Heteroatom Chemistry
Volume 3, Number 1, 1992

# $^{17}O$ NMR Spectroscopy: Proton–Oxygen Coupling in Simple Alcohols at Natural Abundance

Subramanian Chandrasekaran* and David W. Boykin*

*Department of Chemistry, Georgia State University, Atlanta, Georgia 30303-3083 U.S.A.*

*Received 30 August 1991.*

## ABSTRACT

*$^{17}O$ NMR data are reported for 3-pentanol* (**1**), *cyclopentanol* (**2**), *cyclohexanol* (**3**), *and cycloheptanol* (**4**). *The $^{17}O$ NMR signals for* **1–4** *appeared as doublets, shown to arise from proton–oxygen coupling ($^1J_{OH}$ = 76 ± 3 Hz) by proton decoupling experiments. The effect of concentration, temperature, and solvent was examined in detail for* **2**. *Proton–oxygen coupling was observed at low concentrations, decreased at lower temperatures, and was sensitive to solvent.*

## INTRODUCTION

Because oxygen appears in most common organic functional groups, $^{17}O$ NMR spectroscopy has become a valuable method for assessment of structure in organic chemistry [1,2]. Eliel and co-workers have used $^{17}O$ NMR methodology for addressing important questions of conformation and reaction stereochemistry in aliphatic systems [3]. Systematic $^{17}O$ NMR investigations of alcohols have regularly appeared in the literature beginning with the pioneering work by Christ et al. [4]. A recent review describes the factors that influence the $^{17}O$ NMR chemical shifts of alcohols [5]. Prior to the first direct observation of proton to oxygen coupling [6] in intramolecular hydrogen-bonded phenolic ketones, the only previous recognition of proton to oxygen coupling resulted from studies on $^{17}O$-enriched water [7] and line shape analysis of $^{17}O$ NMR data for methanol, ethanol [8], and the enol of neat 2-acetylcyclohexanone [9]. Two bond proton–oxygen coupling has been directly observed for methyl and ethyl formate [10]. Apparently no careful examination of the simple alcohols for proton to oxygen coupling has occurred. We report here, for the first time, directly observed at natural abundance, proton–oxygen coupling constants in the $^{17}O$ NMR spectra for alcohols for which intramolecular hydrogen bonding is not possible. The influence of concentration, temperature, and solvent on proton–oxygen coupling for cyclopentanol is studied in detail.

## RESULTS

$^{17}O$ NMR spectroscopy data, at natural abundance, for 3-pentanol (**1**), cyclopentanol (**2**), cyclohexanol (**3**), and cycloheptanol (**4**) in 0.5 M acetonitrile solution at 75°C show well-resolved proton–oxygen coupling. Figure 1 includes proton coupled and decoupled spectra for **1–2**. In acetonitrile solution the observed $^1J_{OH}$ values for **1–4** are 76 ± 3 Hz.

The influence of concentration on directly observable proton–oxygen coupling using five different concentrations for **2** in acetonitrile as well as the neat liquid is shown in Figure 2. Coupling is not apparent in the neat liquid but is detectable at 5 M and lower concentrations. Table 1 provides the coupling constant values and linewidths for **2** as a function of concentration. The $^1J_{OH}$ values for **2** range from 56 Hz at 5 M concentration and increase to 80 Hz at 0.1 M concentration.

Increasing the temperature of cyclopentanol in acetonitrile solution from 35° to 75°C in 10° steps show that coupling is detectable at 35°C, although resolution is not good, and becomes more clearly

---

In honor of Professor E. L. Eliel's seventieth birthday.

*To whom correspondence should be addressed.

