to this principle, only a single radical product is formed in the frozen solutions, whereas X irradiation of crystalline samples often give rise to a number of different species.

It is interesting to note that despite the fact that the type of radicals formed upon X irradiation strongly depends on the packing of the precursors neighboring molecules, the spin density distribution of the resulting configurations is not seriously affected by the environment. This conclusion is based on the result that the valence-orbital spin densities of the respective configurations lie within a close range for the different compounds. Inspection of Table III reveals that the phosphorus valence s contribution, ρ_s, for all P∴P σ^* radicals in the crystalline solid state lies between 9 and 11% and the corresponding ρ_p value between 21 and 30%. Likewise, narrow intervals are found for the TBP-*e* configurations (ρ_s = 11.5–12.5%, ρ_p = 24–27%), the P∴S σ^* radicals (ρ_s = 12–14%, ρ_p = 37–54%), and the dissociation products (ρ_s = 6–8%, ρ_p = 41–57%). For the P∴P σ^* radicals it is also possible to compare the results from the crystalline state and the THF matrix. It appears that in THF ρ_s has decreased by approximately 0.5% and that the ρ_p values lie in a somewhat larger interval (19–28%).[30] The results demonstrate that the spin density distribution of a specific configuration is fairly constant over the various diphosphine disulfide derivatives and only slightly influenced by its environment. A similar conclusion was obtained in experiments on P∴Cl σ^* radicals.[5]

We conclude that a factor of considerable importance in the radiogenic formation of radicals in molecular crystals is the fact that the reaction cavity can constrain the movements of the precursor and modulate the necessary geometry relaxation that accompanies the formation of a stable radical product. It has been shown that *if the restraint of the environment inhibits the formation of the radical configuration energetically preferred by the isolated molecule, secondary relaxation modes become accessible leading to alternative structures.* This provides a unique possibility to study molecular states that are usually undetected. In agreement with this principle, recent experiments reveal that organic photoreactions in the crystalline state tend to occur with a minimum of deformation of the three-dimensional crystal lattice, being topochemically controlled.[10-14,37] This leads to the conclusion that the intrinsic reactivity of a molecule can be less important than the nature of the packing of its neighboring molecules.

The most illustrative example of this concept is given by our experiments on *meso*-1,2-dibenzyl-1,2-diphenyldiphosphine disulfide (**10**). In its crystalline environment, X irradiation results in the exclusive formation of an electron-capture product in which the extra electron is confined to one of the two contiguous phosphorus moieties (spin-localized). In contrast, X irradiation of the same compound in a frozen THF host matrix gives selectively the spin-delocalized three-electron bond P∴P σ^* radical.

It will be of interest to determine structure–reactivity relationships for radical precursors in the solid state on the basis of a detailed knowledge of their microenvironment.

(39) It is well-known that in protic and etheric solutions it is possible to observe specific electron-gain processes (see e.g., Symons[38]). This is the result of efficient trapping of positive holes created in the radiation process and the generation of highly reactive pretrapped electrons. In the present case there is no evidence of a specific chemical effect of the solvent on the phosphorus-centered radicals or a reaction of the solute with radicals formed from the solvent.

Acknowledgment. This investigation has been supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: ESR spectra of several THF-matrix experiments, angular dependence of ESR field transitions for radicals generated in compounds **5**, **7**, **8**, and **11**, and tables of fractional coordinates, thermal parameters, and molecular geometries of **2**, **7**, and **8** (16 pages); tables of observed and calculated structure factors of **2**, **7**, and **8** (58 pages). Ordering information is given on any current masthead page.

Ab Initio Calculations on the Structure of Pyridine in Its Lowest Triplet State

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Abstract: Recently we have experimentally shown that pyridine-d_5, as a guest in a single crystal of benzene-d_6, adopts a boatlike structure upon excitation into the lowest triplet state T_0. Here MRDCI ab initio calculations are presented that reveal that the observed nonplanarity of the molecule is not caused by the crystal field but is an intrinsic property of pyridine in T_0. The origin of the distortion may be found in the nature of the π-electron system. In the lowest triplet state it is no longer a 6π-electron system as in the ground state but, in first approximation, a 7π-electron system, in which the extra electron occupies a π^* orbital that is strongly antibonding between the nitrogen atom and the ortho carbon atoms. The lowest triplet state can not be simply interpreted as an $n\pi^*$ or a $\pi\pi^*$ state.

