4‘-Hydrazone derivatives of 2,2‘: 6‘,2“-terpyridine : protonation and substituent effects

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Four 4‘-hydrazone derivatives of 2,2‘:6‘,2 “-terpyridine which vary in their N- and C-substitution in the R‘NN=CRPh unit have been prepared and structurally characterized. Protonation studies and solution behaviour of these compounds are described, as well as representative crystal structures of mono- and diprotonated derivatives. In the solid-state structures of each neutral compound, the tpy domain adopts the anticipated trans, trans- conformation, and intramolecular steric factors compete with pi-stacking effects to control the amount to which the C-phenyl substituent twists out of the plane of the tpy unit. When R‘ = H, the imine NH group engages in hydrogen bonding interactions in the solid state, except where R = Ph. In solution, variable temperature H-1 NMR spectroscopy shows that on going from R = Me to Ph (with R‘ = H), the barrier to rotation about the Cpy-Nimi_ bond increases; with R = R‘ = H, the hydrogen bonding capabilities of the solvent to the imine NH influence this dynamic process. In the N-methyl derivative (R = H and R‘ = Me), rotation about the C-py-N-imine bond is facile at room temperature. Protonation of the derivative with R = R‘ = H results in an increase in the activation barrier to rotation, consistent with a greater pi-contribution to the C-py-N-imine bond.
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