1042-7163/92/$3.50 + .25

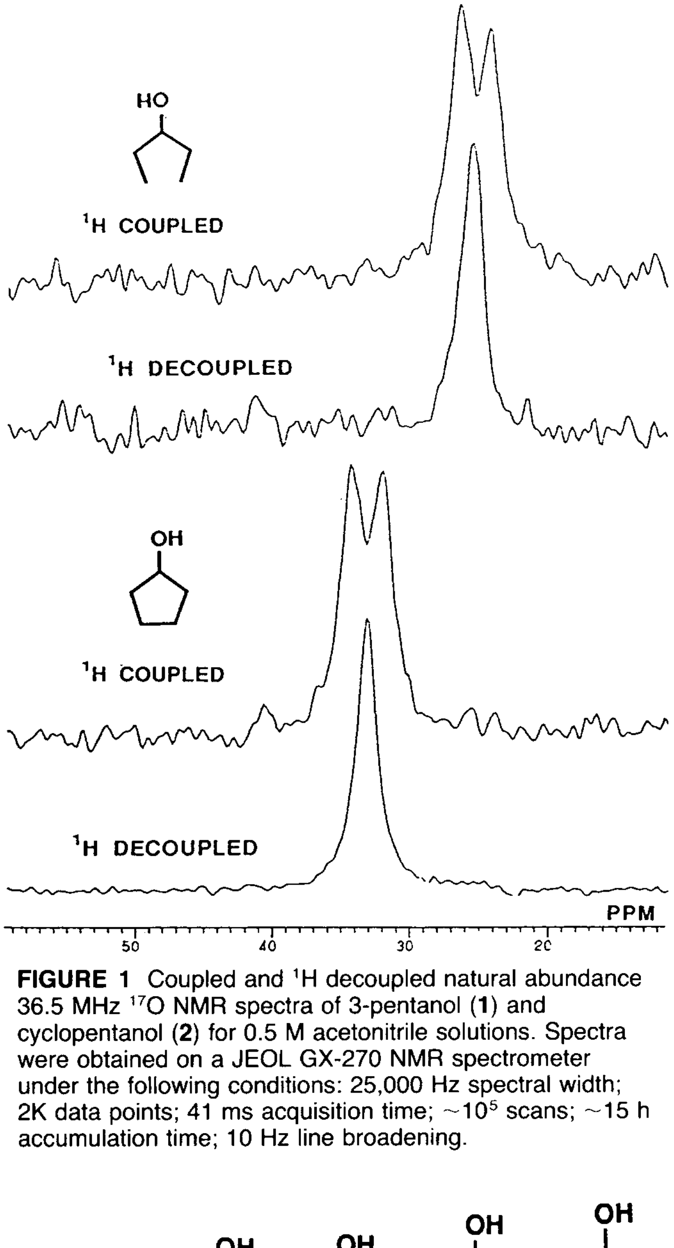
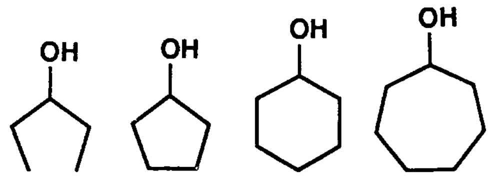


**FIGURE 1** Coupled and ¹H decoupled natural abundance 36.5 MHz $^{17}O$ NMR spectra of 3-pentanol (**1**) and cyclopentanol (**2**) for 0.5 M acetonitrile solutions. Spectra were obtained on a JEOL GX-270 NMR spectrometer under the following conditions: 25,000 Hz spectral width; 2K data points; 41 ms acquisition time; ~$10^5$ scans; ~15 h accumulation time; 10 Hz line broadening.



| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| $\delta_{OH}$ (ppm) | 25.4 | 33.3 | 35.7 | 40.8 |
| $^1J_{OH}$ (Hz) | 79.2 | 79.4 | 73.3 | 73.2 |

observable at 45°C and higher. The apparent $^1J_{OH}$ values for the 0.5 M acetonitrile solution range from 67 Hz at 35°C to 79 Hz at 75°C. Lowering the temperature of **2** in acetonitrile below 35°C reveals that coupling, although reduced, persists at 0°C and disappears at −20°C ($^1J_{OH}$ = 67.1 Hz (25°C); 46.2 Hz (0°C)).

