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Supplementary Material Available: Difference NOE results on $\mathbf{2^+}$; ^{1}H NMR spectra of $\mathbf{2a^+}$, $\mathbf{2b^+}$, $\mathbf{3}_n$·GaBr$_3$, $\mathbf{4}_n{}^+$; and ^{13}C NMR spectra of $\mathbf{3}_n$·GaBr$_3$ (2 pages). Ordering information is given on any current masthead page.

Two-Dimensional Pulse Techniques for Determination of Radio-Frequency Field Strengths and Proton Multiplicities in NMR Spectroscopy

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Heteronuclear multipulse methods range among the most important pulse techniques in modern NMR spectroscopy. These include, for example, two-dimensional (2D) pulse sequences for heteronuclear chemical shift correlation[1-6] or relayed correlation[7-13] spectroscopy and one-dimensional (1D) polarization transfer and editing techniques.[14-18] Common to all these techniques is that radio-frequency (rf) pulses are applied to two nuclear isotopes. Thus, such experiments must be preceded by determinations of the decoupler (usually ^{1}H) and observe rf field strengths.

Observe fields are traditionally calibrated by determining the 180° or 360° pulse widths. Determination of the decoupler rf field strength can be done by various indirect methods[19] which search for zero-crossings of the observed S spin (e.g., ^{13}C or ^{15}N) signal while incrementing the length of decoupler pulses. A very high accuracy can be achieved,[19] but the key experiments (the zero-crossing of S spin signals) are unfortunately associated with low sensitivity.

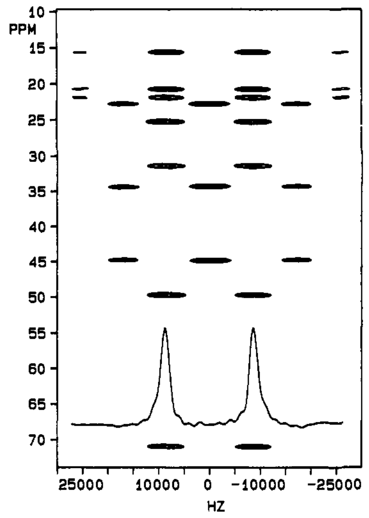

Figure 1. Contour plot (absolute value representation) of a ^{13}C 2D SEMUT spectrum of menthol recorded on a Varian XL-300 NMR spectrometer. A section at 70.8 ppm of a phase-sensitive 2D transformation (zero-filled to 32K points along t_1) is shown as an insert. The decoupler rf field strength determined from such sections of phase-sensitive spectra yields $t_{90}(^1\mathrm{H}) = 29.1 \pm 0.2$ μs for all ten ^{13}C multiplets. This value compares favorably with $t_{90}(^1\mathrm{H}) = 28.8 \pm 0.3$ μs obtained by the more time-consuming 1D SEMUT method.[19] Instrumental time is 3.2 min.

In this paper we introduce two new 2D pulse techniques for fast and accurate calibration of the decoupler rf field strength. In addition the second method can be extended to include calibration of the observe channel in a way which, compared to the 2D observe channel calibration technique suggested earlier,[20] does not exhibit the disturbing modulation effects observed when relaxation between the individual experiments is incomplete.[21]

The first technique, useful in ^{13}C NMR, is a 2D version of SEMUT:[17,18]

$$\begin{array}{lllllllll} I\ (^1\mathrm{H}): & \text{decouple} & | & -\tau- & \theta & -\tau'- & \text{decouple} & & \\ S\ (^{13}\mathrm{C}): & & 90^\circ & -\tau- & 180^\circ & -\tau- & \text{acquire} & & \end{array} \qquad (1)$$

where the $\theta°$ pulse incremented to constitute the evolution period t_1 of the 2D experiment. τ and τ' should be adjusted to $(2\,^1J_{\mathrm{CH}})^{-1}$; they can be chosen unequal ($\tau' < \tau$) to suppress J cross-talk.[18,19] The resulting 2D spectra have the attractive feature that they contain multiplicity information. C, CH, CH$_2$, and CH$_3$ resonances appear as singlets, 1:1 doublets, 1:2:1 triplets, and 1:3:3:1 quartets, respectively. The line separations in these multiplets are determined by twice the decoupler rf field strength. For a separation of ν Hz, the 90° decoupler pulse time is

$$t_{90}(^1\mathrm{H}) = (2\nu)^{-1} \qquad (2)$$

Figure 1 shows a contour plot of a 2D SEMUT spectrum of menthol along with the section through the high-frequency CH carbon resonance.

