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An electron spin-echo envelope modulation study of the lowest triplet state of pyridine- d_5 : Spin-density distribution and structure

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Recently we have shown that the lowest triplet state (T_0) of pyridine, incorporated in a single crystal of benzene, may be studied by electron spin-echo (ESE) spectroscopy. From the nitrogen hyperfine structure in the ESE detected electron paramagnetic resonance (EPR) spectra, we were able to conclude that pyridine, a planar molecule in the ground state, becomes nonplanar upon excitation into T_0 . Here we report the results of a detailed investigation of this distortion and of the electronic nature of the lowest triplet state of pyridine- d_5 . We have performed electron spin-echo envelope modulation (ESEEM) spectroscopy. From the modulation spectra, the electron-nuclear double resonance (ENDOR) frequencies corresponding to the various deuterium nuclei are obtained. Analysis of the dependence of these frequencies on the orientation of the magnetic field with respect to the triplet fine-structure axes system allows for a determination of the deuterium hyperfine and quadrupole tensors. From these tensors and the known nitrogen hyperfine tensor, the structure and spin-density distribution of pyridine in its lowest triplet state are deduced. Pyridine adopts upon excitation into T_0 a boatlike structure, in which the nitrogen atom is tilted by about 40° with respect to the plane through the ortho- and meta-carbon atoms and the para-carbon/para-deuterium fragment by about 10° with respect to this plane. Thereby the hybridization of the ortho-carbon atomic orbitals strongly deviates from that for aromatic hydrocarbons and becomes almost sp^3 ; the hybridization of the atomic orbitals on the other carbon atoms changes much less, while the nitrogen atomic orbitals remain sp^2 hybridized. Approximately half of the spin density is found to be localized on the nitrogen atom with a remarkable distribution over the atomic orbitals: the π orbital carries 40%, the n orbital 10%. The rest of the spin density is distributed over the para- (30%) and ortho-carbon atoms (10% each). The lowest triplet state of pyridine is neither an $n\pi^*$ state nor a $\pi\pi^*$ state, but a state of mixed character as the result of a strong vibronic coupling between the 3B_1 ($n\pi^*$) and 3A_1 ($\pi\pi^*$) states.

I. INTRODUCTION

Pyridine may be considered the prima donna among the aza-aromatic molecules. These molecules differ from their hydrocarbon analogs by the presence of one or more nitrogen atoms in the conjugated system. A nitrogen atom introduces a fairly localized lone-pair orbital with an energy of the same order of magnitude as that of the delocalized π orbitals. Consequently, the lowest triplet state of aza-aromatic molecules need not necessarily be of $\pi\pi^*$ character; it may as well be an $n\pi^*$ state, or there may be states of $n\pi^*$ and $\pi\pi^*$ character so close in energy that they couple vibronically to a lowest triplet state that no longer can be described as an $n\pi^*$ or a $\pi\pi^*$ state.

To study the lowest triplet state of aza-aromatic molecules, optical techniques have commonly been used. More recently transient electron paramagnetic resonance (EPR) has successfully been applied to investigate those aza aromatics that show little or no emission from the lowest triplet

state. From such studies in a magnetic field and in zero field, detailed knowledge has been obtained for many triplet states regarding the magnitude of the zero field splittings, the ordering of the triplet spin sublevels, and the populating and decay rates of these sublevels. Triplet states of aza-aromatic molecules are therefore among the best characterized triplet states of heterocyclic compounds.¹ Nevertheless, even for those molecules, only limited knowledge exists of the spin-density distribution and the structure in the lowest triplet state. It is just these properties we will be concerned with for pyridine.

Spin densities have been obtained from hyperfine structure in EPR spectra. For many aza-aromatic molecules with a lowest triplet state of $\pi\pi^*$ character, proton splittings of the EPR lines have been observed (quinoline,² isoquinoline,² quinoxaline,^{3,4} 1,5-,⁵ 1,6-,⁶ and 1,8-naphthyridine,⁷ acridine,⁸ phenazine⁹). A crude determination of the spin-density distribution subsequently has been made on the basis of the observed hyperfine couplings along one or more of the prin-

principal axes of the zero field splitting tensor by consideration of the anisotropic contribution to these splittings. Information concerning the spin density in the π orbital of the nitrogen nucleus, the more interesting nucleus in aza-aromatic systems, is however limited for $\pi\pi^*$ triplet states. The EPR spectra only showed resolved hyperfine structure owing to the nitrogen nuclear spin when the magnetic field was directed normal to the molecular plane. Consequently, in general not more than one diagonal element of the nitrogen hyperfine tensor could be determined. A more complete picture has been obtained for free-base porphyrin¹⁰ and acridine¹¹ by the use of electron spin-echo envelope modulation (ESEEM) spectroscopy. In this way also the off-diagonal elements of the nitrogen hyperfine tensor could be measured for free-base porphyrin. For acridine- d_9 , on the other hand, the diagonal elements of the hyperfine tensors of the deuterium atoms could be obtained as well, enabling a more accurate determination of the spin-density distribution than had been possible before.

The EPR spectra of triplet states of aza-aromatic molecules of $n\pi^*$ or mixed $n\pi^*$ and $\pi\pi^*$ character showed considerable nitrogen hyperfine splitting along more than one of the principal axes of the fine-structure tensor (pyridazine,¹² pyrimidine,¹³ pyrazine,¹⁴ phthalazine,^{15,16} and 9,10-diazaphenanthrene^{17,18}). Though these splittings for some cases seem to have been consistently interpreted with spin-density distributions obtained from intermediate neglect of differential overlap (INDO) calculations,^{12,15,16,18} an experimental determination of the complete spin-density distribution has not been reported as yet.

Knowledge about structural changes upon excitation into the lowest triplet state is even more scarce for aza-aromatic compounds. For many such molecules, significant structural changes have been hypothesized, in connection with the vibronic coupling between close-lying $n\pi^*$ and $\pi\pi^*$ states. Evidence for the importance of such a vibronic coupling has been deduced from the study of the radiationless decay to the ground state and of the vibronic structure, the polarization, and the solvent dependence of the phosphorescence (pyrazine, pyridazine, 1,2-diazanaphthalene, 2,3-diazanaphthalene, 9,10-diazaphenanthrene).^{12,15,16,18,19} More direct observations concerning the structure in the lowest triplet state are, however, missing as yet.

For pyridine, a lot of effort has been put to the study of its triplet state. Despite all these attempts, the nature of the lowest triplet state T_0 remained a puzzle for many years, mainly because optical transitions to and from this state were nearly undetectable. Evans reported in 1957 the first observation of absorption corresponding to the transition to the lowest triplet state and assigned this state as the 3A_1 state of $\pi\pi^*$ character,²⁰ an assignment that was supported later by Japar and Ramsay's long-pathlength absorption spectrum.²¹ On the other hand, Hoover and Kasha suggested on the basis of studies of the lowest triplet state of substituted pyridines that the lowest triplet state of pyridine should be the 3A_2 state of $n\pi^*$ character.²² Subsequently, it was realized that the apparent absence of phosphorescence could be the result of a vibronic coupling between the 3A_1 ($\pi\pi^*$) and the 3B_1 ($n\pi^*$) states.²³ Such an explanation was supported

by transient absorption studies²⁴ of pyridine vapor that pointed to a fast nonradiative $T_0 \rightarrow S_0$ decay. At nearly the same time, the first observation of phosphorescence of pyridine in the vapor phase at room temperature was reported.²⁵ The quantum yield of this emission was found to be very low indeed ($\sim 10^{-6}$) and the spectrum broad and without structure.²⁶ Together with the reported lifetime ($\sim \mu\text{s}$) these observations corroborated the idea that the lowest triplet state of pyridine could very well be a mixture of an $n\pi^*$ and a $\pi\pi^*$ state.

A breakthrough in the characterization of the lowest triplet state of pyridine came some years ago when we combined electron spin-echo (ESE) spectroscopy with pulsed laser excitation.²⁷ Microwave transitions between the electron spin sublevels of T_0 of pyridine- d_5 , present as a guest in a single crystal of benzene- d_6 , were detected in magnetic field as well as in zero field. The observed energy splitting and ordering of the triplet spin sublevels seemed to indicate a $\pi\pi^*$ character of T_0 , while the magnitude of the nitrogen hyperfine splitting of the EPR lines seemed to be more in line with an $n\pi^*$ state. Most intriguing in this respect was the observation of two distinct triplet species, labeled triplet *A* and triplet *B*. We suggested that these two triplets could be the result of a vibronic coupling between the 3B_1 ($n\pi^*$) state and the 3A_1 ($\pi\pi^*$) state. If strong enough, such a vibronic coupling would result in a double minimum potential energy surface of the lowest triplet state along a distortion coordinate.²⁸ Triplets *A* and *B* were thought to correspond to nuclear configurations belonging to the two energy minima. If this claim could be proved, triplets *A* and *B* would be no less than a direct manifestation of the mixed character of T_0 .

