acyl radical is about as good a leaving group as are benzyl radicals under these conditions.

The behavior of acetate esters also was examined briefly. Acetates quench the absorptions of the solvated electrons with rate constants $k_e' = (2 \pm 0.5) \times 10^9$ M^{-1} s^{-1} in alcohol. Pulse radiolysis of benzyl acetate afforded benzyl radical as the only transient detected optically above 300 nm. The growth of the benzyl absorption was slower than quenching of the solvated electrons and is taken to represent k', the rate of fragmentation of the acetate radical anion (Table I). Thus, the fragmentation of benzyl acetate anion is 30 times faster than that of benzyl benzoate anion. Other considerations, including solvation, spin and charge delocalization, polarizabilities, and steric effects, also are expected to affect the rates of cleavage.[16]

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Configuration-Dependent Photoisomerization of (*E*)-Cinnamamides

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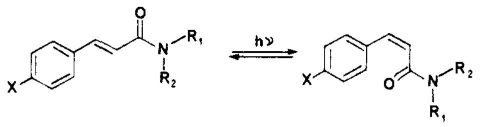
The reactivity of electronically excited molecules is dependent upon the configuration and multiplicity of the excited state.[1] A well-known example of configuration dependence is the Norrish type II reaction of aryl alkyl ketones, which occurs via the $^3n,\pi^*$ but not the $3\pi,\pi^*$ state.[2] Aromatic substituents can alter the energies of these states and thereby affect the reactivity. We have observed that the *E,Z*-photoisomerization efficiencies of a series of (*E*)-cinnamamides are highly dependent upon both N-alkylation and aromatic substitution (eq 1). These results are attributed to the existence of two low-energy $^1\pi,\pi^*$ states, a reactive state with a styrene-like HOMO, and an unreactive state with an amide nonbonding π HOMO. The energy of the former state can be altered by aromatic substituents, while that of the later state can be altered by N-alkylation. This is, to our knowledge, the first instance in which the energies of two states of the same multiplicity can be independently varied via substitution at two different sites in the molecule.



(1)

1: $R_1 = R_2 = H$
2: $R_1 = CH_3$; $R_2 = H$
3: $R_1 = R_2 = CH_3$

While the photoisomerization of (*E*)-cinnamamides has been reported as a method for preparing the (*Z*)-isomers,[3] this process has eluded the mechanistic scrutiny to which cinnamic acid and its esters have been subjected.[4] Absorption spectral data and isomerization quantum yields (Φ_i) obtained from 313 irradiation of 0.01 M dichloromethane solutions of several (*E*)-cinnamamides are summarized in Table I. IR and NMR spectral analyses confirm that the ground states of all of the (*E*)-amides adopt a planar s-trans conformation in solution as in the solid state[5] and are predominantly in monomeric form at the concentrations used in the spectroscopic and photochemical investigations. The marked dependence of Φ_i upon N-alkylation and aromatic substitution stands in contrast to reported results for cinnamic acid and several of its ring-substituted esters, all of which isomerize with $\Phi_i > 0.20$.[4a] Triplet-sensitized irradiations of **3a** or **3b** (0.01 M Michler's ketone, 365 nm) occur with $\Phi_i = 0.55$ and 0.53, respectively, whereas attempted triplet quenching with 1,3-pentadiene (0.2–2.0 M) did not alter Φ_i. Thus we conclude that intersystem crossing is inefficient for the cinnamamides and that the Φ_i values in Table I are determined by partitioning of the nonfluorescent singlet state(s) between isomerization and nonradiative decay.

