

a larger decrease in entropy than transannulation, which is intramolecular. Another factor possibly favoring P-N<sub>ax</sub> interaction when 1 is electrophilically attacked is the already nearly planar configuration of N<sub>ax</sub> in 3 (and very probably in 1) even though the P and N<sub>ax</sub> atoms are separated by the sum of the van der Waals radii. The planarity of bridgehead nitrogens in bicyclics of this type is apparently due to van der Waals interactions among the CH<sub>2</sub> hydrogens.<sup>6,13</sup>

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**Supplementary Material Available:** NMR data, ORTEP drawings, description of the data collection and structure solution, and tables of positional and isotropic thermal parameters, bond distances, and angles for 6-9 (53 pages); listing of observed and calculated structure factors for 6-9 (53 pages). Ordering information is given on any current masthead page.

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### Effects of Inter- and Intramolecular Hydrogen Bonding upon the Structure and Photoisomerization of 3-(2-Pyridyl)propenamides

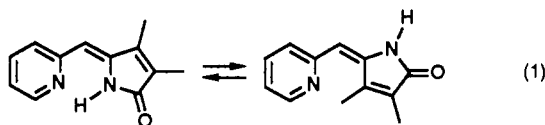
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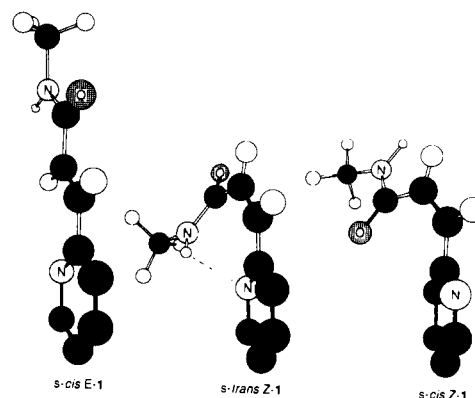
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Intramolecular hydrogen bonding can exert a pronounced effect upon both the thermal<sup>1-5</sup> and photochemical<sup>6-8</sup> equilibria of configurational isomers. For example, the *Z* isomers of enols, enamines, and enamides capable of forming 6-membered intramolecular hydrogen bonds (eq 1) are more stable than their *E* isomers in nonpolar solvents. Disruption of the intramolecular



hydrogen bond by the use of hydrogen bond acceptor solvents such as pyridine or methyl sulfoxide can shift this equilibrium in the direction of the *E* isomer. Photoisomerization of the *Z* isomers of some enols and enamines is reported to yield the *E* isomers, which revert thermally to the *Z* isomers or, in the case of the enols, tautomerize to the corresponding  $\beta$ -dicarbonyl compound, with rates that are subject to acid and base catalysis.<sup>4,5</sup> The *Z* isomers



**Figure 1.** Energy-minimized structures for the low-energy conformers of (*E*)- and (*Z*)-*N*-methyl-3-(2-pyridyl)propenamide. A broken line indicates an intramolecular hydrogen bond.

of  $\alpha$ -pyridyl pyrrolinones are reported to be resistant to thermal or photoisomerization in nonpolar solvents, but undergo photoisomerization in alcohol or acidic solvents, which are presumed to disrupt the intramolecular hydrogen bond (eq 1).<sup>6</sup> While less common, there are also examples of molecules in which 7-membered intramolecular hydrogen bonds influence configurational equilibria.<sup>7,8</sup> We report here preliminary results of our investigation of the effects of intra- and intermolecular hydrogen bonding upon the conformation and photochemical behavior of the isomeric *N*-methyl-3-(2-pyridyl)propenamides (*E*- and *Z*-1, Figure 1) in solution and in the solid state.

