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THE SOLID STATE CHEMISTRY AND SPECTROSCOPY OF SUBSTITUTED CINNAMIC ACIDS AND RELATED MATERIALS

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Abstract The room temperature solid state emission and excitation spectra of polycrystalline samples of cinnamic acids that photodimerize in the solid state have been recorded. The emissions are clearly not molecular and are likely associated with excimers. The potassium and ammonium complex salts of cinnamic acid were found to be unreactive to ultraviolet light. Room temperature emission spectra of polycrystalline samples of these salts reveal both molecular and excimeric emissions.

INTRODUCTION

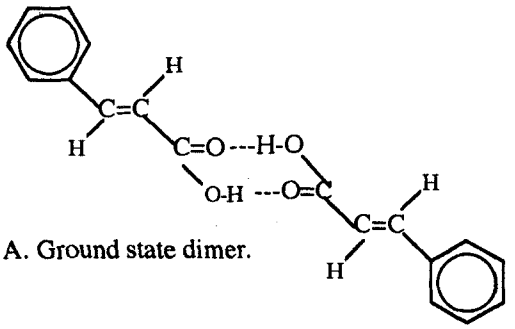
The dimerization of cinnamic acids and derivatives to truxilic and truxinic compounds initiated by ultraviolet light[1] and the polymerization of diacetylenes[2] are the best known examples of organic reactions controlled by solid state structure. In particular, these reactions provide excellent illustrations of the topochemical principle[3] which holds that for reactions to occur in the solid state, the atoms making new covalent bonds should be within about 4.2 Å in the reactant crystal structure.

For the case of the cinnamic acids, the structural requirements for the dimerization and the structures of the dimers are well-established, and an estimate of the solid state quantum yield for photodimerization(Φ = 0.59) has been reported.[4] Recently, it was found that irradiation of α-cinnamic acid in the long wavelength region of its absorption led to a single-crystal-to-single-crystal transformation.[5] Nevertheless, other issues remain unresolved.

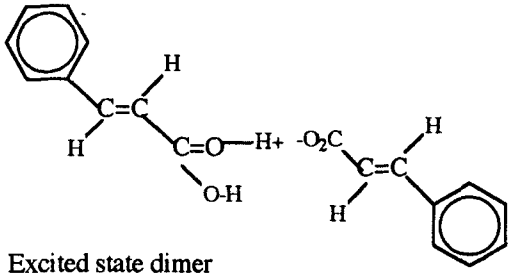
In the structural area, the photodimerization of *p*-bromocinnamic acid has been monitored by Fourier transform infrared(FTIR) spectroscopy, and the results were discussed according to a kinetic model in which monomers have one or two dimeric nearest neighbors during photoconversion.[6] In the course of the study of the crystal structure of an unreactive *p*-chlorocinnamate diacetylene ester, it was noted that both the unreactive ester and reactive *p*-chlorocinnamic acid exhibited room temperature emission spectra that were associated with excimers rather than molecular species.[7] As discussed[7], excimers are

established as reactive intermediates in solid state photodimerizations, yet a detailed structure for an excimer in a cinnamic acid dimerization has not been discussed.

The structure of the excimer is of interest because of the hydrogen bonding of the cinnamic acids. The simplest aromatic carboxylic acid, benzoic acid, also dimerized in the crystal, exhibits a solid state fluorescence spectrum that is clearly molecular in character.[8] The fluorescence studies indicate that in the excited state, the molecule does not possess a center of symmetry due to the increased proton affinity and basicity in the excited state. Figure 1 shows representations of a symmetric ground state and unsymmetric excited state dimers for cinnamic acid.



A. Ground state dimer.



B. Excited state dimer

Figure 1. Structural representations for dimerization in the ground and excited singlet states of cinnamic acid.

