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13C—15N Spin-Spin Coupling Constants in [15N]-Aniline from 13C NMR Spectra

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In connection with current 13C NMR studies on signs and magnitudes of 13C—31P spin-spin coupling constants involving sp^2 hybridized carbon atoms in aromatic and heteroaromatic phosphine derivatives,[1a-c] a comparison with corresponding 13C—15N coupling constants would be of interest. However, in only a very few cases the signs and magnitudes of 13C—15N couplings have been obtained.[2a-d] This note reports on the 13C—15N coupling constants in [15N]-aniline as determined from noise-modulated and single-frequency proton decoupled 13C NMR spectra.

The noise-modulated proton decoupled 13C spectrum of [15N]-aniline in acetone-d_6 is shown in Fig. 1. Assignment of the aromatic carbon resonances followed from a series of single-frequency proton decoupling experiments $(\nu_{H(3)} > \nu_{H(4)} > \nu_{H(2)})^3$ and is in agreement with that proposed earlier for aniline.[4] Under conditions of higher resolution (sweep width 0.5 Hz/cm) all carbon resonances were observed to show additional splittings due to 13C—15N spin-spin interactions. The $J(^{13}C - {}^{15}N)$ coupling constants and 13C chemical shifts are collected in Table 1.

Information on the signs of the 13C—15N coupling constants could be obtained for $^2J(^{13}C(2) - {}^{15}N)$ and $^3J(^{13}C(3) - {}^{15}N)$ using off-resonance and selective proton decoupling techniques as recently described.[1a] In spite of the very small magnitude expected for $^4J(^{15}N - H(3))^5$ the sign of $^3J(^{13}C(3) - {}^{15}N)$ could nevertheless be related to the sign of this coupling constant. As seen from Fig. 2 the sign of the two 13C—15N couplings is found to be the same as for the couplings between 15N and the corresponding ring protons, *i.e.*

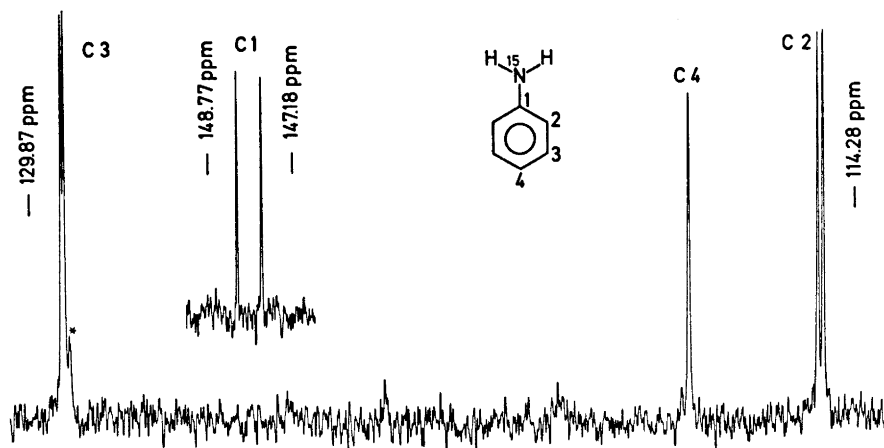*Fig. 1.* Natural abundance 13C NMR spectrum (single scan; 1H noise-decoupled) of [15N]-aniline. The ppm scale is downfield from internal TMS. Peak marked with an asterisk is an impurity.
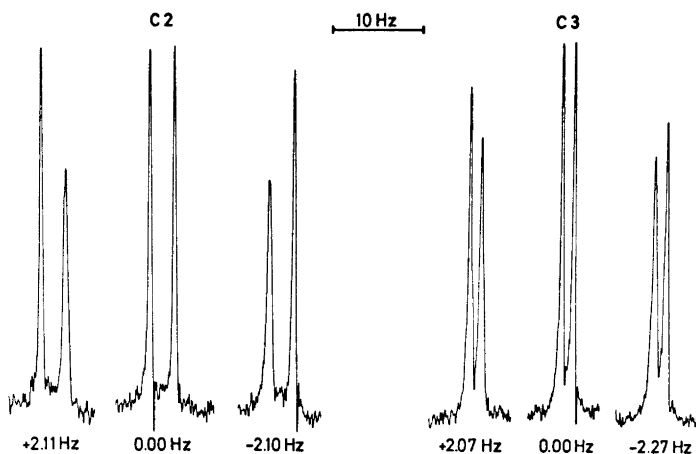
Fig. 2. Single-frequency proton decoupled C(2) and C(3) spectra for relative sign determination of the $^{13}C-^{15}N$ coupling constants (see text). Offsets (Hz) in the decoupling frequencies for H(2) and H(3), respectively, are given below the spectra. Sweep frequency increases from right to left.

Table 1. ^{13}C chemical shifts and $^{13}C-^{15}N$ coupling constants, $J(^{13}C-^{15}N)$, in [^{15}N]-aniline.[a]

Carbon	Chemical shifts[b]	$J(^{13}C\text{-}^{15}N)^{c}$
C(1)	147.98	11.47
C(2)	114.93	− 2.68
C(3)	129.25	− 1.29
C(4)	117.45	0.27

[a] Studied as a (47 % w/w) solution in $(CD_3)_2CO$ (46 % w/w) and $(CH_3)_4Si$ (TMS) (7 % w/w). Temp 32°.

