between the tautomers of methyl-9-hydroxyphenalen-1-one was found to be 154 cm⁻¹, in good agreement with the results from laser-excited fluorescence and fluorescence-excitation spectroscopy.[13,15] The time evolution of the probability density of the initially localized state function demonstrates that, for the symmetric case, the proton or deuteron reaches the other well at the frequencies of their respective gerade–ungerade splittings. For the asymmetric case, three-tenths of a proton, but less than three-hundredths of a deuteron, reaches the other well with each oscillation of frequency equal to the energy difference between the two lowest eigenstates, 5.03×10^{13} and 4.52×10^{13} s, respectively.

Although the introduction of the methyl substituent destroys the symmetry of the double-minimum potential, the rate is fast because the barrier, the interminimal distance, and the difference in energy between the two tautomers are small for this nearly symmetric potential energy profile. This explains the NMR spectra interpreted as showing that methylnaphthazarin does not have proton exchange, but methyl-9-hydroxyphenalen-1-one does.

Tunneling in near symmetric cases deserves special attention. In symmetric cases, one can calculate tunneling from the energy difference between the gerade–ungerade pair. This is so because

the proton will spend equal time in each well, and tunnelling will depend on the frequency with which the proton oscillates between the wells. When the profile is asymmetric, the fraction of the proton that leaks to the other well decreases as the energy difference between the minima increases. It has been found[26] that this fraction depends on the ratio of the energy difference between the minima and the tunneling splitting in the corresponding symmetric case. In the present study the fraction of the proton that leaks to the other well is reduced from unity in the symmetric case to one-third in this nearly symmetric case, while the frequency with which the maximum leakage occurs increases by 60%.

Two-Dimensional Heteronuclear NOE (HOESY) Experiments: Investigation of Dipolar Interactions between Heteronuclei and Nearby Protons

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Abstract: Heteronuclear 2-D NOE (HOESY) experiments were applied to the study of dipolar interactions between heteronuclei and nearby protons. The dipolar interactions between quaternary carbons and protons were studied in two cases: camphor and fluoranthene. Solvent–solute dipolar interactions between phosphorus and protons were investigated for adenosine triphosphate in water. In D_2O, NOEs were observed between α- and β-phosphates and C5′ protons; the α-phsophorus also shows a weak cross peak with H-8′, consistent with the expected anti conformation for ATP in solution.

The nuclear Overhauser effect arises from changes in spin populations due to dipolar relaxation in the presence of double irradiation. For example, applying wide-band ¹H decoupling results in observed ¹³C signals which are enhanced by a factor (NOEF) of up to 1.98, due to the disturbance of the Boltzman distribution of the ¹³C and ¹H dipolar-coupled spins.[1] NOE not only enhances ¹³C sensitivity but also provides valuable information for molecular dynamics[2] and structure elucidation. Since NOE is related to $(r_{AB})^{-6}$, the distance between two dipolar interacting spins A and B can in principle be calculated.

Ernst and co-workers[3-5] developed a homonuclear 2-D experiment to observe NOE phenomena. The technique is able to simultaneously resolve many individual spin NOE effects, even in complex systems.[6]

In preliminary reports our group[7] and Rinaldi[8] presented a heteronuclear 2-D NOE experiment for the investigation of heteronuclear dipolar interactions. The pulse sequence for the heteronuclear 2-D NOE experiment is shown in Figure 1A, and the vector model that describes the *I* spin magnetization is shown Figure 1B. For the simple system of 2 spins, *I* (¹H in this case) and *S* (observed nucleus: ¹³C or ³¹P), the components of *I* magnetization $M(\alpha)$ and $M(\beta)$ corresponding to the two *S* spin states can be represented by the vectors α and β. After an initial 90° (*I*) pulse (Figure 1Ba), the two vectors precess for a period of time, $t_1/2$, and accumulate a relative phase angle of $\pi J t_1$ (Figure 1Bb). Following a 180° pulse on *S*, the two spin-state labels interchange (Figure 1Bc), and further precess for another ($t_1/2$) period, causing the two vectors to become refocused (Figure 1Bd). So far, the two *I* magnetization vectors remain parallel at the end of the evolution period, and no magnetization transfer has occurred; this means that scalar interactions between *I* and *S* have

