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February 16, 1972

To the Graduate Council:

I am submitting herewith a thesis written by Linda Moree Higgins Collins entitled "Spectral Studies of Hydrogen Bonding in Alcohols." I recommend that it be accepted for eighteen quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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We have read this thesis
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Accepted for the Council:

Dean A. Smith
Vice Chancellor for
Graduate Studies and Research

SPECTRAL STUDIES OF HYDROGEN BONDING IN ALCOHOLS

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

by

Linda Moree Higgins Collins

March 1972

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ABSTRACT

The phenomenon of hydrogen bonding in alcohols has been known since the early 1900's. Using three series of alcohols, benzyl alcohols, norbornanols and substituted naphthalene alcohols, it was hoped that some meaningful data could be presented to help clarify and expand some of the theories on alcohol association. The techniques to be utilized were ir and nmr spectroscopies.

The synthetic route for those compounds that were not available as alcohols involved reduction of the corresponding acids to alcohols by use of lithium aluminum hydride. The strengths of the various types of hydrogen bonds, intramolecular and intermolecular, were detected by nmr and ir techniques at various concentrations. The 8-substituted-1-hydroxymethyl-naphthalene slope values (8-Br = 25, 8-Cl = 26, 8-OCH_3 = 13, and 8-CH_3 = 32) made it difficult to interpret the interactions on the basis of nmr alone. It appears that in the nmr studies we observe this difficulty, due to steric, electronic and polarizability effects, of forming the hydrogen bond, and only in the ir data do we get an idea of the actual strength of the hydrogen bond formed. It was observed for 3-endo-phenyl-2-endo-norbornanol that the slope value (8.3) and ir frequency shift (10 cm^{-1}) correlate well with the steric interactions involved in the cis-di-endo compound.

The slope values and frequency shifts give us an idea of the strength of the intramolecular association and the energy relationship between the monomer and dimer. The hydrogen bonding appears to lower the energy of the monomer relative to that of the dimer by virtue of the internal bonds.

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CHAPTER I

INTRODUCTION

Louis Henry[1] was the first scientist to hypothesize the polymerization of compounds; the ability of certain compounds to associate through hydrogen bonding was recognized by Nernst[2] in 1891, and later the concept of hydrogen bonding was explained by Werner.[3] More recently with the development of infrared (ir) and nuclear magnetic resonance (nmr) spectroscopies investigations of hydrogen bonding have expanded to include many types of compounds.

In 1932, Freymann[4] used infrared spectroscopy to observe the intensity and frequency dependence of alcoholic hydroxyls on concentration and temperature. Infrared spectroscopy allows the type of hydrogen bound species to be investigated and the relative strength of these bonds to be followed as a function of concentration. Coggeshall[5] used benzyl alcohol to show that the broad band resulting from association did indeed decrease and eventually disappear on dilution. The standard procedure is to dilute the alcohol with carbon tetrachloride until the peak due to intermolecular association disappears; the free and intramolecular peaks do not change their band positions on dilution. It is possible to assign the type of bonding in an alcohol on the basis of the band position and its shift or lack of shift on dilution. Intramolecular and intermolecular hydrogen bonds are already stretched to a certain extent and require less energy to stretch or extend their bonds than their non-associated counterparts. According to equation (1) the peaks for intra- or inter-molecular hydrogen bonds should occur at shorter wavenumbers than for free peaks (K is wave number):

$$E = Khc \quad . \qquad (1)$$

Ouelette[6,7,8] used nmr spectroscopy to investigate several types of alcohols and their hydrogen bonding properties. He verified that the chemical shift of the hydroxyl proton was linearly related to the concentration as first proposed by Becker, Liddel and Shoolery.[9] By the use of the nonpolar solvent carbon tetrachloride, the usual procedure is to dilute the alcohol and follow the change in chemical shift of the hydroxyl proton. Plots of chemical shift versus concentration reveal important properties of alcohols. By extrapolation to infinite dilution one can obtain the chemical shift of the monomeric hydroxyl proton; this chemical shift is affected only by the proton's magnetic environment. In order to determine something about the steric environment of the hydroxyl proton, the limiting slope of the chemical shift-concentration curve is obtained.

Huggins, Pimentel and Shoolery[10] used phenols in carbon tetrachloride and interpreted their chemical shift data as involving an equilibrium between dimer and monomer. They derived an expression (2) from which the association constant, K, could be calculated by using the slope at zero phenol concentration, $\left(\frac{d\delta}{dx}\right)_{x=o}$, and the chemical shift of the dimer (δ_D) and monomer (δ_M). However, the chemical shift of the dimeric

$$\left(\frac{d\delta}{dx}\right)_{x=o} = 2K\,(\delta_D-\delta_M) \qquad (2)$$

species is not available experimentally without making many assumptions, and the calculations generally have not produced good results. Oki[11] later verified this same theory using relatively unhindered alcohols which formed high order aggregates at high concentrations but which at lower concentrations seemed to reflect an equilibrium between trimer and/or

dimer with monomer, and a large contribution of the monomeric species at infinite dilution.

Steric hindrance at the hydrogen bonding site greatly affects the dimerization equilibrium constants presumably by raising the energy of the dimer relative to the monomer. The energy change is best reflected by the magnitude of the slope for the equilibrium involved; i.e., the magnitude of the slope is directly proportional to the energy difference between the dimer and monomer. This type of relationship was initially demonstrated for some hindered phenols by Somers and Gutowsky.[12]

A. Introduction to the Problem

Intramolecular hydrogen bonding has been aptly revealed by the limiting slope of the chemical shift-concentration plot in nmr spectroscopy and by frequency shifts in infrared spectroscopy. We wished to investigate the possible extension of these spectral tools of intramolecular hydrogen bonding to several series of alcohols. Various types of groups that could intramolecularly interact were to be introduced into the compounds, and the interactions were to be observed by the aforementioned spectral techniques.

Before meaningful calculations of the association constant, K, could be made, it would be necessary to identify each type of hydrogen bond and its relative strength. It was hoped that the infrared technique in conjunction with slope data from the nmr technique would clarify and expand hydrogen bonding theories.

If intramolecular and intermolecular association exist together, then δ_o values, chemical shifts at infinite dilution, would be a weighed

average of the two, and the nmr spectral results for intramolecular hydrogen bonding would be somewhat difficult to analyze.

It was decided to investigate a number of structural features related to inductive, steric, conformation, and pi-interaction effects using slope magnitudes and δ_o positions. This study was to involve disubstituted naphthalene alcohols, disubstituted norbornanols, and some benzyl alcohols. A preliminary study of several of the compounds has been reported by Kleinfelter,[13] but more concentration data were needed to clarify and hopefully verify the meaning of the slopes and δ_o values.

