

CNDO/S-CI-*n*PDQ Studies of the Solvation Effect on the UV Spectra of Pyridine N-Oxide and its Complexes with Proton

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Using the *n*-PDQ model, in which the solvent is simulated by several point dipoles and quadrupoles, we have estimated the shift of the UV bands of pyridine N-oxide (PyO), its cationic acid (PyOH⁺), and homoconjugated cation (PyOHPyO⁺) caused by the solvent (acetonitrile). We have calculated the UV spectra of both unsolvated and solvated species by the CNDO/S-CI and CNDO/S-CI-*n*PDQ method, respectively. We have found that all the bands of all the species under study are blue-shifted on solvation. The most significant is the shift of the long-wave $\pi \rightarrow \pi^*$ bands of pyridine N-oxide.

Introduction

In our previous paper [1] we have calculated the spectra of pyridine N-oxide (PyO), its protonated form (PyOH⁺), and its homoconjugated cation (PyOHPyO⁺) *in vacuo*, using the CNDO/S-CI method with deorthogonalized orbitals (CNDO/SD-CI). This has enabled us to assign the experimentally observed bands to the particular transitions.

In the case of PyO, the first intense band, at about 290 nm, is of $\pi \rightarrow \pi^*$ type and has a redox character (charge-transfer from oxygen to the ring). The second one, at about 255 nm, is the same as 1L_b band of pyridine. The bands below 220 nm are the K bands of benzene ring which are in the region of absorption of most solvents and not so interesting, therefore, from the point of view of the solvation effect. In the case of PyOH⁺ and PyOHPyO⁺ the sequence of the redox and 1L_b bands is reversed due to protonation [1].

The aim of this work is to estimate theoretically the influence of the solvation effect on the UV spectra of the species mentioned above. As a mod-

el solvent we have chosen acetonitrile. To simulate the solvent we have used the *n*-PDQ model [2], in which the solvent is represented by several point dipoles and quadrupoles positioned around the molecule under study. We have applied the CNDO/S-CI method with Del Bene–Jaffé parameters [3] and Nishimoto–Mataga expressions for the integrals [4]. Thirty configurations of successively increasing energy have been considered. To calculate the parameters of the transitions we used CI coefficients corresponding to nondeorthogonalized orbitals.

Methods

Crystallographic geometries of PyO and PyOH⁺ have been taken [5, 6]. As no experimental data exist for the homoconjugated cation PyOHPyO⁺, we have assumed that the geometry of the ring does not change when compared with PyO, while the N–O bond length increases by 0.05 Å with respect to PyO, being still shorter than that of PyOH⁺, as in the case of 2,6-lutidine N-oxide semiperchlorate [7]. Also on the basis of the crystallographic data of the 2,6-lutidine N-oxide homoconjugated cation we have assumed a symmetric hydrogen bond with O···O distance of 2.345 Å [7]. Due to the CNDO/S restrictions we had to assume a planar conformation of the homoconjugated cation.

The point dipoles representing the solvent molecules were positioned at a distance of 3 Å from the species studied (*i.e.* on the van der Waals sphere) so as to get the optimal ground state energy. As the electrostatic potential of a point quadrupole falls off with the distance much faster than that of point dipoles, we thought sufficient to take a point dipole to represent acetonitrile molecules, setting thus the quadrupole moment to zero. We assumed the experimental value of the dipole moment of acetonitrile, of 3.96 D [8]. In the case of PyO and PyOH⁺ two point dipoles were positioned symmetrically in the plane of the ring and directed towards the oxygen atom, the remaining two being placed above and below the ring plane, respectively and directed towards the nitrogen atom. In the case of PyOHPyO⁺ we used one dipole per each heteroatom, antisymmetrically with respect to the plane of the supermolecule.

Results and Discussion

The transition wavelengths and oscillator strengths for both unsolvated and solvated species under consideration are summarized in Table I. As shown, all the bands of all the species are blue-shifted on solvation. Obviously, it can hardly be

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expected that such a simple electrostatic model as we used could give the "exact" positions of the respective bands in acetonitrile solution. On the other hand, it can be assumed that the differences between the shifts of different bands are well reproduced qualitatively.

The most shifted is the long wave $\pi \rightarrow \pi^*$ bands of pyridine N-oxide (from 329 to 325 nm, and from 294 to 291.5 nm, respectively), while the benzene band in all the species is little influenced by the solvation effect (of about 1 nm).

Table I. Calculated absorption spectra of pyridine N-oxide and its complexes with proton.

Species	Unsolvated		Solvated	
	λ [nm]	Oscillator strength	λ [nm]	Oscillator strength
PyO	329	0.020	325	0.020
	294	0.311	291.5	0.301
	217	0.241	216	0.235
PyOH ⁺	252.5	0.082	251.5	0.078
	208.5	0.017	207	0.012
PyOHPyO ⁺	263.5	0.380	263	0.346
	223.5	0.003	222.5	0.0005

The above tendencies are consistent with the experimental data available. Passing from vacuum to solvents of increasing polarity results in a remarkable blue-shifting of the intense $\pi \rightarrow \pi^*$ band observed for pyridine N-oxide [9] and its substituted derivatives [10, 11]. The position of the absorption maximum, which is at about 282 nm for vacuum [9] and nonpolar aprotic solvents like *n*-heptane [11] and *n*-hexane [9], shifts to 275 nm in polar aprotic solvents like acetonitrile [11], and up to 263 nm [12], and 254 nm [13] for polar amphiprotic solvents like ethanol and water. In contrast to this, the position of the 1L_b benzene band is almost independent of the polarity of the solvent [12–14].

It is important to note that our calculations indicate that the weak longest-wavelength band has a $\pi \rightarrow \pi^*$ character, which is consistent both with experiment [15], and with *ab initio* calculations [16]. Some authors [9] assigned to this band a $n \rightarrow \pi^*$ character, based on its large blue-shift in polar solvents [17]. Our calculations have shown that the effect of solvation on this band is significant, in spite of its non- $n \rightarrow \pi^*$ character. Therefore, we can conclude that the solvent-caused shift is not a quantity sufficient to determine whether a band has a $n \rightarrow \pi^*$ or a $\pi \rightarrow \pi^*$ character.

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