I. Introduction

Pyridine presents the simplest molecule among azaaromatic compounds and is considered to be the model for the study of the photochemistry and photophysics of such molecules. Consequently, its lowest excited states have amply been investigated, both theoretically and experimentally. Quantum chemical calculations have been primarily aimed at the localization of the $n\pi^*$-excited states, states that do not occur in the related hydrocarbon benzene. From an experimental point of view, progress was, despite all efforts, limited for a long time. This particularly concerned pyridine's lowest triplet state T_0, due to the virtual impossibility of detecting electronic transitions to and from this state.

In a recent series of papers[1-4] on the lowest triplet state of

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pyridine-d_5 present as a guest in a single crystal of benzene-d_6, we have described how we tackled this problem successfully. Electron spin-echo spectroscopy has allowed us to characterize T_0 to such an extent that it may presently be considered the best documented among all triplet states of azaaromatic compounds. Both the structure, as well as the spin density distribution, as derived from nitrogen and deuterium hyperfine studies, shows unique features that have not been encountered before in aromatic molecules.[4] The planarity commonly observed for aromatic compounds is completely lost in T_0, and pyridine adopts a boatlike structure: the nitrogen atom is tilted by about 40° with respect to the plane spanned by the ortho and meta carbon atoms, while the tilt of the para carbon atom with respect to the same plane amounts to about 10°. In terms of atomic orbitals this structural change upon excitation comes to a rehybridization of the atomic orbitals on the ortho carbon atoms. They are no longer sp^2 hybridized but about sp^3, the hybridization normally observed for saturated hydrocarbons. The meta carbon atoms are on the contrary still approximately sp^2 hybridized, while the nitrogen and para carbon atoms are almost perfectly sp^2 hybridized as in the planar ground state. The spin density distribution over the π and n orbital of the nitrogen atom shows that T_0 is also in this respect peculiar: the π orbital carries about 40% and the n orbital 10% of the total spin density. For an $n\pi^*$ state one would expect the n orbital to carry more spin density than the π orbital, for a $\pi\pi^*$ state only a very small spin density in the lone-pair orbital is expected. The spin density in the lowest triplet state of pyridine seems to point to a state having both $n\pi^*$ and $\pi\pi^*$ character.

The present paper aims at a theoretical foundation of these observations. It concerns a preliminary report of a quantum chemical study of the state T_0. In contrast to previous calculations,[5-8] we no longer confined the geometry of pyridine to that of the ground state in accordance with the conclusion drawn from our experiments. We have performed ab initio configuration interaction (CI) calculations with two questions in mind.

First, is the observed structure an intrinsic property of the lowest triplet state of pyridine? Our experiments have been carried out at low temperature in the solid phase, and one could imagine that the observed distortion is induced by the crystal field. Experimentally this is found to be unlikely because it has been observed that pyridine molecules subjected to quite different crystal fields seem to be analogously distorted. Calculations on the free molecule should definitely settle this point.

Second, what is the electronic nature of the excitation into T_0 and is it possible to get from this a feeling for the origin of the geometry change upon excitation? In the past the assignment of the lowest triplet state of pyridine has been the subject of dispute. Evans suggested that T_0 is the $^3A_1$ state of $\pi\pi^*$ character.[9] Hoover and Kasha, on the other hand, explained the apparent absence of phosphorescence by assuming that T_0 is the $^3A_2$ state of $n\pi^*$ character,[10] but this assignment was later found to be inconsistent with theoretical predictions on the ordering of the states in the triplet manifold.[7] Subsequently it was hypothesized on the basis of transient absorption studies on pyridine vapor that the lowest triplet state might be the $^3A_1$ ($\pi\pi^*$) state perturbed by a vibronic coupling with the $^3B_1$ ($n\pi^*$) state.[11]

The presence of two near-degenerate triplet states has been corroborated by experimental as well as theoretical studies. Low-resolution electron scattering data showed a triplet state at 4.1 eV, while the onset of this spectrum at ~3.7 eV indicated the presence of another triplet state.[12] Japar and Ramsay interpreted their long-pathlength absorption spectrum as arising from two different $T \leftarrow S_0$ band systems separated by about 1700 cm^{-1}.[20] Semiempirical calculations predicted for the planar geometry the $^3A_1$ ($\pi\pi^*$) state to be lowest but to lie within 2000 cm^{-1} of the $^3B_1$ ($n\pi^*$) state.[7] A similar conclusion was obtained from extensive ab initio calculations reported recently.[8] Both calculations do, however, not take into account a possible distortion of pyridine in T_0.