The ESE study in magnetic field²⁷ revealed nitrogen hyperfine splitting of the EPR lines and deep modulations of the echo decay envelope, the latter being indicative of deuterium hyperfine and quadrupole coupling. It was realized that a systematic study of these nitrogen and deuterium interactions might allow for a test of the above hypothesis and, ultimately, even for a determination of the structure and the spin-density distribution of pyridine in T_0 .

The first step on this route consisted of the study of the dependence of the nitrogen hyperfine splitting in the ESE detected EPR spectra on the direction of the magnetic field with respect to the crystal.²⁹ From this study, we obtained the complete hyperfine tensor of the nitrogen atom for both triplet *A* and triplet *B*. The principal axes of both tensors were found not to coincide with the principal axes of the fine-structure tensor. This proved on symmetry grounds that the pyridine molecule in the lowest triplet state can no longer be a planar molecule of C_{2v} symmetry as it is in the ground state. Additionally, comparison of the hyperfine tensors of the nitrogen atom for triplet *A* and triplet *B* supported the idea that *A* and *B* correspond to nuclear configurations distorted with respect to the ground state along the same coordinate, but in opposite sense.

The present paper concerns the second and final step necessary to allow for a complete determination of the spin-density distribution and the molecular structure of pyridine- d_5 in the lowest triplet state. It is based upon the study of the deuterium hyperfine and quadrupole interactions. As we

have mentioned above, the echo decay envelope for pyridine- d_5 present as a guest in a single crystal of benzene- d_6 shows deep modulations, which are indicative of such interactions.³⁰ From a study of these echo decay envelope modulations as a function of the direction of the magnetic field with respect to the crystal, we obtain the hyperfine and quadrupole tensors. Subsequently, it will be shown that particular features of the structural change of pyridine upon excitation into the lowest triplet state can be inferred from a consideration of the tensors of the individual deuterium nuclei. We then combine these tensors with the previously determined hyperfine tensor of the nitrogen nucleus in a model for the whole pyridine- d_5 molecule and in this way find the complete spin-density distribution and geometry of pyridine in its lowest triplet state.

The spin-density distribution shows that almost half of the spin density is localized on the nitrogen atom. In contrast to common expectations for $n\pi^*$ states, the lone-pair orbital carries significantly less spin density than the π orbital on nitrogen. The other half of the spin density is distributed such that the para-carbon atom carries 30% spin density and the two ortho-carbon atoms 10% each. The structure of pyridine in the lowest triplet state is found to be far from planar. The largest distortion occurs at the ortho-carbon atoms. The nitrogen atom is tilted with respect to the plane defined by the ortho- and meta-carbon atoms by about 40° . The atomic orbitals on the ortho-carbon atoms are almost completely rehybridized from sp^2 to sp^3 , while the nitrogen atom remains sp^2 hybridized. This distortion of pyridine upon excitation into T_0 is found to be intrinsic in nature and not induced by the crystal field.

II. EXPERIMENTAL

The pyridine- d_5 /benzene- d_6 mixed crystal was prepared in the usual manner.³¹ All experiments were performed at 1.2 K.

The optical excitation of pyridine- d_5 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 ($34\,373\text{ cm}^{-1}$), the position of the 0-0 band of the $S_1 \leftarrow S_0$ transition of pyridine- d_5 in benzene- d_6 . The laser, operating at 10 Hz, triggers our X-band ESE spectrometer. This spectrometer has already been described in detail before.³²

In ESEEM spectroscopy, two kinds of pulse sequences are commonly used: a two-pulse ($\pi/2-\pi$) and a three-pulse ($\pi/2-\pi/2-\pi/2$) sequence.³⁰ For the two-pulse experiment, the echo height is monitored as a function of the time τ between the first and the second pulse, while for the three-pulse experiment the modulation pattern is obtained as a function of the time T between the second and the third pulse. For the present study of pyridine- d_5 we predominantly made use of two-pulse echoes, while for some selected orientations of the magnetic field, three-pulse experiments were performed as well. This strategy resulted from the following considerations.

(i) Our previous experiments had shown that the sam-

ple photodegradates in the course of time. Consequently the time that we could perform measurements on one crystal was limited to about 200 h. Two-pulse ESEEM spectroscopy has the advantage, as compared to the three-pulse experiment, that the echo is larger for a given value of τ . Therefore, the two-pulse echo enables a faster determination of the modulation patterns with a signal-to-noise ratio (SNR) large enough to allow for a useful transformation into the frequency domain (cf., the next section). The modulation of the echo decay in general has been measured for $700\text{ ns} \leq \tau \leq 10.94\text{ }\mu\text{s}$ in 512 steps of 20 ns.

(ii) The modulation pattern of a two-pulse echo contains, apart from the fundamental frequencies associated with the energy differences between the hyperfine levels, also the sums and differences of those fundamental frequencies.³⁰ On the other hand, in the three-pulse echo modulation experiment, these sum and difference frequencies are absent, but here one has to deal with the "suppression effect": for a given value of τ fundamental frequencies may be suppressed as well. Three-pulse echo experiments have been performed in some cases in order to verify the assignment of frequencies, as obtained from the two-pulse echo decay envelope, as fundamental ones. Those three-pulse echo patterns have been recorded for several values of τ in order not to miss any of the fundamental frequencies.

The benzene crystal has four molecules in the unit cell. As is known from our previous studies, pyridine may occupy each of these four sites. Of those sites only one has been studied. We have recorded the modulation patterns for the triplets A and B at this site for a large number of orientations of the magnetic field $\mathbf{B}_0$ in the three principal planes of the fine-structure tensor, the $x'y'$, $y'z'$, and $z'x'$ planes. The modulation experiments have been performed on both the high-field as well as the low-field EPR line.

It did not prove possible to measure the modulation patterns for every orientation of $\mathbf{B}_0$ in the three planes mentioned above. This was mainly due to the overlap of the signals of the eight EPR lines resulting from two distinguishable triplet species in each of the four sites. Also, in the $y'z'$ plane, the intensity of the EPR signal turned out to decrease dramatically when $\mathbf{B}_0$ was rotated away from either the y' or the z' principal axis.

III. TREATMENT OF THE DATA

For the transformation of a time domain signal to the frequency domain, commonly a fast Fourier transform (FFT) is used. As indicated before, we have recorded the modulations of the echo decay envelope only for $10\text{ }\mu\text{s}$, which corresponds to a truncation of the time domain signal (cf., $T_2 \sim 10\text{ }\mu\text{s}$). Application of the FFT would then lead to a poor spectral resolution. The modulation patterns have therefore been transformed into the frequency domain using the maximum entropy method (MEM) as developed by Burg³³ and introduced into the analysis of ESEEM data by van Ormondt *et al.*³⁴ If the MEM is used, a truncation of the time domain signal has no effect on the frequency resolution. As an example, we show in Fig. 1(a) a modulation pattern recorded for triplet A and a certain orientation of $\mathbf{B}_0$. In Figs.

1(b) and 1(c) are shown the frequency domain spectra obtained by the MEM and the FFT, respectively. It is observed that the use of the MEM not only enhances the spectral resolution, but also results in a higher SNR.

After correction for the exponential background decay of the echo, the modulation patterns were transformed with a so-called Burg order of 260,³³ which is approximately half of the number of data points (512). A peak in the frequency spectrum generated in this way was considered true if its intensity was larger than 1% of the peak with the largest intensity. The Burg method may give rise to distortions in the relative intensities of the peaks and may generate spurious signals in the frequency spectrum.³³ Several trial runs

FIG. 1. (a) Modulation of the two-pulse electron spin echo envelope for the high-field transition of triplet *A* for B_0 in the $x'y'$ plane with $\angle(B_0, x') = 60^\circ$. (b) Frequency spectrum obtained using the maximum entropy method. (c) Frequency spectrum obtained using the fast Fourier transform method.

were made to obtain the optimum Burg order and the peaks in the frequency spectrum generated by the MEM were always checked against the intensity of the (much less-resolved) peaks in the corresponding frequency region of the FFT spectrum.

In pyridine- d_5 for most orientations of B_0 we have to deal with five magnetically inequivalent deuterium atoms. Each deuterium ($I = 1$) causes a splitting of every electron spin state into three nuclear spin sublevels. Consequently we expect for a general orientation of B_0 30 fundamental frequencies: 5×3 frequencies deriving from the $m_s \approx 0$ level and 5×3 frequencies deriving from the $m_s \approx +1$ or -1 level. Apart from those fundamental frequencies, the two-pulse echo modulation pattern also contains the sums and differences. Though the fundamental frequencies are of larger intensity than the combination frequencies, the presence of the latter makes it difficult to unravel the frequency spectra. Therefore we looked in the first instance for traces involving the most intense peaks in the plots of the frequencies vs the orientation of B_0 . With those frequencies, the sums and differences were calculated and looked for in the spectra. If other traces of lesser intensity could be recovered by such an assignment, the principal traces were kept. In this way most of the observed frequencies ($>90\%$) could be interpreted. As a typical example, we present in Fig. 2(a) all the measured frequencies and the intensities of the corresponding peaks in the frequency spectra for the $m_s \approx 0 \leftrightarrow m_s \approx -1$ transition of triplet *A* and B_0 in the $z'x'$ plane. An analysis of this plane showed that almost all of these frequencies derive from six fundamental traces belonging to the para-deuterium atom. If these fundamental frequencies and their combinations are removed from the plot, Fig. 2(b) is generated. In this figure, only very few unexplained frequencies remain, nearly all of them corresponding to low-intensity peaks in the spectrum.

