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PSEUDO-JAHN–TELLER DISTORTION OF PYRIDINE IN ITS LOWEST TRIPLET STATE

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We have performed an electron spin echo detected electron paramagnetic resonance study of the nitrogen hyperfine interaction in the lowest triplet state of pyridine. It is concluded that the molecule is non-planar in this state owing to pseudo-Jahn–Teller coupling between the $^3B_1(n\pi^*)$ and the close-lying $^3A_1(\pi\pi^*)$ states.

1. Introduction

Recently we reported the first magnetic resonance study of the lowest triplet state of pyridine present as a guest in a single crystal of benzene [1]. Interestingly, two kinds of triplets were observed, henceforth called A and B, with slightly different zero-field splittings and large differences in triplet sublevel lifetimes. We suggested that these triplets A and B might originate from a strong vibronic coupling between the two lowest triplet states of pyridine, causing a double minimum in the potential energy surface of the lowest triplet state along the active distortion coordinate. In this picture the two nuclear configurations belonging to the two energy minima become distinguishable in the benzene crystal as triplets A and B since they are frozen out in slightly different crystal fields. The observation of A and B offers an excellent opportunity to study the vibronic coupling between close-lying $n\pi^*$ and $\pi\pi^*$ states [2], because the lowest triplet state of pyridine was found to be an $n\pi^*$ state, most probably the $^3B_1$ state, considerably admixed with the close-lying $^3A_1(\pi\pi^*)$ state.

A way to investigate our hypothesis concerning the nature of the lowest triplet state of pyridine, and particularly our proposition of vibronic coupling, is to study the dependence of the nitrogen hyperfine splitting on the orientation of the magnetic field with respect to the molecule. For both A and B the spin axes coincide within experimental accuracy with the molecular symmetry axes of the undistorted planar molecule. If our hypothesis concerning the nature of A and B is correct, one would expect the orientational dependence of the nitrogen hyperfine interaction to be different for A and B as they correspond to two differently distorted nuclear configurations.

Electron spin echo (ESE) detected EPR spectroscopy enabled us to make a complete orientation study of the nitrogen hyperfine splitting in the two triplets A and B of pyridine-d_5 dissolved in benzene-d_6. Here we describe the results of this investigation which clearly show that pyridine in a benzene host crystal is non-planar in its lowest triplet state, the nitrogen atom being tilted out of the molecular plane as compared to the ground state.

2. Experimental procedure

The optical excitation was provided by the frequency-doubled output of a Quanta Ray PDL-1 dye laser, using sulforhodamine B as a dye, pumped by a Quanta Ray DCR-2 frequency-doubled Nd : YAG laser. With this laser system we obtained 5 mJ pulses at 290.9 nm (34373 cm^{-1}), the position of the 0–0 band of the $S_1 \leftarrow S_0$ transition of pyridine-d_5 in benzene-d_6. The

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laser operates at 10 Hz and triggers our X-band ESE spectrometer, which has already been described in detail [3]. Typical durations of the $\pi/2$ and π pulses are 50 and 100 ns, respectively, with a power of 20 to 40 W.

From our previous study it is known that pyridine occupies four magnetically inequivalent positions in the benzene crystal. Experiments were performed on only one of these sites. Unfortunately, EPR signals of the various sites and of the two triplets A and B overlap for certain orientations of the magnetic field. For this reason the deuterated sample was investigated because the width of the EPR lines in such a sample is much smaller than for the corresponding protonated sample.

Choosing different time intervals between the $\pi/2$ and π pulses proved to be a valuable tool in selectively suppressing EPR signals. This is due to a destructive interference caused by the hyperfine interactions with the deuterium nuclei [4]. In this way, we could measure the position of the resonance fields with an accuracy of at least 0.3 mT (3 G).

The pyridine-d_5/benzene-d_6 mixed crystal was prepared in the usual manner [1,5]. All hyperfine data were collected at 1.2 K from one sample.

3. Results and discussion

As a typical example of the nitrogen hyperfine splitting we show in fig. 1 an ESE detected EPR spectrum with the magnetic field along the z-axis. The orientational dependence of such hyperfine splittings for the triplets A and B was investigated by monitoring the EPR spectra with the magnetic field being rotated in three mutually orthogonal planes, the xy, yz and zx planes as defined in fig. 1. The high-field ESE signals kept a much better signal-to-noise ratio than the low-field signals when the magnetic field was rotated away from an extreme orientation. Consequently, in the zx plane the $m_S \approx 0$ to $m_S \approx +1$ transition was studied, in the xy plane the $m_S \approx 0$ to $m_S \approx -1$ transition, and in the yz plane the $m_S \approx 0$ to $m_S \approx +1$ transition around the z extreme and the $m_S \approx 0$ to $m_S \approx -1$ transition around the y extreme. Apart from some orientations for which only two peaks could be identified, the mean field difference between the three hyperfine peaks was taken as a measure of the nitrogen hyperfine splitting.