Both *E*- and *Z*-1 are crystalline solids which are unchanged by prolonged irradiation in the solid state or by heating at their melting points. The molecular packing modes for *E*- and *Z*-1 (Figure 2) are similar to that for *N*-methylcinnamide<sup>9</sup> in that chains of molecules are hydrogen bonded via a glide plane.<sup>10</sup> *E*-1 exists in the *s*-cis enone conformation and is nearly planar in the solid state, having pyridyl-vinyl and vinyl-amide dihedral angles of 6.2° and 2.2°, respectively. The corresponding dihedral angles for *Z*-1 are 6.7° and 70.1°. The vinyl-amide dihedral angle is much larger than those previously reported for conjugated amides<sup>9</sup> and presumably is necessary to minimize intermolecular contacts between the chains of (intermolecularly) hydrogen-bonded molecules.

Analysis of the IR and <sup>1</sup>H NMR data for *E*-1 indicates that its solution conformation is similar to that in the solid state (planar *s*-cis).<sup>11</sup> The N-H chemical shifts for *E*-1 in deuteriochloroform and methyl sulfoxide are  $\delta$  5.71 and 8.25, respectively, and N-H irradiation results in large NOEs for the  $\alpha$ -vinyl hydrogens, but not for the aromatic hydrogens, in both solvents (36.6% and 11.8%, respectively). In contrast, the spectral data for *Z*-1 are indicative of intramolecular hydrogen bonding in dichloromethane, but not in methyl sulfoxide solution. The N-H chemical shifts for *Z*-1 in deuteriochloroform and methyl sulfoxide are  $\delta$  11.25 and 9.3, respectively. N-H irradiation in deuteriochloroform solution results in a small NOE for the  $\alpha$ -vinyl hydrogen (0.9%) and a large NOE for the aromatic hydrogen adjacent to nitrogen (6.3%), whereas, N-H irradiation in methyl sulfoxide solution results in a large NOE for the  $\alpha$ -vinyl hydrogen (8.3%) and a small NOE for the aromatic hydrogen adjacent to nitrogen (1.8%). These

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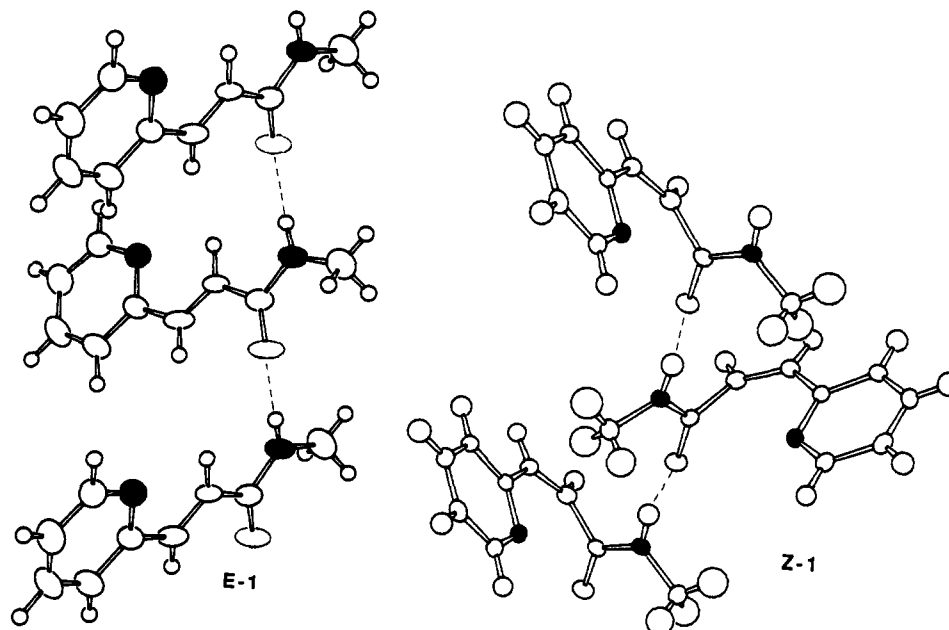
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(10) *E*-1: mp 108-110 °C, orthorhombic; space group *Pbca*, *a* = 9.370 (3) Å, *b* = 11.003 (2) Å, *c* = 16.906 Å, *V* = 1743 (1) Å<sup>3</sup>, *Z* = 8,  $\mu_{\text{calcd}}$  = 0.78 cm<sup>-1</sup>,  $\rho_{\text{calcd}}$  = 1.236 g/cm<sup>3</sup>; 2192 unique reflections, *R* = 0.045, *R*<sub>w</sub> = 0.044. *Z*-1: mp 72-74 °C; monoclinic; space group *P2<sub>1</sub>/c*, *a* = 10.838 (2) Å, *b* = 8.712 (2) Å, *c* = 9.849 (4) Å, *V* = 838.6 (5) Å<sup>3</sup>, *Z* = 4,  $\mu_{\text{calcd}}$  = 0.81 cm<sup>-1</sup>,  $\rho_{\text{calcd}}$  = 1.284 g/cm<sup>3</sup>; 1826 unique reflections, *R* = 0.038, *R*<sub>w</sub> = 0.049. An Enraf-Nonius CAD-4 with Mo K $\alpha$  was used.