For some orientations it proved possible to assign frequencies directly to the sum and difference of two fundamental frequencies on the basis of their phase factors. The combination frequencies of two fundamental frequencies are known to have phase factors that differ by 180° .³⁰ As a final check, the assignment of the fundamental traces was confirmed by performing three-pulse echo experiments in some selected orientations.

A full analysis of the data resulted in fundamental traces corresponding to the various deuterium atoms. All traces in each of the three fine-structure principal planes belonging to one deuterium have together been fitted to the following spin Hamiltonian:

$$\hat{\mathcal{H}} = -g_D\beta_n B_0 \cdot \hat{\mathbf{I}} + \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{I}} + \hat{\mathbf{I}} \cdot \mathbf{P} \cdot \hat{\mathbf{I}}, \quad S = 1, \quad I = 1. \quad (1)$$

For the evaluation of this spin Hamiltonian, the expectation values of the electron spin angular momentum operator $\hat{\mathbf{S}}$ need to be calculated. Depending upon the trace under consideration, this concerns the expectation values in the $m_s \approx +1$, $m_s \approx 0$, or $m_s \approx -1$ state. These have been calculated from the electron spin Hamiltonian parameters of triplet *A* or *B* as they have been obtained before,²⁷ and the measured strength and orientation of B_0 . Thereupon, the

FIG. 2. (a) Measured frequencies for the $m_s \approx 0 \leftrightarrow m_s \approx -1$ transition of triplet *A* for B_0 in the $z'x'$ plane. Frequencies are labeled according to their intensity relative to the frequency of largest intensity for a given orientation: $\square$ 100%–75%; $\triangle$ 74%–50%; $\circ$ 49%–25%; $\bullet$ 24%–1%. (b) Remaining frequencies after removal of principal frequencies and sums and differences corresponding to the para-deuterium atom [cf. Fig. 4(c)].

elements of the hyperfine (*A*) and quadrupole (*P*) tensors were calculated by a nonlinear least-squares fit of the modulation frequencies to Eq. (1). In doing so, the modulation frequencies were given a weight factor. This weight factor was determined on the one hand by the intensity of the peak in the frequency spectrum and on the other hand by the extent to which for a certain orientation of B_0 combination frequencies of these fundamental frequencies were observed. In the fit, the hyperfine tensor was assumed to be symmetric, while for the quadrupole tensor only five elements were fitted because it is a traceless and symmetric tensor.

IV. RESULTS

In the following, a number of axes systems are used, which for reasons of clarity are defined here: The axes *x*, *y*, and *z* refer to the molecular symmetry axes of pyridine in the planar ground state (see Fig. 3); the axes x' , y' , and z' to the principal axes of the fine-structure tensor, while doubly primed axes x'' , y'' , and z'' refer to the principal axes of the hyperfine tensor of a nucleus under consideration.

In Fig. 4, we show for triplet *A* and for triplet *B* the fundamental traces which have been identified as originating from the para-deuterium atom of pyridine- d_5 . For this deuterium atom, traces deriving from the $m_s \approx 0 \leftrightarrow m_s \approx -1$ transition could be found in all the fine-structure principal planes. The curves in this figure are the result of a fit as described above. We note that both the measured and the calculated traces show deviations from the commonly observed sinusoidal shape, in particular in the $z'x'$ plane. This is caused by two factors. First, under the present experimental conditions, we are not in the high-field limit. Consequently, the expectation values of the electron spin angular momentum in the triplet sublevels deviate from +1, 0, and -1 and its components in the $x'y'z'$ axis system do not vary sinusoidally upon a rotation of the magnetic field in a fine-structure plane, in particular for the $m_s \approx 0$ level. Secondly, there is an experimental factor that is responsible for the smaller wiggles in the traces. Since for many orientations of the magnetic field the EPR lines of different sites and/or different trip-

FIG. 3. Pyridine- d_5 and the molecular axes system xyz .

FIG. 4. Angular dependence of the ENDOR frequencies of the para-deuterium atom for the $m_s \approx 0 \leftrightarrow m_s \approx -1$ transition of triplet *A* and *B*. In (a) B_0 is rotated in the $x'y'$ plane, in (b) in the $y'z'$ plane, and in (c) in the $z'x'$ plane. Closed and open circles represent the frequencies deriving from the $m_s \approx 0$ level and $m_s \approx -1$ level, respectively. The drawn lines result from a fit according to Eq. (1) corresponding to the para-deuterium hyperfine and quadrupole tensors in Table I; dashed lines for $m_s \approx 0$, solid lines for $m_s \approx -1$.

let species happened to overlap, we were often forced to switch from one nitrogen hyperfine line to another upon changing the direction of $\mathbf{B}_0$ in order to have a "free" line.

For the $m_s \approx -1$ level, the angular dependence of the ENDOR frequencies in the $z'x'$ plane clearly differs from that observed in the $x'y'$ and $y'z'$ planes. Neither for triplet *A*, nor for triplet *B* do the orientations, for which the ENDOR frequencies are extreme, coincide with the z' (x') direction. In addition, the traces for *A* and the traces for *B* are approximately mirror symmetric, the $y'z'$ plane being the mirror.

The extremes of the hyperfine interaction are displaced from x' and z' for triplet *A* by $+8^\circ$ and for triplet *B* by -8° .

The fits of the para-deuterium traces according to Eq. (1) lead to the tensors *A* and *P* as given in Table I. In first instance, all six elements of *A* and all five elements of *P* were fitted. These initial calculations showed that the $x'y'$ and $y'z'$ elements of both *A* and *P* were smaller than their standard deviation. Consequently, these elements were put to zero in subsequent fits. This means that the y'' axis of the para-deuterium tensor, both for triplet *A* and for triplet *B*, is found to

TABLE I. Values in kHz of the elements of the hyperfine (*A*) and quadrupole (*P*) tensors of the deuterium nuclei present in pyridine- d_5 for triplet *A* and triplet *B*. In the hyperfine tensors of the ortho- and meta-deuterium atoms, the upper sign of A_{xy} holds for D_0 and D_m , the lower sign for $D_{o'}$ and $D_{m'}$ (see Fig. 3). The value of P_{zz}/h has been determined from $(P_{xx}/h + P_{yy}/h + P_{zz}/h) = 0$. The values in parentheses give the standard deviation in the value of the element.

Deuterium	A_{xx}/h	A_{xy}/h	A_{yy}/h	A_{zx}/h	A_{yz}/h	A_{zz}/h	Triplet
Para	-2428(5)	0	-4135(3)	-235(7)	0	-750(4)	<i>A</i>
	-2451(7)	0	-4159(5)	228(14)	0	-767(13)	<i>B</i>
Meta	-440(33)	$\pm 120(60)$	835(34)	...	...	...	<i>A</i>
Ortho	1834(37)	$\mp 424(40)$	3359(26)	-141(11)	...	1475(16)	<i>A</i>
	1669(42)	...	...	79(34)	...	1402(54)	<i>B</i>
Deuterium	P_{xx}/h	P_{xy}/h	P_{yy}/h	P_{zx}/h	P_{yz}/h	P_{zz}/h	Triplet
Para	$\pm 53(2)$	0	$\pm 53(2)$	$\pm 6(3)$	0	∓ 106	<i>A</i>
	$\pm 57(4)$	0	$\pm 58(3)$	$\pm 5(3)$	0	∓ 115	<i>B</i>

coincide with the fine-structure y' axis. In addition, from these initial calculations the frequencies occurring in the $m_s \approx 0 \leftrightarrow m_s \approx +1$ transition could be predicted. Thereupon we were able to assign frequencies present in the ESEEM spectra of this transition to the para-deuterium atom. These frequencies were added in subsequent fits with the appropriate weights. The final results, given in Table I, derive from the calculation in which the $x'x'$, $y'y'$, $z'x'$, and $z'z'$ elements of **A** and **P** were fitted to the data measured for both transitions. The $A_{zx'}$ and $P_{zx'}$ elements clearly differ from zero, which confirms that indeed the principal axes of both the hyperfine and the quadrupole tensor of the para-deuterium in the fine-structure $z'x'$ plane are rotated with respect to the z' and x' axes.

