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THE CONFORMATIONS OF CIS-CYCLODODECENE. EVIDENCE FROM DYNAMIC NMR SPECTROSCOPY AND ITERATIVE FORCE-FIELD CALCULATIONS

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Summary cis-Cyclododecene shows conformational barriers of 7 and 9.6 kcal/mol and exists as a mixture of two unsymmetrical conformations, labelled [$1_{ene}2333$] and [$1_{ene}2342$].

cis-Cyclododecene (I) is a readily available compound and is valuable as a synthetic intermediate,[1] yet nothing is known concerning its conformational properties. Indeed, very little is known about the conformations of the large-ring cycloalkenes in general.[2] The relationship of the conformations of the cycloalkenes to those of the corresponding cycloalkanes is of interest, since much is known about the latter subject.[3,4] We now report on the conformations of I as evidenced from dynamic NMR spectroscopy and iterative force-field calculations.

The 251-MHz ^1H NMR spectra (in $CHCl_2F$) of I at various temperatures are shown in Figure 1. The allylic hydrogen absorption changes from a single line (δ 2.14) at -12°C, to two bands (δ 1.80, 2.45) of equal intensities at -94°C ($T_c \simeq -65°C$, $\Delta G^{\ddagger} \simeq 9.6$ kcal/mol). The high-field band in turn splits into two new bands at -150°C while the low-field band only broadens. The olefinic hydrogen absorption of I which is a single line (δ 5.35) at -12°C gives rise to two bands (δ 5.32, 5.63) in the ratio of ca. 2:1 ($\Delta G° \simeq 0.2$ kcal/mol) at -150°C, ($T_c \simeq 128°C$, $\Delta G^{\ddagger} \simeq 6.8$ kcal/mol) and this clearly indicates that more than one conformation are populated at this temperature.

The 63.1-MHz ^{13}C NMR spectra of I in the temperature range from -5 to -150°C exhibit rather simple changes in the olefinic region, whereas those in the aliphatic region are complex. The sharp band of the olefinic carbons (δ 131.2) at -5°C, broadens as the temperature is lowered, and gives rise to three chemical shifts (δ 128.9, 131.7 and 133.0) at -150°C, in an intensity ratio of 2:1:2 respectively. The absorption at 131.7 ppm is slightly broader than the other two absorptions and

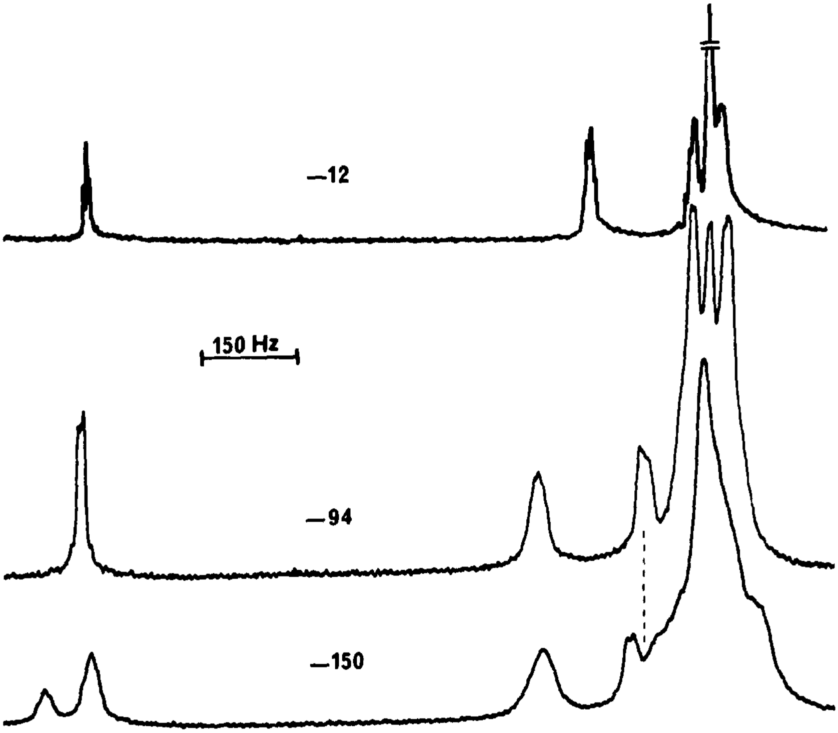


Figure 1. 251 MHz ^{1}H NMR spectra of I in $CHCl_2F$ at various temperatures.