In the calculations we have considered the states which in C_{2v} symmetry correspond to the $^3B_1$ ($n\pi^*$) state and the 1,2 $^3A_1$ ($\pi\pi^*$) states. The 1 $^3B_2$ state, which is of lower energy than the 2 $^3A_1$ state,[8] is not of interest here. In our calculations on the distorted molecular structures, this B_2 state becomes of a different symmetry than the B_1 and A_1 states and thus can not couple with these states. For the planar molecule it will be shown that the $^3B_1$ and 1 $^3A_1$ state are near-degenerate. Calculation of the potential energy surfaces of the three triplet states along out-of-plane coordinates shows that T_0 indeed is intrinsically unstable with respect to distortions in which the nitrogen atom is tilted with respect to the plane of the ortho and meta carbon atoms, the geometry of minimum energy occurring for an angle of 35°. According to the present calculation, a tilt of the para carbon atom on the other hand increases the energy of T_0. This behavior will be rationalized on the basis of the nature of the molecular orbitals that participate in the electronic transition.

II. Computational Details

The calculations start from a planar geometry of C_{2v} symmetry as it has been determined for the ground state.[13] Distortions of the molecule along two (model) out-of-plane coordinates have been considered. In the first the nitrogen atom has been rotated around the axis through the two ortho carbon atoms. The angle by which the nitrogen atom has been rotated with respect to the planar molecule will be designated by α, and the distortion will be called the N-distortion. The second out-of-plane coordinate concerns the para carbon atom that has been rotated around the axis through the two meta carbon atoms. In doing so the para hydrogen atom has been rotated by the same amount as the para carbon atom and consequently has been kept in the plane spanned by the para and the two meta carbon atoms. This rotation angle will be indicated by β and the distortion labeled the C-distortion. While rotating the nitrogen atom or the para carbon and hydrogen atoms, the rest of the molecule has been kept in its planar ground-state geometry. This modeling of the respective distortion coordinates represents an idealized description of the experimentally observed structural changes upon excitation into T_0.

A distortion of the molecule as mentioned above lowers the symmetry from C_{2v} to C_{1h}. Though it is then no longer correct to label the triplet states with B_1 and A_1, since they both become of A′ symmetry, we will for the sake of clarity continue to label states and orbitals with the symmetry labels of C_{2v}.

For the carbon atoms and the nitrogen atom the (9s,5p) basis, contracted according to Dunning to the [4s,2p] Cartesian Gaussian basis set, has been used.[14] For the hydrogen atoms the (5s) set contracted to [2s] has been employed.[15] With this atomic orbital (AO) basis set we obtained for the ground state with a planar geometry an SCF energy of −246.5519 H. This compares favorably with earlier calculations that used basis sets of similar quality but slightly different geometries.[8]

The CI calculations have been performed with the CRAY-XMP version of the Wuppertal–Bonn multireference single- and double-excitation CI (MRDCI) method with configuration selection and energy extrapolation to the generated MRDCI space.[16] The energy corresponding to the full CI space within the AO basis has been estimated by the formula given in.[17] The complete set of the 70 molecular orbitals

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(MOs) has not been used in the CI calculations, but a truncated set of 59 orbitals obtained by discarding the 11 σ-type virtual orbitals of highest energy has been used. Of these 59 orbitals, the lower 11 σ-type orbitals have been kept doubly occupied, resulting in a CI in which 20 electrons have been correlated.

