ELECTRONIC AND VIBRATIONAL SPECTRA OF A FLEXIBLE MOLECULE HELD AT DIFFERENT CONFORMATIONS: APPLICATION OF CONFORMATIONAL POLYMORPHISM

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The spectrum of a flexible molecule changes with its conformation. In gas and solution phases, it is difficult to obtain significantly different conformations for study without resorting to chemical substitution. A unique approach to studying the conformation-spectrum relationship is through the solid-state phenomenon of conformational polymorphism - the existence of several crystal forms of the same molecule in which the molecule adopts significantly different conformations. 5-Methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile has several conformational polymorphs of different colors within a narrow (¡ 2 kJ/mole) energy range, including Forms R (red prisms, mp 106.2 deg. C), Y (yellow prisms, mp 109.8 deg. C), OP (orange plates, mp 112.7 deg. C), and ON (orange needles, mp 114.8 deg. C). Following Y-ON-OP-R, the thiophene ring undergoes a 126 deg. torsion, passing from being nearly perpendicular to being nearly parallel to the o-nitroaniline part of the molecule. Polarized single-crystal absorption spectra of different polymorphs were recorded using a modified Raman microscope. Miller indices were determined from crystal profile angles and conoscopic interference figures. The visible absorption band correlates with the intramolecular charge-transfer transition of the o-nitroaniline chromophore. While essentially unperturbed in Form Y (the perpendicular conformer), this band is increasingly red-shifted as the thiophene ring becomes more parallel with the o-nitroaniline chromophore. The conformational difference leads to significantly different CN stretch frequencies. The conformation-spectrum relationship was used to investigate molecular conformations in solution and supercooled melt.