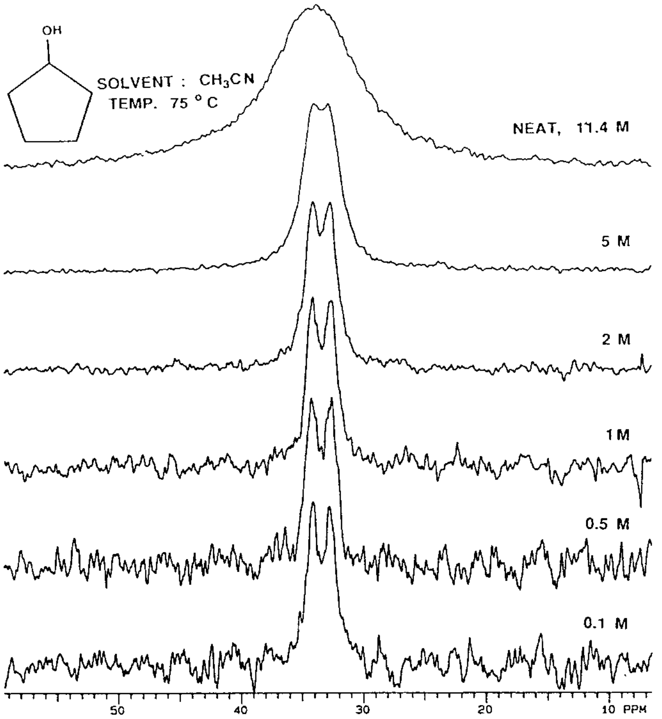


**FIGURE 2** Effect of concentration on proton-oxygen coupling of cyclopentanol (**2**). Spectra were obtained on a Varian VXR-400 NMR spectrometer under the following conditions: 54.2 MHz observation frequency; 3382 Hz spectral width; 2K data points; 303 ms acquisition time; 246,000 scans (25 h) for 0.1 M sample and 12,000 (71 min) for all the other concentrations; 10 Hz line broadening.

The influence of solvent on $^1J_{OH}$ for **2** at 75°C is illustrated in Figure 3 for acetonitrile, toluene, pyridine, and triethylamine, and the $^1J_{OH}$ and linewidth values are found in Table 2. Proton to oxygen coupling is readily detected in toluene ($^1J_{OH}$ = 73 Hz) and acetonitrile ($^1J_{OH}$ = 79 Hz) at 75°C, but in pyridine and triethylamine solutions coupling is not observed. At 45°C, **2** exhibits coupling in acetonitrile ($^1J_{OH}$ = 73 Hz), but no coupling is apparent in diethylamine.

## *DISCUSSION*

For proton–oxygen spin–spin coupling, constants may be smaller than $^{17}O$ quadrupolar broadening and consequently in certain cases direct detection of coupling would not be possible even under optimum conditions. It has been common practice in $^{17}O$ NMR spectroscopy to employ concentrated solutions (including neat liquids) and to apply large broadening factors to acquired data that could obscure otherwise detectable proton-oxygen coupling. As illustrated by Figure 1, it is possible to detect directly $^1J_{OH}$ for simple alcohols in acetonitrile solution using an exponential broadening factor of only 10 Hz (see Experimental). Proton de-

**TABLE 1** Concentration Effects on $^1J_{OH}$ for Cyclopentanol (**2**) at 75°C[a]

| *Concentration* | $^1J_{OH}$ *(Hz)*[b] | $\upsilon_{1/2}$ *(Hz)*[c] |
|---|---|---|
| neat[d] | — | 529 |
| 5 M | 56.0 | 194 |
| 2 M | 69.3 | 160 |
| 1 M | 74.5 | 157 |
| 0.5 M | 78.8 | 141 |
| 0.1 M | 79.8 | 145 |

[a] 12,000 scans were used for data collection at all concentrations except 0.1 M, which required 246,000 scans.

[b] Directly observed proton–oxygen coupling in hertz.

[c] Band-width at half-height in hertz.

[d] ~11.4 M.

coupling experiments (Figure 1) demonstrate that the doublet $^{17}$O signals are the result of proton–oxygen coupling.

It is clear from Figure 2 that the value of $^1J_{OH}$ increases as the concentration decreases presumably because of a decrease in self-association. Our lower limit for natural abundance $^{17}$O NMR measurements was 0.1 M solution because data acquisition at this concentration required ~25 h. Studies at lower concentrations will require enrichment of the alcohol. The influence of temperature on the direct observation of proton–oxygen coupling for **2** is similar to that noted for concentration effects.

