a retention time of 7 min and 20 sec. Isolation of **30** and **31** by preparative vpc gave samples whose infrared spectra were identical with the infrared spectral of authentic samples of **30** and **31**.

2-Methylpyrrole (33).—To a round-bottomed flask fitted with a side arm for distillation and a thermometer to observe actual pot temperature was added 170 ml of diethylene glycol and 30 g of potassium hydroxide pellets. The flask was heated with a free flame until the potassium hydroxide began to fuse and dissolve. A magnetic stirrer was used to stir the solution. After the potassium hydroxide had all dissolved, the flask was cooled and 14.8 g of 2-pyrrolecarboxaldehyde was added followed by 22 ml of 95% hydrazine. The flask was then heated with a heating mantle. At 130° distillation began and distillate was collected until the pot temperature reached 200°. This required 1.5 hr. The distillate was poured into 100 ml of water and extracted three times with 75-ml portions of ether. The ethereal extracts were combined, dried over anhydrous magnesium sulfate, filtered, and the ether evaporated *in vacuo* to give 11.7 g of crude product. The crude product was fractionated through a Vigreaux column to give 9.0 g (75%) of water-white **33**, bp 149°.

2-Methylpyrrolidine (30).—In a glass bomb was placed 20 ml of glacial acetic acid, 4.0 g of 2-methylpyrrole, and 0.5 g of commercial Adams catalyst. The ampoule was flushed several times with hydrogen and then pressurized to 49.2 lb with hydrogen. After 5 hr, 85% of the theoretical amount of hydrogen had been consumed. On continued shaking overnight, only another 2% was consumed. The viscous yellow oil was filtered through a sintered-glass funnel and the catalyst washed with a small amount of acetic acid. The filtrate was then diluted with 50 ml of water and then made strongly basic with sodium hydroxide, with external ice cooling. The basic solution was then extracted three times with 50-ml portions of ether. The ether solutions were combined, dried over anhydrous magesium sulfate, filtered, and concentrated to 30 ml by evaporation. The solution was then distilled and the fraction boiling from 90 to 92° was collected. The water-white liquid weighed 0.8 g (19%).[18]

Registry No.—**1**, 13118-58-6; **5**, 5044-49-5; **7**, 13118-60-0; **30**, 765-38-8; **33**, 636-41-9.

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Conformational Analysis. LVI. Chlorocyclohexane and 1-Chloro-1-methylcyclohexane[1,2]

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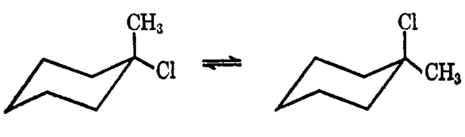
From studies on chlorocyclohexane, 1-chloro-1-methylcyclohexane, *cis*- and *trans*-4-*t*-butyl-1-chlorocyclohexane, *cis*- and *trans*-4-*t*-butyl-1-chloro-1-methylcyclohexane, and 1-chloro-1,4,4-trimethylcyclohexane, the conformational energy of chlorine was determined by a study of the molar absorbance of the C–Cl stretching frequency in the infrared, supplemented by variable-temperature infrared spectroscopy and equilibrium measurements, to be 0.4 kcal/mole, favoring the equatorial conformation when the chlorine was secondary, and it was found that, when the chlorine and methyl were geminal, the conformational energy was 1.1 kcal/mole, favoring the chlorine axial and methyl equatorial.

The conformational energies of substituents on cyclohexane rings have been widely studied, both because of the wide occurrence and importance of this ring system, and also because of the simplicity of the theoretical treatment of the data so obtained.[3,4] During the last few years, both the accuracy obtainable in the experimental measurements, and also the theoretical interpretation of the conformational energies available have continuingly increased, so that now energies of the order of 0.2 kcal/mole are often attainable by measurement, and they provide stringent tests of current conformational theory.[5,6]

While the first step in studying the conformational energies of groups was concerned with securing and understanding average numerical values for these quantities, it is now clear that the values are not constant to within experimental error, but vary with the immediate molecular environment,[9,10] sometimes with more distant molecular environment,[11] and also with intermolecular environment.[12]

If conformational energies were strictly additive, then by knowing the conformational energy of a methyl group, together with that of a chlorine atom, one could make accurate predictions regarding the equilibrium shown. While the additivity of the conformational energies might be assumed as a first approximation, the available theory indicates that it would not in general be exactly correct.[13] The present work reports an experimental study of this problem.



