Effect of Donors and Acceptors on the Twist Angle of Bis(bipyridine)ruthenium(II) 3,4-Diamino-3′,4′-diimino-3′,4′-dihydrobiphenyl. A Bifunctional Biphenyl Derivative and a Potential Molecular Switch

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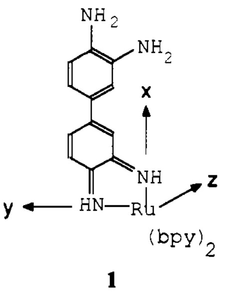
The biphenyl linkage offers a useful building block toward the design of molecular switches, where the rate of electron transport through the molecule may be modified by the degree of twist between the two phenyl groups.[1] We demonstrate here, using AM1 calculations on a model compound, how this twist angle may be dramatically influenced by solvent, in the complex $[Ru(bpy)_2(dadib)]^{2+}$ (**1**), where dadib = 3,4-diamino-3′,4′-diimino-3′,4′-dihydrobiphenyl and bpy = 2,2′-bipyridine[2] (previously called [RuQ,CAT]), which shows extreme solvatochromic behavior in a visible region electronic transition. Lewis acid (or hydrogen bond donor) solvents cause the twist angle to approach 90°, while Lewis base (hydrogen bond acceptor) solvents cause it to approach 0°.

Dissolving species **1** into the strongly hydrogen bond donating solvent water, or adding acceptor species such as H^+ or BF_3 to solutions of **1**, causes the spectrum to appear like that in Figure 1a (water), apparently containing only one strong band. Strong electron donor, or hydrogen bond acceptor (Lewis base), solvents, on the other hand, clearly give rise to two strong bands whose relative intensity varies with solvent (Figure 1b, DMSO = dimethyl sulfoxide).

The metal to ligand charge-transfer (MLCT) transitions of **1**, as labeled in Figure 1, are assigned as follows: bands I, II, Ru d → π^* diimine MLCT from two different ruthenium d orbitals; band III, Ru d → bpy(π^*) MLCT. The assignments are based on studies of related benzoquinonediimine complexes[3,4] and resonance Raman (rR) studies.[5,6] Briefly, FTIR and rR spectra show two skeletal, believed to be largely Ru–N, stretching vibrations associated with the two chemically nonequivalent Ru–NH═ bonds. A resonance Raman excitation profile (Figure 2) reveals that band I shows rR enhancement of the Ru–N vibration at 578 cm^{-1} and also enhancement of some internal quinonediimine deformations,[5] and is assigned[3,4] as $d_{xz} \rightarrow$ BQDI(π^*) (BQDI = benzoquinonediimine) (see **1** for reference frame), while band II shows enhancement of the Ru–N vibration at 618 cm^{-1} and is assigned as $d_{yz} \rightarrow$ BQDI(π^*).[7] The rR data demonstrate that transition I lies very close to transition II in the spectrum in water; it is evidently obscured by transition II in this medium. Excitation into III enhances bipyridine vibrations.



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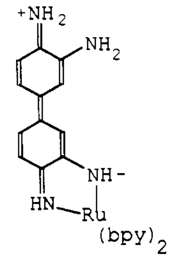

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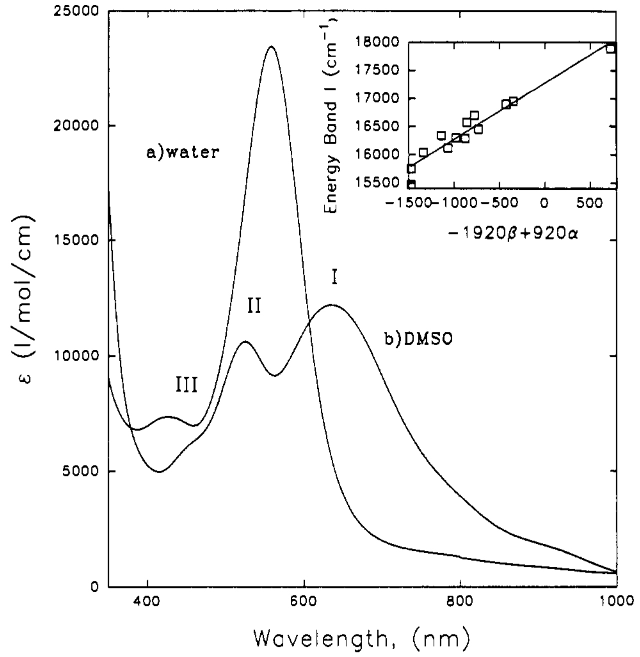

Figure 1. Electronic spectra of complex **1** in water (a) and in dimethyl sulfoxide (b). Band I in the water spectrum is obscured by band II therein. The inset shows the solvatochromism of band I plotted as a function of Taft and Kamlet α and β parameters. The solvent on the upper right is water, and that on the lower left is DMSO.