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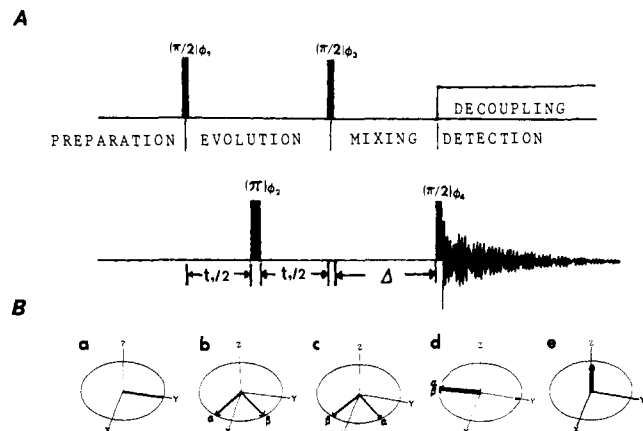(8) Rinaldi, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 5167.

A

B

Figure 1. (A) The pulse sequence of the heteronuclear 2-D NOE (HOESY) experiment. (B) A vector model describes I (^{1}H) spin magnetization. The usual equilibration delay establishes the equilibrium magnetization of I and S spins. A 90° (I) pulse flips the I spins into the xy plane where their components, α and β, precess during t_1 according to the resonance frequencies of the chemically distinct nuclei. If there is coupling between the I and S spins, this is removed by a 180° (S) pulse at $t_1/^2$. At the end of the t_1 period, the I spins are frequency labeled.

been removed, and only cross relaxation through dipole–dipole interaction gives rise to signals originating from nuclei correlating with each other. The second 90° proton pulse then creates longitudinal I spin magnetization (Figure 1Be) with amplitude proportional to cos ($2\pi\delta_H t_1$), where δ_H is the proton's chemical shift, followed by a mixing time, Δ. During the mixing period, cross relaxation leads to exchange of magnetization between I and S spins through dipolar interactions. The interval Δ is kept fixed and the signal recorded right after the 90° observe pulse as a function of t_2. As in other 2-D spectroscopy methods, the experiment is repeated for a set of equally incremented t_1 values. A two-dimensional Fourier transformation of the data matrix $S(t_1,t_2)$ then produces the desired frequency domain spectrum.[9]

Quaternary carbons in most medium- to large-sized organic molecules are relatively inefficiently relaxed, yet their NOEs will still be sizable or even full (at least at low magnetic fields), reflecting dipolar relaxation due to protons on neighboring carbons. For protonated carbons, because of strong coupling between the carbon and directly attached proton(s), it is easy to assign the spectra with either 1-D techniques[10–12] or 2-D techniques (heteronuclear shift correlated spectroscopy). As for quaternary carbons, which lack strong coupling with protons, fewer spectral assignment methods can be applied. Therefore, it is of interest to use the HOESY experiment, which simultaneously evaluates heteronuclear NOE contributions from all of the protons and gives the connectivity between (quaternary) carbon and proton spectra.

Experimental Section

Camphor and fluoranthene were purchased from Aldrich and solutions 2 M in CDCl$_3$ and Me$_2$SO-d_6 were prepared, respectively. Data were acquired at 90.56 MHz on a Bruker WM-360 WB spectrometer (equipped with an Aspect-2000A computer) in 20-mm sample tubes. The heteronuclear 2-D NOE experiments were carried out with the pulse sequence described above. The pulse width for ^{1}H was calibrated with the method described by Bax[13] to be 60 μs. In order to separate the positive and negative modulation frequencies (hence quadrature detection in F_1), suppress the unwanted axial peaks,[14] and cancel out the image along $F_1 = 0$, a 16-step phase cycling was applied (Table I).