The assignment of the frequencies belonging to the two meta-deuterium atoms is not as clear cut as for the para-deuterium atom. In the frequency spectra deriving from the $m_s \approx 0 \leftrightarrow m_s \approx -1$ transition, no indications were found for traces belonging to these atoms. For the $m_s \approx 0 \leftrightarrow m_s \approx +1$ transition, three-pulse echo experiments showed in which frequency region the six ENDOR frequencies for each of the two meta-deuterium atoms are situated. Inspection of the frequency spectra obtained with the two-pulse echo experiments revealed in these regions only broad peaks, which for the larger part could not definitely be assigned as deriving from the meta-deuterium atoms. Moreover, the frequency

spectra in the $z'x'$ plane are dominated for this transition by the frequencies of the ortho-deuterium atoms (*vide infra*), which forced us to consider only the $x'y'$ plane.

In Fig. 5 traces belonging to the meta-deuterium atoms of triplet **A** for the $m_s \approx 0 \leftrightarrow m_s \approx +1$ transition in the $x'y'$ plane are shown. For triplet **B**, the corresponding traces could not be found. The frequencies for triplet **A** have been taken as the maximum of those broad lines mentioned above that could uniquely be identified as originating from one of the two meta-deuterium atoms, though it is not known from which of the two. On this basis, the $A_{xy'}$ element was not determinable, but the $A_{xx'}$ and $A_{yy'}$ elements could be obtained. Subsequently, an estimate of the $A_{xy'}$ element was made by the use of the data of the three-pulse echo experiments. The resulting $A_{xx'}$, $A_{xy'}$, and $A_{yy'}$ elements are given in Table I.

In Fig. 6, we show the traces which we have assigned to the two ortho-deuterium atoms. These traces derive from the $m_s \approx 0 \leftrightarrow m_s \approx +1$ transition. For triplet **A**, we have identified traces in both the $x'y'$ and the $z'x'$ plane. For triplet **B** traces have been identified in the $z'x'$ plane. Though the frequencies in the $z'x'$ plane [Fig. 6(a)] seem at first sight to point to one deuterium, the frequencies of triplet **A** in the $x'y'$ plane [Fig. 6(b)] clearly prove that we actually have to do with the two deuterium atoms. The traces of these two atoms in the $x'y'$ plane are mirror symmetric with respect to the x' axis. We have to conclude that the two ortho-deuterium atoms are equivalent apart from being at opposite sites of the $z'x'$ plane. For orientations near the y' axis, the frequencies of only one deuterium atom seem to be present. This is due to the same phenomenon as observed for the meta-deuterium atoms, namely that for these orientations, only broad peaks have been observed. For the ortho-deuterium atoms, we have been able to obtain an accurate value for the $A_{xy'}$ element, since the traces do show two ortho-deuterium atoms for orientations around the x' axis in the $x'y'$ plane. In summary, the data points of Fig. 6(b) around the y' axis have been used to determine the $A_{yy'}$ element, while $A_{xy'}$ has been primarily determined from the data near the x' axis.

The result of the fit of the traces in Fig. 6 to Eq. (1) is given in Table I. For triplet **A** we had initially hoped to obtain at least part of the **P** tensor for these deuteriums. Trial runs indicated, however, that the elements of this tensor were too dependent on the value of the A_{yz} and P_{yz} elements which in second order are important in the $x'y'$ and $x'z'$ planes. Due to the fact that the traces have not been identified in all the three planes, it proved only possible to determine the **A** tensor, with the exception of the A_{yz} element, and not the **P** tensor. For triplet **B**, we have found the $x'x'$, $z'x'$, and $z'z'$ elements of the hyperfine tensor. Since for neither triplet a quadrupole tensor could be obtained, the fits indicated by the lines in Fig. 6 do not reproduce the, experimentally observed, quadrupole splitting.

V. THE STRUCTURE AND SPIN-DENSITY DISTRIBUTION OF PYRIDINE- d_5 IN THE LOWEST TRIPLET STATE

In this section, we deduce the structure and spin-density distribution of pyridine in its lowest triplet state from an

FIG. 5. Angular dependence of the ENDOR frequencies of the meta-deuterium atoms for the $m_s \approx 0 \leftrightarrow m_s \approx +1$ transition of triplet **A**. B_0 is rotated in $x'y'$ plane. The circles represent the frequencies deriving from the $m_s \approx +1$ level. For reasons of clarity, the fit of the frequencies, represented by the solid line and corresponding to the hyperfine tensor in Table I, has been drawn only for meta-deuterium atom D_m (see Fig. 3).

analysis of the deuterium tensors obtained in the previous section and the hyperfine tensor of the nitrogen nucleus reported previously.²⁹ We first examine the hyperfine and quadrupole tensors of the individual deuterium atoms. In this way, we gain insight into some characteristic features of pyridine in T_0 without the need to consider the entire molecule. Subsequently, we set up an orbital model for the distorted pyridine molecule as a whole in its lowest triplet state and calculate within this model the hyperfine tensors of the deuterium atoms and the nitrogen atom. To allow for a fit of the calculated to the experimental tensors, we have to establish the relation between the axes system xyz , in which the hyperfine tensors are calculated in our model, and the axes system $x'y'z'$ in which the experimental hyperfine tensors are defined. It will be shown that the mutual orientation of both axes systems can be obtained from an analysis of the hyperfine tensor of the nitrogen atom.

A. Deuterium hyperfine and quadrupole interactions

1. Para-deuterium

The hyperfine and quadrupole tensors of the para-deuterium atom (cf., Table I) show that the only nonzero off-diagonal element in the $x'y'z'$ axes system is the $z'x'$ element. For this deuterium atom, the y'' axis is therefore coincident with the y' axis while the x'' and z'' axes are rotated with respect to the fine-structure principal axes in the $z'x'$ plane, as has been found previously for the principal axes of the hyperfine tensor of the nitrogen atom.²⁹ If pyridine would

have been planar in the lowest triplet state, the axes x' , y' , and z' would have coincided on symmetry grounds with x , y , and z . The principal axes x'' , y'' , and z'' would have been along x , y , and z and thus along x' , y' , and z' as well. Since this is not the case, it can be concluded that pyridine in the lowest triplet state is not planar. The observation that y'' is coincident with y' proves that the symmetry plane perpendicular to the plane of pyridine in the ground state is preserved and points to a structure of the molecule in the lowest triplet state with C_{1h} symmetry.

In Table II, the eigenvalues and eigenvectors of the hyperfine and quadrupole tensors of the para-deuterium atom are given for triplets A and B . In view of the discussion that follows, the hyperfine tensor has been split into a diagonalized anisotropic part and an isotropic part.

Let us first consider the anisotropic part of the hyperfine tensor, which is determined by the magnetic dipole-dipole interaction between the triplet electron spin and the nuclear spin of the para-deuterium atom. Such a magnetic dipole-dipole interaction can, in general, be expressed by

$$\frac{1}{h} \mathbf{A} - \frac{1}{3h} \text{Tr } \mathbf{A} \mathbf{E} = g_n \beta_n g_e \beta_e \sum_i \rho_i \left\langle \varphi_i \left| \frac{3\hat{r}\hat{r} - \mathbf{E}}{r^3} \right| \varphi_i \right\rangle \\ \equiv g_n \beta_n g_e \beta_e \mathbf{H}. \quad (2)$$

Here $|\varphi_i\rangle$ represents the atomic orbitals on the nitrogen and carbon atoms; $\mathbf{r} = \mathbf{r}_n - \mathbf{r}_e$; $\hat{r} \equiv \mathbf{r}/|\mathbf{r}|$; $\hat{r}\hat{r}$ is a dyadic tensor; and $\mathbf{E}$ is the unit matrix. In this expression the spin-density

FIG. 6. Angular dependence of the ENDOR frequencies of the ortho-deuterium atoms for the $m_s \approx 0 \leftrightarrow m_s \approx +1$ transition for a rotation of $\mathbf{B}_0$ in (a) the $z'x'$ plane (triplets A and B) and (b) the $x'y'$ plane (triplet A). Circles and lines in (a) are defined as in Fig. 4. In (a) the frequencies of both deuterium atoms overlap; in (b) they become different and are represented by, respectively, circles for the ortho-deuterium atom D_o and squares for the ortho-deuterium atom D_e [open and closed as in (a)]. The lines in (b) result from the fit to Eq. (1) corresponding to the hyperfine tensors given in Table I; the solid line and dashed lines belong to the open and closed circles, respectively, the dotted line to the squares (see also the text).

TABLE II. Principal values (kHz) and principal axes in the $x'y'z'$ axes system of the anisotropic hyperfine tensor and the quadrupole tensor of the para-deuterium nucleus of triplet *A* and triplet *B*. The isotropic contribution to the hyperfine tensor is given by $\text{Tr } A/3h$ (kHz).