CHAPTER II

EXPERIMENTAL

Benzyl alcohol was obtained from Eastman Organic Chemicals, bp 204°. 2-Methoxybenzyl alcohol was obtained from Aldrich Chemical Corporation, bp 121°_{11}. 2-Hydroxymethylnaphthalene, mp 79-81° (lit.,[14] mp 80-80.5°), 8-methoxy-1-hydroxymethylnaphthalene, mp 87.5-89° (lit.,[15] mp 88-89°), 8-methyl-1-hydroxymethylnaphthalene, mp 92-93° (lit.,[15] mp 93-94.5°), 8-bromo-1-hydroxymethylnaphthalene, mp 86-87° (lit.,[15] mp 88-89°), 8-chloro-1-hydroxymethylnaphthalene, mp 81-82° (lit.,[15] mp 81.5-83°), and 1-hydroxymethylnaphthalene, mp 59-60° (lit.,[15] mp 59-60°) were prepared by Dr. P. H. Chen.[15] 1-Cyclohexyl-2-exo-norbornanol, mp 70-73° (lit.,[16] mp 70-73°), was prepared by J. M. Miller, 1-Phenyl-2-exo-norbornanol, mp 67-69° (lit.,[17] mp 69.5-70°) and 7-anti-phenyl-2-exo-norbornanol, mp 89-90° (lit.,[18] mp 89-90°) were available from prior research by others. 7-syn-Phenyl-2-exo-norbornanol, mp 89-90° (lit.,[18] mp 89-90°) was prepared by G. Sanzero using the method of J. M. Miller.[16] Some ir spectral values were obtained from L. P. Joris' work at Princeton University.

A. Preparation of Compounds

1. o-Methylbenzyl Alcohol

8.23 g (.0605 moles) of o-toluic acid, Eastman Organic, mp 107° was added with stirring to 5.83 g (.153 moles) of lithium aluminum hydride and 50 ml of anhydrous ether. After all of the o-toluic acid had been added, the solution was stirred overnight at room temperature, after which the

excess lithium aluminum hydride was destroyed by adding cold water to the cooled solution. The ether solution was dried over anhydrous sodium sulfate. The ether was removed on a rotatory evaporator, and a white solid formed from the cooled viscous oil which remained. 5.61 g (.0458 moles), 72.0% yield of the alcohol was obtained. The melting point was 35-36° (lit.,[19] mp 35-36°).

2. 1-Hydroxymethylnaphthalene

The standard reduction method as outlined in part one of this chapter was employed. 1.14 g (.0299 moles) of lithium aluminum hydride was added to 20 ml of anhydrous ether, and to this cooled solution was added 3.16 g (.0184 moles) of solid 1-naphthoic acid, mp 160-1° from J. T. Baker Co. The crude oil was treated with ligroine and on cooling 1.88 g (.0119 moles), 71.2% yield, of a white crystalline solid appeared, mp 59-60° (lit.,[20] mp 59-60°).

3. 2-Methoxy-1-hydroxymethylnaphthalene

Using the procedure outlined in part one of this chapter, 3.06 g (.0152 moles) of 2-methoxy-1-naphthoic acid, mp 177-178°, obtained from C. F. Cheng,[21] was reduced using 1.68 g (.0433 moles) of lithium aluminum hydride in 30 ml of anhydrous ether. 2.22 g (.0118 moles), 78.2% yield, of the solid white alcohol was obtained with a melting point of 100-1° (lit.,[22] mp 100-101°).

4. 1-Methoxy-2-hydroxymethylnaphthalene

Using the method outlined in part one of this chapter, .195 g (.000965 moles) of 1-methoxy-2-naphthoic acid sample, mp 126-127.5°,

obtained from C. F. Cheng,[23] was reduced with 2.70 g (.0711 moles) of lithium aluminum hydride in 30 ml of ether. After recrystallization from ether, .133 g (.000706 moles), 69.4% yield, of the light brown solid alcohol was obtained. The melting point was 64-66°.

5. 2-Methoxy-3-hydroxymethylnaphthalene

Using the procedure in part one of this chapter, 1.06 g (.00525 moles) of a sample of 2-methoxy-3-naphthoic acid, mp 69-70°, donated by C. F. Cheng,[24] was reduced by 1.033 g (.0272 moles) of lithium aluminum hydride in 30 ml of anhydrous ether. After recrystallization from ethanol .829 g (.00443 moles), 78.3% yield, of the solid alcohol with melting point of 69-70° (lit.,[25] mp 71-72°) was obtained.

6. 3-exo-Phenyl-2-exo-norbornanol

Using the method outlined by J.M. Miller[26] 5.42 g (.0284 moles) of 3-exo-phenyl-2-endo-norbornanol, mp 42.5-43.5°,[27] was dissolved in reagent grade acetone and the internal temperature of -5° to -15° was maintained while 15 ml of 8 N chromic acid was added dropwise. 4.55 g (.0244 moles), 86.1% yield, of the colorless oily ketone was obtained. This ketone was reduced by the method outlined in part one of this chapter, using 1.20 g (.0317 moles) of lithium aluminum hydride in 30 ml of ether. 3.60 g (.0192 moles) of a cloudy oil resulted which had approximately 45% of the desired di-exo product determined by nmr analysis. 1.50 g (.00698 moles), 41.8% yield, of the alcohol was obtained after chromatographing with alumina. The di-exo compound was verified by comparison of the nmr spectrum with the spectrum of a pure reference sample.

7. 3-endo-Phenyl-2-endo-norbornanol

Using the standard method, 2.03 g (.0109 moles) of 3-endo-phenyl-2-norbornanone, bp 125-8°,[28] (kindly furnished by G. Sivils), was reduced with 1.83 g (.0487 moles) of lithium aluminum hydride in 30 ml of ether. After recrystallization of the crude product from ligroine 1.83 g (.00973 moles), 89.3% yield, of the di-endo compound was obtained. The white solid had a melting point of 69-71° (lit.,[29] mp 71-72°).

B. Techniques

1. Infrared Dilution Techniques

Infrared spectra for the 3600-3000 cm^{-1} region were recorded on a Perkin-Elmer Model 257 grating spectrometer calibrated against polystyrene standard. A variable path length sodium chloride cell (Variable Cell XL-O, series No. 0085) allowed the addition of solvent for the dilutions. In order to measure the position of the hydroxyl peak, scans were run at "times ten" settings and peaks were calibrated relative to known peak values of polystyrene.

For symmetrical hydroxyl peaks the centers were determined by inspection, and the average of eight to ten peaks was used. For hydroxyls that appeared as shoulders, the graphical values obtained by Joris were used.

The alcohol was weighed in a tared vial, carbon tetrachloride was added, and the resulting solution was transferred to the cell. After each spectrum was run, more carbon tetrachloride was added, by means of a calibrated syringe, and the solution was mixed thoroughly again before rerunning the ir spectrum. It was possible to have a volume of approx-

imately ten milliliters when the cell was full.

Normal runs consisted of fast scanning of the 3600-3000 cm^{-1} region. At points approaching infinite dilution, the expanded scale (x 10) was used with the known peaks at 3027.1 and 3001.7 cm^{-1} of polystyrene as reference. In all cases duplicate determinations were obtained using new samples.