Table I. Phase Cycling Used in the HOESY Experiment

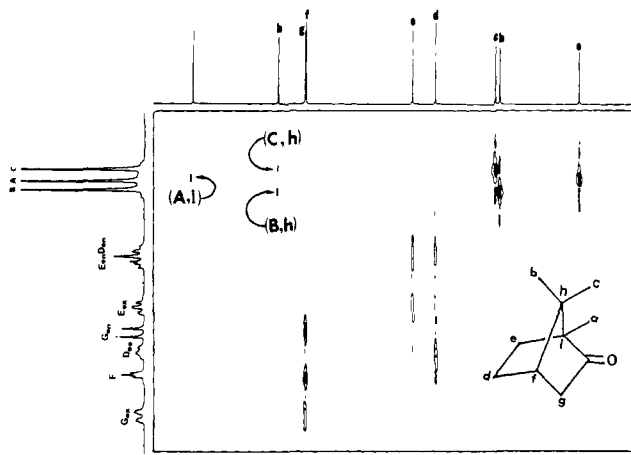| expt no.	ϕ_1	ϕ_2	ϕ_3	ϕ_4	receiver
1	x	x	x	x	x
2	x	x	y	y	$-x$
3	x	x	$-x$	nx	x
4	x	x	$-y$	$-y$	$-x$
5	y	x	y	x	x
6	y	x	$-x$	y	$-x$
7	y	x	$-y$	$-x$	x
8	y	x	x	$-y$	$-x$
9	$-x$	x	$-x$	x	x
10	$-x$	x	$-y$	y	$-x$
11	$-x$	x	x	$-x$	x
12	$-x$	x	y	$-y$	$-x$
13	$-y$	x	$-y$	x	x
14	$-y$	x	x	y	$-x$
15	$-y$	x	y	$-x$	x
16	$-y$	x	$-x$	$-y$	$-x$

Figure 2. Contour plot of the HOESY spectrum for camphor. The mixing time Δ was 2 s. The spectral width in the F_2 dimension (^{13}C) was 5400 Hz. The increment time ($t_1/^2$) was set to be 684 μs which made the spectral width in F_1 dimension = 730 Hz. For each value of t_1, 64 FIDs (each FID consisting of 1K data points) were accumulated. Zero filling in the F_1 dimension was executed once to make it contain 128 points. Three cross peaks arising from dipolar interactions between quaternary carbons and nearby protons are marked by parentheses.

Since quad detection was operating in F_1, the proton transmitter frequencies were set to the center of the ^{1}H chemical shift regions of interest, minimizing the required acquisition frequency and required data storage, as well as optimizing decoupling.[15]

For the efficiency of the experiment time with respect to sensitivity to be maximized, the repetition delay, D_1, was set to be 1.3 times that of the mean proton T_1.[16] Because the signals of primary interest originate from dipolar interactions between quaternary carbons and neighboring protons (of methyl groups), the mixing time was set equal to that of the methyl proton T_1.[3] A shifted sine bell[17] digital filtering function was applied in both dimensions to improve spectral resolution.

Results and Discussion

1. HOESY Experiment on Camphor. Figure 2 shows the contour plot of a heteronuclear 2-D NOE experiment on camphor. All of the cross peaks in the 2-D display originate from heteronuclear dipolar interactions. For protonated carbons, dipolar interactions are much stronger (from their inverse proportionality to r^6) than for quaternary carbons. At this high magnetic field,

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(13) Bax, A. *J. Magn. Reson.* **1983**, *52*, 76.
(14) Bax, A.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 501.