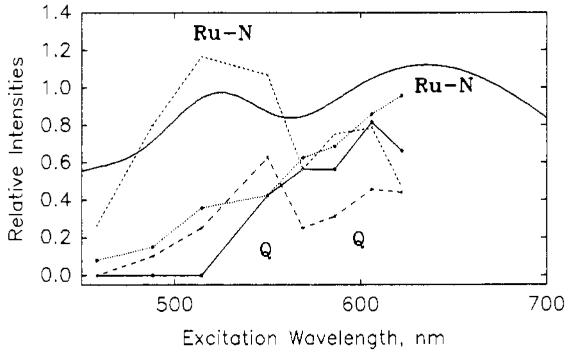

Figure 2. Excitation profile of resonantly enhanced vibrations in the DMSO solution spectra of bis(bipyridine)ruthenium(II) 3,4-diamino-3′,4′-diimino-3′,4′-dihydrobiphenyl. Short hatched and dotted lines refer to skeletal Ru–dioxolene modes, believed to be mostly Ru–N at 618 and 578 cm^{-1}, respectively, maximizing under the lower and higher wavelength transitions, respectively. Internal quinonediimine modes at 1466 (solid line) and 1284 cm^{-1} (long hatched line) tend to maximize under the longer wavelength transition.

Band I is highly solvatochromic, with total shift of 2500 cm^{-1} between the two most extreme solvents (water, DMSO). Band II (a shoulder of imprecise energy in many solvents) is less solvatochromic, total shift 1500 cm^{-1}. The shift of band I does not correlate with any combination of the Gutmann donor (DN) or acceptor (AN) numbers,[8] nor the Reichardt polarity parameter E_T,[9] but does correlate with a dual parameter fit of the Taft and Kamlet hydrogen bond donor (α) and hydrogen bond acceptor

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(1) Woitellier, S.; Launay, J. P.; Joachim, C. *Chem. Phys.* **1989,** *131,* 481.

(2) Auburn, P. R.; Lever, A. B. P. *Inorg. Chem.* **1990,** *29,* 2551.

(3) Masui, H.; Auburn, P. R.; Lever, A. B. P. *Inorg. Chem.* **1991,** *30,* 2402.

(4) Masui, H.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1993,** *32,* 258.

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(β) parameters (Figure 1, inset):[10]

$$E(\text{band I}) = -1920(\pm 200)\beta + 920(\pm 110)\alpha + 17270(\pm 165) \quad (R = 0.97;\ 13\ \text{solvents})$$

With increasing hydrogen bond donicity (increasing α), transition I shifts to the blue (Figure 1a). With increasing hydrogen bond acceptor power (increasing β), it shifts to the red e.g. spectrum in DMSO (Figure 1b). These solvatochromic changes are a consequence, as shown by AM1 calculations, of changes in the twist angle between the two rings of the biphenyl linkage such that Lewis acids (water, protons, BF_3) interacting with the diamino end of the molecule cause a larger twist angle, while Lewis bases (DMSO) tend to make the biphenyl derivative more nearly planar.

In the flattened molecule, conjugation of the benzoquinonediimine ring with the diaminophenyl ring causes the imino groups to be electronically very different and lowers the effective symmetry of the local ruthenium diimino chromophore. In the twisted molecule, the two imino functions are electronically much more similar, raising the local symmetry. Thus, the complex containing the twisted chromophore has an electronic spectrum similar to[3,4] $[(bpy)_2Ru\text{–benzoquinonediimine}]^{2+}$.

In the lower (local to ruthenium) symmetry of the flattened molecule the two dπ orbitals perpendicular to the benzoquinonediimine plane may be considered quantized along the Ru–NH= bond axes and transitions from each to the ligand LUMO are allowed by symmetry and overlap leading to two relatively strong Ru(dπ) → dadib(π^*) transitions.

AM1[11] semiempirical calculations were performed in order to demonstrate that donor or acceptor modifications to the amine end of the molecule could cause the changes in twist angle postulated (see refs 12 and 13 for related analyses). In the absence of good basis functions for the ruthenium center, the molecule was modeled using a BF_2 fragment to mimic the net electron acceptor character of the $[(bpy)_2Ru]^{2+}$ fragment.[14]

The effect of hydrogen bond donors and acceptors on the biphenyl ligand twist angle results from changes in the availability of the *p*-amino lone pair for π-conjugation. In $[BF_2(dadib)]^+$ the p-amino group is shown, by AM1 calculation, to be unusually flat (angle HNH = 117.9°) indicating a great deal of lone pair donation into the diaminophenyl ring. The electron-rich diaminophenyl ring can then, in turn, donate some of its π-electron density to the electron poor benzoquinonediimine ring, via resonance structure **2**. In doing so, however, the dadib ligand must approach planarity, and hence steric repulsion between the 2,2′ and 6,6′ hydrogen atoms must be overcome.[15]

Table I. Inter-Ring Distances and Torsion Angles[a]

donor/acceptor[b]	interaction	distance (Å)	angle (deg)
H^+	e^- acceptor	1.49	46.2
BF_3[c]	e^- acceptor	1.458	33.3
H_2O[d]	H-bond donor	1.445	31.6[e]
none		1.434	25.5
DMF (O)	H-bond acceptor	1.425	23.0
NH_3	e^- donor	1.426	23.0
Cl^-	e^- donor	1.374	2.2

[a] Unless otherwise noted, all systems were fully geometry optimized. [b] Donor or acceptor interacts specifically with the *p*-amino group. [c] B–N distance constrained to 2.0 Å. [d] It was necessary to constrain the NHO angle to be linear, as AM1 prefers water to act as a hydrogen bond acceptor in this case, whereas the solvatochromism data show it acting as a hydrogen bond donor (large α value). [e] SM1 calculation shows a twist angle of 43°; see text.

