# Conformational Inversion Rates in the Dimethylcyclohexanes and in Some *cis*-Decalins

**Don K. Dalling, David M. Grant,*[1] and LeRoy F. Johnson**

*Contribution from the Department of Chemistry, University of Utah,*
*Salt Lake City, Utah 84112, and from the Instrument Division,*
*Varian Associates, Palo Alto, California 94303.* *Received October 2, 1970*

**Abstract:** Carbon-13 magnetic resonance (cmr) data over the temperature range 211–318°K has been used to study the kinetic process associated with conformational inversion in some dimethylcyclohexane and decalin ring systems. Rate constants and activation enthalpies and entropies are reported for 1,1-, *cis*-1,2-, *trans*-1,3-, and *cis*-1,4-dimethylcyclohexane and for the parent and 9-methyl-*cis*-decalin. The results may be rationalized in terms of previous data on similar systems and steric interactions. The advantages of cmr technique in kinetic studies of conformational interconversions are delineated.

Nuclear magnetic resonance has been used extensively for the determination of the thermodynamic parameters associated with conformational equilibration of hydrocarbons such as cyclohexane and related compounds.[2] Most studies have utilized protons[3–16] or fluorine-19[17–21] magnetic resonance. In this work we would like to suggest and to investigate the use of carbon-13 magnetic resonance (cmr) as an alternative to that of $^{1}$H or $^{19}$F which, under favorable circumstances, offers some unique and desirable advantages.

Proton resonance has proved very useful for the investigation of conformational equilibration, but it suffers from two deficiencies. First, proton resonances usually exhibit complex, homonuclear spin–spin splittings which create difficulty in determining rate constants from the line width and the coalescence temperature studies normally used. This problem has been circumvented in numerous cases by extensive deuteration and subsequent double resonance of the deuterium.[22] The second limitation arises from the fact that the chemical-shift changes exhibited by protons in different conformers are generally small. This tends to limit the temperature range over which the approximate equations used for calculating equilibration rate constants can be employed. The rate constants must be determined accurately over a wide range of temperature in order to calculate the activation parameters (other than the Gibbs free energy of activation, $\Delta G^{\ddagger}$) with any accuracy. Fluorine, which has a much greater sensitivity to molecular environment and thus exhibits much larger chemical shifts between conformers, has been substituted for hydrogen in somewhat successful attempts to overcome the small chemical-shift difficulty. A problem does arise with this approach, however, since fluorine is much heavier and somewhat larger than hydrogen, thereby raising the question as to whether the parameters determined by $^{19}$F resonance will in fact apply to the original, unsubstituted molecules.

Many of the above difficulties might be avoided by investigating the temperature dependence of the natural abundance, proton-decoupled cmr spectra of conformationally equilibrating hydrocarbons. The principal advantages are the following: (1) molecules of interest may be examined directly without the need for extensive deuteration; (2) there is often more than one equilibrating resonance in a molecule which can provide useful corroborative data; (3) there are often nonequilibrating sites in a molecule which are convenient for use in determining reference line widths; and (4) the chemical shifts between carbon resonances in a single conformer and thus between carbon resonances which interchange environments are in general sufficiently large and varied to provide a rather wide range for temperature study. The larger chemical shifts provide an additional advantage in that the coalescence temperature of carbon resonances will be correspondingly higher than those of protons, making the temperature range of interest more accessible. A disadvantage of utilizing cmr in rate studies (when compared with pmr techniques) is that there is a large number of compounds, such as cyclohexane, which, because of symmetry, do not have carbon resonances which average between two environments, thus making the method inapplicable in these cases. As subjects for a preliminary study, we have chosen the four dimethylcyclohexanes (1,1-, *cis*-1,2-, *trans*-1,3-, and *cis*-1,4-) and two decalins (*cis*- and 9-methyl-*cis*-) which are intercon-

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(1) University of Utah.

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(21) J. T. Gerig and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2791 (1966).