The effect of N-alkylation upon the electronic structure of the cinnamamides was investigated with Gaussian 82 calculations.[6] The frontier orbitals include a styrene-like HOMO (π_S) and LUMO (π^*) for **1a–3a**, similar to those previously reported for methyl cinnamate.[4b] In addition, there are the two high lying orbitals observed by Turner and co-workers[7] for the amides of formic and acetic acid: the carbonyl oxygen lone pair (n_O) and the approximately nonbonding antisymmetric π_N. The nodal properties and approximate atomic coefficients of the π orbitals are shown in Chart I and the orbital energies summarized in Table II. While the energies of the n_O, π_S, and π^* orbitals are relatively insensitive to N-alkylation, the energy of π_N is seen to increase with N-alkylation, as previously observed for simple amides.[7] The π_S orbital lies well above π_N or n_O in cinnamamide (**1a**), whereas in acrylamide the π(C=C) orbital lies below n_O and π_N.[8]

The presence of two high-lying π-orbitals should result in two singlet states (π_S,π^* and π_N,π^*), which should not mix significantly due to the lack of overlap between the π_N and π_S orbitals. The π_S,π^* state would be expected to isomerize efficiently, as it does in the case of the cinnamic esters,[4a] whereas the π_N,π^* state retains a higher C=C bond order and thus should resist isomerization. The effects of aromatic substituents on λ_{max} (Table I) support the assignment of the UV absorption band to a $\pi^* \leftarrow \pi_S$ transition. The $\pi^* \leftarrow \pi_N$ transition is not resolved but may be responsible for long-wavelength tails and shoulders.

While the relative energies of the π_S,π^* and π_N,π^* states will depend upon the extent of configuration interaction, we assume as our working hypothesis that the lowest singlet of **1a** is the reactive π_S,π^* and the lowest singlet of **3a** is the unreactive π_N,π^* state. This hypothesis provides a conceptually simple framework for understanding the consequences of N-alkylation and aromatic substitution. N-Alkylation should lower the energy of the π_N,π^* state but have little effect on the energy of the π_S,π^* state (Table II). The electron-donating methoxy group should raise the π_S energy and thus lower the energy of the π_S,π^* singlet state (but not π_N,π^*). A large red shift in the long-wavelength absorption band of **1b** vs **1a** and **3b** vs **3a** and a dramatic increase in Φ_i, especially in the case of **3b** vs **3a**, are, in fact, observed. Conversely, the electron-withdrawing trifluoromethyl group should lower the π_S energy and thereby raise the energy of the π_S,π^* state. The blue-shifted absorption bands of **1c** vs **1a** and **3c** vs **3a** and the decrease in Φ_i for **1c** vs **1a** conform to this prediction. Raising the π_S,π^* energy should have no effect on Φ_i in the case of **3c** vs **3a**, if the lowest singlet is π_N,π^* in both cases.

Additional support for the two singlet hypothesis comes from the effect of BF_3 complexation upon Φ_i. All of the amides form stable BF_3 complexes ($K > 1000$) with red-shifted absorption compared to the free amide and all of the Lewis acid complexes have $\Phi_i \geq 0.35$ ($\Phi_i = 0.55$ for **3a**:BF_3). Gaussian 82 calculations

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Table I. Absorption Spectral Data[a] and Isomerization Quantum Yields[b]

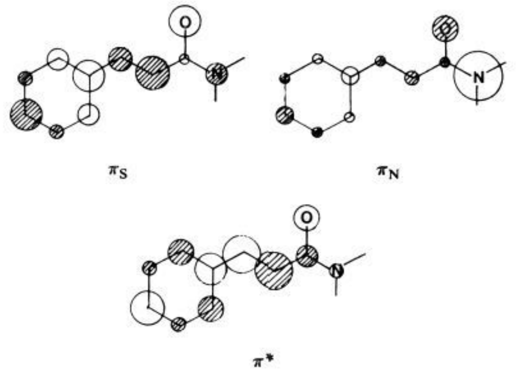
amide	X	R_1	R_2	λ_{max}	$10^{-4}\epsilon$	Φ_i
1a	H	H	H	273	1.87	0.25
1b	OCH_3	H	H	290		0.51
1c	CF_3	H	H	268	2.80	0.07
2a	H	CH_3	H	272	3.43	0.03
3a	H	CH_3	CH_3	277	2.02	0.01
3b	OCH_3	CH_3	CH_3	292	2.41	0.26
3c	CF_3	CH_3	CH_3	270	3.40	0.01

[a] Absorption spectrum in dichloromethane solution. [b] Data for 313-nm irradiation of 0.01 M amide in dichloromethane solution.

