Figure 2. (A) Absorption and (B) electrochromic spectra for [(NH$_3$)$_5$Ru]$_2$pz^{5+}(C$_7$H$_7$SO$_3^-$)$_5$ in 50% (v/v) glycerol/D$_2$O, 77 K. F$_{ext}$ = 4 × 10^5 V/cm; χ = 90°.

spectrum, though the zeroth and first derivatives also contribute, indicating that the transition moment and polarizability changes are non-negligible. $|\Delta\mu_A|$ calculated from this analysis is (28 ± 2)/f D (debye), and p-$\Delta\mu_A$ = (27 ± 2)/f D, indicating that $\Delta\mu_A$ and the transition dipole moment are essentially collinear.

The near-infrared absorption and electrochromic spectra of [(NH$_3$)$_5$Ru]$_2$pz^{5+} are shown in Figure 2. The electric field causes the low-energy side and the peak of the absorption band to decrease in a manner that is well modeled by a negative zeroth derivative, while the high-energy side of the absorption increases in a field. The $\Delta A(\nu)$ spectrum does not satisfactorily decompose into a simple linear combination of derivatives of the *overall* absorption band. Qualitatively, however, there is little evidence that a second derivative and hence $\Delta\mu_A$ contributes significantly to the $\Delta A(\nu)$ line shape, especially on the low-energy side which lacks the large, positive signature of the second derivative.

A large $\Delta\mu_A$ should accompany a true intervalence transition involving a large redistribution of electronic charge density from one metal center to the other. In [(NH$_3$)$_5$Ru]$_2$(4,4'-bpy)$^{5+}$, the observed $|\Delta\mu_A|$ of 28/f D indicates that the states involved are highly dipolar and the unpaired electron is substantially localized. For the limiting case of full charge transfer over 11.3 Å (the Ru–Ru distance),[2] $|\Delta\mu_A|$ will be 54 D. While very large, the experimentally measured value of $|\Delta\mu_A|$ is significantly smaller than this upper limit.[18] This difference suggests that the limiting case is an over-simplification and that metal–ligand and metal–metal interactions may be more complex and significant than initially thought.[2,11]

The absence of an observable contribution by $|\Delta\mu_A|$ to the $\Delta A(\nu)$ spectrum for the near-IR band of [(NH$_3$)$_5$Ru]$_2$pz^{5+} indicates that there is little net movement of the centers of charge associated with this transition. This result directly demonstrates that the metal centers are so strongly coupled to each other that the unpaired electron is delocalized over both, even at 77 K; this description is consistent with a large body of indirect experimental evidence for this complex.[1,2,11,19,20] The low-energy portion of the absorption band decreases in intensity in an electric field, indicating an effect solely due to a perturbation of the transition dipole moment. At higher energies, the band behaves in a com-

plicated manner, suggesting that multiple bands exist that behave differently in a field. Variations across the near-IR band have also been noted in MCD spectra at low temperature;[21] electrochromism is likewise often useful for selectively detecting weak transitions which are sensitive to an electric field.

Electrochromism offers a wealth of information on the changes in electrostatic properties associated with transitions between states in mixed-valence complexes. In tandem with a detailed theoretical analysis,[22] these will be explored more fully in a subsequent paper covering both metal-to-ligand and intervalence charge-transfer transitions of mono- and binuclear ruthenium complexes.

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Solvation-Controlled Diastereofacial Selectivity in Alkylations of Bicyclic Lactam Enolates

Kathleen A. Durkin and Dennis Liotta*

*Department of Chemistry, Emory University
Atlanta, Georgia 30322*

Recent work by the Meyers group has suggested the possibility of stereoelectronic effects playing a role in diastereofacially selective alkylations of the enolate carbon in the bicyclic [3.3.0] lactam **1**.[1] Meyers describes numerous cases where alkylation leads to impressive endo selectivity (Figure 1).[2] Careful examination of the geometry of **1**, by molecular modeling techniques, suggests that the two faces are sterically very similar with the endo face slightly less accessible. The origin of the observed endo selectivity is therefore unclear.

One possibility that has been presented invokes stereoelectronic control via the Cieplak effect.[3,4] This effect, which is purported to occur in σ bond forming reactions, involves stabilization of the transition state in question via orbital mixing of the incipient σ^* orbital with a proximal electron-rich σ bond. Although work done by le Noble et al. on adamantyl systems has suggested that this type of stereoelectronic control is real, the magnitude and generality of this effect remain incompletely documented.[5,6] Moreover, other work done by Meyers on systems very similar to the lactam **1** has yielded results that are inconsistent with the Cieplak model.[1]

Our goal was to use molecular orbital techniques to examine the lactam **1** in alkylation reactions in order to determine the nature of the facial bias. Semiempirical calculations (AMPAC)[7] were chosen since the number of atoms preclude a complete ab initio study of the reaction surface. The AM1 Hamiltonian[8] was used in all cases except those where a lithium counterion was used. In these cases MNDO[9] was applied.