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[1] Paper LV: N. L. Allinger, L. W. Chow, and R. A. Ford, *J. Org. Chem.*, **32**, 1994 (1967).

[2] This research was supported by Grant GP 4290, from the National Science Foundation.

[3] J. A. Hirsch in "Topics in Stereochemistry," N. L. Allinger and E. L. Eliel, Ed., Vol. I, Interscience Publisher, Inc., New York, N. Y., 1967, p 199.

[4] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 435.

[5] For a discussion of the current methods of physical measurement of conformational energies, see ref 4, p 129.

[6] For a recent review and discussion of the status of the theory of conformational analysis, see ref 4; more recent papers are ref 7–9.

[7] J. B. Hendrickson, *J. Am. Chem. Soc.*, **86**, 4854 (1964).

[8] K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

[9] N. L. Allinger, M. A. Miller, F. A. Van-Catledge, and J. A. Hirsch, *ibid.*, in press.

[10] (a) E. L. Eliel and T. J. Brett, *ibid.*, **87**, 5039 (1965); (b) E. L. Eliel, S. H. Schroeter, T. J. Brett, F. J. Biros, and J. C. Richer, *ibid.*, **88**, 3327 (1966).

[11] D. H. R. Barton, F. McCapra, P. J. May, and F. Thudium, *J. Chem. Soc.*, 1297 (1960).

[12] See ref 3 for a recent summary.

[13] That this is the case follows as an extension of the discussion given in ref 9. The detailed theoretical treatment will be published elsewhere.

Discussion and Results

As a typical example of substituents with which the additivity of conformational energies might be studied with respect to their variation upon geminal substitution, we chose the methyl group and the chlorine atom. The main experimental technique employed was infrared spectroscopy, and other physical methods have been used to give supplementary information when possible.

The infrared spectra of simple, acyclic chlorides have been studied in some detail by Krimm and co-workers.[14] These workers found that there was a very definite relationship between the C–Cl stretching frequency, and two features of the molecular structure in the vicinity of the halide. The first feature found to be significant was the primary, secondary, or tertiary nature of the halide. The second feature of importance was the number of vicinal hydrogens which were oriented *anti* to the halide. In the symbolism of Krimm, the compound *t*-butyl chloride is tertiary, and necessarily has three hydrogens *anti* to the chlorine, and hence is given the symbol T_{HHH}. The halogen in *sec*-butyl chloride is secondary and would show two conformations, one in which there are two hydrogens *anti* to the chlorine, and one in which there is one hydrogen and a carbon *anti* to the chlorine. These conformations would be referred to as S_{HH}, and S_{CH}, respectively. For each conformation there would be a C–Cl stretching frequency within a given range.

If we extend these ideas of Krimm to cyclic systems, we can predict that cyclohexyl chloride will show two C–Cl stretching frequencies, one from the axial chlorine, which should be near the range characteristic of the S_{HH} conformation, and another from the equatorial chlorine, which results from the S_{CC} conformation. Because the cyclohexane ring does not have the dihedral angles between vicinal substituents exactly 60°, the absorption frequencies may vary somewhat from those of the acyclic analogs. For reference purposes, the appropriate frequencies are summarized in Table I.

TABLE I

THE C–Cl STRETCHING FREQUENCIES (RECIPROCAL CENTIMETERS OF DIFFERENT STRUCTURAL TYPES[a]

P_H	P_C	
648–657	723–731	
S_{HH}	S_{CH}	S_{CC}
608–615	661–678	749–758
T_{HHH}	T_{CHH}	T_{CCH}[b]
561–581	611–620	650–700

[a] Reference 14. [b] Extrapolated from T_{HHH} and T_{CHH}.

