High-resolution Variable-temperature ^{1}H and ^{13}C NMR of a 1,8-Bis-*gem*-substituted Cyclotetradecane

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Cyclotetradecane-1,8-dione-bis(ethylene ketal) has been investigated by variable temperature ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra reveal two conformational processes with corresponding activation free energies of 38.3 (0.8) kJ mol^{-1} and 31 kJ mol^{-1}, respectively. The low energy process is also visible in the ^{13}C NMR spectra; the free energy barrier is found to be 31.6 (0.8) kJ mol^{-1} at $-103°$. Based on observed lineshape changes and chemical shift arguments we conclude that the title compound exists in a diamond lattice [3434] conformation with the *gem*-dioxa substituents on corner positions. Conformational interconversion modes are discussed.

Cyclotetradecane belongs to the family of "large-membered" rings in which transannular nonbonded repulsions are absent.[1] Cyclotetradecane is thought to be conformationally homogeneous and have the rectangular diamond lattice conformation.[2] An examination of the conformation of this hydrocarbon using ordinary molecular models (*e.g.* Dreiding models) is not very fruitful, and the molecule appears to be exceedingly flexible, even if non-bonded atoms are kept reasonably far apart. A semiquantitative strain-energy calculation carried out by Dale,[3] however, suggests that the diamond lattice or [3434] conformation is distinctly lower in energy than any other conformation.

Cyclotetradecane has been investigated by variable temperature ^{13}C NMR.[4] In the first attempt,[4a] the spectrum at low temperature $(-132 °C)$ of the natural abundant ^{13}C compound contains peaks of an approximately 4:1:2 intensity ratio. In the second attempt,[4b] four well-resolved lines in the ratio of 2:2:2:1 are observed for (1-

^{13}C)cyclotetradecane. These results are consistent with a [3434] conformation. A successful interpretation of the lineshape changes requires that the low-temperature spectrum must be assigned correctly, which is difficult in the present case, because two low-field lines are separated by only 0.6 ppm.

We now report a study of the temperature dependence of ^{1}H and ^{13}C NMR spectra of cyclotetradecane-1,8-dione-bis(ethylene ketal) (I).
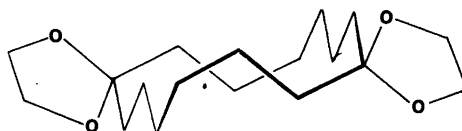
I

This compound has many features similar to the parent hydrocarbon. It is a 1,1,8,8-tetrasubstituted cyclotetradecane and only one conformer is possible on the lowest energy [3434] ring conformation, since the geminal substituents are restricted to corner positions.

EXPERIMENTAL

Cyclotetradecane-1,8-dione-bis(ethylene ketal) was prepared by azeotropic distillation from a mixture of the diketone and ethylene glycol in benzene containing a little p-toluene-sulfonic acid, in the same way as described for other ketones by Hartley.[5] Cyclotetradecane-1,8-dione was prepared from suberic acid by ketene cyclization.[6]

NMR Spectra. NMR spectra were obtained on a superconducting solenoid spectrometer operating at 59 kG.[7] The proton spectra were obtained with standard 5-mm sample tubes in a frequency-sweep mode. The ^{13}C spectra are Fourier transforms of accumulated free-induction decays and were obtained with 10-mm tubes with the magnetic field locked on a ^{19}F peak of the solvent. A 1:1 mixture of $CHCl_2F$ and $CHClF_2$ was used as solvent. All temperatures were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample and connected to a Newport Laboratories digital thermometer reading to 0.1 °C and accurate to 0.2 °C. The variable temperature unit was calibrated with methanol, and for very low temperatures with a thermocouple situated inside the spinning sample tube. The chemical shifts are referenced to internal tetramethylsilane.

Free energies of activation were calculated from rate constants by the absolute rate theory with a transmission coefficient of 1. The rate constants were obtained at the coalescence temperatures of the separated peaks in the ^1H NMR spectra by the expression $k = \Pi\Delta v/\sqrt{2}$.* The erros given in the text are our best estimates of 90 % confidence limits and include possible systematic errors and the effects of couplings and natural line widths. As a result of high power (*ca.* 10W) used for decoupling protons in the ^{13}C spectra, the temperature measurements associated with these spectra are of lower accuracy (± 3 °C) than those of the ^1H spectra (± 1 °C). The accuracy (0.8 kJ mol^{-1}) of the free-energy barriers obtained from the ^{13}C spectra was entirely adequate for determining a correspondence with one of the two barriers obtained in the ^1H spectra.