(15) One reviewer suggested performing a proton 180° pulse in the middle of the mixing time (Bolton, P.H. *J. Magn. Reson.*, **1982**, *48*, 336) in order to improve S:N by the square root of two.
(16) Bax, A. "Two Dimensional Nuclear Magnetic Resonance in Liquids"; Reidel: Boston, 1982.
(17) Wanger, G.; Wüthrich, K.; Tschesche, H. *Eur. J. Biochem.* **1978**, *86*, 67.

Table II

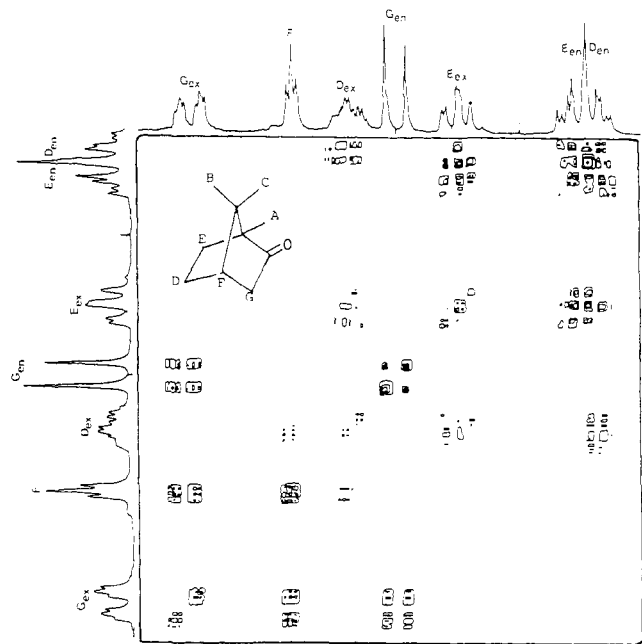|	carbon								
	a	b	c	d	e	f	g	h	i
T_1	4.4	4.6	4.0	3.2	3.6	6.3	4.1	17.1	17.2
NOEF	2.0	2.0	2.0	2.0	1.9	1.9	1.8	1.1	0.9

Figure 3. The COSY spectrum of camphor. The three isolated methyl protons at high field are not shown. Spectral acquisition parameters were the following: 730 Hz in both dimensions, the mixing pulse was set to be 60° tip angle (4.5 μs, 128 spectra, 16 scans each) and were accumulated and zero filling was executed along the F_1 dimension to make both dimensions consist of 512 data points, a sine bell filtering function in both dimensions was applied, and symmetrization was executed after the 2-D transformation.

chemical shift anisotropy becomes an important relaxation mechanism for quaternary sp² (C=O) carbons. Also, spin rotation is an important relaxation mechanism for sp² or even sp³ quaternary carbons in small molecules like camphor. This latter effect reduces the NOEs for quaternary carbons h and i in camphor. Futhermore, incomplete relaxation of quaternary carbons (a pulse repetition time that is short compared with $5T_1$ for these carbons, i.e., ca. 85 s!) makes the quaternary carbon signals in camphor hard to detect in the HOESY experiment. Despite their smaller amplitude, when the contour plot levels are set appropriately, signals from NOE's to the quaternary carbons are clearly observed (Figure 2). The quaternary carbon h, for example, shows dipolar interactions with protons in the B and C methyl groups.

¹³C spin–lattice relaxation time (T_1) and NOEF (nuclear Overhauser enhancement factor, NOE − 1) data for 2 M camphor in CDCl₃ are shown in Table II.

