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Investigation of the photochemistry and photophysics of para-substituted tertiary thiocinnamamides

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Abstract

We report the synthesis and photochemical investigation of a new series of compounds, the tertiary, *p*-substituted thiocinnamamides. The synthesis centers on a one-pot conversion of the corresponding cinnamamide to the thiocinnamamide via Lawesson's reagent. Results of semi-empirical calculations predict a frontier orbital structure for the thiocinnamamides that is similar to the analogous cinnamamides. One important difference is the inclusion of the sulfur non-bonding orbital as the highest occupied orbital of the thiocinnamamides. The oxygen non-bonded orbital of the cinnamamides is considerably lower in energy, and does not contribute significantly to the frontier orbital structure. The absorption and emission spectra were measured and are described. The quantum yields for E-Z photoisomerization at various wavelengths were measured and the quantum yields were not found to vary with wavelength. The photostationary states were measured and found to depend on the absorbance of the E and Z isomers at the irradiation wavelength as was expected. Analysis of photoproducts and triplet quenching studies suggest the importance of a triplet state in the photoreactivity of the tertiary thiocinnamamides. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Thiocinnamamide; Quantum yield; Photo-products

1. Background

The photochemistry of the thiocinnamamide family of compounds has received relatively little attention in the literature [1–5]. Condorelli et al., have focused investigations on the primary thiocinnamamide and poly aromatic derivatives. They found essentially invariant quantum yields and photostationary states (E/Z isomer ratios) with differing wavelength of irradiation, solvent and triplet quenchers. They proposed a singlet state deactivation mechanism involving twisting about the C=C double bond [1,2]. This compares well to the photoisomerization of the primary cinnamamides, reported by Lewis et al. which also exhibited essentially invariant quantum yields and photostationary states with changes in excitation wavelength [3,4]. Ionescu et al., report minor differences in thiocinnamamide quantum yield and photostationary state with varying excitation wavelength in ethanol, but in general, their data agree with the results and conclusions of Condorelli et al. [5].

In contrast, the tertiary amides as reported by Lewis et al., exhibit interesting substituent dependent photochemical behavior [3,4]. This dependence of the quantum yield for photoisomerization on the para substituent derives from two energetically closely spaced highest occupied orbitals localized over two different regions of the molecule (styryl and amide moieties) [3,4]. The relative energy of these orbitals is calculated and experimentally shown to depend on the nitrogen and para- substitution pattern. Excitation from the styryl HOMO leads to efficient isomerization. Excitation from the amide HOMO leads to much lower isomerization efficiency [3,4].

The thiocinnamamides were chosen for study to examine the effect of sulfur substitution into the cinnamamide structure on the photochemistry. The higher energy of the sulfur frontier orbitals is expected to result in a red shift in the absorption spectrum and higher importance of non-bonding orbitals in the observed photochemistry compared to the oxygen counterpart. The higher energy frontier orbitals should also result in considerably different mixing of the styryl and thioamide conjugated orbitals compared to the cinnamamides as will be discussed below. In addition, sulfur may increase the spin-orbit coupling between singlet and triplet states and increase the importance of the triplet state to the photochemistry of the thiocinnamamides [10]. The tertiary thioamide derivatives were chosen for initial investigation because the contribution of the thiol imine form of

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the tertiary thiocinnamamide are reduced compared to the primary and secondary thioamides, reducing the probability of secondary thermal reactions [6].

We report here the results of our investigation of the photochemistry of the tertiary thiocinnamamides and the effect of para substitution on the photoisomerization efficiency. Comparisons are made to the tertiary cinnamamides, which exhibit substitution dependent photochemistry and in some cases, wavelength dependent quantum yields. [3,4]

