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TRANS-CYCLOHEPTENE: SPECTRAL CHARACTERIZATION AND DYNAMIC BEHAVIOR

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Abstract: We have produced *trans*-cycloheptene via a singlet exciplex of the *cis* isomer and have obtained NMR and UV spectra of this strained cyclic alkene. This ring system undergoes a pseudorotation process with a barrier of 10.0 kcal/mole. The UV spectrum suggests a substantial twist to the double bond, but interestingly the vinyl H-H coupling constant implies a 180° dihedral angle for the vinyl protons.

Trans-cycloalkenes have long piqued the interest of the chemical community as a measure of the amount of strain that can be placed across a double bond. Cyclooctene is the smallest ring system that can accommodate a *trans* double bond and remain thermally stable at room temperature.[1] More recently *trans*-cycloheptenes[2] and even *trans*-cyclohexenes[3] have been hypothesized as intermediates during pulsed laser photolysis experiments.

Trans-cycloheptene (I) was originally detected by trapping with diphenylisobenzofuran when produced via an elimination of a thiocarbamate.[4] Early indication of photochemical production came from the presence of methanol trapping products during the photolysis of the *cis* isomer.[5] In a series of more recent papers Inoue developed what appears to be a singlet exciplex mechanism to form *trans* cyclic olefins from their *cis* counterparts.[6] While I was not spectroscopically observed, adding acidic methanol to previously photolyzed solutions 0.01M in both *cis*-cycloheptene and methylbenzoate led to ether trapping products. Addition of the acidic methanol after variable delay times gave a *trans* - *cis* barrier of 17.4 kcal/mole[6c] *though this was apparently complicated by the presence of* oxygen.[6d]

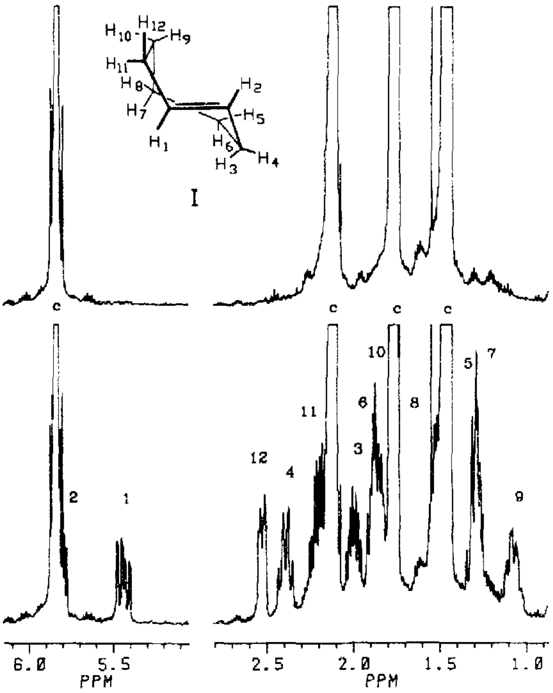

Figure 1. Bottom: 400MHz ^1H NMR spectrum at -90° of a 5:1 *cis:trans* cycloheptene mixture produced after 30 min photolysis. *Cis* peaks are labeled with a c while the trans resonances are numbered according to the figure. Top: Same sample at -90° after warming to -30° for 10 min.

Photolysis of a *cis*-cycloheptene copper(I) triflate complex gave the *trans* complex as shown by NMR, Raman and UV.[7] Further NMR spectroscopic examination of this complex by Michl's group showed that the ring was lacking in symmetry and showed the dynamic behavior predicted by force-field calculations.[8] Unfortunately release of the *trans* species from coordination to the copper was difficult. It was accomplished with trimethylphosphite in acetone solution, but paramagnetic impurities made it difficult to observe the NMR spectra[9] and other spectroscopic tools were not useful considering the mixture of species present. However a species was seen with seven ^{13}C resonances which decayed to the *cis* isomer upon warming. Neither dynamic NMR nor the vinyl proton coupling constant could be observed because of the paramagnetic broadening present, but it was felt, based on the chemistry of the *trans*-cyclooctene complex, that the freed species was I. The thermal decay rates observed were faster than the rates reported by Inoue and no methanol trapping products could be obtained.[9]

We felt that this important member of the strained cycloalkenes had not been well characterized and that the spectroscopic parameters would be helpful to our understanding of these systems. We decided to see if spectroscopically observable I could be generated via Inoue's singlet exciplex method. In fact we have used this method to obtain the complete proton NMR assignment, the ring dynamics and the UV spectrum of this critical molecule.