From Figure 2, we can assign the ¹H spectrum from a known ¹³C spectrum (or vice versa). The full assignment for the 1-D spectrum (in the F_1 dimension) of camphor is shown in Figure 2, which is quite different from the assignment done by Grant et al. from the deuterium spectrum of camphor.[18] The variance of the two assignments is shown below:

ref 18	D_{exo}	D_{endo}	F	D_{exo}
this study	D_{endo}	D_{exo}	D_{exo}	F

For our assignment of the ¹H camphor spectrum to be confirmed, a COSY experiment was performed with a $90°$–t_1–α acquisition pulse sequence.[19] Four-step phase cycling was used

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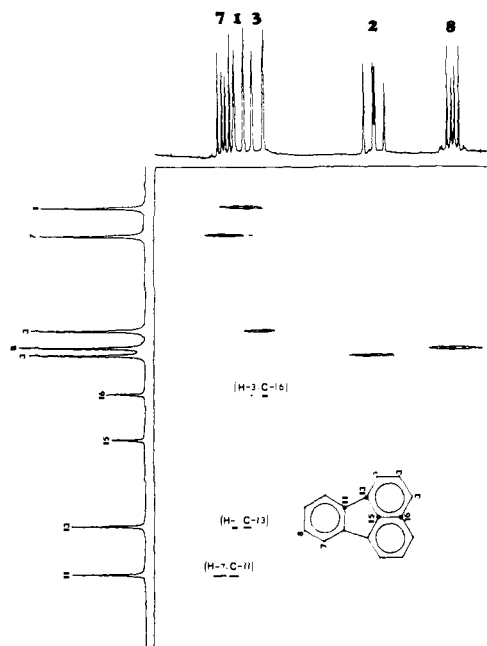(19) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981,** *44,* 542.

Figure 4. The contour plot of a HOESY spectrum of fluoranthene. Spectral acquisition parameters are the following: 2 s for mixing time, 2315 Hz in F_2 (¹³C) dimension, and 64 spectra (128 scans each) were accumulated with a t_1 increment to make 240 Hz in the F_1 dimension. The dipolar interactions between three quaternary carbons and nearby protons clearly show up as cross peaks labeled in parentheses.

to have quad detection in F_1 and cancel the axial peaks.[16] To search for cross peaks near the principal diagonal, the mixing pulse (α) was chosen to be 60° to reduce the relative intensity of parallel transitions while still obtaining good sensitivity. Figure 3 shows the COSY experiment of camphor. The conventional spectrum appears along the principal diagonal ($F_1 = F_2$). Any two resonances at frequencies f_A and f_B connected by a scalar (spin–spin) coupling have cross peaks at (f_A, f_B) and (f_B, f_A). For example, along F_1, the proton F has two sets of cross peaks indicating that it couples to protons G_{ex} and D_{ex}, respectively, as shown in Figure 3. If the assignment in ref 18 was correct, this resonance would be assigned as D_{ex}, but there is no geminal coupling (with D_{en}) or vicinal coupling (with E_{ex} and E_{en}) indicated by cross peaks in the COSY spectrum (Figure 3). Also the line assigned as E_{ex} in ref 18 (our assignment D_{endo}) would need to show a cross peak with the peak assigned to D_{ex} (our F) which is absent. No evidence of cross peaks between lines assigned to D_{endo} and D_{exo}[18] are present in the COSY spectrum. Going through the connectivity for each proton spin in Figure 3, the scalar coupling connectivities of this COSY experiment are consistent with our assignments and dipolar connectivities in the heteronuclear 2-D NOE experiment.

2. HOESY Experiment on Fluoranthene. Jones et al.[11] used broad-band decoupling in a 1-D measurement of overall ¹³C{¹H} NOE to assign the four quaternary carbon resonances of fluoranthene. However, this technique requires (1) the use of geometry arguments (difficult in a complicated system) to estimate the NOE for each quaternary carbon and (2) the assumption that relative contributions of all relaxation mechanisms other than dipolar, ξ, are the same for all quaternary carbons (this is not easily sustained, as ξ may represent several different relaxation processes). Moreover, this technique will fail when different quaternary carbons have the same, or very close, NOE. In Jones' low-field (15.1 MHz for carbon) experiment, two quaternary carbons had the same NOE (C-11 C-11 and C-13) in fluoranthene. But at high field (90.56 MHz) as demonstrated in Table III, there are three quaternary carbons (C-11, C-13, and C-16) having the same or very close *low* NOE values (CSA dominates at high field for quaternary carbons), which made assignment more difficult from measurement of overall ¹³C{¹H} NOE. The HOESY technique is able to avoid these problems and also provides unique connectivities for quaternary carbons and nearest protons. Figure