2. Methods

The thiocinnamamides are readily prepared from the corresponding cinnamamides. The appropriate cinnamic acid, purchased from Aldrich, and thionyl chloride (excess) was refluxed for several hours. Distillation of the solution to remove the excess thionyl chloride affords the cinnamic acid chloride in nearly quantitative yield. Addition of 25% secondary amine in water to an ether solution of the cinnamic acid chloride gives the cinnamamide in greater than 90% isolated yield after recrystallization from chloroform. Column chromatography of the cinnamamides on silica gel, eluting with chloroform, afforded the E-isomers in >99.9% purity by GC. Refluxing the cinnamamides and Lawesson's reagent in toluene for 4–6 h, followed by column chromatography of the reaction mixture on silica gel, eluting with chloroform, gives the corresponding thiocinnamamide in 75–90% isolated yield [7–9]. Further chromatography of the thiocinnamamide on silica gel, eluting with diethylether, affords the E and Z isomers in >99% purity. Prep TLC just prior to photolysis is required of several derivatives to achieve >99.9% purity of the E isomer. The thiocinnamamides studied for this report were characterized fully. NMR (proton and carbon), IR (KBr wafer), GC-MS and elemental analysis were all consistent. NMR were recorded on a Gemini 200 spectrometer with a Gemini 2000 system upgrade. IR spectra were recorded on a Mattson-ATI Genesis FT-IR.

The NMR spectral details are as follows (in ppm): *N*,*N*-dimethylthiocinnamamide, ^{1}H, 3.4 (s, 3H), 3.6 (s, 3H) 7.15, 7.8 (dd, 2H) 7.35, 7.65 (m and m, 5H), ^{13}C, 41, 43, 126, 128, 129, 130, 136, 144, 197; *N*,*N*-dimethyl-*p*-methoxythiocinnamamide,^{1}H, 3.4 (s, 3H), 3.6 (s, 3H), 3.85 (s, 3H), 7.05, 7.85 (dd, 2H), 6.9, 7.5 (dd, 4H), ^{13}C, 42, 42, 55, 114, 122, 127, 128, 129, 130, 144, 160, 198; *N*,*N*-dimethyl-*p*-trifluoromethylthiocinnamamide, ^{1}H, 3.4 (s, 3H), 3.6 (s, 3H), 7.1, 7.8 (dd, 2H), 7.6 (m, 4H), ^{13}C, 42, 45, 121, 126, 128, 129, 139, 141, 160, 196.

The IR spectral details are as follows (in cm^{-1}): *N*,*N*-dimethylthiocinnamamide, 3100–3000 (b, m), 2934 (b, m), 1628 (m), 1601 (w), 1517 (m), 1505 (m), 1393 (m), 1294 (m), 1143 (m), 984 (m), 857 (m); *N*,*N*-dimethyl-*p*-methoxythiocinnamamide, 3100–3000 (b, m), 2950–2850 (b, m) 1629 (w), 1604 (m), 1514 (m), 1394(m), 1273 (s), 1252 (s), 1178 (m), 1152 (m), 1029 (m), 826 (m); *N*,*N*-dimethyl-*p*-trifluoromethylthiocinnamamide, 3100–3000 (b, m), 2950–2850 (b, m), 1632 (m), 1613 (m), 1503 (m), 1407(m), 1309 (s), 1288 (m), 1165 (m), 1066(m), 824 (w)[1].

Mass spectra were measured for the title compounds. Ionization (EI +) resulted in parent peaks of 191, 259, 205 for the *N*,*N*-dimethyl thiocinnamamide, *N*,*N*,-dimethyl-4′-trifluoromethylthiocinnamamide, and *N*,*N*-dimethyl-4′-methoxythiocinnamamide, respectively.

Elemental analyses of the three compounds were in agreement with calculation (in parentheses), (%C, %H, %N) 68.11(69.1) 6.78(6.8) 7.02(7.3); 54.62(55.6) 4.69(4.7) 5.09(5.4); 62.73(65.1) 7.13(6.8) 5.37(6.3) for *N*,*N*-dimethyl thiocinnamamide, *N*,*N*-dimethyl-4′-trifluoromethylthiocinnamamide, and *N*,*N*-dimethyl-4′-methoxythiocinnamamide, respectively.

Absorption spectra were recorded on a Perkin–Elmer Lambda 3B spectrophotometer. Spectrochemical or HPLC grade solvents were used without further purification.

Emission spectra were recorded on a Gilford Fluoro IV spectrophotometer. Spectrochemical or HPLC grade solvents were used without further purification.