2. Nuclear Magnetic Resonance Studies

In all cases the Varian A-60 nmr spectrometer was used. The temperature at probe depth was obtained by using a spinning ethylene glycol sample and using the plots of A. L. Van Geet.[30]

Samples were weighed in tared vials after which carbon tetrachloride was added and the vials were reweighed. The solution was mixed thoroughly, and a portion was weighed in a tared nmr tube. Two or three drops of tetramethylsilane (TMS) were also weighed in the nmr tube. The nmr tube containing the mixed solution was allowed to spin for at least ten minutes at probe depth before obtaining the spectrum. The trace of the hydroxyl chemical shift (δ) versus TMS was run three or four times per concentration so that an average chemical shift could be obtained.

The concentration was changed by weighing additional carbon tetrachloride in the nmr tube. This process was continued until the hydroxyl peak remained constant relative to TMS, or until the peak position could not be recorded with certainty.

CHAPTER III

DISCUSSION OF RESULTS

Kleinfelter[13] has reported the limiting slope, $(d\delta/dx)_{x=o}$, and the chemical shift of the monomer, δ_m, for several norbornanols. Some of these data were reported with a minimum number of experimental points, and dilution (nmr and ir spectroscopy) studies on a number of these compounds and two other series of alcohols determined at temperatures of 33.5 ± 0.8°C (nmr) and room temperature for ir spectra are discussed below.

A. Nuclear Magnetic Resonance Studies

The nmr spectral technique provides the limiting slope and chemical shift of the monomer. Since δ_o is sensitive to structural features in the molecule, the limiting slope is a better criterion for the strength of the intramolecular hydrogen bond. In general as the strength of the intramolecular hydrogen bond increases there is a downfield shift of δ_o. The exception to this rule exists when a phenyl ring is present in the molecule, and the aromatic ring acts as an electron pair donor in the hydrogen bonding process.[31] "Ring current effects"[32] and the random distribution of the molecules can also cause the hydroxyl hydrogen to be shielded by the induced magnetic field of the phenyl ring. As the strength of the intramolecular hydrogen bond increases, the limiting slope value decreases. The slope values are felt to give an approximation of the energy difference between the monomer and dimer. As the slope becomes smaller, the equilibrium constant for dimerization becomes smaller. A lower equilibrium constant is to be expected when intra-

molecular hydrogen bonding is possible, because the energy of the monomer is lowered relative to that of the dimer.

Comparing the benzyl alcohols in Table I, one notices that benzyl alcohol (I) and its two ortho substituted counterparts, o-methyl (II) and o-methoxy (III), have slope values of 54, 36 and 18, respectively. Benzyl alcohol, the parent compound for the study, has the largest slope and can have only one intramolecular hydrogen bond (OH---π) possible at infinite dilution. The slope value implies a weak intramolecular hydrogen bond and a large energy difference between monomer and dimer. In II and III steric factors may influence the energies of the various conformations, and there is the increased possibility for the hydroxyl hydrogen to move closer to the pi cloud of the phenyl ring. In each case the slope decreases. Since III has an added site for hydrogen bonding, the ethereal oxygen, it should presumably intramolecularly bond to the oxygen more so than to the benzene ring since the former bond type is generally stronger.[33] The chemical shifts at infinite dilution for I and II are approximately the same, 0.95 and 0.93 respectively, but when the methyl group is replaced by a methoxy group, as in III, the structural change causes deshielding of the hydroxyl proton to 1.59 δ_o.

When the hydroxymethylnaphthalenes, IV and V (Table II), are compared with I ($d\delta/dx = 54$) one notices that their slopes are only slightly smaller, IV ($d\delta/dx = 45$) and V ($d\delta/dx = 51$). One might expect a more acidic hydroxyl proton to exist due to the added ring in the naphthalene system. The only evidence for any difference in the two systems is in the chemical shifts at infinite dilution where the naphthalene hydroxyl protons have their chemical shifts further upfield. Although the slope

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA FOR SOME BENZYL ALCOHOLS

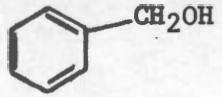
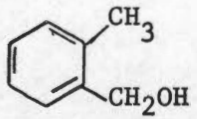
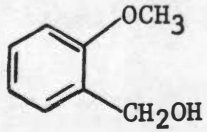
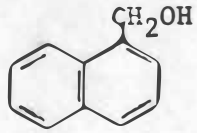
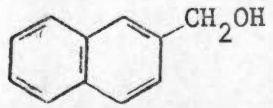
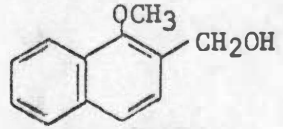
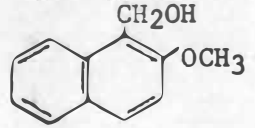
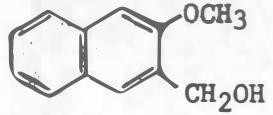
Alcohol	Code	Structure	δ_o, p.p.m.	$(d\delta/dx)_{x=o}$
Benzyl	I		0.95	54
o-Methylbenzyl	II		0.93	36
o-Methoxybenzyl	III		1.59	18

TABLE II

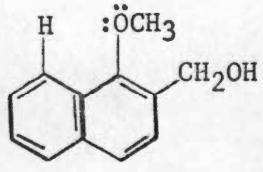
NUCLEAR MAGNETIC RESONANCE DATA FOR SOME DISUBSTITUTED NAPHTHALENES

Naphthalene	Code	Structure	δ_o, p.p.m.	$(d\delta/dx)_{x=o}$
1-Hydroxymethyl	IV		1.16	45
2-Hydroxymethyl	V		1.16	51
1-Methoxy-2-hydroxymethyl	VI		1.46	46
2-Methoxy-1-hydroxymethyl	VII		1.36	21
2-Methoxy-3-hydroxymethyl	VIII		1.73	25

differences between IV and V may not be significant, it is noted that IV does have the added possibility for OH---π bonding at the point of ring fusion, a position of high electron density, which should increase the tendency for intramolecular hydrogen bonding. A slightly smaller slope is noticed for IV. However, the δ_o's for both compounds being the same value contradict such an explanation.

Compound VIII, 2-methoxy-3-hydroxymethylnaphthalene, has a limiting slope of 25 compared to II, o-methoxybenzyl alcohol, with a slope of 22. These two compounds are quite similar, and models reveal that both compounds are so similar structurally that they should have essentially the same limiting slope values. The slope differences obtained in this research are too small to be considered significantly different. In both cases the hydroxyl proton is significantly deshielded by the methoxy group (δ_o of 1.73 ppm vs δ_o of 1.16 ppm for IV or V).