Table III. 90.56-MHz ^{13}C Relaxation Data for 2 M Fluoranthene in $CDCl_3$

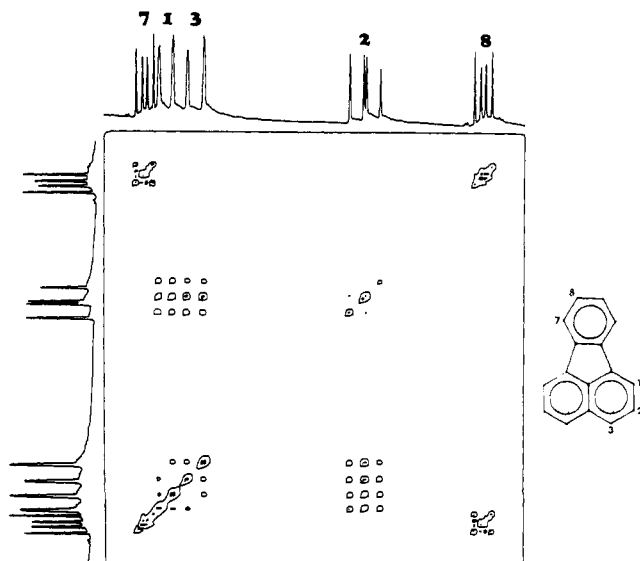|	carbon								
	C-1	C-2	C-3	C-7	C-8	C-11	C-13	C-15	C-16
T_1	2.4	2.4	2.1	2.5	2.2	16.1	15.6	15.1	11.6
NOEF	1.73	1.98	1.86	1.72	1.86	0.33	0.34	0.15	0.33

Figure 5. The contour plot of a COSY spectrum of fluoranthene. The spectral width was 240 Hz. The data set consisted of 512 points in both dimension. For each value of t_1, 64 FIDs were accumulated. A sine bell window function and symmetrization have been applied. It is worth noting that H-7 is clearly scalar coupled with H-8; this confirmed that H-7 has the most deshielded chemical shift.

4 shows the HOESY spectrum of fluoranthene; among the four quaternary carbons only C-13, C-11, and C-16 give cross peaks; these are due to dipolar interactions from the nearest protons H_1, H_7, and H_3, respectively, and correspond nicely along the F_1 dimension. However, the innermost carbon C-15, has no cross peak since it is far removed from any proton (and lacks significant dipolar relaxation at this magnetic field—see below). The protonated carbons give intense cross peaks, owing to strong dipolar interaction between these carbons and their directly attached protons. Table III lists ^{13}C T_1 and NOEF data for 2 M fluoranthene.

All protonated carbon NOEs are close to full (some minor contributions are due to either chemical shift anisotropy relaxation—sp^2 carbons—or another mechanism), while the quaternary carbon NOEs are very small. The C-15 carbon is observed to have the smallest NOEF (0.15) which is only half that seen for the remaining three quaternary carbons. This is consistent with the HOESY experiment in Figure 4, where no cross peak was found for C-15. Wehrli[20] and Levy[21] found that dipolar relaxation rates for quaternary carbons were related to the number of geminal protons. C-16 has two geminal protons (H_3) and relaxes faster (T_1 = 11.6 s) than do C-11 and C-13 (T_1s ~ 16 s), each of which has only one geminal proton.