The MO set used in the CI expansion of the $^3B_1$ ($n\pi^*$) and the two $^3A_1$ ($\pi\pi^*$) states derives from an SCF calculation on the $^5B_1$ state (... $(2b_1(\pi))^2(11a_1(n))^1(1a_2(\pi))^1(3b_1(\pi^*))^1(2a_2(\pi^*))^1$). This choice is based upon the following observations:

(i) The electronic state we are primarily interested in is the $^3B_1$ ($n\pi^*$) state. Consequently we have tried to use as MO basis the SCF orbitals of the ...$11a_1(n)3b_1(\pi^*)$ configuration. In C_{2v} symmetry such an SCF calculation is well possible, but upon distorting the molecule convergence is much more difficult, up to the point that for α or $\beta \geq 15°$ no convergence could be obtained anymore. Trial SCF calculations with ground-state SCF orbitals show that this behavior has to be attributed to a mixing of the ...$11a_1(n)3b_1(\pi^*)$ configuration with the ...$2b_1(\pi)\cdot 3b_1(\pi^*)$ configuration. Consequently, the lowest triplet state for a distorted geometry can not be described as a dominant one-configuration state upon distortion but should be considered as a two-configuration state for which convergence problems are commonly observed in a single-configuration SCF calculation.

(ii) CI calculations with an MO basis consisting of ground-state SCF orbitals show a large dependence of the MRDCI energies and MRDCI expansions of the wave functions of the triplet states on the number of reference configurations. In the MRDCI method[16] a set of configurations with the proper symmetry is generated from the single and double excitations for a given set of reference configurations. Subsequently the generated MRDCI space is truncated by a selection of configurations on the basis of an energy-lowering criterium. The effect of the discarded configurations on the energy is taken into account via a perturbation treatment. For such a perturbation treatment, it is essential that the zeroth-order wave function, obtained by diagonalizing the CI matrix in the basis of the reference configurations, is a good approximation to the CI expansion in which also the selected configurations from the MRDCI space are used. We observed on the contrary that for nonplanar geometries the overlap between zeroth order and final CI expansions was too low and varied dramatically as a function of the number of reference configurations.

(iii) Calculations on the lower excited triplet and singlet states of benzene have shown that an adequate way to circumvent problems associated with two-configuration states is to use the SCF orbitals of a quintet state.[18,19] For this state the singly occupied orbitals are chosen as the ones that are singly occupied in either of the two configurations. For the lowest triplet state of pyridine this would mean a state in which $11a_1(n)$, $2b_1(\pi)$, $3b_1(\pi^*)$, and another π^* orbital are singly occupied because the mixing of the ...$11a_1(n)3b_1(\pi^*)$ configuration mainly occurs with the ...$2b_1(\pi)3b_1(\pi^*)$ configuration. Use of such quintet MOs led, however, to the same problems as encountered for the ground-state SCF orbitals.

(iv) Only the $^5B_1$ state mentioned above has been found to generate SCF orbitals that meet the criteria to properly perform the MRDCI calculations.

In the calculations a set of reference configurations has been used that consisted of the 27 configurations, of which the magnitude of the coefficient in the CI expansion is larger than 0.05 in the $^3B_1$ state or larger than 0.10 in either of the two $^3A_1$ states for any of the geometries considered in our calculations. Selection of the generated configurations on the lower three roots of the CI with the reference configurations with an energy threshold of 15 μH resulted in CI expansions that varied in size between 3000 and 8000 configurations out of 4 437 166. For the planar molecule two separate calculations have been performed, one for the $^3B_1$ state and one for the $^3A_1$ states. In these calculations the same set of reference configurations has been used albeit that the configurations have been divided into the two symmetry classes.

III. Results and Discussion

In Figure 1 we show the calculated potential energy surfaces of the $^3B_1$ ($n\pi^*$) and the 1,2 $^3A_1$ ($\pi\pi^*$) states as a function of the rotation angles α and β. In Table I some characteristics are given of the CI calculations for the planar geometry of C_{2v} symmetry.

