triphenyldisilane. The solid was mixed with 50 ml. of absolute ethanol and 50 ml. of 10% hydrochloric acid and stirred at room temperature for 1 hr. The suspension was extracted with ether. Evaporation of the solvent left a solid which was slurried with ethanol and filtered. The insoluble material was recrystallized from ethanol several times to give 10.1 g. (60.3%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 107–110° (mixture melting point). The ethanol-soluble portion proved to be 5.20 g. (37.6%) of triphenylsilanol, m.p. 152–154° (mixture melting point). Further elution of the chromatographic column with ethyl acetate gave an additional 2.50 g. (18.1%) of triphenylsilanol.

Reaction of Chlorotriphenylsilane and Chlorotrimethylsilane with Sodium in Refluxing Xylene.—A mixture of 29.5 g. (0.10 mole) of chlorotriphenylsilane, 10.9 g. (0.10 mole) of chlorotrimethylsilane, 2.30 g. (0.10 g. atom) of sodium and 150 ml. of xylene was heated at reflux temperature for 5 hr. As refluxing started, the sodium melted and the solution became dark blue in color. After the solution had cooled, it was poured into ethanol. The suspended white solid was filtered, washed with water and ether, and dried to give 3.30 g. (12.7%) of hexaphenyldisilane, m.p. 360–365° (mixture melting point). The organic layer from the filtrate was subjected to the usual chromatographic work-up. From the petroleum ether (b.p. 60–70°) eluates was obtained 15.2 g. (45.4%) of crude 1,1,1-trimethyl-2,2,2-triphenyldisilane melting over the range 101.5–107°. Recrystallization from ethanol gave 14.4 g. (43.2%) of pure disilane, m.p. 106.5–109° (mixture melting point, infrared spectrum). Elution of the column with benzene, ethyl acetate and with ethanol gave a total of 8.15 g. (29.5%) of triphenylsilanol, m.p. 150–151.5° (mixture melting point).

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The Rate of the Chair–Chair Interconversion of Cyclohexane[1,2]

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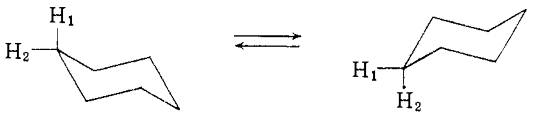
The low temperature proton magnetic resonance spectrum of cyclohexane shows separate axial and equatorial resonances as broad bands, each of which exists as a broad band with unresolved fine structure. The rate of the chair–chair interconversion at the temperature of half-peak separation (−66.7°) is $k = 52.5$ sec.$^{-1}$. Assuming the boat form as an unstable intermediate in this process, $\Delta F^{\ddagger}$ is 10.1 kcal./mole.

Introduction

One of the basic quantities of use in conformation analysis[3] is the facility with which one chair conformation may be converted to the other chair conformation. All chemical information suggests that this interconversion is rapid, and estimates based upon qualitative energetics[4] and upon spectroscopic assignments[5] have been made. Shoppee estimated the barrier to be 9–10 kcal./mole and Beckett, Pitzer and Spitzer estimated the barrier to be 14 kcal./mole.



Other investigators have been concerned with the chair–boat energy difference. Estimates have ranged from 2–10 kcal.,[3,4,6–8] with the boat being less stable.

Recently, a direct experimental method has given the value of 5.3 kcal. for this difference.[9] Another type of measurement which appears useful for these constants is the ultrasonic relaxation method. Recent studies have demonstrated the utility of this method in determining the energy difference between conformers in 2-methylpentane and related compounds as well as the energy barrier between them.[10] Similar studies of cyclohexane derivatives[11,12] have not been carried out as a function of temperature, though these quantities would appear to be accessible for such compounds by this method. However, ultrasonic relaxation fails when two conformers are of equal energy.

A further method is extremely useful in cases of rapid interconversion of two (or more) isomers. This is nuclear magnetic resonance. Several situations have been investigated by this technique; inversion of ethylenimines,[13,14] *cis*- and *trans*-alkyl nitrites[15] and hindered rotation in amides.[16] At high temperatures, the spectrum obtained is the weighted time average of the two isomers; at low temperatures the spectrum is the summation for the individual isomers. The pertinent theoretical considerations are summarized by Pople, Schneider and Bernstein.[17]

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[1] Originally published in preliminary form; F. R. Jensen, D. S. Noyce, C. H. Sederholm and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960); presented, in part, at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

[2] Supported, in part, by the National Science Foundation.

