at The Johns Hopkins University. An exchange of comments and experimental data greatly helped us in our work, which is fully acknowledged. The very similar results obtained by their group[9] and ours using different experimental procedures is a good check on the accuracy of the data.

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## A Nuclear Magnetic Resonance Study of OH···π Hydrogen Bonding[1]

*Sir:*

Jackman[2] has stated that "because of the magnitude of the shifts associated with hydrogen bonding, nuclear magnetic resonance will doubtless prove to be a valuable alternative to infrared spectroscopy for the investigation of structural features which permit such an interaction." Intramolecular OH···π hydrogen bonding has been aptly demonstrated in the infrared,[3a] but limited study of such interactions has been extended to nmr.[3b] The initial results on an nmr study of the hydrogen-bonding tendencies of 13 norbornanols are summarized in Table I. During the course of this research it was learned in conversation with Collins and Benjamin that they too have observed the phenomenon to be discussed in one compound, 7-*syn*-phenylnorbornane-7-*anti*,2-*exo*-diol.[4]

**Table I.** Hydrogen Bonding Data for Some Norbornanols

| Compd | Norbornanol[a] | $(d\gamma/dx)x = 0$ | $\gamma_0$, ppm | $\Delta_1$[b] | $\sigma_H$[c] | $\Delta\mu$, $cm^{-1}$[d] |
|---|---|---|---|---|---|---|
| **1** | *exo-* | 34 | 0.82 | ...... | .... | ... |
| **2** | *endo-* | 33 | 0.83 | ...... | .... | ... |
| **3** | 3-*endo*-Ph-2-*exo*- | 42 | 1.10 | 0.28 | .... | ... |
| **4** | 3-*exo*-Ph-2-*endo*- | 30 | 1.20 | 0.37 | .... | ... |
| **5** | 7-*anti*-Ph-2-*exo*- | 58 | 0.90 | 0.08 | .... | ... |
| **6** | 1-Ph-2-*endo*- | 12 | 1.14 | 0.31 | 0.06 | 19[e] |
| **7** | 1-Ph-2-*exo*- | 2.8 | 0.91 | 0.09 | 0.19 | 30[e] |
| **8** | 3-*endo*-Ph-2-*endo*- | 5.4 | 1.02 | 0.19 | 0.18 | 10 |
| **9** | 3-exo-Ph-2-*exo*- | 2.9 | 0.58 | −0.24 | 0.52 | 30 |
| **10** | 7-*syn*-Ph-2-*exo* | 4.0 | 0.26 | −0.56 | 0.64 | 28 |
| **11** | 2-*exo*-Ph- | 7.2 | 1.24 | 0.41 | .... | ... |
| **12** | 2-*endo*-Ph- | 11 | 1.30 | 0.48 | .... | ... |
| **13** | 1-Cyclohexyl-2-*exo*- | 17 | 0.81 | −0.01 | .... | ... |

[a] The O–H resonance frequencies were determined for six to eight concentrations of alcohol ranging from *ca.* 0.10 to below 0.01 mole fraction. [b] $\Delta_1$ is the difference between the O–H signal at infinite dilution and the O–H signal for the parent alcohol, **1** or **2**. [c] $\sigma_H$ is the difference between the O–H signal at infinite dilution and that observed for **3**, **4**, or **5**. This was done to compensate for the inductive effect of phenyl. [d] Infrared. [e] D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960, p 94.

A number of structural features related to inductive, steric, conformational, and π-interaction effects can be revealed by an examination of the magnitude of the slope $(d\gamma/dx)x = 0$ and the position of $\gamma_0$. These are summarized as follows:

(1) Those bicyclic secondary alcohols incapable of intramolecular OH··· π bonding have their $\gamma_0$'s at lower fields than **1** and **2**, presumably due to the inductive effect of phenyl. This effect falls off with distance as shown by comparison of **3** and **4** with **5**.