Quantum yields of photoisomerization from the E and Z-isomers were measured by irradiation at 254 nm (fluorescent lamp), 313 nm (K_2CrO_7/pyrex filter of a 450 W Hanovia lamp) and 366 nm (fluorescent lamp) to low (<10%) conversion and subsequent sample analysis by GC. Chemical actinometry was used to measure light intensity for the relative quantum yield calculations. *Trans*-Stilbene in methylene chloride was used as the actinometer at 254 and 313 nm [3,4]. E-*p*-Methoxy-*N*,*N*-dimethylcinnamamide in methylene chloride was used at 366 nm [3,4]. Solutions were prepared and checked by absorption spectrometry to ensure the solution absorbed all light at the appropriate wavelengths. Sample solutions were prepared in spectrochemical or HPLC grade solvents and checked by absorption spectroscopy to ensure the solution absorbed all incident light at the irradiation wavelength. Samples prepared for irradiation under N_2 were bubbled for 15 min with dry N_2 prior to irradiation. Photostationary states were also measured at 254, 313 and 366 nm using appropriate fluorescent lamps or an Oriel high pressure lamp and Corning glass filters.

Irradiation reaction solutions were analyzed in triplicate by GC. A Varian 3400 GC with FID detector and a 100% methylated polysiloxane (DB-1) capillary column (30 m, 25 μm) was used. Photoproducts were also analyzed by

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[1] The IR results for the thiocinnamamides are quite different from the comparable cinnamamides as expected. The chief difference is the signal for the thiocarbonyl moiety. The S-C bond is much longer and weaker than the C-O and therefore results in a characteristic IR frequency much lower than the carbonyl. The low frequency of the thiocarbonyl also results in a decrease in mixing with the conjugated alkene. It is therefore unlikely that the characteristic shifts of conjugated enone systems will be of use in determining the conformations of the thiocinnamamides.

Table 1
Semi-empirical calculation data for E-*N*,*N*-dimethylthiocinnamamide using Hyperchem 5.01 (see Footnote 2) [6]

E-*N*,*N*-Dimethylthiocinnamamide				
Singlet calculation				
Wavelength (nm)	344.62	278.45	215.18	
Oscillator strength	0.798	0.643	0.351	
Triplet calculation				
Wavelength (nm)	726.56	343.01	294.68	
Oscillator strength	0.149	0.01	0.078	
Singlet calculation	LUMO –1	HOMO 0	SHOMO 1	THOMO 2
Zindo(s) (eV)	−1.13509	−7.55901	−7.83147	8.79875
Zindo(1) (eV)	3.723522	−6.7124	−7.03666	−7.91177
PM3 (eV)	−1.63715	−8.1826	−8.46168	−9.18701
Triplet calculation				
Zindo(1) (eV)	0.724013	−4.89301	−7.49545	

Table 2
Semi-empirical calculation data for E-*N*,*N*-dimethyl-*p*-trifluoromethylthiocinnamamide using Hyperchem 5.01 (see Footnote 2) [6]

E-*N*,*N*-Dimethyl-*p*-trifluoromethylthiocinnamainide				
Singlet calculation				
Wavelength (nm)	346.44	279.24	223.18	216.26
Oscillator strength	0.772	0.709	0.045	0.305
Triplet calculation				
Wavelength (nm)	310.26			
Oscillator strength	0.988			
Singlet calculation	LUMO −1	HOMO 0	SHOMO 1	THOMO 2
Zindo(s) (eV)	−1.44409	−7.79243	−8.05714	−9.04545
Zindo(1) (eV)	2.973581	−7.13052	−7.43243	−8.44941
PM3 (eV)	−2.07737	−8.4174	–8.75166	–9.58406
Triplet calculation				
Zindo(1) (eV)	0.076931	−5.3605	−8.1192	

Table 3
Semi-empirical calculation data for E-*N*,*N*-dimethyl-*p*-methoxythiocinnamamide using Hyperchem 5.01 (see Footnote 2) [6]

E-*N*,*N*-Dimethyl-*p*-methoxythiocinnamainide				
Singlet calculation	350.80	283.24	218.41	
Wavelength (nm)	0.942	0.540	0.336	
Oscillator strength				
Triplet calculation				
Wavelength (nm)	315.86			
Oscillator strength	0.636			
Singlet calculation	LUMO −1	HOMO 0	SHOMO 1	THOMO 2
Zindo(s) (eV)	−1.08132	−7.4887	−7.7074	−8.61898
Zindo(1) (eV)	3.866445	−6.59691	−6.79613	−7.49732
PM3 (eV)	−1.56695	−8.10083	−8.38201	−8.98007
Triplet calculation				
Zindo(1) (eV)	1.072267	−4.39837	−6.95234	

GC/MS. A Varian Saturn 2000 GC/MS system was used (GC system described previously).

