Nuclear Magnetic Resonance Line-Shape and Double-Resonance Studies of Ring Inversion in Cyclohexane-d_{11}[1]

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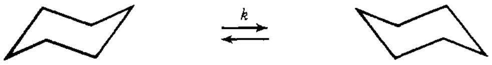
Abstract: Kinetic parameters were obtained for ring inversion in cyclohexane-d_{11} by two different nmr methods: (a) line-shape analysis and (b) double resonance. A field-frequency lock spectrometer operating at 60 Mc/sec was used for all measurements. Rate constants were calculated from −117 to −24° and covered a range of over half a million. The values of ΔF^*_{cb}, ΔH^*, and ΔS^*_{cb} for the chair-to-boat process were found to be 10.3 and 10.8 kcal/mole and 2.8 eu, respectively. The results do not agree with the recent spin-echo work of Allerhand, Chen, and Gutowsky as far as ΔS^*_{cb} is concerned.

Cyclohexane holds a central position in the theory of conformational analysis.[2] There is therefore a special interest in the kinetic parameters for the chair–chair interconversion (ring inversion, Ia ⇄ Ib) in this hydrocarbon. All the experimental data which have been obtained about this process come from nuclear magnetic resonance studies[3] on cyclohexane or cyclohexane-d_{11}. There is general agreement about the order of magnitude of the rate constant (k) and therefore also of the Gibbs' free energy of activation (ΔF^*) for inversion (Table I). The situation is different for the energy of activation (ΔE^*), the enthalpy of activation (ΔH^*), or the entropy of activation (ΔS^*). These parameters are obtained from the temperature dependence of k, or ΔF^*, and this requires accurate measurements of k over as wide a temperature range as possible.[4] There has in fact been some disagreement about the precise values (say ±0.1 kcal/mole) of ΔH^* or ΔE, and consequently the value of ΔS^*, obtained from the relationship, $\Delta S^* = (\Delta H^* - \Delta F^*)/T$, has also been uncertain. It was particularly disturbing that the recent spin-echo work of Allerhand, Chen, and Gutowsky (ACG)[3f] on cyclohexane-d_{11} gave much lower values of ΔH^* and ΔS^* than the previous high-resolution nmr studies on the same compound. The appreciably negative value of ΔS^* obtained by ACG was also puzzling and unexpected.[3a]



Ia Ib

Cyclohexane-d_{11} is a particularly favorable system for the study of rates by both the spin-echo and high-resolution methods. Compared to the extremely complex spectrum of cyclohexane at low temperatures (*e.g.*, −100°), the proton spectrum of cyclohexane-d_{11}, under the same conditions, consists of two broadened lines which become very sharp when the deuterium nuclei are decoupled from the proton by irradiation at the deuteron resonance frequency.[3d,e] These two sharp lines, which are of equal intensities, broaden as the temperature is raised and then merge to a single very broad band at the coalescence temperature (T_c). At still higher temperatures, the band narrows and ultimately becomes extremely sharp, and this is the state of the spectrum of cyclohexane-d_{11} at room temperature. The determination of rate constants at temperatures where the spectrum differs significantly from one sharp line or two sharp lines is quite straightforward. We will refer to this procedure as the line-shaped method.

The results of Bovey, *et al.*,[3e] were obtained over a rather narrow temperature range (−75 to −47°). Even though the rate constants are very close to those determined by ACG by the spin-echo method, the two sets of data define appreciably different slopes on an Arrhenius plot. Our own previous results[3d] were obtained over the temperature range −94 to −32°, but they suffered from considerable scatter.[5] The aim of the present work was to obtain, by high-resolution nmr, more accurate data and over a wider temperature range than had been possible with previously available instrumentation and techniques. In particular, the use of a spectrometer with an internal field-frequency lock[6] allows slow sweeps to be used, and thus undistorted line shapes can be obtained. The recent double-resonance technique of Forsén and Hoffman[7] enables much smaller rate constants to be measured than the conventional line-shaped method, and thus greatly extends the temperature range where accurate measurements are available, particularly if T_1 is long, as is indeed the case with C_6HD_{11}.

Results

A. Line-Shaped Method. Line widths of C_6HD_{11} and TMS at various temperatures are given in Table II.

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(1) This research was supported by the National Science Foundation, Grant No. GP 3780.

(2) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers Inc., New York, N. Y., 1965, Chapter 2; M. Hanack, "Conformation Theory," Academic Press Inc., New York, N. Y., 1965, p 87.

(3) (a) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960): **84**, 386 (1962); (b) R. K. Harris and N. Sheppard, *Proc. Chem. Soc.*, 419 (1961); (c) S. Meiboom, paper presented at the Symposium on High Resolution Nuclear Magnetic Resonance, Boulder, Colo., July 1962; (d) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964); (e) F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *ibid.*, 146 (1964); *J. Chem. Phys.*, **41**, 2041 (1964); (f) A. Allerhand, F. Chen, and H. S. Gutowsky, *ibid.*, **42**, 3040 (1965).

(4) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 378; see also ref 3f.

(5) The rate constants obtained in the slow-exchange region for ring inversion in cyclohexane-d_{11} were incorrectly calculated in our previous work[3d] (see also M. Ahmad, Ph.D. Thesis, University of Ottawa, 1963: and F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, **87**, 3147 (1965)) and were too small by a factor 2. A redetermination of the activation parameters is not very meaningful as there is much scatter in the recalculated data which leads to comparatively large limits of error of ΔH^* and ΔS^*.

(6) R. Freeman and D. H. Whiffen, *Proc. Phys. Soc.* (London), **79**, 794 (1962).

(7) S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963).

Table I. Activation Parameters for Ring Inversion in Cyclohexane and Cyclohexane-d_{11}

Compound	Temp range, °C	ΔF^*_{cb},[a] kcal/mole	$\Delta H^* \approx \Delta E - RT$,[b] kcal/mole	ΔS^*_{cb},[b] eu	Ref
C_6H_{12}	. . .	10.1	11.5 ± 2	(4.9)[c]	3a
C_6H_{12}	−70 to −20	10.3	9.0 ± 0.2	−6.5 ± 1.0	3b[d]
C_6H_{12}	. . .	10.7	11.5	4.9	3c
C_6HD_{11}	−94 to −32	10.3	10.9 ± 0.6	2.9 ± 2.3	3d
C_6HD_{11}	−75 to −47	10.2	10.5 ± 0.5	1.4 ± 1.0	3e
C_6H_{12}	−60 to −25	10.3	9.1 ± 0.5	−5.8 ± 2.4	3f
C_6HD_{11}	−98 to +25	10.3	9.1 ± 0.1	−5.8 ± 0.4	3f
C_6HD_{11}	−117 to −27	10.22	10.8	2.8	This work

[a] At −67°. [b] Errors in ΔH^* and ΔS^* are discussed in the text. [c] Calculated on the basis of an unsymmetrical transition state. A cyclohexene-like transition state (see text) gives a calculated ΔS^* of 3.6 eu. [d] See also ref 3d for additional information on these values.

