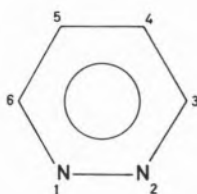


N. M. R. STUDIES OF NITROGEN CONTAINING MOLECULES.

II. The spectrum of pyridazine and approximate additivity of the nitrogen effect on the H-H coupling constants of azines.

The proton N. M. R. spectrum of pyridazine



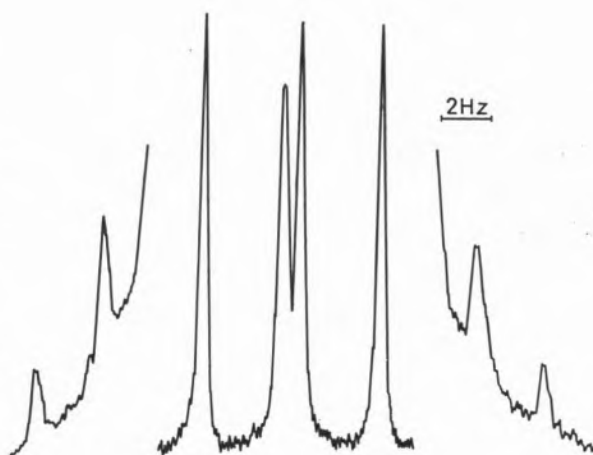
was firstly reported by TORI & OGATA (1). Because only four out of the twelve lines expected for each of the absorption signals arising from the 4,5-protons and the 3,6-protons were observed, values for the coupling constants had to be obtained from the spectra of ^{13}C containing molecules (natural abundance). However, these spectra were not well resolved and the analysis was incorrect (2). Better ^{13}C -H spectra were obtained and a more correct analysis was made by one of the authors (2). We now present a spectrum of pyridazine (pure liquid), recorded on a Varian HA-100 spectrometer, which shows the four weak previously undetected outer lines expected for the signals of 4,5- and 3,6-protons (Figure).

Several sweep-frequency spectra were run in both directions, and mean positions for the various lines computed. This mean spectrum was analyzed as an AA'BB' system yielding the following coupling constants:

$$\begin{aligned} J_{34} &= 5.07 \text{ Hz} \\ J_{35} &= 1.88 \\ J_{36} &= 1.38 \\ J_{45} &= 8.34 \end{aligned}$$

The estimated uncertainty is ± 0.02 Mz. These values agree, within the experimental error, with those previously reported, except for J_{45} which was quoted as 8.0 Hz (2). This difference was found to be due to a small error of calibration of one of the ^{13}C -H spectra.

The present values for the coupling constants are not only more reliable than those previously obtained but also do not involve any uncertainty on the relative signs. The analysis of the ^{13}C -H spectra leaves the sign of J_{36} uncertain; the present spectrum unambiguously shows that J_{36} has the same sign of the other coupling constants (positive). This is inferred from the position of the outer lines with respect to the more intense quartet lines. The positive sign for J_{36} is in accordance with an approximate additivity of the nitrogen effect on the proton coupling constants of azines, as is shown below.



Spectrum of the 4,5-protons of pyridazine.

Comparison of the H-H coupling constants of pyridine (3) and benzene (4) shows that replacement of a CH group by a N atom causes the following changes on the J_{HH} values: -2.68 (J_{23}), $+0.46$ (J_{24}), $+0.32$ (J_{25}), -1.51 (J_{26}), $+0.11$ (J_{34}), -0.01 (J_{35}). The coupling constants for benzene are: $J_{\text{ortho}} = 7.56$, $J_{\text{meta}} = 1.38$, $J_{\text{para}} = 0.68$. If we assume that, in diazines, the effect of each N atom is the same as in pyridine, then the J_{HH} values for those molecules will be as shown in the table.

	Calculated	Observed
Pyrimidine	$J_{24} = 0.33$	~ 0 (5)
	$J_{25} = 1.32$	1.5
	$J_{45} = 4.99$	5.0
	$J_{46} = 2.30$	2.5
Pyridazine	$J_{34} = 4.99$	5.07
	$J_{35} = 1.83$	1.88
	$J_{36} = 1.32$	1.38
	$J_{45} = 7.78$	8.34
Pyrazine	$J_{23} = 2.20$	~ 2.5
	$J_{25} = 1.32$	~ 1.5
	$J_{26} = 0.14$	~ -0.2

The approximate values quoted for pyrazine are deduced from the spectrum of methyl-pyrazine (6). The spectrum of pyrazine itself consists of a single line and its ^{13}C -H spectrum is difficult to analyze; the only information that has been possible to obtain from the latter (7) is

$$J_{23} + J_{25} + J_{26} = 3.7 \text{ Hz}$$

in agreement with the individual values quoted. The agreement between the calculated J_{HH} values for diazines and the experimental data is satisfactory.

ACKNOWLEDGEMENTS

The authors thank the Comissão de Estudos de Energia Nuclear of the Instituto de Alta Cultura, Portugal, for research grants.

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Recebido 19. Março. 1969

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