Application of Homonuclear INDOR to a Study of the PMR Spectrum of ^{15}N-pyrrole

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(Z. Naturforsch. **26 a**, 1187—1189 [1971]; received 15 March 1971)

Homonuclear INDOR method has been applied to investigate the assignment of some lines of the PMR spectrum of ^{15}N-pyrrole to the transitions in the energy level diagram of the AA'BB'C spin system. This study, based on the characters of some connected transitions and the corresponding line positions, shows that the couplings $^1J_{NH}$, $^2J_{NH}$ and $^3J_{NH}$ carry the same signs, which is in accordance with a result obtained by the tickling method.

Introduction

The determination of the absolute signs of indirect spin-spin couplings in the high resolution NMR spectrum of a multi-spin system is not possible using an analysis based on the conventional Hamiltonian including only chemical shifts and spin-spin couplings. If the relaxation effects are ignored, the frequencies and intensities of the lines in high resolution single and double resonance spectra are invariant to a change in sign of all spin-spin couplings [1]. On the other hand, the topological structure of the nuclear spin energy level diagram and the assignment of the spectral lines to transitions between these levels, depend on the relative signs of the nuclear spin couplings, which can be obtained using different double resonance methods [1].

The homonuclear tickling double resonance technique has been applied before [2] to investigate the relative signs of the couplings J_{NH} in ^{15}N-pyrrole, and then the spectral regions having lines with common energy levels were recognizable. This was sufficient to determine the relative signs of the couplings J_{NH}, which all appear to have the same sign. However, the final assignment of the observed lines to transitions in the energy level diagram requires the definition of the progressive or regressive character of the connected transitions, which can be studied e. g. with the homonuclear INDOR method [1, 3].

In INDOR experiment, the frequency ω_1 of the observing or monitoring field H_1 is set exactly on resonance of some spectral line, while the frequency ω_2 of the perturbing field H_2 is swept over the rest of the spectral region. The obtained INDOR spectrum represents the intensity of the observed line as a function of the perturbing frequency ω_2. In order to interpret the INDOR spectrum unambiguously, the line under study should be a well-resolved single line, which corresponds to a non-degenerate transition [1, 3].

Whenever the perturbing frequency corresponds to a transition which is regressive relative to the monitored transition, the result is a decrease in the intensity of the monitored line, or a negative INDOR signal. The intensity increases, or a positive INDOR signal appears, when a progressive transition is perturbed.

Experimental

The sample, whose preparation has been described elsewhere [4], contained, in addition to ^{15}N-pyrrole (96 per cent enriched) and TMS, a small amount of water and diethylether as impurity. The measurements were performed on a Varian HA-100 spectrometer, which was modified with a VKZ-4354-001 kit supplied by Varian. The frequency sweep spectra were recorded with the sweep velocity 0.4 Hz/sec. The field-frequency ratio was stabilized by locking to internal TMS. The lock frequency was produced by manual oscillator in the V-4354 unit. An external Hewlett-Packard 200 AB oscillator gave the observing frequency ω_1. Both the observing and the perturbing frequencies were measured with the V-4315 built-in frequency counter. The perturbing frequency was obtained from the sweep oscillator in the V-4354 A unit. The intensity of the field H_1 was adjusted just below the saturation level of the monitor line, the amplitude of the perturbing frequency being 0.4 – 0.6 mG. The temperature in the probe was +31 °C.

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Results

In the AA′BB′CX spectrum of ^{15}N-pyrrole there can be found four single lines suitable for the investigation of connected transitions and of the relative signs of the couplings J_{NH} by INDOR method. These lines (1 and 206) appear as the outer components of the NH quintuplets. The PMR spectrum can be treated as two AA′BB′C sub-spectra [2, 4] corresponding to the $+1/2$ and $-1/2$ spin values of the ^{15}N nucleus. The nitrogen-proton couplings are included in the effective Larmor frequencies

$$\nu_A^* = \nu_A \pm {}^3J_{NH}/2\,,$$
$$\nu_B^* = \nu_B \pm {}^2J_{NH}/2\,,$$
$$\nu_C^* = \nu_C \pm {}^1J_{NH}/2\,,$$

which replace the ordinary chemical shifts in the numerical calculations. Using the absolute values of the chemical shifts and of the couplings, produced by the previous sub-spectral analysis [4], the sub-spectra I and II (corresponding to the + and − signs in the formulas above) were calculated with the eight different combinations of signs for the couplings J_{NH}. The same [5] positive sign was used for all the proton-proton couplings in calculations, which were performed with the ABCDE 15-program [6] and an IBM 360/30 computer.

