Intramolecular charge transfer in aminosubstituted phthalides: theoretical quantum-chemical calculations and experimental study.

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The introduction of electron donating amino substituent to the aromatic ring of non-fluorescent phthalide (Pd) results in a strong change of electronic spectrum due to ground state interaction of lone pair electrons from nitrogen atom with the π-system, giving rise to a long-wave charge transfer (CT) absorption band [1]. The nature of the interaction and therefore the extent of coupling between the substituent and the phthalide depend on the position of the amino group at the ring. Aminophthalides with dimethyamino (DMA) group substituted at ring positions different than the para orientation in relation to the carbonyl group (4-DMAPd, 6-DMAPd and 7-DMAPd) have similar UV absorption spectra indicating that the electronic structure of those molecules resemble that of phthalide modified with CT transition from DMA to the Pd ring. Substitution with DMA group at 5 position (5-DMAPd) generates completely different electronic structure displaying UV spectrum characteristic for dimethylaniline linked to the lactone ring.

Absorption spectra of non-para DMAPds consist of three clearly separated bands and differ from the phthalide absorption spectrum by the presence of a long-wave CT band (with maximum in hexane at 31870 cm\textsuperscript{-1} and at 29450 cm\textsuperscript{-1} for 4-DMAPd and 6-DMAPd, respectively). Absorption spectrum of the ρ-derivative, 5-DMAPd, significantly differs both from that of phthalide and from the non-para derivatives: the first absorption band in n-hexane lies deeper in UV (band maximum at 35340 cm\textsuperscript{-1}) and includes two closely lying electronic transitions (S\textsubscript{0} → S\textsubscript{1} and S\textsubscript{0} → S\textsubscript{2}, as verified by magnetic circular dichroism spectroscopy and by semiempirical DFT calculations).

DFT and CASSCF methods have been used for geometry optimization and estimation of energies of vertical electronic transitions.

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