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DOI

[10.1016/0022-2860\(88\)80058-9](https://doi.org/10.1016/0022-2860(88)80058-9)

Publication date

1988

Published in

Journal of Molecular Structure

[Link to publication](#)

Citation for published version (APA):

Buma, W. J., Groenen, E. J. J., Schmidt, J., & de Beer, R. (1988). Electron Spin Echo spectroscopy of the photo-excited triplet state of pyridine. *Journal of Molecular Structure*, 173, 249-252. [https://doi.org/10.1016/0022-2860\(88\)80058-9](https://doi.org/10.1016/0022-2860(88)80058-9)

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ELECTRON SPIN ECHO SPECTROSCOPY OF THE PHOTO-EXCITED TRIPLET STATE OF PYRIDINE

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SUMMARY

Magnetic resonance experiments on the elusive triplet state of pyridine as a guest in a single crystal of benzene have been performed with the help of pulsed laser excitation and Electron Spin Echo techniques. From a study of the ^{14}N and ^2D hyperfine interactions it is concluded that the molecule is non-planar owing to pseudo Jahn-Teller coupling between the $^3\text{B}_1(\text{n}\pi^*)$ and the close lying $^3\text{A}_1(\pi\pi^*)$ states.

INTRODUCTION

The combination of pulsed, tunable dye lasers with Electron Spin Echo (ESE) techniques provides a powerful tool for studying short-lived photo-excited triplet states. In addition to the fact that the transient species often are too scarce for detection by cw EPR methods the ESE technique also exploits the strong spin polarization that accompanies laser flash excitation resulting from the spin-level selectivity of the intersystem crossing process. In addition ESE is an attractive method to study hyperfine interactions. The hyperfine splittings can be obtained either by applying an additional, pulsed rf field and observing the effect on the echo intensity or by Fourier Transform of the oscillatory pattern of the echo decay envelope. A great advantage of the latter method is that no resonant field is required and that the lack of an appreciable nuclear transition moment is not a limiting factor.

Here we illustrate the aspects of the laser flash/ESE method mentioned above, with a study on pyridine. For the first time it has been possible to perform a magnetic resonance study on the elusive triplet state of this molecule using these techniques.

RESULTS

The virtual absence of phosphorescence for pyridine has hampered the study of its lowest triplet state T_0 for a long time. By using ESE spectroscopy in combination with pulsed laser excitation we have been able to observe the magnetic resonance spectrum of T_0 of pyridine- d_5 in a benzene- d_6 host crystal at 1.2 K [1]. From the ESE signals the zero-field parameters were determined, the sublevel lifetimes and their relative populating rates. On the basis of these data it was concluded that T_0 of pyridine is a mixture of $n\pi^*$ and $\pi\pi^*$ character.

Interestingly, the ESE detected EPR spectrum shows the presence of two triplets with only slightly different zero-field splittings. This observation led us to the hypothesis that these two triplets, henceforth called A and B, might originate from two nuclear configurations belonging to two energy minima on the potential energy curve of T_0 . Since the hyperfine interaction is a sensitive measure of the local structure of a molecule we studied the dependence of the nitrogen and deuterium hyperfine splitting on the orientation of the magnetic field with respect to the pyridine molecule.

The nitrogen hyperfine splitting is found to be the same for A and B for all orientations of the magnetic field in the xy and yz planes (see fig. 1 for the definition of the axis system). However the orientational dependence in the zx-plane is clearly different for A and B. The maxima are displaced with respect to the z-axis, in opposite directions for A and B. A careful analysis [2] shows that the triplet pyridine molecule is deformed such that the nitrogen is tilted above (A) or below (B) the yz plane, this plane being the molecular plane corresponding to the planar ground state.

Fig.1. The axis system in pyridine.

Deuterium hyperfine interaction, much smaller than that due to nitrogen, does not lead to resolved structure in the EPR spectrum. The ESE technique, however, provides an alternative way to study such interactions because small interactions cause oscillations in the decay of the electron spin echo intensity as a function of the time between the excitation pulses. The corresponding spectrum shows the ENDOR frequencies. We have performed an orientation study of such two-pulse echo envelope modulation patterns. Since the decay of the echo signal occurs in a limited time interval we have applied maximum entropy analysis to these data instead of the conventional Fourier Transformation [3].

A complete description of the quantitative analysis of the deuterium ENDOR frequencies will be published in the near future. In the present context we only describe one result derived from those frequencies that we have recognized to correspond to the para deuterium atom. It appears that the principal directions of the hyperfine tensor of this particular atom are rotated in the zx plane, in opposite directions for the triplets A and B. This result clearly proves that pyridine is distorted in T_0 into a chair-like hexagon. Indicating the position of the nitrogen for triplet A as above the yz plane, the para deuterium is to be found below this plane. For triplet B the opposite situation occurs.

The next question that arises is how this conclusion is related to the hypothesis of a strong vibronic interaction. In C_{2v} symmetry the lowest triplet states of pyridine are $n\pi^*$ and $\pi\pi^*$ states of B_1 and A_1 orbital symmetry. Vibronic coupling therefore requires a b_1 vibrational mode. The observed deformation indeed is compatible with a change in geometry along a b_1 mode.

Finally we emphasize that ESE spectroscopy has enabled us to study the lowest triplet state of pyridine that remained in darkness for 25 years. The equilibrium geometry of pyridine in this state is found to correspond to a chair-like conformation. A complete description of the structure, based upon the data presented above and the analysis of the hyperfine and quadrupole interaction for the ortho and meta deuterium atoms is forthcoming.

ACKNOWLEDGEMENT

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) and by "de Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)" with financial aid from "de Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.)".

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