Competition for the lone pair by external Lewis acids can then markedly increase the twist angle. Conversely, π-enriching the amino group via interaction with Lewis bases permits an increased contribution of resonance form **2**, thereby decreasing the twist angle. Evidence for the participation of resonance structure **2** in the mechanism of the observed solvatochromism is obtained from the calculated structures and charges of the model $[BF_2(dadib)]^+$ system, where donors or acceptors interact specifically with the p-amino group. For example, Table I lists the inter-ring distance and twist angles for $[BF_2(dadib)]^{2+}$ associated with various donors and acceptors. The two species, Cl^- donor and H^+ acceptor, lead to almost flat and twisted configurations, respectively. All other structural parameters and charges are consistent. Moreover the *meta* imino nitrogen group puckers and becomes formally sp^3 with the Cl^- donor (see **2**), while both imino functions are sp^2 and planar in the protonated species.

The effect of aqueous solvation can also be obtained computationally through a dielectric continuum model. We chose the semiempirical solvation model SM1, recently introduced by Truhlar,[16] to investigate the effect of aqueous solvation on the $[BF_2(dadib)]^+$ twist angle. In addition to calculating solvation enthalpy, SM1 introduces terms in the Fock matrix to allow for solvent-induced perturbations to the electronic structure of the molecule. The SM1-corrected AM1-optimized twist angle for $[BF_2(dadib)]^+$ is 43° (aqueous solvation), affording further support for the solvent-induced twisting mechanism. At the time of writing, however, SM1 was not parametrized for solvents other than water.

One may now conclude that in the more planar molecules band II is associated with a transition from the dπ orbital aligned with the Ru–NH= fragment (d_{yz}), while band I involves the dπ orbital aligned along the Ru–NH$^-$ fragment, d_{xz}. The latter interaction will destabilize the dπ orbital to a degree dependent upon the build up of negative charge on this NH fragment, which, in turn, is dependent upon the degree of planarity. Thus, band I will red shift as the solvent interaction forces the molecule toward planarity.

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(5) Metcalfe, R. A.; Dodsworth, E. S.; Lever, A. B. P.; Pietro, W. J.; Stufkens, D. J. To be submitted for publication.

(6) The resonance Raman spectra were measured with a Dilor XY Raman spectrometer using a SP 2016 argon laser and a CR 590 dye laser with Rhodamine 6G and Coumarin 6 as dyes.

(7) Assumes C_{2v} symmetry with respect to the bisector of the diimino ring, collinear with the *z* axis, and with the diimino ring, contained within the *xz* plane.

(8) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1980.

(9) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, Germany, 1968. Reichardt, C.; Harbusch-Gornert, E. *Liebigs Ann. Chem.* **1983**, 721.

(10) Kamlet, M. J.; Abboud, J. L. M.; Abraham, R. W.; Taft, J. *J. Org. Chem.* **1983**, *48*, 2877.

(11) All semiempirical calculations were performed at AM1 level using the Spartan 2.0 system of programs (Wavefunction Inc., Irvine, CA) on a Silicon Graphics 4D/35 Personal Iris. Equilibrium geometries were determined by full Cartesian gradient optimization. Constrained optimizations were performed by the method of Baker. (Baker, J. *J. Comput. Chem.* **1992**, *13*, 240). Of the various semiempirical formalisms currently defined, AM1 has proven to be the most reliable when studying hydrogen-bonded systems. Moreover, our main objective is to probe the electronic structure of the $[BF_2(dadib)]^+$ moiety as a function of amino lone pair availability, and we are less concerned with accurate reproduction of hydrogen bond geometry. In addition, conformational preferences and the barrier to internal rotation about non-amide bonds are well reproduced by AM1. Trends in ligand conformation induced by subtle electronic structure changes should certainly be meaningful. Atomic charges were obtained by fits to molecular electrostatic potentials (MEP) using a modified version of CHELP (Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894). Atomic charges derived by this method mimic the quantum mechanical MEP and are superior to conventional Mulliken charges for describing one-electron properties.

(12) Cativiela, C.; Garcia, J. I.; Elguero, J.; Elguero, E. *Gazz. Chim. Ital.* **1991**, *121*, 477.

(13) Haga, M. A.; Ano, T. A.; Yamabe, S. S. *Inorg. Chem.* **1991**, *30*, 3843.

(14) NDDO based semiempirical programs are not parametrized yet for use with transition metals. The BF_2^+ unit was used in order to mimic the positive charge of the $Ru(bpy)_2^{2+}$ unit as well as its electron acceptor ability.

(15) Almlof, J. *Chem. Phys.* **1974**, *6*, 135.

(16) Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 8305.