Table II. Frontier Orbital Energies (hartrees)

amide	n_0	π_N	π_S	π^*
1a	−0.3183	−0.2976	−0.2531	0.2014
2a	−0.3177	−0.2816	−0.2531	0.2013
3a	−0.3144	−0.2683	−0.2510	0.2017

Chart I. Frontier Molecular Orbitals



using protonation as a simple model for BF_3 complexation show that the π_N energy (but not π_S or π^*) is drastically lowered by protonation of the carbonyl oxygen. This should result in a reactive lowest π_S,π^* singlet for all of the amide–BF_3 complexes.

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A New Class of Chelating Agents

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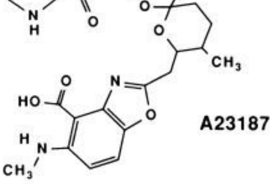
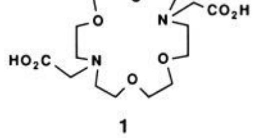
Classical chelating agents bearing carboxylate groups such as EDTA, crown ethers[1] **1**, and ionophores[2] such as A23187 share a common structural feature: only the anti lone pairs of the carboxylate achieve contact with the metal ions in the complex (eq 1). This is a constraint imposed by their molecular shapes.





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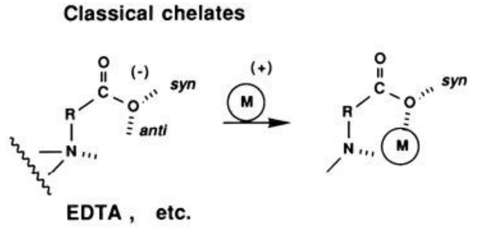
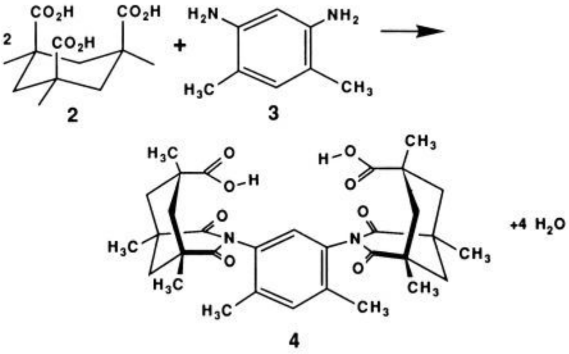


(1)

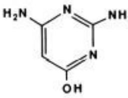
Stereoelectronic considerations,[3] however, indicate that the syn lone pairs are more basic, and this is supported by calculations,[4] structures of simple metal carboxylates in the solid state,[5] and the orientation of carboxylates at enzyme active sites.[3] Here we present structures in which the syn lone pairs are available for binding and report on their behavior as chelating agents.

The new structures are rapidly and efficiently assembled by condensation of Kemp's[6] triacid **2** with appropriate aromatic diamines such as *m*-xylidine diamine **3** (eq 2).[7] The resulting



(2)

diacid **4** can be obtained by merely heating the two components in the absence of solvent. Other diamines, **5** → **8** were also converted to the corresponding diacids by this procedure.[8] When



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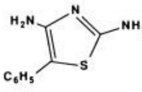

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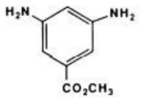

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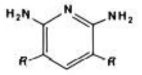

8a R=H
8b R=$CH_2C_6H_5$

substituents ortho to the amines are present, as in **3** or **8b**[9] rotations about the C_{aryl}–N_{imide} bonds become hindered in the condensation products, and the carboxyl groups are constrained to the conformation in which the OH bonds converge.[10] This may be seen in the crystal structure of the diacid derived from **8b** (shown below in Figure 1).[11] Even without these restraining elements, intra-

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[8] All new compounds were characterized by a full complement of high resolution spectra. Compound **4** showed decomposition at >400 °C; other diacids derived from **5**; mp 225; from **6**, mp 199–202; from **7**, mp 270 dec; from **8a**, decomposition at >330 °C; from **8b**, mp 328–329. These structures are within the scope of U.S. Patent no. 4 698 425.

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