

mates⁹ the separation between molecules in intermolecular interactions.

In the hopes of shedding light on the above questions, we carried out ab initio calculations on the amine-SO₂ interactions using a valence shell "double ζ " 431-G basis set.¹⁰ We optimized the energy with respect to three intermolecular parameters for NH₃-SO₂ and CH₃NH₂-SO₂ (MA) and then optimized only $R(N-S)$ for (CH₃)₂NH(DMA)-SO₂ and TMA-SO₂. The results of the geometry searches and Morokuma component analysis¹¹ at $R(N-S) = 2.45$ Å are presented¹² in Table I. The results are interesting and help to answer the questions posed above. (1) The order of gas phase amine-SO₂ affinities is TMA > DMA > MA > NH₃. We carried out a more complete geometry optimization of the SO₂ complex of NH₃ and MA than the SO₂ complexes of DMA and TMA; thus we expect that the order of interaction energies will be preserved upon complete geometry optimization. Further improvement of the basis set is likely (a) to increase the polarization energy and to increase the differences between the amines and (b) to decrease the electrostatic energies and to improve the overall agreement between the ΔE (calculated) and ΔE (experimental).¹³ (2) The $R(N-S) = 2.36$ Å for TMA-SO₂ is in much better agreement with the experimental value $R(N-S) = 2.06$ Å. The calculated difference in energy between $R(N-S) = 2.06$ and 2.36 Å is only 3 kcal/mol out of a total calculated ΔE of -15 kcal/mol.¹⁴ However, since the addition of polarization functions usually increases intermolecular separations in H-bonded complexes,^{9,13} it isn't clear how definitive our calculated gas phase $R(N-S)$ is. We hope that these results will stimulate microwave spectral studies on TMA-SO₂ in the gas phase. TMA-SO₂ also may be an example where correlation effects on the minimum energy structure are much larger than calculated for Li⁺OH₂, F⁻OH₂, and (H₂O)₂.¹⁵

Another fascinating finding is that the charge-transfer component (Table I) is the key to the methyl substituent effect in these systems, in contrast to the methyl substituent effect on proton affinities⁴ (polarization key), amine vs. amide basicity (exchange repulsion key),⁶ and most H-bond energies (electrostatic dominated).^{9,13} Geometry optimization of the amine-Li⁺ interactions at the 431-G level showed that, in that case, $R(N-Li)$ was practically the same for all the amines.⁶ The biggest difference between the relative magnitudes of the energy components of amine-Li⁺ and amine-SO₂ interactions is the small size of the charge-transfer term in the former case and its significant contribution to the attraction in the latter case.

Further studies are in progress on these systems, in particular on amine-F₂ and amine-Cl₂ interactions, where STO-3G calculations predict NH₃ to be a stronger base than TMA.^{16,17} Is that result real and are F₂ and Cl₂ very different Lewis acids than I₂, or is this another example of the inability of STO-3G to correctly represent the methyl substituent effect in these prototype "charge-transfer" complexes? In addition, more complete geometry optimization on TMA-SO₂ with a more extensive basis set seems worthwhile to do.¹⁸ However, even at this stage, the qualitative difference between amine-SO₂ and amine-Li⁺ studied with double ζ basis sets and the amine-SO₂ complex basis set dependence is very intriguing.

