Crystal structure, spectroscopic, and theoretical investigations of excited-state proton transfer in the doubly hydrogen-bonded dimer of 2-butylamino-6-methyl-4-nitropyridyne*N*-oxide.

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Streszczenie

The crystal structure of 2-butylamino-6-methyl-4-nitropyridine N-oxide (2B6M) was resolved on the basis of X-ray diffraction. Solid 2B6M occurs in the form of a doubly hydrogen-bonded dimer with squarelike hydrogen-bonding network composed of two intra- (2.556(2) A) and two intermolecular (2.891(2) A) N-H...O type hydrogen bonds. The molecule thus has both a protonable and a deprotonable group that led us to investigate the possibility of an excited-state proton transfer (ESIPT) reaction in different solvents by means of experimental absorption, steady state, and time-resolved emission spectroscopy. The results were correlated with quantum mechanical TD-DFT and PM3 calculations. Experimental and theoretical findings show the possibility of an ESIPT reaction in polar solvents. It is demonstrated that in particular the emission spectra of 2B6M are very sensitive to solvent properties, and a large value of the Stokes shift (about 8000 cm(-1)) in acetonitrile is indicative for an ESIPT process. This conclusion is further supported by time-resolved fluorescence decay measurents that show dual exponential decay in polar solvents. Vertical excitation energies calculated by TD-DFT reproduce the experimental absorption maxima in nonpolar solvents well. The majority of electronic transitions in 2B6M is of pi --> pi* character with a charge shift from the electron-donating to the electron-accepting groups. The calculations show that, due to the charge redistribution on excitation, the acidity of the amino group increases significantly, which facilitates the proton transfer from the amino to the N-oxide group in the excited state.

Słowa kluczowe

Absorption, Fluorescence, Oligomers, Solvents, energy