Solvent effects on spin–spin coupling are well-documented [11]. For conformationally fixed systems, solvent-induced variation of coupling constants is attributed to changes in the electronic structure of solute molecules [11,12]. The $^1J_{OH}$ values in toluene (73 Hz) and acetonitrile (79 Hz) are marginally consistent with the trends for $^1J_{CH}$ and $^1J_{NH}$, which increase with solvent polarity [12–14]. Figure 3 demonstrates that coupling for **2** is not detected in pyridine and triethylamine solutions, despite an 11-h accumulation. In the case of $^1J_{NH}$ the hydrogen bonding ability of the solvent was considered important [14]. Pyridine is a well-known hydrogen bond acceptor; however, in the case of **2** proton exchange may be approaching the time scale of the experiment because coupling is questionable. Alternatively, the lack of well-resolved coupling in pyridine might be the result of quadrupolar broadening in the relatively more viscous solvent (linewidth = 195 Hz). The data obtained for **2** in solvents of similar viscosities but different hydrogen-bonding capabilities (acetonitrile and triethylamine at 75°C, Table 2, and acetonitrile and diethylamine at 45°C, Table 2) showed that coupling was not directly observed in triethylamine and diethylamine, even though the linewidths were similar in all three solvents. This finding suggests that one-bond, oxygen-proton coupling may not be observable in solvents capable of strong hydrogen bond interactions. In conclusion, it appears that the optimum conditions for observing $^1J_{OH}$ for alcohols are acetonitrile solutions at 75°C using small broadening factors during data processing. Instrument time constraints suggest 0.5 M solutions for natural abundance studies; however, enrichment of the alcohol will be necessary to determine $^1J_{OH}$ at concentrations for which self-association is minimal.

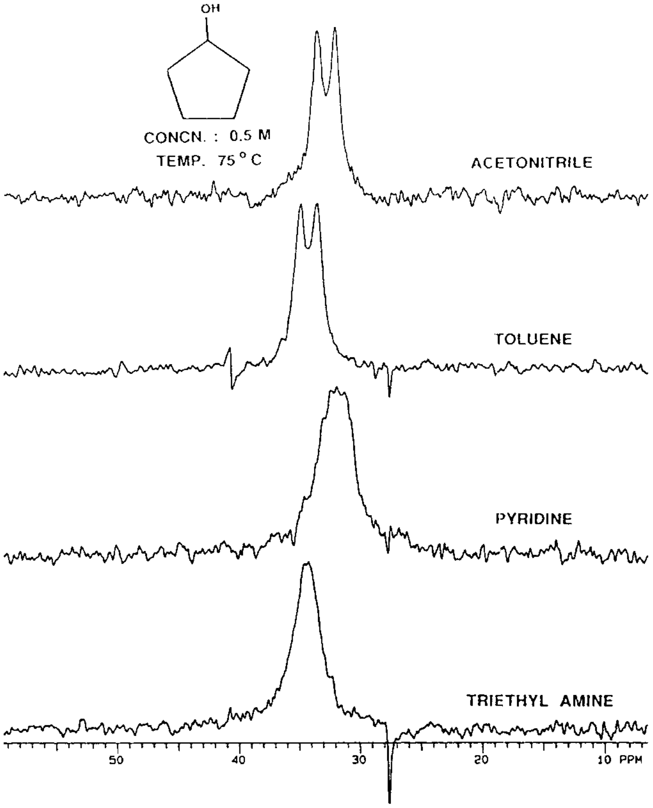


FIGURE 3 Effect of solvent, acetonitrile, toluene, pyridine, and triethylamine on proton–oxygen coupling of cyclopentanol (**2**) in 0.5 molar solutions at 75°C. Spectral conditions were identical to those for Figure 2 except that the number of scans was 64,000 (6.3 h) for acetonitrile, 122,000 (12.0 h) for toluene, 109,000 (10.7 h) for pyridine, and 113,000 (11.1 h) for triethylamine.