3. Results and discussion

Semi-empirical calculations were carried out for the thiocinnamamide derivatives prepared in this study[2]. Several methods were used including PM3, ZINDO/1 and ZINDO/S. The results for the parent (-H) tertiary thiocinnamamide are presented in Tables 1–3 and depicted in Fig. 1. The results calculated for the *p*-methoxy and *p*-trifluoro tertiary thiocinnamamides are qualitatively similar to the results of the parent compound and are not shown. The three methods listed result in frontier orbitals for the cinnamamides similar to those reported by Lewis et al. using Gaussian 86. We conducted calculations on the corresponding cinnamamides to test the methods. The frontier orbitals of the cinnamamides consist of a styrene localized π^*, a styrene localized π and an amide localized π. The energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is 12.33 eV and the energy difference between the HOMO and second highest occupied orbital (SHOMO) is 0.32 eV. The orbital energy values are presented for general, relative comparison purposes only. The localized π orbitals exhibit greater mixing than observed for the results from an STO-3G ab initio calculation with no CI included. This data is consistent, though, with further work done by Lewis et al. incorporating CI into the calculation [3,4]. The methods reproduce the results of the more rigorous ab initio calculations performed by Lewis et al. so the calculations performed on the thiocinnamamides may be of use in predicting the photophysical and photochemical properties of the thio derivatives in the singlet state. The lowest unoccupied orbital calculated for *N*,*N*-dimethylthiocinnamamide is a styrene π^* orbital similar to the cinnamamide system. The highest occupied orbital is a sulfur n orbital. The next two occupied orbitals correspond to the styryl and amide π systems of the cinnamamides. The HOMO–LUMO energy gap is less than the corresponding cinnamamide (10.43 eV vs. 12.33 eV), consistent with a shift of the absorption spectrum to longer wavelength. The energy difference between the amide localized orbital and the styryl localized orbital is considerably larger (0.97 eV) than that exhibited by the tertiary cinnamamide (0.34 eV). The relative orbital energies calculated for the tertiary cinnamamides show a reversal in the ordering of the π_{amide} and π_{styryl} orbitals upon para substitution with an electron donating group [3,4]. There is no comparable reordering of orbitals when comparing the

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[2] Hyperchem 5.01 copyright Hypercube, PM3, RHF semi-empirical calculation with Configuration Interaction (singly excited, 3 occupied, 3 unoccupied orbitals included). Hyperchem 5.01 ab initio calculations with a minimal basis set result in unreasonable orbital calculations presumably due to the large molecular size and therefore large basis functions required for these molecules (file storage problem). The thioamide group was locked in a planar conformation, similar to the amide group (amide resonance) (6).