The carbon-13 assignments of fluoranthene in Figure 4 (F_1 dimension) are consistent with the literature.[22,23] However, the proton assignment is somewhat different from that assigned by Heffernan et al.[24] in either carbon tetrachloride or acetone as solvent. To resolve this discrepancy, J-resolved and COSY spectra were acquired; the COSY spectrum is shown in Figure 5. Figure 6 shows a simulated spectrum with LAOCOON5. Both 2-D ex-
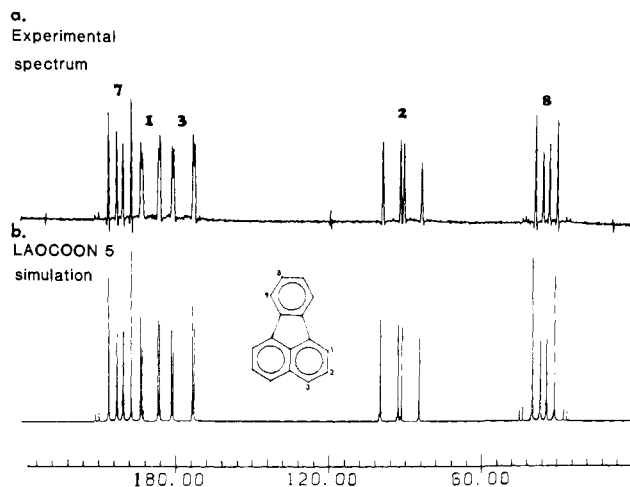
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Figure 6. The assignment of the ^1H spectrum of fluoranthene: (a) experimental (resolution enhanced) and (b) calculated spectrum at 360 MHz as a 2 M solution in $CDCl_3$. The scale is in Hz and is arbitrarily set to zero at the right-hand limit.
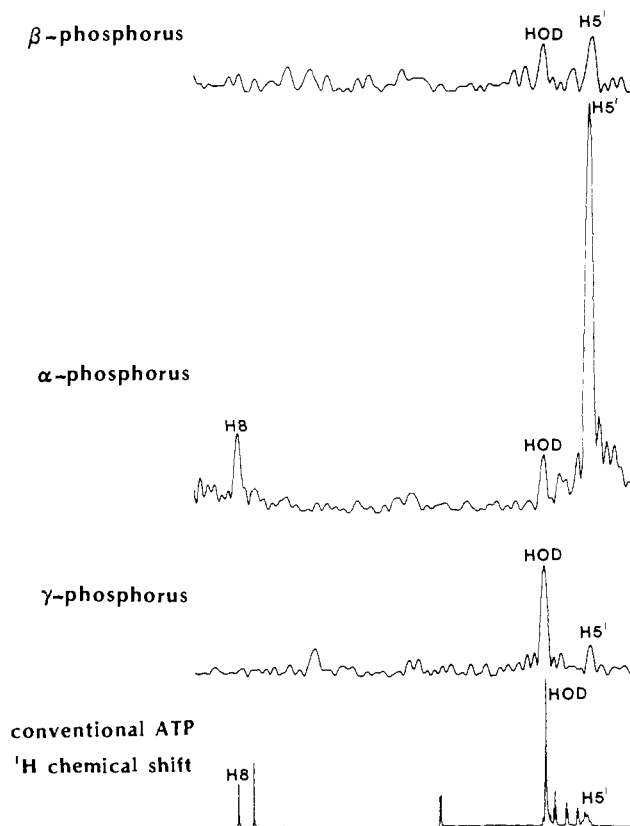

Figure 7. Slices along the three phosphorus chemical shifts of the contour plot of a HOESY spectrum for 0.5 M ATP in phosphate buffer (100% D_2O). In the conventional ^1H spectrum of ATP, the lower field H-8 and H-1 are not shown. The highest intensity is seen for γ-phosphorus to the HOD peak, which reflects strong dipolar interactions between that group and the water protons. See ref 7 for acquisition parameters.

periments are consistent with our experimental spectrum and assignment (Figure 6a).

