

liquid boiling at 85–94° (0.3 mm.). Redistillation afforded 3.9 g. (71%) of XV, b.p. 89–91.50° (0.2 mm.), n^{24}_D 1.5380.

Anal. Calcd. for $C_{15}H_{21}Cl$: C, 76.09; H, 8.94; Cl, 14.97. Found: C, 75.94; H, 8.85; Cl, 14.82.

A solution of 7.3 g. (0.031 mole) of XV in 30 ml. of ethanol was hydrogenated over 5% palladium on charcoal at room temperature and several atmospheres of pressure. Hydrogen was slowly absorbed for 20 hr. The solution was filtered, the solvent was distilled at

atmospheric pressure, and the residue (5.74 g.) was subjected to preparative gas chromatography (205°, 20% silicone on Chromosorb W, Perkin-Elmer Model 154 vapor fractometer). The major component (of six) was collected; it had an infrared spectrum identical with that of VIII obtained from cyclization of X.

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Mechanism of Conformational Changes in Medium-Sized Rings. Nuclear Magnetic Resonance Studies of 1,1,4,4-Tetramethyl-6,7-benzocycloheptene

Ernest Grunwald¹ and Elton Price

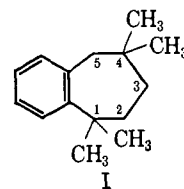
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The n.m.r. spectrum of racemic 1,1,4,4-tetramethyl-6,7-benzocycloheptene at low temperatures is that of a mixture of two racemic conformational isomers called *d,l-B* and *d,l-C*. Evidence is presented that the seven-membered ring is in the boat conformation in the *B*-isomer, and in the chair conformation in the *C*-isomer. The equilibrium constant, $K = [C]/[B]$, was obtained from the n.m.r. data and is represented by the equation, $\log K = -0.026 + 69.2/T$; $\Delta H^\circ = -317 \text{ cal.}$; $\Delta S^\circ = -0.12 \text{ e.u.}$ From observations of proton exchange, two separate conformational changes could be characterized. The first is isomerization without racemization, $d-C \rightleftharpoons d-B$ and $l-C \rightleftharpoons l-B$. Kinetic results are: $\log k_{C \rightarrow B} = 10.919 - 2134/T$; $\Delta H^* = 9.3 \text{ kcal.}$; and $\Delta S^* = -10 \text{ e.u.}$ The second is racemization of the *C*-isomer, $d-C \rightleftharpoons l-C$. Kinetic results are: $\log k_{d-C \rightarrow l-C} = 12.847 - 2870/T$; $\Delta H^* = 12.6 \text{ kcal.}$; and $\Delta S^* = -1 \text{ e.u.}$ To rationalize these results, a notation has been developed that introduces appropriate plus or minus signs into the chemical structural formula. With this notation it becomes easy to represent all stable and metastable ring conformations and to characterize the conformational changes as simple wagging motions that invert specific carbon atoms of the ring.

Substances consisting of molecules with medium-sized rings often produce highly temperature-dependent n.m.r. spectra.^{2–4} The spectra indicate that there is exchange of nuclei between different resonance frequencies, the rate of which increases with the temperature. In most such cases it is reasonable to assume that the exchange results from the interconversion of specific conformational isomers of the ring. This

theory has been applied successfully to relatively simple and symmetrical rings, such as cyclohexane^{2,5,6} or cyclohexyl fluoride,⁴ where the exchange is a simple, first-order process.

In this paper we discuss conformational changes in more complex rings of lower symmetry, where the exchange can involve several first-order processes in parallel. Our specific example is the hydrocarbon 1,1,4,4-tetramethyl-6,7-benzocycloheptene (I).^{7a} Hart and co-workers^{7b} had noted, as early as 1960, that the



proton magnetic resonance (p.m.r.) spectrum of I becomes strongly temperature dependent below 0°, showing the characteristics that are usually associated with exchange between different conformational species. When Hart described these observations to us, we decided to undertake a quantitative study. He helped us by supplying, first a purified, then a doubly purified, sample of I, and by thoughtful comment. Our p.m.r. measurements were made on 5–10 wt. % solutions of I in carbon disulfide.

Compound I is well suited for the study of intramolecular motions by the p.m.r. method because there are several nonequivalent kinds of protons to provide diagnostic chemical shifts, yet the spin-spin interactions are relatively simple. In particular, the four methyl groups in each molecule have character-

(1) Chemistry Department, Brandeis University, Waltham, Mass.
(2) F. R. Jensen, D. C. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960).
(3) N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962).
(4) F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *ibid.*, **40**, 3099 (1964). This article contains a bibliography of earlier work.

(5) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, **145** (1964).

(6) F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *ibid.*, 146 (1964).

(7) (a) H. Hart and J. L. Corbin, *J. Am. Chem. Soc.*, **87**, 3135 (1965); (b) H. Hart, private communication.

istically different proton chemical shifts, but spin-spin interaction is insignificant because the nearest nonequivalent protons are removed by two aliphatic carbon-carbon bonds. Also, the nonequivalent protons at C-5 give a simple spectrum of the AX or AB type, which involves only one spin-spin interaction.⁸

The p.m.r. spectrum of I shows clearly that there are two stable conformational isomers. Proton exchange is found to involve two separate conformational changes that can be characterized on the basis of the p.m.r. spectrum. Quantitative data are reported for the relevant equilibrium and rate constants over a wide temperature range. Much of the paper is devoted to establishing the conformation of the two isomers and to finding a reaction mechanism that would predict precisely those conformational changes that are observed. In this connection, a useful notation is developed that introduces appropriate plus or minus signs into the chemical structural formulas. With this notation it becomes easy to obtain the complete set of stable and metastable ring conformations, and to describe the probable mechanism of their interconversion.

Qualitative Features of the P.m.r. Spectrum

Figure 1 shows the dramatic changes that take place in the p.m.r. spectrum of I between 40 and -71° . In these and subsequent records, the resonance frequencies are near 60.0 Mc. and decrease from left to right. The resonances on the far left have been assigned to the phenyl protons because of their relatively low chemical shifts. The other resonances, which are due to the aliphatic protons, divide themselves into four distinct regions, with relative intensities 2:4:6:6, as shown most clearly by the spectrum at 40° . These four subdivisions of the spectrum can be assigned to specific protons, as shown in Figure 1, on the basis of chemical shifts, intensities, and an analysis of the low-temperature spectrum. In this figure and elsewhere in this paper, we use the letters α , β , and γ to denote position with respect to the benzene ring; e.g., $\gamma\text{-CH}_2$ is at ring-position 3, or $\beta\text{-C}(\text{CH}_3)_2$ is at ring-position 4.