To avoid foldings, the ω_1 spectral width must be larger than 6 times the decoupler rf field strength, $\gamma_I B_2/2\pi$ (Hz); for our spectrometer we use increments $\Delta t_1 = 16.7$ μs, corresponding to about 60 kHz. After the standard t_2 Fourier transformation, the imaginary (dispersive) part is discarded and the t_1 data apodized by using a Lorentzian to Gaussian transformation followed by zero-filling to typically 1024 points. For the sake of generality, a complex Fourier transformation is then applied along t_1 where the real part represents the 2D SEMUT spectrum; for other 2D calibration techniques (vide infra) the 2D spectrum is found as the imaginary part. The number N of t_1 increments determines the accuracy of the calibration. We typically employ $N = 32$ (i.e., $t_1^{\max} = 534$ μs, which yields an accuracy of about 1% for the 90°

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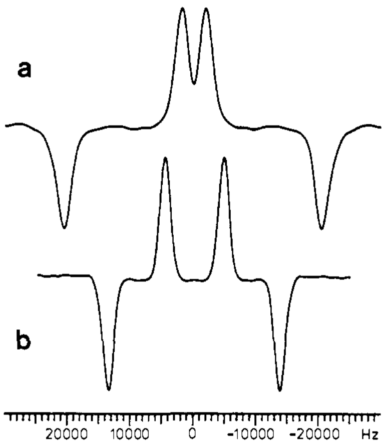

Figure 2. Sections through phase-sensitive ^{15}N 2D SINEPT spectra of pyridine obtained with simultaneous θ_1, θ_2 incrementation and employing $N = 32$ zero-filled to 32K. (a) $\kappa = 1.0$, $\Delta t_1 = 16.7$ μs; (b) $\kappa = 0.4$, $\Delta t_1 = 20.0$ μs.

pulse width. The total recording time for 2D SEMUT with concentrated samples and $N = 32$ is a few minutes.

Pulse sequence 1 should not be employed if polarization transfer enhancement is essential for sensitivity reasons. In addition, the sequence is unsuitable for calibration via long-range couplings because complicated multiplet patterns may occur. ^{15}N NMR of pyridine is an example where polarization transfer enhancement and calibration via long-range couplings are required. For this purpose we introduce the 2D version of INEPT[14,15] or SINEPT:[19]

$$\begin{aligned} I(^{1}\text{H}):&\quad \theta_{2x} - \frac{\tau}{2} - (180^\circ) - \frac{\tau}{2} - \beta_{y} - \tau' - \text{decouple}\\ S(^{15}\text{N},{}^{13}\text{C}):&\quad -\frac{\tau}{2} - (180^\circ) - \frac{\tau}{2} - \theta_{1} - \tau' - (180^\circ) - \tau' - \text{acquire} \end{aligned} \tag{3}$$

The refocusing pulses in parentheses should be employed if approximate knowledge about the rf field strengths is available.[22] β is adjusted to the estimated value for a 90° rotation (not critical). The delays τ and τ' are selected as for INEPT[14,15] when one-bond couplings are exploited. Otherwise, $\tau = \tau' = (4J)^{-1}$, where J is the largest relevant homo- or heteronuclear long-range coupling constant. Incrementation of one of the θ pulses while keeping the other constant ($\sim$90°) leads to an antiphase doublet with splitting determined by the corresponding rf field strength.