Results and Discussion

When a 0.25M solution in d_6-dimethylether of *cis*-cycloheptene with 0.01M methylbenzoate is photolyzed at -90° twelve new resonances are observed in the ^1H NMR spectrum.[10] Upon warming to -30° these resonances quickly decay with a concomitant increase in the *cis*-cycloheptene resonances (Figure 1). This suggests that the metastable species observed is the *trans* isomer. Confirmation of this assignment comes from the ring flipping process as revealed by dynamic NMR (Figure 3).[10] Thus we see the predicted totally unsymmetric *trans*-cycloheptene structure having twelve different hydrogens which undergo pairwise exchange via the ring psuedorotation.

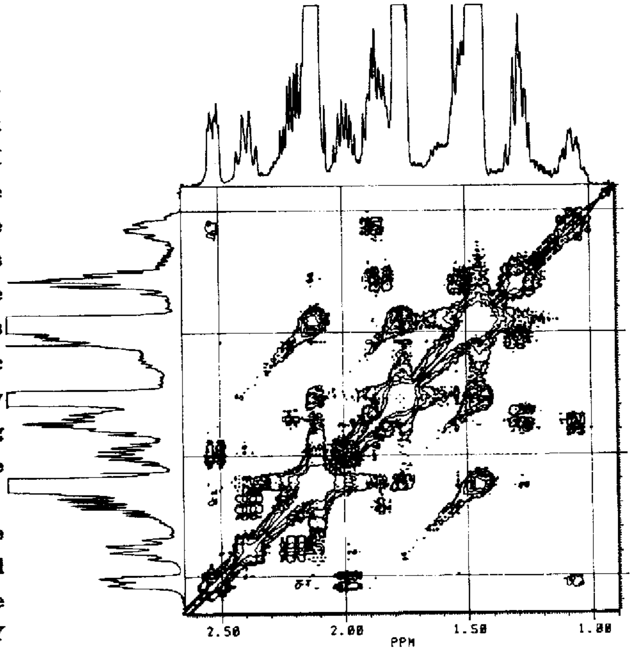

Figure 2. ^1H homo-NOESY 2D-NMR spectrum at -90° of the upfield region of a 4:1 *cis:trans* cycloheptene mixture.[11]

We have been able to assign all twelve resonances to the predicted MMPMI structure and obtain most of the coupling constants. The connectivities determined by a 2-D homo COSY spectrum allows sixty-four possible permutations of assignment patterns of the hydrogens. All but sixteen can be eliminated by considering the pairs of hydrogens that interconvert during the ring flip process, and of this set all but two assignment patterns can be eliminated by single-frequency decoupling experiments.[11]

TABLE 1: Chemical Shifts and Coupling Constants of Trans Cycloheptene in d_6-Dimethylether.

Hydrogen	Shift (ppm)	Coupling Constants (Hz)
1	5.43	$J_{1,2}$=18.0, $J_{1,4}$=1.1, $J_{1,11}$=10.9
2	5.80	$J_{2,3}$=5.7, $J_{2,4}$=10.2
3	1.99	$J_{3,4}$=11, $J_{3,6}$=6
4	2.38	$J_{4,5}$=10, $J_{4,6}$=0.5
5	1.28	
6	1.88	
7	1.28	$J_{7,9}$=10, $J_{7,10}$=6
8	1.51	$J_{8,9}$=2.2, $J_{8,10}$=6
9	1.06	$J_{9,10}$=11, $J_{9,11}$=11 $J_{9,12}$=4.8
10	1.85	$J_{10,11}$=5.2, $J_{10,12}$=0.5
11	2.19	$J_{11,12}$=10.9
12	2.52	$J_{1,12}$=2.8