The simplicity of the aliphatic p.m.r. spectrum at 40° (Figure 1) suggests that each of the carbon atoms C-1 to C-5 is inverting rapidly, so that there is effective averaging of chemical shifts at each ring position. As the temperature decreases, each of the four resonances changes gradually into a multiplet of lines. However, near -70° the line structure reaches a low-temperature limit and then undergoes no further qualitative change down to temperatures as low as -101° . The spectrum indicates clearly that the hydrocarbon I is a mixture of two stable conformational isomers that are present in a ratio of roughly 2:1. Our analysis of the spectrum in terms of two isomers is shown schematically by the open and closed triangles in Figure 2. The α - and $\beta\text{-C}(\text{CH}_3)_2$ protons each produce two two-line spectra, and the $\alpha\text{-CH}_2$ protons produce two AX spectra. The intensities of the lines are also consistent with the presence of two isomers.

The processes that take place above -70° are shown most clearly by the resonance assigned to the $\beta\text{-C}(\text{CH}_3)_2$ protons (Figure 3). In the spectrum at -81.0° ,

lines 1 and 4 are substantially of equal intensity (there is some overlapping of lines) and result from the two nonequivalent methyl groups at C-4 in the more stable isomer, which we shall call isomer C. Analogously, lines 2 and 3 result from the two nonequivalent methyl groups at C-4 in the second isomer, which we shall call isomer B. As the temperature rises, two distinct kinetic processes can be recognized. Up to *ca.* -35° , the only process that is significant is a conformational isomerization, $\text{C} \rightleftharpoons \text{B}$, which proceeds without racemization. This process is inferred from the following facts. There is an exchange of protons between lines 1 and 3; there is an exchange of protons between lines 2 and 4; and the corresponding rates of exchange are precisely equal. Thus Figure 3 shows that at -34.6° the original four-line spectrum is collapsed into two broad lines, one at the weighted-average frequency of lines 1 and 3, the other at that of lines 2 and 4. Analysis of the widths of these lines shows that the rates of exchange are equal. One line is broader than the other because the chemical shifts are not equal

$$|\delta_1 - \delta_3| > |\delta_2 - \delta_4|$$

As the temperature increases in small steps above -35° the two broad lines described above first become narrower. However, near -33° the width reaches a minimum, and above this temperature a new process becomes dominant that somehow produces proton exchange between the two lines. Thus at -20.2° we find a barely resolved doublet (Figure 3), and at -18° we find collapse into a single line that becomes very narrow as the temperature approaches 40° (Figure 1). A detailed analysis of the phenomenon will be given in a later section. This analysis indicates, with high probability, that the new proton exchange is specifically between lines 1 and 4. If this be granted, then the process involves only the more stable isomer C, and it produces an exact inversion of chemical shifts of the two methyl groups at C-4. The only plausible process consistent with this description is one in which the molecules of C are converted to their mirror image, that is, *d*-C \rightleftharpoons *l*-C. In this process, each of carbon atoms C-1 to C-5 inverts its configuration.

In the preceding analysis we have emphasized the resonance of the $\beta\text{-C}(\text{CH}_3)_2$ protons, but it should be noted that the changes observed in the other parts of the p.m.r. spectrum are congruent.

In summary, the hydrocarbon I is a mixture of two conformational isomers, called B and C. There are two distinct rate processes that produce an effect on the p.m.r. spectrum; B is in dynamic equilibrium with C by a mechanism that produces no racemization, and C, and only C, will undergo a process that interconverts the *d*- and the *l*-form.

Structure and Mechanism

In this section we wish to develop an explanation for the preceding highly specific facts. First, by applying existing theory⁹⁻¹¹ we shall develop a convenient

(9) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961); **86**, 4854 (1964).

(10) (a) W. G. Dauben and K. S. Pitzer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 1; (b) F. H. Westheimer, Chapter 12 of ref. 10a.

(11) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.

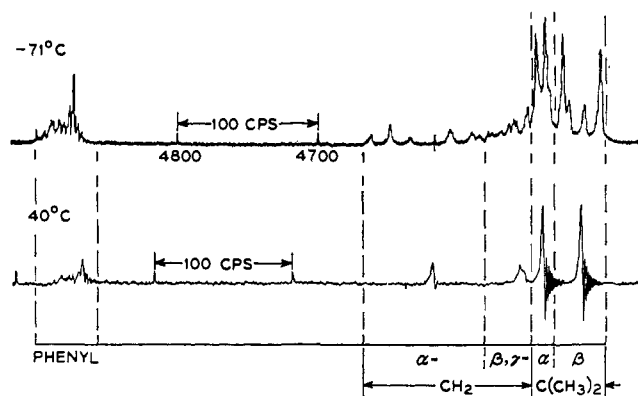


Figure 1. P.m.r. spectrum of 1,1,4,4-tetramethyl-6,7-benzocycloheptene in 5 wt. % solution in carbon disulfide. The resonance frequencies are near 60.0 Mc. and decrease from left to right.

notation that will enable us to write down the complete set of stable and metastable conformations of the seven-membered ring in I. Next, we shall consider a probable mechanism for the interconversion of these conformations. Finally, after appropriate assignment of conformational structure, we shall show that our theory predicts precisely those interconversion processes that are observed, and no others.

Notation. We now wish to develop a distinctive notation for representing each stable and metastable ring conformation. The notation is based on general theory of potential energy in carbon rings,⁹⁻¹¹ but the theory is applied only qualitatively, to count and characterize those ring conformations in which the potential energy is at a minimum. Our procedure is as follows. First, we consider how many potential minima there would be due to torsional strain alone. Then we eliminate those torsional minima that would result in excessive angle strain. Finally we eliminate those minima that would result in excessive nonbonded repulsion. The set of minima that remains after these operations will represent all conformations that are either stable or only slightly metastable, that is, all of the conformational isomers that might conceivably be observed.

Figure 4 shows Newman projection formulas¹² of adjacent atoms in a ring. The atoms are placed so that the endocyclic bond to the first atom comes from the right. If both atoms are saturated carbon atoms, there will be three torsional potential minima for the conformation of the endocyclic bonds: *gauche* (+) (Figure 4a), *gauche* (-) (Figure 4b), and *trans*. However, to avoid excessive angle strain in the ring, some of the torsional potential minima must be eliminated. If the ring is of medium size, it cannot close without much strain if any of the endocyclic bonds are *trans*. Thus only two conformations are relevant, *gauche* (+) and *gauche* (-), and we shall use the following notation. To indicate *gauche* (+) we shall write a *plus* sign in the structural formula next to the line that indicates the bond between the given carbon atoms.