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 (12) We carried out the component analysis at a number of geometries, but report only the values at a common reference geometry here. $R = 2.45$ Å was chosen because it was between the minima for NH₃ and TMA. All of the energy components are very distance dependent (much more so than the total energy) and increase in magnitude as $R(N-S)$ decreases; thus, if one had used different $R(N-S)$ for comparison of the different methyl amines, the interpretation of the results would have been much more ambiguous.
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 (14) This difference in $R(N-S)$ appears a bit too large to be a crystal packing effect, since the TMA-SO₂ complexes form separated 1:1 complexes in the crystal. The difference in $R(O\cdots O)$ for (H₂O)₂ gas phase and H₂O (ice) is only 0.2 Å, and this shortening in the crystal would be expected to be accentuated by the extended tetrahedral H-bonding network.
 (15) G. Dierksen, W. Kraemer, and B. Roos, *Theor. Chim. Acta*, **36**, 249 (1975), and O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, **64**, 1361 (1976), find that correlation effects stabilize (H₂O)₂ by ~1 kcal/mol and decrease O \cdots O by ~0.1 Å.
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 (17) The limited results of ref 13 on H₃N \cdots ClF compared with CH₃NH₂ \cdots Cl-F suggest that ClF as a Lewis acid might form a stronger complex to NH₃ than TMA.
 (18) In particular, it will be interesting to compare the observed (68°) and calculated β (we assumed the same value as in methylamine-SO₂, 85°) as well as to look at changes in some of the intramolecular degrees of freedom upon complex formation. For example, in the crystal¹ complex, one C-N is 1.52 Å, the other two 1.48 Å; there is also significant asymmetry in the S-O bonds.

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¹³C-¹H Cross-Polarization in Liquids

Sir:

The observation of ¹³C NMR spectra of organic solids using proton-carbon cross-polarization¹⁻³ yields remarkable improvements in resolution and sensitivity. We report here preliminary results which demonstrate the advantageous use of this pulse technique in ¹³C NMR spectroscopy of organic liquids. In the cross-polarization experiment on liquid samples, spin-spin coupling is responsible for the magnetization transfer; hence we introduce the abbreviation JCP for J cross-polarization.

The JCP experiment contrasts with the pulsed ¹³C FT NMR experiment in three important ways. First, pulse repetition rates are governed by the proton longitudinal relaxation times T_1 rather than those of the carbon nuclei. Second, approximately a fourfold signal enhancement is predicted owing primarily to the ratio of the magnetogyric ratios for ¹H and ¹³C. Third, the indirect spin-spin couplings, J_{CH} , modulate the amplitude of JCP spectra obtained as a function of cross-polarization time. The first two features are well known from the solid-state cross-polarization experiment. The third is a consequence of the mechanism of polarization transfer: in contrast

to solid-state cross-polarization, here magnetization is coherently exchanged among ^{13}C nuclei and coupled protons with frequency comparable to J_{CH} . A related JCP experiment was considered first by Hartmann and Hahn,⁴ who developed the theory and determined $^1J_{\text{PH}}$ in hypophosphorous acid ($\text{HPO}(\text{OH})_2$) by observing the proton magnetization in a proton-phosphorus cross-polarization experiment. More recently, Ernst and co-workers⁵ have incorporated a type of cross-polarization process in two-dimensional FT experiments.

In our JCP experiment the protons are spin locked along a resonant rf field of strength B_1^{H} following a $\pi/2$ proton rf pulse. Simultaneously rf field B_1^{C} is applied very near the carbon Larmor frequency. The field strengths are balanced so that the respective nutation rates are identical, i.e., $\gamma^{\text{H}}B_1^{\text{H}} = \gamma^{\text{C}}B_1^{\text{C}}$, where the γ 's are the magnetogyric ratios. When the matching (called the Hartmann-Hahn condition⁴) is met exactly, ^{13}C and ^1H nuclei will exchange polarization periodically, keeping total polarization constant. For CH, CH_2 , and CH_3 groups with proton-carbon coupling constants $^1J_{\text{CH}}$ (in hertz), the intensities of the proton-decoupled carbon magnetization, M_{C} , as a function of cross-polarization time, τ , are