Cyclohexyl chloride was indeed found to show two bands with frequencies of 685 and 731 cm^{-1}, which were assigned, respectively, to the axial and equatorial chlorines. The 4-*t*-butylcyclohexyl chlorides have been previously reported,[15] and they were found to show the corresponding stretching frequencies at 693 and 727 cm^{-1}, respectively. Since the molar absorbances of the C–Cl stretching frequencies are not the same for equatorial and axial halides, it was necessary for these quantities to be determined in order to assign an equilibrium constant to chlorocyclohexane from the observed ratio of the band intensities. The molar absorbancies of these bands were established by comparative measurements with the 4-*t*-butyl derivatives, which is essentially the method of Price,[16] and independently the enthalpy of the conformational isomerization was determined by measuring the variation in the ratio of the band intensities as a function of temperature, which has previously been described by Kozima and Sakashita.[17] It was found that at room temperature the ratio of the areas of the C–Cl stretching bands for the *cis*- to *trans*-*t*-butyl compounds was 0.038:0.047. For cyclohexyl chloride itself, the ratio of the respective bands was 0.025:0.050, which gives an equilibrium constant of 2.0, favoring the equatorial chlorine. This equilibrium constant corresponds to a free-energy difference, $\Delta G° = 0.4$ kcal/mole, and the value is in good agreement with other measurements previously reported by others.[3]

The same approach was then used to study the conformational equilibrium of 1-chloro-1-methylcyclohexane. To this end, 1-chloro-1-methyl-4-*t*-butylcyclohexane was prepared as a mixture of *cis* and *trans* isomers, and the latter were separated by preparative vpc. Utilizing Table I, it is seen that the axial chloride is of the form T_{HHH}, which should absorb near the region 561–581 cm^{-1}. The equatorial chloride is of the type T_{CCH}, which was not studied by Krimm and co-workers, but by extrapolating the other values in the table it can be predicted to absorb at a frequency higher than 630 cm^{-1}. Of the two compounds isolated, one showed a single, strong peak at 555 cm^{-1}, and it was assigned the axial conformation. The other isomer showed two peaks, one at 670 and the other at 540 cm^{-1}, with an intensity ratio of 2:1. From the presence of the peak at 670 cm^{-1} and the absence of a corresponding peak in the other isomer, this isomer was assigned the geometry with the equatorial chlorine. These compounds have subsequently been reported by Greene and co-workers,[18] and they made the same structural assignment on the basis of the rates of elimination of these compounds upon treatment with base. With these compounds the axial chloride gave the stronger absorption peak, in the ratio of 0.065:0.026, the reverse order of intensities from that found with the secondary halides.

The spectrum of 1-chloro-1-methylcyclohexane was then recorded, and a medium band was noted at 656 cm^{-1}, together with two strong bands at 565 and 545 cm^{-1}. It seemed clear that the band at 656 cm^{-1} was the equatorial C–Cl stretching frequency, but it was uncertain just what the interpretation of the 545–565-cm^{-1} doublet was. Both of these frequencies changed their absorption intensities relative to that at 656 cm^{-1} when the temperature of the solution was changed, and hence it appeared that both of these frequencies were due to the axial isomer. Using the 545-cm^{-1} frequency as the C–Cl frequency for that of the axial isomer, an equilibrium constant of 2.94 (favoring this isomer) was calculated from room-temperature measurements, while if the 565-cm^{-1} band was

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[14] J. J. Shipman, V. L. Folt, and S. Krimm, *Spectrochim. Acta*, **18**, 1603 (1962).

[15] F. D. Greene, C-C. Chu, and J. Walia, *J. Am. Chem. Soc.*, **84**, 2463 (1962).

[16] R. A. Pickring and C. Price, *ibid.*, **80**, 4931 (1958).

[17] K. Kozima and K. Sakashita, *Bull. Chem. Soc. Japan*, **31**, 796 (1958).

[18] A. Fang, M.S. Thesis, Massachusetts Institute of Technology, 1965.

assigned to the axial isomer the equilibrium constant was 2.0. Thus, the axial chlorine conformer was calculated to be the more stable one by 0.64 or 0.40 kcal/mole, depending on which band was used.

The equilibrium was then studied by measuring the spectrum of the compound at −80°. The enthalpy of the equilibrium was calculated in the usual way,[19] and it was found to be 0.34 or 0.25 kcal/mole, depending as before upon which band was assigned to the axial chlorine. The compound appeared as though it might be crystalline at −80°, however, and, if it was, these values are of doubtful significance.