Here we demonstrate the experiment with simultaneous incrementation of θ_1 and θ_2 which results in a doublet of doublet four-line pattern in the ω_1 dimension of the 2D spectrum. The apparent "J splittings" reflect the rf field strengths of the applied two fields. To avoid overlap of the four components, one of the doublet splittings may be scaled, e.g., by incrementing θ_1 according to $\theta_1 = \kappa\theta_2$. The relevant section through the 2D ^{15}N spectrum of pyridine by using $\kappa = 1.0$ and 0.4 is shown in Figure 2. This experiment yields $t_{90}(^{1}\text{H}) = 26.4 \pm 0.2$ μs and $t_{90}(^{15}\text{N}) = 22.1 \pm 0.2$ μs which compare favorably with 1D[19] results: $t_{90}(^{1}\text{H}) = 26.2 \pm 0.3$ μs and $t_{90}(^{15}\text{N}) = 22.1 \pm 0.3$ μs.

We should note that instrumental imperfections can affect the results of the 2D calibration techniques. It is therefore recommended, once and for all, to compare the 2D result with the result of a detailed equivalent 1D calibration.[19] This yields a scaling factor to put on future rf field strengths determined by the 2D techniques.[23] As a consequence, instrumental imperfections are unimportant for routine applications of the presented techniques.[24]

In conclusion, we have in this paper introduced simple 2D pulse techniques for calibration of rf field strengths with significantly higher sensitivity and shorter performance time than 1D methods yielding equivalent information. The time saving can easily reach an order of magnitude for samples of low inherent sensitivity. The multiplicity information in ^{13}C 2D SEMUT spectra makes the performance of separate editing experiments[16-18] superfluous, which results in additional time saving. Furthermore, the ideas presented in this paper can be extended to the more sensitive heteronuclear "inverse" experiments with proton detection.

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Registry No. Menthol, 89-78-1; pyridine, 110-86-1.

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[22] Inaccurate 180° pulses do not affect the calibration. To improve sensitivity the S spin 180° pulses can be replaced by composite pulses.

[23] On modern spectrometers (e.g., the Varian XL-300 applied in this research) such scaling factors are close to 1.

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Thiocarbonyl *S*-Sulfides, a New Class of 1,3-Dipoles[†]

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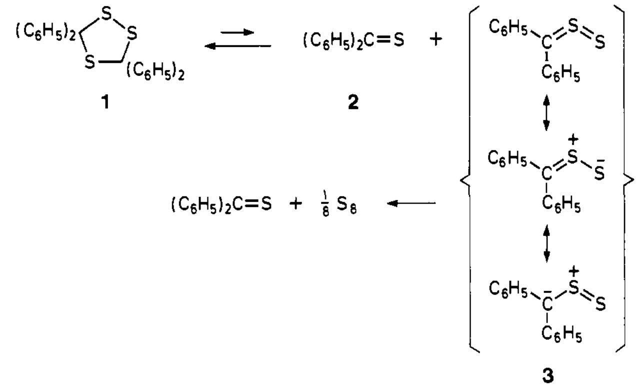
The rich literature on "thiosulfines", $R_2C{=}S{=}S$,[1] oddly contrasts the scant experimental observations of their transient occurrence. In our opinion, this report offers the first unequivocal evidence for their existence.

According to Staudinger,[2] 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) decomposes above the mp 124 °C to give thiobenzophenone (**2**) and sulfur. $\Delta H^\circ_f = 92.0$ kcal mol^{-1} for singlet sulfur atom, $S(^{1}D_2)$,[3] forbids a concerted fragmentation into two thiobenzophenones and an S atom. Instead, a 1,3-dipolar cycloreversion may furnish thiobenzophenone *S*-sulfide (**3**) and **2**. In the absence of reaction partners, the molecules of **3** may undergo mutual transfer of the terminal sulfur; long sulfur chains are built up which may roll around and eliminate cyclooctasulfur. *We succeeded in intercepting both dissociation products by cycloaddition.*



Warm solutions of the colorless **1** turn deep blue indicating **2** as dissociation product. After reacting **1** with 4 equiv of dimethyl acetylenedicarboxylate 4 h at 60 °C, ^{1}H NMR analysis indicated 68% of **4** (s, H1, δ 5.14) and 83% of **7** (s, OCH_3, 3.41). Chromatography on silica gel separated the colorless 1*H*-2-benzothiopyran derivative **4**, mp 91–92 °C, the Diels–Alder adduct of **2**,[4] and the light-yellow dimethyl 3,3-diphenyl-3*H*-1,2-dithiole-

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[†] Dedicated to Professor Leopold Horner on the occasion of his 75th birthday.

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