(12) (a) M. S. Newman, *J. Chem. Educ.*, 32, 344 (1955). (b) The present notation is consistent with the notation of J. B. Hendrickson in a recent article that appeared after our manuscript had been completed: *J. Am. Chem. Soc.*, 86, 4854 (1964). However, Hendrickson uses the + to denote the conformation that we call *gauche* (-), and *vice versa*.

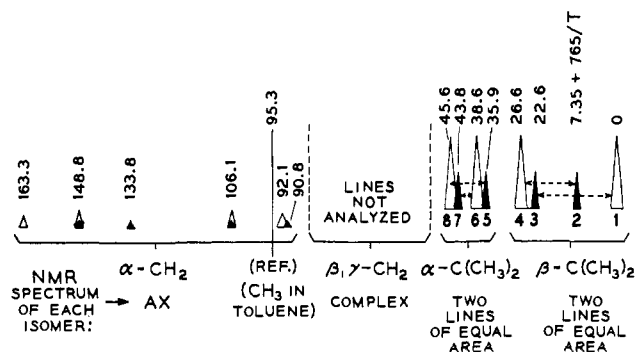


Figure 2. Schematic representation of the low-temperature p.m.r. spectrum of 1,1,4,4-tetramethyl-6,7-benzocycloheptene, showing line assignments and differences of line frequencies. The resonance frequencies are near 60.0 Mc. and actually decrease from left to right. The solid triangles represent the spectrum of isomer B, the open triangles represent that of isomer C. Note the numbering of the lines, which begins on the right.

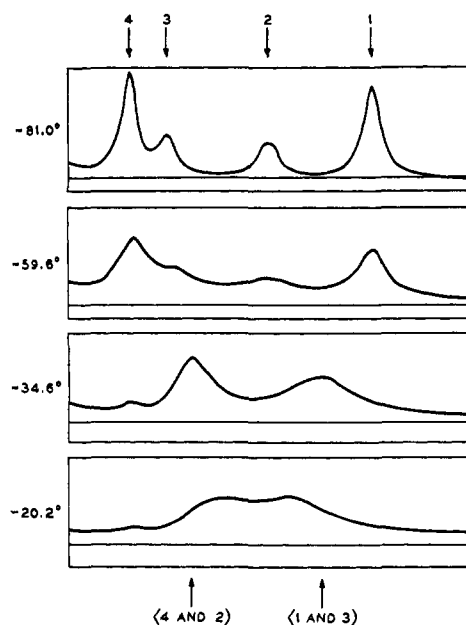


Figure 3. P.m.r. spectrum of the β -C(CH₃)₂ protons at various temperatures. The lines are numbered as in Figure 2.

Similarly, to indicate *gauche* (-) we shall write a *minus* sign. Examples are shown in Figure 5.^{12b}

The requirement that the ring must close without much strain also introduces another constraint. The number of plus and minus signs in the ring (n_+ and n_-) must be balanced, that is, $n_+ - n_- = 0$ (if $n_+ + n_-$ is even), $n_+ - n_- = \pm 1$ (if $n_+ + n_-$ is odd), or $n_+ - n_- = 0$, with one bond eclipsed (if $n_+ + n_-$ is odd). The physical picture to justify this constraint is that the carbon atoms must form a ring, not a helix, and that all dihedral angles in the ring must be fairly close to $\pm 60^\circ$.

Finally, to avoid excessive nonbonded repulsion, we shall impose another constraint. We shall rule out all conformations in which three or more consecutive bonds are all *gauche* (+) or all *gauche* (-). Thus we shall not consider any isomers with the conformational sequence (+++) or (---), because the energy of such isomers is presumed to be too high.

If the ring contains C=C, we shall assume that

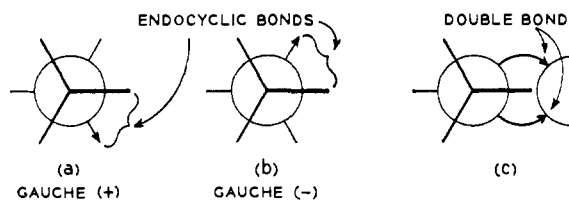


Figure 4. Projection formulas showing stagger of endocyclic bonds to adjacent carbon atoms in a small ring: a, right-handed stagger (+); b, left-handed stagger (-); c, a possible conformation when one endocyclic bond is single and the other is double. The arrow indicates the direction of advance around the ring, i.e., from ring position n to $n + 1$.

the only stable conformation is one in which the endocyclic single bonds adjacent to the double bond are *cis*. This conformation is indicated unambiguously in the conventional way of writing structural formulas, and no new notation is required.

Single bonds adjacent to a double bond have conformational properties that are quite different from those of bonds between saturated carbon atoms. Rotation about the bond between the trigonal and the tetrahedral atom is virtually free in molecules like toluene and nitromethane,¹³ and is opposed only by a small potential barrier in less symmetrical molecules, e.g., carbonyl compounds.¹⁴ Thus, in Figure 4c we shall assume that the torsional strain is essentially independent of the angle between the endocyclic bonds. The value that this angle actually assumes is then determined entirely by the conformation of the rest of the molecule, so as to minimize angle strain and nonbonded repulsion. On this basis, a single bond that is adjacent to a double bond will not increase the number of metastable conformations that are available to the molecule, since there is only one potential minimum for every metastable arrangement of the other bonds.¹⁵ Since our notation is intended to characterize different metastable isomers rather than suggest precise geometries, we shall not add a special symbol in the structural formula next to such a bond.

Conformational Isomers. It is now a simple matter to write down the set of stable or metastable isomers of I. According to the rules just laid down, each of the four bonds between ring positions 1 and 5 can be either plus or minus. The other bonds are not labeled. Moreover, the number of plus and minus bonds must balance. It follows from eq. 1 and 2 that $n_+ = n_-$

$$n_+ + n_- = 4 \quad (1)$$

$$n_+ - n_- = 0 \quad (2)$$

$= 2$. Thus the number of isomers is equal to the number of arrangements of two plus signs and two

(13) (a) K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 803 (1943); (b) E. Tannenbaum, R. J. Myers, and W. D. Gwinn, *J. Chem. Phys.*, **25**, 42 (1956).

(14) See, for example, W. Tabor, *ibid.*, **27**, 974 (1957); J. D. Swalen and C. C. Costain, *ibid.*, **31**, 1562 (1959); R. W. Kilb, C. C. Linn, and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957); L. C. Krisher and E. B. Wilson, Jr., *ibid.*, **31**, 882 (1959).