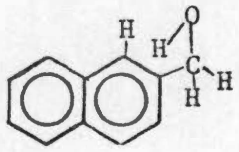
In the case of VI, 1-methoxy-2-hydroxymethylnaphthalene, the "peri effect"[34] should exert an appreciable effect upon the orientation of the groups at the 1- and 2-positions and consequently upon the hydrogen bonding orientations. The peri hydrogen presumably forces the lone pair electrons of the oxygen to be orientated away from the proton of the hydroxyl; therefore, the only intramolecular hydrogen bonding possible is that from an OH---π interaction. This weaker hydrogen bond is revealed



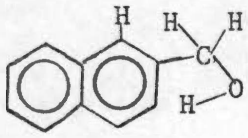
VI

by a slope of 46, which is close to the unsubstituted cases. This leads

one to conclude that only a slight increase in OH---π hydrogen bonding has occurred. The difference between a δ_o of 1.46 in VI and the 1.16 value of V is due partly to the addition of a methoxy group. In order to help explain the δ_o values the following structures can be used. Both cases are equally probable. In case Vb, the hydroxyl proton signal would

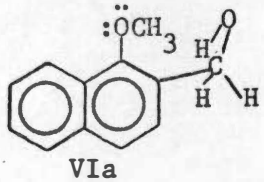


Va

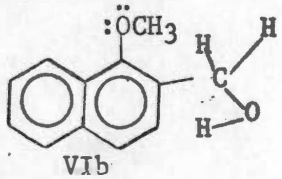


Vb

be further downfield due to its greater distance from the point of ring fusion. In case VIa, the energy requirement is too large for a significant



VIa



VIb

contribution from this species. However, the energy of VIb is less than VIa; i.e., it is preferred conformation. Since VIb would be the preferred species, the downfield shift of the hydroxyl proton may be rationalized. Molecular models for 2-hydroxymethylnaphthalene (V) and VIII (Table II, page 13) show that their hydroxyl protons (on the average) are even further removed from the point of ring fusion than VII (Table II) and should have their δ_o's at even lower field positions. For VIII there is also the OH---O bond which may exert a larger deshielding effect because of electron withdrawal of the ethereal oxygen. In addition, as will be shown from an analysis of the ir data, VII appears to have a predominance of OH---π bonding. Presumably this interaction will cause greater shielding of the hydroxyl proton. A molecular model of 2-methoxy-1-hydroxymethylnaphthalene (VII) shows that the lower energy orientational conformation

along the C-OH bond axis should be the one in which the proton of the hydroxyl group is over the ring fusion position. The slope value of 21 indicates relatively strong intramolecular hydrogen bond or bonds are formed compared to III, VI, or VIII. Therefore, the chemical shift value of 1.36 δ may result from shielding of the hydroxyl proton by the ring current effect when the hydroxyl proton is above the plane of the phenyl ring.

1,8-Substituents are not coplanar with the naphthalene ring, and as the size of the 8-substituent increases, the 1-hydroxymethyl group is forced further out of the plane. This brings the hydroxyl closer to the pi electron cloud of the naphthalene ring and results in an increase in the strength of the OH---π hydrogen bond. The 1- and 8-positions in naphthalene are said to be peri to each other. Due to naphthalene's geometry, the substituents are in closer proximity to each other than similar groups located ortho to one another. This closeness causes the unique properties called "peri effects."[34]

Compounds IX (8-methoxy-1-hydroxymethylnaphthalene), XI (8-bromo-1-hydroxymethylnaphthalene), and XII (8-chloro-1-hydroxymethylnaphthalene) all have the possibility of forming six-membered ring structures via OH---X interactions. On the basis of steric interactions[35] alone one would expect the small methoxy group to have the largest slope, but the data from this research show that IX has the smallest slope ($d\delta/dx$ = 13). Therefore, some other effect must be operating such as the energetically more favorable OH---O hydrogen bond. E_s values for bromine and methyl are identical (0.00) and these groups should show the same steric interaction in XI and X. The slopes of these two imply that the steric influence is not the only effect

that needs consideration. In the case of XI, there seems to be an OH---X hydrogen bond formed. It has been shown in other 1,8-disubstituted naphthalenes that the ring may buckle in order to adopt the best arrangement for large groups at these positions.[34] The slope values for compounds X, XI, and XII all are similar, and one could conclude that the monomer and dimer energies are close together in each compound. On the basis of steric size and electron donor ability one would expect the slope of the chloro substituted compound to be much larger than that of the bromo compound. Since this is not observed one assumes that the smaller size of the chloro group may make it more readily available for OH---X bonding in comparison with XI. The structural differences of the various substituents is obvious from the vast difference in chemical shifts of the monomer at infinite dilution. Compounds XI and XII have similar structural features, δ_o's of 1.75 and 1.74 ppm's respectively, while IX with the large deshielding influence from the ethereal oxygen of the methoxy group has a δ_o value of 2.42 ppm. X, with its δ_o of 1.13 ppm, is very close to the unsubstituted compound, IV, with its value of 1.16 ppm. The data for compounds IX through XII are shown in Table III, p 18.

From the results of this research, it was generally observed that the norbornanols capable of OH---π bonding exhibited much smaller slopes and δ_o values than did the naphthalene or benzyl alcohols studied. Both slopes and δ_o values are reported in Table IV.

As in the other compounds studied, alcohols capable of intramolecular hydrogen bonds (OH---π type) exhibit smaller slopes than their structurally similar isomers where such bonding is precluded. For example, 3-<u>exo</u>-phenyl-2-<u>exo</u>-norbornanol (XVII) has a slope of 3.2 ppm/mole percent compared

TABLE III

NUCLEAR MAGNETIC RESONANCE DATA FOR SOME 1,8-DISUBSTITUTED NAPHTHALENES

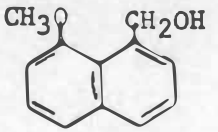
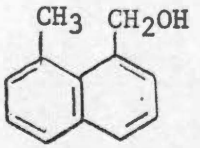
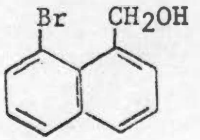
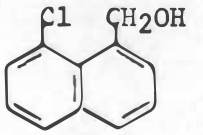
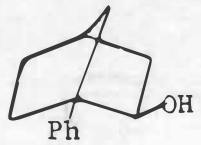
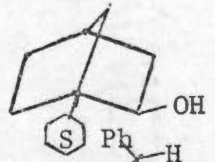
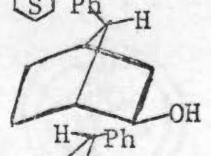
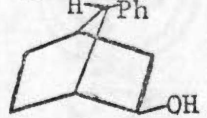
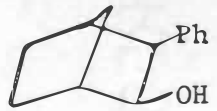
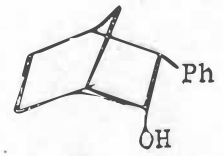
Naphthalene	Code	Structure	δ_o, p.p.m.	$(d\delta/dx)_{x=o}$
8-Methoxy-1-hydroxymethyl	IX		2.42	13
8-Methyl-1-hydroxymethyl	X		1.13	32
8-Bromo-1-hydroxymethyl	XI		1.75	25
8-Chloro-1-hydroxymethyl	XII		1.74	26

TABLE IV

NUCLEAR MAGNETIC RESONANCE DATA FOR SEVERAL NORBORNANOLS

Norbornanol	Code	Structure	δ_o, p.p.m.	$(d\delta/dx)_{x=o}$
1-Phenyl-2-<u>exo</u>-	XIII		0.93	3.0
1-Cyclohexyl-2-<u>exo</u>-	XIV		0.84	16
7-<u>anti</u>-Phenyl-2-<u>exo</u>-	XV		0.90	61
7-<u>syn</u>-Phenyl-2-<u>exo</u>-	XVI		0.24	4.7
3-<u>exo</u>-Phenyl-2-<u>exo</u>-	XVII		0.55	3.2
3-<u>endo</u>-Phenyl-2-<u>endo</u>-	XVIII		1.00	8.3

to the slope of 42 ppm/mole percent for 3-*endo*-phenyl-2-*exo*-norbornanol.[13] The smaller slope for XVII indicates that the equilibrium constant for its dimerization is less than that of its *trans* isomer; it also implies that a reasonably strong OH---π interaction must form for the more stable monomer to result.

