



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

### The Interaction of Cinnamic Acids with $^{60}\text{Co}$ Gamma Radiation

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Version of record first published: 21 Dec 2006

To cite this article: Jeffrey M. Njus, Chantana Sae-Lim & Daniel J. Sandman (2006): The Interaction of Cinnamic Acids with  $^{60}\text{Co}$  Gamma Radiation, *Molecular Crystals and Liquid Crystals*, 456:1, 55-61

To link to this article: <http://dx.doi.org/10.1080/15421400600786330>

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## The Interaction of Cinnamic Acids with $^{60}\text{Co}$ Gamma Radiation

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*In the interest of expanding our knowledge of the interaction of cinnamic acid and its derivatives with ionizing radiation, (E)-cinnamic acid and several of its chlorinated and brominated derivatives were exposed to  $^{60}\text{Co}$  gamma radiation. Dimer yields were estimated from integration of the proton NMR signals of the irradiated material. (E)-Cinnamic acid itself is relatively unreactive. The largest yield of dimer was obtained with p-bromocinnamic acid where exposure to a dose of 116 megarads led to a 24% yield.*

**Keywords:** cinnamic acid dimerization; gamma radiation; heavy atom effect

### INTRODUCTION

In the investigation of solid-state reactions, our current level of understanding behooves the researcher to study each reaction with all available probes: heat, ultraviolet light, ionizing radiation, and pressure. The structural basis of the photodimerization of cinnamic acids with ultraviolet light [1] is well known. Attempts to study the dimerization process thermally are made difficult by the sublimation that occurs

This work was supported in part by the Petroleum Research Fund under Grant 40263-AC7. Ms. Mary Montesalvo of the Radiation Laboratory of the University of Massachusetts Lowell facilitated access to the  $^{60}\text{Co}$  source. Chantana Sae-Lim thanks the government of Thailand for a fellowship. The authors thank Professor B.M. Foxman (Brandeis University) for useful discussions in the course of this work. He also facilitated access to the Gammacell at Brandeis University when D.J.S. was employed at GTE Laboratories Incorporated.

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on heating. Cinnamic acid has typically been regarded as relatively unreactive to ionizing radiation [2,3]. A relative lack of reactivity is not surprising because aromatic compounds are much more resistant to radiation than alkanes and alkenes [4]. Yet, ionizing radiation produces higher excited states as well as ionization. The higher excited states might rapidly decay to the lowest singlet state by Kasha's Rule and that state should lead to dimerization. Such was the situation when it was reported [5] that electron beam irradiation (1 MeV, 0.5 mA) of (*E*)-cinnamic acid with a 500 Mrad dose gave truxillic acid in 58% yield.

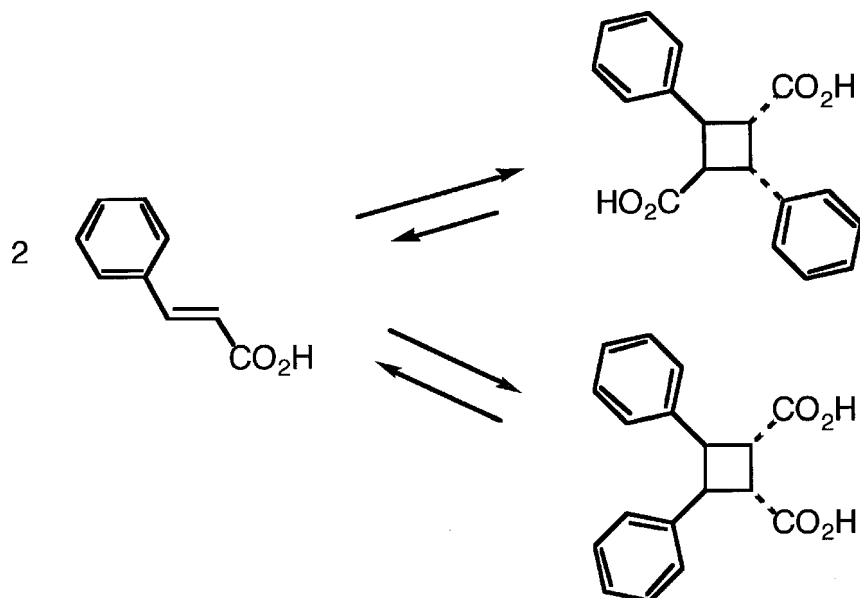
In the interest of learning more about the reactivity of (*E*)-cinnamic acids with ionizing radiation, we have exposed (*E*)-cinnamic acid and several of its chloro and bromo derivatives to  $^{60}\text{Co}$  gamma radiation. This line of inquiry uses a heavy atom strategy. In the interaction of  $\gamma$ -radiation with matter, the photoelectric effect and Compton scattering are major processes. Both of these processes are more probable for materials with high atomic numbers [6]. Hence, it would be expected that molecular structures containing heavy atoms that are involved in the electronic structure would be more reactive to  $\gamma$ -radiation than similar molecular structures lacking a heavy atom, other things (*e.g.*, crystal structure in the solid state) being equal. Earlier, the role of heavy metal atoms in the reaction of metal propynoates with  $^{60}\text{Co}$   $\gamma$ -radiation [7,8] was discussed.