From Figure 1 it is clear that the planar ground-state geometry of pyridine is not a stable geometry for the lowest triplet state. The energy of this state is lowered upon the N-distortion, the geometry of lowest energy being found for a rotation of approximately 35°. By this rotation, pyridine is stabilized in comparison to the planar geometry by about 1500 cm^{-1}. The potential energy surface of the lowest triplet state is remarkably flat. Even for large values of α the energy does not increase considerably, and

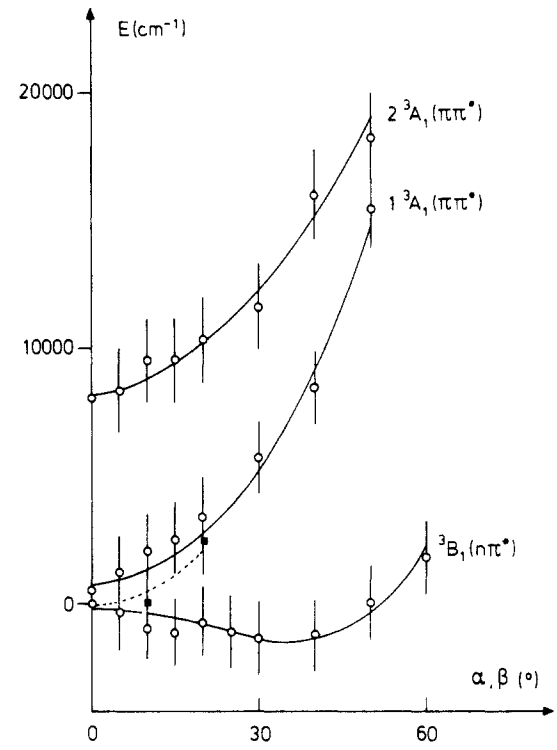

Figure 1. Potential MRDCI energy of the $^3B_1$ ($n\pi^*$) and 1,2 $^3A_1$ ($\pi\pi^*$) states as a function of the angles α of the N-distortion (circles and solid lines) and β of the C-distortion (squares and dashed line). The lines result from a polynomial fit but serve no purpose other than a guide to the eye. The zero of energy corresponds to the energy of the $^3B_1$ state in the planar geometry.

Table I. Characteristics of the CI Calculations of the $^3B_1$ and 1,2 $^3A_1$ States for the Planar Geometry (1 H = 219 474.62 cm^{-1})

	$^3B_1$	1^3A_1	2^3A_1
no. ref config	14	13	13
no. generated config	1 222 076	1 420 703	1 420 703
threshold T (μH)	15	15	15
no. selected config at T	3246	3479	3479
E_{rc}[a] (H)	−246.4429	−246.4204	−246.3801
$E(T)$[b] (H)	−246.5824	−246.5316	−246.5021
$E(T = 0)$[c] (H)	−246.6879	−246.6808	−246.6467
extrapolation uncertainty (H)	0.0053	0.0064	0.0072
$E(T = 0) + E_{DAV}$[d] (H)	−246.7058	−246.7035	−246.6692
$\sum_{i=1}^{no.\ ref} c_i^2$[e]	0.9270	0.9126	0.9154

[a] Energy after CI with only the reference configurations. [b] Energy at lowest threshold T. [c] Energy extrapolated to $T = 0$. [d] Energy extrapolated to $T = 0$ including the Davidson correction.[17] [e] Sum of squared contributions of the reference configurations in the final CI expansion.

it is only for values of $\alpha > 50°$ that the energy gets higher than that for the planar geometry. In contrast to the energy lowering observed for the N-distortion, there is no indication that a similar effect occurs along the C-distortion coordinate.

The energy of the two $^3A_1$ states has been found to increase with increasing value of α. The calculation of the potential energy surfaces of these two states for a variation of the angle β turned out to be subject to the same problems described in Section II for a CI calculation with the ground-state SCF orbitals: the final CI expansion of for example the 1 $^3A_1$ state showed too much of an overlap with the zero-order expansion of the 2 $^3A_1$ state. As will be shown below, it is likely however that also along the C-distortion coordinate the energy minimum of these states coincides with the planar nuclear configuration.

Correlation effects within the combined σ–π-electron system underlie the stabilization of the lowest triplet state as a function of the nitrogen displacement angle α. This becomes clear when we consider the potential energy surfaces of Figure 2. These have been calculated by using for the CI expansion only the reference configurations, which mainly consist of $n\pi^*$ and $\pi\pi^*$ excitations.