(2) Phenyl-substituted secondary alcohols which are incapable of intramolecular OH···π bonding show slopes related to dimer–monomer equilibria which are equal to and greater than those for the unsubstituted parent compounds. The values of 30, 42, and 58 for **4**, **3**, and **5**, respectively, suggest an order of decrease in steric factors which presumably raises the energy difference between the monomeric and dimeric species.[5]

(3) Particularly noteworthy are the $\gamma_0$ positions for **7**–**10**, all of which show essentially complete bonding to the benzene ring in their infrared spectra at infinite dilution. The $\gamma_0$'s all occur at higher fields relative to those incapable of such interactions. In addition, while **7**, **9**, and **10** show approximately equivalent $\Delta\mu$'s indicative of the strength of the OH···π bond, their $\gamma_0$'s occur at quite different fields, the magnitudes of the differences being reflected by $\sigma_H$.

(4) All secondary alcohols which demonstrate complete OH···π bonding in the infrared exhibit very small slopes relative to the other secondary alcohols. The values range from 2.8 to 5.4 and reflect a reduction in the energy difference between the monomer and dimer. That this reduction in energy is due to both the intramolecular interaction lowering the energy of the monomer and a steric effect raising the energy of the dimer was shown from the slope of 17 exhibited by **13**, the 1-cyclohexyl analog of **7**. Assuming that the bulk of a cyclohexyl group is larger than that of phenyl, then the OH···π bond in **7** causes at least a sixfold decrease in the slope.

The reasons for the relative equivalence of the $\Delta\mu$'s for alcohols **7**, **9**, and **10** and the variance of their $\gamma_0$ values stem from the differences between the infrared and nmr absorption processes. An examination of Dreiding models and measurements of both the approximate distance and the angle from the center of the benzene ring to the hydroxyl hydrogen aids in explaining these differences. The measurements are included in Table II.

In both the infrared and nmr the maximum interaction is experienced when the OH bond is oriented

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(1) This research was supported in part by a grant from the National Science Foundation.

(2) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p 68.

(3) (a) P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958); (b) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **35**, 1552 (1962); R. J. Ouellette, D. L. Marks, and D. Miller, *J. Am. Chem. Soc.*, **89**, 913 (1967).

(4) C. J. Collins and B. M. Benjamin, *ibid.*, **89**, 1652 (1967).

(5) B. G. Somers and H. S. Gutowsky, *ibid.*, **85**, 3065 (1963).

toward the $\pi$-cloud loop on the ring carbon atoms. In the infrared the differences between the positions of the OH group above the plane of the $C_2$–$C_1$–$C_6$ carbon atoms in **7**, **9**, and **10** are not sufficient to reflect any significant differences in the OH$\cdots\pi$ bonds. In the nmr, however, maximum shielding of a hydrogen is experienced when it is held close to the center of the aromatic ring where the induced ring currents cause increased shielding.[6] The degree of shielding of a proton by an isotropic group of electrons is known to depend on both $r$ and $\theta$.[7]

**Table II.** Shielding Parameters for OH$\cdots\pi$ Bonded Alcohols

| Norbornanol[a] | a (ring radii) | | | | | |
|---|---|---|---|---|---|---|
| | $Z$ | $P$ | $r$ | $\theta$[b] | $\sigma_H$, ppm | $\Delta\mu$, cm$^{-1}$ |
| **10** | 1.4 | 0.8 | 1.6 | 29 | 0.64 | 28 |
| **9** | 1.4 | 1.1 | 1.8 | 38 | 0.52 | 30 |
| **7** | 1.6 | 1.3 | 2.1 | 39 | 0.19 | 30 |
| **8** | 1.4 | 1.1 | 1.8 | 38 | 0.18 | 10 |

[a] The $Z$ axis is normal to the plane of the aromatic ring at its center, and the $P$ axis is in the plane of the ring, both measured in ring radii (1.39 A) (see C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958)). Then $r$ measures the distance of $Z_0$, $P_0$ to the H atom. [b] $\theta$ is the angle between the $Z$ axis at $P_0$ and the H atom.

Table II shows that **10**, corresponding to the smallest values of $r$ and $\theta$, reflects the greatest shielding, as expected. While $\theta$ is approximately the same in **7** and **9**, the greater $r$ value for the former alcohol apparently leads to the lesser degree of shielding.

The values of $r$ and $\theta$ have been measured assuming that the preferred benzene ring-hydroxyl hydrogen orientation is that of maximum interaction with the hydrogen perpendicular to the $P$ axis. On this basis, the experimental data for **8** initially appear to be out of line when compared to its di-*exo*-analog **9**. In **8** the phenyl orientation for maximum OH$\cdots\pi$ interaction is one in which an *o*-phenyl hydrogen displays an unfavorable steric interaction with the *endo*-5 hydrogen. To relieve the steric strain the benzene ring can rotate somewhat, thus increasing the value of $\theta$ and decreasing considerably the extent of the OH$\cdots\pi$ interaction evidenced by nmr and infrared.