Another interpretation of the spectrum of axial 1-chloro-1-methylcyclohexane was also reasonable, and was entertained at this point. The Raman spectrum of the compound has been reported,[20] and shows a line at 275 cm^{-1}. It is possible that the overtone of this frequency enters into Fermi resonance with the C–Cl stretching frequency. If so, then the total area under the doublet should more properly be used as a measure of the amount of axial conformation present. When the calculations were carried out on this basis, a free-energy change of 0.9 ± 0.2 kcal/mole at room temperature was calculated, and, from further studies described below, this value is believed to represent the free-energy change corresponding to the equilibrium in question. As a check on this point, 1,4,4-trimethylcyclohexyl chloride was prepared, and its infrared spectrum in this region was examined. The equilibrium constant should be the same for this compound as it is for 1-chloro-1-methylcyclohexane itself, and it seemed unlikely that the complicating effect of the extraneous band would be present. It was found that this compound showed only one band (at 540 cm^{-1}) which could be attributed to the axial chlorine. The equilibrium constant for this compound was calculated from the room-temperature measurements as previously described for 1-chloro-1-methylcyclohexane, and was found to have the value 5.9. This equilibrium constant corresponds to a value of $\Delta G° = 1.1$ kcal/mole, favoring the conformation with the chlorine axial.

Finally, the equilibrium constant between *cis*- and *trans*-1-chloro-1-methyl-4-*t*-butylcyclohexane was measured by treatment of these isomers with concentrated hydrochloric acid at room temperature, followed by an analysis of the mixture by gas chromatography. In this way a value for $\Delta G°$ of 1.1 kcal/mole was obtained.

On the basis of these several independent measurements it was concluded that the free-energy change for the axial → equatorial chlorine in the 1-chloro-1-methylcyclohexane system is +1.1 ± 0.2 kcal/mole. This number differs slightly from what one would calculate assuming the additivity relationship for the conformational energies of methyl and chlorine as determined from measurements when they are attached to secondary carbon atoms (1.7–0.4 = 1.3 kcal/mole), but the difference is not really outside the limits of experimental error.

Experimental Section

All melting points and boiling points are uncorrected. The infrared spectra were obtained from solutions in carbon disulfide on a Beckman Model IR-4 recording spectrophotometer, a Perkin-Elmer Model 137 spectrophotometer (both with sodium chloride optics), Perkin-Elmer 621 (grating) spectrophotometer, or Perkin-Elmer Infracord with potassium bromide (800–450 cm^{-1}) optics. For gas chromatographic analysis, three standard columns of 6 ft × 8 mm Pyrex tubing were employed. Column A was packed with 10% by weight of polyglycol E-20,000 (Dow Chemical Co., Midland, Mich.) suspended on base-washed firebrick, and column B was packed with 15% polyglycol E-9,000 (Dow Chemical Co.) on base-washed firebrick. Column C was packed with XF-1150 (G.E. nitrile silicone fluid) on base-washed firebrick.

***cis*- and *trans*-4-*t*-Butylcyclohexyl Chloride.**[21]—In a 200-ml three-necked flask equipped with a mechanical stirrer, 5 g of 4-*t*-butylcyclohexanol (1:4 *cis–trans* mixture) was dissolved in 50 ml of anhydrous ether. Six grams of tri-*n*-butylamine was added. Four grams of thionyl chloride in 15 ml of anhydrous ether was then added with stirring over a period of 1 hr. The mixture was stirred at room temperature for 3 hr and poured into ice water. The ether layer was washed with saturated sodium bicarbonate solution and with water, and dried over magnesium sulfate. The ether solution was filtered and the solvent was removed. Distillation through a 1-ft Podbielniak column with partial reflux head gave 2 g [bp 59–61° (13 mm)] of 4-*t*-butylcyclohexene and 1.9 g [bp 62–65° (4 mm)] of 4-*t*-butylcyclohexyl chloride.

The chloride fraction was analyzed by gas phase chromatography on column C, an XF-1150 column at 110° and 9 psi. Peaks showed at 2.9 (4-*t*-butylcyclohexene), 16, and 20 min. The 16-min fraction was collected and its infrared spectrum was identical with the spectrum of *cis* compound published by Greene.[21]

Anal. Calcd for $C_{10}H_{19}Cl$: C, 68.76; H, 10.88. Found: C, 68.76; H, 10.74.

