structures with a C_{2h} symmetry rather than localized electronic structures with different bending at phosphorus.

The electrochemical oxidation of different diphosphines is under investigation in order to get more information concerning the mechanism of stabilization of the corresponding cation radicals and their reactivity.

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High-Resolution NMR with a Surface Coil

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Topical nuclear magnetic resonance is a method by which chemical shift spectra are obtained from a spatially selected region inside an intact system. Surface coils have been widely used for attaining spatial selectivity, by taking advantage of the strongly varying rf intensity at different distances from the coil.[1-9] Frequency resolution in this type of spectroscopy and related volume-selective approaches[10,11] remains a serious problem, which is typically overcome by shimming the magnet for each NMR region being observed or moving the sample so that the observed region lies in a preset homogeneous spot of the magnet.[10]

In this paper we demonstrate the first application of SHARP NMR spectroscopy[12] to obtain high-resolution heteronuclear NMR spectra in an inhomogeneous field with a surface coil. This method employs the detection of single-quantum echoes with coherence transfer methods[13-16] or heteronuclear echoes[12] in double-quantum[16,17] evolution. It eliminates the need for shimming altogether, yielding very sharp lines close to the frequency of the heteronuclear spins. Figure 1 shows an illustrative SHARP spectrum of ethanol in an inhomogeneous field and compares it to the normal ^{13}C and ^{1}H spectra. The narrow lines and high sensitivity of SHARP greatly enhance the applicability of surface coil and volume selective NMR to nonhomogeneous samples.

The pulse sequence used here for the case of ^{13}C (S) and ^{1}H (I) is illustrated in Figure 2. The concept is the generation of signal as a function of an evolution time, t_1, which contains chemical shift information but has field inhomogeneity effects

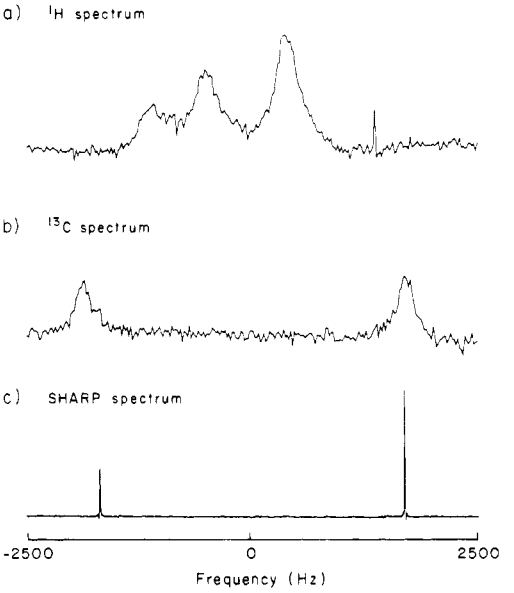

Figure 1. Surface coil spectra of a 2-mm bulb sample of ethanol, enriched to 25% in ^{13}C at each position, one ^{13}C per molecule. (a) ^{1}H spectrum (1 min); (b) ^{13}C spectrum with 10-ms proton presaturation and proton decoupling (2 h); (c) SHARP spectrum obtained by the method of Figure 2 and with the spectrometer phase inverted, to give $\delta = (\delta_C - \delta_H)/4$ (1 h). Spectra were taken on a 360-MHz spectrometer.