Triplet <i>A</i>	$A_{x''x''}/h = -23$	$A_{y''y''}/h = -1698$	$A_{z''z''}/h = 1721$	$\text{Tr } A/3h = -2438$
	0.991	0.000	-0.136	
	0.000	1.000	0.000	
	0.136	0.000	0.991	
Triplet <i>B</i>	$A_{x''x''}/h = -22$	$A_{y''y''}/h = -1700$	$A_{z''z''}/h = 1722$	$\text{Tr } A/3h = -2459$
	0.991	0.000	0.132	
	0.000	1.000	0.000	
	-0.132	0.000	0.991	
Triplet <i>A</i>	$P_{x''x''}/h = \pm 53$	$P_{y''y''}/h = \pm 53$	$P_{z''z''}/h = \mp 106$	
	0.999	0.000	-0.039	
	0.000	1.000	0.000	
	0.039	0.000	0.999	
Triplet <i>B</i>	$P_{x''x''}/h = \pm 57$	$A_{y''y''}/h = \pm 58$	$A_{z''z''}/h = \mp 115$	
	0.999	0.000	0.031	
	0.000	1.000	0.000	
	-0.031	0.000	0.999	

matrix ρ is assumed to be diagonal, the diagonal elements being designated by ρ_i with $\sum_i \rho_i = 1$.

We observe that for the para-deuterium atom, the ratio of the $A_{x''x''}/h$, $A_{y''y''}/h$, and $A_{z''z''}/h$ elements is to a very good approximation 0: -1: +1. This proportionality has been observed as well for protons in planar aromatic hydrocarbons and can easily be rationalized as follows: Consider a C-H fragment with the proton in the nodal plane of the π molecular orbital. Consider a local axis system $x''y''z''$; let the x'' axis be perpendicular to the plane defined by the C-H fragment and the carbon atoms to which this fragment is bonded, the y'' axis in the plane and perpendicular to the C-H bond, and the z'' axis is the axis in the direction of the C-H bond. If the spin density on the ipso-carbon atom, i.e., the carbon atom to which the proton is bonded, is much larger than the spin density on the neighboring atoms, the only relevant term in the summation in Eq. (2) is the one in which $|\varphi_i\rangle$ is the π orbital on the ipso-carbon atom. This results from the r^{-3} dependence of the magnetic dipole-dipole interaction. The integral cannot easily be evaluated analytically, but the point spin model³⁵ has proved to be an adequate way to circumvent this problem. In this model, the ratio 0: -1: +1 ($A_{x''x''}/h$: $A_{y''y''}/h$: $A_{z''z''}/h$) is reproduced when, for a C-H bond length of 1.085 Å, the π spin density distribution on the carbon atom is represented by two point spins located at $x'' = +0.7665$ Å and $x'' = -0.7665$ Å, each carrying half of the spin density of the carbon atom.

The fact that we observe the same ratio for the para-deuterium atom in pyridine- d_5 apparently means that a description of the anisotropic hyperfine tensor of this deuterium atom including only the interaction of the deuterium nucleus with the electron spin density on the para-carbon

atom is reasonable in first order. If we do so, for the moment, we calculate from the value of $\frac{1}{2}(|A_{y''y''}| + |A_{z''z''}|)$ an approximate value of the spin density on the para-carbon atom of $\rho_p = 0.33$, both for triplet *A* and for triplet *B*.

The assumptions underlying the explanation of the 0: -1: +1 ratio would imply that the para-deuterium, the para-carbon, and the meta-carbon atoms to a good approximation are all in the same plane. Additionally, the z'' axis of the hyperfine tensor of the para-deuterium would within this model coincide with the direction of the C_p-D_p bond. From the eigenvectors in Table II, one should then conclude that the bond from the para-carbon atom to the para-deuterium atom makes an angle of -7.8° with the z' axis for triplet *A* ($+7.6^\circ$ for triplet *B*). We will come back to this point later on.

Next we consider the isotropic part of the hyperfine tensor of the para-deuterium atom. The McConnell relation³⁶ states that the isotropic part of the hyperfine tensor of a deuterium atom in a planar aromatic molecule is proportional to the spin density in the π orbital of the ipso-carbon atom, with a proportionality constant Q_{CD}^D in the range of -9.2 – -11.5 MHz. The combination of the value of ρ_p calculated from the anisotropic hyperfine interaction with the observed isotropic hyperfine interaction leads to a value of -7.4 MHz for Q_{CD}^D . This is fairly high compared to the commonly observed values. The isotropic hyperfine interaction actually measures the spin density in the s orbital of the deuterium atom, which is sensitive to the hybridization of the atomic orbitals on the ipso-carbon atom. The relatively high value of Q_{CD}^D for the para-deuterium atom might therefore indicate that the hybridization of the para-carbon atom slightly deviates from sp^2 and that the para-deuterium atom

is not exactly in the nodal plane of the π orbital of the para-carbon atom. This slight nonplanarity is still compatible with the observed ratio of 0: - 1: + 1 because the anisotropic contribution to the hyperfine tensor is much less sensitive to small deviations from planarity than the isotropic contribution.

The diagonalized quadrupole tensor shows axial symmetry. The direction of the C_p-D_p bond in the fine-structure principal axes system can be determined from the eigenvectors because the unique axis should point along this bond.³⁷ From the quadrupole tensor, we therefore have to conclude that the C_p-D_p bond makes an angle in the $z'x'$ plane of -2° and $+2^\circ$ with respect to the z' axis for triplet *A* and triplet *B*, respectively. The approximate analysis of the anisotropic hyperfine tensor given above suggested a value of -7.8° (triplet *A*) and $+7.6^\circ$ (triplet *B*) for this angle. This value resulted from the assumption that the C_p-D_p bond is in the plane defined by the para- and meta-carbon atoms. This assumption is apparently not fully correct as is clear now from the consideration of the quadrupole tensor and the description of the isotropic hyperfine interaction. The too large value for the rotation angle could have been caused also by the neglect of contributions of the spin density on the other carbon atoms, in particular the meta-carbon atoms, to the anisotropic hyperfine tensor of the para-deuterium nucleus. It will appear that these contributions are negligible indeed.

2. Meta-deuterium

For this deuterium atom, the hyperfine tensor has not been determined to such an extent that any quantitative conclusion can be drawn about the spin density and hybridization on the meta-carbon atoms from this tensor as such. The absence in most orientations of frequencies belonging to the meta-deuterium atoms does indicate, however, that probably the meta-carbon atoms carry only a small fraction of the total spin density.

3. Ortho-deuterium

The hyperfine tensors of the two ortho-deuterium atoms are compatible with a C_{1h} symmetry of pyridine in the lowest triplet state. The A_{zx} elements are equal for both atoms; the A_{xy} elements are equal in magnitude, but different in sign.

The hyperfine tensors for these nuclei have not been determined completely enough, neither for triplet *A* nor for triplet *B*, to allow for an approximate description of their anisotropic parts as was possible for the para-deuterium atom. Interesting conclusions may nevertheless be drawn from a consideration of the isotropic part of the hyperfine tensor of triplet *A* [$(1/3h)\text{Tr } \mathbf{A} = 2224 \text{ kHz}$]. Use of the McConnell relation with the negative Q_{CD}^D values commonly applicable for planar aromatic molecules leads to a spin density on the ortho-carbon atoms in the range of -0.19 – -0.24 . These values are unrealistic and far larger than any negative spin density ever observed. We have to conclude that for the ortho-deuterium nuclei the McConnell relation with common Q_{CD}^D values apparently is not valid. On the

other hand, if the spin density on the ortho-carbon atoms would be positive, the isotropic hyperfine contribution would point to a large positive Q_{CD}^D value.

A positive Q_{CD}^D value implies that the deuterium atom is not in the nodal plane of the π orbital on the ipso-carbon atom. Hereby the s orbital of the deuterium can actually participate in the π molecular orbital leading to a direct spin density at the deuterium nucleus. This results in a positive contribution to the isotropic hyperfine tensor^{38–40} instead of the negative contribution arising from the exchange coupling in the McConnell model. For the para-deuterium atom, discussed above, we found a Q_{CD}^D value slightly less negative than those observed for planar aromatic hydrocarbons, suggesting a slight deviation from planarity. For the ortho-deuterium atoms, we observe a positive Q_{CD}^D value, which means that the positive contribution to the isotropic hyperfine tensor dominates the negative one. We have to conclude that the pyridine molecule is strongly distorted at the ortho-carbon sites. This will appear to be one of the most salient features of the structural change of pyridine upon excitation into T_0 .