Table II. Line Widths of C_6HD_{11} and TMS and Rate Constants for Chair–Chair Interconversion

Temp, °C	Line widths[a] C_6HD_{11}	Line widths[a] TMS	Sweep rate[b]	k, sec^{-1}
−24.0	0.74	0.30	1.78	2490
−34.4	1.44	0.33	3.57	1150
−42.5	2.80	0.52	3.57	566
−61.4	Coalescence temp		. .	64
−77.9	2.44	0.40	10	6.4
−81.8	1.62	0.35	3.57	4.0

[a] In cps. [b] In cps/min.

The sweep rates used to obtain the spectra are also given. Typical spectra are shown in Figures 1 and 2. Comparisons of experimental spectra with computer-calculated spectra are shown in Figures 2 and 3. At least six separate measurements of the line widths of both C_6HD_{11} and TMS were made at each temperature.

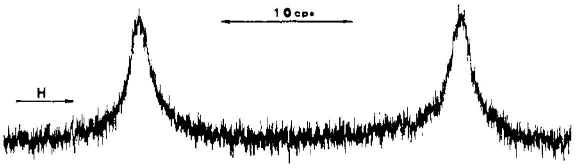

Figure 1. Nmr proton spectrum of cyclohexane-d_{11} at −77.9°, with deuterons decoupled.

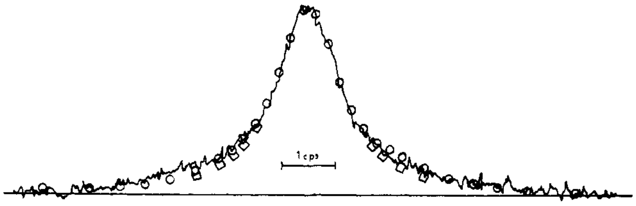

Figure 2. Nmr proton spectrum of cyclohexane-d_{11} at −35.3°, with deuterons decoupled. The circles represent points calculated with k = 1150 sec^{-1}, $T_2{}^0$ = 30 sec, and a broadening function based on the TMS line. The squares represent points calculated with the same k, but with T_2 = 0.86 sec. Where squares and circles coincide, only circles are shown.

B. Double-Resonance Method. Figures 4 and 5 show decay and recovery curves at different temperatures. Figures 6 and 7 show typical plots of log functions of the decay and recovery of magnetization against time. Table III gives the values of T_1 and k, calculated as described in the Discussion, at various temperatures.

Table III. Lifetimes (τ_A), Spin-Lattice Relaxation Times (T_{1A}), and Rate Constants (k) for Ring Inversion in C_6HD_{11} by the Double-Resonance Method

Temp, °C	Lines observed and modes[a]	τ_A, sec	T_{1A},[b] sec	k,[b] sec^{-1}
−96.9	lf and hf, dec and rec	3.8	25 ± 2	0.27 ± 0.03
−100.4	hf, dec and rec	9.0	23 ± 1	0.11 ± 0.01
−105.3	lf and hf, dec and rec	14.1	29 ± 2	0.071 ± 0.004
−107.3	lf, dec	26	32	0.039
−112.1	lf[c]	74	. . .	0.014
−116.7	lf[c]	236	. . .	0.004

[a] lf = low field, hf = high field, dec and rec = decay and recovery of magnetization. [b] The errors are the standard errors of the mean for several experiments at the same temperature. [c] The ratio of magnetization only was measured; τ_A and k were calculated with an assumed T_{1A} of 27 sec.

Discussion

Calculation of Rates from Line Widths and Coalescence Temperature. As mentioned previously,[4] the determination of ΔH^* or ΔE requires k to be measured accurately and over a wide temperature range. To obtain k at as high a temperature as possible, the line shape, or more simply the line width, of a fairly narrow line has to be measured. Since the instrumental or magnetic-field inhomogeneity was of the order of 0.3 to 0.4 cps, conditions were chosen where this amount was a comparatively small correction in the observed line width. Therefore, spectra were taken at several temperatures in the vicinity of −30° where line widths

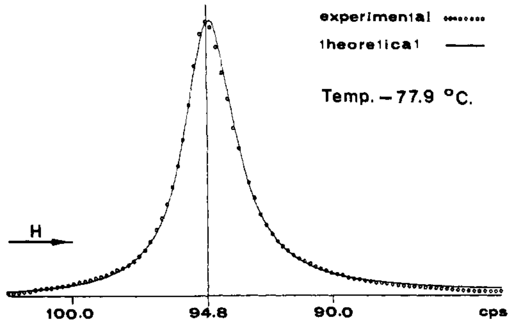

Figure 3. Comparison of the line shape of cyclohexane-d_{11}. The "experimental points" are taken from a smooth curve drawn through the low-field peak of Figure 1. The theoretical line corresponds to k = 6.2 sec^{-1} and T_2 = 0.80 sec.

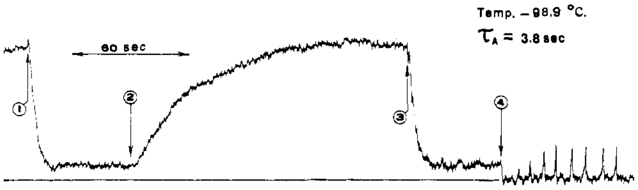

Figure 4. Decay and recovery of magnetization of the high-field line of cyclohexane-d_{11}. Arrows 1 and 3 show the application of a saturating radiofrequency field at the frequency of the low-field line; arrow 2, the removal of the field. Arrow 4 shows the beginning of a field sweep to observe the low-field line, which is rapidly (manually) swept successively upfield and downfield.

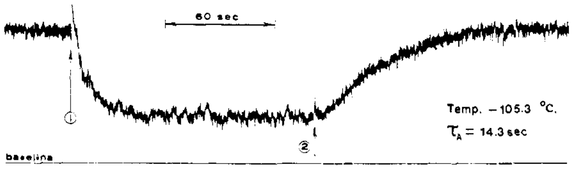

Figure 5. Decay and recovery of magnetization for the high-field line of cyclohexane-d_{11}. Arrow 1 shows the onset of saturation of the low-field line, and arrow 2 the removal of the saturating field.