3. HOESY Experiment and Intermolecular Interactions: ATP. Adenosine triphosphate (ATP) plays an essential role in the

metabolism of living organisms. It is the prime energy source for most endergonic biological systems and participates in numerous enzymatic reactions. As we presented in our preliminary report,[7] the HOESY experiment is able to evaluate solvent and intramolecular proton dipolar relaxation for the three phosphates in ATP. We ran the HOESY experiment for 0.5 M ATP in fully deuterated phosphate buffer (100% D_2O, repeated lyophilizations). Figure 7 shows individual slices at three phosphorus signals along the F_1 dimension (proton chemical shift) in the HOESY experiment. Each phosphorus slice has a small peak corresponding to the HOD peak, due to the small number of residual solvent protons in the sample. The γ-phosphorus slice gives the highest HOD intensity which may be due to (a) the terminal phosphorus being most accessible to the water and (b) in the buffer (pH 5.6), there still being one proton attached to the γ-phosphorus through oxygen (pK_a for γ-phosphorus in ATP are 4.1 and 6.5[25]).

In the α-phosphorus slice, two intramolecular dipolar interactions are indicated: (a) with H-5′ protons, close to the sugar ring, and (b) with the H-8 proton of the base. This is consistent with the anti conformation being populated, which is expected for solutions of ATP.[26]

Conclusions

The heteronuclear 2-D NOE experiment should prove to be a powerful albeit sometimes demanding experiment for structural elucidation and conformational analysis, both in ^{13}C and ^{31}P NMR spectroscopy. It should be noted that this experiment gives information through space (dipolar interaction) rather than through bonds (J coupling). For carbon-13, it provides information about dipolar interactions between quaternary carbons and nearby protons. A disadvantage of the HOESY experiment for relatively weak NMR nuclei (e.g., ^{15}N, ^{13}C) is that in order to detect cross peaks a concentrated sample may be necessary. This is especially true for nonprotonated sp^2 or sp- hybridized atoms at high magnetic fields, where NOEs may be quite small.

The HOESY technique should prove useful for the study of molecular conformation and solvent–solute interactions in a variety of chemical and biological systems. Since the observed nucleus is not limited to ^{13}C or ^{31}P, HOESY experiments are also expected to have significant potential in studies of peptides (^{15}N), organometallics and metalloenzymes[8] (spin $^1/_2$ metals), and solvation studies of inorganic spin $^1/_2$ ions.

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H$_2$ Photoproduction by Nafion/CdS/Pt Films in H$_2$O/S^{2-} Solutions

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Abstract: We report the construction, characterization, and evaluation of a novel system for photocatalytic hydrogen generation that comprises semiconductor (CdS) crystallites embedded in a polymer (Nafion) matrix that also contains a hydrogen-evolution catalyst (Pt). Hydrogen-production efficiencies from water containing a sacrificial electron donor (sulfide ion) were greater than those commonly obtained with unsupported colloidal or powdered semiconductors under similar conditions. Several factors dramatically influence performance: the crystalline form and surface composition of the semiconductor and the extent of catalyst dispersion throughout the film.

Photocatalytic and photosynthetic reactions at semiconductor particles provide the possibility of the utilization of solar energy for the promotion of useful chemical reactions.[1,2] Photoreactions at these particles are based on the production of electrons and holes (e^-h^+) upon absorption of light; these can react with species in solution to produce oxidized and reduced forms. These particulate systems are of interest because they are generally easy to fabricate, are potentially inexpensive, and have a large surface area which facilitates efficient light absorption and heterogeneous charge (e^- and h^+) transfer to solution species. CdS is an interesting semiconductor material that has been studied as an electrode material; many studies of particulate systems involving CdS have also been reported.[3-12]

Particle systems have several disadvantages, however. Since they are dispersed in the solvent system, they are inconvenient to use in continuous-flow systems. They may also tend to flocculate and settle out with time. A previous brief communication[13]

described the production and immobilization of CdS in a polymer (Nafion) matrix and its use for the photocatalyzed reduction of

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