RESULTS AND DISCUSSION

The ^1H NMR spectra of I at various temperatures are given in Fig. 1. The spectrum above -53 °C consists of a resonance for ethylene ketal bridge protons at 3.83 ppm, ring protons α to the ketal groups at 1.55 ppm and the rest of fourteen-membered ring protons in the range of 1.47 to 1.24

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*This expression is strictly valid for an exchange process between two equally populated sites and where exchange is the only broadening effect; errors resulting from coupling and natural line-width effects are least when the chemical shift difference is greatest. The experimental data available are not suitable for obtained meaningful values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, even though the errors in $\Delta G^{\ddagger}$ are not large. (Anet, F. A. L. and Anet, R., *Dynamic Nuclear Magnetic Resonance Spectroscopy*, In Cotton, F. A. and Jackman, L. M., Eds., Academic, New York 1975, p. 543).
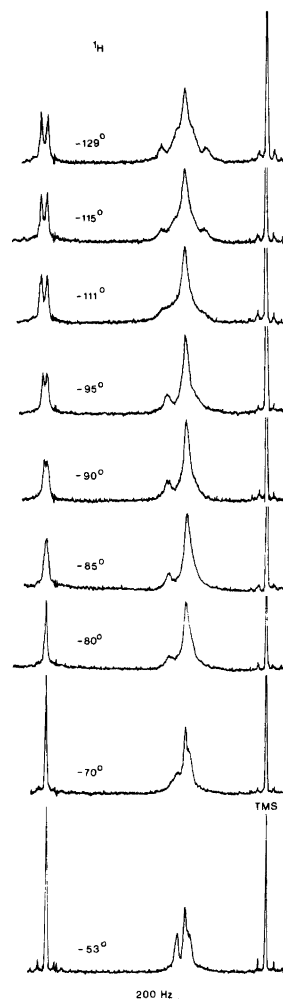

Fig. 1. The 251 MHz ^1H NMR spectra of I (3.5 % in a 1:1 mixture of $CHCl_2F$ and $CHClF_2$) at various temperatures.

ppm. Below -75 °C, the α protons split into two resonances, ($\Delta v = 120$ Hz; the high field portion is hidden), with a corresponding activation free energy ($\Delta G^{\ddagger}_{-75°C}$) of 38.3 (0.8) kJ mol^{-1}. The same process is visible in the ethylene ketal bridges with a coalescence temperature of -84 °C; the $\Delta G^{\ddagger}_{-85°C}$ is 38.8 (0.8) kJ mol^{-1}. Below -95 °C, a second process is visible. The most reasonable interpretation is that the band at $\delta = 1.73$ splits into two resonances with a separation of 34 Hz (where the high field portion is hidden). The lower energy

Table 1. Dynamic NMR data.

Nucleus	Probe	T_c K	$\Delta\nu$ Hz	$\Delta G^{\neq}$ kJ mol^{-1}
^{1}H	protons α to ketal bridge	198	120	38.3(0.8)
^{1}H	ethylene glycol units	189	27	38.8(0.8)
^{1}H	protons α to ketal bridge	162	~34	~31
^{13}C	α carbons	170	260	31.6(0.8)

process is calculated to have a $\Delta G^{\neq}$ of about 31 kJ mol^{-1} at -111 °C. The changes in the rest of the spectrum are too complex for analysis. The ^{1}H NMR data are listed in Table 1.

