not as widely used as the above methods, have also been applied to cycloalkenes.[5] Structures for both isomers of cyclooctene have been calculated with a MINDO/2′ program and are in agreement with experimental data with *t*-C_8H_{14} calculated to exist in the twist form with a double-bond dihedral angle of 128.4°.[22]

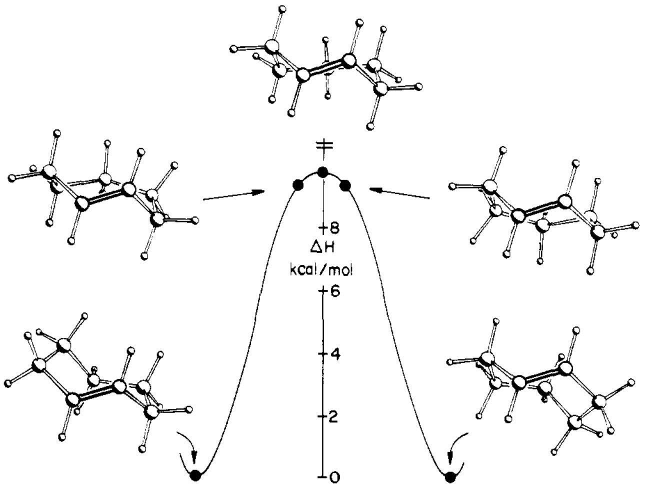

Figure 7. Representation of structural changes undergone by *t*-C_7H_{12} during pseudorotation (MOLBD III).

In our hands, MNDO and MOLBD III both gave distorted chair conformations for *t*-C_7H_{12} (Figures 3 and 6), in good agreement with the structure previously calculated by Ermer's method[4b] and by the MM1 method of Allinger.[32] MNDO, MOLBD III, and Ermer's calculation gave double-bond torsion angles which are significantly smaller than the 125° originally calculated by Allinger and Sprague.[19a] The heats of formation are also larger than their reported value of 18.67 kcal/mol.

Ermer's method produced an additional C_2 minimum energy conformation **14** of C_2 symmetry and found it to be 7.4 kcal/mol higher in energy than the chair conformation.[4b] Using MOLBD III, we found this same geometry to lie nearly 12 kcal/mol higher in energy than the unsymmetrical equilibrium geometry of Figures 3 and 6, and not to correspond to a local minimum. Our attempts to find a local minimum of C_2 symmetry using MOLBD III were unsuccessful.

The important result of the calculations is the fact that they all obtained a chair conformation as the energy minimum rather than the C_2 twist form as is the case for *t*-C_8H_{14}. In this regard, minor discrepancies in the structural parameters, or even the larger differences found in the heats of formation, assume a secondary importance.

Conformational Automerization. The calculated transition state for the conformational automerization of *t*-C_7H_{12}·CuOTf has a twofold axis of symmetry bisecting the double bond and passing through C5 (Figure 4). As a result, the carbon atoms within the pairs (C1 C2), (C3 C7), and (C4 C6) are equivalent. The difference between the MOLBD and MNDO methods is insignificant.

The most direct way in which this transition-state structure can be reached from either the starting or the final equilibrium geometry is a distortion of the kind displayed in Figure 7; on going from the left-hand side to the transition state located in the center, C5 moves up while C6 moves down. The opposite is true when starting on the right-hand side. The two equilibrium geometries are related by a 180° rotation; hence the automerization process is a pseudorotation. In order to help the reader to visualize the motion involved, we have added to Figure 7 two of the intermediate structures reached near the transition state along the "direct" reaction path, namely, the one reached when the torsion angle 4567 is driven from its initial value of 84.1° (MOLBD, Figure 3) to a value of −10.0° and its counterpart on the product side (the energy profile shown is not the minimum energy path). Finally, a physically more meaningful display of the type of motion involved in the reaction is shown in Figure 8. Here, the two

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[27] Our attempts to grow crystals of CuOTf complexes suitable for X-ray analysis have not been successful.

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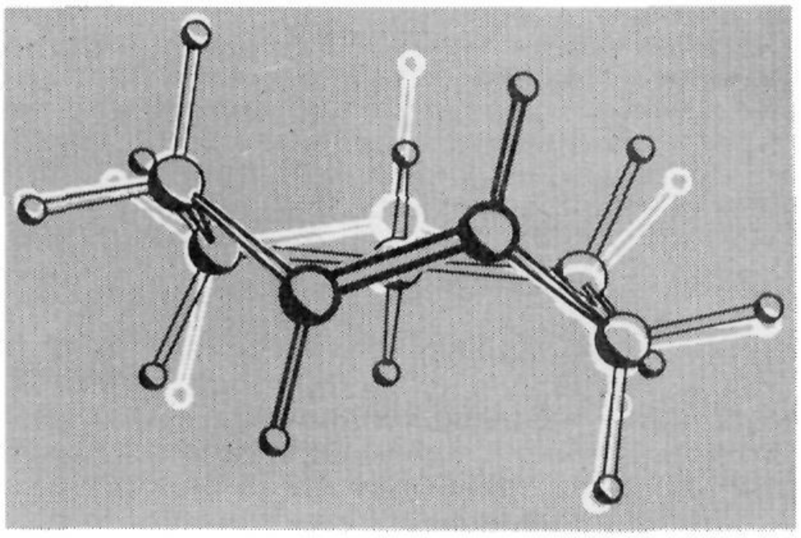