(15) It should be emphasized that we are describing an approximation, but one that is necessary to keep the complexity of the problem within manageable bounds. Once we admit that there is more than one potential minimum, we shall probably have to admit also that there might be more than two minima. We should note, also, that the time-scale of the p.m.r. experiment is long enough to permit effective averaging of conformations across low barriers.

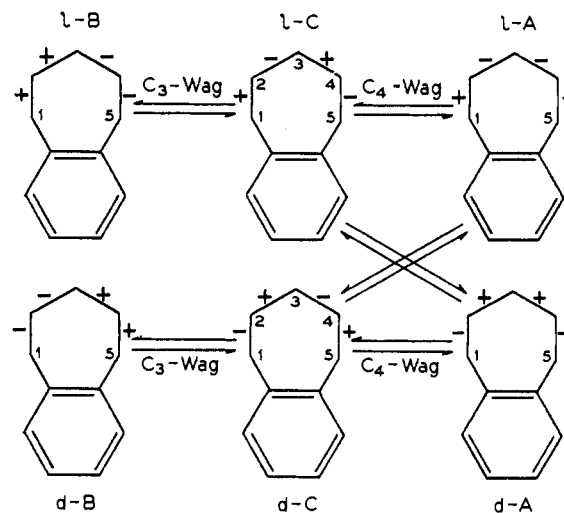


Figure 5. The stable and metastable conformations of 1,1,4,4-tetramethyl-6,7-benzocycloheptene (methyl groups are not shown). The arrows indicate those interconversions that involve simple wagging motions, that is, motions in which the stagger of adjacent bonds in the ring changes from (+-) to (-+), or *vice versa*.

minus signs among four nonequivalent sites. There are six such arrangements, as shown in Figure 5. In this figure, the methyl groups have been left out for greater clarity, but the substituents at each ring position are the same as in I.

The six isomers divide themselves into three *d,l*-pairs labeled B, C, and A, respectively. Perspective drawings of these isomers are presented in Figure 6. In isomer C, the seven-membered ring exists in the chair form; in isomer B, it exists in the boat form.

Mechanism of Interconversion of Conformations. The preceding notation is particularly useful for characterizing the mechanism of the intramolecular rate processes. Here the reactant is the substrate molecule in one potential minimum, and the product is the same molecule in some other potential minimum. Since the conformations that correspond to potential minima are subject to constraints (eq. 1 and 2 above), the possible changes of conformation are subject to derivative constraints. Only those changes are possible in which $\delta n_+ = 0$ and $\delta n_- = 0$. If the process converts the conformation of one bond from *gauche* (+) to *gauche* (-), then there must be a compensating change from *gauche* (-) to *gauche* (+) in the conformation of some other bond.

In addition to the constraint that $\delta n_+ = \delta n_- = 0$, which is independent of reaction mechanism, there are further constraints that are imposed by the specific reaction mechanism. This is because each reaction mechanism postulates a specific relationship of the sites in the molecule where the conformational changes can take place. In the present case, the ring is sufficiently inflexible so that pseudo-rotation of the entire ring skeleton can be ruled out.¹⁶ Perhaps the simplest conceivable mechanism for changing the ring conformation is a wagging motion that inverts a single carbon atom in the ring. Figure 7 shows how this process is

(16) Pseudo-rotation can be formally described in terms of our notation as a process in which the entire set of *plus* and *minus* signs advances by one site, that is, each sign advances from its original site to the next labeled site. The advance of the signs is either uniformly clockwise or uniformly counterclockwise.

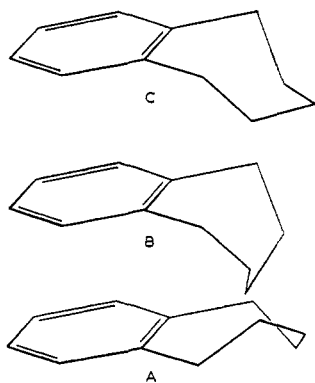


Figure 6. Perspective drawings of conformational isomers of benzocycloheptene. Drawings A, B, and C depict the same molecules as do the corresponding structural formulas with (+) and (-) signs in Figure 5.

represented in terms of our notation. The two endocyclic bonds to the atom in question change from (+-) to (-+), or *vice versa*. The essential feature of this mechanism is that the conformational changes take place in adjacent bonds, whose conformations must be of opposite sign. Thus in Figure 5 the isomer labeled *l*-B has only one set of adjacent bonds whose conformations are of opposite sign, namely those next to ring-position 3. Hence this isomer can undergo a wagging motion that inverts a carbon atom *only* at C-3. The product can be predicted easily, as follows: The (+-) sequence around C-3 changes to (-+), while the signs of the other bonds remain the same. On this basis it is found that *l*-B is converted into *l*-C.

Similarly, the isomer labeled *l*-C can undergo a wagging motion that inverts a carbon atom at either of the ring-positions 2, 3, and 4. The reader will satisfy himself that the respective products are *d*-A (C-2 wag), *l*-B (C-3 wag), and *l*-A (C-4 wag). The isomer labeled *l*-A can undergo this type of motion either at C-2 or at C-4, the respective products being *d*-C and *l*-C, and so on. Figure 5 shows the complete set of changes in ring conformation that are permitted by this mechanism.

It is obvious from even a cursory inspection of Figure 5 that this simple approach succeeds in reproducing the most striking qualitative feature of the observed rate processes, namely their high specificity. Moreover, by making one mild additional assumption, we can bring the theory into exact correspondence with experiment. The assumption that must be made is that conformation A is somewhat less stable than B and C, and for this reason the A-isomer has not been observed in the p.m.r. spectrum. Conformation B must then be assigned to the isomer that we have called B; and conformation C must be assigned to isomer C. Thus, according to Figure 5, the B-molecules, which are optically active, can undergo only one reversible rate process: a change into the corresponding optical form of C, without racemization. This description fits the process that has a large effect on the p.m.r. spectrum below about -33° . In addition, the theory predicts a second process in which the *d*- and the *l*-form of C interconvert by a mechanism that involves two wags in succession, one at C-2 and the other at

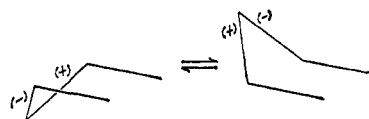


Figure 7. The change from (-+) to (+-) in the stagger of adjacent bonds represents the simple wagging motion of the central carbon atom.

C-4, with the A-conformation as a metastable intermediate. This description fits the process whose effect on the p.m.r. spectrum becomes noticeable above about -33° . Finally, the theory predicts that there should be no other processes, and none are observed.