$$M_{\text{C}} = \begin{cases} M_{\text{H}} \sin^2 \left(\frac{\pi J \tau}{2} \right) & \text{CH} \quad (1a) \\ M_{\text{H}} \sin^2 \left(\frac{\pi J \tau}{\sqrt{2}} \right) & \text{CH}_2 \quad (1b) \\ M_{\text{H}} \left[\frac{1}{2} \sin^2 \left(\frac{\pi J \tau}{2} \right) + \frac{1}{2} \sin^2 \left(\frac{\pi J \tau \sqrt{3}}{2} \right) + \frac{1}{4} \sin^2 (\pi J \tau) \right] & \text{CH}_3 \quad (1c) \end{cases}$$

where M_{H} is the magnetization of the coupled protons. The maximum ^{13}C magnetization corresponds to that of the coupled protons, yielding a fourfold enhancement of CH and CH_2 carbon signals and somewhat more for CH_3 groups. Equation 1 is modified slightly for nonresonant irradiation as well as for a violation of the Hartmann-Hahn condition.

We have examined several organic liquids using JCP, including heptane, methylcyclohexane, 3-methyl-3-hydroxy-1-butene, propargyl alcohol, ethylene glycol, formic acid, and acetylene in acetone. These resonances involved carbon-proton couplings ranging from a few hertz to 250 Hz. Figure 1 shows JCP spectra of propargyl alcohol (3-hydroxy-1-propyne) for cross-polarization times of 1 to 32 ms. For these data, Fourier analysis of the cross-polarization intensity as a function of τ for the C_1 and C_3 resonances yields couplings of 270 and 145 Hz, respectively, using eq 1. The J couplings observed from conventional coupled ^{13}C spectra are $^1J_{\text{CH}} = 250.8$ Hz for C_1 and $^1J_{\text{CH}} = 148.4$ Hz for C_3 . The $^2J_{\text{CH}}$ coupling of 49.0 Hz for C_2 could not be extracted with the limited τ range presently available. A similar analysis was carried out for $^1J_{\text{CH}}$ of the methyl group of 3-hydroxy-3-methyl-1-butene. Equation 1c predicts a three-frequency modulation of the methyl signal, at $J/2$, $J\sqrt{3}/2$, and J . Fourier analysis resolved the low-frequency peaks with frequencies corresponding to a J of 132 and 135 Hz. The high frequency peak at J was not resolvable as it is near the middle peak and only one half its intensity. The coupled spectrum gives a value of $J_{\text{CH}} = 128$ Hz.

Interestingly, for samples meeting certain criteria, the JCP experiment has utility in quantitative ^{13}C NMR. In the JCP experiment, the cross-polarization enhancement is always present; the magnitude of J governs only the periodicity of the intensity. From known values of J , eq 1 may be used to calculate weighting factors for respective line intensities at a particular τ . If only two types of carbon are of interest the appropriate pair of equations may be numerically solved for a τ

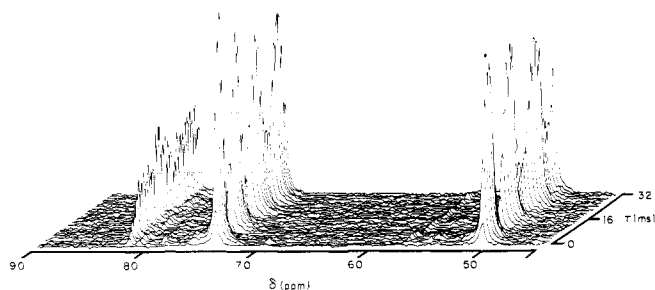


Figure 1. The effect of cross-polarization time, τ , on the intensity of the ^{13}C NMR spectrum of propargyl alcohol (HCCCH_2OH). τ ranges from 1 to 32 ms in 1-ms increments. Each spectrum is the central region of the Fourier transform of 12 signal averaged FID's digitized into 2048 points with a computer dwell time of 166 μs . The pulse repetition time was 15.3 s. The data were multiplied by the function $f = \exp(-iK)$, $K = 3 \times 10^{-3}$, before transformation. The periodic intensity behavior is discussed in the text.