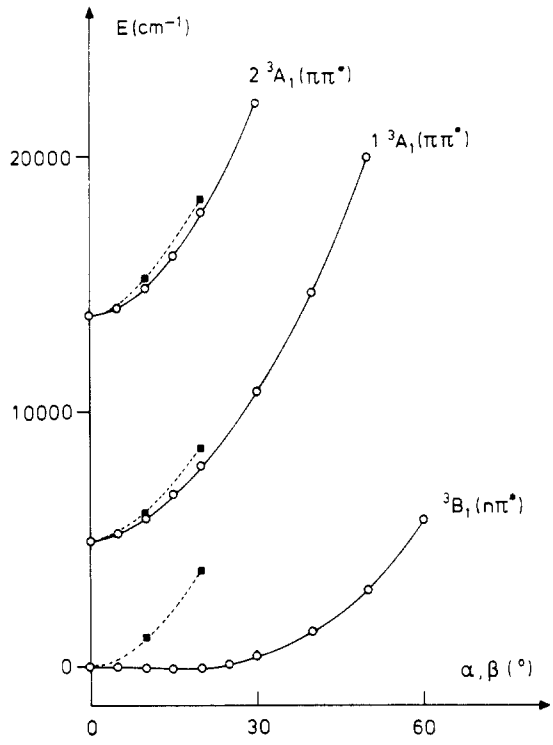

Figure 2. Potential energy of the $^3B_1$ ($n\pi^*$) and 1,2 $^3A_1$ ($\pi\pi^*$) states as a function of the angles α of the N-distortion (circles and solid lines) and β of the C-distortion (squares and dashed lines). The energy has been calculated in a CI calculation with only the reference configurations. The zero of energy corresponds to the energy of the $^3B_1$ state in the planar geometry.

In this calculation the lowest triplet state qualitatively still shows the same features as in Figure 1, but the stabilization energy along the N-distortion coordinate is much less. For both $\pi\pi^*$ states the energy is minimum for the planar geometry. Though we have not been able to calculate in the "complete" CI energy dependence of these states for the C-distortion, the results as drawn in Figure 2 give reason to believe that for this distortion also the energy of the $\pi\pi^*$ states increases with increasing value of β.

Next we describe the results obtained for the planar geometry and subsequently consider why this geometry is unstable in the lowest triplet state. In C_{2v} symmetry the $^3B_1$ ($n\pi^*$) state and the 1 $^3A_1$ ($\pi\pi^*$) state are nearly degenerate according to our MRDCI calculations (ΔE = 500 cm^{-1}; cf. Figure 1). On the other hand we observed that this separation is sensitive to the inclusion of σ–π and σ–σ-correlation effects, because a calculation with only the reference configurations yielded an energy difference between the two states of 5000 cm^{-1}. In a recent communication, Kitao and Nakatsuji reported SAC-CI calculations on the planar pyridine molecule that revealed a similar behavior.[8] They found the 1 $^3A_1$ ($\pi\pi^*$) state to be the lowest triplet state both in a calculation in which only the π and n electrons are correlated and in a calculation in which also the σ electrons are taken into account. For the first calculation a separation of 10 000 cm^{-1} had been calculated, but in the second calculation the separation decreased to 1200 cm^{-1}. Experimentally no firm evidence exists on the position of the two states relative to each other. Electron scattering and absorption data seem to suggest that the two lower triplet states are close to each other, the energy difference being of the order of 2000 cm^{-1}.

As to the question whether in C_{2v} symmetry the $^3B_1$ ($n\pi^*$) state or the 1 $^3A_1$ ($\pi\pi^*$) state is lowest, the above-mentioned experiments give no clue. We have calculated that the lowest triplet state is the $^3B_1$ ($n\pi^*$); other theoretical studies have assigned it as the 1 $^3A_1$ ($\pi\pi^*$) state.[5-8] Though from a calculational point of view the ordering in C_{2v} symmetry may be of interest, the question is hardly relevant experimentally. The lowest triplet state of pyridine in the geometry of lowest energy is neither of these states but an A′ state with both $n\pi^*$ and $\pi\pi^*$ character.