Recalling that the amount of isomer C is nearly twice that of isomer B, our theory implies that the chair form of I is somewhat more stable than the boat form. This conclusion fits in nicely with recent work¹⁷ concerning the stable conformations of the structurally similar ketone, 1,2-benzocyclohepten-5-one. The seven-membered ring in this compound is believed, on the basis of electric dipole moment measurements and theoretical calculations, to exist only in the chair and the boat form, with an equilibrium ratio of roughly 10 to 1.

Quantitative Results

In this section we summarize our quantitative analysis of the p.m.r. data in the following parts: positions of the p.m.r. lines, widths of the lines in the absence of exchange broadening, equilibrium constants ΔH° and ΔS° for the equilibrium $B \rightleftharpoons C$, rate constants ΔH^{\ddagger} and ΔS^{\ddagger} for the process $l\text{-}B \rightleftharpoons l\text{-}C$ or $d\text{-}B \rightleftharpoons d\text{-}C$, and rate constants ΔH^{\ddagger} and ΔS^{\ddagger} for the process $d\text{-}C \rightleftharpoons l\text{-}C$. The analysis is based on p.m.r. records made at 26 different temperatures between -101 and 36° , eighteen of which were in the range -70 to -5° where the effects of the rate processes are most pronounced. Most of the results are based on measurements involving lines 1 through 4 (Figure 2), which have been assigned to the $\beta\text{-C}(\text{CH}_3)_2$ protons. However, the rest of the p.m.r. spectrum was also examined at most of these temperatures without finding any inconsistencies. All measurements were made on 5-10 wt. % solutions of I in carbon disulfide.

The calculations are simple enough to be made with a desk calculator. However, several iterations are required because the variables are interdependent. For example, the line positions have to be corrected at some temperatures for small displacements caused by chemical exchange. These corrections require a knowledge of the rates of exchange. The rates, in turn, cannot be known accurately without an accurate knowledge of the line positions. Fortunately, there are temperature ranges in which the interdependence of certain variables is slight, so that it is possible to begin the iterations with a set of values that are already quite accurate.

P.m.r. Line Positions. All resonance frequencies are near 60.0 Mc. and all frequency differences are reported at constant applied magnetic field. The results of our measurements at several temperatures between -101 and -60° are listed in Figure 2 on a

(17) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, 27, 722 (1962).

scale whose origin coincides with the center of line 1 at each temperature. On this scale, all but one of the resonance frequencies are independent of the temperature within a standard deviation of ± 0.1 c.p.s. The exception is line 2, whose frequency decreases systematically from 11.7 at -101° to 10.8 c.p.s. at -64° . Without investigating the physical mechanism for this phenomenon we assumed a linear dependence on $1/T$ ($^\circ\text{K}$). The empirical equation given in Figure 2 was obtained by the method of least squares from data at nine temperatures. All line positions were corrected, when necessary, for small displacements resulting from chemical exchange (see eq. 16 in the Appendix).

Line Width in the Absence of Exchange Broadening. We use the symbol $1/T_2$ to denote the effective p.m.r. line half-width (in radians/sec.) in slow-passage records in the absence of exchange broadening. This quantity was measured for the $\beta\text{-C}(\text{CH}_3)_2$ protons at -101 , -89 , -81 , and -76° (average of lines 1 and 2, Figure 2), and also at 36° , at which temperatures any line broadening due to exchange is at most a small correction term. The final corrected results are represented accurately by eq. 3. The constant term,

$$\frac{1}{T_2} = 0.50 + 0.0358 \text{ antilog}(419.0/T) \quad (3)$$

0.50, in eq. 3 is our estimate of the contribution to the line width from factors that depend on the measuring instrument, such as inhomogeneity of the magnetic field and radiation damping. The specific value, 0.50, is based on the difference that we usually find between slow-passage and spin-echo measurements of $1/T_2$ in other systems. The exponential term in eq. 3 should be a good approximation to the "natural" $1/T_2$.

In the intermediate temperature range where exchange broadening is considerable, values of $1/T_2$ were estimated by interpolation from eq. 3.

Thermodynamic Constants for the Equilibrium $B \rightleftharpoons C$. The equilibrium constant, $K = [\text{C}]/[\text{B}]$, was measured over a very wide temperature range, from -101 to -12° . Results are listed in Table I. Between -101 and -64° , lines 1 and 2 (Figure 2) are quite well resolved, and K can be obtained by measuring the ratio of the respective areas. Between -37 and -30° , the $\beta\text{-C}(\text{CH}_3)_2$ resonance is collapsed into two lines (Figure 3) whose separation, $\langle\delta_{4,2}\rangle - \langle\delta_{1,3}\rangle$, depends on the mole fraction of B in the B-C mixture, and therefore on K . The relevant equation is 4 and the relevant resonance frequencies, δ_1 , δ_2 , δ_3 , and δ_4 , are those of the uncollapsed lines, as listed in Figure 2. In our final calculations based on eq. 4, a small correction was applied to $\langle\delta_{4,2}\rangle - \langle\delta_{1,3}\rangle$ to allow for

$$\langle\delta_{4,2}\rangle - \langle\delta_{1,3}\rangle = [K(\delta_4 - \delta_1) + (\delta_2 - \delta_3)]/(1 + K) \quad (4)$$

line displacements due to chemical exchange. (See eq. 17 in the Appendix.)

Above ca. -15° , the β - and $\alpha\text{-C}(\text{CH}_3)_2$ proton resonances are both collapsed by exchange into single lines, and K can be derived from the corresponding line separation, $\langle\delta_\alpha\rangle - \langle\delta_\beta\rangle$. The relevant equation is 5, and the relevant resonance frequencies, $\delta_1 \dots \delta_8$, are those listed in Figure 2.

$$\langle\delta_\alpha\rangle - \langle\delta_\beta\rangle = [K(\delta_8 + \delta_6 - \delta_4 - \delta_1) + (\delta_7 + \delta_5 - \delta_3 - \delta_2)]/2(1 + K) \quad (5)$$

Unfortunately, the three different methods (ratio of areas, eq. 4 and eq. 5) cannot be compared directly because their temperature ranges do not overlap. However, the plot of the experimental values of $\log K$ vs. $1/T$ appears to be continuous, so that the methods are at least internally consistent (see Table I).

On applying the method of least squares to all the data, we obtain the following results (eq. 6). The

$$\log K = -0.026 + 69.2/T \quad (6)$$

standard error of fit = ± 0.02 log unit, $\Delta H^\circ = -317$ cal., $\Delta S^\circ = -0.12$ e.u., and $K^{298} = 1.61$.

