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THE STATIC AND DYNAMIC CONFORMATIONAL PROPERTIES OF *CIS, CIS,TRANS* -1,5,9-CYCLODODECATRIENE

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Abstract : *cis, cis, trans*-1,5,9-Cyclododecatriene (**1**) exists as a mixture of one symmetrical conformation (C_2-symmetry) and two rapidly interconverting unsymmetrical conformations (and their two mirror image conformations). Copyright © 1996 Published by Elsevier Science Ltd

The four stereoisomers of 1,5,9-Cyclododecatriene are of significant synthetic and theoretical interest.[1,2] The conformational features of three of these stereoismers have been elucidated, while those of the *cis, cis trans* -1,5,9-cyclododecatriene (**1**) have remained elusive.[1,3] We now report on conformational properties of **1** as evidenced by dynamic NMR spectroscopy [4] and iterative force-field calculations.[1,5]

The 251-MHz ^1H NMR spectrum of **1** consists of four broad multiplets at -5°C, which broaden appreciably as the temperature is lowered, reaching maximum width at -60°C and giving rise to overlapping multiplets at -170°C.[6] The low temperature ^1H NMR spectra of **1** are too complex for any meaningful interpretation, however the observed dynamic NMR effect indicates that a conformational process with a barrier of 9.9 kcal/mol must occur in **1**.

The 63.1-MHz ^{13}C NMR spectra of **1** in the temperature range from -5 to -170°C are shown in figure 1.[7] Each of the allylic and vinylic carbon resonances splits into two lines (total of twelve lines) at -92°C (T_c= -60°C, $\Delta G^{\neq}$ = 10.2 kcal/mol). The relative intensities of the allylic and vinylic absorptions change appreciably over the temperature range from -70 to -130°C (figure 2) without any apparent broadening in line width and no new peaks were observed down to -170°C .[8] Hence the change in relative intensities is due to entropy effects.[9]

Force-field calculations indicate that the lowest energy conformation in **1** is the symmetrical conformation **1A** (C_2-symmetry) followed by the two unsymmetrical conformations **1B** and **1C** (figure 3), both of which have virtually the same calculated strain energy (0.9 kcal/mol less stable than **1A**).[10] The two conformations **1B** and **1C** as well as their mirror image conformations **1B*** and **1C*** can interconvert via a calculated energy barrier of only 5.2 kcal/mol relative to the strain energy of the lowest energy conformation **1A**. Hence this interconversion (**1B** == **1C** == **1C*** == **1B***) should be fast on the NMR time scale even at -170°C, leading to time-averaged C_s-symmetry for the two unsymmetrical conformations **1B** and **1C** and only three allylic and three vinylic carbon absorptions should be observed for these two conformations. Force-field calculations indicate that the interconversion of conformations **1A** and **1B** can occur via a calculated barrier of 10.0 kcal/mol relative to the strain energy of conformation **1A**,[11] in excellent agreement with the experimental (free energy) barrier observed in the ^1H and ^{13}C NMR spectra of **1**.