A solution of 1 g of a *cis–trans* mixture of chloride and 1 g of potassium hydroxide in 5 ml of 95% of ethanol was heated at reflux for 19 hr. The mixture was poured into water and extracted with petroleum ether (bp 30–60°). Washing and drying of the petroleum ether solution and removal of solvent afforded 0.7 g of oil, which on vpc analysis showed a peak at 2.9 (4-*t*-butylcyclohexene), and peaks at 16 and 20 min with a ratio of 1:2. The latter peak was collected and its infrared spectrum was identical with that of the *trans* compound obtained by Greene.[21]

***cis*- and *trans* 4-*t*-Butyl-1-methylcyclohexanol.**—Magnesium shavings (4.85 g) in anhydrous diethyl ether (100 ml) were treated with methyl iodide until all the magnesium had reacted. The reagent than was cooled in an ice bath to 5°. A solution of 15.4 g of 4-*t*-butylcyclohexanone (mp 52[22]) in 20 ml of diethyl ether was added at such a rate that the internal temperature did not exceed 5°. After the addition was complete the cooling bath was removed, and the stirring was continued for an additional 2 hr. The reaction mixture was allowed to stand overnight at room temperature, cooled again, and treated with a saturated aqueous ammonium chloride solution until a clear separation of salt occurred. The internal temperature was not allowed to exceed 5° during this addition.

The solution was filtered and the ether solution was dried with magnesium sulfate, filtered, and concentrated *in vacuo* at room temperature.

A 3.0-g sample of the above product was dissolved in hexane and chromatographed on 150 g of Merck chromatographic grade alumina. The column was developed with hexane–benzene mixture (100:100%) and the elution was effected with benzene. The first eluate contained the *trans*-1-methyl-4-*t*-butylcyclohexanol, mp 69–70° (6.2 g from hexane) (lit.[22] mp 71°). The second eluate contained *cis*-1-methyl-4-*t*-butylcyclohexanol, which had mp 91–92° (from petroleum ether, 6.0 g) (lit.[22] mp 97.8°).

***cis*- and *trans*-1-Methyl-4-*t*-butylcyclohexyl Chloride.**—1-Methyl-4-*t*-butylcyclohexanol (1.3 g) in 20 ml of diethyl ether was treated with dry hydrogen chloride (5 g) overnight. The solution was washed with saturated aqueous sodium bicarbonate and dried over anhydrous calcium chloride. After filtration the solvent was evaporated and the chloride fraction was analyzed by vpc on column B at 120° and 6 psi. Peaks resulted at 17 and 21 min with a ratio of 5.9:1. The 17-min peak was collected and had an infrared spectrum identical with that of the com-

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[19] Reference 4, p 147.

[20] H. J. Hageman, Ph.D. Thesis, University of Leiden, 1965.

[21] F. D. Greene, C. C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964).

[22] W. J. Houlihan, *ibid.*, **27**, 3861 (1962).

pound assigned the *trans*-4-*t*-butyl-1-methylcyclohexyl chloride structure by Greene.[23]

Anal. Calcd for $C_{11}H_{21}Cl$: C, 70.02; H, 11.14. Found: C, 70.29; H, 11.21.

A solution was prepared from 1 g of 4-*t*-butyl-1-methylcyclohexyl chloride (*cis–trans* mixture) in 5 ml of ethyl alcohol and was added to 650 mg of freshly prepared sodium methoxide. The mixture was refluxed overnight, and was poured into ice water and extracted with ether. The ether layer was separated and washed with water. After drying of the solution and removal of the solvent, vpc analysis of the residue showed a peak at 4 min (4-*t*-butyl-1-methylcyclohexene) followed by peaks at 17 and 21 min in the ratio 1:1. The latter was collected and the infrared spectrum was identical with that of the compound assigned the *cis* structure by Greene.[23]

1-Methylcyclohexyl Chloride.—1-Methylcyclohexyl chloride was prepared from 1-methylcyclohexanol [bp 49–50° (8 mm)] and concentrated hydrochloric acid according to Brown,[24] bp 30–31° (6 mm) [lit[24]. bp 65.2–65.5° (44 mm)].