## EXPERIMENTAL SECTION

Cinnamic acid and its derivatives were used as received from Aldrich Chemical Company. Their crystalline phase was established by X-ray powder diffraction in earlier studies. Truxillic and truxinic acids were prepared by uv irradiation [9] as previously described. Proton NMR spectra were recorded on Bruker 500 or 250 MHz spectrometers. The compounds were irradiated in screw cap vials in the presence of air at ambient temperature. The dose rate was 0.76 Mrad/hr. The irradiated solids were dissolved in an appropriate solvent and their NMR spectra were recorded. The product yield was obtained from the relative areas of the olefinic signals of the cinnamic acid and the aliphatic protons of the dimer. Obtaining the yields of the irradiation experiments by integration of the  $^1\text{H}$  NMR spectra is clearly a more accurate method than solvent extraction [3] of the irradiated solid.

## RESULTS AND DISCUSSION

The products of dimerization of the cinnamic acids are illustrated in Figure 1. The compounds that were exposed to  $\gamma$ -radiation are listed

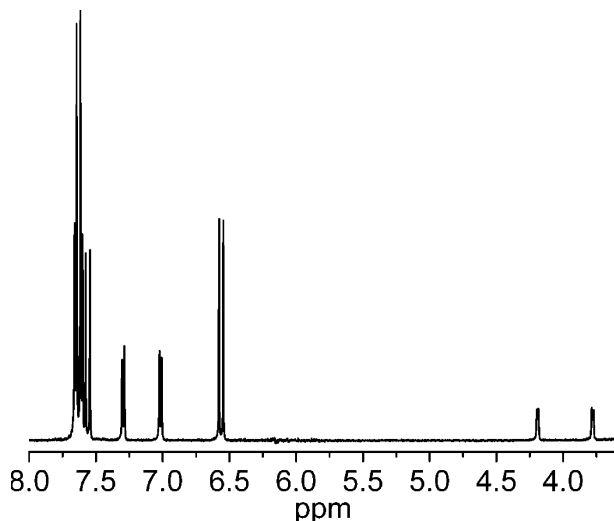


**FIGURE 1** Cinnamic acid, its dimerization to truxillic and truxinic acids and the reverse processes.

in Table 1 along with the radiation dose and the product yield. The radiation dose was a minimum of 50 Mrad as this is the dose used to polymerize diacetylene monomers to completion when possible. Integration of the proton resonances of the vinylic protons of the reactant and the aliphatic protons of the dimer was used to obtain the yields. With respect to Table 1, the largest yield of dimer was obtained with

**TABLE 1** Cinnamic Acids and their Dimers, the Dose of  $\gamma$ -Radiation they Received, and the Product Yield

| Starting compound                     | Dose of $^{60}\text{Co}$ , Mrad | Yield of product |
|---------------------------------------|---------------------------------|------------------|
| <i>E</i> -Cinnamic acid               | 50                              | 0.8–5.6%         |
| 4-Chlorocinnamic acid                 | 50                              | 8.1%             |
| 4-Bromocinnamic acid                  | 50                              | 7.1%             |
| 2,4-Dichlorocinnamic acid             | 50                              | 0.0%             |
| 2,4-Dichlorocinnamic acid             | 116                             | 20%              |
| 4-Bromocinnamic acid                  | 116                             | 24%              |
| Truxillic acid                        | 50                              | 0.03%            |
| 4,4'-Dichloro- $\beta$ -truxinic acid | 50                              | 0.4%             |
| 4,4'-Dibromo- $\beta$ -truxinic acid  | 50                              | 1.3%             |



**FIGURE 2** Expanded region of the proton NMR spectrum (DMSO- $d_6$  solution) of *p*-bromocinnamic acid irradiated with 116 Mrad  $^{60}\text{Co}$  gamma radiation. The two multiplets located in the 3.5–4.5 ppm range are the methine protons of the truxinic acid. The doublets near 6.6 and 7.6 ppm are alkene protons of *p*-bromocinnamic acid.

4-bromocinnamic acid with a dose of 116 Mrad, and the yields of dimers were typically higher with cinnamic acids with halogen substituents than without. The  $^1\text{H}$  NMR spectrum of the products of  $\gamma$ -radiation of 4-bromocinnamic acid is displayed in Figure 2.