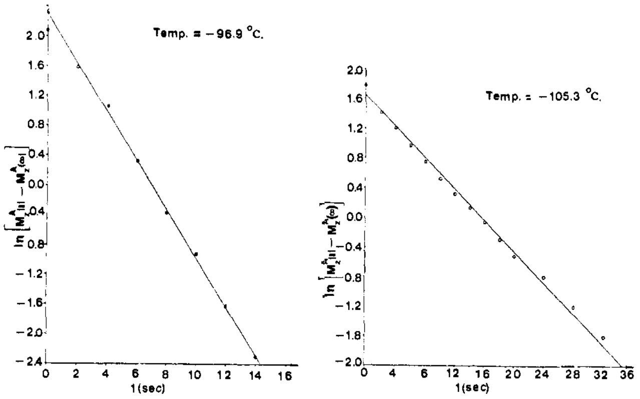

Figure 6. Logarithmic plots (base e) of the decay of magnetization shown in Figures 4 and 5. The units of the vertical coordinates are arbitrary. The slopes of the lines give τ_{1A} = 3.0 and 9.5 sec at −96.9 and −105.3°, respectively.

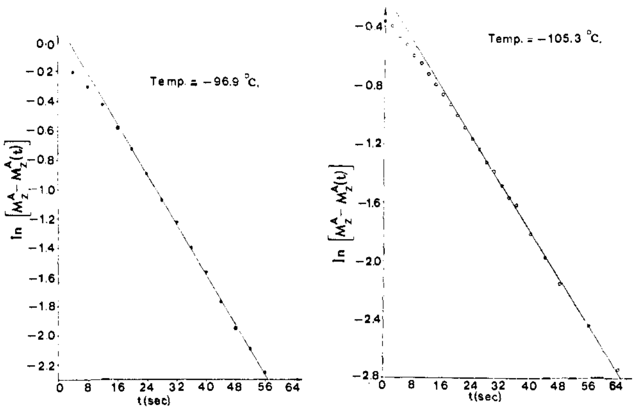

Figure 7. Logarithmic plots (base e) of the recovery of magnetization shown in Figures 4 and 5. The units of the vertical coordinates are arbitrary. The slopes of the straight lines give T_{1A} = 23.5 and 24.8 sec at −96.9 and −105.3°, respectively.

of C_6HD_{11} varied from about 0.9 to 0.8 cps. Similarly, at the lowest temperatures where the line-shape method can be applied, the spectra consist of pairs of slightly broadened lines. In the present work, measurements were made at *ca.* −80°, where the line widths were *ca.* 2 cps.

The value of k was also measured near T_c, in order to obtain a check on the values obtained at lower and higher temperatures.

Values of k at −27 to −42° were calculated by the fast exchange approximation[8]

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

where ν_{AB} is the chemical shift between protons in equatorial and axial sites, and $\delta\nu$ is the line width at half-height when all broadenings other than that resulting from ring inversion are zero. In actual practice, the line is broadened by magnetic-field inhomogeneities of about 0.3 cps, and by a finite T_2^0. The transverse relaxation time in the absence of exchange, T_2^0, is equal to T_1 when the relaxation mechanism is the direct dipole–dipole interaction and the line width is narrow compared to the magnitude of this interaction, as is true under our conditions.[9] Even at −100°, the value of T_1 for C_6HD_{11} in dilute carbon disulfide solution is about 25 sec. At higher temperatures, T_1 is undoubtedly even longer.[3f] Thus the broadening resulting from a finite T_2^0, which is equal to $1/\pi T_2^0$, is less than 0.02 cps and is therefore negligible. For tetramethylsilane (TMS), we estimate[10] that T_1 is longer than 10 sec, so that $1/\pi T_2^0$ for TMS is no more than 0.03 cps. Therefore, the observed line width of TMS gives a measure of magnetic-field inhomogeneities, and it can be substracted from the observed line width of C_6HD_{11} to obtain the corrected line width, $\delta\nu$, for substitution in eq 1. The value of ν_{AB} (28.7 cps) used in eq 1 was obtained at −100°, but since this value is temperature independent from −100 to at least −80°, we feel that the value at −30° cannot be in error by more than 0.2 cps. The resulting error in k is then less than 2% and can be neglected compared to other errors.

In the low end of the temperature range, k can be calculated from the slow-exchange approximation,[8] eq 2, where $\delta\nu$ is the corrected line width of either line of C_6HD_{11}, and is obtained in a way analogous to that described for the fast-exchange region.

$$k = \pi\delta\nu \qquad (2)$$

The coalescence temperature (T_c) was also determined. The rate constant at T_c can be calculated by eq 3. Magnetic-field inhomogeneities of the order

$$k = \pi\nu_{AB}/\sqrt{2} \qquad (3)$$

existing in the present work have almost no effect on the observed spectrum at this temperature and can be ignored.

The calculated rate constants are given in Table II.

Calculation of Line Shapes. While it was anticipated that eq 1 to 3 would be excellent approximations[11]

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[8] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965, p 481; F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964).

[9] A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, Oxford, 1961, p 292.

[10] Neat TMS is reported to have T_1 = 17 sec at 25°: F. A. Bovey, quoted by W. A. Moniz, W. A. Steele, and J. A. Dixon, *J. Chem. Phys.*, **38**, 2418 (1963).

[11] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

and therefore that the values of k so obtained would be accurate, more rigorous calculations were undertaken to support this point. We have used for this purpose a computer program for exchange between multiple sites, kindly made available by Professor M. Saunders of Yale University. For cyclohexane-d_{11}, there are only two sites and there is no spin coupling. The equation describing the line shape for this situation can be rigorously stated[8] and is actually not very complicated, even when a finite T_2 ($T_2^A = T_2^B$) is used. It is usual to take T_2 to describe the line width in the absence of exchange and to include in T_2 not only T_2^0, but also a quantity T_2' dependent on the magnetic-field inhomogeneity, as

$$1/T_2 = 1/T_2^0 + 1/T_2'$$

The use of T_2' assumes that the line shape caused by the magnetic-field inhomogeneity is Lorentzian, which is often not true. In any case, the procedure is not really correct, and what should be done is to first calculate the line shape with T_2^0, and then to put in the inhomogeneity broadening by a convolution function, as has been done by Saunders[12] in his program. We have used both procedures, but we have found that the more lengthy convolution calculations are not needed when the line shape of a reference compound, *e.g.*, TMS, is reasonably good, *i.e.*, close to Lorentzian.

Figures 1 and 2 show typical spectra. Some comments about the way these spectra were measured are desirable at this point. The radiofrequency field was set well below saturation, and this was determined to be so in two ways: (a) at the same sweep rate the intensity of the band could be increased at least threefold by increasing the radiofrequency field, and (b) no decrease of intensity with time was noted when the field was rapidly adjusted to the center of the band. Thus we can safely ignore perturbations due to a finite radiofrequency magnetic field. This test was made for both the lines of C_6HD_{11} and TMS at all temperatures where spectra were taken.