1,4,4-Trimethylcyclohexyl Chloride.—4,4-Dimethylcyclohexanone (240 mg) underwent the Grignard reaction as described for 4-*t*-butylcyclohexanone. The formation of 1,4,4-trimethylcyclohexanol was verified by the disappearance of 1680-cm^{-1} band. The alcohol (200 mg) was dissolved in 5 ml of dry ether and treated with 70 mg of anhydrous hydrogen chloride at 0°. The reaction mixture was allowed to stand overnight and was diluted with ether, washed with water, and dried over magnesium sulfate. The solvent was removed *in vacuo*, and vpc analysis using column B at 120° and 9 psi gave a peak with a retention time of 5 min. This fraction was collected.

Anal. Calcd for $C_9H_{17}Cl$: C, 67.29; H, 10.59. Found: C. 68.08; H, 10.39.

Registry No.—Chlorocyclohexane, 542-18-7; 1-chloro-1-methylcyclohexane, 931-78-2; *cis*-4-*t*-butyl-1-chlorocyclohexane, 13131-74-3; *trans*-4-*t*-butyl-1-chlorocyclohexane, 13145-48-7; *cis*-4-*t*-butyl-1-chloro-1-methylcyclohexane, 13145-49-8; *trans*-4-*t*-butyl-1-chloro-1-methylcyclohexane, 13131-75-4; 1-chloro-1,4,4-trimethylcyclohexane, 13145-50-1.

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[23] Professor F. D. Greene, private communication.

[24] H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951).

Conformational Analysis. X.[1] Determination of Intramolecular Hydrogen Bonding by Hydroxyl Proton Magnetic Resonance[2]

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Dilution studies of the hydroxyl proton magnetic resonance of a number of isomeric alcohols containing the bicyclo[2.2.1]heptane skeleton have been made, and the limiting chemical shift–concentration dependence relationships have been determined. In the compounds investigated, a distinction has been made between pairs of isomers in which one compound can intermolecularly hydrogen bond to an acceptor site and the second compound cannot. Compounds which are intramolecularly hydrogen bonded exhibit small limiting slopes compared with isomeric compounds which cannot intramolecularly hydrogen bond. The compounds which cannot intramolecularly hydrogen bond to an acceptor site may intermolecularly hydrogen bond to it. The degree of intermolecular hydrogen bonding is indicated by the difference in the observed chemical shift concentration curve from that predicted from model compounds lacking the acceptor site.

The hydroxyl proton magnetic resonance has been examined quantitatively for only a few simple compounds. This widely occurring resonance has been ignored as a result of its concentration dependence. At concentrations normally employed in nmr, the hydroxyl signal is a time average of a weighted average of the various hydrogen-bonded species present in solution. We have shown in several reports that the chemical shift of the hydroxyl proton is linearly related to concentration in carbon tetrachloride in the 0.015–0.002 mole fraction range.[4] By extrapolation to infinite dilution, the chemical shift of the monomeric hydroxyl proton can be determined. At infinite dilution the chemical shift is solely a function of magnetic environment, and this resonance signal has been used as a conformational probe in the cyclohexane series.[4] However, the limiting resonances for a large number of simple alcohols investigated in this laboratory have been shown to be located in a relatively narrow high-field region. Therefore, another method was sought in order to provide additional structural information from the nmr of alcohols. An alternate approach, which offers a quantitative method of evaluating the steric environment of the hydroxyl proton, involves the use of the limiting slope of the chemical shift–concentration curve. This technique has been shown to be useful in determining the steric environment of the hydroxyl group in some rigid bicyclic compounds.[5]

The limiting-slope method is derived from the early work of Becker, Liddel, and Shoolery,[6] who carried out a detailed study of the dilution shift of the hydroxyl proton of ethanol in carbon tetrachloride. With decreasing concentration the hydroxyl resonance shifts to a higher field and the dilution curve linearly approaches a limiting value at infinite dilution. The linear relationship has been interpreted in terms of a

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[1] Conformational Analysis. IX: R. J. Ouellette, D. L. Marks, and D. Miller, *J. Am. Chem. Soc.*, **89**, 913 (1967).

[2] The authors acknowledge a grant from the Petroleum Research Fund of the American Chemical Society in support of this research.

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[6] E. D. Becker, V. Liddel, and J. N. Schoolery, *J. Mol. Spectry.*, **2**, 1 (1958).