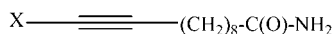
Since the yield of truxillic acid decreased [5] at electron beam doses greater than 500 Mrad, we chose to inquire if the dimer was reactive to radiation. As shown in Table 1, the largest amount of cinnamic acid was obtained with the Br-substituted truxinic acid, 1.3% yield. This invited the question as to whether the dimers were stable under UV irradiation. Under conditions (254-nm light) [9] where 4-bromocinnamic acid was converted to dimer in 90% yield, the Br-substituted truxinic acid converted to monomer in 1.5% yield.

While (*E*)-cinnamic acid has the  $\alpha$ -crystal structure and the halogenated cinnamic acids have the  $\beta$ -structure [1], it appears that the major reason for the results in Table 1 is the heavy atom effect. While it is also apparent that both electron beams [5] and  $^{60}\text{Co}$   $\gamma$ -radiation can convert cinnamic acid to its dimer, the doses involved are very large. Ultraviolet irradiation and sunlight remain the methods of choice to carry out this dimerization for synthetic purposes.

It was suggested [5] that the interaction of electron beams with cinnamic acid to give truxillic acid proceeds via the same lowest excited state as the photochemical dimerization. While this suggestion is plausible, as discussed above, it may well be oversimplified. The potential of ionizing radiation to produce excited states that are electric dipole forbidden is at the heart of this suggestion. In addition, it is appropriate to note that the excited state leading to dimerization may be more complex than the lowest singlet of monomeric (*E*)-cinnamic acid. The fluorescence of solid cinnamic acids [9,10] is clearly not molecular and may be excimeric.

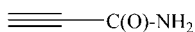
While the presence of halogens in the cinnamic acid molecular structure enhances reactivity toward  $\gamma$ -radiation, it is not the only example of this type. The molecular structures given in Figure 3 provide several additional examples. While N-propargylcarbazole is relatively unreactive to  $\gamma$ -radiation, N-(3-bromo-2-propynyl)carbazole [11] reacts. The term "relatively unreactive" means that, after exposure to radiation, the solid retained its original color and its melting point is not changed. Ultimately, everything is reactive to ionizing radiation. Again, 10-undecyanamide [12] is relatively unreactive to  $\gamma$ -radiation, 11-bromo-10-undecyanamide [13] reacts. Vacuum sublimed crystals of

## Cinnamic Acids and Gamma Radiation

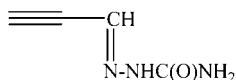


X = H, 10-undecyanamide

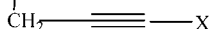
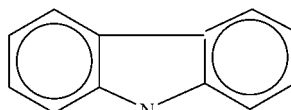
X = Br, 11-bromo-10-undecyanamide



Propiolamide

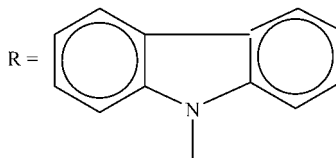
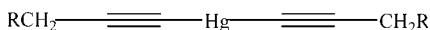


Propiolaldehyde semicarbazone



X = H, N-propargylcarbazole

X = Br, N-(3-bromo-2-propynyl)-carbazole

R =  $\text{---}(\text{CH}_2)_3\text{---O---C}(\text{O})\text{---NH---C}_2\text{H}_5$ 

**FIGURE 3** Molecular structures and names of solid compounds that were exposed to  $^{60}\text{Co}$   $\gamma$ -radiation.

the semicarbazone of propionaldehyde and propiolamide [14] are relatively unreactive, but crystals of these compounds obtained from chlorinated solvents show reactivity that was traced to the presence of solvent in crystalline defects. The presence of short intermolecular contacts between alkyne carbons in the crystal structures of 10-undecyanamide [12] and the semicarbazone of propionaldehyde [14] is not sufficient to render these compounds reactive to  $\gamma$ -radiation. They are also melt-stable. Certain aromatic acetylenes, *e.g.*, 1,4-diethynylbenzene [15], are reactive to  $\gamma$ -radiation, but p-ethynylbenzoic acid, with a linear chain crystal structure [16], is unreactive to both  $\gamma$ -radiation and UV light.

While the above examples show the effectiveness of halogen atoms in imparting solid state reactivity to otherwise unreactive molecular structures, the presence of a heavy atom in a molecular structure is not sufficient to impart significant reactivity. The mercury compounds [17] in Figure 3 are relatively unreactive to  $\gamma$ -radiation.

While (*E*)-cinnamic acid is relatively unreactive to radiation, its molecular structure contains an  $\alpha,\beta$  unsaturated aromatic acid that undergoes a 2 + 2 cycloaddition.  $\alpha,\beta$  Unsaturated acids such as sorbic and muconic give some dimer and also oligomer on exposure [18] to  $\gamma$ -radiation. Acenaphthene is an  $\alpha,\beta$  unsaturated aromatic compound that undergoes a 2 + 2 cycloaddition [19] under the influence of  $\gamma$ -radiation.

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