that gives correct relative intensities. For example, the $^1J_{\text{CH}}$ couplings in *n*-heptane are all 125 ± 2 Hz. At a τ of 5.66 ms, obtained from eq 1b and 1c, the cross-polarization amplitudes of the CH_3 and CH_2 signals should yield correct relative intensities. In the JCP experiment on heptane at a τ of 5.66 ms, the integrated intensities of all spectral lines were found to be correct to within $\pm 2\%$. This τ also corresponds to a predicted maximum in the intensity for the CH_2 signals. At this cross-polarization time we observed a signal-to-noise ratio in the JCP experiment 4 ± 0.2 times that of an FT experiment in which NOE was suppressed. Hence, for certain restricted cases, e.g., for two carbons with different J_{CH} or many carbons with similar J_{CH} 's (such as saturated hydrocarbons), a substantial time saving can be achieved. Under other circumstances the full fourfold enhancement may not be simultaneously obtained for all spectral lines and, further, the theoretical time savings may be tempered by the requirement of determining J_{CH} 's in advance.

A paramagnetic relaxation reagent is frequently used to allow increased pulse repetition rates and to suppress NOE in the quantitative FT experiment. Protons, because of their large γ and closer approach to the paramagnetic center, are more efficiently relaxed than are carbon nuclei. We have verified that, on a sample doped with paramagnetic reagent, more rapid pulsing rates are possible for the JCP experiment compared with the FT experiment; furthermore, the JCP enhancement is retained.

In the JCP experiments reported here, a Varian HA-100 modified for FT was employed. Receiver artifacts and any residual FT signal were removed.⁶ Single-frequency cross-polarization fields were used with broad-band proton decoupling during data acquisition. The single coil is double tuned for 100 and 25 MHz with an rf field, $\gamma B_1/2\pi$, of 3 kHz at both frequencies. Quadrature phase detection was used in all experiments, as was sample spinning.

Several important details in the JCP experiment need to be examined. The constraints on matching the Hartmann-Hahn condition are far more severe than is the case for solids. In solids, a mismatch of the order of the proton-proton dipolar field is tolerable, whereas for liquids the effective mismatch should be smaller than the J_{CH} coupling involved, which is at least two orders of magnitude smaller than dipolar interactions. For example, to obtain accurate matching for single bond coupling, we must set the fields to within 0.2 db for ^{13}C resonances within 500 Hz of the carrier. We note that increasing the rf fields severalfold should give proper matching across the entire carbon chemical shift range provided the Hartmann-Hahn condition can be well met.

Central to the success of the JCP experiment is the homogeneity of the rf fields. In our spectrometer the ^1H and ^{13}C

excitations are produced by the same transmitter coil to keep the ratio of the two rf fields constant everywhere within the active sample volume.⁷

With careful consideration to the experimental details, ¹H-¹³C cross-polarization of liquid samples can be an effective technique for determining ¹³C NMR spectra. Further time savings may be realized by reducing *T*₁ of the coupled protons with a paramagnetic reagent, without significantly affecting carbon line widths. Analysis of the periodicity of the carbon magnetization in the JCP experiment can be used to assign ¹³C resonances from *J*_{CH} values under conditions of proton decoupling. The JCP method should be useful in obtaining the NMR spectra of other low γ nuclei in natural abundance such as ¹⁵N. The predicted enhancement factor is 9.9 at the maxima of the cross-polarization signals for NH and NH₂ groups, ideally yielding a time saving of ~100 over conventional FT spectroscopy (6.3 if full NOE is realized). Because of the negative magnetogyric ratio of ¹⁵N, a diminution of intensity is possible for ordinary proton-decoupled FT experiments when nondipolar mechanisms contribute to longitudinal relaxation. This difficulty is avoided in the JCP experiment.