A second important point is the sweep rate used to measure the spectra. In general, the spectra of C_6HD_{11} were symmetrical and showed no trace of ringing. For the TMS band extremely slow sweeps are necessary to remove all traces of ringing, because the line is very sharp, and this very slow rate becomes inconvenient when the much wider C_6HD_{11} line is observed. The sweep rate chosen was a compromise and the TMS line shape used in the convolution analysis was smoothed to remove the remnants of ringing. Twenty-one intensity values at intervals of 0.24 cps were used to describe the line shape of TMS. Ample frequency response was generally used, and consequently the spectra are somewhat noisy; however, a smooth curve can be easily drawn by eye through the noise.

Figures 2 and 3 show spectra calculated by Saunders' program, with values of k obtained by the line-width method and with magnetic-field inhomogeneities considered in the two ways described above.

In Figure 3 the line shape of the TMS was very close to Lorentzian, and indeed the calculated and observed spectra agree very closely when the magnetic-field inhomogeneity is described by an effective T_2.

Figure 2 shows a calculated spectrum which fits somewhat less well with the experimental spectrum when this kind of description is used, but where somewhat better agreement can be obtained by the convolution procedure. In this particular experiment, the line shape of TMS was poorer than in the experiment shown in the previous figure. Also, the line width of C_6HD_{11} is narrower by about a factor of two in Figure 3 than in Figure 2. The effects of poor line shape are in general most noticeable with a particular line width. The humps at the base of the band of C_6HD_{11} in Figure 4 reflect the presence of appreciable intensity at distances of 1 to 2 cps from the center of the TMS line. Although this intensity is small when measured simply by height, it is appreciable when integrated intensities (*i.e.*, areas), are considered. Thus, when the central line is broad, as in the C_6HD_{11} band, the humps on the sides have appreciable heights when compared to the height at the center of the band. In the convolution procedure, it is important to obtain a correct base line for measuring the line shape of the TMS peak; otherwise the results may be no better than if an effective T_2 had been used.

A poor line shape often corresponds, very roughly, to the superposition of two Lorentzian lines of very different widths. This phenomenon (the so-called base-line rise) has been given some attention recently by instrument makers. Resolution should not be described only by line width at half-height but also by the width at other points, which give some indication of the line shape. The width at 0.5% height (*e.g.*, at the height of the ^{13}C satellites for a compound such as chloroform), or 0.1% height, gives an excellent measure or departure from a Lorentzian line shape. A non-Lorentzian line shape is evident in virtually all published experimental nmr spectra. The effect is particularly obvious when a computer-calculated line shape is also given.[13] Of course, these calculated spectra use an effective T_2 to give the corrected line width at half-height. The reporting of resolution in terms of line widths at half-height, and at say 0.5% height, would seem very desirable in accurate work.

Figure 2 clearly shows that even when the reference line has a comparatively bad line shape, the line width at half-height is virtually the same for a given k when calculated with an apparent T_2 as when the convolution method is used. Although the use of computer-calculated line shapes undoubtedly is capable of giving the most accurate rate constants, this procedure would seem to be worthwhile only in extremely accurate work, which would also require very precise temperature control and measurement. All the results given in Table II were actually obtained under conditions such that the line shape was considerably better than in the experiment just described.

Calculation of Rates by the Double-Resonance (Relaxation) Method. Eigen[14] and others have done much recently to develop relaxation methods for obtaining kinetic data on systems which are initially at equilibrium. Most of this work has dealt with ultrafast reactions, but slower reactions can also be studied. The

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[12] M. Saunders, private communication; C. S. Johnson, Jr., *Advan. Magnetic Resonance*, 1, 33 (1965).

[13] J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 3896 (1965).

[14] M. Eigen and L. De Maeyer, "Investigation of Rates and Mechanisms of Reactions," Part II, 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 18.

principle of the method is to disturb the equilibrium in some way, and then to measure the approach to a new equilibrium value. The double-resonance method of Forsén and Hoffman[7] (FH) for obtaining rates in an exchanging system is actually a relaxation method of a novel kind.

It is possible to change the relative population of the two spin states, $+^1/_2$ and $-^1/_2$, for protons in a certain site, say B, in a number of ways, *e.g.*, by saturation with a strong radiofrequency magnetic field. If these protons are transferred by an exchange process to another site, say A, the relative spin population at this site will change, and the change can be followed by measuring the intensity of the proton band for site A by means of a weak radiofrequency magnetic field. The intensity at site A does not reach zero, because spin-lattice relaxation tends to maintain the relative population of the spin states at its thermal equilibrium value. In the simple case of two sites with equal numbers of protons and equal spin-lattice relaxation times (T_1), the following effects are observed when the protons at site B are instantaneously saturated. The intensity of the band of protons at site A decreases and reaches a new value, which is significantly different from the old value, or from zero, only when the lifetime of protons in either site is comparable to T_1. Thus the range of lifetimes which can be measured is severely limited, but it is a range which is virtually inaccessible by the line-shape method.

In their experimental procedure, FH used a rapid repetitive scan in the field-sweep mode. Because of the changing magnetic field, a large radiofrequency field is required to saturate nuclei at site B, so that it is necessary that site A be well separated from site B. FH also used a nonspinning, and hence a fairly low resolution procedure, to avoid ringing of the line at site A. This mode of operation would be difficult to apply when the separation of A from B is less than 30 cps, as it is in C_6HD_{11}.

Since our spectrometer was equipped with an internal field-frequency lock which prevented field drifts from occurring, it was possible to adjust the magnetic field so that protons at site A were at resonance at the observing frequency. Spinning was used and a very sharp line was therefore given by these protons, but it was nevertheless possible to "sit" on top of the line. Satisfactory signal-to-noise ratios were achieved even though extremely low-radiofrequency magnetic fields were used to avoid saturation. Tests for saturation were made by the method described in the previous section. Protons at site B also gave a sharp line, which was therefore saturated very easily even by a fairly small radiofrequency field. This second irradiation had no *direct* effect on the intensity of the line given by protons at site A.

It is now necessary to present the equations which are applicable to our experiments; more general systems have been discussed by FH.[7,15] It is convenient to use the magnetization (*e.g.*, $M_z^A(t)$) of protons in a given site (A) at a given time (t) in the direction of the static magnetic field (H_z). The magnetization depends on the relative spin population and is zero when the protons are saturated. The band intensity of the protons in a given site, measured by using a weak radiofrequency field, is proportional to the magnetization for that site. The equilibrium magnetization at site A in the absence of saturating radiofrequency fields will be denoted by M_z^A.