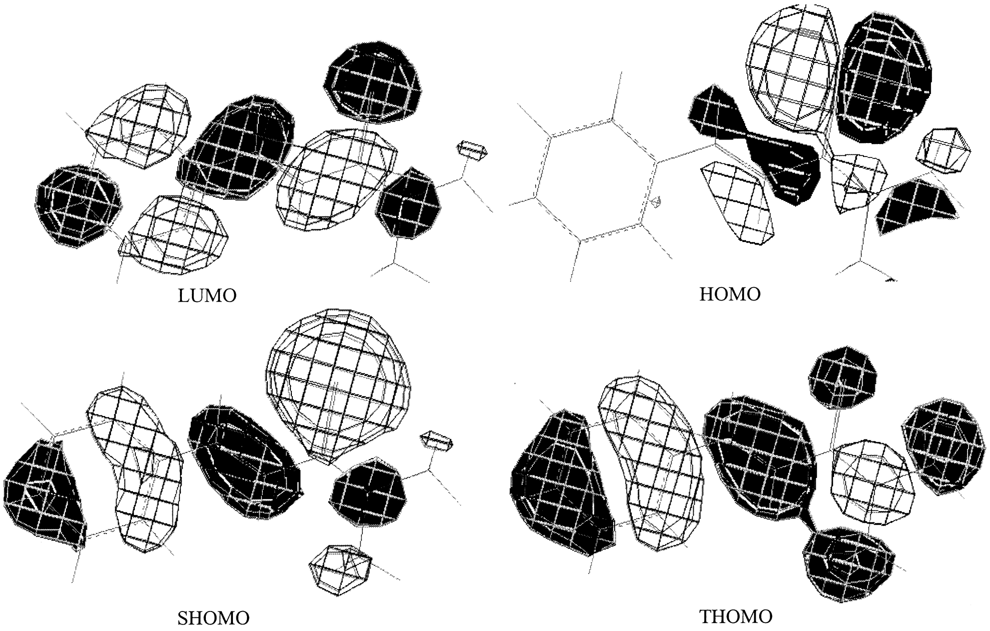
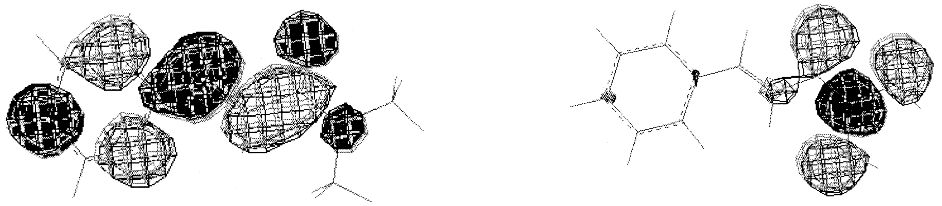


Fig. 1. Lowest unoccupied (LUMO), highest occupied (HOMO), second highest occupied (SHOMO) and third highest occupied (THOMO) molecular orbitals of *N*,*N*-dimethylthiocinnamamide calculated with ZINDO(1).

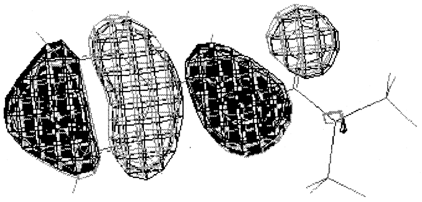
calculated relative energies in the thiocinnamamides derivatives, the energy gap between the amide and styryl moieties is too large. This is a fundamental difference between the cinnamamides and thiocinnamamides. Also, unlike the tertiary cinnamamides, the calculated frontier orbitals of the tertiary thiocinnamamides exhibit differences in the magnitude of mixing of the styryl and amide orbitals. The derivatives show strong mixing of the ‘thioamide’ and ‘styryl’ localized π orbitals. As stated above, the order of the orbitals does not change, i.e. the sulfur n localized orbital is the HOMO followed by the thioamide localized orbital. This fundamental difference in the singlet state frontier orbital structure of the tertiary thiocinnamamides vs. the tertiary cinnamamides would predict that the thiocinnamamides exhibit little dependence on para substitution. Also, the tertiary thiocinnamamides may be expected to exhibit lower photoisomerization efficiencies in the singlet state than the corresponding cinnamamide due to the nature of the lowest energy transitions, both of which have strong modes of coupling with the environment [3,4,6,10,12]. Calculations of the first excited triplet state using ZINDO(1) for the three thiocinnamamide derivatives used in this study result in similar frontier orbitals. The LUMO is a styrene localized π^*, the HOMO is a sulfur non-bonding localized molecular orbital, and the SHOMO is a styrene localized π (Fig. 2). The molecular orbitals calculated for the comparable cinnamamides show similar differences between cinnamamide and thiocinnamamide to those seen in the singlet results (Fig. 2). The triplet state calculation results suggest the triplet state reactivity of the thiocinnamamides used in this study may be similar to the comparable cinnamamides if the transition is π, π^*, therefore, the thiocinnamamides would be expected to isomerize efficiently and with no dependence on para substituents. Coupling between the π, π^* and n, π^* state of the thiocinnamamide may lower the observed quantum yield for photoisomerization by decreasing the triplet lifetime or increasing competitive side reaction pathways. The ZINDO/S method electronic spectrum calculation correlates well with the measured absorption spectrum of the tertiary thiocinnamamides (Tables 1–3). The calculated oscillator strength of the long wavelength band is higher than observed. Results of semi-empirical calculations of the Z-isomers are similar to the results of the E-isomers, with differences due to the non-planarity of the Z-isomer [3,4].