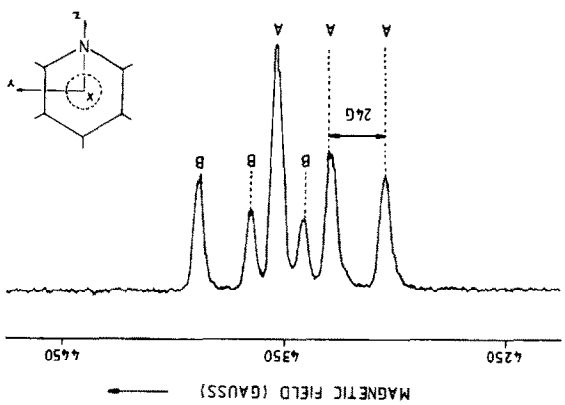

Fig. 1. The ^{14}N hyperfine structure of the high-field transition with $B_0 \| z$. The six peaks belong to the two triplet species A and B.

In fig. 2 we show the observed angular dependence of the nitrogen hyperfine splitting in the three planes for the two triplets A and B. As can be seen from this figure, there are certain regions where the hyperfine splitting could not be measured as a result of too large an overlap of signals from various sites and triplets or because the echo intensity decreased dramatically beyond the extremes, which was particularly the case in the yz plane. Fig. 2 shows that the orientational dependence of the hyperfine splitting for triplets A and B is the same in the xy and yz planes within the experimental accuracy. However, in the zx plane, A and B clearly behave differently. The maxima are displaced with respect to the yz plane, for A to the positive side and for B to the negative side.

These hyperfine data have been quantitatively analysed using the following spin Hamiltonian:

$$H_S = |\mu_e| B_0 \cdot \mathbf{g}_e \cdot S + S \cdot \mathbf{D} \cdot S + S \cdot \mathbf{A} \cdot I,$$

$$S = 1, \quad I = 1, \tag{1}$$

where the symbols have their usual meaning. In this model the nuclear Zeeman energy and the quadrupole term for the nitrogen have been neglected. This is justified because in the field region were we measured, the nuclear Zeeman energy is at most 1.5 MHz and the quadrupole splitting is of the same size [6,7]. This is an order of magnitude smaller than the measured hyperfine splittings, which vary between 15 and 70 MHz.

The hyperfine splitting in the $m_S \approx 0$ level, often negligible, turns out to reach values up to 3 MHz in the

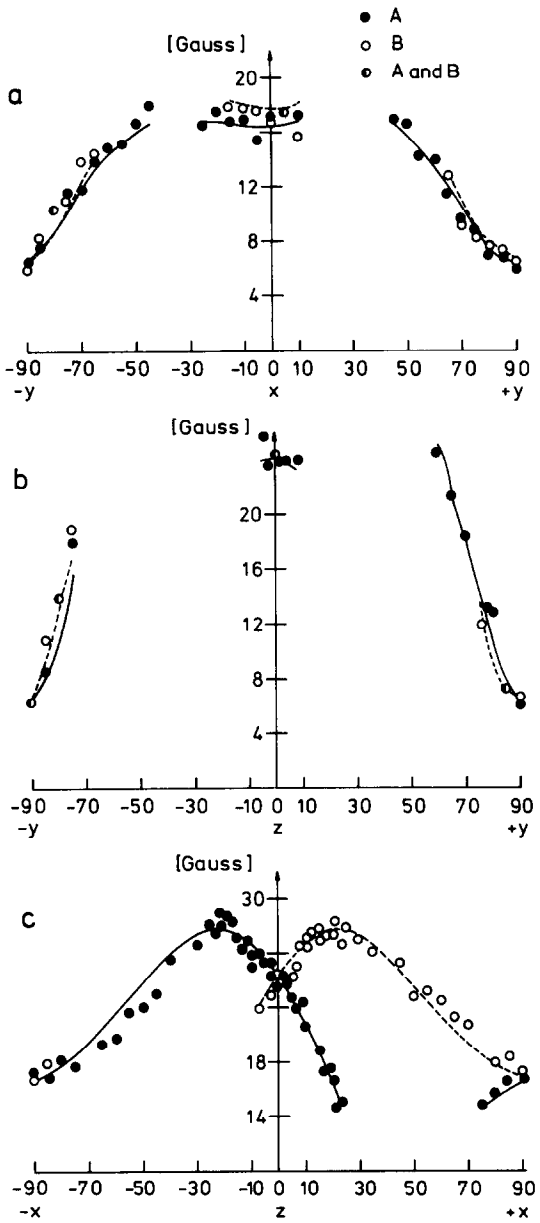

Fig. 2. Angular dependence of the nitrogen hyperfine splitting for a rotation of B_0 in (a) the xy plane, (b) the yz plane, and (c) the zx plane. The closed circles represent the measured splittings for triplet A, the open circles for triplet B. The drawn lines correspond to a fit according to eq. (1); full lines for A, dashed lines for B.

present case as a result of imperfect quantization of the electron spin along the external field. These splittings have to be taken explicitly into account, although experimentally we observe only three hyperfine lines for a certain electron spin transition. Each line is composed of three transitions from the three nuclear spin levels in $m_S \approx 0$ to one of the nuclear spin levels in $m_S \approx +1$ or -1. The position of the maximum of this line is determined by the relative contributions of these three transitions.