## *EXPERIMENTAL*

The alcohols **1–4** (Aldrich) were dried over anhydrous potassium carbonate, filtered, and distilled prior to the preparation of NMR samples. Acetonitrile, toluene, and pyridine were anhydrous gold label solvents under nitrogen (Aldrich). Diethylamine and triethylamine were dried over potassium hydroxide and distilled prior to use. Proton coupled and broad band decoupled $^{17}$O NMR spectra of 3-pentanol (**1**), cyclopentanol (**2**), cyclohexanol (**3**), and cycloheptanol (**4**) were obtained on 0.5 M solutions in acetonitrile at 75°C on a JEOL GX-270 NMR spectrometer in a 10-mm broad band probe operating at 36.5 MHz; 25,000 Hz spectral width, 2K data points, 90° pulse angle (28 $\mu$s pulse width), 250

**TABLE 2** Solvent Effects on ${}^1J_{OH}$ for Cyclopentanl (2) at 0.5M and 45° and 75°C[a]

| *Solvent* | *Temperature, °C* | $\epsilon^b$ | $\eta^c$ | ${}^1J_{OH}$ *(Hz)*[i] | $\upsilon_{1/2}$ *(Hz)*[j] |
|---|---|---|---|---|---|
| $(CH_3CH_2)_2NH$ | 45 | 3.60 | 0.367[d] | — | 158 |
| $CH_3CN$ | 45 | 35.8 | 0.345[d] | 72.9 | 164 |
| toluene | 75 | 2.38 | 0.526[e] | 72.7 | 150 |
| $CH_3CN$ | 75 | 35.8 | 0.345[d] | 78.8 | 141 |
| pyridine | 75 | 12.3 | 0.974[f] | — | 195 |
| $(CH_3CH_2)_3N$ | 75 | 2.42[g] | 0.394[g,h] | — | 153 |

[a] Values are based upon 64,000 scans $CH_3CN$ and 125,000, 122,000, 109,000, and 113,000 scans for diethylamine, tolune, pyridine, and triethylamine, respectively.

[b] Dielectric constants at 25°C taken from CRC Handbook of Chemistry and Physics, 67th Ed., 1986.

[c] Viscosity values taken from CRC Handbook of Chemistry and Physics, 67th Ed., 1986.

[d] $\eta$ values at 25°C.

[e] $\eta$ value at 30°C.

[f] $\eta$ value at 20°C.

[g] Taken from Lange's Handbook of Chemistry, 12th edition, 1979.

[h] $\eta$ value at 15°C.

[i] Directly observed proton–oxygen coupling in hertz.

[j] Band-width at half-height in hertz.

μs acquisition delay, 41 ms acquisition time, and ~$10^5$ scans. The FIDs were zero-filled to 8 K data points before multiplication by an exponential window with a line broadening factor of 10 Hz and Fourier transformation. The data point resolution is estimated to be 6.1 Hz. The spectra are referenced to external deionized water (0 ppm) at 75°C. Proton-coupled $^{17}O$ NMR spectra of **2** (concentration, temperature, and solvent effects) were obtained on a Varian VXR-400 NMR spectrometer in a 10-mm broad band probe operating at 54.2 MHz with 3382 Hz spectra width, 2K data points, 90° pulse angle (30 μs pulse width), 50 μs acquisition delay, and 303 ms acquisition time. The FIDs were zero-filled to 4 K data points before multiplication by an exponential window with a line broadening factor of 10 Hz and Fourier transformation. The data point resolution is estimated to be 1.8 Hz. The spectra are referenced to external deionized water (0 ppm) at the appropriate temperatures (75°C and 45°C). The error in the coupling constant is estimated to be ±2 Hz.

## *ACKNOWLEDGMENTS*

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the NSF Instrumentation Program (CHEM-8409599).