(22) For examples see ref 6, 8, and 15.

verting between conformers of equal energy and thus have equal populations and lifetimes. These compounds in their two interconverting isomeric forms are given as follows for the convenience of the reader.

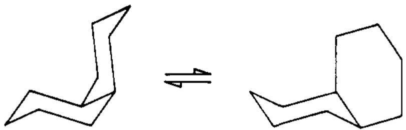
1,1-

cis-1,2-

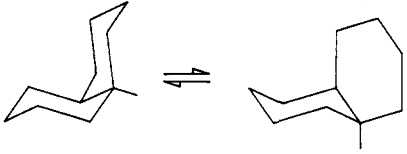
trans-1,3-

cis-1,4-

cis-



cis-9-methyl-



## Experimental Section

The dimethylcyclohexanes used in this study were procured on loan from the American Petroleum Institute or purchased from standard commercial sources; all were of very high purity as indicated by their proton and cmr spectra. The *cis*-decalin sample was obtained from K and K Laboratories and was found to have a few per cent of *trans*-decalin impurity. The sample of *cis*-9-methyldecalin was synthesized by Dr. E. G. Paul at the University of Utah and his help is acknowledged. The neat liquids had been vacuum degassed and sealed in 5 mm o.d. sample tubes but the tubes were opened for introduction of a capillary of $^{13}$C enriched methyl iodide for use as an internal field-frequency lock, and they were not resealed.

The $^{13}$C spectra were run using a Varian HA-100 spectrometer operating at 25.14 MHz. Frequency-swept spectra were obtained with a V-3530 RF/AF sweep unit and proton noise decoupling was accomplished with a V-2512-1 heteronuclear spin decoupler. Sweep widths covered were between 500 and 1000 Hz and the sweep time for each scan was 100 sec. A Varian C-1024 time averaging computer was used for multiple scan accumulation of the spectra, generally three–six scans. A V-6040 temperature controller was calibrated using a direct reading thermocouple potentiometer, and the same settings were used for each compound.

The temperature dependence of the $^{13}$C spectrum of *cis*-decalin is presented in Figure 1 as an example of the type of spectra obtained in this study.

## Results and Calculations

The rate constants for conformational inversions were determined by the method of line shapes,[23] as described by Anet and Bourn.[15] The data for the compounds studied are presented in Table I along with the relevent spectral parameters required in the calculation of the rate constants.

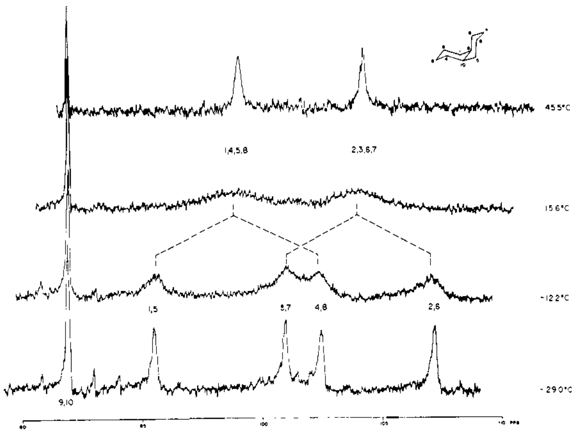


Figure 1. Carbon-13 magnetic resonance spectra for *cis*-decalin are portrayed as a function of temperature. The very sharp peak due to C-9,10 exhibits no kinetic averaging due to identical chemical environments in both conformational forms. The remaining eight carbons give rise at low temperatures to a four-line spectrum which collapses into two lines under rapid kinetic averaging at higher temperatures. Neither the low-temperature nor high temperature methylene singlets are as sharp as the bridgehead peaks due to residual kinetic effects.