Rate Constants for the $B \rightleftharpoons C$ Interconversion. We define a relaxation time τ such that

$$\frac{1}{\tau} = k_{B \rightarrow C} + k_{C \rightarrow B} \quad (7)$$

The k values denote first-order rate constants for the reversible process $B \rightleftharpoons C$ (which proceeds without racemization), and are related to the equilibrium constant by eq. 8. Between -68 and -62° , both k

$$k_{B \rightarrow C}/k_{C \rightarrow B} = K \quad (8)$$

values could be obtained independently from the broadening of lines 1 and 2. The applicable equations are those for life-time broadening (eq. 9). $1/T_2'$

$$\begin{aligned} \frac{1}{T_2'} - \frac{1}{T_2} &= k_{C \rightarrow B} \text{ (line 1)} \\ &= k_{B \rightarrow C} \text{ (line 2)} \end{aligned} \quad (9)$$

is the experimental line half-width (in radians/sec.), and $1/T_2$ is calculated from eq. 3. Since K is already known (eq. 6), we can test the accuracy of the k values by means of eq. 8. In fact, the ratios $k_{B \rightarrow C}/k_{C \rightarrow B}$ agreed well with the independent measurements of K ; discrepancies were always less than 5% and apparently random.

At higher temperatures, only one kinetic parameter could be evaluated. Between -62 and -55° , $k_{C \rightarrow B}$ could still be measured *via* eq. 9. Between -55 and -50° , τ could be measured from the separation of lines 1 and 4. This method makes use of eq. 16 in the Appendix. Between -41 and -34.6° , τ could be measured from the half-widths of the two lines into which lines 1 through 4 are collapsed in this temperature range. This method makes use of eq. 18 in the Appendix. The two lines afford two independent values of τ that were generally in reasonable agreement. In these calculations, a small correction was made to allow for life-time broadening due to the second process, racemization. This correction became significant above -40° and was made by subtracting from the experimental line width an amount equal to $(2\lambda)^{-1}$, where λ was calculated from eq. 12. (See next section.)

By utilizing eq. 6-8, rate constants, k , were calculated from the relaxation times, τ . An Arrhenius plot of the results for $k_{C \rightarrow B}$ is shown in Figure 8. On applying the method of least squares, we obtain the following

Table I. Equilibrium Constants for Boat-to-Chair Interconversion of 1,1,4,4-Tetramethyl-6,7-benzocycloheptene (I) in CS₂

Temp., °C.	K, [C]/[B]	Method ^a	Temp., °C.	K, [C]/[B]	Method ^a
-109.8	2.47	A	-64.5	1.84	A
-88.8	2.27	A	-37.3	1.97	B
-81.0	2.17	A	-34.6	1.95	B
-75.8	1.99	A	-29.8	1.82	B
-72.4	2.05	A	-12.6	1.81	C
-67.4	1.97	A			

^a A, ratio of areas, p.m.r. lines 1 and 2; B, eq. 4; C, eq. 5.

results (eq. 10). The standard error of fit = ±0.03

$$\log k_{C \rightarrow B} = 10.919 - 2134/T \quad (10)$$

log unit, $\Delta H^*_{C \rightarrow B} = 9.3$ kcal., $\Delta S^*_{C \rightarrow B} = -10$ e.u.

Rate Constants and Mechanism for the Racemization.

As a result of the process that we have just discussed, the original four β -C(CH₃)₂ p.m.r. lines are averaged into two lines of equal intensity, namely line a = (line 1 + line 3) average and line b = (line 4 + line 2) average.

Above -35° there is a second process that results in further averaging and causes lines a and b to collapse into a single line. We recognize three distinct molecular mechanisms that could produce this effect. (1) Racemization of the C-isomer, $d\text{-C} \rightleftharpoons l\text{-C}$, would produce exchange between lines 1 and 4. (2) Racemization of the B-isomer, $d\text{-B} \rightleftharpoons l\text{-B}$, would produce exchange between lines 2 and 3. (3) Interconversion of the appropriate *d* and *l* forms of B and C would produce proton exchange simultaneously between lines 1 and 2 and between lines 3 and 4. This process is the optical antipode to the previously described process that produces the averaging into lines a and b. That is, if the previously described process is represented as [$d\text{-B} \rightleftharpoons d\text{-C}$; $l\text{-B} \rightleftharpoons l\text{-C}$], then this process must be represented as [$d\text{-B} \rightleftharpoons l\text{-C}$; $l\text{-B} \rightleftharpoons d\text{-C}$].

In each of processes 1 to 3, a specific subset of the protons that are averaged in line a exchanges with a specific subset of those that are averaged in line b, thereby causing lines a and b to collapse. However, there are quantitative differences, especially with respect to the speed of the final collapse into a single, sharp line as the temperature is raised. These differences are diagnostic and enable us to select process 1 as the only process that can reproduce our data with reasonable accuracy.

To obtain this result, we analyzed the spectrum of the β -C(CH₃)₂ protons in two temperature ranges in which certain simplifying assumptions could be made. Let us introduce a relaxation time, λ , to express the speed of the formal process: protons of line a \rightleftharpoons protons of line b. Then, in the range from -25 to -10°, the proton exchange is characterized by the following inequalities: $1/\tau \gg |\delta_4 - \delta_2|, |\delta_3 - \delta_1|$; $1/\lambda \leq |\delta_a - \delta_b|$. The physical significance of these inequalities is that there is efficient averaging by the τ -process into lines a and b, but further averaging by the λ -process is rather ineffectual and leads at best to a broad single line in which lines a and b just fail to be resolved. To interpret the p.m.r. spectrum between -25 and -10°, we therefore adopted a model in which proton exchange with relaxation time λ takes place in an 1:1 doublet consisting of lines a and b. λ can be derived from the spectrum by established methods¹⁸ provided

that the line width in the absence of exchange by the λ process is known. We expressed the latter as a sum (average width of lines a and b, $\langle w \rangle$), if there were no

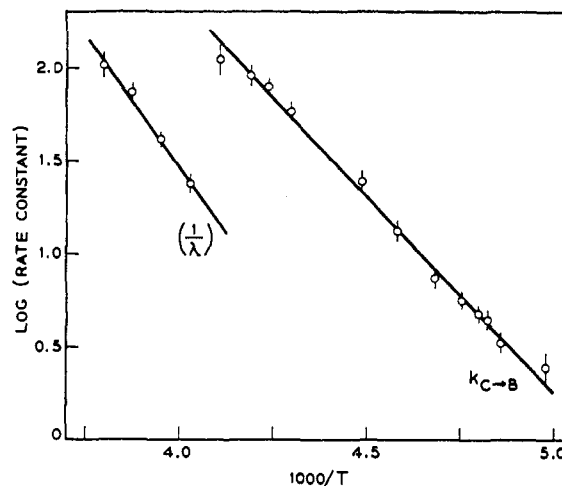


Figure 8. Arrhenius plots based on p.m.r. data. See text for explanation of symbols.