B. Coupling between the molecular and the fine-structure axes system: The nitrogen hyperfine interaction

To get any further in the elucidation of the structure of pyridine- d_5 in its lowest triplet state, we have to go beyond the one-center approximation for the anisotropic hyperfine tensors. We set up a model for the molecule as a whole, calculate the anisotropic hyperfine tensors in terms of a number of parameters describing the geometry and the spin-density distribution, and fit these parameters by comparison of the calculated hyperfine tensors with the experimentally determined tensor elements. Such a procedure of course requires the knowledge of the experimental hyperfine tensors in a molecule-fixed coordinate system. The experimental tensors have, however, been determined in the principal axis system of the fine-structure tensor whose orientation relative to the molecule we do not know. We therefore have to fix first the mutual orientation of those axes systems in order to be able to transform all hyperfine tensors calculated in a molecule-fixed axis system to the principal axis system of the fine-structure tensor. We will show that this can be done by considering the hyperfine tensor of the nitrogen atom, a tensor that we have obtained previously and reproduce in Table III.²⁹

To describe the anisotropic part of the hyperfine tensor of the nitrogen atom according to Eq. (2), one in principle has to take into account contributions deriving from all atomic orbitals $|\varphi_i\rangle$ carrying spin density. Because these contributions are proportional to r^{-3} , the one-center contributions, i.e., φ_i on nitrogen, dominate for a spin-density distribution in which the nitrogen carries a major part of the total spin density. The spin-density distribution as we have calculated it (*vide infra*) indeed shows that these one-center contributions account for more than 99% of the anisotropic hyperfine tensor. This allows us to consider the anisotropic hyperfine tensor of the nitrogen atom without explicitly tak-

TABLE III. Principal values (MHz) and principal axes of the anisotropic hyperfine tensor in the $x'y'z'$ axes system of the nitrogen nucleus of triplet *A* and triplet *B*. The isotropic contribution to the hyperfine tensor is given by $\text{Tr } A/3h$ (MHz) (Ref. 29).

Triplet <i>A</i>	$A_{x''x''}/h = -11.6$	$A_{y''y''}/h = -23.2$	$A_{z''z''}/h = 34.8$	$\text{Tr } A/3h = 41.3$
	0.868	0.000	0.497	
	0.000	1.000	0.000	
	-0.497	0.000	0.868	
Triplet <i>B</i>	$A_{x''x''}/h = -13.1$	$A_{y''y''}/h = -22.0$	$A_{z''z''}/h = 35.1$	$\text{Tr } A/3h = 40.8$
	0.897	0.000	-0.442	
	0.000	1.000	0.000	
	0.442	0.000	0.897	

ing into account spin densities other than those on the nitrogen atom itself.

Assume that the spin density on the nitrogen atom is distributed among two orbitals: the π orbital $|\varphi_\pi\rangle$ and the nonbonding orbital $|\varphi_n\rangle$ which carry spin densities ρ_π and ρ_n , respectively. Assume further for the moment that the nitrogen is sp^2 hybridized as it is in the planar ground state. Define a molecule-fixed axes system $\xi\eta\zeta$ such that $|\varphi_\pi\rangle$ corresponds to $|2p_\xi\rangle$ and $|\varphi_n\rangle$ to $\sqrt{\frac{1}{3}}|2s\rangle + \sqrt{\frac{2}{3}}|2p_\xi\rangle$. Take for the $2s$ and $2p$ orbitals, Slater orbitals with exponent $\alpha/2 = Z/2a_0$, with Z being the effective nuclear charge and a_0 the Bohr radius. The integrals in Eq. (2) can now be calculated analytically and we find for the elements of the tensor **H**

$$\begin{aligned} H_{\xi\xi} &= \frac{\alpha^3}{60} \left(2\rho_\pi - \frac{2}{3}\rho_n \right), \\ H_{\eta\eta} &= \frac{\alpha^3}{60} \left(-\rho_\pi - \frac{2}{3}\rho_n \right), \\ H_{\zeta\zeta} &= \frac{\alpha^3}{60} \left(-\rho_\pi + \frac{4}{3}\rho_n \right). \end{aligned} \quad (3)$$

The tensor **H** is diagonal, in other words the principal axes of the calculated nitrogen hyperfine tensor are along ξ , η , and ζ . Comparison of this tensor with the experimental one allows us to relate the molecule-fixed axes ξ , η , and ζ to the experimentally determined principal axes x'' , y'' , and z'' of the hyperfine tensor of the nitrogen atom.

In Table III, we resume the eigenvalues and eigenvectors of the nitrogen hyperfine tensor for triplets *A* and *B*. The principal axes of these tensors that we have labeled with z'' and x'' are rotated in the $z'x'$ plane with respect to the principal axes of the fine-structure tensor by $+30^\circ$ for triplet *A* and -26° for triplet *B*.

We have noted that the zx plane remains a symmetry plane upon distortion. Consequently, y' coincides with y and from our definition of ξ , η , and ζ it follows that η coincides with y as well. Hereby y' is along η . Since y'' is found to be parallel to y' , η needs then to be identified with y'' . As to the other two axes, we are left with the possibilities that ξ corresponds either to x'' or to z'' and, complementary, ζ to z'' or to x'' , respectively. In Fig. 7 these two possibilities are sketched

for triplet *A*, which we will discuss in detail in the following: If ξ is identified with x'' [choice (i)], the n -orbital points in the z'' direction and we find that it makes an angle of $+30^\circ$ with the z' axis in the $z'x'$ plane. For choice (ii), in which ξ is identified with z'' , the n orbital is directed along the x'' direction. In this case, the angle between the n orbital and the z' axis is -60° .

If we can now distinguish between the two possible identifications, we will have fixed the direction of the axes system $\xi\eta\zeta$ with respect to the principal axes system of the fine-structure tensor. This means that we are able to transform any tensor defined in a molecule-fixed coordinate system for which the relative position with respect to $\xi\eta\zeta$ is known, into the principal axes system of the fine-structure tensor.

The axes identification indicated by (ii) is correct. To show this, we first calculate the spin densities on the nitrogen atom from Eq. (3) and the experimental eigenvalues of the anisotropic nitrogen hyperfine tensor. For Z , we take a value of 4.35 which has been found before to lead to an adequate description of anisotropic hyperfine tensors for the nitrogen atom.¹⁰ For choice (i), we thus calculate $\rho_\pi = 0.07$ and $\rho_n = 0.55$, while for choice (ii), $\rho_\pi = 0.37$ and $\rho_n = 0.11$ is obtained. From the isotropic part of the nitrogen hyperfine tensor (41 MHz), we can also calculate the spin density in the n orbital, the only orbital having s character. For unit

FIG. 7. The two possible orientations of the π and n orbital of the nitrogen atom in the $z'x'$ plane under the assumption of sp^2 hybridization.

spin density in a nitrogen $2s$ orbital, the isotropic hyperfine interaction has been determined to be 1062 MHz.⁴¹ We then find $\rho_n = 0.12$. The agreement with the value obtained above for choice (ii) is striking and unambiguously proves that Fig. 7 (ii) represents the actual situation. Or from another point of view: if choice (i) would have been correct, i.e., if ρ_n instead of 0.11 would have been 0.55, we would have measured an isotropic contribution to the nitrogen hyperfine tensor of 195 MHz, which is in flagrant contrast with the observed value of 41 MHz. Apart from the axes identification, we have in this way also obtained spin densities on the nitrogen atom that, considering the one-center character of the anisotropic hyperfine tensor of the nitrogen atom, are almost correct.

One point in the foregoing analysis deserves some attention. The analysis was based upon the assumption that the nitrogen atom remains sp^2 hybridized upon excitation into T_0 . Since pyridine is no longer planar in its lowest triplet state, one might argue that the hybridization on the nitrogen is not sp^2 anymore, but tends towards sp^3 . However, a deviation from sp^2 hybridization would introduce $2s$ character into the π orbital of the nitrogen atom. Even a slight s character of this π orbital would already lead to isotropic hyperfine interactions that are incompatible with the experiment,⁴² and we can safely conclude that also in T_0 the hybridization of the atomic orbitals of the nitrogen atom is well described by sp^2 .

Finally we note that for triplet B , the same considerations apply. From a similar calculation for this triplet, we find the spin densities $\rho_n = 0.08$ and $\rho_\pi = 0.36$. The angle between the n orbital and the z' axis is here $+64^\circ$.

C. Structure and spin densities

In this section, we will go beyond the one-center approximation for the description of the anisotropic hyperfine tensors and finally derive the structure of pyridine- d_5 in its lowest triplet state and the complete spin-density distribution in this state. We set up a model for the entire molecule in terms of "spin-hybrid" orbitals on the nitrogen and various carbon nuclei.

The model is based upon the following assumptions.

1. The geometry of pyridine in T_0

We take the bond lengths within the six-membered ring to be equal: $R_{CC} = R_{CN} = 1.37$ Å. For a planar pyridine molecule, this corresponds to a regular hexagon. To describe the structure in the lowest triplet state we introduce two angles α and β (see Fig. 8). Starting from the planar hexagon, we keep the ortho- and meta-carbon atoms fixed and allow for a rotation of the nitrogen atom around the axis through the ortho-carbon atoms by the angle α and of the para-carbon atom around the axis through the meta-carbon atoms by the angle β . During the rotation over β , the C_p-D_p bond is kept in the mirror plane of the molecule and in the plane defined by the para- and meta-carbon atoms. The direction of the C_o-D_o and C_m-D_m bonds is fixed by the hybridization of the atomic orbitals on the ortho- and meta-carbon atoms, respectively (see below). The bond length R_{CD} is taken to be 1.08 Å. We are well aware that this geom-

etry represents a rather idealized structure. The geometry of pyridine in the ground state, e.g., already slightly deviates from a regular hexagon, both the bond lengths as well as the bond angles.⁴³ In the end, however, we are not concerned with subtle details of the structure, but wish to find out what are the decisive structural changes upon excitation into T_0 .