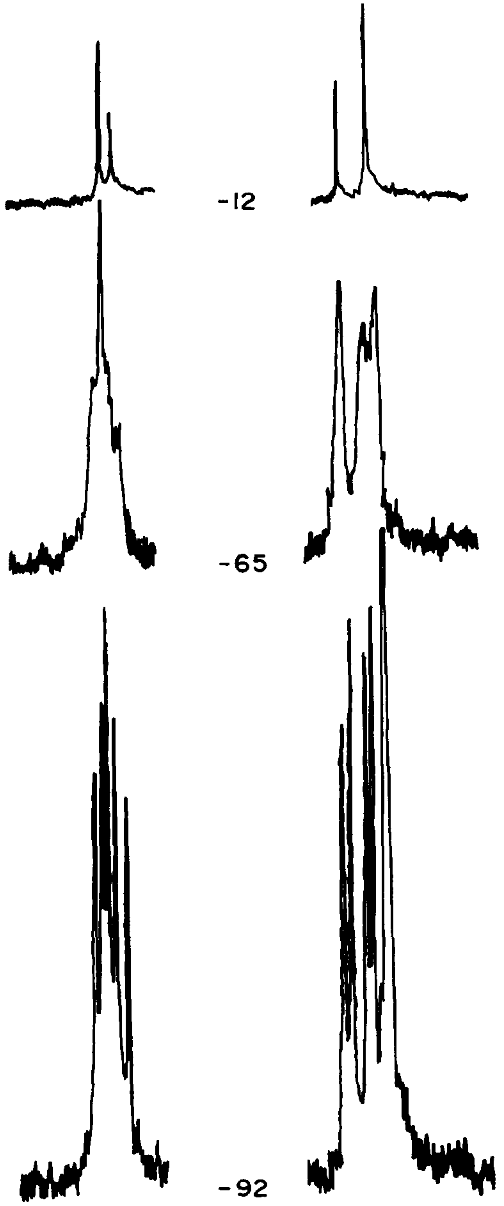
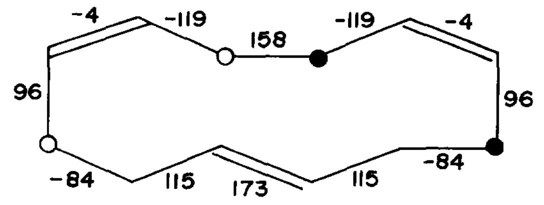
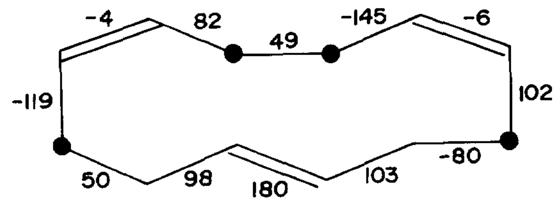


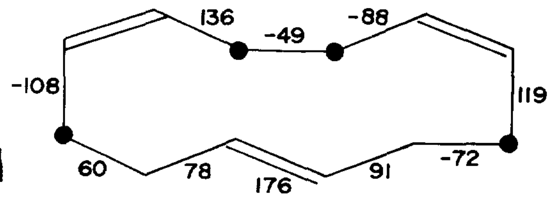
Figure 1: 63.1-MHz ^{13}C NMR spectra of *cis,cis,trans*-1,5,9-Cyclododecatriene (**1**) in $CHCl_2F/CHClF_2$ (4:1) at various temperatures.



1 A (6.9 kcal/mol)



1B (7.8 kcal/mol)



1C (7.8 kcal/mol)

Figure 3: Calculated torsional angles and total strain energies of the low energy conformations of *cis, cis, trans*-1,5,9-Cyclododecatriene (**1**).