At temperatures somewhat above coalescence the approximate equation used for calculating rate constants ($k$) was

$$k = \pi \nu_{AB}^2/2\delta\nu \qquad (1)$$

where $\nu_{AB}$ is the chemical shift in hertz between carbons which interchange environments due to conformational inversion, and $\delta\nu$ is the corrected line width at half-height (in hertz), *i.e.* the width which is due only to conformational interchange. A correction is needed to compensate for broadening due to a finite transverse relaxation time, magnetic field inhomogeneities, and sweep rate broadening. The latter two contributions undoubtedly dominate line widths of nonexchanging carbons since effects due to relaxation processes are negligible for carbons in hydrocarbon liquids as a result of their relatively long relaxation times. In any case, compensation was made for all factors other than exchange by subtracting the values of reference line widths from those affected by kinetic averaging. The widths of reference lines are also given in Table I.

At the coalescence temperature, the rate is given by

$$k = \pi \nu_{AB}/\sqrt{2} \qquad (2)$$

and the coalescence temperatures given in Table I are accurate to better than ±5°. This error produces scatter in $\Delta G^{\ddagger}$ of only about ±0.2 kcal/mol.[16]

At temperatures below coalescence where the two lines of each pair are broad but not overlapping, eq 3 may be used to calculate the rate constant

$$k = \pi \delta\nu \qquad (3)$$

where $\delta\nu$ is calculated as before except that the width of the two lines was averaged before subtracting the reference.

Because of variability of the homogeneity with temperature and the relatively low signal-to-noise ratio attainable with naturally abundant carbon-13, consistent resolution was difficult to maintain, but the usual inhomogeneity broadening was less than 2.5–3.0 Hz. Since very accurate line shapes for narrow lines required more time averaging than we chose to do, line

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[23] (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965, Chapter 9; (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 10.