In view of the above discussion, a possible mechanistic scheme for dimerization might be the following:

$$(Ar\text{-}CH{=}CH\text{-}CO_2H)_2 \xrightarrow{h\nu} Ar\text{-}CH{=}CH\text{-}CO_2H_2 + Ar\text{-}CH{=}CH\text{-}CO_2^-$$

$$Ar\text{-}CH{=}CH\text{-}CO_2H_2 + Ar\text{-}CH{=}CH\text{-}CO_2^- \longrightarrow \text{Excimer}$$

$$\text{Excimer} \longrightarrow \text{Cyclobutane Dimer*}$$

$$\text{Cyclobutane Dimer*} \longrightarrow \text{Cyclobutane Dimer}$$

$$\text{Excimer} \longrightarrow (\text{Ar-CH=CH-CO}_2\text{H})_2 + h\nu'$$

In the above scheme, the detailed structure of the excimer is not specified, and it may include more than one hydrogen-bonded dimer in a linear chain structure. It is assumed that the excimer is singlet in character. The species "Cyclobutane Dimer*" represents a dimer formed at a geometry other that at equilibrium. This would be consistent with the crystallographic studies[5] that reveal dimer geometry changing as a function of conversion of monomer to dimer.

EXPERIMENTAL SECTION

Ultraviolet spectra were recorded on a Varian Cary 17 spectrophotometer using 1 cm. cells. Emission spectra were recorded on the SLM 8000 spectrometer at ambient temperature as previously[7] described. Thermogravimetric analysis was carried out on a DuPont 2950 instrument. FTIR spectra were obtained on a Perkin Elmer 1760 instrument using samples dispersed in KBr pellets. A Rigaku 300 diffractometer was used to obtain X-ray powder diffraction data.

Preparation of 4,4'-Dichloro-β-truxinic Acid. This compound was prepared as previously described.[7] In acetonitrile solution, the uv spectrum exhibited the following: λ_{max}(nm)(ε): 277(430); 268(610);261(550). Samples of this compound did not give a significant emission spectrum either in solution or the solid state.

Ammonium hydrogen dicinnamate and potassium hydrogen dicinnamate. These salts were prepared as previously described.[9] They were identified from their X-ray powder patterns. In the course of attempting to record a capillary tube melting point of the potassium salt, it was noted that a white solid sublimed off the sample. Thermogravimetric analysis revealed that the sample lost 46.2% of its weight between room temperature and 220°C. The calculated weight per cent of cinnamic acid in this solid is 43.3%. The uv spectrum of the potassium salt in ethanol(1.15×10^{-5}M) exhibited the following: λ_{max}(nm)(ε x 10^{-4}): 295(sh)(0.47); 271(1.83); 266(1.83); 260(sh)(1.61). The FTIR spectra of these salts were very similar between 2000 and 400 cm^{-1} and include the following significant absorptions (cm^{-1}): 1687, 1622, 1576, 1495, 1449, 1390, 980, 880, 770, 707, 690, 585, 530, 490.

RESULTS AND DISCUSSION

a. Cinnamic Acid Emission Spectra

The room temperature solid state emission and excitation spectra of a series of polycrystalline samples of cinnamic acids that photodimerize in the solid state[1] have been recorded. The results are summarized in Table I.

TABLE I. Solid State Emission Spectra of Cinnamic Acids

Compound	λ_{max}, nm, Emission	λ_{max}, nm, Excitation
α-cin acid	411	361
β-cin acid	409, 425	358, 374
4-Cl-cin acid	409	371
2,4-Di-Cl-cin acid	409	378
2,6-Di-Cl-cin acid	409	362
4-Br-cin acid	412	372

The data in Table 1 indicate generally similar emissions for these cinnamic acids that are clearly not molecular in character and likely excimeric. As indicated previously for *p*-chlorocinnamic acid,[7] the spectra are not highly structured. The presence of the heavy Cl and Br atoms is clearly not effective in stimulating an intersystem crossing to a triplet state. The emission spectra given in Table 1 are not due to covalent dimers. Excitation of polycrystalline 4,4'-dichloro-β-truxinic acid[7](a cyclobutane dimer) between 270-300 nm gave no significant emission.

b. Preparation, Characterization, and Reactivity of Complex Cinnamate Salts

In view of the presence of the hydrogen-bonded dimer structure in all reactive phases of cinnamic acids, it is of interest, in view of the above mechanistic discussion, to study a phase in which the hydrogen-bond pattern is disrupted. The use of a metal salt or an ammonium ion would be an approach to this.

