

DETERMINATION OF COUPLING CONSTANTS OF NITROGEN IN AMINO GROUP OF NITROANILINES BY MEANS OF RELAXATION TIMES IN ROTATING FRAME

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One-bond coupling constants of amino nitrogen in 2-, 3- and 4-nitroanilines have been calculated on the basis of ^1H and ^{13}C relaxation times in rotating frame ($T_{1\rho}$) which are affected by interaction with rapidly relaxing ^{14}N nucleus. A method has been suggested and tested for calculation of ^{14}N — ^{13}C couplings with elimination of effects of other relaxation mechanisms. Dependence of $^1J(^{14}\text{N}^{13}\text{C})$ on position of nitro group in the aromatic nucleus has been observed.

Measurement of nuclear relaxation times in rotating frame (spin-locking) represents an efficient method of study of slower exchange processes taking place in organic compounds. One of the mechanisms affecting the $T_{1\rho}$ values is the spin coupling of the examined nucleus with a rapidly relaxing quadrupole nucleus. Contribution of relaxation of the quadrupole nucleus to the relaxation time $T_{1\rho}$ of the examined nucleus in the molecule can be expressed in the form¹

$$(T_{1\rho}^{\text{sc}})^{-1} = 4(\pi J)^2 I(I + 1) T_{11} / (3(1 + \omega_1^2 T_{11}^2)), \quad (1)$$

where J means the coupling constant of the examined nucleus with the quadrupole nucleus having a spin I ; T_{11} means spin-lattice relaxation time of the quadrupole nucleus, and ω_1 is amplitude of the spin-locking field in the frequency units ($\omega_1 = \gamma B_1$). From Eq. (1) it follows that $T_{1\rho}^{\text{sc}}$ is directly proportional to ω_1^2 . From the slope of this straight line and from the value $T_{1\rho}^{\text{sc}}(\omega_1^2 = 0)$ it is possible to evaluate the coupling constant J as well as the spin-lattice relaxation time of the quadrupole nucleus T_{11} . One of the important applications of this method is the determination of ^{14}N — H and ^{14}N — ^{13}C coupling constants which, in most cases, are only accessible indirectly from the ^{15}N interactions. In the present communication the said procedure is used for determination of the coupling constants in isomeric nitroanilines.

EXPERIMENTAL

2-, 3- and 4-nitroanilines were measured in 10 mm tubes as saturated solutions in hexadeuterioacetone. All the measurements were carried out on a JEOL FX-100 FT NMR spectrometer at

22°C. The spin-lattice relaxation times were obtained by the inversion recovery method. The relaxation times in rotating frame were measured by the pulse sequence described in ref.². Amplitude of the spin-locking field B_1 was determined by measuring the time needed for a 180° pulse. The signal intensities were determined from the spectra taken at 200 Hz (^1H) or 300–600 Hz (^{13}C) spectral width using 2 048 data points. The ^{13}C spectra were measured with the single frequency proton decoupling, external lithium lock being used. The ^{14}N NMR spectra were recorded at 7.14 MHz with the proton noise decoupling. 8 192 data points, a spectral width of 10 kHz and 50 ms interval between pulses were used. The inaccuracy of the calculated ^{14}N —H and ^{14}N — ^{13}C coupling constants due to random error was about 2 and 0.5 Hz, respectively. The error in the relaxation times of nitrogen is 5 to 10%.

RESULTS AND DISCUSSION

The ^1H $T_{1\rho}$ measurements were used to study the one-bond ^{14}N —H interactions in NH_2 group of 3- and 4-nitroanilines. In 2-nitroaniline the proton signal of amino group was overlapped by that of aromatic protons, and its intensity could not be determined reliably. Results of the measurements are given in Table I. Besides the spin coupling with ^{14}N nucleus the relaxation times $T_{1\rho}$ are also affected by other relaxation mechanisms which are presumed to contribute equally¹ to both $T_{1\rho}$ and T_1 values. Comparison of these values reveals that the contribution of the coupling with ^{14}N nucleus to the relaxation of NH_2 protons in the rotating frame is considerable, so that Eq. (2) can be used¹ for sufficiently accurate calculation of $T_{1\rho}^{\text{sc}}$

$$(T_{1\rho}^{\text{sc}})^{-1} = T_{1\rho}^{-1} - T_1^{-1}, \quad (2)$$

where the expression T_1^{-1} represents contribution of the other rapid relaxation processes to the overall relaxation in the rotating frame. The calculated coupling constants $^1J(^{14}\text{NH})$ (Table I) agree well with the directly measured³ values $^1J(^{15}\text{NH})$. For 3-nitroaniline the measured absolute value was $^1J(^{15}\text{NH}) = 83.0$ Hz, that for

TABLE I

^1H Relaxation times and calculated one-bond ^{14}N —H coupling constants and ^{14}N spin-lattice relaxation times in NH_2 group of nitroanilines

Compound	T_1 s	$T_{1\rho}$ (ms) at ω_1 , rad s ⁻¹						$^1J(^{14}\text{NH})$ Hz	^{14}N T_1 ms
		2 000	4 000	6 000	8 000	10 000	12 000		
3-NO ₂	1.75	41	87	160	250	345	460	61	0.41
4-NO ₂	1.81	39	78	148	245	310	450	65	0.43

4-nitroaniline was 88.9 Hz, and recalculation with the use of gyromagnetic ratios gives the respective values ${}^1J({}^{14}\text{NH}) = 59.2$ Hz and 63.4 Hz.