2. The spin-density distribution

We assume that the spin-density distribution in T_0 can be described by five parameters: three spin densities ρ_p , ρ_m , and ρ_o are allocated to the π -type orbitals on the para-, meta-, and ortho-carbon atoms, respectively, and two spin densities ρ_π and ρ_n to the π and the lone-pair orbital on the nitrogen atom.

3. The hybridization of the atomic orbitals

The atomic wave functions carrying the spin densities have been taken as hybrids of $2s$ and $2p$ Slater atomic orbitals on the nitrogen and carbon centers.⁴⁴ The nitrogen atom and the para-carbon atom are both considered to be sp^2 hybridized. For the nitrogen atom, this is well justified above, but for the para-carbon atom the analysis in Sec. V A 1 suggested a small deviation from sp^2 hybridization. Test calculations showed, however, that the incorporation of a rehybridization of the para-carbon atom hardly affected the results of the forthcoming calculations. For the ortho- and meta-carbon atoms, the hybridization is taken to change with the geometry of pyridine in accordance with the generally accepted link between molecular shape and hybridization.⁴⁵ We have determined the hybridization for the ortho- and meta-carbon atoms from the angles α and β , respectively, under the assumption that the three σ type orbitals on these carbon atoms are equivalent and that the set of hybrids on each carbon atom is normalized to one $2s$ orbital and three $2p$ orbitals. This procedure not only fixes the hybrid character and the direction of the π orbitals, but also the direction of the σ bonds towards the ortho- and meta-deuterium atoms.

4. Calculation of the anisotropic hyperfine tensors

The anisotropic hyperfine tensors of the nitrogen and the deuterium nuclei are calculated according to Eq. (2). For this calculation, the one-center contribution of the spin density on the nitrogen atom to the hyperfine tensor of this atom is analytically calculated as described in Sec. V B. The other contributions to the hyperfine tensor of the nitrogen nucleus and the contributions to the hyperfine tensors of the deuterium nuclei are determined using the point-spin-density model (cf., Sec. V A 1). In the past, the application of the point-spin-density model to pure π orbitals has been justified more empirically than theoretically.³⁵ For other kinds of orbitals, such an empirical justification does not exist. Models were proposed in terms of more than two point spins and/or different density distributions over the two lobes of an orbital.^{44,46,47} We have chosen to locate in the case of the carbon atoms two point spins at $+0.7660$ and -0.7660 Å in the direction of the π orbital; in the case of the nitrogen atom two point spins at $+0.6079$ and -0.6079 Å in the direction of the π orbital and two point-spins at the same

distances in the direction of the n orbital. These coordinates correspond to the average distance of an electron in a hybrid consisting of $2s$ and $2p$ Slater orbitals for carbon ($Z = 3.45$) and nitrogen ($Z = 4.35$), respectively. For such a Slater hybrid, it can be shown that $\langle r \rangle$ is independent of the hybridization. Though therefore $\langle r \rangle$ does not alter with a change of hybridization, the position of the point spins does (cf., assumption 3). The spin density in the orbital is distributed among the two point spins in proportion to the electron density distribution over the two lobes of the orbital. After calculation of the anisotropic hyperfine tensors in the molecule-fixed axis system, they have been transformed to the fine-structure principal axes system in accordance with the mutual orientation of both axes systems as derived in the previous section.

To obtain the parameters α , β , ρ_n , ρ_o , ρ_m , and ρ_p from the experimentally determined anisotropic hyperfine tensors, we apply the above model in an iterative way. By a nonlinear least-squares procedure, the angles and spin densities are adjusted until the correspondence between experimental and calculated tensors is optimum. This has been done subject to two boundary conditions. First, the spin densities are normalized to one; secondly, the angles α and β are restricted to be such that the hybridization of the ortho- and meta-carbon atoms is within $[sp^2, sp^3]$. For the hyperfine tensors of which not all diagonal elements are available, a transformed tensor was fitted. For the meta-deuterium atoms of triplet *A*, e.g., only the elements in the $x'y'$ plane have been determined. Consequently, in the fit, $(A_{xx'} - A_{yy'})$ and $A_{xy'}$ were considered, hereby circumventing the introduction of another variable measuring the isotropic contribution to this hyperfine tensor.

Initial calculations in which both α and β were fitted showed a large correlation between these variables. This can be understood on the basis of the spin densities that result from these fits. The spin density on the meta-carbon atoms turns out to be almost negligible. Consequently, the anisotropic hyperfine tensor of the para-deuterium atom consists merely of the contribution of the spin density on the para-carbon atom. The direction of the principal axes of the hyperfine tensor of the para-deuterium atom therefore depends only on the angle β . Similarly, the anisotropic hyperfine tensor of the nitrogen atom is determined by the spin density on the nitrogen atom and the direction of the hyperfine tensor of the nitrogen atom depends only on α . The mutual orientation of the principal axes systems of both hyperfine tensors is fixed by the experiment. Consequently, for a certain value of α , the angle β is no longer free. Indeed this was observed in

our calculations and therefore we choose as the only independent geometrical variable in later calculations the angle α , the angle β being determined from the relation between the principal axes systems of the two experimentally obtained hyperfine tensors.

The final result of the iterative process is given in Table IV for triplet *A*. It is seen that the nitrogen atom carries almost half of the spin density, while the other half is distributed very unequally over the carbon atoms: the para-carbon atom has 0.28 spin density, the two ortho-carbon atoms each 0.11, while the two meta-carbon atoms have almost zero spin density. The structure of pyridine in its lowest triplet state as it follows from the fit of the hyperfine data to the model is drawn in Figs. 8 and 9. We observe that the pyridine molecule is heavily distorted, the nitrogen atom being tilted with respect to the plane spanned by the ortho- and meta-carbon atoms by 41° . This implies that the ortho-carbon atoms are almost sp^3 hybridized. The hybridization on the meta-carbon atoms deviates much less from sp^2 .

For triplet *B*, it did not prove possible to obtain a reliable fit. For this triplet, the angles α and β cannot be determined accurately because not enough hyperfine data are available. Still, the spin densities on the nitrogen and para-carbon atoms as derived in Sec. V B and V A 1 are not expected to change dramatically in a fit of the whole molecule. Additionally, comparison of magnitude and sign of the hyperfine tensor elements of triplet *B* with those of triplet *A* reveals that the hyperfine tensors of both triplets are related by a mirror symmetry with respect to the $y'z'$ plane. Consequently it is reasonable to conclude that the intrinsic structure of triplet *B* is qualitatively the same as that of triplet *A*. The position of triplet *B* in the crystal is roughly the mirror image of that of triplet *A* with the $y'z'$ plane being the mirror.

Our conclusions based on the consideration of the individual tensors are well reflected in the results obtained from our fit, both as regards the spin densities and the structure. The ortho-carbon atoms deviate far from sp^2 hybridization which we qualitatively predicted on the basis of the isotropic contribution to the hyperfine tensor of the ortho-deuterium atom. The nitrogen spin-density distribution is about the

TABLE IV. Structure parameters and spin-density distribution of pyridine- d_5 in triplet *A*.

$\alpha = -41 \pm 4^\circ$
$\beta = -11 \pm 4^\circ$
$\rho_n = 0.11 \pm 0.01$
$\rho_o = 0.35 \pm 0.01$
$\rho_p = 0.11 \pm 0.02$
$\rho_m = 0.02 \pm 0.02$
$\rho_p = 0.28 \pm 0.01$

FIG. 8. Projection of the molecular structure of pyridine- d_5 in triplet state *A* on the $z'x'$ plane. The symbols *o* and *m* represent the projection of the ortho- and meta-carbon atoms on this plane, the ortho- and meta-deuterium atoms have not been drawn.

FIG. 9. Molecular structure of pyridine- d_5 in triplet state *A*.

same as obtained before, while ρ_p is found to be only a little lower. The value of ρ_m (0.02) explains why frequencies belonging to the meta-deuterium atoms hardly show up in the ESEEM spectra.

We have noted before that the isotropic contributions to the hyperfine tensors of the ortho-deuterium atom and to a lesser extent of the para-deuterium atom gave rise to Q_{CD}^D values that one would not have expected for deuterium atoms in aromatic hydrocarbons. Our explanation was that owing to a rehybridization of the corresponding carbon atomic orbitals, the deuterium atoms are not in the nodal plane of the π orbitals. The s orbital of the deuterium atom consequently overlaps with the π electron system, giving rise to altered Q_{CD}^D values. Now that we have obtained the spin densities on the carbon atoms from our fit of the anisotropic hyperfine tensors, we can estimate the "direct" spin density in the deuterium s orbital. A unit spin density in such an orbital gives rise to an isotropic hyperfine contribution of +218 MHz.⁴⁸ From our fit, it is seen that the ortho-carbon atoms have spin density 0.11, which, with a Q_{CD}^D value of -10.3 MHz, would cause an isotropic contribution of -1.12 MHz to the hyperfine tensors of the ortho-deuterium atoms if the ortho-carbon atoms would be sp^2 hybridized. Experimentally, this contribution is +2.22 MHz and we estimate for the "direct" spin density $(2.22 + 1.12)/(218) = 0.015$, which is in the order of magnitude to be expected. Likewise we calculate for the "direct" spin density in the para-deuterium s orbital 0.002, in accordance with the

much smaller deviation from sp^2 hybridization for the para-carbon atom as suggested in Sec. V A 1.