In conclusion, it has been shown that numerous structural features related to the magnitude of inductive, steric, and conformational effects in bicyclic systems can be probed by an examination of relative values of the slope ($(d\gamma/dx)x = 0$) and the OH signal at infinite dilution ($\gamma_0$). The nmr analysis of $\pi$-interaction effects appears to be superior to the infrared method, since the former method better reflects the differences in structure. This analysis should be useful as an analytical tool for structural assignments and as an instrument for detecting the extent of interaction of aromatic rings and other unsaturated systems with functional groups and thereby elucidating physical and chemical behavior.

**Acknowledgment.** The infrared hydrogen bonding measurements of **6** and **7** by Lewis Robinson and of **8**, **9**, and **10** by Louis Joris are sincerely appreciated.

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[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, London, 1965, p 140.

[7] H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).

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## O–H Chemical Shift, Conformation, and Electron Delocalization in Protonated Carbonyl Compounds[1]

*Sir:*

While studying classical and nonclassical carbonium ions in $SO_2$–$FSO_3H$–$SbF_5$ we have observed the C=O—H proton signal in the nmr spectra of various protonated aldehydes, ketones, and carboxylic acids. In the usual nmr observations of such species, rapid proton exchange with the medium averages the C=O—H proton signal with the solvent signal. In very acidic media at sufficiently low temperatures, however, such proton exchange becomes slow enough to permit nmr observation of the C=O—H proton resonance. The C=O—H signal for protonated acetone was first observed by MacLean and Mackor[2a] in HF–$BF_3$ at −75°, while very recently Birchall and Gillespie[2b] have reported protonated acetone in $FSO_3H$–$SbF_5$, several acetophenones in $FSO_3H$, and $CH_3COOH$, $CH_3CH_2COOH$, and $C_6H_5COOH$ in $FSO_3H$–$SbF_5$. Still more recently, MacLean and Mackor[2d] have reported protonation of formic acid in HF–$BF_3$.

The C=O—H proton nmr signal represents a powerful tool in the study of substituent or electron-delocalization effects, and thus it represents a new tool in the study of nonclassical species. Besides casting some light on the electronic distribution in the protonated species, the C=O—H nmr signal furnishes information regarding conformation and configuration. In the present communication we illustrate some of the kinds of protonated species we have observed and the information derived from the spectra (Table I).

The nmr[3] of acetaldehyde in $SO_2$–$FSO_3H$–$SbF_5$ at −52° shows two doublets, integrating together for one O–H proton, one at $\delta$ 14.78 ($J$ = 8.5 cps) and the other at $\delta$ 15.14 ($J$ = 18.5 cps), in *ca.* 5:1 ratio, respectively. This is interpreted as an equilibrium mixture of *syn* and *anti* conformational isomers I and II. The assignment of the $\delta$ 14.78 doublet to the *syn* isomer and the $\delta$ 15.14 doublet to the *anti* isomer is based on an assumed steric preference of I over II and an analogy between *syn* and *anti* coupling constants ($J_{anti} > J_{syn}$) and *cis* and *trans* olefinic coupling constants ($J_{trans} > J_{cis}$). The spectrum of protonated methyl ethyl ketone at −60° shows two O–H singlets, one at

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[1] (a) Research supported in part by the National Science Foundation; (b) research sponsored in part by the U. S. Army Research Office (Durham).

[2] (a) C. MacLean and E. L. Mackor, *J. Chem. Phys.*, **34**, 2207 (1961); (b) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965); (c) these authors have shown that the C=O—H chemical shift in substituted acetophenones is quite sensitive to *para* substituents and follows a $\rho\sigma^+$ relationship; (d) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. MacLean, *Chem. Commun.*, 898 (1966); (e) our observations and interpretation of the behavior of protonated HCOOH are the same as those of Hogeveen, *et al.*

[3] All chemical shifts ($\delta$) are reported in parts per million downfield from TMS using internal $CH_2Cl_2$ ($\delta$ 5.30) as the secondary standard.