The described method of $T_{1\rho}^{\text{sc}}$ calculation cannot be used in the ${}^{13}\text{C}$ measurements. The ${}^1J({}^{14}\text{N}{}^{13}\text{C})$ coupling constants are substantially smaller than ${}^1J({}^{14}\text{NH})$, hence the contribution of the coupling with ${}^{14}\text{N}$ nucleus to the overall relaxation of ${}^{13}\text{C}$ nucleus in rotating frame is relatively small. Effects of other processes affecting T_1 and $T_{1\rho}$ as well as those of systematical errors of the measurements cause that the $T_{1\rho}^{\text{sc}}$ calculation *via* Eq. (2) is loaded with a large error. Therefore, in calculations of the ${}^{14}\text{N}$ — ${}^{13}\text{C}$ couplings one of the unknown parameters present in Eq. (1), *i.e.* the relaxation time of ${}^{14}\text{N}$ nucleus of amino group, was calculated independently from the ${}^{14}\text{N}$ signal half width according⁴ to Eq. (3)

$$T_1 = T_2 = (\pi W_{1/2})^{-1}, \quad (3)$$

where T_1 and T_2 stand for the spin-lattice and spin-spin relaxation times of ${}^{14}\text{N}$ nucleus, respectively, and $W_{1/2}$ means the ${}^{14}\text{N}$ signal width at half height. The $T_{1\rho}^{\text{sc}}$ values were expressed from the modified relation (2)

$$(T_{1\rho}^{\text{sc}})^{-1} = T_{1\rho}^{-1} - (T'_1)^{-1}, \quad (4)$$

where the $(T'_1)^{-1}$ constant independent of ω_1 represents all remaining contributions to relaxation in rotating frame. Its value was chosen in such way that the dependence $T_{1\rho}^{\text{sc}}$ vs ω_1^2 according to Eq. (1) might give the relaxation time of ${}^{14}\text{N}$ nucleus calculated from Eq. (3). The contribution of NO_2 nitrogen relaxation to the measured values

TABLE II

${}^{13}\text{C}$ Relaxation times, ${}^{14}\text{N}$ spin-spin relaxation times and calculated one-bond ${}^{14}\text{N}$ — ${}^{13}\text{C}$ coupling constants for CNH_2 group in nitroanilines

Compound	T_1 s	$T_{1\rho}(\text{s})$ at ω_1 , rad s^{-1}					${}^{14}\text{N } T_2$ ms	${}^1J({}^{14}\text{N } {}^{13}\text{C})$ Hz
		1 000	2 000	4 000	6 000	7 000		
2- NO_2	34.5	0.80	1.25	2.40	4.65	6.5 ^a	0.50	10.9
3- NO_2 ^b	2.78	0.90	1.00	1.35	1.65	1.73	0.44	8.9
4- NO_2 ^b	3.01	0.70	0.81	1.30	1.57	1.70	0.43	10.5

^a At $\omega_1 = 8\,000$ rad s^{-1} . ^b With addition of chromium(III) acetylacetonate.

of $T_{1\rho}$ is negligible because its relaxation time is relatively long and the couplings with the $C_{(1)}$ carbon are small.

Table II gives the relaxation times T_1 and T_{1e} measured at $C_{(1)}$ atom of the studied nitroanilines and those of amino nitrogen atom calculated from Eq. (3). The relaxation times of nitrogen atom calculated from the half width of signals agree (within the experimental error) with the spin-lattice relaxation times found from the ^1H T_{1e} measurements (Table I). Concentration of 2-nitroaniline solution was sufficiently high, so intensities of ^{13}C signals could be read from the spectra measured at a single pulse. Concentration of 3- and 4-nitroaniline solutions was lower, and accumulation of spectra was necessary to obtain sufficient signal/noise ratio. To reduce the measurement time of the T_{1e} data, chromium(III) acetylacetonate was added to the two samples, whereby the spin-lattice relaxation time of $C_{(1)}$ atom was shortened to a value about 3 s. Although the addition of the relaxation reagent represents a further contribution to the ^{13}C relaxation times, this contribution does not depend on ω_1 and is eliminated in the expression of T_{1e}^{sc} by Eq. (4).

Fig. 1 gives the dependences T_{1e}^{sc} vs ω_1^2 for the $C_{(1)}$ atom of the nitroanilines, Table II gives the calculated coupling constants $^1J(^{14}\text{N}^{13}\text{C})$. Agreement of the calculated coupling constant of 4-nitroaniline with the value $^1J(^{15}\text{N}^{13}\text{C}) = 14.9$ Hz, i.e. $^1J(^{14}\text{N}^{13}\text{C}) = 10.7$ Hz (measured with an ^{15}N -enriched sample⁵) confirms correctness of the chosen evaluation method. The high value of this coupling constant as compared with $^1J(^{14}\text{N}^{13}\text{C}) = 8.2$ Hz found in aniline⁶ is explained by the increase of the N-C bond order of amino group caused by NO_2 substituent⁵. From comparison of the calculated $^1J(^{14}\text{N}^{13}\text{C})$ values it follows that the effect of nitro group is similar in 2-nitroaniline, whereas in 3-nitroaniline it is substantially weaker.

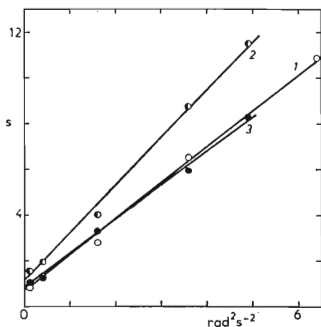


FIG. 1

Dependence T_{1e}^{sc} vs $\omega_1^2 \cdot 10^{-7}$ for $C_{(1)}$ atom of 1 2-nitroaniline, 2 3-nitroaniline and 3 4-nitroaniline

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