**Table I.** Experimental Data and Rate Constants

| Compound ($\nu_{AB}$)[a] | Temp,[b] °C | Carbons | Line width[j] | Ref line | Line width[j] | $k$, sec$^{-1}$ |
|---|---|---|---|---|---|---|
| 1,1-Dimethylcyclohexane | 15.6 | $CH_3$ | 5.4 | 1 + 4 av | 3.0 | 39,600 |
| | 0.8 | $CH_3$ | 7.3 | 1 + 4 av | 3.4 | 24,400 |
| ($\nu_{ae}$ = 246) | −12.2 | $CH_3$ | 17.7 | 1 + 4 av | 3.0 | 6,470 |
| | −29.0 | $CH_3$ | 58.5 | 1 + 4 av | 3.3 | 1,720 |
| | −36 ± 2 | $CH_3$ | | Coalescence[c] | | 546 |
| | −62.0 | $CH_3$ | 12.8[d] | 1 + 4 av | 4.1 | 27.3 |
| *cis*-1,2-Dimethylcyclo- | 0.8 | $CH_3$ | 6.0 | *e* | 3.8 | 32,100 |
| hexane | −12.2 | 3,6 | 6.0 | *e* | 3.8 | 7,140 |
| ($\nu_{1,2}$ = 36.7[f]) | −12.2 | 4,5 | 5.8 | *e* | 3.8 | 2,010 |
| ($\nu_{3,6}$ = 100 ± 10) | −12.2 | $CH_3$ | 16.4 | *e* | 3.8 | 5,600 |
| ($\nu_{4,5}$ = 160 ± 10) | −29.0 | 1,2 | 6.0 | *e* | 3.8 | 982 |
| ($\nu_{ae}$ = 212 ± 10) | −29.0 | 3,6 | 12.4 | *e* | 3.8 | 1,830 |
| | −29.0 | 4,5 | 26.4 | *e* | 3.8 | 1,780 |
| | −29.0 | $CH_3$ | 35.0 | *e* | 3.8 | 2,260 |
| | −42.9 | 1,2 | 7.4 | *e* | 3.8 | 588 |
| | −42.9 | 3,6 | 40.0 | *e* | 3.8 | 434 |
| | −42.9 | 4,5 | 84.0 | *e* | 3.8 | 501 |
| | −42.9 | $CH_3$ | 98.0 | *e* | 3.8 | 749 |
| | −63 ± 5 | 1,2 | | Coalescence | | 81.5 |
| | −58 ± 5 | 3,6 | | Coalescence | | 222 |
| | −54 ± 5 | 4,5 | | Coalescence | | 355 |
| | −49 ± 5 | $CH_3$ | | Coalescence | | 471 |
| *trans*-1,3-Dimethyl- | −29.0 | 4,6 | 9.8 | 2 + 5 av | 4.9 | 3,920 |
| cyclohexane | −42.9 | 4,6 | 36.0 | 2 + 5 av | 4.5 | 610 |
| ($\nu_{4,6}$ = 110.6) | −42.9 | $CH_3$ | 58.0 | 2 + 5 av | 4.5 | 500 |
| ($\nu_{1,3}$ = 32.9 ± 1.0) | −56.4 | 1,3 | 19.0 | 2 + 5 av | 5.4 | 125 |
| ($\nu_{CH_3}$ = 130.4) | −55 ± 5 | 4,6 | | Coalescence | | 246 |
| | −60 ± 3 | 1,3 | | Coalescence | | 73.1 |
| | −46 ± 3 | $CH_3$ | | Coalescence | | 290 |
| | −62.0 | 4,6 | 26.0 | 2 + 5 av | 5.5 | 64.4 |
| | −62.0 | 1,3 | 31.6 | 2 + 5 av | 5.5 | 82.0 |
| | −62.0 | $CH_3$ | 27.1 | 2 + 5 av | 5.5 | 67.9 |
| *cis*-1,4-Dimethylcyclo- | −12.2 | $CH_3$ | 5.3 | *g* | 2.9 | 13,000 |
| hexane | −29.0 | 1,4 | 13.5 | *g* | 2.9 | 4,180 |
| ($\nu_{2,3,5,6}$ = 52.0) | −29.0 | $CH_3$ | 13.9 | *g* | 2.9 | 2,840 |
| ($\nu_{1,4}$ = 168.0) | −42.9 | 2,3,5,6 | 11.0 | *g* | 2.9 | 524 |
| ($\nu_{CH_3}$ = 141.0) | −42.9 | 1,4 | 70.0 | *g* | 2.9 | 661 |
| | −42.9 | $CH_3$ | 45.0 | *g* | 2.9 | 741 |
| | −56.4 | 2,3,5,6 | 39.5 | *g* | 2.9 | 116 |
| | −59 ± 3 | 2,3,5,6 | | Coalescence | | 116 |
| | −50 ± 5 | 1,4 | | Coalescence | | 373 |
| | −54 ± 5 | $CH_3$ | | Coalescence | | 313 |
| | −62.0 | 2,3,5,6 | 27.6 | *g* | 2.9 | 77.6 |
| | −62.0 | 1,4 | 27.4 | *g* | 2.9 | 77.0 |
| | −62.0 | $CH_3$ | 25.4 | *g* | 2.9 | 70.7 |
| *cis*-Decalin | 45.5 | 1,5,4,8 | 7.5 | 9,10 | 2.8 | 10,000 |
| ($\nu_{1,4,5,8}$ = 173.0) | 45.5 | 2,6,3,7 | 7.0 | 9,10 | 2.8 | 8,990 |
| ($\nu_{2,3,6,7}$ = 155.0) | 27.1 | 1,5,4,8 | 26.8 | 9,10 | 2.5 | 1,930 |
| | 27.1 | 2,6,3,7 | 24.6 | 9,10 | 2.5 | 1,710 |
| | 15.6 | 1,5,4,8 | 56.2 | 9,10 | 3.0 | 884 |
| | 15.6 | 2,6,3,7 | 51.5 | 9,10 | 3.0 | 778 |
| | 8 ± 5 | 1,5,4,8 | | Coalescence | | 384 |
| | 5 ± 5 | 2,6,3,7 | | Coalescence | | 344 |
| | 0.8 | 1,5[h] | 80.0 | 9,10 | 3.3 | 241 |
| | 0.8 | 2,6[h] | 73.5 | 9,10 | 3.3 | 221 |
| | −12.2 | 1,5,4,8 | 22.6 | 9,10 | 4.0 | 58.4 |
| | −12.2 | 2,6,3,7 | 27.2 | 9,10 | 4.0 | 72.9 |
| | −29.0 | 1,5,4,8 | 6.8 | 9,10 | 3.9 | 9.1 |
| | −29.0 | 2,6,3,7 | 6.8 | 9,10 | 3.9 | 9.1 |
| 9-Methyl-*cis*-decalin | 45.5 | 1,8 | 22.5 | 9 + 10 av | 3.1 | 7,310 |
| ($\nu_{1,8}$ = 300.5) | 45.5 | 3,6 | 8.0 | 9 + 10 av | 3.1 | 7,210 |
| ($\nu_{4,5}$ = 8.4 ± 0.5) | 27.1 | 1,8 | 88.5 | 9 + 10 av | 2.8 | 1,660 |
| ($\nu_{3,6}$ = 150.0) | 27.1 | 3,6 | 26.3 | 9 + 10 av | 2.8 | 1,500 |
| ($\nu_{2,7}$ = *i*) | 0.8 | 3,6 | 150 | 9 + 10 av | 3.1 | 241 |
| | 8 ± 5 | 1,8 | | Coalescence | | 668 |
| | −20 ± 5 | 4,5 | | Coalescence | | 18.7 |
| | −5 ± 5 | 3,6 | | Coalescence | | 333 |
| | −29.0 | 4[h] | 9.2 | 9 + 10 av | 3.9 | 16.7 |
| | −29.0 | 3,6 | 7.2 | 9 + 10 av | 3.9 | 10.4 |