The values of $A_{\mu\nu}$ ($\mu,\nu = x,y,z$), assuming **A** to be symmetric, were iteratively determined from a non-linear least-squares fit of the experimental data to eq. (1). For each triplet the observed values of B_0 corresponding to all hyperfine lines for all orientations of B_0 served as the input data. Assuming an initial **A** matrix, for each value of B_0 a complete diagonalisation of (1) was performed which yielded nine energy eigenvalues. The transition energy corresponding to the hyperfine line at that value of B_0 was then calculated as the weighted sum of the transition energies belonging to the three transitions from the three nuclear spin levels in $m_S \approx 0$ to one of the nuclear spin levels in $m_S \approx +1$ or -1. The weight factors were taken proportional to the transition probability as derived from the transition moment operator $\boldsymbol{S} \cdot \boldsymbol{B}_1$ in which $\boldsymbol{B}_1$ is the applied microwave field. The transition energy obtained in this way was compared to the microwave frequency, which was fixed in the experiments. This procedure was repeated, adapting the **A** matrix, until the difference between the experimental and calculated values of the microwave frequency, squared and summed over all hyperfine lines corresponding to one triplet, was a minimum.

Both a six-parameter fit and a four-parameter fit with the constraints $A_{xy} = A_{yz} = 0$ were carried out. In the six-parameter fit, the values of A_{xy} and of A_{yz} turned out to be insignificant relative to their standard deviations. The **A** matrices, resulting from the four-parameter fit, are given in table 1. The A_{xz} elements are most noteworthy. They are of the same order of magnitude as the diagonal elements and have opposite sign for triplets A and B.

Table 1
Nitrogen hyperfine matrix elements of triplets A and B. Standard deviations are given in parentheses. Matrices are defined in the spin axes system

Triplet	A_{xx}/h (MHz)	A_{xz}/h (MHz)	A_{yy}/h (MHz)	A_{zz}/h (MHz)
A	41(2)	20(3)	18(3)	65(2)
B	37(5)	-19(5)	19(3)	67(4)

Finally, as an independent check, the hyperfine splittings for all orientations were calculated again from the final set of $A_{\mu\nu}$ values using the eigenfield algorithm of Belford [8]. The drawn lines in fig. 2 represent the hyperfine splittings calculated in this way. Although the relative signs of the matrix elements are unique, the absolute sign of the matrix cannot be determined from EPR experiments. Results of other nitrogen hyperfine studies suggest however that the signs are as given [6,7]. At first sight the standard deviations in the matrix elements may seem rather large. Even the largest one is however still within the accuracy of our field measurements.

The results described above indicate that pyridine is non-planar in its lowest triplet state. The observed rotation of the hyperfine axes in the zx plane with respect to the spin axes reveals that the triplets A and B correspond to pyridine molecules in which the nitrogen is tilted above and below the yz plane, respectively, as compared to the planar ground state. This distortion of pyridine must derive from a strong vibronic interaction within the triplet manifold. Our observation therefore allows a discussion of the electronic nature of the lowest triplet state and of the spectroscopic properties of pyridine.

From the EPR spectra and zero-field data, the lowest triplet state was suggested to have both $n\pi^*$ and $\pi\pi^*$ character [1]. The $\pi\pi^*$ state is the $^3A_1$ state, but quantum-chemical calculations showed some ambiguity as to the nature of the $n\pi^*$ state, being either the $^3B_1$ or the $^3A_2$ state [9]. The symmetry of the distortion indicates the vibronic coupling mode to have b_1 symmetry, which means that the lowest triplet state is a mixture of the $^3B_1(n\pi^*)$ and the $^3A_1(\pi\pi^*)$ states. Although the symmetry of the vibronically active mode is now well established as b_1, this still leaves several possibilities, from which the low-frequency "boat" vibration seems the most probable candidate [10].

Additionally, our results corroborate earlier speculations [10,11] that the extremely weak phosphorescence in the gas phase [11] could be accounted for by a rapid radiationless decay to the ground state owing to the so-called proximity effect [12]. According to this theory, the vibrational mode active in the coupling between close-lying $n\pi^*$ and $\pi\pi^*$ states acts as an efficient acceptor of vibronic energy, thereby enhancing the radiationless decay rate. Evidence for such effects has been found in the vibronic structure, polarisation and solvent dependence of phosphorescence [2,13]. For pyridine we observe an actual distortion of the molecule in its lowest triplet state which is a direct manifestation of a strong vibronic coupling. Pyridine thus clearly meets the requirements for the proximity effect to work, qualitatively accounting for the (virtual) absence of phosphorescence.

Finally, we emphasize that this nitrogen hyperfine study has shown the pyridine molecule to be non-planar in its lowest triplet state. We have determined the complete nitrogen hyperfine matrix, but are as yet not able to quantify the distortion, because the spin density distribution is unknown. To allow such a detailed description we are investigating the deuterium hyperfine interaction in the triplets A and B via electron spin echo envelope modulation spectroscopy.

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