[b] In ppm downfield from internal TMS with errors ± 0.01 ppm.

[c] In Hz with errors ± 0.03 Hz. Signs determined as described in the text.

$^{3}J(^{15}N-H(2))$ and $^{4}J(^{15}N-H(3))$, respectively. Similar results have been obtained for the corresponding $^{n}J(^{13}C-X)$ and $^{n+1}J(^{1}H-X)$ coupling constants in benzene,[6] monofluorobenzene,[7] and triphenylphosphine derivatives,[1c] ($n=2$ and 3; $X=^{1}H$, ^{19}F, and ^{31}P). Thus, as these are all known to be positive, one may assume, taking into account the negative magnetogyric ratio of the ^{15}N isotope, that $^{2}J(^{13}C-^{15}N)$ and $^{3}J(^{13}C-^{15}N)$ $(X=^{15}N)$ are negative in sign. Several selective

proton decoupling experiments were performed in order to obtain the sign of the one-bond $^{13}C(1)-^{15}N$ coupling. However, due to long-range $^{13}C(1)-^{1}H$ couplings to both the amino and *meta* protons the results were not conclusive.

Assuming the dominance of the Fermi contact mechanism, Binsch *et al.*[2a,b] suggested the relationship (1) (based on the average triplet excitation energy approximation)

$$80 \ ^{1}J(^{13}C-^{15}N) = s_{C}s_{N} \qquad (1)$$

between the magnitude of $^{1}J(^{13}C-^{15}N)$ and the product of percentage of s-characters, s_C and s_N, in the carbon and nitrogen hybrid orbitals of a $C-N$ bond. Although empirical expressions such as (1) should be utilized with awareness of their limitations, the application of (1) in the case of [^{15}N]-aniline seems justified [2a,b] by the "normal" nitrogen chemical shift [2c] observed for this compound. Using $^{1}J(^{13}C-^{15}N) = 11.47$ Hz and $s_C = 33 \%$ one arrives at a s_N character of 28 % for the hybrid nitrogen orbital in the $C-N$ bond of [^{15}N]-aniline. The same value was recently estimated for the s-character of the nitrogen hybrid orbital in the $N-H$ bonds from studies of $^{1}J(^{15}N-^{1}H)$ coupling constants in a series of anilines,[5] using an empirical relationship [2a] similar to (1). Thus from $^{1}J(^{13}C-^{15}N)$ further evidence for a nitrogen hybridization intermediate

between tetrahedral (sp^3) and trigonal (sp^2) in aniline is obtained.

Comparison of the reported $J(^{13}C - ^{15}N)$ values with $^{13}C - ^{31}P$ couplings in phenyl phosphorus compounds[1c] (e.g. phenylphosphine) will form part of a subsequent paper.

Experimental. ^{13}C spectra were recorded on a Varian XL-100-15 spectrometer operating in the c.w. mode at 25.2 MHz. Internal field-frequency lock was provided by the ^2H resonance of acetone-d_6 used as solvent. Carbon line positions were measured relative to the carbon resonance of internal TMS using a sweep width of 0.5 Hz/cm. Noise-modulated and single-frequency proton decoupling experiments were performed by means of the Varian Gyrocode spin decoupler. The sample solution was contained in a 12 mm tube sealed under vacuum.

[^{15}N]-Aniline (98 % enriched) was obtained from Ministerio de Industria Junta de Energia Nuclear, Spain.

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Proton Magnetic Resonance Analysis of the *trans* Isomer of 2-Chloro-4-methyl-1,3,2-dioxaphospholane and the *cis* and *trans* Isomers of 2-Chloro-4,5-dimethyl-1,3,2-dioxaphospholane

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Goldwhite[1] has found evidence from PMR spectra for the presence of geometric isomers in 2-chloro-4-methyl-1,3,2-dioxaphospholane (I). The mixed isomers showed two doublets for the C–CH$_3$ absorption at 0.95 and 1.20 ppm, indicating different environment around the methyl group in the two isomers. The C–CH$_3$ absorption of the corresponding phosphate isomers seemed to indicate similar position of the 4-methyl substituent. Gagnaire and co-workers[2] have reported the PMR spectra of the isomers of 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholane (II), where the *cis* and *trans* forms were prepared from *meso*- and D,L-2,3-dimethylbutandiol, respectively. The proton-proton coupling constants and the phosphorus-proton coupling constants involved were obtained from double resonance experiments. This paper reports the PMR analysis of the *trans*-isomer of I and the *cis* and *trans* isomers of II, using the iterative computer program UEAITR.[3] This program adds iterative evaluation of input parameters to an earlier program (UEA-NMRII), which makes use of magnetic equivalence factoring to reduce the size of certain matrices.

The PMR spectrum of 2-chloro-4-methyl-1,3,2-dioxaphospholane (I) shows that there are two kinds of methyl groups in magnetically different environments in the ratio 1 : 4. It is unlikely that the different environments arise from a stable nonplanar conformation of the ring, since studies of 1,3-dioxalanes[4,5] and 1,3-dioxasulfolanes[6] suggest that flexing of these five-membered rings is rapid. The most reasonable interpretation of the spectrum is that a relatively stable pyramidal stereochemistry at phosphorus leads to two kinds of methyl groups in the compound, *cis* and *trans* to the 2-chloro-substituent. The