exchange by the λ -process) consisting of two terms, $1/T_2$, plus a term for exchange broadening by the τ -process

$$\langle w \rangle = \frac{1}{T_2} + \tau[(\delta_4 - \delta_2)^2 + (\delta_3 - \delta_1)^2]K/2(1 + K)^2 \quad (11)$$

Values of $1/T_2$, K , and τ at the experimental temperatures were calculated from eq. 3, 6, 7, 8, and 10. Values of λ were obtained in this way with good precision at four temperatures. An Arrhenius plot of the results is shown in Figure 8. The least-squares line fitting these data is eq. 12.

$$\log (1/\lambda) = 12.863 - 2847/T \quad (12)$$

The second temperature range in which the interpretation of the p.m.r. spectrum becomes relatively simple is characterized by the inequalities $1/\tau \gg |\delta_4 - \delta_2|, |\delta_3 - \delta_1|$; $1/\lambda \gg |\delta_a - \delta_b|$. In this range there is efficient averaging by both processes. In practice, these inequalities are satisfied above about 5°.

Before writing any equations, it is helpful to consider the physical situation. Both λ and τ are small (relative to the inverse line separations) and are approaching zero as the exchange broadening of the doubly averaged p.m.r. line approaches zero. More-

(18) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **84**, 4664 (1962).

over, in the limit that $\tau = 0$ the exchange broadening is proportional to λ , and in the limit that $\lambda = 0$ the exchange broadening is proportional to τ .¹⁹ It is therefore convenient to develop the line half-width, $1/T_2'$, as a Taylor series expansion in the variables λ and τ about the point $\lambda = \tau = 0$. Recalling that $1/T_2' = 1/T_2$ at that point, we write eq. 13. If λ

$$\frac{1}{T_2'} = \frac{1}{T_2} + \left(\frac{\partial(1/T_2')}{\partial\lambda} \right)_{\tau=0} \cdot \lambda + \left(\frac{\partial(1/T_2')}{\partial\tau} \right)_{\lambda=0} \cdot \tau + \dots \quad (13)$$

and τ are sufficiently small, we can neglect terms of second order and higher.

We propose to use eq. 13 to determine the mechanism of the λ -process. The strategy is as follows. Suppose we measure $1/T_2'$ at a temperature at which eq. 13 applies. We already have empirical equations for predicting T_2 , λ , and τ at this temperature. We already know the mechanism of the τ -process (collapse into lines a and b), and we know, therefore, that for $\tau = 0$ and $\lambda \ll |\delta_a - \delta_b|^{-1}$

$$\frac{1}{T_2'} = \frac{1}{T_2} + \frac{\lambda(\delta_a - \delta_b)^2}{4}$$

hence $\partial(1/T_2')/\partial\lambda = (\delta_a - \delta_b)^2/4$. This leaves only one unknown quantity, $\partial(1/T_2')/\partial\tau$, which can therefore be calculated. The result can then be compared with theoretically predicted values for each of the mechanisms 1 to 3.

According to mechanism 1, the λ -process would collapse lines 1 and 4 but leave lines 2 and 3 intact. At $\lambda = 0$ and $\tau = \infty$, the β -C(CH₃)₂ resonance would be a triplet, with chemical shifts δ_2 , δ_3 , and $(\delta_1 + \delta_4)/2$, and relative line intensities 1, 1, and 2K, respectively. According to mechanism 2, the λ -process would collapse lines 2 and 3 but leave lines 1 and 4 intact. At $\lambda = 0$ and $\tau = \infty$, the β -C(CH₃)₂ resonance would be a triplet, with chemical shifts δ_1 , δ_4 , and $(\delta_3 + \delta_2)/2$, and relative line intensities K, K, and 2, respectively. According to mechanism 3, the λ -process would collapse lines 1 and 2 as well as lines 3 and 4. At $\lambda = 0$ and $\tau = \infty$, the β -C(CH₃)₂ resonance would be a 1:1 doublet, with chemical shifts $(K\delta_1 + \delta_2)/(1 + K)$ and $(K\delta_4 + \delta_3)/(1 + K)$. It is clear, therefore, that each mechanism leads to a different set of resonance lines for $\lambda = 0$ and $\tau = \infty$. As τ decreases, these lines will collapse into a single line, but the magnitude of the exchange broadening for a given small value of τ will depend on the mechanism.

Table II summarizes the theoretical prediction of $[(1/T_2') - (1/T_2)]$ for each mechanism and compares values obtained at 5° with experiment. The expressions for $\partial(1/T_2')/\partial\tau$ (at $\lambda = 0$) were derived for us by Dr. S. Meiboom, to whom we now express our appreciation publicly. This derivation employed a convenient method, developed by Dr. Meiboom²⁰ and based on Bloch equations modified for exchange,²¹

(19) When either λ or τ is zero, we have in effect only one relaxation process. By hypothesis, we are considering the region of exchange narrowing where the line width increases linearly with the relaxation time.

(20) S. Meiboom, unpublished research, Bell Telephone Laboratories, Inc., Murray Hill, N. J.

(21) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. M. McConnell, *ibid.*, **28**, 430 (1958).

that can handle n.m.r. problems of any degree of complexity in the fast-exchange limit.

The comparison of theory with experiment is given in the last two columns of Table II. The error estimates correspond approximately to two standard deviations. It is clear that mechanism 1 is the only one that fits with a reasonably high probability.

If we accept mechanism 1, we are able to convert the formal rate constant, $1/\lambda$, into a real rate constant, $k_{d-C \rightarrow l-C}$. The conversion is made by eq. 14. The

$$k_{d-C \rightarrow l-C} = \frac{1 + K}{K} \times \frac{1}{2\lambda} \quad (14)$$

data summarized by the empirical eq. 12 then give rise to a new empirical equation (15); $\Delta H^* = 12.6$

$$\log k_{d-C \rightarrow l-C} = 12.847 - 2870/T \quad (15)$$

kcal., $\Delta S^* = -1$ e.u.

Activation Entropies. It follows from eq. 10 and 15 that there is a marked difference of activation entropies: $\delta\Delta S^* = \Delta S^*_{d-C \rightarrow l-C} - \Delta S^*_{C \rightarrow B} = 9 \pm 3$ e.u. A difference of this magnitude is unusual for two quite similar first-order processes. We now wish to show, however, that the reaction mechanism detailed in Figure 5 provides a natural explanation.