(11) *E*-1: IR (CCl<sub>4</sub>)  $\nu_{\text{N-H}}$  3450,  $\nu_{\text{C=O}}$  1675 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.96 (d, 3 H), 5.71 (br s, 1 H), 6.97 (d, *J* = 15.2 Hz, 1 H), 7.25 (t, 1 H), 7.37 (d, 1 H), 7.62 (d, *J* = 15.2 Hz, 1 H), 7.70 (t, 1 H), 8.62 (d, 1 H). *Z*-1: IR (CCl<sub>4</sub>)  $\nu_{\text{N-H}}$  3220,  $\nu_{\text{C=O}}$  1655 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.92 (d, 3 H), 6.16 (d, *J* = 13.6, 1 H), 6.65 (d, *J* = 13.6, 1 H), 7.30 (t, 1 H), 7.39 (d, 1 H), 7.79 (m, 1 H), 8.64 (d, 1 H), 11.25 (br s, 1 H).



**Figure 2.** Crystal structures of hydrogen-bonded arrays of (*E*)- and (*Z*)-*N*-methyl-3-(2-pyridyl)propenamide. Nitrogen atoms are shaded, and broken lines indicate intermolecular hydrogen bonds.

results support the assignment of *s*-cis and *s*-trans enone conformations for *Z*-1 in dichloromethane and methyl sulfoxide solutions.<sup>12</sup>

Energy-minimized structures for the *s*-trans and *s*-cis conformations of *Z*-1 obtained using the MM2 force field as modified by Ponder<sup>13</sup> are shown in Figure 1.<sup>14,15</sup> No energy minimum could be located for geometries similar to that for *Z*-1 in the solid state. The *s*-trans conformer is calculated to be more stable (by 0.32 kcal/mol) and more planar than the *s*-cis conformer. The calculated intramolecular hydrogen bond length in the *s*-trans conformer is 2.19 Å, which is longer than that for the intermolecular hydrogen bond in the solid state (2.03 Å), and the torsion angle of the hydrogen bond deviates significantly from planarity.<sup>16</sup> While this is clearly a very weak hydrogen bond, it is sufficiently strong to overcome the normal *s*-trans conformational preference of the *Z*-cinnamamides.<sup>15</sup> Iodine atom catalyzed isomerization of *Z*-1 in dichloromethane solution results in its quantitative conversion to *E*-1. Thus, the 7-membered intramolecular hydrogen bond in *Z*-1, unlike the 6-membered hydrogen bond in the  $\alpha$ -pyridyl pyrrolinones (eq 1),<sup>6</sup> is not sufficiently strong to render *Z*-1 thermodynamically more stable than *E*-1.