In our case, the bands of axial and equatorial protons at low temperatures have equal intensities, and consequently the proton populations at the two sites are equal, and the average lifetimes in the two sites, τ_A and τ_B, are also equal. Furthermore, $k = 1/\tau_A = 1/\tau_B$.

The magnetization at site A, $M_z^A(t)$, after the instantaneous application of a strong radiofrequency field at site B at $t = 0$, is given by

$$M_z^A(t) = M_z^A[(\tau_{1A}/\tau_A)\exp(-t/\tau_{1A}) + \tau_{1A}/T_{1A}] \quad (4)$$

where T_{1A} is the spin-lattice or longitudinal relaxation time and τ_{1A} is given by

$$1/\tau_{1A} = 1/T_{1A} + 1/\tau_A \quad (5)$$

An equilibrium value of $M_z^A(t)$ is reached asymptotically at $t = \infty$ and is given by

$$M_z^A(\infty) = M_z^A\tau_{1A}/T_{1A} \quad (6)$$

Upon substitution of eq 6 in eq 4, eq 7 is obtained. Consequently a plot of the log of the right-hand side of eq 7 against t will give a straight line. From the slope

$$M_z^A(t) - M_z^A(\infty) = M_z^A(\tau_{1A}/\tau_A)\exp(-t/\tau_{1A}) \quad (7)$$

of this line, τ_{1A} can be calculated. The ratio $M_z^A(\infty)/M_z^A$ is easily available experimentally and gives τ_{1A}/T_{1A} (eq 6), so that τ_{1A} and T_{1A} can be obtained. Equation 5 then gives τ_A which is equal to $1/k$.

When the strong radiofrequency field at B is removed, the magnetization at A recovers its initial thermal equilibrium value, but not in a simple exponential fashion. The expressions for the magnetizations at A and B are given by eq 8 and 9. The values of c_1 and c_2 are

$$M_z^A(t) = M_z^A + c_1\exp(-\lambda_1 t) + c_2\exp(-\lambda_2 t) \quad (8)$$

$$M_z^B(t) = M_z^B + c_1[(1/\tau_{1A}) - \lambda_1)]\tau_B\exp(-\lambda_1 t) + c_2[(1/\tau_{1A}) - \lambda_2)]\tau_B\exp(-\lambda_2 t) \quad (9)$$

determined by the initial conditions, which are given by eq 10, when the saturating field at B is removed at time

$$M_z^B(0) = 0 \text{ and } M_z^A(0)/M_z^A = \tau_{1A}/T_{1A} \quad (10)$$

$t = 0$. Thus, eq 11–13 can be obtained.[7]

$$c_1 = M_z^A[\lambda_2(T_{1A} - \tau_{1A})/(\lambda_1 - \lambda_2)T_{1A}] \quad (11)$$

$$c_2 = M_z^A[\lambda_1(T_{1A} - \tau_{1A})/(\lambda_2 - \lambda_1)T_{1A}] \quad (12)$$

$$c_1/c_2 = -\lambda_2/\lambda_1 \quad (13)$$

Values of λ_1 and λ_2 are given by solving the following determinant for λ.

$$\begin{vmatrix} (1/\tau_{1A} - \lambda) & -1/\tau_B \\ -1/\tau_A & (1/\tau_{1B} - \lambda) \end{vmatrix} = 0$$

Although in principle the nuclei may have different relaxation times in the two sites, in practice the values obtained from the decay curves show that within experimental error (10–15%) they are the same and have an average value over the temperature range of 27 sec. Since, even at the lowest rates measured from the recovery curve, the lifetime is only 14 sec, it follows that

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(15) S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, 40, 1189 (1964).

in this temperature range the value of $1/\tau_{1A}$ in eq 2 will be dominated by the value of τ_A, and, as $\tau_A = \tau_B$, it follows that to a good approximation $\tau_{1A} \approx \tau_{1B}$. The determinant then becomes

$$\begin{vmatrix} (1/\tau_{1A} - \lambda) & -1/\tau_A \\ 1/\tau_A & (1/\tau_{1A} - \lambda) \end{vmatrix} = 0$$

and solving this gives $\lambda_1 = 1/\tau_{1A} + 1/\tau_A$ and $\lambda_2 = 1/\tau_{1A} - 1/\tau_A = 1/T_{1A}$.

When exchange is very fast one obtains $\lambda_1 = 2/\tau_A$ and $\lambda_2 = 1/T_{1A}$ corresponding to eq 18 of ref 7 with $P_A = P_B = {}^1/_2$.

According to eq 5, the recovery curve for $M_z^A(t)$ will approximate to a single and easily soluble exponential if $\lambda_1/\lambda_2 = -c_2/c_1 >> 1$. The exponential with the smallest c value will have the largest λ value, and its effect on $M_z^A(t)$ will quickly decay to zero leaving $M_z^A(t)$ as a function of the remaining exponential.

Under these conditions eq 8 reduces to

$$M_z^A(t) - M_z^A = c_2 \exp(-t/T_{1A}) \qquad (14)$$

If $\lambda_1/\lambda_2 = 2$ is set as a lower workable limit and T_{1A} taken to be 27 sec, this puts an upper limit of 13 sec ($k = 0.08$ sec^{-1}) on τ_A. The lowest rate where recovery of magnetization was studied is slightly lower than this value, $k = 0.07$ sec^{-1}, *i.e.*, $\tau_A = 14.3$ sec. The recovery curve at this temperature is shown in Figure 7, and it can be seen that the plot of ln $(M_z^A - M_z^A(t))$ against time approximates very well to a straight line in the region of $t > 16$ sec. The slope of this line gives T_{1A} (eq 14).

At temperatures between −110 and −116°, where the ratio $M_z^A(\infty)/M_z^A$ is approaching unity, the curves become very shallow and difficult to measure accurately. Furthermore, the recovery curve in this region is a function of two exponentials as discussed above and as a consequence is more difficult to interpret. However, it is still possible to measure $M_z^A(\infty)/M_z^A$ reasonably accurately and, if a value of T_1 is assumed, τ_A can be calculated. The values in Table III at temperatures of −112.1 and −116.7° were calculated in this manner using $T_{1A} = 27$ sec, a value which is the mean T_{1A} found between −97 and −107°. Values of τ_A, T_{1A}, and k are given in Table III. It can be seen that over the temperature range −97 to −117°, k changes by a factor of slightly over 50.