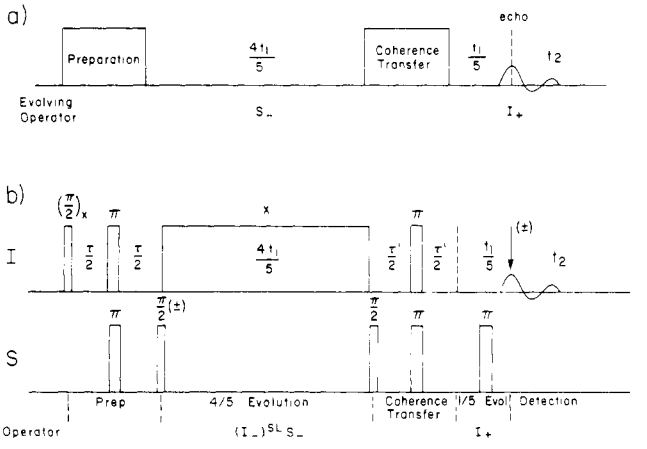

Figure 2. Pulse sequence used for SHARP spectra. (a) Schematic sequence showing a period of proton-decoupled S-spin evolution, followed by a proton evolution period $^1/_4$ as long. (b) Details of the coherence transfer steps between protons and S spins. Preparation times τ, τ' were chosen to be equal to $^1/_2J_{IS}$. A constant purging pulse of 8 ms was used before the evolution period to dephase unwanted nonsatellite magnetization. The symbols $\pi/2$ (±) and ↓ (±) indicate that two experiments differing in phase by 180° are subtracted on alternate shots to further suppress nonsatellite signal.

completely removed. This can be achieved by noting that $\gamma_H/\gamma_C = 3.997 \simeq 4$, so that proton nuclei will dephase (or rephase) about 4 times as rapidly as carbon nuclei in a given magnetic field. Thus, by allowing ^{13}C to dephase for $4t_1/5$ and ^{1}H to rephase for $t_1/5$, an echo is produced at the end of t_1. The sequence in Figure 2 has precisely this effect, with the added feature that magnetization is both initiated and detected in the proton spin system, hence maximizing sensitivity. Thus, there are two coherence transfer steps, one to prepare, from I_x, heteronuclear double-quantum coherence, I_xS_x, and the second to transfer coherence back to I_x for eventual detection. The data are collected point-by-point and Fourier transformed with respect to $4t_1/5$. The chemical shifts are given by

$$\delta = -\delta_C + \delta_H/4$$

Heteronuclear coupling is completely removed, while homonuclear coupling is scaled by $^1/_4$ and is not resolved in Figure 1. Thus,

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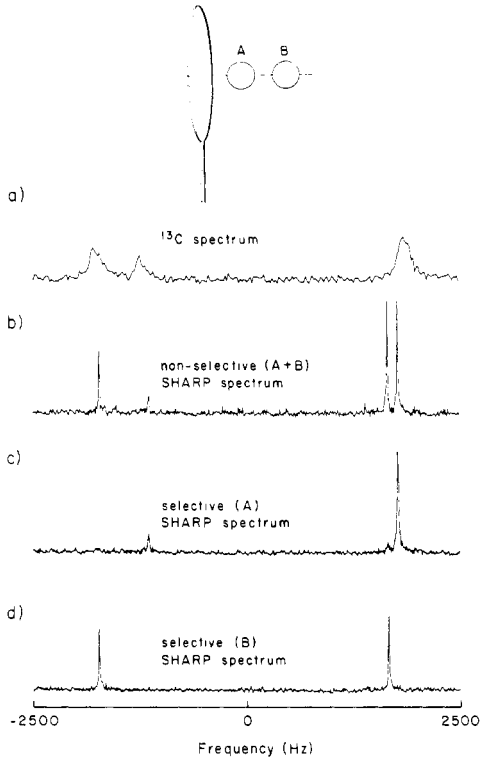

Figure 3. Surface coil selectivity experiment on two capillary tubes, A and B, placed on axis at 2 and 4 mm from the surface coil. The first contained 3-μL saturated solution of a mixture of 50% 2-^{13}C- and 50% 3-^{13}C-enriched alanine; the second contained 2 μL of ethanol enriched to 25% at C_1 and C_2 on different molecules. (a) ^{13}C spectrum, with 10-ms proton presaturation and proton decoupling. (b) SHARP spectrum, pulse times intermediate between A and B. (c) SHARP spectrum, pulse times set for A. (d) SHARP spectrum, pulse times set for B.

a single resonance is obtained for each ^{13}C position, and the signal to noise is that of satellite protons. The approach is applicable to all pairs of coupled nuclei, provided that the coherence transfer time, τ, and the relative lengths of the t_1 subintervals are adjusted in accordance with the J coupling and the ratio of the magnetogyric constants, respectively.