The ^{13}C NMR spectra of I are shown in Fig. 2. The spectrum at ambient temperature contains the following resonances: at 63.5 ppm for the carbons in the ethylene ketal bridges; at 34.9 ppm for carbons α to the quaternary carbons; at 27.2 and 22.5 ppm for the carbons β and γ to the quaternary carbons. The assignment of which resonances correspond to the β and γ carbons is not straightforward, as will be discussed later. The quaternary carbons which resonate at 110.8 ppm are not shown. The spectrum at -143 °C shows that there are two types of α, β and γ carbons. The resonance from the quaternary carbons remains a single line. The chemical shifts for the carious resonances are listed in Table 2. The activation free energy fro the ^{13}C visible process is 31.6 (0.8) kJ mol^{-1} at -103 °C calculated from a separation of 260 Hz for the α carbons. The ^{13}C NMR data are included in Table 1.
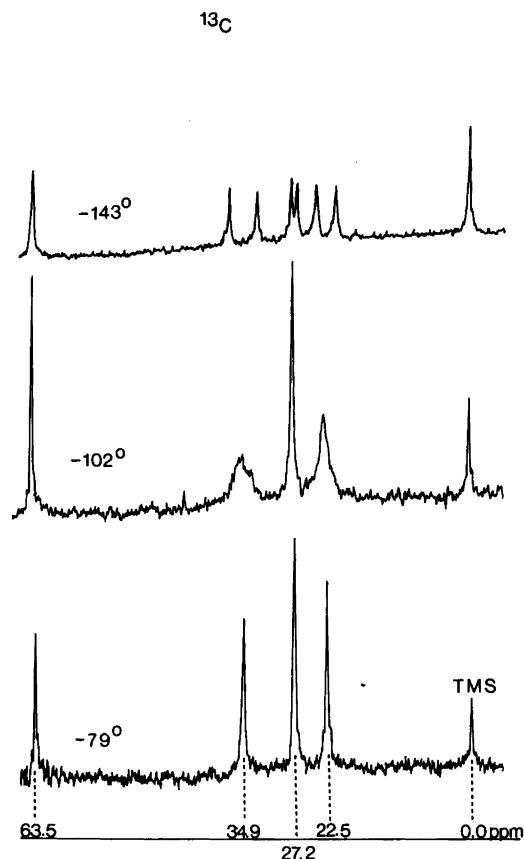

Fig. 2. The 63.1 MHz ^{13}C NMR spectra of I at various temperatures, with the protons noise decoupled.

Table 2. ^{13}C chemical shifts and effects.

Conformational sites[a]	Observed chemical shifts[b] -79 °C	-143 °C	Observed splitting	Chemical shift effects[c]	Predicted splitting
quaternary	110.7	110.8		$2V_g$	
α	34.9	36.1	4.3	$\gamma+V_g+2V_t$	$\gamma-V_t=4.2$
α'		31.8		$2\gamma+V_g+V_t$	
γ'	27.2	27.4	0.5	$2V_g$	$\gamma-V_g+V_t=2.3$
γ		26.9		$\gamma+V_g+V_t$	
β	22.5	23.8	3.0	$3\gamma+2V_t$	$V_g-V_t=2.7$
β'		20.8		$3\gamma+V_g+V_t$	

[a] As given in Fig. 3. [b] In parts per million downfield from Me$_4$Si. [c] Includes the effect from the *gem*-dioxa substituents, γ = 5 ppm, V_g = 3.5 ppm, V_t = 0.8 ppm.

The observation derived from the ^{1}H NMR data is supported by the ^{13}C NMR spectra. As expected, only the lower energy process is observed with both probes.

[13]C chemical shifts in saturated hydrocarbons show regular features that are relatively well understood,[8] at least from an empirical point of view. In the conformation of the compound under discussion, two contributions to the ^{13}C NMR shifts should be of importance, namely the γ and the "vicinal – gauche" (V_g) effect. The γ effect results in an upfield shift of about 5 ppm for the terminal carbons in a gauche butane fragment. The V_g effect occurs for the two central carbons in the same fragment, and results in an upfield shift, but is somewhat smaller (3.5 ppm) than the γ effect. A third effect, V_t, has also been postulated, and occurs for the central carbons in an anti butane fragment, but its magnitude (ca. 0.8 ppm upfield) is much smaller than that of either the γ or the V_g effect. Still another complication is to what extent the oxygen atoms will contribute differently to the γ-, V_g- and V_t-effects compared to methyl or methylene groups. We have not tried to differentiate between oxygen atoms and methylene groups in this respect. It has been found that the γ effect varies considerably in magnitude and depends on the precise structure of the compound examined.