To begin, we consider the physical significance of $\delta\Delta S^*$. The process $C \rightleftharpoons B$ does not result in racemization. Hence the parameter, $\Delta S^*_{C \rightarrow B}$, is a formal quantity that describes the behavior of two separate, real processes, $d-C \rightarrow d-T^*$ and $l-C \rightarrow l-T^*$, where T^* denotes the transition-state complex. Reflection will show that the over-all entropy change, $\Delta S^*_{C \rightarrow B}$, is equal to ΔS^* for either of these real processes. We may suppose, therefore, that the two processes giving rise to $\delta\Delta S^*$ involve identical initial states ($d-C$), and that $\delta\Delta S^*$ measures the entropy difference of the two transition states.

According to Figure 5, the process $d-C \rightarrow d-B$ involves a C-3 wag. The process $d-C \rightarrow l-C$ involves two wags in succession, one at C-2 and the other at C-4. In the transition state for the C-3 wag, the hydrogen atoms at C-3 are eclipsed on one side by the hydrogen atoms at C-2 and on the other side by the methyl groups at C-4. As a result, we expect a high barrier to rotation of the methyl groups in this transition state.

In the process $d-C \rightarrow l-C$, the C-2 wag inverts a CH₂ group while the C-4 wag inverts a C(CH₃)₂ group. Because of the greater bulk of the latter, we expect the C-4 wag to be more difficult, energywise, and rate determining. In the transition state of the C-4 wag, the methyl groups are eclipsed by hydrogen atoms on each side. Hence the conformation of each methyl group is analogous to that of a methyl group in toluene or in nitromethane¹³; the potential energy is high but is nearly independent of the angle of rotation, that is, the methyl groups are nearly free to rotate.

We believe that the difference in the rotational freedom of the methyl groups in the two transition states accounts for the major part of $\delta\Delta S^*$. Judging by experimental entropy data for dimethyl compounds and by theoretical tabulations,^{10a,13a} the effect should be on the order of 4–8 e.u.

Table II. Reaction Mechanism of the λ -Process

Mechanism	$[\partial(1/T_2')/\partial\tau]$ for $\lambda = 0^a$	$(1/T_2' - 1/T_2)$, sec. ⁻¹ at 5°	
		Calcd., eq. 13 ^{b,c}	Obsd. ^c
1	$-[(\delta_2' + \delta_3')(\delta_1' + \delta_4')/2 + \delta_2'\delta_3'/K]$	3.51 ± 0.66	3.18 ± 0.50
2	$-[(\delta_2' + \delta_3')(\delta_1' + \delta_4')/2 + \delta_1'\delta_4'/K]$	5.78 ± 0.83	3.18 ± 0.50
3	$[(\delta_4' - \delta_1') + (\delta_3' - \delta_2')/K]^2 K/16$	4.31 ± 0.69	3.18 ± 0.50

^a δ_i' is the chemical shift of the i th n.m.r. line, in radians/sec., relative to the average chemical shift, δ_0 , of all β -C(CH₃)₂ protons. That is, $\delta_i' = \delta_i - \delta_0$, where $\delta_0 = [K(\delta_1 + \delta_4) + (\delta_2 + \delta_3)]/2(1 + K)$. The values of δ_1' and δ_2' are negative, those of δ_3' and δ_4' are positive. ^b $\lambda[\partial(1/T_2')/\partial\lambda] = 3.30$; $\tau[\partial(1/T_2')/\partial(\tau)] = 0.21$ (1), 2.48 (2), 1.01 (3). ^c Error estimates correspond to two standard deviations.

Appendix

In this section we wish to give some useful p.m.r. spectral relationships for proton exchange between two chemical shifts. These relationships are special solutions of a more general equation given by Gutowsky and Saika.²² The mathematics is straightforward, and only the final results will be reported.

Let the chemical shifts that are involved in the exchange be δ_A and δ_B , and let the corresponding proton fractions be p_A and p_B ($p_B = 1 - p_A$). Let the average chemical shift of the A-B proton system be δ_0 , where $\delta_0 = p_A\delta_A + p_B\delta_B$. Let τ be the relaxation time for exchange, that is, $\tau^{-1} = \tau_A^{-1} + \tau_B^{-1}$.

When τ is very large, there are two p.m.r. lines with maxima at δ_A and δ_B , respectively. As τ decreases, these maxima move closer together, and eventually the lines merge. While the two resonances are still quite apart, the positions of the maxima, d_A and d_B ,

(22) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953), eq. 17.

are given by eq. 16, provided that $1/T_2 \ll |\delta_A - \delta_B|$. After the resonances are coalesced, and if

$$d_A - \delta_0 = (\delta_A - \delta_0) \left[1 - \frac{1}{1 + (\delta_B - \delta_A)^2 \tau^2} \right] \quad (16a)$$

$$d_A - d_B = (\delta_A - \delta_B) \left[1 - \frac{1}{1 + (\delta_B - \delta_A)^2 \tau^2} \right] \quad (16b)$$

$\tau^{-1} > ca. |2\delta_A - 2\delta_B|$, the position, d_0 , of the maximum of the combined line is given by eq. 17. If

$$d_0 - \delta_0 = p_A p_B (p_B - p_A) (\delta_B - \delta_A)^2 \tau^2 \quad (17)$$

$d_A > p_B$, then it follows from eq. 17 that $(d_0 - \delta_0)$ and $(\delta_A - \delta_0)$ have the same algebraic sign.

Under the conditions where eq. 17 applies, the line half-width, $1/T_2'$, is given by eq. 18.

$$\frac{1}{T_2'} = \frac{1}{T_2} + p_A p_B (\delta_A - \delta_B)^2 \tau \times [1 + (p_A p_B - [p_B - p_A]^2) (\delta_A - \delta_B)^2 \tau^2] \quad (18)$$

Ring Inversion in Cyclohexene¹

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The proton n.m.r. spectrum of cyclohexene-cis-3,3,4,5,6,6-d₆ has been measured in bromotrifluoromethane solution at various temperatures down to -170°. The band of H-4 and H-5 broadens at about -150° and separates into two bands at -164°. The rate constant for ring inversion at -164° is 45 sec.⁻¹ and the nature of the inversion process is discussed. The chemical shift difference between axial and equatorial protons in cyclohexene is estimated to be 24 ± 2 c.p.s.

Introduction

In recent years the rates of ring inversion in saturated, six-membered rings have been extensively studied by nuclear magnetic resonance (n.m.r.) spectroscopy. The compounds investigated include cyclohexane,³

substituted cyclohexanes,⁴ and derivatives of piperidine,⁵ piperazine,⁶ 1,2-dioxane,⁷ and 1,2-dithiane.⁷ All these compounds exist in chair conformations and the rates of inversion are such that the n.m.r. measure-

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