As a test for complete saturation in site B, it is useful to know that at the high rate found at −97°, $M_z^A(0)$ should decay to a value of $M_z^A(\infty)$ which is very small. The fact that it does so (Figure 4) is a good indication that site B is almost wholly saturated. As a further check we examined the signal from site B at the finish of one of the site A decay curves (Figure 4). This was accomplished by quickly moving the variable frequency ν_2 so that the spectrum was effectively field-swept through the recording frequency ν_1 in the direction which brings site B into resonance at ν_1. This simultaneously sweeps the saturating frequency ν_3 off resonance because $\nu_1 - \nu_3$ is fixed so that the signal at B begins to recover as soon as ν_2 is changed. The recovery can be followed by repeatedly sweeping through the resonance. We found that the fastest time in which it was possible to move from A to B without breaking the field-frequency lock was about 4 sec. By this time B had partially recovered, but, by extrapolating the peak intensities back to $t = 0$, it was possible to determine that B was originally completely saturated when A was being observed.

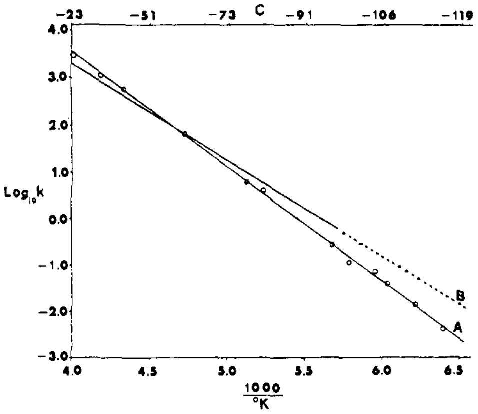

Figure 8. Arrhenius plot for ring inversion in cyclohexane-d_{11}. The slope of line A corresponds to an activation energy (ΔE) of 11.24 kcal/mole. Line B (full line) is identical with the line drawn by ACG except that the region above −23° is not shown. The dashed portion of B is an extrapolation to temperatures not investigated by ACG.

The values of T_1 for cyclohexane-d_{11} in carbon disulfide solution (12%) given in Table III are longer than would be expected on the basis of ACG's work. However, ACG used a more concentrated solution (1:1 by volume), which contained a higher density of magnetic nuclei, and which was also probably more viscous than our solution. These factors[9] tend to shorten T_1.

Activation Parameters for Ring Inversion in Cyclohexane. The rate constants for ring inversion, k, obtained by both the line-shape and the double-resonance methods are given in Tables II and III and are shown as an Arrhenius plot in Figure 8. The best straight line (A) through these points was calculated by a least-squares analysis. All our data fall very close to this line, even though k varies by a factor of over half a million. The point at the highest temperature and the points at the two lowest temperatures are considered to be somewhat less accurate than the rest of the data, but exclusion of these points does not significantly alter the slope of the best line through the remaining data.

It is significant that the points obtained by the line-shape method, which was used from −82 to −24°, define the same line as the points derived from the double-resonance method, which was employed over a very different temperature range, namely −117 to −97°. We feel that this agreement is an excellent test of the accuracy of all our data.

It is very likely that a boat or twist boat is an intermediate in the chair–chair interconversion.[16] Therefore, the observed rate constant k is equal to ${}^1/_2 k_{cb}$, where k_{cb} is the rate constant for the chair-to-boat (or twist boat) process. This follows clearly from the fact that of the molecules which become boats, one-half will revert to their initial chair forms and one-half

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(16) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961); R. Bucourt and D. Hainaut, *Bull. Soc. Chim. France*, 1366 (1965). For recent reviews of ring inversion, see L. W. Reeves, *Advan. Phys. Org. Chem.*, 3, 187 (1965); J. E. Anderson, *Quart. Rev.* (London), **19**, 426 (1966); F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964); also ref 2.

will go to the inverted chair forms. Since the chair-to-boat process presumably involves only a single barrier, in contrast to the chair-to-chair process which involves two equal barriers, it is simpler to use parameters which refer to the chair-to-boat process in the discussion of ring inversion. The values of ΔF^*_{bc} and ΔS^*_{bc} given in Table I are for the chair-to-boat process and were calculated from k_{cb} $(=2k)$. The values of ΔH^* and ΔE, also given in Table I, are the same for the chair-to-chair and chair-to-boat processes and are therefore not subscripted.

Since $\Delta E = \Delta H^* + RT$, we might expect the Arrhenius plot not to give a straight line over an extended range of temperatures, provided that ΔH^* is temperature independent, or at least that its temperature dependence does not cancel with the RT term. However, since the value of RT varies only by about 0.1 kcal/mole at the extremes of the temperature range from its mean value, a curvature would scarcely be noticeable.

We have not given statistical limits of errors on the kinetic parameters, because we have probably not eliminated all forms of systematic error to the point where random errors have become dominant. Our somewhat subjective estimate of the "standard errors" in ΔH^* and ΔS^* are ± 0.1 kcal/mole and 0.5 eu, respectively.

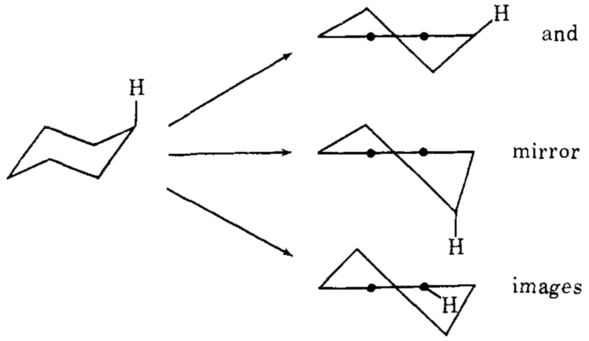
Our value of ΔF^*_{bc} is in excellent agreement with previously obtained values (Table I). For the other activation parameters, ΔH^*, ΔE, and ΔS^*_{bc}, there is excellent agreement with recent high-resolution work,[3d,e] but not with ACG's spin-echo results.[3f] Figure 8 shows the nature of the discrepancy. The value of k found by us (line A) and by ACG (full line B) are in excellent agreement at temperatures near T_c. At temperatures much higher than T_c, ACG's values are lower than ours, while the reverse is true at temperatures much lower than T_c. If the results of ACG were correct, then our observed line broadening at both -30 and $-80°$ should have been about 50% greater than actually found. It is very difficult indeed to find an effect which would cause this kind of error. Most effects,[11] such as saturation due to the use of too high a radiofrequency field, cause line broadening. In the temperature range where we have used the double-resonance method, the values of k found by us are about three times smaller than are predicted by an extrapolation of ACG's results.