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[a] In hertz (±2 Hz) except as noted. In the cases studied here the chemical shift, $\nu_{AB}$, between interconverting conformers remained constant over the relevant temperature ranges, even though the shift values relative to $CH_3I$ varied appreciably as a result of the temperature dependence of the $CH_3I$ shift value. [b] ±1.0° except as noted. [c] Data given before coalescence temperatures were treated by the fast exchange approximation; those given afterward were treated by the slow exchange approximation. [d] All line widths given below coalescence are averages of the two lines except as noted. [e] No reference line was available in this compound; the line width of the narrowest line measured at 45.5° was used. [f] The removal of coalescence was never achieved for this resonance signal; the value given was calculated using the set of parameters given in the Ph.D. Thesis of D. K. Dalling, University of Utah, 1969, p 62. [g] No reference line was available in this compound; the average of all three resonance line widths at 45.5° was used. [h] Only one line width was used here, since the other half of the pair overlapped another resonance severely; see Figure 1. [i] The removal of coalescence was never achieved for this signal. Use of the parameters noted in footnote *f* above was not considered justified, since the value $\nu_{AB}$ must be <3 Hz. [j] Hertz.

**Table II.** Activation Parameters from Least-Squares Regression Analysis of Rate Data

| Compound | Temp range, °K | $\Delta H^{\ddagger}$,[a] kcal/mol | $\Delta S^{\ddagger}$,[b] eu | $\Delta G^{\ddagger}$,[c] kcal/mol | Corr coeff | *F* test of variance |
|---|---|---|---|---|---|---|
| 1,1-Dimethylcyclohexane | 211.2–288.8 | 11.3 | 3.7 | 10.2 | 0.995 | 410 |
| *cis*-1,2-Dimethylcyclohexane | 211.2–274.0 | 9.3 | −3.5 | 10.3 | 0.961 | 170 |
| *trans*-1,3-Dimethylcyclohexane | 211.2–244.2 | 11.1 | 4.5 | 9.8 | 0.976 | 163 |
| *cis*-1,4-Dimethylcyclohexane | 211.2–261.0 | 11.0 | 4.1 | 9.8 | 0.991 | 624 |
| *cis*-Decalin | 244.2–318.7 | 13.6 | 3.5 | 12.6 | 0.999 | 4731 |
| 9-Methyl-*cis*-decalin | 244.2–318.7 | 12.4 | −0.7 | 12.6 | 0.994 | 678 |

[a] ±0.7 kcal/mol; for discussion of errors see text. [b] ±3 eu; for discussion of errors see text. [c] Calculated at 298° using the parameters of this table.

widths giving a $\delta\nu$ of <2.0 Hz were not utilized in any of the calculations.