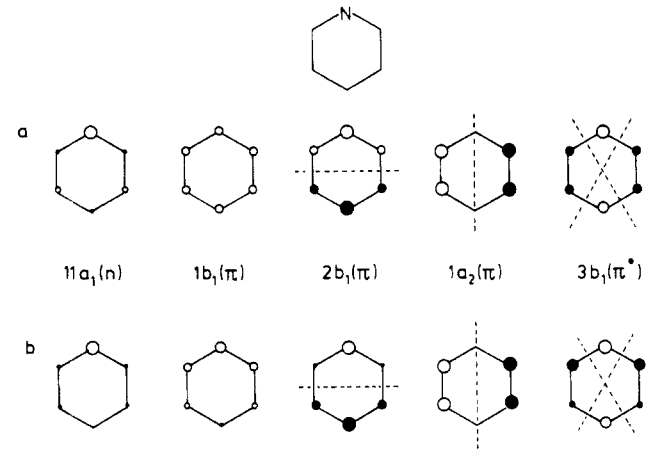

Figure 3. Schematic representation of the important MOs that participate in the lowest triplet state. The SCF orbitals of the ground state are given in a, those of the $^3B_1$ ($n\pi^*$) state in b. The circles are a measure for the participation of the AOs on an atom in the MO.

To assess the question why for the lowest triplet state the planar geometry is not the one of minimum energy, we consider the form of the molecular orbitals. In Figure 3 we compare the form of the lone-pair orbital and of the four important π orbitals involved in the $n\pi^*$ excitation as they result from SCF calculations on the ground state (Figure 3a) and on the $^3B_1$ ($n\pi^*$) state (Figure 3b) for the planar molecule. In the π orbitals for the ground state (Figure 3a) one may well recognize the related orbitals for benzene. The lone-pair orbital is largely localized on the nitrogen atom, and there are minor contributions from atomic orbitals on all the carbon atoms, in accordance with earlier calculations.[21] In C_{2v} symmetry the dominant contribution to the $^3B_1$ state is the configuration resulting from the excitation of an electron from the n orbital to the $3b_1(\pi^*)$ orbital. The latter orbital is in the ground state antibonding between the nitrogen atom and the two ortho carbon atoms and between the para and the two meta carbon atoms. It is plausible that upon excitation of the molecule a geometrical relaxation will take place in such a way that the antibonding character becomes reduced. This might very well rationalize the observed distortion of pyridine along the N out-of-plane coordinate.

Such a reasoning would also predict an energy lowering upon the C-distortion. The orbitals for the ...$11a_1(n)3b_1(\pi^*)$ configuration show why this is less likely to occur. From Figure 3b we see that the n orbital is essentially not changed in character: it is still localized on the nitrogen atom, the delocalization over the carbon atoms being slightly less than in the ground state. The $3b_1(\pi^*)$ orbital, however, changes considerably. It is still antibonding between the same atoms as in the ground state, but the antibonding character between the nitrogen and ortho carbon atoms has increased, whereas the antibonding character between the para and the meta carbon atoms has diminished. Moreover, it is seen that for the $2b_1(\pi)$ orbital, which remains doubly occupied in this excitation, the bonding character between the nitrogen and the ortho carbon atoms also reduces compared to the same orbital in the ground state, while the bonding character between the para and meta carbon atoms remains the same. Consequently, a rotation of the para carbon/para hydrogen fragment is not expected to stabilize the lowest triplet state as much as a rotation of the nitrogen atom.

Our experimental results have established that the nitrogen atom is tilted with respect to the plane spanned by the ortho and meta carbon atoms by 40°, the atomic orbitals on the ortho carbon atoms being almost sp^3 hybridized. In our calculations we find the geometry of lowest energy at α = 35°, which is in surprisingly good agreement with the experiment, given the approximations in the calculation. Moreover the calculations have been performed on the free molecule, while the experimental structure has been

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derived in the presence of a crystal field. The most serious limitation of our calculations in this respect concerns the ortho carbon atoms that are only allowed to rehybridize partially, because the ortho hydrogen atoms have been kept fixed in the positions they occupy in the planar geometry. Experimentally we have observed that the para carbon/para deuterium fragment is rotated as well, albeit only by about 10°. Our calculations do not reproduce this observation, although the potential energy surface of Figure 1 is rather flat for small values of β (the energy for $\beta = 10°$ is almost equal to the energy in the planar geometry). Consequently, it may well be that also the C-distortion would have led to an energy lowering of the lowest triplet state if the hybridization on the meta carbon atoms would have been relaxed.