Final assignment rests upon the 2-D homo-NOESY spectrum shown in Figure 2.[12] In the upfield region pictured strong cross peaks are seen at 1.06-1.88, 1.28-1.51, 1.28-1.85, 1.99-2.52, and 2.19-2.38 ppm caused by the chemical exchange between the paired protons. Additional cross peaks at 1.85-2.19, 1.06-2.52, 1.51-1.85 and 1.51-1.88 ppm show that these hydrogens are near one another spatially. Using as a basis the MMPMI calculated structure, of the two remaining possible assignments only the hydrogen assignment pictured above in Figure 1 would be expected to have these cross peaks in the NOESY spectrum. The chemical shifts and coupling constants are listed in Table 1. We have also obtained the ^{13}C NMR shifts of the seven carbons of I which match precisely with those reported by Michl's group demonstrating that they had indeed produced I. It is interesting that we see isomerization rates[11] about the same as those observed by Michl's group,[9] but faster than those reported by Inoue.[6c]

The dynamic ring flip process has been calculated by Michl to go through a C_2 symmetric transition state. As seen in Figure 3 using a modified Binch DNMR program[13] we simulated the vinyl region by using an unsymmetrical six spin system. As far as we know this is the largest spin system simulated and we were forced to use double precision on a Cray XMP/24[14] in order to avoid numeric instability problems. The simulation gave a $\Delta G^\ddagger$ of 10.0±0.1 kcal/mole for the ring flip process. Unfortunately the temperature range over which the dynamic NMR is observed is too narrow for accurate determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. Most of the error in our measurement comes from an estimated temperature error of 2° especially for the higher temperature spectra which had to be taken quickly since the lifetime of the *trans* species was only minutes at -30°.

Unlike Michl we find using MMPMI[15] that the lowest energy pathway for ring inversion is through a second unsymmetrical minimum. While this conformer of *trans* is predicted to be bound by only 0.5 kcal/mole and may therefore not actually be a minimum it is calculated to be 4.9 kcal/mole lower than the C_2 symmetric transition state calculated by Michl.[8] The barrier is calculated by MMPMI to be 7.7 kcal/mole.

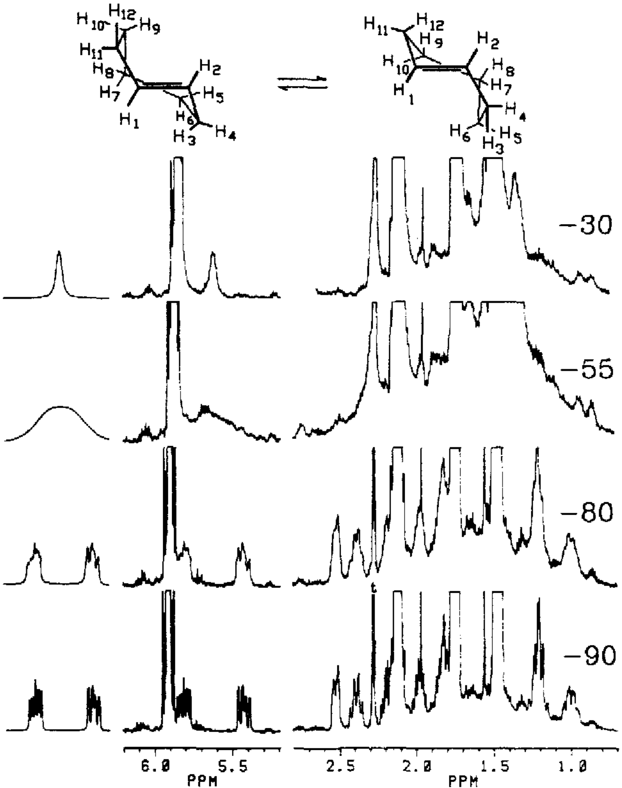

Figure 3. Right: Dynamic NMR spectra from -90° to -30° of I. The methyl of d_8-toluene is labeled with a t in the lowest spectrum.[10] Left: Simulated vinyl region.