Irradiation of *E*-1 in several solvents (dichloromethane, acetonitrile, and water) results in its quantitative conversion to *Z*-1, while irradiation in tetrahydrofuran, ethanol, or methyl sulfoxide solution results in isomerization of both isomers. Photodegradation of the isomer mixture occurs in tetrahydrofuran and ethanol solution, prior to reaching the photostationary state. Photostationary states and isomerization quantum yields obtained upon irradiation in the long-wavelength ( $\lambda_{\max} = 280\text{--}290\text{ nm}$ )  $\pi, \pi^*$  absorption band are reported in Table I, along with more limited data for the *N*-methyl-3-(3-pyridyl)propenamides (*E*- and *Z*-2).

(12) Complete solution spectral data and their analysis will be provided in a full paper.

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(14) Conformational analysis of several cinnamamides indicates that the solution enone conformations of the *E* and *Z* isomers are *s*-cis and *s*-trans, respectively.<sup>15</sup>

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(16) Both the *s*-trans and *s*-cis conformers of *Z*-1 have approximately planar amide and alkene groups. Calculated dihedral angles for the pyridyl-ethylene are 12.4° and 29.4° and for the enone are 28.8° and 31.7°, respectively.

**Table I.** Photostationary States and Quantum Yields for Photoisomerization

amide	solvent	$\beta^a$	$\Phi_{E,Z}^b$	$\Phi_{Z,E}^b$	PSS, % $Z^c$
1	CH <sub>2</sub> Cl <sub>2</sub>	0.10	0.21	<10 <sup>-3</sup>	99
	CH <sub>3</sub> CN	0.31			98
	H <sub>2</sub> O	0.47		<10 <sup>-3</sup>	99
	THF	0.55	0.05	0.07	<i>d</i>
	CH <sub>3</sub> CH <sub>2</sub> OH	0.75	0.12	0.04	<i>d</i>
	(CH <sub>3</sub> ) <sub>2</sub> SO	0.76	0.06	0.06	80
2	CH <sub>2</sub> Cl <sub>2</sub>	0.10	0.16	0.28	65
	CH <sub>3</sub> CN	0.31			65
	H <sub>2</sub> O	0.47			62

<sup>a</sup> Values from ref 18. <sup>b</sup> Quantum yields determined using monochromatic 313-nm irradiation of deoxygenated 0.05 M amide solutions, <10% conversion. <sup>c</sup> Photostationary state determined using Pyrex-filtered (>300 nm) irradiation. <sup>d</sup> Amides are unstable to prolonged irradiation in these solvents.

The latter is sufficient to establish that the photoisomerization of *E*- and *Z*-2 is not highly solvent dependent.<sup>17</sup>

Of the common solvent parameters, only the Taft solvatochromic  $\beta$  parameter<sup>18</sup> (hydrogen bond acceptor, Table I) provides an interpretable correlation with the quantum yields for photoisomerization of *Z*-1. Photoisomerization is observed in solvents of comparable or greater  $\beta$  value than that of pyridine ( $\beta = 0.64$ ). We assume that, like methyl sulfoxide, all such solvents disrupt the intramolecular hydrogen bond and thereby "switch on" photoisomerization. The photochemical stability of *Z*-1 in water is particularly interesting in view of the greater solvent polarity of water vs ethanol or methyl sulfoxide and hydrogen bond donor strength of water vs ethanol. It is possible that the free energy of solvation of the amide carbonyl group by water is actually larger for the more exposed *s*-trans vs *s*-cis enone conformation (Figure 1).

While there are numerous examples of one-way *E,Z* photoisomerization in which the thermodynamically less stable configurational isomer is converted to the more stable isomer,<sup>8,19</sup> this is, to our knowledge, the first example of counterthermodynamic

(17) The photoisomerization of cinnamamides is reversible in several solvents.<sup>15</sup>

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one-way photoisomerization. While the photostability of Z-1 is clearly related to weak intramolecular hydrogen bonding in the ground state of Z-1, the role of the hydrogen bond in the non-radiative decay of the excited state remains to be elucidated.