Figure 8. Black: the calculated (MOLBD III) transition-state geometry for the pseudorotation of free *trans*-cycloheptene. White: the geometry reached from the transition state upon displacement in the direction of the reaction coordinate (the normal mode with imaginary frequency).

superimposed structures indicate the direction of motion along the reaction coordinate at the transition state, i.e., the one normal mode of the transition state which has a negative force constant.

Conclusions

The ^{13}C DNMR behavior of the CuOTf complex of *trans*-cycloheptene shows that the equilibrium geometry of the olefin has no symmetry elements. The results of molecular mechanics and semiempirical quantum mechanical calculations show free t-C_7H_{12} to have an unsymmetrical chair equilibrium geometry.

It is proposed that the observed dynamical process is due to conformational automerization (pseudorotation) of the olefin. The calculated $\Delta G^{\ddagger}$ values for the automerization of the free olefin are 10.5 and 8.6 kcal/mol, using MOLBD and MNDO, respectively. They are in excellent agreement with the experimental value of 9.47 ± 0.20 kcal/mol found for t-C_7H_{12}·CuOTf at 299 °C, particularly in view of the fact that quantum mechanical calculations of this type are known generally to underestimate activation barriers.[22,30a] In principle, the agreement may be only apparent in that the calculation is on the free olefin and the measurement on a complexed olefin. As noted above, however, extrapolation of previous experience with similar olefins and complexes suggests strongly that the effects of the complexation on conformational mobility of the cycloalkenes are minor.

Experimental Section

The cycloalkene complexes were prepared according to ref 12 and 13. The ^{13}C NMR spectra were run on a Varian SC-300 spectrometer using dried, degassed diethyl ether as solvent. The probe temperature was calibrated with a ^{13}C chemical shift thermometer and has an absolute uncertainty of ±1 °C at the lowest temperature. The line-shape analysis employed a program based on the method of Nakagawa.[33] The error limits in the rate constants were taken from simulated spectra corresponding to values which are clearly either too fast or too slow based on visual fitting. The values of the free energy of activation were calculated from the Eyring equation, $\Delta G^{\ddagger}$ (cal mol^{-1}) = $1.9872T(23.7600 + \ln T - \ln k)$. The DNMR kinetic data for t-C_7H_{12}·CuOTf and c-C_8H_{14}·CuOTf are presented in the table.

The molecular mechanics calculations used the MOLBD III program[16] with modifications similar to those reported in ref 31. The MNDO calculation was done using the standard program of Dewar.[17]

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Registry No. 2, 69515-66-8; **3**, 69496-00-0; **5**, 85761-20-2; **7**, 51826-48-3; **8**, 85735-19-9.

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Study of Electron Distributions of Molecular Orbitals by Penning Ionization Electron Spectroscopy

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Abstract: Penning ionization electron spectroscopy (PIES) has been used to study spatial electron distributions of individual molecular orbitals. On the basis of comparison of observed band intensities with electron densities of ab initio molecular orbitals, a simple principle for orbital activities in Penning ionization has been established; the outer orbital which is exposed outside the van der Waals surface is active and the inner orbital which is localized inside the van der Waals surface is inactive. Penning ionization can be considered as an electrophilic reaction of rare gas atoms in metastable states with sample molecules. It is concluded that PIES is a sensitive method for probing orbital electron densities at the very frontier of the molecule where the molecule is attacked by the reagent.

The concept of the molecular orbital (MO) stems from the early days of the quantum theory. Its importance has been supported by a vast accumulation of experimental results and also by successful applications of quantum chemical methods to various problems. Although molecular orbitals are introduced on purely theoretical grounds, recent developments in photoelectron spectroscopy have made it possible to relate molecular orbitals to observed ionization bands for most closed-shell molecules.[1-3] Further, observed ionization potentials can be compared with theoretical orbital energies in many cases where Koopmans' theorem[4] is valid. This enables us to consider that individual electron energy levels in molecules can be observed experimentally. On the other hand, phenomena, which directly reflect orbital functions for "individual" molecular orbitals, have eluded observation hitherto, although "total" electron densities have been

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