[3] For a recent review, see M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter I by W. G. Dauben and K. S. Pitzer.

[4] C. W. Shoppee, *J. Chem. Soc.*, 1138 (1946).

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[9] W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, **82**, 1255 (1960).

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Results

In the present study, we have examined the low temperature proton magnetic resonance spectrum of cyclohexane in carbon disulfide solution. The single sharp peak observed at room temperature progressively broadens as the temperature is lowered. At a temperature of −64°, it has changed to a single broadly rounded peak with a width at $^1/_2$ maximum intensity of 31 c./s. At −70° separation into two peaks is clearly evident. At −100° the spectrum (Fig. 1) shows two bands which are separated by about 27 c./s. Each band shows splitting into two major peaks of separation 5–7 c./s. In addition, the broad nature of the peaks clearly indicates additional splittings which are incompletely resolved. The complex nature of the spectrum is clearly to be expected, with a great many lines expected within the region of 20–30 cycles.

The peak at low field is assigned to the equatorial protons and the peak at high field to the axial protons. This assignment is consistent with other equatorial and axial assignments.[18] It is to be further noted that the axial (high field) peak is broader than the equatorial peak. This, likewise, is to be expected, since axial–axial coupling constants are larger than equatorial–axial or equatorial–equatorial coupling constants.[19]

The two bands do not have equal areas and therefore cannot be individually assigned, one to equatorial and one to axial protons. However, the interaction of these two protons is probably sufficiently small that little error is introduced in the calculation by such an assignment.

Discussion

The separation of the single peak into two bands is clear evidence that the rate of the chair–chair interconversion has been slowed sufficiently at low temperatures so that the mean lifetime in any given conformation is larger than the inverse frequency separation due to the two kinds of hydrogens.

TABLE I

AXIAL (ν_a) AND EQUATORIAL (ν_e) PROTON RESONANCE SIGNALS FOR CYCLOHEXANE AT VARIOUS TEMPERATURES[a]

Temp., °C.	ν_a, c./s. to TMS	ν_e, c./s. to TMS	Av. ν_a, ν_e; c./s. to TMS	$(\nu_a - \nu_e)$, c./s.
−55	(Time avg.	signal only)	−85.2	. .
−64.8	−80.3	−90.6	−85.4	10.3
−66.6	−79.3	−92.0	−85.6	12.7
−68.0	−75.9	−94.8	−85.3	18.9
−82	−72.4	−97.9	−85.1	25.5
−105	−71.8	−99.1	−85.4	27.3

[a] The solution was 3 *M* cyclohexane in carbon disulfide containing 0.04 ml. of TMS (tetramethylsilane)/ml. of solution.

Two general methods are available for the measurement of rate processes by n.m.r.[15,17]

The first method involves the measurement of the width of the time average signal at temperatures above the temperature of coalescence. In the present case, this process is complicated in that the separate resonances at low temperature are split into many signals. The observed variation of line width occurs over a sufficiently broad temperature range to calculate the enthalpy of activation.[15] Unfortunately, the rate factors obtained were subject to large error and the enthalpy of activation was found to be 11.5 ± 2 kcal./mole. Further attempts are underway to improve these results, and the experiments are not described in more detail in the present paper. However, it should be noted that if the difficulties can be overcome and the enthalpy of activation accurately determined, then the entropy of activation can also be determined since the free energy