In the past the empirical Arrhenius eq 4, where $k_r$ is

$$k_r = A \exp(-E_a/RT) \qquad (4)$$

the rate constant, $A$ the frequency factor, and $E_a$ the activation energy, has often been used to treat rate data. However, as Harris and Sheppard have pointed out,[4b] discussion usually centers around the enthalpy, $\Delta H^{\ddagger}$, and the entropy, $\Delta S^{\ddagger}$, of activation as derived from the Eyring equation (5) of absolute reaction rate theory.

$$k_r = (\kappa kT/h)\exp(-\Delta G^{\ddagger}/RT) = \kappa(kT/h)\exp(\Delta S^{\ddagger}/R)\exp(-\Delta H^{\ddagger}/RT) \qquad (5)$$

Thus $-R \ln (hk_r/kT\kappa)$ was plotted against $10^3/T$, giving a slope of $\Delta H^{\ddagger}$ and an intercept of $-\Delta S^{\ddagger}$. The actual values were calculated by least-squares linear regression analysis, and the data for *cis*-decalin are plotted in Figure 2 as a typical example of the scatter in data found for the compounds in this study. The results are summarized in Table II.

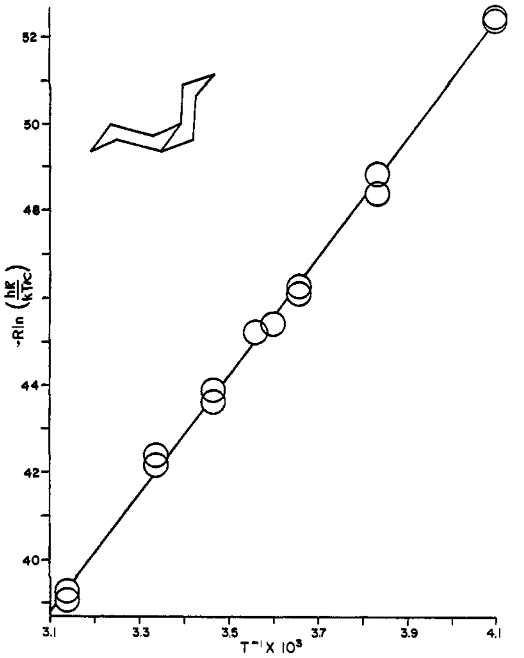

Figure 2. Logarithmic *vs.* $1/T$ plot for *cis*-decalin.

The transmission coefficient, $\kappa$, is introduced into eq 5 as a convenient means of accounting for the metastable boat configurations which double the maxima in the energy barriers to inversion. A compound in this configuration may revert to its original conformation, rather than completing the conformational inversion. For example, 1,1-dimethylcyclohexane converts from the chair form to a flexible or boat form which is considered to have the same probability of returning to its original state as of completing the conversion to the mirror image. As the experiment measures the rate of chair-to-chair conversion, it is necessary to use a $\kappa = 0.5$ if the correct values for $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ are to be obtained from the chair-to-chair rate data. Figure 3 presents representations of energy *vs.* inversion coordinate for the two types of compounds used in this study. In both compounds the double maxima in the barrier gives rise to a $\kappa$ of 0.5. The situation is somewhat more complicated for *cis*-decalin, as it has at least three metastable forms instead of one (see Figure 3) giving rise to four separate energy barriers which must be traversed before the complete chair–chair to chair–chair conversion has been completed.[24]