Compound XV, 7-*anti*-phenyl-2-*exo*-norbornanol, does not have the structural arrangement needed for an intramolecular hydrogen bond. Consequently, the large slope value of 61 is not surprising. The chemical shift at infinite dilution occurs at 0.90 ppm which shows only a slight inductive electron withdrawal (2-*exo*-norbornanol, δ_o = 0.82 ppm).[13] Changing the phenyl group from the 7-*anti*-position to the 7-*syn*-position (XVI) causes some drastic changes due to the steric effect of the phenyl ring and to the OH---π bond which can form. Both of these effects probably combine to decrease the energy difference between the dimer and the monomer. The slope value decreases more than ten fold due to these effects. The orientation of the hydroxyl proton must be such that it lies well within the shielding cone of the phenyl ring, δ_o = 0.24 ppm.

Steric effects are also involved in XIII (1-phenyl-2-*exo*-) and XIV (1-cyclohexyl-2-*exo*-) which are identical in their group positions. In only one case, XIII, is OH---π bonding possible. One would therefore suspect the slope values to be drastically different; however, the slope of XIII is 3.0 and the slope of XIV is 16. From these values one must conclude that a considerable steric interaction between the 1-substituent in one molecule and the hydroxyl group in the second molecule raises the energy of the dimer relative to that of the monomer.[13] At the concentrations normally used the dimer would be the energetically preferred species.

Compounds XVII (3-exo-phenyl-2-exo-) and XVIII (3-endo-phenyl-2-endo-) appear to be much more alike because in both compounds the groups are cis to each other. From this research we note that their slopes and chemical shifts are quite different. When both the phenyl and hydroxyl groups are in the endo position, as in XVIII, the interaction of one of the ortho protons of the phenyl group with the 5-endo hydrogen may be large and may force the phenyl group to rotate such that a smaller degree of OH---π bonding would result when compared to XVII. This seems to be verified by the δ_o of 1.00 for XVIII; the slope values suggest that the monomer energy of XVIII is not lowered as much as that of XVII.

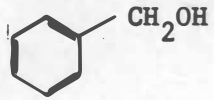
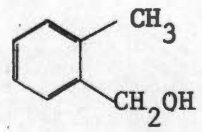
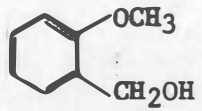
B. Infrared Studies

The use of ir dilution techniques for hydrogen bonding studies was used in conjunction with the nmr spectral measurements at various concentrations. From the ir spectral data, the concentrations where monomer-dimer equilibria change to higher order species are ascertainable. This technique also allows the determination of the types and magnitudes of the hydrogen bonds in the compounds. In general, the greater the strength of the hydrogen bond, the larger will be the frequency difference between the free peak and the intramolecularly hydrogen bound peak ($\Delta\nu$, cm^{-1}). In a number of cases the free peaks appeared as shoulders on the intramolecular peaks; the values used for the free peaks in these cases were those obtained by Joris using graphical separation of the peaks. In Tables V-VII the peak values obtained by Joris are included for comparison; they are the values in parentheses.

From the data in Table V one can obtain the types of hydrogen bonds and their strengths. Compounds I ($\Delta\nu$ = 19 cm^{-1}) and II ($\Delta\nu$ = 18 cm^{-1})

TABLE V

INFRARED SPECTRAL DATA FOR SOME BENZYL ALCOHOLS

Alcohol	Code	Structure	Free Peak[a]	Bonded Peak[a]	$\Delta\nu$[a]	Rel. Abs.
Benzyl	I		3632 (3631)	3617 (3615)	19[b]	1.0 1.4
o-Methylbenzyl	II		None	3618	18[b]	---
o-Methoxybenzyl	III		3630 (3642)	3606 (3607)	36[c]	1.0(1.0)[d] 1.5(2.0)[d]

[a]Values are given in cm^{-1}.

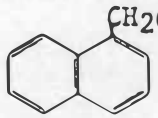
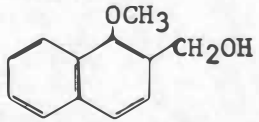
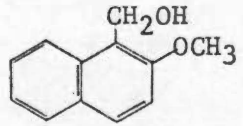
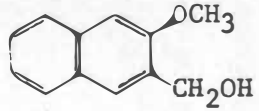
[b]Estimated from a free peak of 3636 cm^{-1}.

[c]Estimated from a free peak of 3642 cm^{-1} (Joris' graphical separation method).

[d]Integrated absorption peaks determined by Joris.

TABLE VI

INFRARED SPECTRAL DATA FOR SOME DISUBSTITUTED NAPHTHALENES

Naphthalene	Code	Structure	Free Peak	Bonded Peak	Δν	Rel. Abs.
1-Hydroxymethyl	IV		3628 (3631)	3617 (3617)	19[a]	1.0 1.3
2-Hydroxymethyl	V		3629 (3631)	3614 (3615)	22[a]	1.0 1.2
1-Methoxy-2-hydroxymethyl	VI		3629 (3631)	3617 (3618)	19[a]	1.0 1.4
2-Methoxy-1-hydroxymethyl	VII		None	3618	18[a]	---
2-Methoxy-3-hydroxymethyl	VIII		3636 (3642)	3607 (3607)	35[b]	1.0(1.0)[c] 1.6 (2.0)[c]

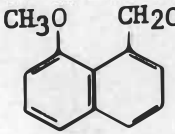
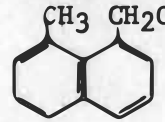
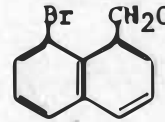
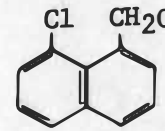
[a]Estimated from free peak of 3636 cm^{-1}.

[b]Estimated from free peak of 3642 cm^{-1} (Joris' graphical separation method).

[c]Integrated absorption peaks determined by Joris.

TABLE VII

INFRARED SPECTRAL DATA FOR SOME 1,8-DISUBSTITUTED NAPHTHALENES

Naphthalene	Code	Structure	Free Peak	Bonded Peak	Δν	Rel. Abs.
8-Methoxy-1-hydroxymethyl	IX		3634 (3640)	3587 (3590)	53[a]	1.0(1.0)[d] 2.1(1.0)[d]
8-Methyl-1-hydroxymethyl	X		3631 (3631)	3613 (3613)	24[b]	1.0 1.5
8-Bromo-1-hydroxymethyl	XI		3639 (3639)	3610 (3614) 3590 (3592)	29[c] 49[c]	1.0(1.0)[d] .9(.4)[d] 1.3(1.4)[d]
8-Chloro-1-hydroxymethyl	XII		3636 (3639)	3604 (3609)	35[c]	1.0(1.0)[d] 1.4(1.5)[d]

[a]Estimated from a free peak of 3640 cm^{-1}.