The transitions, which have a common energy level with the single lines 1 and 206 of the NH proton, have the same numbers in the sub-spectra calculated with the different alternatives of signs of the couplings J_{NH}. They are marked with thicker lines in Fig. 1, which shows the schematic energy level diagram of an AA′BB′C spin system and contains all the transitions whose intensity is >0.010 and which are calculated with the parameters produced by earlier sub-spectral analysis [4]. In Table 1 appear the frequencies of the connected transitions with line 1 in the lower-field NH quintuplet or with line 206 of the higher-field NH quintuplet. The frequencies were calculated with the different alternative signs of the couplings J_{NH}. This table shows that for both the NH lines a regressive and a progressive transition in the spectral parts of the CH$_\alpha$ and CH$_\beta$ protons is to be found.

The observed and calculated PMR spectra of ^{15}N-pyrrole together with the results of two INDOR experiments are shown in Fig. 2. The INDOR spectrum presented in Fig. 2 a is obtained by monitoring line number 1 in the lower-field NH quintuplet. In this spectrum the negative intensity changes appear at the positions of the lowest-field components of the CH$_\alpha$ and CH$_\beta$ protons. This confirms that these components include lines which are situated in the energy level diagram regressively relative to line 1. The comparison of the observed negative INDOR line positions to the calculated frequencies of the regressive lines 3 and 4, presented in Table 1, shows that it is only when all the couplings J_{NH} have the same sign that the negative INDOR signals appear at both the observed positions. The positive INDOR lines lie at the positions which also simultaneously correspond to the calculated frequencies of the progressive transitions 13 and 15. The frequencies of lines 208 and 209, calculated with the

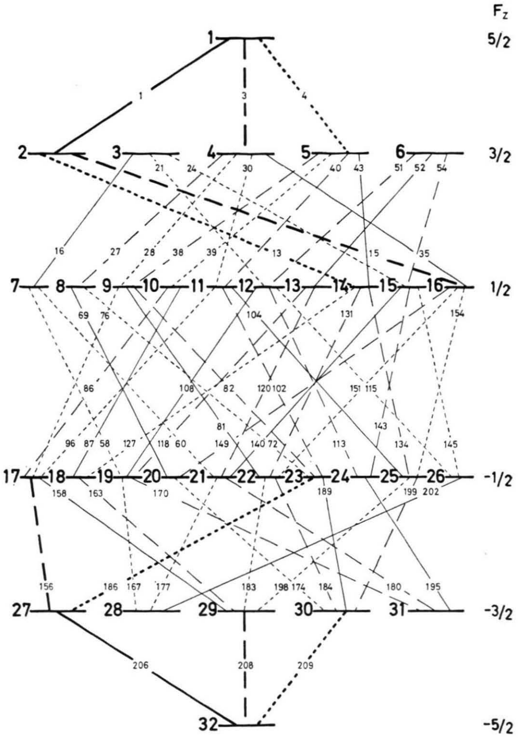

Fig. 1. The schematic energy level diagram of an AA′BB′C spin system containing all the transitions whose intensity is > 0.010 and which are calculated with the same signs of the couplings J_{NH}. Transitions belonging to the NH, CH$_\alpha$ and CH$_\beta$ protons are shown with ———, — — — —, and - - - - lines, respectively. The connected transitions studied are marked with thicker lines.