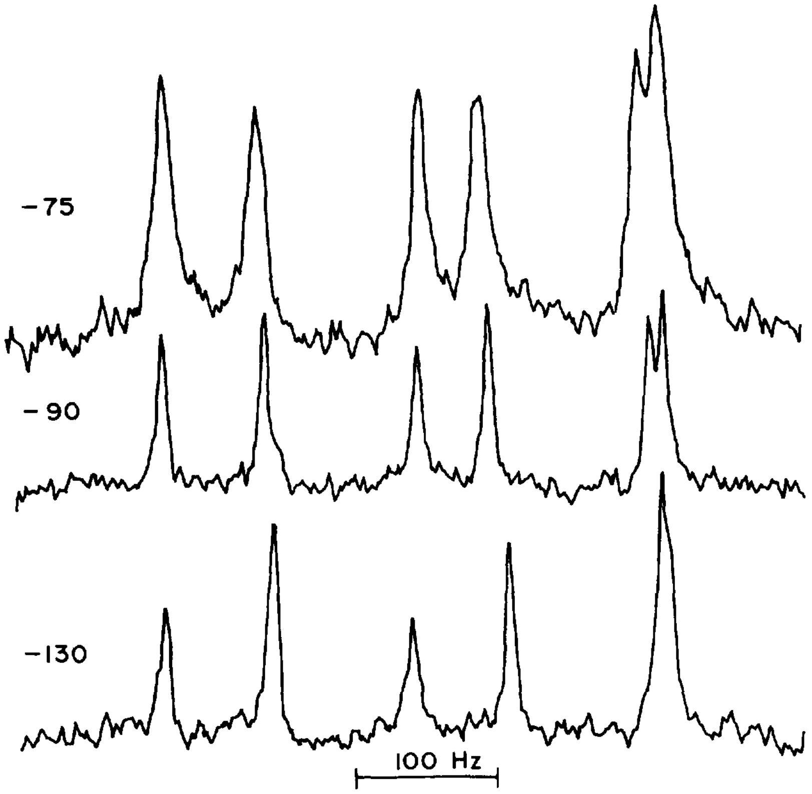


Figure 2 : 63.1 MHz ^{13}C NMR spectra of the aliphatic region of *cis, cis, trans* -1,5,9-Cyclododecatriene in $CHCl_2F/CHClF_2$ (4:1) at various temperatures.[8]

The ^{13}C NMR spectrum of **1** at -170°C can thus be rationalized in terms of a mixture of one symmetrical conformation **1A** and two rapidly interconverting unsymmetrical conformations **1B** and **1C** (as well as **1B*** and **1C***). The conformational process which is observed in the dynamic ^1H and ^{13}C NMR spectra of **1** must then involve the interconversion of the preferred conformation **1A** with **1B** and **1C** and their mirror image conformations. This interconversion leads to time-averaged C_{2v} -symmetry in **1** and results in the mutual exchange of all the different carbons on the one hand and all the different hydrogens on the other.

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4. All NMR spectra were measured on a superconducting selenoid spectrometer operating at 59 kG. ^{1}H NMR spectra were obtained in a frequency sweep mode, while ^{13}C NMR spectra were obtained by the Fourier transform technique with the protons noise decoupled. For variable temperature studies a mixture of $CHFCl_2$ and CHF_2Cl(4:1) was used as a slovent, and a ^{19}F peak of the slovent was employed for lock purposes. In both ^{1}H and ^{13}C NMR spectra tetramethylsilane was used as an internal reference.

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6. The ^{1}H NMR spectrum of **1** at -15°C consists of four broad multiplets with the following chemical shifts: δ (ppm) 2.05, 2.13, 5.36, and 5.49.

7. Owing to chemical shift coincidences, the ^{13}C NMR spectrum of **1** in the fast exchange region consists of four instead of the expected six resonances. At -12°C, the following chemical shifts are exhibited: δ(ppm) 27.3, 31.0, 129.8 and 131.2. At -92°C the spectrum consists of the following chemical shifts: δ (ppm) 25.8, 26.0, 27.9, 28.6, 30.3, 31.4, 128.9, 130.3, 131.0, 131.4, 131.7 and 132.5.

8. The change in relative intensities of the allylic absorptions in the ^{13}C NMR spectra of **1** was monitored over the temperature range from -70 to -170°C under the following experimental conditions: 45° pulse angle, 2K data points, 2015 Hz spectrum width, and an exponential broadening function corresponding to 4Hz broadening. In order to avoid any reflected peaks from the vinylic carbons or solvents a long pulse was employed. Such a pulse was used to excite the allylic carbons only while the remaining carbons in the spectrum were unaffected.

9. The symmetry and mixing contributions to entropy of the symmetrical conformation **1A** is zero (-R ln2 + R ln2) and for the two unsymmetrical conformations **1B** and **1C** is 2.8 eu (R ln2 + R ln2). For the equilibium **1A** == [**1B** + **1C**], the equilibirum constant (K) was obtained from the expanded ^{13}C NMR spectra of the allylic carbons.[6] Hence at -90°C, K = 0.88, $\Delta G^{o} = 50$ cal/mol and $\Delta H^{o} = 560$ cal/mol, while at -75 and -130°C, K= 1.05 and 0.61 respectively.

10. The vibrational frequencies of all the conformations of **1** were calculated and in each case 3N-6 real vibrational frequencies were obtained indicating that each of these conformations corresponds to a true (local) energy minimum with respect to any small geometric distortion; For the conformational transition states 3N-7 real frequencies were obtained.

11. The interconversion of conformations **1A** and **1B** occur via conformation **1D** as an intermediate and psudorotation partner. **1D** has a calculated total strain energy of 12.1 kcal/mol and exhibits the following torsional angles (starting from the torsional angle of the *trans* double bond) : 173, 115, -70, 96, -3, -111, 158, -114, 4, -9, 77, and -1.

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