The UV spectra pictured in Figure 4 show a species red-shifted from *cis*-cycloheptene which is produced upon photolysis with methylbenzoate (A) and decays upon warming (B).[16] Thus, the difference spectrum (C) in the figure represents the absorption of I, but this spectrum is complicated by a negative absorption due to the cis cycloheptene which is produced upon decay of the *trans* as well as the presence of the sensitizer, methylbenzoate. Thus the absolute red-shift from the *cis* isomer for I cannot be determined, though a 40 - 50 nm red-shift is consistent with the spectrum we find and with the shifts observed for the *trans* isomers of 1-phenylcycloheptene[17] and 2-cycloheptenone.[18] These shifts along with those of other *trans* cyclic alkenes have been interpreted as deriving from the twisting of the double bonds in the *trans* isomers. This twist is accompanied by a raising of the ground state and a lowering of the excited state because the minimum energy excited state for an alkene is the 90° twisted form. There appears to be a smooth progression in the *cis* to *trans* red-shift of 11 nm for cyclooctenes, about 50 nm for cycloheptenes and 100 nm for cyclohexenes.[17]

A crystal structure of an allylic substituted *trans*-cyclooctene shows an 18° twist and substantial pyramidalization (24°) of the vinyl carbons. MMPMI apparently underestimates the response of molecular geometry to the induced ring strain since 14.2° and 13.8° are predicted for the twist and pyramidalization angles respectively for *trans*-cyclooctene.

For I MMPMI predicts 25.6° and 23.4° for the twist and pryamidalization angles which again might be low. Indeed our UV result suggests a large twist for *trans*-cycloheptene, but interestingly our vinyl H-H coupling is large implying a 180° dihedral angle between the hydrogens. This is not a contradiction because MMPMI calculations[15] indicate that twisting and pyramidalization offset one another so that a nearly 180° (178°) dihedral angle is maintained for the H's while the $C_7C_1C_2C_3$ angle is predicted to be quite small (131°). One might expect this pyramidalization would lead to different ^{13}C-H coupling constants for the vinyl carbons between the *cis* and the strained *trans* isomers, but surprisingly this is not observed for the either the cycloheptene or cyclooctene isomers.[9]

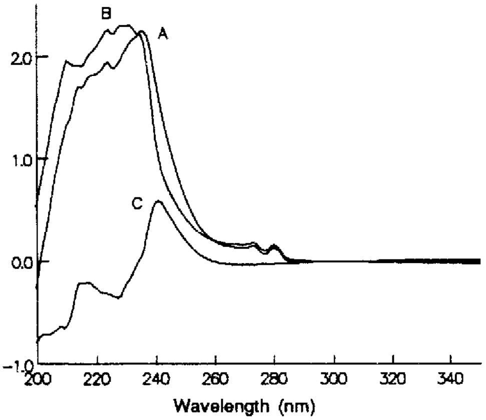

Figure 4. A. UV spectrum at -90° of photolyzed sample.[16] B. UV spectrum after warming and recooling. C. Subtraction of A and B.

Summary

We have spectroscopically characterized *trans*-cycloheptene and have shown that the species produced via Inoue's singlet exciplex mechanism[6] and by substitution with trimethylphosphite of the *trans*-copper(I) triflate complex[9] is I. The complete proton assignment of I could be made and the dynamic ring flip process observed. The UV spectrum shows a 40-50 nm red-shift which indicates substantial twist about the double bond while the vinyl proton coupling shows that these hydrogens have very close to a 180° dihedral angle. Thus as seen in *trans*-cyclooctene the vinyl carbons twist and pyramidalize to accommodate the strained ring and thereby create the 180° H-H dihedral angle.

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10. All spectra were obtained on a Bruker AM-400 NMR spectrometer with probes modified for improved low temperature capability. Dynamic NMR samples were prepared with the same concentrations as previous samples but in a 3:1 mixture of d_6-dimethylether:d_8-toluene in order to reveal the entire vinyl region of I.
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16. UV samples were prepared by photolyzing 0.6 ml of a HPLC grade pentane solution of 0.025M *cis*-cycloheptene and 0.001M methylbenzoate for 6 min at -118°. This sample was then diluted by rapid cannulation directly into a cuvette containing 2.5 ml of pentane pre-cooled to -100°. UV spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer.
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