We examined the reaction surfaces for the endo and exo monoalkylation of methyl iodide to the naked enolate of **1** (no

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8163

CH₃

a) LDA · R'X
b) LDA · R''X

CH₃

R'
R''

O

O

1 (A = B = hydrogen)
2 (A or B = methyl, B or A = hydrogen)
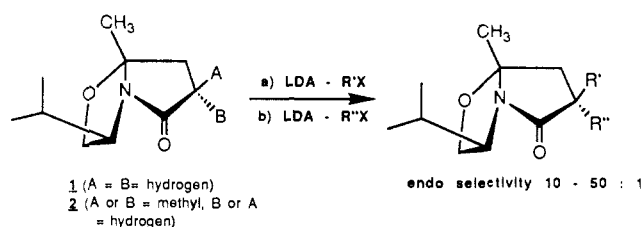
endo selectivity 10 · 50 : 1

Figure 1. Alkylation of bicyclic [3.3.0] lactams.

counterion). The transition state (ts) for each reaction was located as a saddle point on the reaction surface and unequivocally identified by a FORCE calculation yielding one negative force constant with the major vibration along the axis of the S_N2 reaction. The endo ts was found to have a heat of formation of –69.9 kcal/mol while the exo was found to have a heat of formation of –70.2 kcal/mol. Within calculation error, these are essentially the same.

Since Meyers has observed generally higher selectivity in the addition of the second alkyl group, we considered the possibility that facial bias might be more manifest in these cases. The transition states for the endo and exo addition of methyl iodide to the monomethylated lactam **2** were located and found to have identical heats of formation at –75.9 kcal/mol. In looking for a possible steric bias, we also considered the modification to **1** where the ring juncture methyl group was replaced by hydrogen. The ts for the exo methylation was located and has a heat of formation of –58.1 kcal/mol. The corresponding endo ts has a virtually identical heat of formation of –58.4 kcal/mol. We therefore conclude that *no portion of the structural framework of these lactam enolates exerts any significant steric or electronic control on the diastereofacial selectivity observed in the alkylation reactions of these bicyclic lactams.*

We next considered the possibility that the observed diastereoselectivity stemmed from factors external to the enolate structure. In particular, if the counterion (lithium) exhibits preference for one of the enolate faces, it could interfere with the approach of an electrophile to that face. In order to probe this, an unsolvated lithium was included in the calculations.[10,11]

If the oxygen–lithium bond in the enolate of **1** is allowed to completely optimize, the lithium preferentially bridges the enolate carbon and oxygen atoms. This may result from the artificial lack of external solvation, since physical studies of lithium enolates show that the most stable species involves little interaction with the enolate carbon.[12] We do, however, notice an exo preference of 0.8 kcal/mol with the lithium out of plane by approximately 33°.

MOPAC[13] (MNDO) calculations involving lithium species solvated with 12-crown-4 resulted in transition-state geometries verified by FORCE calculations. The transition state for the endo addition of methyl iodide to the solvated lithium enolate of **1** was 0.7 kcal/mol more stable than the corresponding exo transition state. The same result was found for the transition states involving methyl iodide addition to the solvated lithium enolate of **2**, i.e., the endo transition state was found to be 0.7 kcal/mol more stable than the exo transition state. This difference clearly shows a preference for endo addition.

Assuming that the change in entropy is the same for each endo and exo reaction pair, a difference of 0.7 kcal/mol in the heat of formation for reactions run between –100 and –78 °C corresponds to a product ratio of 88:12. Thus, a great deal of the selectivity seen in these reactions can be explained solely through consideration of preferential exo solvation, presumably due to favorable electrostatic interactions between the lithium and the pyramidalized nitrogen.[14] In addition, the 12-crown-4 case is

the one expected to give the lowest selectivity since the solvation of the lithium involves one of the least sterically encumbered solvation shells possible. In a solution enolate, in which the steric effects due to solvation are much greater, the facial bias could be more substantial. These results seem to confirm the conclusion that the diastereofacial selectivity results from the nature of the enolate solvation.

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Enhanced Photoacidities of Cyanonaphthols

Laren M. Tolbert* and Jeanne E. Haubrich

*School of Chemistry and Biochemistry
Georgia Institute of Technology
Atlanta, Georgia 30332-0400*

That the acidities of aromatic alcohols are enhanced upon photoexcitation has been recognized for several decades and has been the basis for several mechanistic and technological applications.[1] Among these are photopolymerization,[2] photodepolymerization,[3] pH jump experiments,[1d,4] and biological probes of the environment around proteins[5] and micelles.[6] Most of these studies have concentrated on the commercially available 1- and 2-naphthols, their sulfonated derivatives, and 8-hydroxy-1,3,6-pyrenetrisulfonate. Förster pK_a values[7] of substituted phenols have been determined,[8] but for many applications phenols are not suitable because their absorption frequency is too high and fluorescence is weak. Naphthols exhibit excited-state pK_a (pK_a^*) values in the range 0–3 and thus limit proton-transfer studies to aqueous solvents.[1] In fact, previous studies of naphthol derivatives in aqueous alcohols[9] and in the gas phase[10] indicate that a cluster

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