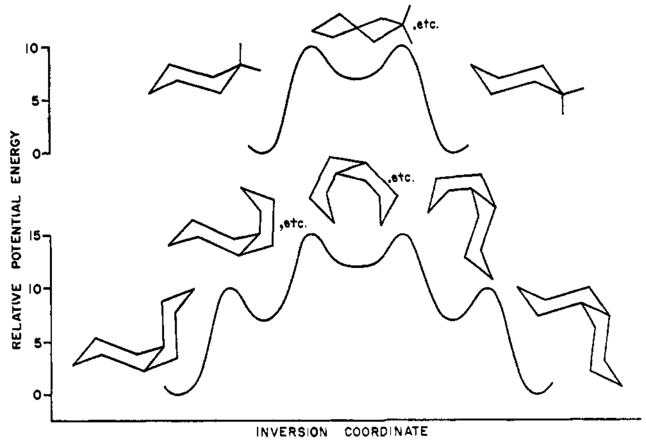

Figure 3. The energetics of ring inversion are shown schematically for 1,1-dimethylcyclohexane (upper trace) and *cis*-decalin (lower trace). Representative structures are given for each of the minima in the reaction coordinate.

The error limits specified in Table II are not statistical ones, but rather represent an estimate of probable errors from scatter in the data. The only available direct comparison of the results with literature values is for 1,1-dimethylcyclohexane and *cis*-decalin. Friebolin, *et al.*,[8a] using a deuterated analog of the 1,1-dimethyl compound, determined values for $\Delta G^{\ddagger}$ of 10.4 and 10.5 kcal/mol at about −60°. The value determined by the use of the parameters of Table II for

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(24) A $\kappa = 0.5$ is justified in this case with the assumption that if the first and fourth barriers are sufficiently lower than the second and third barriers then the boat–chair and chair–boat metastable configurations will make no effect on the transmission coefficient.

$\Delta G^{\ddagger}$ at the same temperature is in excellent agreement, being 10.5 kcal/mol. Jensen and Beck,[8b] using a theoretical estimate of $\Delta S^{\ddagger}$ of 2.5 eu and a measured $\Delta G^{\ddagger}$ of 12.8 kcal/mol at −18°, calculated a $\Delta H^{\ddagger}$ of 13.4 kcal/mol for *cis*-decalin. At −18°, a value of 12.7 kcal/mol is calculated for $\Delta G^{\ddagger}$ for *cis*-decalin using the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of Table II. The free-energy results for *cis*- and 9-methyl-*cis*-decalin also compare well with those determined by Gerig and Roberts[21] for the various conformers of the 2,2-difluoro-substituted *cis*-decalins ($\Delta G^{\ddagger}$ = 11.6–12.4 and 12.0–12.8 kcal/mol for compounds analogous to *cis*-decalin and to 9-methyl-*cis*-decalin, respectively). The average $\Delta H^{\ddagger}$ of 13.9 kcal/mol and $\Delta S^{\ddagger}$ of 5.3 eu calculated from Gerig and Roberts[21] data for the low-energy conformations of the three *cis*-decalins also are in excellent agreement, but their results for the low-energy conformation of the 3,3-difluoro-9-methyl cis compound ($\Delta H^{\ddagger}$ = 9.8 kcal/mol and $\Delta S^{\ddagger}$ = −10 eu) differ considerably from ours. It is presumed that their large negative values for $\Delta S^{\ddagger}$ account for the discrepancy, or else some unexplained fluorine substituent effect is influencing the kinetic parameters in those compounds having both methyl and fluorine substituents.