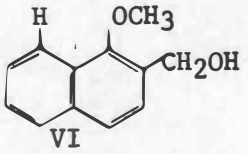
[b]Estimated from a free peak of 3636 cm^{-1}.

[c]Estimated from a free peak of 3639 cm^{-1}.

[d]Integrated absorption peaks determined by Joris.

have OH---π bonds of approximately the same strength. The large methyl in II evidently restricts the hydroxyl proton to a position over the edge of the phenyl ring, and does not allow a free hydroxyl even at infinite dilution. This piece of evidence helps to verify the interpretation of the nmr values. The slope value of 36 for II suggests some intramolecular association when compared with I (see Table I, p 12). The lack of a free hydroxyl peak in the ir spectrum indicates that OH---π association does exist. Some of the decrease in slope may be caused by the steric effect of the o-methyl group. Compound III ($\Delta\nu$ = 36 cm^{-1}) has a strong OH---O hydrogen bond. The slope value of 22 observed was the smallest of the benzyl alcohols studied, and thus the two values combine to indicate a strong intramolecular association. At the same time, however, about 40% of the hydroxyl exists free at infinite dilution. Possibly the smaller methoxy group does not restrict the conformation in the same manner as did the methyl group.

Compounds IV-VII (Table VI, p 23) have hydrogen bonds of approximately the same strength and type (OH---π). For the compounds without the methoxy substituents, one notices a slightly larger percent of free hydroxyl. For VI the "peri effect" has forced the most energetically favorable arrangement



VI

to be the one with the lone pair electrons of the methoxy group oriented away from the hydroxyl proton. This value is close to that of IV and V which have only the possibility of OH---π bonding. The ir and nmr spectral results also complement each other in this case (see page 14). Compound VII shows no free hydroxyl; from an examination of molecular models one might expect a

possible OH---O hydrogen bond or OH---π bond. From the Δν value (18 cm^{-1}) and the peak position of 3618 cm^{-1}, one draws the conclusion that the interaction is of the OH---π type.

VIII has the most favorable arrangement for OH---O bonding because the "peri effect" no longer restricts the arrangement of the groups, and the molecule is flat.[34] A strong OH---O interaction (Δν = 35 cm^{-1}) results.

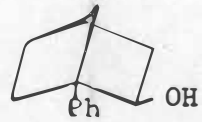
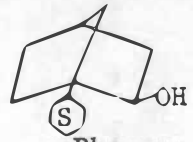
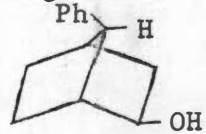
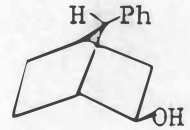
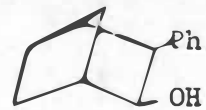
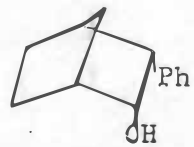
In the case of 1,8-disubstituted naphthalenes (Table VII, p 24) the bonding appears to be affected by the steric interactions between the 1- and 8- groups. In compounds IX-XII some type or types of hydrogen bonding interaction exist, but a more noticeable observation is that each has at least 30% of the free hydroxyl. The fact that the frequency shift for the 8-bromo compound (Δν = 49 cm^{-1}) is greater than that of the 8-chloro compound (Δν = 35 cm^{-1}) may be due to the difference in the atomic size and polarizability between the bromine and chlorine. The bromine atom in XI, atomic radius 1.14 Å, is closer to the hydroxymethyl group than is the chlorine in XII, atomic radius 1.00 Å,[15] and the bromine may force the hydroxymethyl group to move out of the plane of the naphthalene ring. The arrangement of the bromine (or any other 8-substituent) and hydroxymethyl cannot be in the same plane with the naphthalene ring. However, the optimum O---O distance for hydrogen bonding, 2.2 to 3.4 Å, can still be attained, and presumably the hydrogen bond strength can be maximized. The slope values of the bromo and chloro compounds are relatively close in value, 25 and 26 respectively. It may be that the nmr slope value reflects the difficulty of the Br to get in close enough to bond to the hydroxyl proton, and only in the ir data do we observe the approximate strength of the OH---Br bond once it has formed. The 8-bromo compound also experiences OH---π

interaction ($\Delta\nu$ = 29 cm^{-1}), which appears to be stronger than the OH---π hydrogen bond in the 8-methyl compound ($\Delta\nu$ = 24 cm^{-1}). One might conclude then that steric size as well as electronegativity of the 8-substituent influences the hydrogen bonding. The 8-methoxy, IX, frequency shift of 53 cm^{-1} was the largest observed in this research. The smaller size of the methoxy group should give the best OH---O arrangement and allow maximum OH---O hydrogen bonding. From the lack of a bonded peak at approximately 3620-10 cm^{-1} one would conclude that an OH---π hydrogen bond is lacking. Consequently this compound has the best arrangement and the strongest intramolecular hydrogen bond for this series.

In the norbornanol series studied the only type of intramolecular hydrogen bonds were those of the OH---π type. The strongest interactions were those of compounds XIII and XVII (Table VIII). The only compounds that exhibited free peaks were XIV and XV. The frequency shift for XVI (32 cm^{-1}) is not surprising when compared with the nmr slope value of 4.7. The slope may, of course, be due largely to steric effects. The δ_o value of 0.24 for XVI, 7-<u>syn</u>-phenyl-2-<u>exo</u>-norbornanol, shows the phenyl and OH must interact quite strongly when compared to 7-<u>anti</u>-phenyl-2-<u>exo</u>-norbornanol, δ_o = 0.90. Both techniques indicate rather strong intramolecular association. In ir spectroscopy the maximum effect exists when the proton is oriented over the edge of the ring while in nmr spectroscopy the maximum effect operates when the proton is over the center of the phenyl ring. One might also expect the frequency shifts of XVII and XVIII to be closer in value. The di-<u>endo</u> compound, XVIII, has a $\Delta\nu$ of 10 cm^{-1} which indicated a weak intramolecular hydrogen bond. In order for maximum OH---π interaction to occur in XVIII an <u>o</u>-hydrogen of the phenyl must interact with the

TABLE VIII

INFRARED SPECTRAL DATA FOR SEVERAL NORBORNANOLS

Norbornanol	Code	Structure	Free Peak[a]	Bonded Peak[a]	$\Delta\nu$[a]
1-Phenyl-2-<u>exo</u>-	XIII		----	3587	33[b]
1-Cyclohexyl-2-<u>exo</u>-	XIV		3620	----	---
7-<u>anti</u>-Phenyl-2-<u>exo</u>-	XV		3619	----	---
7-<u>syn</u>-Phenyl-2-<u>exo</u>-	XVI		----	3589	32[b]
3-<u>exo</u>-Phenyl-2-<u>exo</u>-	XVII		----	3587	33[b]
3-<u>endo</u>-Phenyl-2-<u>endo</u>-	XVIII		----	3610	10[b]

5-endo- hydrogen. To relieve this strain the phenyl ring must rotate somewhat and thereby considerably decrease the extent of OH---π interaction. This was also observed to cause a larger slope, 8.3, for the di-endo compound in comparison with the slope for the di-exo compound of 3.2.