VI. DISCUSSION

The results of the previous section have shown that the structure of pyridine in T_0 strongly deviates from that in the ground state. In the ground state, the geometrical arrangement of the atoms in the six-membered ring roughly corresponds to a regular hexagon. Upon excitation into T_0 the molecule is found to distort to a boatlike structure: the nitrogen atom is no less than 40° tilted with respect to the plane of the ortho- and meta-carbon atoms; the para-carbon and para-deuterium atoms are tilted as well with respect to this plane albeit to a much lesser extent. The present results show that in T_0 the hybridization of the atomic orbitals on the nitrogen atom remains well described by sp^2 , while the hybridization of the para-carbon atom deviates only slightly from sp^2 . The hybridization of the ortho-carbon atoms on the other hand changes dramatically: in the triplet state it becomes almost sp^3 as compared to the sp^2 hybridization in the ground state. The bond angles on the ortho-carbon atoms in the triplet state are about 112° (cf., 120° for sp^2 and 109° for sp^3 hybridization).

We have described the molecular geometry of pyridine in the lowest triplet state with respect to the molecular plane defined by the ortho- and meta-carbon atoms. Our experiments have been performed on a doped single crystal of benzene in which the planar ground-state pyridine molecules substitutionally replace benzene molecules.⁴⁹ Given the large distortion upon excitation into T_0 , the position and orientation of the triplet pyridine molecule within its benzene cavity is not obvious. The principal axes of the fine-structure tensor are found to be parallel to the symmetry axes of the (hypothetical) benzene molecule that has been replaced by a pyridine molecule.²⁷ For a molecule of C_{2v} symmetry, this would have been a logical observation. In that case, the molecular yz plane would have coincided with the $y'z'$ plane. Because pyridine is no longer planar in T_0 , the observed near coincidence of the fine-structure axes and the benzene symmetry axes has to be considered merely fortuitous. The hyperfine data (cf., Sec. V) led to an orientation of the triplet pyridine molecule with respect to the fine-structure axes as indicated in Fig. 8 for triplet *A*. From the orientation of the distorted molecule with respect to the principal axes of the fine-structure tensor and the orientation of those axes with respect to the benzene crystal axes, we conclude that the orientation of the plane spanned by the ortho- and meta-carbon atoms of pyridine changes by about 20° upon excitation into T_0 (see Fig. 8), in opposite directions for triplets *A* and *B*.

The considerations presented above regarding the distortion of pyridine in T_0 were based upon measurements in the solid phase. The question may arise whether the distortion is an intrinsic property of the lowest triplet state or induced by the crystal field. Experimental support for the intramolecular nature of the geometry change stems from additional observations during our ESE studies. Though the

major fraction of pyridine molecules is substituted in such a way that their twofold axes are nearly parallel to the crystal b axis, there is found to be a minor fraction of pyridine molecules that has its twofold axes rotated by $\pi/3$. In an ESE detected $S_1 \leftarrow S_0$ excitation spectrum, they show up with their 0-0 transition shifted by 196 cm^{-1} to the red as compared to the major fraction.³² When these molecules are excited again, two triplet species are observed in the ESE detected EPR spectrum. The nitrogen hyperfine splitting of the EPR lines for these triplet species shows them to be distorted in a way similar to that observed for triplets A and B . Apparently, pyridine molecules that feel quite a different crystal field deform in a comparable way when excited to their lowest triplet state. This strongly supports the intrinsic nature of the observed distortion. *Ab initio* calculations, which will be described in detail elsewhere,⁵⁰ reveal that indeed in the free molecule the energy of T_0 becomes lower for a distortion along an out of plane coordinate that tilts the nitrogen atom out of the plane defined by the ortho- and meta-carbon atoms. This behavior seems to be driven by the character of the π orbital to which the excitation takes place. It is an orbital which is strongly antibonding between the nitrogen atom and the ortho-carbon atoms and about nonbonding between the carbon atoms.

All observations point to a description of the two triplets A and B in terms of triplet pyridine molecules distorted along the same coordinate, but in opposite direction. This corroborates the vibronic coupling picture outlined in the introduction in which triplet A and B correspond to the two minima in a double minimum potential.²⁹ The fact that the lowest triplet state of pyridine may be looked upon in terms of a strong vibronic coupling between an $n\pi^*$ and a $\pi\pi^*$ state qualitatively accounts for the observed rapid radiationless decay from the lowest triplet state.^{26,51}

Also the spin-density distribution, most notably that on the nitrogen atom, supports a lowest triplet state of mixed $n\pi^*$ and $\pi\pi^*$ character. We have shown that the total spin density on the nitrogen atom is 0.46. Such a large spin density is commonly taken as evidence for an $n\pi^*$ state. A value for the spin density in the n orbital of about 0.5 may be expected in that case under the assumption that the n orbital is localized on the nitrogen atom. Though for T_0 of pyridine the total ρ is 0.46, the value of ρ_n is found to be only 0.11. The main contribution to the spin density on nitrogen stems from ρ_π . The observed distribution over the two atomic orbitals clearly indicates that the lowest triplet state of pyridine is neither a pure $n\pi^*$ nor a pure $\pi\pi^*$ state.

Significant distortions of aza-aromatic molecules upon excitation into the lowest triplet state have not been observed before. For the diazabenzenes, the geometry in the lowest triplet state is still under discussion. In pyridazine (1,2-diazabenzene), the absence of phosphorescence might be due to a vibronic coupling.¹² Hartree-Fock calculations indicate that a molecular geometry with an out of plane twisted configuration of the nitrogen atoms is of minimum energy in the lowest triplet state.⁵² Though not fully understood, configuration interaction calculations seem to suggest on the other hand a planar geometry; the nonplanarity is compensated for by the delocalization of the electrons over the carbon

atoms in the molecule.⁵² EPR studies on pyrimidine (1,3-diazabenzene)¹³ reveal that the principal axes of the fine-structure tensor might be rotated in the plane of the molecule, which would indicate a loss of symmetry compared to the ground state. Also the splitting of the EPR line as a result of the hyperfine interaction of the triplet electron spin with the nuclear spins of the protons and nitrogen atoms has been interpreted as deriving from a molecular geometry in which the twofold axis is lost as a symmetry element. Finally, for pyrazine (1,4-diazabenzene), an out of plane distortion of the molecule has repeatedly been suggested,⁵³⁻⁵⁶ though recent excitation studies in a supersonic jet⁵⁷ yielded no evidence for such a distortion.

In recent years, Terazima, Yamauchi, and Hirota have investigated the lowest triplet state of many nonradiative aza-aromatic molecules.^{15-18,58} For all the molecules they studied, it was reported that the directions of the principal axes of the fine-structure tensor coincide with the molecular symmetry axes as expected for the planar molecule. The nitrogen hyperfine splittings, which were observed along the fine-structure principal axes, were interpreted by means of INDO calculations as arising from an undistorted planar molecule. Our results on pyridine show, however, that one should be careful in drawing definite conclusions as to whether the molecule is distorted upon excitation on the mere basis of the diagonal elements of a hyperfine tensor.

VII. CONCLUSIONS

ESEEM spectroscopy has enabled us to investigate the hyperfine and quadrupole tensors of the deuterium atoms of pyridine- d_5 . In combination with the previously obtained hyperfine tensor of the nitrogen atom, this allowed us to determine the complete structure and spin-density distribution of pyridine in the lowest triplet state. The results show a heavily distorted molecule in which the nitrogen atom is tilted by approximately 40° with respect to the plane through the ortho- and meta-carbon atoms. About 50% of the spin density is localized on the nitrogen atom. The distribution of this spin density over the atomic orbitals on this atom resembles neither that expected for an $n\pi^*$ nor for a $\pi\pi^*$ state. Both the structure and the spin-density distribution reveal that the lowest triplet state is a state with a mixed electronic character, resulting from a strong vibronic coupling between the 3B_1 ($n\pi^*$) and the 3A_1 ($\pi\pi^*$) state.

Now that the lowest triplet state of the model compound of aza-aromatic molecules has been well characterized, it is interesting to investigate in more detail the lowest triplet state of diaza-benzenes. Such studies can indicate to what extent the electronic nature of the lowest triplet state of pyridine is reflected in such molecules. One of the most intriguing molecules in this respect is pyrimidine, for which the zero field splitting tensor and the observed hyperfine splittings seem to indicate a loss of symmetry upon excitation into the lowest triplet state. Presently, we are therefore performing an ENDOR study of the lowest triplet state of pyrimidine.

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