The temperatures in our experiments, as mentioned in the Experimental Section, were determined very carefully, furthermore, if the temperature measurements were at fault, it is very peculiar that this would not be true near T_c, since our results at this temperature agree closely with those of ACG and of Bovey, *et al.*[3e]

The most likely causes of discrepancy between ACG's and our data are systematic errors. Since we have employed two entirely different methods for measuring rate constants, and both methods give essentially the same set of kinetic parameters, it is scarcely conceivable that systematic errors are important in our results. On the other hand, ACG employed a single method, which is undoubtedly most accurate near T_c, but which becomes less accurate at both higher and lower temperatures. At the moment, we do not know that systematic errors are present in ACG's data, and we have no specific suggestion to make about the precise nature of any possible systematic errors. Gutowsky, *et al.*, have recently analyzed the errors which could be present in their previous spin-echo results[11] and conclude that large errors should not occur under the conditions of their experiment. However, ACG have pointed out that their spin-echo measurements were obtained at a low frequency (26.85 Mc/sec) and on a not very elaborate instrument. It would therefore appear very desirable that this spin-echo work be repeated at a higher frequency (say 60 Mc/sec) and with the best instrumentation available. It is perhaps significant that in a previous spin-echo study at 60 Mc/sec, Meiboom[3c] found a positive ΔS^*_{cb} (Table I), unlike that found by ACG. The high-resolution and the spin-echo methods must of course give the same results if all errors are eliminated from both procedures. We feel that our data on ring inversion in C_6HD_{11} are the most accurate available at the present time.

Our observed ΔH^* of 10.8 kcal/mole is a little smaller than the 12.7-kcal/mole energy difference between the chair and half-chair forms calculated by Hendrickson.[16] However, the calculations assume an internal angle of 109.5° for the chair, whereas the true internal angle is 111.6°, and Bucourt and Hainaut[16] have shown that calculations taking this difference into account lead to a slightly lower energy for the boat form than found by Hendrickson. Since the half-chair has several internal angles that are much larger than 110°, the effect in this case will be an appreciable lowering of the energy. Thus, ΔH^* should be somewhat smaller than the calculated 12.7 kcal/mole, in agreement with observation.

One satisfying aspect of the present results is that the entropy of activation, ΔS^*_{cb}, is slightly positive as would be expected on symmetry grounds.[3a] Thus, if a cyclohexene-like transition state (II), as suggested by Hendrickson,[16] is accepted, it is clear that C_6HD_{11}, say in H-axial form, has six distinct paths for reaching the transition state, as shown below. This can also be seen to be true because there are three different types of carbon atoms in the transition-state structure, which furthermore exist in *d* and *l* forms. If inversion took place *via* only one of these six structures, $\Delta S^*_{cb} \approx 0$, provided that the vibrational and rotational contributions to the entropy are closely similar in the ground and transition states, as is likely. Since inversion takes place *via* any of the six possible transition states, $\Delta S^*_{cb} = R \ln 6 = 3.6$ eu. Thus, the value of ΔS^*_{cb} found by ACG requires a vibrational and rotational contribution of -9.4 eu to ΔS^*_{cb}. Since the vibrational entropy of cyclohexane is only 9.3 eu,[17] this does not appear to



II

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

be probable. Our present results give $\Delta S^*_{cb} = 2.9$ eu, which is in the range of values expected from our discussion. We have assumed a transmission coefficient of one in the absolute rate theory expression for k_{cb}, a procedure generally followed by other workers,[3] including ACG.

There are a number of examples, *e.g.*, 1,1-difluorocyclohexane,[11,18] perfluorocyclohexane,[19] and N,N-dimethylformamide,[20] where early work showed more or less large negative entropies of activation, whereas more accurate later work showed positive or only very slightly negative entropies of activation. It appears that there are only very few systems which have been studied by nmr where ΔS^* is known to the nearest entropy unit, or where ΔH^* is known to 0.1 kcal/mole. It has been suggested[21] recently that rate constants obtained by the line-shape method with cyclohexane-d_{11} might be in error because an Overhauser effect, caused by the decoupling field at the deuteron resonance frequency, might affect the "proton relaxation time." The theory of the nuclear Overhauser effect is well established.[9] The primary effect is to change the equilibrium population of spin states; thus the total intensity is affected, but the line shape does not change. The spin-lattice relaxation time, T_1, is unaffected. It is true that "T_2," if measured by the line width does change when the deuterons are irradiated, but this is because of decoupling, not because of an Overhauser effect. In fact, the undecoupled line[3] (Figure 9) is far from Lorentzian, and thus it cannot be described even by an effective T_2. The inherent T_2 is T_2^0, which as pointed out earlier is equal to T_1 when the relaxation mechanism is the direct dipole–dipole interaction, as is undoubtedly true in the present case. When exchange takes place either very rapidly or very slowly, the line or lines are Lorentzian and an exchange contribution to T_2 can be formulated. This contribution cannot be affected by an Overhauser effect. Because of the small frequency range of the deuterons in cyclohexane-d_{11}, estimated to be about 5 cps, it is extremely easy to obtain complete decoupling, even when the deuteron frequency is offset from its best value by 10 cps or more. Thus decoupling should be complete irrespective of the rate of ring inversion.

Christiansen[22] has objected recently to the cyclohexane-like transition state (II) for ring inversion in cyclohexane, claiming that only a planar transition state is consistent with infrared spectral data. He has also questioned the use of nmr to obtain rate constants for ring inversion. Neither of these objections is well-founded in our opinion. Christiansen's arguments against II imply that the absolute rate theory does not apply to this system. In any case, a nonplanar transition state is consistent with the infrared data, as Beckett, Pitzer, and Spitzer[17] showed many years ago. The nmr results prove that protons in cyclohexane are in two different sites and that there is an exchange of protons between the two sites. If the chair form of cyclohexane is accepted, then the only exchange process not involving bond breaking is chair–chair interconversion, *i.e.*, ring inversion.

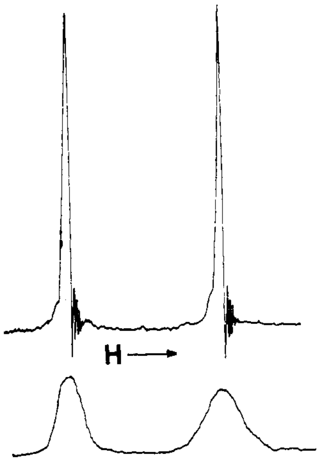

Figure 9. Proton nmr spectrum of cyclohexane-d_{11} at −100°: lower curve, without deuterium decoupling; upper curve, with deuterium decoupling. The separation between the peaks is 28.7 cps (0.462 ppm).