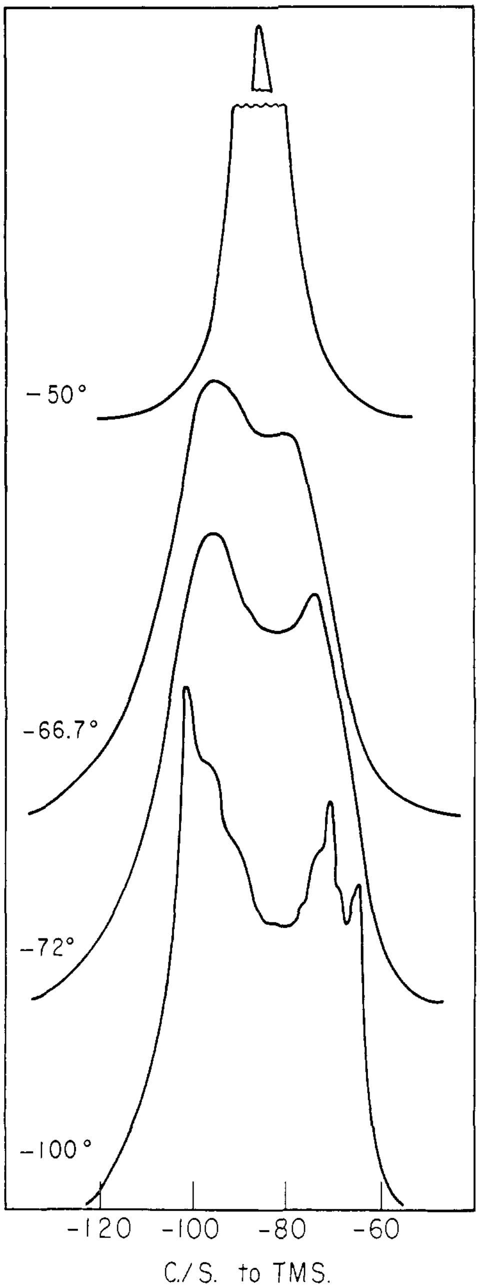

Fig. 1.—Proton resonance spectrum of cyclohexane.

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(17) 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, p. 218 ff., 365 ff.

(18) Reference 17, p. 390.

(19) S. Brownstein and R. Miller, *J. Org. Chem.*, **24**, 1886 (1959).

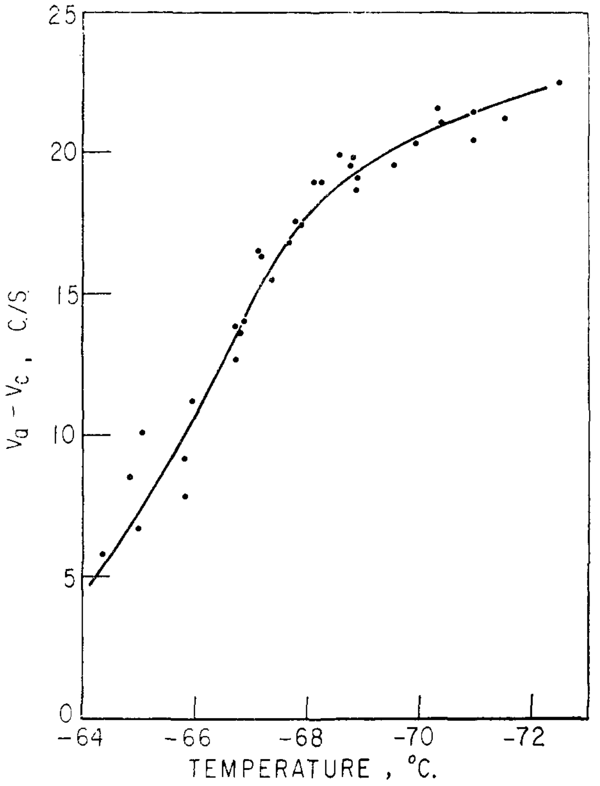

Fig. 2.—Separation of signals for axial and equatorial cyclohexane protons at various temperatures.

of activation can accurately be determined by the line separation method (described below).

The second method is to measure the line separations in the region of the transition from a single time average signal to complete separation of the resonances of the individual protons. This process occurs in the temperature range immediately below the temperature of coalescence. In using this method, it is necessary to know the maximum separation of the resonances. The results reported here are primarily by this line separation method.

Using this method, the rate constant for the interconversion can be accurately determined by measuring the line separation.[17] The major part of the separation occurs over approximately a 6° temperature interval. It is improbable that sufficiently accurate temperature and rate measurements can be made over this small temperature interval using presently available methods to give a reliable enthalpy of activation. By applying the Eyring equation and by making the usual assumption that the transmission coefficient is one, the free energy of activation can be calculated. This procedure was adopted in the present study.