## *REFERENCES*

[1] (a) D. W. Boykin (ed): *$^{17}O$ NMR Spectroscopy in Organic Chemistry*; CRC Press, Boca Raton, FL, 1991; (b) D. W. Boykin, A. L. Baumstark, *Tetrahedron, 45,* 1989, 3613. (c) W. G. Klemperer: *Application of $^{17}O$ NMR Spectroscopy to Structural Problems*, in J. B. Lambert, F. G. Riddell (eds): *The Multinuclear Approach to NMR Spectroscopy*, Reidel, Dordrecht, Holland, pp. 245–260 (1983); (d) J.-P. Kintzinger: *Oxygen $^{-17}NMR$*, in P. Laszlo (ed): *Newly Accessible Nuclei*, Academic Press, New York, Vol. 2, pp. 79—104 (1983); (e) J.-P. Kintzinger: *Oxygen MNR. Characteristic Parameters and Applications*, in P. Diehl, E. Fluck, R. Kossfeld (eds): *NMR-17, Oxygen-17 and Silicon-29*, Springer-Verlag, New York, pp. 1–64 (1981).

[2] A. L. Baumstark, D. W. Boykin: $^{17}O$ NMR Spectroscopy: Applications to Structural Problems in Organic Chemistry, in A. L. Baumstark (ed): *Advances in Oxygenated Processes*, JAI Press, Greenwich, Vol. III, pp. 141–176 (1991).

[3] (a) E. L. Eliel, K.-T. Liu, S. Chandrasekaran, *Org. Magn. Reson., 21,* 1983, 179; (b) E. L. Eliel, S. Chandrasekaran, L. E. Carpenter, III, J. G. Verkade, *J. Am. Chem. Soc., 108,* 1986, 6651; (c) M. Manoharan, E. L. Eliel, *Magn. Reson. Chem., 23,* 1985, 225; (d) E. L. Eliel, K. M. Pietrusiewicz, L. M. Jewell, *Tetrahedron Lett.,* 1979, 3649; (e) B. Gardillo, E. L. Eliel, *J. Am. Chem. Soc., 113,* 1991, 2172.

[4] H. A. Christ, P. Diehl, H. R. Schneider, H. Dahn, *Helv. Chim. Acta, 44,* 1961, 865.

[5] S. Chandrasekaran: $^{17}O$ NMR Spectroscopy of Single Bonded Oxygen: Alcohols, Ethers and Their Derivatives, in D. W. Boykin (ed): *$^{17}O$ NMR Spectroscopy in Organic Chemistry,* CRC Press, Boca Raton, FL, pp. 141–203 (1991).

[6] D. W. Boykin, A. L. Baumstark, M. Beeson, *J. Org. Chem., 56,* 1991, 1969.

[7] (a) J. Reuben, A. Tzalmona, D. Samuel, *Proc. Chem. Soc.* 1962, 353; (b) S. W. Rabideau, H. G. Hecht, *J. Chem. Phys., 47,* 1967, 544; (c) H. G. Hertz, R. Klute, *Z. Phys. Chem., 69,* 1970, 101; (d) G. D. Mateescu, G. M. Benedikt, *J. Am. Chem. Soc., 101,* 1979, 3959; (e) G. D. Mateescu, G. M. Yvars, T. Dular: Water, Ions and O-17 Magnetic Resonance Imaging, in P. Lauger, L. Packer, V. Vasilescu (eds): *Water and Ions in Biological Systems,* Birkhauser Verlag, Basel-Bos-

ton-Berlin, pp. 239–250 (1988).
[8] H. Versmold, C. Yoon, *Ber. Bunsenges, Phys. Chem., 76,* 1972, 1164.
[9] M. Gorodetsky, Z. Luz, Y. Mazur, *J. Am. Chem. Soc., 89,* 1967, 1183.
[10] C. Delseth, J. P. Kintzinger, T. T. Tam Nguyen, W. Niederberger, *Org. Magn. Reson., 11,* 1978, 38.
[11] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry,* 2nd Ed., VCH, Weinheim, 1988.
[12] P. E. Hansen, *Prog. NMR Spectroscopy, 14,* 1981, 175.
[13] S. Watanabe, I. Ando, *Bull. Chem. Soc. Jpn., 54,* 1981, 1241.
[14] L. Paolillo, E. D. Becker, *J. Magn. Reson., 2,* 1970, 168.