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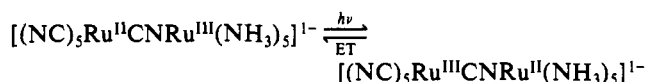
**Supplementary Material Available:** ORTEP representations, tables of atomic coordinates, thermal parameters, bond angles, and bond distances for E-1 and Z-1 (12 pages). Ordering information is given on any current masthead page.

### Picosecond Infrared Study of Ultrafast Electron Transfer and Vibrational Energy Relaxation in a Mixed-Valent Ruthenium Dimer

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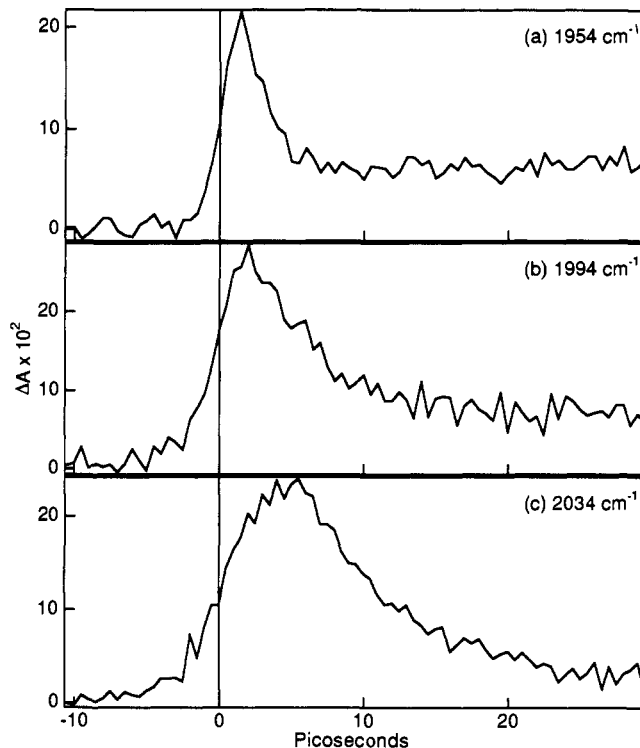
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Mixed-valent transition-metal dimers have become key systems for understanding many fundamental aspects of electron-transfer dynamics.<sup>1</sup> The mixed-valent dimer  $[(\text{NC})_5\text{Ru}^{\text{II}}\text{CNRu}^{\text{III}}(\text{NH}_3)_5]^{1-}$  is an interesting member of this class. In this complex, the ruthenium centers are strongly coupled through a short cyanide bridge, but because the  $[(\text{NC})_5\text{Ru}^{\text{III}}\text{CNRu}^{\text{II}}(\text{NH}_3)_5]^{1-}$  state of this systems lies approximately 8000  $\text{cm}^{-1}$  higher in energy, the odd electron is localized on the ruthenium cyanide center.<sup>2</sup> Optical excitation into the metal-metal charge-transfer (MMCT) band leads to reduction of the ruthenium ammine site. This state is highly unstable with respect to back electron transfer:



The MMCT excitation is followed by back electron transfer, which may occur on very short time scales, allowing one to observe effects due to ultrafast reorganization processes, to discern excited state/ground state coupling phenomena, and to test modern electron-transfer theories. In this communication, we report a picosecond infrared study of the dynamics of  $[(\text{NC})_5\text{Ru}^{\text{II}}\text{CNRu}^{\text{III}}(\text{NH}_3)_5]^{1-}$  following MMCT optical excitation.<sup>3</sup> We observe the terminal  $\text{RuC}\equiv\text{N}$  stretching vibrational frequency, which is sensitive to the oxidation state of the ruthenium cyanide center and also, because of anharmonicity, to the degree of vibrational excitation of this mode. Our observations allow us to observe unambiguously the formation and decay of the MMCT excited state and, by observing the energy flow out of this state, to address the more general issues of vibrational coupling and energy-transfer dynamics.