We further note that SHARP spectroscopy inherently exhibits some spatial selectivity. This was demonstrated on two capillary tubes, containing alanine and ethanol, placed at different distances from the coil. Figure 3a shows the ^{13}C spectrum after a single pulse. It is nonselective and poorly resolved; resonances from both tubes appear, but the methyl groups on alanine and ethanol are not separated. Figure 3b–d are SHARP spectra. The spectrum in Figure 3b is nonselective and was obtained by setting the pulses in Figure 2 for a point halfway between the two tubes. The spectra in Figure 3c,d were obtained by setting the pulses for the first and second tubes, respectively; distinction of the contents of the two tubes illustrates a spatial separation of high resolution.

The technique described here yields high-resolution spectra that are easy to interpret and that can be combined with methods of accurate spatial selection designed for heteronuclear systems.[6,7,11] It should therefore prove a useful addition to topical NMR. Other pulse sequences have been designed which can retain or remove either heteronuclear or homonuclear couplings or both,[12] and this provides additional information and resolution. Background water does not interfere, since it has no heteronuclear coupling. The technique could be used for natural abundance studies of isotopes such as ^{13}C and ^{15}N or for following the metabolic pathway of specifically labeled compounds such as lactic acid, glucose, or drugs.

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Structures and Raman Spectra of Two Crystalline Modifications of Dithiodiglycolic Acid

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Prompted by the observations of Lord and Yu[1]that the Raman spectra of lysozyme, ribonuclease, and α-chymotrypsin differed in the S–S stretching region near 500 cm^{-1}, there have been a number of attempts to establish how this frequency varies with the conformation proximate to the S–S bond in molecules containing CCSSCC fragments.[2] For almost a decade, however, an unresolved conflict over this question has persisted in the literature.

Sugeta, Go, and Miyazawa[3-5] proposed that bands having Raman shifts larger than the typical 505–510 cm^{-1} arise from disulfide conformations having one (525 cm^{-1}) or two (540 cm^{-1}) carbon atoms anti to distal sulfurs, i.e., one or two CCSS torsion angles of about 180°. Van Wart and Scheraga,[6-8] however, assigned these bands to conformations having either one (525 cm^{-1}) or two (540 cm^{-1}) quite small CCSS torsion angles, roughly in the range 20–50°.

Van Wart and Scheraga[6] rejected the Sugeta assignments because the spectrum they recorded for a solid sample of dithiodiglycolic acid, $HOOCCH_2SSCH_2COOH$, had a disulfide stretching frequency of 508 cm^{-1}, while an unpublished crystallographic study made by Frank[9] in Parthasarathy's laboratory gave a molecular structure having C_2 symmetry with CCSS torsion angles of 167°. This information, together with a survey of protein conformations that revealed significant numbers of CCSS torsion angles in the 20–40° range, then led Van Wart and Scheraga to propose their alternative correlation scheme.

We recently began a series of studies in which we have obtained both the Raman spectra and the structures of a number of mesocyclic disulfides. The results, which will be published in due course, have all supported the Sugeta, Go, and Miyazawa rather than the Van Wart and Scheraga correlations. For example, in the centrosymmetric molecule 1,2,6,7-tetrathiacyclodecane, the two CCSS torsion angles are 37° and −62° [10] and the disulfide stretching frequency is 502 cm^{-1} rather than the 525 cm^{-1} that the Van Wart and Scheraga correlations would have predicted. Findings such as this have caused us to question the experimental evidence on which the Van Wart and Scheraga correlations were based.

We now report that dithiogdiglycolic acid can be obtained in two different crystalline modifications, depending upon the method of crystallization. Form I, which is obtained uniquely only when an aqueous solution of the compound is allowed to evaporate through a small orfice for a matter of weeks, crystallizes in the

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