## Discussion

With the exception of *cis*-1,2-dimethylcyclohexane, all of the activation parameters for the dimethylcyclohexanes fall within experimental error of the very precise activation parameters ($\Delta H^{\ddagger}$ = 10.8 kcal/mol and $\Delta S^{\ddagger}$ = 2.8 eu) reported by Anet and Bourn.[15] This agreement is a little surprising in light of the fact that each of these three compounds possesses an axial methyl group which produces steric repulsion energy of 1.7 kcal/mol in the ground state due to interaction with 3,5 axial protons.[25] Thus, it might have been expected that the energy barrier to inversion would be decreased for the dimethyl compounds relative to the cyclohexane parent because of the more energetic ground state of the methyl-substituted species. It can only be concluded, therefore, that the activated flexible forms are also destabilized by methyl groups relative to the corresponding cyclohexane transition state which presumably is a half-chair with four carbons in a near-planar configuration. Hendrickson[26] made an estimate of 12.7 kcal/mol for the inversion barrier of cyclohexane due to various steric features, *i.e.*, changes in dihedral angles causing increased bond eclipsing, distortion of normal valency angles, and nonbonded repulsions between hydrogen atoms. Of these three contributions, the torsional distortion was found to constitute the greater part of the inversion barrier. Harris and Sprague observed[16] that chain branching increases such torsional barriers by 0.7 kcal/mol in going from propane to isobutane. Thus, if both methyl groups contribute that much torsional strain to the barrier to inversion and thereby destabilize the activated species by about 1.4 kcal/mol, then the lack of a difference in energy barriers between the parent and dimethyl compounds is rationalized for the trans-1,3-, cis-1,4-, and 1,1-dimethyl species.

The situation for the cis-1,2 molecule is, of course, more complex since the additional gauche interaction between the methyl groups contributes another 0.9 kcal/mol (approximately) of nonbonded repulsion energy above that found in *trans*-1,3- or *cis*-1,4-dimethylcyclohexane. Furthermore, the adjacent methyls may force the ring flattening to be found essentially at the four unsubstituted ring carbons. The considerably reduced $\Delta H^{\ddagger}$ (9.3 kcal/mol) does support the relative destabilization expected for the ground state, and the lower entropy of activation (−3.5 eu) does seem consistent with the decreased freedom proposed for ring inversion in the transition state. It is interesting that the apparently lower enthalpy and entropy of activation for this compound, however, does give rise to a $\Delta G^{\ddagger}$ which is coincidentally comparable to the other dimethyl species at 298°K.

The above arguments rest on the supposition that the energy difference between the various nonequivalent half-chair forms is not sufficient to favor a lower energy transition state significantly. This is supported by the entropy results, which are not less than that found for cyclohexane ($\Delta S^{\ddagger}$ = 2.8 eu[15]) except in the cis-1,2 compound, as would be expected if there was one half-chair of much lower energy than all others. Since the error limits of the $\Delta S^{\ddagger}$'s are rather large it is hazardous to draw too many conclusions from the entropy values, but is significant that the $\Delta S^{\ddagger}$'s for all compounds are in a reasonable range for the structure of the proposed activated state.

As a result of potential energy calculations there was some debate earlier as to whether the ground state of *cis*-decalin is a two-chair[21] or a two-boat[27] configuration. The rather high barrier found for this compound is in agreement with other recent evidence[21] in favor of the two-chair conformation. A double-boat form of *cis*-decalin would have a conformational barrier considerably less[21] than that found in Table II.

Measurements[28] of the energy of the boat form of cyclohexane relative to the chair form gave an energy difference of 4.8 kcal/mol. If the heights of the two barriers of the inversion coordinate of *cis*-decalin given in Figure 3 are about the same as that of cyclohexane, 10 kcal/mol, and the first well is about 5 kcal/mol above the ground state, then the measured free energy of activation should be about 15 kcal/mol, which is in reasonable accord with that found experimentally. Some reduction, however, in the height of the second barrier may occur from ring–ring interactions once one boat form has been introduced into the structure.

One might be concerned that proton decoupling would cause errors in the shape of the $^{13}$C resonance lines, and thus in the rate constants, because of nuclear Overhauser effects, but this has been shown to be untrue for pmr.[15] The same is assumed to be valid for cmr, as long as the decoupling is complete which was the case in this study.

It is concluded that cmr is a valuable tool in the investigation of kinetic processes, especially in the study of conformational interconversions.

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