Besides the above mentioned rehybridization there is another effect that could influence the distortion of pyridine in its lowest triplet state. Though we have calculated that the $^3A_1$ states are not susceptible to out-of-plane distortions, it is to be expected that for the 1 $^3A_1$ state in-plane structural changes do occur. This state is the analogue of the $^3B_{1u}$ ($\pi\pi^*$) state in benzene, which is vibronically coupled to the $^3E_{1u}$ state. Both experimental[22-24] and theoretical[18,19] evidence exists that benzene in the $^3B_{1u}$ state is distorted along an in-plane vibrational coordinate. McWeeny and Peacock have pointed out that for the $\pi\pi^*$ states in azabenzenes similar behavior is to be expected.[25] A vibronic coupling of the 1 $^3A_1$ and 2 $^3A_1$ (the analogue of one of the components of the $^3E_{1u}$ state in benzene) states in pyridine may consequently be anticipated and such a coupling would indirectly influence the mixing of the $^3B_1$ ($n\pi^*$) and the 1 $^3A_1$ ($\pi\pi^*$) states.

The question arises whether the out-of-plane distortion found for the lowest triplet state of pyridine can be regarded as a typical phenomenon for electronic states in azaaromatics that, uncoupled, are of $n\pi^*$ character. For this kind of molecules vibronic interactions between $n\pi^*$- and $\pi\pi^*$-triplet states[26-28] and a possible nonplanar geometry[29-31] have repeatedly been suggested. Except for pyridine, though, no direct evidence is available for such distortions. Many quantum chemical calculations have been reported over the years that concerned the excitation energies of azaaromatic compounds. Unfortunately, virtually no calculations considered the possible instability of the lowest triplet states of $n\pi^*$ character with respect to out-of-plane distortions. Terazima et al. recently performed a geometry optimization of the lowest triplet state of pyridazine (1,2-diazabenzene).[32] Within the Hartree–Fock approximation they found a minimum in the energy for an out-of-plane twisted configuration of the nitrogen atoms. This tendency toward nonplanarity seemed, however, to be compensated by the inclusion of electron correlation, which, in our opinion, can not well be understood on the basis of the reported wave function.

An azaaromatic molecule in its ground state is planar as a consequence of the stabilization energy that results from a delocalization of the π electrons. Upon $n\pi^*$ excitation an electron is excited from the n orbital to a π^* orbital. In $n\pi^*$ states the π-electron system is consequently no longer aromatic. For example, for the azabenzenes a 7π-electron system results that does not obey the $4n + 2$ rule. Since it is the extra electron that reduces the resonance stabilization, a possible distortion will be bound up with the nature of the π^* orbital involved in the excitation. In pyridine this π^* orbital has been observed to be antibonding between the nitrogen and the ortho carbon atoms and to a lesser extent between the para and the meta carbon atoms. The observed and calculated distortion of the molecule in the lowest triplet state is such that this antibonding character becomes reduced. For pyridazine the π^* orbital is one that is virtually localized on the two nitrogen atoms and strongly antibonding between these atoms.[32] At least at the Hartree–Fock level, the optimized geometry for pyridazine suggests that the antibonding character of this π^* orbital may determine the structure in the lowest triplet state for this molecule as well.

For azaaromatic molecules in $n\pi^*$-excited states one should thus be aware of a possible out-of-plane distortion of the molecule. The above considerations indicate that such a structural change seems to be governed by the antibonding character of the π^* orbital.

IV. Conclusions

The present ab initio calculations have led to the conclusion that the free pyridine molecule in its lowest triplet state is not planar as it is in the ground state. Upon excitation the molecule becomes heavily distorted along an out-of-plane vibrational coordinate by which the nitrogen atom is tilted with respect to the plane of the ortho and meta carbon atoms. This conclusion is in good agreement with the experimentally determined structure of pyridine in the lowest triplet state in a benzene crystal. The nature of the MOs indicates that the distortion presents the answer of the molecule to an increased antibonding character in the π-electron system upon excitation. From another point of view one might interpret the structural change as the result of a strong vibronic coupling between the $^3B_1$ ($n\pi^*$) and the 1 $^3A_1$ ($\pi\pi^*$) states, states that are nearly degenerate in the planar geometry. Due to this coupling the lowest triplet state is neither an $n\pi^*$ state nor a $\pi\pi^*$ state but a state of mixed character.

Acknowledgment. This work was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Scientific Research (NWO).

Registry No. Pyridine, 110-86-1.

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