



The impact of solvent polarity on intramolecular proton and electron transfer in 2-alkylamino-4-nitro-5-methyl pyridine *N*-oxides.

Autorzy

Anna Szemik-Hojniak

Łukasz Wiśniewski

Irena Deperasińska

A. Makarewicz

Lucjan Jerzykiewicz

Aniela Puszko

Yuval Erez

Dan Huppert

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The crystal structure of 2-butylamino-4-nitro-5-methyl pyridine N-oxide (2B5M) and solution studies of both 2B5M and 2-methylamino-4-nitro-5-methyl pyridine (2M5M) N-oxide are presented. Steady-state absorption and emission measurements were employed for both molecules while a picosecond fluorescence up-conversion technique was used to follow the dynamic behavior of the 2M5M system. The experimental methods were complemented by DFT and TD DFT B3LYP/6-31G(d,p) calculations involving ground and excited-state optimization which in the case of the smaller 2M5M molecule were extended to the CAM-B3LYP/6-31G(d,p) method. The solvent effect is incorporated by applying the polarizable continuum (PCM) model. The data reveal that the 2B5M molecule crystallizes in the monoclinic space group P2(1)/c and its crystal lattice is composed of monomers with intramolecular N-H...O [2.572(3) Å] hydrogen bonds, connected into a polymer network by weak intermolecular C-H...O [3.2-3.4 Å]-type interactions. Quantum-chemical calculations show that the aminoalkyl substituent in aminoalkyl-pyridine N-oxides is a specific determinant of the CT nature of the lowest-lying excited electronic $\pi\pi^*$ state, distinguishing them from other nitroaromatic compounds. The results of both picosecond fluorescence up-conversion experiments in different solvents and quantum-chemical calculations suggest that in nonpolar media the ESIPT process in 2M5M is favored, while in polar acetonitrile, the $N^* \rightarrow PT^*$ transition demands barrier-crossing and thus unfavorable thermodynamic conditions do not allow the ESIPT to occur. The signals of picosecond fluorescence up-conversion of 2M5M are solvent- and emission-wavelength dependent. The three time components found in a weakly polar isooctane-dioxane mixture have been attributed to solvation dynamics (~ 500 fs), and to relaxation of N^* and PT^* forms while in acetonitrile, a very rapid fluorescence decay with a time constant (2.3-4.0 ps) indicative of the presence of the normal (N^*) form was observed. Much shorter fluorescence lifetimes in alcohols (a few picoseconds) and in D(2)O (less than 200 fs) than in aprotic solvents suggest that in protic media, the solvent molecules participate in the ESIPT, bridging between the methylamine group and the N-oxide group of 2M5M.

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