HIGH RESOLUTION STARK SPECTROSCOPY OF MODEL DONOR-ACCEPTOR AMINOBENZONITRILES IN THE GAS PHASE.[a]

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Electronic communication between donor-acceptor systems is prevalent in many chemical processes. Unfortunately, an accurate description of the changes in molecular geometry responsible for intramolecular charge transfer (ICT) is difficult to ascertain. Reported here are the S_0, L_a, and L_b electronic state structures and dipole moments of two model ICT systems, 4-(1H-pyrrol-l-yl)benzonitrile (PBN) and 4-(1-pyrrolidinyl)benzonitrile (PDBN), as measured by rotationally resolved electronic spectroscopy. As was observed for phenylpyrrole,[a] the unsaturted rings of PBN become collectively more planar following excitation with UV light, in support of the planar ICT model. However, in PDBN the twist/inversion angle between rings is nearly zero in both the ground and excited electronic states. The unperturbed dipole moments measured here, taken in conjunction with available solvatochromism data, provide an estimate for the polarization, dispersion, and charge transfer contributions to solvent-mediated excited state stabilization.

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[a]J.A. Thomas, J.W. Young, A.J. Fleisher, L. Álvarez-Valtierra, and D.W. Pratt, *J. Phys. Chem. Lett.* **1**, 2017 (2010).