C. Infrared and Nuclear Magnetic Resonance Correlations

One of the objectives of this research was to determine the species present in the alcohols at various concentrations in the nmr spectra so that dimerization constants could be calculated. It was hoped that a correlation of the species present in the ir spectra could be applied to the nmr results. In the calculations normally done it is assumed that at approximately 2.0 mole percent and below the same sort of species are present. As one can see from an examination of Table IX, this assumption does not hold in all cases. For example, in either 3-endo-phenyl-2-endo-norbornanol or 3-exo-phenyl-2-exo-norbornanol the polymer or oligmer species is no longer apparent at concentrations of approximately 0.55 mole percent while for 1-phenyl-2-exo-norbornanol or 1-cyclohexyl-2-exo-norbornanol the sample must be diluted to approximately 0.30 mole percent or below for the higher ordered species to disappear. Therefore, one cannot work at the same concentrations for all species and do meaningful calculations and interpretations. In Table IX ε_m is either the free hydroxyl peak or the intramolecular species that occurs at highest frequency.

Another important observation is that as the sample is diluted, the peak due to the higher ordered species (ε_{o+p}) is shifted closer to the monomer peak (ε_m), and the former peak also decreases in intensity. This implies that the equilibria shifted toward the monomer-dimer position.

TABLE IX

INFRARED DILUTION DATA

Compound	Mole %	ε_m [a]	ε_{o+p} [b]
1-Phenyl-2-exo-norbornanol	.71	1.0	.15 (3448 cm^{-1})
	.35	1.0	.02 (3471 cm^{-1})
	.29	1.0	----
1-Cyclohexyl-2-exo-norbornanol	.54	1.0	.20 (3500 cm^{-1})
	.39	1.0	.10 (3501 cm^{-1})
	.30	1.0	----
3-endo-Phenyl-2-endo-norbornanol	1.0	1.0	.36 (3472 cm^{-1})
	.70	1.0	.20 (3477 cm^{-1})
	.60	1.0	----
3-exo-Phenyl-2-exo-norbornanol	1.1	1.0	.26 (3473 cm^{-1})
	.88	1.0	.16 (3476 cm^{-1})
	.55	1.0	----
7-anti-Phenyl-2-exo-norbornanol	.41	1.0	.16 (3491 cm^{-1})
	.29	1.0	.07 (3496 cm^{-1})
	.13	1.0	----
7-syn-Phenyl-2-exo-norbornanol	.27	1.0	----
o-Methoxy-benzyl alcohol	1.58	1.0	.72 (3466 cm^{-1})
	.61	1.0	.40 (3498 cm^{-1})
	.37	1.0	----
o-Methylbenzyl alcohol	1.22	1.0	.74 (3413 cm^{-1})
	.56	1.0	.12 (3486 cm^{-1})
	.35	1.0	----
Benzyl alcohol	1.52	1.0	.64 (3481 cm^{-1})
	.59	1.0	.21 (3494 cm^{-1})
	.50	1.0	----
1-Hydroxymethylnaphthalene	.57	1.0	.50 (3477 cm^{-1})
	.36	1.0	.30 (3492 cm^{-1})
	.24	1.0	----
2-Hydroxymethylnaphthalene	.62	1.0	.48 (3480 cm^{-1})
	.38	1.0	.25 (3490 cm^{-1})
	.30	1.0	----

TABLE IX (Continued)

Compound	Mole %	ε_m [a]	ε_{o+p} [b]
1-Methoxy-2-hydroxymethyl-naphthalene	.34	1.0	.36 (3514 cm^{-1})
	.26	1.0	.35 (3518 cm^{-1})
	.16	1.0	----
2-Methoxy-1-hydroxylmethyl-naphthalene	.51	1.0	.19 (3491 cm^{-1})
	.27	1.0	.07 (3506 cm^{-1})
	.23	1.0	----
2-Methoxy-3-hydroxymethyl-naphthalene	.32	1.0	.24 (3492 cm^{-1})
	.26	1.0	.20 (3493 cm^{-1})
	.23	1.0	----
8-Methoxy-1-hydroxymethyl-naphthalene	.28	1.0	.11 (3476 cm^{-1})
	.21	1.0	.08 (3477 cm^{-1})
	.17	1.0	----
8-Methyl-1-hydroxymethyl-naphthalene	.33	1.0	.30 (3478 cm^{-1})
	.27	1.0	.20 (3482 cm^{-1})
	.22	1.0	----
8-Bromo-1-hydroxymethyl-naphthalene	.48	1.0	.28 (3483 cm^{-1})
	.33	1.0	.15 (3492 cm^{-1})
	.22	1.0	----
8-Chloro-1-hydroxymethyl-naphthalene	.17	1.0	----

[a] Extinction coefficient of monomer.

[b] Extinction coefficient of dimer.

In general one would expect to see a reversal of curvature in the nmr spectra at the concentration where the monomer-dimer equilibria exist, and this is observed in a large number of cases. Figure 1 is an example of this correlation. The small arrows indicate where the ir technique shows infinite dilution has been reached. In this research it was possible to control the temperature for nmr dilutions, but a controlled temperature ir cell was not available, and therefore some error was involved in trying to relate exactly the contribution of the species present between the two techniques.

Another limitation was the volume required to begin an ir spectrum. In the case of the 8-chloro-1-hydroxymethylnaphthalene and 7-syn-phenyl-2-exo-norbornanol insufficient sample was available to determine the exact concentration at which infinite dilution occurs. Also, there were lower limits on the nmr concentrations since after a certain point the peaks could not be measured. Compounds 8-bromo-1-hydroxymethylnaphthalene, 8-methyl-1-hydroxylmethylnaphthalene, 1-phenyl-2-exo-norbornanol, and 7-syn-phenyl-2-exo-norbornanol had this physical limitation.

The compounds which could not be correlated due to one or more of the above limitations were 1-hydroxymethylnaphthalene, 1-methoxy-2-hydroxymethylnaphthalene, 8-methyl-1-hydroxymethylnaphthalene and 3-exo-phenyl-2-exo-norbornanol. For the other compounds studied it appears that the point of change in curvature of the nmr curve corresponds to the ir infinite dilution point. However, this change in curvature does not occur at the same concentration for all compounds. Due to these limitations it was not felt that meaningful dimerization constants could be calculated.