In the preliminary report of these results,[1] the average lifetime (τ) was calculated by observing the temperature at which the lines coalesce into a single broadly rounded maximum, and applying the relation

$$\tau = \frac{\sqrt{2}}{2\pi(\nu_a - \nu_e)} = \frac{1}{k}$$

This method has recently been used by other workers.[20,21]

The parameters have been redetermined for cyclohexane using a slightly different procedure which should give improved accuracy. The free energy of activation by this alternate procedure differs slightly ($\approx$0.4 kcal.) from that originally reported.

In the newly adopted procedure, the line separation (ν_a-ν_e) is plotted as a function of temperature. An S-shaped curve results. Since the peak separation changes most rapidly with temperature in the region of half the maximum separation, the rate constant is calculated at the temperature of half separation using the appropriate function.[22] The total rate constant (k) for the process is calculated for cyclohexane to be 105 sec.$^{-1}$ at the half peak separation temperature of −66.7°. A plot of the data is given in Fig. 2. The above rate constant is the total for the forward and reverse reactions and since these constants are identical, the desired rate constant for the chair–chair interconversion is 52.5 sec.$^{-1}$.

From an examination of models and consideration of energy interactions, various workers have concluded that the most probable path of chair–chair interconversion for cyclohexane involves the boat form as a stable intermediate.[4,5] This conclusion seems to be well founded, for it is difficult to conceive of a lower energy pathway since one end of the molecule can be changed almost independent of the other. However, once the boat form is obtained, it appears highly likely that interchange of boat forms may occur more rapidly than conversion of boat to chair form. Once the boat form is obtained, there is an equal probability that any hydrogen will go to axial and equatorial forms in the resulting chair. This situation then requires a resulting statistical factor of two in calculating the rate constant for the conversion of chair to boat and, therefore, the rate constant this reaction is 105 sec.$^{-1}$ at −66.7°.

Sources of possible error are temperature measurement, instrumental error, the determination of the centers of the signals for partial and complete separation, and the assumption that the transmission coefficient is one in the Eyring equation. In three separate experiments, the half separation was found to occur within 0.3° of the same temperature. Since the thermocouple was carefully calibrated (see Experimental part) and the results were highly reproducible, it is believed that the limit of uncertainty is ±0.5°. This value includes uncertainty due to instrumental error. Possible error due to difficulty in locating the centers of the signals is more difficult to assess. In the temperature range where the main separation occurs (−65° to −70°), the reported positions are for the maxima at the signals. This approximation should be nearly correct as the signal peaks are nearly symmetrical. However, the peaks are broad and rounded, and the maxima are not clearly defined. At the lower temperatures, the centers of mass do not occur at the maxima

[20] L. W. Reeves and K. O. Strømme, *J. Can. Chem.*, **38**, 1241 (1960).

[21] G. Claeson, G. M. Androes and M. Calvin, *J. Am. Chem. Soc.*, **82**, 4428 (1960).

[22] Reference 17, p. 224.

and the peaks are not symmetrical. No serious attempt was made to analyze the fine structure of the spectrum. As the centers of the signals at low temperature were visually approximated, the value given for the maximum separation at low temperature has an uncertainty of about ± 3 c./s., $(\nu_a\text{-}\nu_e)_{max}$ = 27.3 ± c./s. It is estimated that error in the rate constant due to this difficulty is less than 10% and is probably much less. No attempt was made to assess the validity of the assumption that the transmission coefficient is unity. The above considerations lead to k = 105 ± 10 sec.$^{-1}$ at −66.7 ± 0.5°.

From this result, $\Delta F^{\ddagger}$ for the conversion of the chair to the boat form is calculated to be 10.1 ± 0.1 kcal. mole at −66.7°. This value is 0.4 kcal./mole higher than that reported in the preliminary account.[1] The value for $\Delta H^{\ddagger}$, 11.5 ± 2 kcal./mole, for this process by the line broadening procedure given above has such a large experimental uncertainty that $\Delta S^{\ddagger}$ can not be calculated from these values. It seems reasonable that $\Delta S^{\ddagger}$ can be reliably estimated. Of the factors which contribute to entropy (molecular vibration, translational motion, etc.) the only factor which it is reasonable to expect makes a significantly different contribution in the ground and transition states is symmetry. The chair form of cyclohexane has a symmetry number of six; the proposed transition state has a symmetry number of one and exists as a D,L-pair. From these considerations, $\Delta S^{\ddagger}$ is estimated to be 4.9 e.u., and, hence, $\Delta H^{\ddagger}$ 11.1 kcal./mole.