Ultrafast visible pump/infrared probe experiments were performed as described previously.<sup>4</sup> A visible pump pulse at 600



**Figure 1.** Transient decays obtained at (a) 1954, (b) 1994, and (c) 2034  $\text{cm}^{-1}$  from 0.04 M dimer in  $\text{D}_2\text{O}$ . See Table I for appropriate rise and decay times. Offsets remaining at long times are due to thermal transients and do not affect the fits obtained.

**Table I.** Rise and Decay Times for the Best Fit to Data from 1954 to 2060  $\text{cm}^{-1}$ <sup>a</sup>

wavelength ( $\text{cm}^{-1}$ )	rise time (ps)	fall time (ps)
1954	0.1	0.7
1974	0.3	1.9
1994	0.6	3.6
2014	0.7	4.6
2034	1.4	5.9
2060 <sup>b</sup>	0.0	6.9

<sup>a</sup> Values given correspond to the best fit obtained when convolving the instrument response (typically a 3–4 ps FWHM  $\text{sech}^2$  function) with a biexponential function; estimated relative error is  $\pm 0.5$  ps.  
<sup>b</sup> Ground-state bleach.

nm (2 ps, 50–100  $\mu\text{J}/\text{pulse}$ ) is followed by an infrared probe pulse (2 ps, 10–100 nJ/pulse, FWHM 8  $\text{cm}^{-1}$ ) generated by difference frequency mixing of the visible pulse with a 532-nm pulse in a  $\text{LiIO}_3$  crystal. Time resolution<sup>5</sup> is obtained by optical delay, and the infrared difference frequency is changed by tuning the frequency of the dye laser. The sodium salt of  $[(\text{NC})_5\text{Ru}^{\text{II}}\text{CNRu}^{\text{III}}(\text{NH}_3)_5]^{1-}$  was synthesized by literature methods.<sup>6</sup> The visible spectrum consists of a broad (FWHM 4500  $\text{cm}^{-1}$ ) MMCT band centered at 683 nm ( $\epsilon = 2800 \text{ M}^{-1} \text{ cm}^{-1}$ ). In the ground state, the terminal  $\text{RuC}\equiv\text{N}$  stretch is observed at 2053  $\text{cm}^{-1}$  (FWHM = 23  $\text{cm}^{-1}$ ,  $\epsilon = 2500 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>7</sup>

Upon excitation at 600 nm, we observe an ultrafast (instrumentally limited,  $\tau < 0.5$  ps) decrease in the  $\text{RuC}\equiv\text{N}$  absorbance for the ground state at 2053  $\text{cm}^{-1}$ . The recovery is fit by convolving the instrument response with a  $6 \pm 1$  ps exponential. Simultaneous

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(1) See, for example: (a) *Mixed-Valence Compounds*; Brown, D. B., Ed.; D. Reidel: Dordrecht, The Netherlands, 1980. (b) Creutz, C. *Prog. Inorg. Chem.* 1983, 30, 1.

(2) Estimated from redox potentials for the appropriate monomer pairs; see: Haim, A. *Inorg. Chem.* 1985, 14, 113.

(3) The photophysics of a related molecule,  $[(\text{NC})_5\text{Fe}^{2+}\text{CNRu}^{3+}(\text{NH}_3)_5]^{1-}\text{Na}^+$ , have recently been investigated using femtosecond visible spectroscopy: Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Dong, Y.; Hupp, J. T. *J. Phys. Chem.* 1991, 95, 5712.

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(5) Using deconvolution techniques we estimate that we can resolve ca. 500 fs events, given typical signal to noise ratios.

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(7) In  $C_{4v}$  symmetry there should be more than one band in this region. Compounds of this type, however, often show only one IR-active  $\text{MC}\equiv\text{N}$  stretching vibration, perhaps because of their closeness to  $O_h$  symmetry (see for example: Siddiqui, S.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* 1987, 26, 3101). The bridging cyanide stretch is observed at 2118  $\text{cm}^{-1}$  and is ca. 50 times weaker than the terminal stretch.