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(18) All new compounds gave correct elemental analyses and IR and NMR spectra consistent with the structure. All optical rotations were recorded at 5461 Å with a Bendix-Ericson Model 143A polarimeter using chloroform as a solvent. An authentic sample of 1-methyl-2,2-diphenylcyclopropane[7] gave $[\alpha] \pm 151°$ (c 1.18).

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Sensitivity Enhancement in ^{15}N NMR: Polarization Transfer Using the INEPT Pulse Sequence

Sir:

In a previous communication[1] a new pulse sequence was described which allows the NMR signals of nuclei with low magnetogyric ratio to be enhanced by the transfer of polarization from protons scalar coupled to the weak nucleus. This technique has now been evaluated for the case of a simple ^{15}N spectrum in natural abundance, that of the blocked dipeptide benzyloxycarboxylglycylglycyine methyl ester, giving substantial improvements in sensitivity both for proton coupled and for decoupled spectra.

Three main factors contribute to the low sensitivity of ^{15}N NMR: the low natural abundance (0.37%), its low resonant frequency, and the negative sign of its magnetogyric ratio. The first of these can only be overcome by the use of isotopically enriched materials, but the problems caused by the other two factors can be alleviated to some extent by suitable experimental methods. The use of wide-band proton decoupling can lead to an increase in the ^{15}N signal of up to four times, by the nuclear Overhauser effect;[2] however, since the magnetogyric ratios of the proton and the ^{15}N nucleus have opposite signs, if the dipole–dipole mechanism on which the Overhauser effect depends does not dominate the ^{15}N T_1, then proton irradiation can actually reduce or entirely suppress the signal. This situation is sufficiently common that many nitrogen spectra must be run using gated proton decoupling[3] in order to suppress the Overhauser effect.

A more satisfactory solution to the problem is to transfer spin polarization from protons to ^{15}N via proton–nitrogen scalar couplings. Not only does this lead to a tenfold increase in the ^{15}N polarization owing to the higher magnetogyric ratio of the proton, but an additional improvement in sensitivity can result from the faster spin-lattice relaxation of protons, since this governs the rate at which experiments may be repeated. Cross polarization via Hartmann–Hahn contact in the rotating frame is familiar in solid-state NMR[4,5] and has recently been applied to liquid-state high-resolution NMR with considerable success.[6-9] The principal disadvantage of this technique is its sensitivity to any mismatch between the proton and nitrogen radio frequency fields, which makes necessary the construction of probe coils doubly tuned for ^{15}N and protons, a procedure which reduces the basic ^{15}N sensitivity. This problem can be avoided by the use of the INEPT pulse sequence[1] (insensitive nuclei enhanced by polarization transfer).

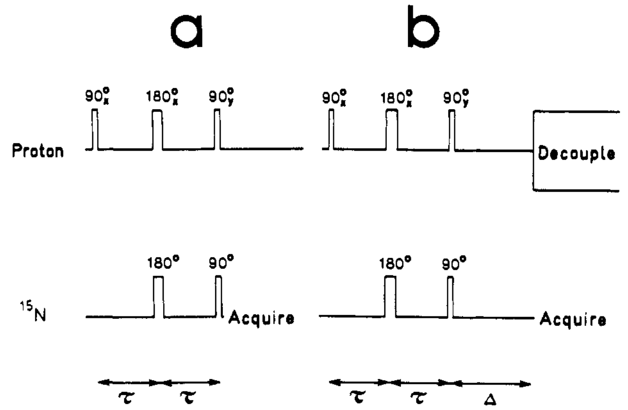

Figure 1. Pulse sequences used for obtaining INEPT enhanced spectra (a) without proton decoupling and (b) with proton decoupling. For the spectra of Figure 2a τ was 2.5 ms and Δ5 ms.