While light-induced reactivity of metal salts of cinnamic acid was reported long ago[10], the crystal structures of the materials reported are unknown, and it is not at all clear that the reactive materials are single crystallographic phases. There is only one report of a reactive metal cinnamate where the crystal structure is given, and this work involves the sodium salt of *o*-chlorocinnamic acid dihydrate.[11]

It is highly desirable to study a phase where the crystal structure is established, and one structural study of this type has been reported. The structure of the ammonium cinnamate-cinnamic acid complex salt has been reported.[9] The structure reveals that the α carbons of the cinnamate groups are separated by 3.82Å, clearly within distances for topochemical reactivity.[1] Additionally, potassium also forms a complex salt that is isomorphous to the ammonium complex salt.[9] The early report[10] suggested that the acid salts were reactive to ultraviolet light and sunlight.

The above potassium and ammonium complex salts were prepared as previously described.[9] They were identified by their X-ray powder diffraction patterns . An attempt

to study the thermal reactivity of the complex potassium salt revealed that cinnamic acid quantitatively sublimed from the solid.

Both salts were irradiated with ultraviolet light at both 254 and 370 nm wavelengths for times that would completely dimerize *p*-chlorocinnamic acid.[7] Comparison of the Fourier-transform infrared(FTIR) spectra before and after irradiation revealed that these materials were unreactive to uv light at both wavelengths.

Since the optimal orientation for reactivity of either simple or complex metal or ammonium salts of cinnamic acids is not known, it was of interest to study the emission spectra of these salts. Polycrystalline samples of both salts were excited at wavelengths from 260-370 nm. The strongest emission spectra were observed with 295 nm excitation, and both salts gave similar spectra. The emission spectra revealed two distinct features: a maximum at 330 nm and a weaker maximum near 390 nm. A representative spectrum is shown as Figure 2. The emission near 390 nm is also observed with excitation from 340-370 nm. The excitation spectrum for the 330 nm emission revealed a maximum at 300 nm, probably associated with a shoulder in the absorption spectrum rather than the maximum near 271 nm. The excitation spectrum for the longer wavelength emission involves a weak maximum near 295 nm and a broad feature from 315-360 nm.

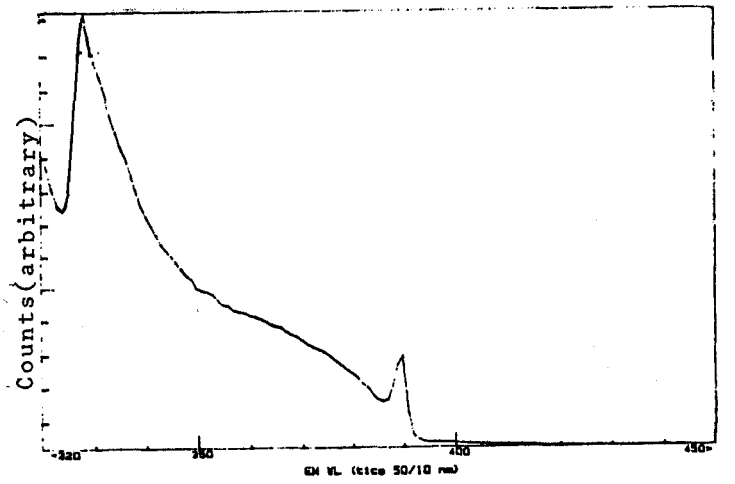


Figure 2. Emission spectrum of K^+H^+ cinnamate complex salt with excitation at 295 nm.

The emission near 330 nm is clearly molecular in origin and appears novel, as all other solid state emissions from cinnamate materials appear to be excimeric in character, as

noted above. The emission near 390 nm is presumed to be excimeric, as it is similar to those reported previously[7] and noted in Table 1.

The reactive double bonds in sodium *o*-chlorocinnamate are parallel and generally in an orientation that would be regarded as near optimal for reactive neutral cinnamic acids.[11] It is thus possible that the K^+ and NH_4^+ complex cinnamates are unreactive for structural reasons because the potentially reactive double bonds are almost orthogonal.[9] It is also conceivable that the necessary motion for reaction in the K^+ and NH_4^+ complex cinnamates is restricted due to ionic interactions in these crystals. It is clear that electronic excited states are produced in these salts and that some of their energy is released by fluorescence. Yet it is not clear what type of relationship, if any, exists between the molecular and excimeric emissions observed in these salts and their lack of reactivity.

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