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Published on Web 05/25/2004

On the Nature of the Low-Lying Singlet States of 4-(Dimethyl-amino)benzotrile

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Abstract: 4-(*N,N*-Dimethyl-amino)benzotrile (DMABN) is a prototype molecule for dual fluorescence. The anomalous emission has been attributed to an intramolecular charge-transfer (ICT) state, and the structure of the latter is still subject to some controversy. We applied a recently developed analytical gradient code for the approximate coupled-cluster singles-and-doubles method CC2 in combination with accurate basis sets to address this problem. Fully optimized excited state structures are presented for the ICT state and the so-called locally excited state, and recent transient IR and Raman measurements on the excited states are interpreted by means of calculated harmonic frequencies. Strong evidence is found for an electronic decoupling of the phenyl and the dimethyl-amino moiety, resulting in a minimum structure for the ICT state with a twisted geometry. In contrast to previous findings, the structure of this state is, at least in the gas phase, not C_{2v} symmetric but distorted towards C_s symmetry. The distortion coordinate is a pyramidalization of the phenyl carbon atom carrying the dimethyl-amino group. The results from the CC2 model are supported by single-point calculations using more elaborate coupled-cluster models (CCSD, CCSDR(3)) and by CASSCF calculations.