Despite the uncertainties enumerated above, we have found it quite useful to compare the observed chemical shifts in I with those calculated from chemical-shift effects present in an appropriate conformation, namely the [3434] conformation as shown in Fig. 3. The results are given in Table 2. With arguments using chemical-shift effects we find that
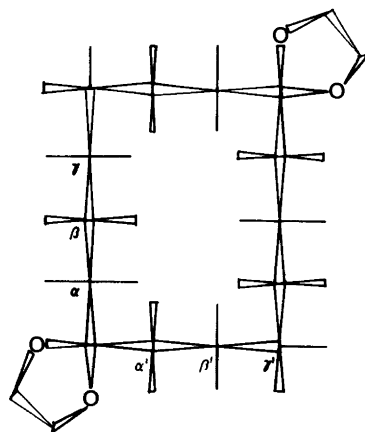

Fig. 3. Wedge representation[3] of the [3434] conformation of I. The letters α, α', β, β', γ and γ' refer to carbon sites.

the β carbons are more shielded than the γ carbons.* The agreement between observed and predicted splitting of the resonances is excellent for the α- and the β-carbons, but not so good for the γ-carbons. The chemical shift for the quaternary carbons in I (100.8 ppm) agrees well with the shift for C-2 in 2,2-dimethyl-1,3-dioxolane (108.5 ppm).[9]

The available results preclude detailed com-

*This is consistent with the situation in cyclotetradecane itself. The middle carbon on the 4-side in the [3434] conformation has a relative intensity of 1 and can therefore be assigned (δ 23.1). The resonance at δ 21.4 probably belongs to the carbons on the 3-side, see Ref. 4a.
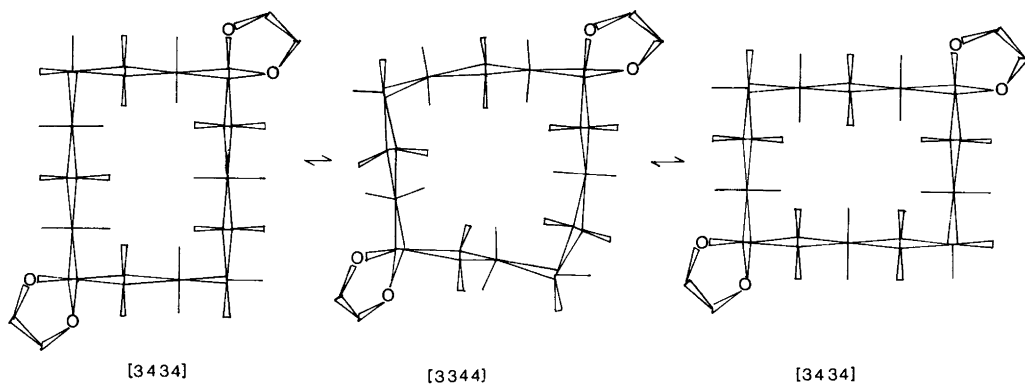

Fig. 4. Partial pseudorotation itinerary for the [3434] conformation of I which averages carbon sites and leaves geminal hydrogens non-equivalent.

parisons, and a larger body of data is needed for determination of γ-, V_g- and V_t-values in large ring compounds. Nevertheless, the assignments made in Table 2 show reasonable agreement with the [3434] conformation having substituents at corner positions.*

Finally, we may consider the line-shape changes in both the ${}^1H$ and the ${}^{13}C$ NMR spectra at intermediate temperature. The lowest energy pseudorotation mechanism for the [3434] conformation with 1,8-bis-*gem*-substituents, involves, according to Dale's semiquantitative calculations,[3] the following itinerary: [3434]→ [3434]→[3434] as shown in Fig. 4. This leads to exchange of the carbon atom sites, but the methylene hydrogens remain geminally non-equivalent. It is worth noticing that the barrier calculated from the ${}^{13}C$ spectrum agrees very well with the low-temperature process in the ${}^1H$ spectrum. To achieve site exchange so as to reach the high-temperature spectrum requires passage over barriers with higher energies, because the *gem*-dioxa substituents can no longer remain at relatively unhindered corner positions. The present analysis leads to a free energy of activation for the overall high energy process of $38.3\,(0.8)\,kJ\,mol^{-1}$ at $-57\,°C$. The precise nature of the barriers involved in the high-energy process is difficult to predict at this stage and will be the topic of future empirical force-field calculations. However, it suffices to state that the difference between the high- and low-energy process of only $7.1\,kJ\,mol^{-1}$, indicates that *gem*-dioxa substituents require much less space than *gem*-dimethyl groups.**

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*Infrared spectroscopy and dipole moment studies also suggest that this conformation is the exclusive one in solution. Alvik, T., Borgen, G. and Dale, J. *Acta Chem. Scand. 26* (1972) 1805.

**A discussion of the effect of placing *gem*-dimethyl groups on conformational energies and barrier heights has been done by Dale (*Acta Chem. Scand. 27* (1973) 1149) and by Anet and Anet, Ref. 4b, p. 562.

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