The available evidence indicates that the boat form of cyclohexane is twisted or skewed.[23] From an examination of models it appears reasonable that the transformation from the chair to the boat form occurs by a twisting motion at a carbon atom. This type of motion appears to lead to a reaction pathway involving a minimum amount of interactions and bond angle distortion, and results in a twisted boat. The molecular arrangement in the transition state can be visualized as the structure approximately half way between the chair and twisted boat forms.

The major thermodynamic parameters for the chair–boat–chair interconversion are now known and are shown in the accompanying diagram (Fig. 3). The value for the enthalpy change in the chair–boat interconversion is the average of the values obtained by the interconversion of *cis*- and *trans*-1,3-di-*t*-butylcyclohexane (5.9 kcal./mole, no corrections for interactions),[24] by combustion of locked ring systems (5.5 kcal./mole, after corrections for non-cancelling interactions in the model compounds),[23] and by careful calculation of the difference of the interactions in the chair and boat forms (5.1 kcal./mole).[25]

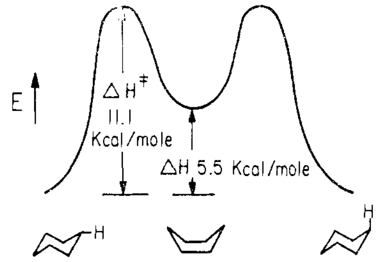

Fig. 3.—Energy relationships in cyclohexane.

The accompanying energy diagram does not include the energy for the boat–boat interconversion as this value is unknown. However, it is reasonable that this energy is less than that required for the boat–chair interconversion (5.6 kcal./mole).

Experimental

The measurements were carried out with a Varian Associates HR-60 n.m.r. spectrometer operated at 60 Mc. The spectrophotometer was housed in an air conditioned room. The magnet was cooled by a recirculating water supply whose temperature was automatically monitored.

Band separations were measured by the conventional side band technique. The spinning sample tube was maintained at the desired temperature between room temperature and −140° using a variation of the procedure of Piette and Anderson.[15]

Temperature measurement was made indirectly by means of a thermocouple glued to the inside wall of the probe insert, about 1" above the insert winding, which measured the coolant gas temperature. The thermocouple–potentiometer system was sensitive to temperature changes of about 0.05°.

The temperature measuring device was calibrated for actual temperature of the sample, by comparing the coolant gas thermocouple voltage with the voltage of a thermocouple placed in an open spinning sample tube containing carbon disulfide. The sample was consistently warmer than the temperature recorded. Plots of mv. of the coolant gas thermocouple *vs.* actual sample temperature were constructed. This particular design in which the thermocouple wire was sealed directly to the probe insert gave highly reproducible results. The temperature measurements were surprisingly precise and showed scatter of < ±0.3°. No difference was noted whether the desired temperature was approached from higher or lower temperatures. The thermocouple was calibrated against ice, a Dry Ice–acetone-bath and at temperatures 0° to −60° with a mercury–thallium eutectic thermometer which had been calibrated by the National Bureau of Standards. The correction was in no instance greater than 0.5° from the value in standard tables.

A possible source of error in the temperature measurement involves possible cooling of the solvent in the sample tube by heat being conducted away by the thermocouple. In order to keep this loss to a minimum, No. 34 wire was used for the thermocouples. In order to test for possible error, the above results were compared with those obtained using a thermocouple of larger wire, No. 24, in the sample tube. The results using the wires of different size compared closely. Since the larger wire should give greater heat losses and since no differential was observed, it is probable that the error introduced by heat conduction of the thermocouple is negligible.

The cyclohexane was purified by fractionation and then recrystallization and showed m.p. 5.4–6.8°. A carbon disulfide solution of cyclohexane (3 *M*) and tetramethylsilane (TMS, 0.04 ml./1 ml. of solution) was prepared. The solution was injected by means of a syringe into a 5 mm. o.d. thin-walled Pyrex tube to a depth of about 1.25". After flushing with nitrogen, the tube was sealed with a flame. Care was taken to ensure obtaining a symmetrical seal in order to obtain optimum uniform spinning.

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