Figure 1 illustrates the pulse sequences used to obtain enhanced proton coupled and decoupled spectra by the INEPT method. The mechanism of the basic experiment has already been described in detail;[1] a ^{15}N modulated proton spin echo is used to invert one ^{15}N satellite of each proton directly coupled to nitrogen, which leads to the full proton Boltzmann spin polarization appearing across the connected ^{15}N transitions. This leads to proton coupled multiplet intensity ratios of $-1{:}+1$ for NH groups, $-1{:}0{:}+1$ for NH_2, and $-1{:}-1{:}+1{:}+1$ for NH_3. Since proton decoupling immediately after the ^{15}N 90° pulse would collapse the antiphase signals and hence lose any enhancement, the extra delay in Figure 1b is inserted in order to bring the multiplet components in phase before the onset of decoupling. The optimum value for the delay τ is $1/(4J_{\rm NH})$, while that for Δ is $1(2J_{\rm NH})$ for doublets and $1/(4J_{\rm NH})$ for triplets. Since most one-bond proton–nitrogen couplings lie in the range of 60–90 Hz and the polarization transferred shows only a sine dependence on J, a single value of τ generally suffices to give good enhancements for all protonated nitrogens.

Spectra of a 1 M solution of blocked glycylglycine[10] in deuteriochloroform obtained using the pulse sequences of Figure 1 are shown in Figure 2a. For comparison, spectra obtained by conventional methods using the same total time of 10 min are shown in Figures 2b and 2c. Figure 2b shows the spectra obtained with Overhauser enhancement, using gated decoupling to obtain an enhanced spectrum.[11] In separate experiments the nuclear Overhauser enhancement was found to be the theoretical maximum of -4 within experimental error. Figure 2c shows a proton coupled spectrum obtained without nuclear Overhauser enhancement, and a proton decoupled spectrum obtained using only 40-s time averaging with continuous proton decoupling, in order to show the effect of removing the Overhauser enhancement without the need for artificially long interpulse delays. All experimental conditions were chosen to optimize sensitivity for the different techniques employed, using proton and nitrogen T_1 values of 1 and 3 s, respectively, estimated from progressive saturation experiments.

Spectra were obtained using the low-band multinuclear system of a Bruker WH 400 spectrometer, operating at 40.5 MHz for ^{15}N with 15-mm-diameter sample tubes. The only nonstandard feature of the spectrometer used was the provision of a computer-controlled 90° phase shift on the decoupler channel. The pulse sequence was generated using a machine code patch to the standard Bruker FT NMR software.

Despite the low pulse power ($\nu_1 = 1.6$ kHz for ^{15}N) of the particular broad-band probe used, ~80% of the predicted

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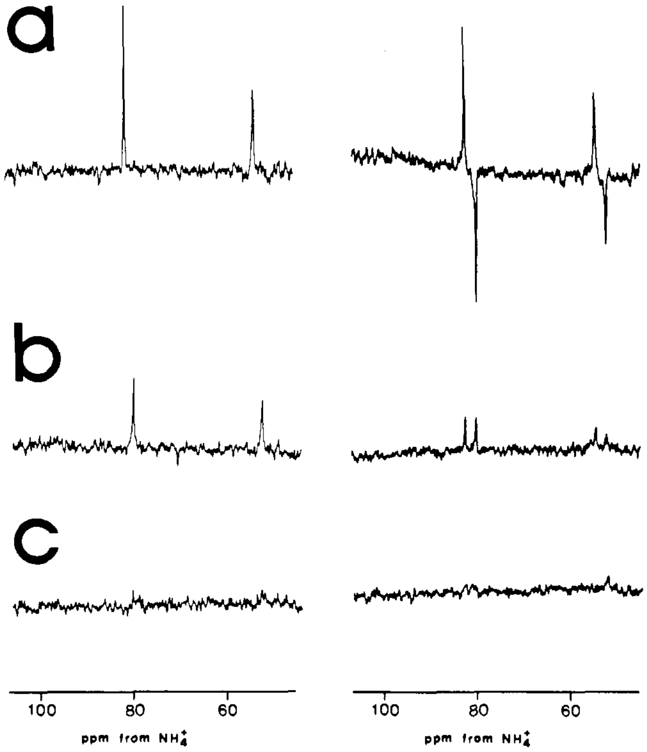