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A Phosphoranoxide¹ Anion—Direct Observation and Isolation of a Stable Model for the Postulated Intermediate in Nucleophilic Substitution at Tetracoordinated Phosphinoyl Phosphorus

Sir:

The most thoroughly studied reaction of tetracoordinated phosphorus compounds, such as **1**, which contain a P=O bond, is nucleophilic substitution at phosphorus.² It is generally accepted that a reaction of this type involves apical approach of the nucleophile and formation of a trigonal bipyramidal (TBP) intermediate, or transition state, such as **2**. The direct observation of such a TBP intermediate, with an equatorial oxy anion, has remained an elusive goal.^{3b} We here report such an observation.

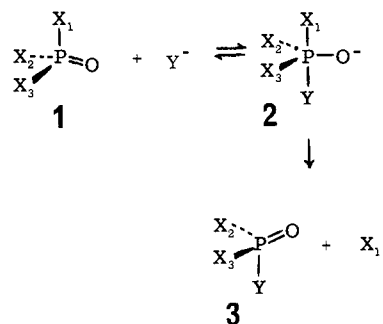
Only recently have reports appeared of compounds whose solution spectra³ and reaction products⁴ suggest that they belong to the class of hydroxyphosphoranes, conjugate acids of **2**. One such compound has been isolated as a crystalline solid.⁵

The hydroxyphosphoranes for which evidence has been reported all have alkoxy or carboxy ligands to phosphorus which

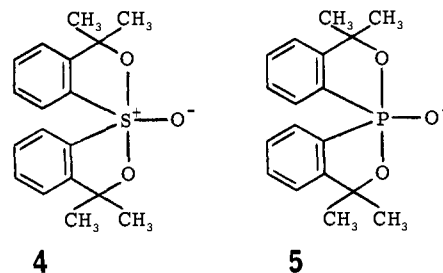
Table I. ³¹P NMR of Mixtures of **6** and **7**

Solvent	temp, °C	chemical shift, ppm	line width, Hz	rel concn
10% TFA in CDCl ₃	28	+81.9	5	
CH ₃ OH	28	+50.9	220	
CDCl ₃	28	+45.6	140	
C ₅ H ₅ N	28	-12.4	320	
CH ₃ OD	28	+54.9	54	
CH ₃ OD	5	+54.2	24	~50
		-26.3	100	1
CH ₃ OD	-10	+53.7	20	8.5
		-26.3	40	1
CH ₃ OD	-30	+52.7	8	3.3
		-26.7	15	1
CH ₃ OD	-50	+52.7	5	2.5
		-27.0	5	1

are easily eliminated to generate a P=O bond (vide infra). These hydroxyphosphoranes are destroyed (as in **2** → **3**) by treatment with base,⁵ even bases as weak as pyridine or dimethyl sulfoxide.^{3d} The conversion of these hydroxyphosphoranes to observable phosphoranoxide anions has therefore not been accomplished.



Our observation of stability in sulfurane oxides,⁶ such as **4**,⁶ suggested to us that isoelectronic phosphoranoxide anions, such as **5**, having all the structural features⁷ responsible for the stability of the analogous **4**, might be sufficiently stabilized by these structural features to allow their direct observation. We report evidence confirming this view.



A crystalline compound^{8,9} having either structure **6** or **7** was prepared by the indicated route (Scheme I). Examination of the ³¹P NMR spectrum of the reaction mixture in tetrahydrofuran (THF) prior to hydrolysis (aqueous ammonium chloride) reveals a sharp signal at -20.8 ppm, attributable to the magnesium salt of **5**. Solution ¹H and ³¹P NMR spectra of **6**, or **7**, show clear evidence for a dynamic equilibrium between **6** and **7**, present in ratios dependent on solvent and temperature (Table I). The intermediate rate of **6**-**7** exchange evidenced by the single broad ³¹P peak seen at room temperature is slowed at lower temperatures, to give separate sharp peaks for **6** and **7**. Peak area ratios show increasing amounts of the ring tautomer, hydroxyphosphorane **6** (ca. -27 ppm) relative to open-chain tautomer **7** (ca. +52 ppm) in CH₃OD