THE PHOTOPHYSICS OF 1,8-(BISDIMETHYLAMINO)NAPHTHALENE: INTERNAL CHARGE TRANFER WITH A TWIST

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The photophysical properties of the excited states of 1,8-(bisdimethylamino)naphthalene have been investigated by a combination of experimental spectroscopic methods and ab initio calculations. The experiments show that the lowest excited singlet state is a state with dominant internal charge transfer character that gives rise to weak emissive properties, a strong solvent dependence of the emission, and transient absorption spectra that carry the signature of the steady-state absorption spectra of the naphthalene radical anion. The ab initio calculations support the interpretation of the experimental studies, and enable us to put their results into a broader perspective. They explain the order of the lower excited states of 1,8-(bisdimethylamino)naphthalene and related compounds as well as the role of intramolecular relaxation upon excitation, thereby elucidating the large Stokes shift already observed in nonpolar solvents. Transient absorption experiments on the femtosecond timescale elucidate the dynamical processes such as intramolecular large-amplitude motions, solvent relaxation, and vibrational cooling that occur after excitation.