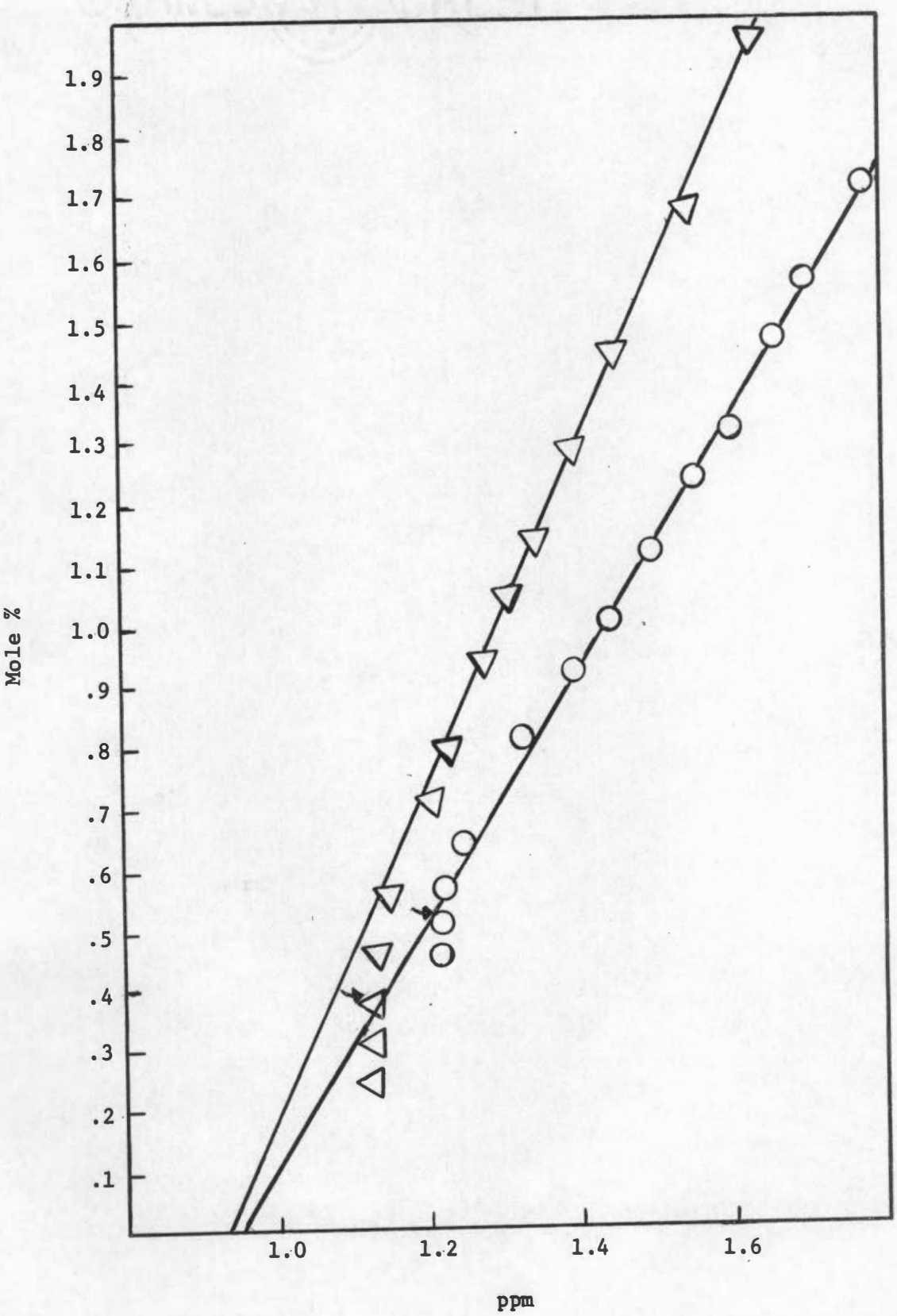


Figure 1. Nmr slope curves for benzyl alcohol, O, and o-methylbenzyl alcohol, Δ.

Toward the end of this research it was decided that a brief discussion was needed on the controversy over the utility of frequency shifts as a measure of hydrogen bonding strengths.

Baker[37] looked at the frequency shifts for ~~several~~ ortho substituted halophenols and found that the frequency shift and trans/cis ration increased with the increasing atomic number of the halogen. On the basis of electronegativity alone the $\Delta\nu$ values would be expected to be of the inverse order; therefore, it appears that the polarizability of the halogen is more important. The fact that both the trans/cis ratio and $\Delta\nu$ shift increase in the same order appears to argue against the ~~applicability~~ of Badger's rule.[38] Baker[39] later used similar systems, and the results indicated that the order of increasing hydrogen bond is I<F<Br<Cl. This could be rationalized by assuming that the small fluorine couldn't get close enough to the hydroxyl group for a strong bond to form, and the balance between optimum interacting distance and minimum repulsive interaction is reached in chlorine. West and Schleyer[40] actually measured the heats of formation for several alkyl halides and compared those values with the frequency shifts (Table X, values in parentheses). The $-\Delta H_f^\circ$ values decrease in the order F>Cl>Br while the reverse is noticed for the spectra order shift. According to Schleyer's explanation the lack of correlation between $\Delta\nu$ and $-H_f^\circ$ can be rationalized because $-\Delta H_f^\circ$ measures the total interaction, A-H--B-Y; i.e., the strength of the H--B bond which is partially compensated by the weakening of the A-H and B-Y bonds while $\Delta\nu$ measures only the weakening of the A-H bond. In a given series if the donor atom, A, is kept the same then $\Delta\nu$ and $-H_f^\circ$ may correlate for minor changes in the proton acceptor, Y.

TABLE X

FREQUENCY SHIFTS AND $-\Delta H_f^\circ$ FOR SEVERAL ACCEPTOR BASES

Acceptor Bases	$\Delta\nu$ (PFP)		$-\Delta H_f^\circ$ (PFP)	
Cyclohexyl F	(53)[a]		(3.1)[a]	
Cyclohexyl Cl	(66)[a]	71	(2.2)[a]	2.12
Cyclohexyl Br	(82)[a]	90	(2.0)[a]	1.96
Cyclohexyl I	(86)[a]	95	(1.7)[a]	1.46
n-Butyl Cl		62		1.93
n-Butyl Br		71		1.82
n-butyl I		78		1.55
Anisole		169		3.13
Bibenzyl ether		249		4.59
Dioxane		252		5.10
Diethyl ether		285		5.57
Tetrahydrofuran		292		5.75

[a]From Schleyer's work (ref. 40); all other values are from Arnett (ref. 41).

Recently Arnett and Schleyer[41] (see Table X) obtained the frequency shifts and $-\Delta H_f^\circ$ values for p-fluorophenol (PFP) and other hydroxy compounds in various acceptor bases. The halogen acceptor bases followed the trend of Schleyer's earlier paper.[40] For most of the other compounds the frequency shifts (excluding OH--π) seem to correlate with the $-\Delta H_f^\circ$ values.

Definitely $\Delta\nu$ and $-\Delta H_f^\circ$ measure different processes, and the exact relation between the values is still not clear. Drago has been the leading exponent of the opposite interpretation of the results[42] of Arnett and Schleyer. Positive proof from both groups to support their conflicting interpretations has been announced, but has yet to appear.

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