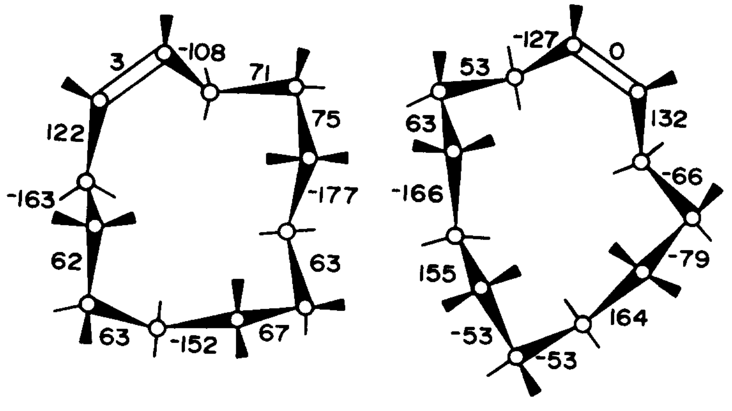
this is most probably due to an overlap of two bands. The low-temperature ^{13}C spectrum of I can be rationalized in terms of two conformations in a ratio of 2:1 ($\Delta\underline{G}° \simeq 0.2$ kcal/mol); the lines at 128.9 and 133.0 ppm are ascribed to the major conformation, and the overlapping lines at 131.7 ppm are assigned to the minor conformation. The barrier ($\Delta\underline{G}^{\ddagger}$) of the conformational process associated with the dynamic NMR effect at -120°C is of the order of 7.0 kcal/mol, in agreement with the lower o the two barriers obtained from the ^{1}H spectra.

In order to obtain further evidence for the conformations of I we turned to iterative force-field calculations.[5] Altogether seven different conformations of I have been computed (Table 1).[6] The $[1_{ene}2333]$ conformation is of lowest energy, followed by the $[1_{ene}2342]$, $[1_{ene}2423]$ and $[1_{ene}3233]$ respectively (Figure 2). Hence the major and minor conformations observed in the ^{13}C NMR spectrum of I at -150°C are the $[1_{ene}2333]$ and $[1_{ene}2342]$ respectively. On the assumption that the only mechanism of exchange is the interconversion of these two conformations and their mirror images (i.e., $[1_{ene}2333] \rightleftharpoons [1_{ene}2342] \rightleftharpoons [1_{ene}2342]^* \rightleftharpoons [1_{ene}2333]^*$) the barrier observed in both the ^{13}C and ^{1}H NMR spectra ($\Delta\underline{G}^{\ddagger} \simeq 7$ kcal/mol) can then be ascribed to the separation of these two conformations. At temperatures above ca. -120°C the interconversion of the two conformations of I

Table 1. Calculated Strain Energies (kcal/mol) of Various Conformations of cis-Cyclododecene (I) and Some Conformational Transition States of Cyclododecane (II).

Conformation[a] (I)	RSE[b]	Conformational Transition State[c] (II)	RSE[d]
$[1_{ene}2333]$	0.0	$[\underline{1}2333]^{\ddagger}$	0.0
$[1_{ene}2342]$	0.6	$[\underline{1}2342]^{\ddagger}$	2.0
$[1_{ene}2423]$	1.6	$[\underline{1}2423]^{\ddagger}$	4.8
$[1_{ene}3233]$	2.1	$[\underline{1}3233]^{\ddagger}$	0.0
$[1_{ene}353]$	2.9		
$[1_{ene}2234]$	4.7		

[a] All conformations have $\underline{C}_1$ symmetry; see Note 6 for nomenclature. [b] Strain energy relative to that of the $[1_{ene}2333]$ conformation of I, whose total strain energy is 9.9 kcal/mol. [c] See Reference 4 for nomenclature. [d] Strain energy relative to that of the $[\underline{1}2333]^{\ddagger}$ transition state of II.



$[1_{ene}2333]$ $[1_{ene}2342]$

Figure 2. Torsional angles of the $[1_{ene}2333]$ and $[1_{ene}2342]$, conformations of cis-cyclododecene.

must be rapid on the NMR time scale and only the time-averaged chemical shifts are observed. The second conformational process ($\Delta G^{\ddagger} \simeq 9.6$ kcal/mol), which is observed only in the ^{1}H spectra, gives rise to, for example, site exchange of the inner- and outer-allylic (gem) hydrogens. The pathway for this exchange is not clear at the present time, but it must lead, in conjunction with the first process, to a time-averaged C_{2v} symmetry.

The four lowest-energy conformations of I are related to the four lowest conformational transition states in cyclododecane (II) in the manner shown in Table 1. In both systems there is always present a one-bond side which has a torsional angle close to zero. Because of their structural differences, I and the cyclododecane transition states have significantly different calculated strain-energies.

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References and Notes

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(6) The nomenclature used to describe the various conformations of *cis*-cyclododecene is an extension of the shorthand notation proposed by Dale[2,4] for the conformations of the cycloalkanes. The numbers of bonds on consecutive sides of a conformation are concatenated and placed in square brackets, starting with the *cis*-double bond, which gives rise to a one-bond side and is marked by the subscript "ene". The direction around the ring is so chosen that the second number is the smallest possible.

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