Experimental Section

Cyclohexane-d_{11} was obtained from Merck Sharp and Dohme of Canada Ltd. No isotopic species other than C_6HD_{11} were evident in the low-temperature spectra, even under conditions that ^{13}C satellites of C_6HD_{11} were clearly visible. The sample for rate measurements was a 12% solution of C_6HD_{11} in carbon disulfide with 5.3% methylene chloride added to provide a suitable lock signal, and 1% tetramethylsilane (TMS) added as a reference peak. The solution was placed in a 5-mm thin-wall nmr tube which had been modified by the addition of a spherical glass bead of 5-mm diameter to the bottom of the tube so as to reduce thermal contact between the solution and the Teflon supporting cup at the bottom of the insert when the tube was in the probe of the spectrometer. The tube was subjected to several freeze-pump-thaw cycles to degas the solution and was then sealed. The height of the solution in the tube was 3.0 cm.

The variable-temperature probe was built from a design by Shafer[23] and is similar but somewhat more elaborate than that described by Brownstein.[24] Temperature measurements were made from a thermocouple constructed from 33-gauge copper and constantan wires. One junction was kept in an ice-water mixture, and the other was sealed with epoxy cement in a hole made in the wall of the probe insert at a height about 1.8 cm above the center of the receiver coil. The generated emf's were measured with a Leeds and Northrup potentiometer, No. 8677, and the corresponding temperatures were obtained from an emf–temperature table.[25] The thermocouple was calibrated at the sublimation temperature of solid carbon dioxide[25] (−78.62° at 760 mm) by the method given by Scott. This temperature was also measured on a Leeds and Northrup platinum resistance thermometer, No. 8163, and was found to be within 0.1° of the published value.[25]

The temperature measured at the insert was slightly lower than the actual temperature inside the sample tube owing to inflow of heat resulting from thermal contact with the bottom of the insert. To make this difference as small as possible, a large flow of coolant gas was used. Nitrogen gas from boiling liquid nitrogen was mixed with dry cylinder nitrogen gas, which was kept at a constant flow of 8 l./min. The temperature was varied by changing the flow of cold nitrogen. The total flow of nitrogen was about 20 and 80 l./min at −50 and −100°, respectively.

Temperature corrections between the inside and outside of the sample tube were determined by inserting a second thermocouple

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into an open sample tube containing the same height of carbon disulfide as contained in the sealed sample tube. The corrections were 1.5 and 0.7° at −50 and −100°, respectively, when the temperature was measured by the second thermocouple at the height of the receiver coil. At the very bottom of the tube the temperature was 1° warmer than at the receiver coil. The temperature gradient along the axis of the tube near the receiver coil was less than 0.3 °/cm. Samples spinning changed the temperature by less than 0.1°. The temperature was also unaffected by the presence of radiofrequency power used for deuterium decoupling. Temperature corrections were obtained for all the temperatures at which rates were measured.

All the spectra were obtained on a Varian HR60 spectrometer operating at 60 Mc/sec and modified by the addition of a second audio phase/detector[26] working at a variable frequency (ν_2) obtained from a General Radio interpolation oscillator, No. 1107A. The 60-Mc/sec transmitter frequency was frequency modulated at the frequency ν_2, and the output of the radiofrequency receiver was phase detected so as to obtain a dispersion mode signal. This signal was amplified by a Philbrick amplifier and applied in the correct sense to the pickup coils of the superstabilizer. The signal from the methylene chloride was used for locking the magnetic field to a frequency (60 Mc/sec $\pm\ \nu_2$) by the procedure just described. Thus a stabilized field sweep can be obtained by sweeping the frequency ν_2. For this purpose we used a 2-rpm synchronous motor fitted with gears ranging in reduction ratio from 1:1 to 50:1. Sweep rates as low as 4 cps/min were obtained by driving the main dial of the oscillator. Still lower sweep rates, down to 0.713 cps/min, were obtained over a sweep width of 20 cps, when the subsidiary dial was driven. Frequency measurements showed that the oscillator scale was linear with rotation.

Spectra were obtained *via* phase detection at a fixed frequency (ν_1) of about 2000 cps of the Varian integrator, which was used in the side-band mode. A variable attenuator was employed to control the intensity of the magnetic-field modulation at the frequency ν_1. For the double-resonance studies, a third frequency ν_3, was obtained from a Hewlett-Packard oscillator, Model 200AB, which had been modified by the attachment of several potentiometers to the RC circuit so as to allow precise settings of the frequency. This frequency was applied to the modulation input of the 60-Mc/sec transmitter, *via* a Hewlett-Packard 350D attenuator. In these experiments a notch filter, consisting of a series high-Q inductance–capacitor circuit tuned to ν_3, was connected across the output of the radiofrequency receiver.

Deuterium decoupling was accomplished with an NMR Specialties, Inc., Model HD60 spin decoupler. This instrument is essentially a single side-band suppressed-carrier radiofrequency generator which makes use of a 9.2-Mc/sec crystal-controlled oscillator. An audio oscillator was used to generate and adjust the side-band frequency. The radiofrequency power was increased until no further change was observed in the line being decoupled. Since the deuteron resonance spectrum in C_6HD_{11} was only a few cycles per second wide, even at low temperatures, very little power was required to obtain complete decoupling. At room temperature, the line width of the proton spectrum, with deuteron decoupling, of C_6HD_{11} was identical with that of TMS. The line width at half-height of TMS was in the range of 0.2 to 0.5 cps, depending on the care used in the adjustment of the field homogeneity

The frequency stability of the various audio oscillators was found to be excellent provided that these instruments had reached thermal equilibrium in a temperature-controlled environment.

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Investigation of Singlet–Triplet Transitions by the Phosphorescence Excitation Method. IV. The Singlet–Triplet Absorption Spectra of Aromatic Hydrocarbons

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Contribution from the Department of Chemistry, University of California, Riverside, California. *Received July 21, 1966*

Abstract: The phosphorescence excitation method is used to investigate the singlet–triplet absorption spectra of 45 representative aromatic hydrocarbons. From this preliminary study we have obtained singlet–triplet spectra which should be of general use. We have also obtained information regarding molecular vibrational frequencies of triplet-state molecules; energy transfer in halogenated benzene crystals; the triplet-state properties of iodo-substituted benzenes and evidence for uncertainty principle broadening of the S → T absorption spectra; external heavy-atom effects on S → T transitions of guest molecules in heavy-atom host crystals; detection of low-yield photochemical reactions; the assignment of the lowest triplet state in polyacenes; and substituent effects on S → T transitions.

Although it has been over 20 years since Lewis and Kasha first published their classic paper in which they identified the phosphorescent states of organic molecules as triplet states,[3] it has only been in recent years that many implications of their work have been fully appreciated. The current interest in the triplet state of organic molecules has been generated by recent developments in a number of fields, including photochemistry,[4–8] spectroscopy,[9–13] photobiology,[14–17] and

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