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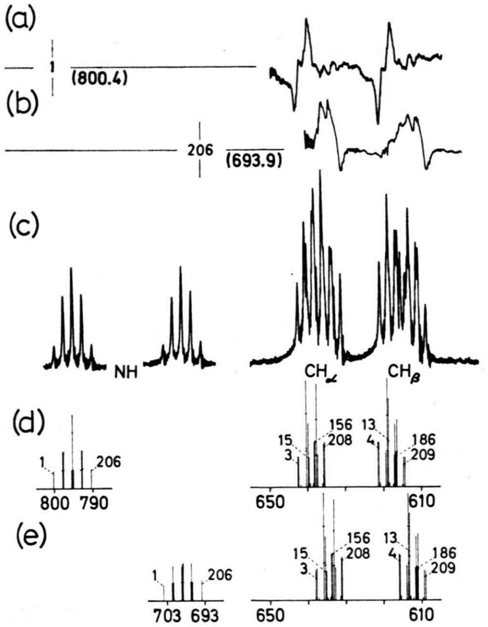

Fig. 2. INDOR spectrum of ^{15}N-pyrrole obtained by monitoring (a) line 1 at 800.4 Hz and (b) line 206 at 693.9 Hz from TMS at 100 MHz. (c) the normal frequency sweep PMR spectrum of ^{15}N-pyrrole. (d) and (e) the theoretical sub-spectra I and II calculated by assuming the same signs for all J_{NH}. The positions of the connected transitions of lines 1 and 206 are shown by line numbers.

J_{NH}'s having the same sign, correspond to the negative INDOR lines (in Fig. 2 b) observed when line 206 in the higher-field quintuplet is monitored. At the calculated positions of lines 156 and 186, which are progressive relative to line 206, appear positive INDOR signals.

The order of the transitions having a common energy level with lines 1 or 206, presented in Fig. 1, is confirmed by the observed INDOR spectra. They show, in accordance with the earlier double resonance experiments[2], that the couplings $^1J_{\mathrm{NH}}$, $^2J_{\mathrm{NH}}$, and $^3J_{\mathrm{NH}}$ in ^{15}N-pyrrole have the same signs. Using selective double resonance, GAGNAIRE et al.[7] have drawn the conclusion that the couplings $^1J_{\mathrm{NH}}$ and $^3J_{\mathrm{NH}}$ in di-t-butyl-2,5 ^{15}N-pyrrole also carry the same signs.

Table 1. The calculated and observed INDOR line frequencies for monitor lines 1 at 800.4 Hz (in the lower-field NH quintuplet) and 206 at 693.9 Hz (in the higher-field NH quintuplet).

Monitor line freq.	INDOR lines numb.	calculated frequency * − − − + + +	− + + + − −	− + − + − +	− − + + + −	observed freq.
1 800.4	3 r	642.4	637.9	637.9	642.4	642.2(−)
	4 r	621.0	615.6	621.0	615.7	620.6(−)
	13 p	618.6	613.2	618.5	613.2	617.6(+)
	15 p	639.8	635.3	635.4	639.8	638.8(+)
206 693.9	156 p	633.7	638.3	638.2	633.8	633.9(+)
	186 p	611.5	616.9	611.5	616.8	611.2(+)
	208 r	631.1	635.6	635.6	631.2	631.2(−)
	209 r	609.0	614.4	609.0	614.3	608.9(−)

r = regressive connected transition,
p = progressive connected transition,
(−) = negative INDOR line,
(+) = positive INDOR line,
* = signs of couplings J_{NH} in order $^1J_{\mathrm{NH}}$, $^2J_{\mathrm{NH}}$, and $^3J_{\mathrm{NH}}$.

Acknowledgements

The author wishes to thank the Neste Oy for the use of their Varian HA-100 spectrometer, and Mr. P. EENILÄ, M. A., and Mrs. M. JOKINEN (Research Center of Neste Oy, Kulloo) for skilfull assistance in the measurements. He is indebted to Prof. P. TUOMIKOSKI for discussions on the manuscript and to Mr. E. PÄÄKKÖNEN, M. A., for assistance with the English. This work has been financially supported by the National Research Council for Sciences.

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