Figure 2. Proton decoupled and coupled spectra of a 1.0 M solution of benzyloxycarboxylglycylglycine methyl ester in deuteriochloroform, obtained (a) using the INEPT pulse sequence, (b) with nuclear Overhauser enhancement, and (c) without Overhauser enhancement. With the exception of the decoupled spectrum c all spectra represent the result of 10-min time averaging; the decoupled spectrum c is equivalent to that which would be obtained in 10 min in the absence of the nuclear Overhauser effect. Chemical shifts measured with respect to saturated aqueous ammonium nitrate were 81.6 and 53.8 ± 0.1 ppm downfield for peptide and amide resonances, respectively.

signal enhancement was obtained. The sensitivity improvement factors for proton coupled and decoupled spectra were 15 and 8, respectively, over the unenhanced spectra, and 4 and 2, respectively, over spectra obtained with nuclear Overhauser enhancement. The INEPT method is thus particularly suited to the measurement of proton coupled spectra and to the study of systems with less than the full nuclear Overhauser effect, offering in some cases an improvement in total acquisition time of more than two orders of magnitude.

Cross-polarization methods in solution cannot solve all ^{15}N sensitivity problems, relying as they do on the existence of resolvable proton-nitrogen couplings which may not be available for unprotonated nitrogens or in chemically exchanging systems. Nevertheless the great sensitivity gains possible in suitable systems make cross polarization a very attractive proposition; the INEPT pulse sequence offers a simple way of making this available on existing instrumentation. Many variations on existing techniques are possible using an INEPT sequence as a preparation, including ^{15}N relaxation studies. A related pulse sequence has been used for detecting multiple quantum transitions with enhanced sensitivity,[12] while recently a modified INEPT sequence has been used in the first two-dimensional NMR experiments on ^{15}N.[13]

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Analysis and Optimization of Gas-Phase Reactions. 13.[1,2] Silatoluene

Sir:

Silabenzene and its derivatives, repeatedly postulated as reaction intermediates[3-5] and one of which was finally generated unambiguously,[3] according to the literature[6] have so far eluded spectroscopic detection and characterization. According to quantum chemical calculations,[7-10] the parent compound is expected to be a thermodynamically stable[7] singlet[8] molecule with Si-C distances shortened by ~0.1 Å[8-10] with respect to the single bond length and should exhibit a first ionization potential of ~8.2 eV.[11]

After numerous futile attempts, tenacity, and especially a newly designed heated inlet system, which allows gas-phase flow pyrolysis of compounds to take place at ~1 cm above the ionization region of the photoelectron spectrometer,[12] helped to achieve the goal. Starting from 1-methyl-1-allyl-1-silacyclohexa-2,4-diene,[3,4] with propene as an advantageous leaving molecule[13] in the thermolysis,[4] the change in the PE spectroscopic molecular fingerprints upon pyrolysis (Figure 1) reveals two bands at 7.7 and 9.1$_5$ eV. A third band centered at 10 eV coincides with the first band of propene (Figure 1).

The two low-energy bands emerging in the PE spectrum of the pyrolysis mixture are assigned to the lowest radical cation states of silatoluene on the basis of the following arguments. A low first ionization energy is predicted according to first-order perturbation of benzene—inserting a silicon center should yield for C_5H_5SiH 8.2 eV,[11] and additional attachment of a methyl group should further lower the ionization energy by ~0.4 eV[14]—to amount to ~7.8 eV for $C_5H_5SiCH_3$. In contrast, the second ionization potential should remain approximately constant and be comparable to $IE_2 = 9.15$ eV of toluene.[14] Both expectations are in full accord with a Koopmans correlation, $IE_n = -\epsilon_j^{SCF}$, of MNDO eigenvalues (Figure 1).

Additional support is supplied by mass spectroscopic investigation: the oven used in the PE spectrometer heated inlet system could be fixed at a distance of ~18 cm from the ionization chamber of a Varian MAT CH7. The predominant

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