Absorption spectra were recorded for the thiocinnamamide derivatives prepared and the data is summarized in Table 4. The absorption spectrum of *N*,*N*-dimethyl thiocinnamamide (E and Z), the *N*,*N*-dimethyl-*p*-trifluoromethyl thiocinnamamide (E and Z) and N,N-dimethyl-*p*-methoxy thiocinnamamide (E and Z) are shown in Figs. 3–5. The tertiary thiocinnamamides exhibit a broad absorption band with an extended tail to long wavelength well into the visible region. This gives the thiocinnamamides a yellow appearance. The tertiary thiocinnamamides studied here do not exhibit the detailed band structure observed with the primary thiocinnamamide in the main (270–290 nm) transition band [1,2]. The wavelength of maximum absorbance (λ_{max}) for the Z-isomers is shifted 10 nm to shorter wavelength compared to the E-isomers. The extinction coefficients at λ_{max} ($\varepsilon_{\lambda_{max}}$) for the Z-isomers are 90% of the E-isomers. The λ_{max} and $\varepsilon_{\lambda_{max}}$ data are consistent with the primary thiocinnamamide results [1,2]. The wavelength maxima differences of the Z and E isomers of the thiocinnamamides are less than the comparable cinnamamides (10 nm vs. 20 nm) [1–4].

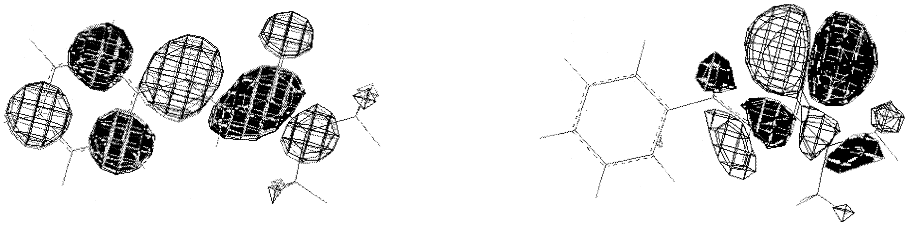


N,N-Dimethylcinnamamide LUMO

N,N-Dimethylcinnamamide HOMO

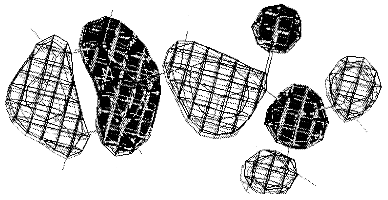


N,N-Dimethylcinnamamide SHOMO



N,N-Dimethylthiocinnamamide LUMO

N,N-Dimethylthiocinnamamide HOMO



N,N-Dimethylthiocinnamamide SHOMO

Fig. 2. Lowest unoccupied (LUMO), highest occupied (HOMO), and second highest occupied (SHOMO) molecular orbitals of *N,N*-dimethylcinnamamide and *N,N*-dimethylthiocinnamamide calculated with ZIND(1).

The extinction coefficients of the E and Z-cinnamamides vary much more than the thiocinnamamides, presumably due to the varying HOMO–LUMO transition of the cinnamamides [3,4]. A series of solvents of differing polarity were used to probe the nature of the transitions. A small (5–8 nm) blue shift was observed for the long wavelength band (360 nm) and the main absorption band (270 nm) of *p*-methoxy and parent thiocinnamamide as the solvent polarity was increased. This is characteristic of a strong n, π^* component to the transition. The long wavelength band (>360 nm) does not shift to the blue when comparing the E to Z isomers. This is consistent with the assignment of the long wavelength band as an n, π^* localized on the thioamide portion of the molecule. The absorption spectra results of the three derivatives studied here are in general agreement with the earlier results of Condorelli et al. [1,2].

The tertiary thiocinnamamides studied exhibited no measurable emission in the UV–Vis region. Thioketones are known to exhibit $S_2 \rightarrow S_0$ fluorescence [10], but the thiocinnamamides presumably have efficient internal conversion decay modes coupled with efficient isomerization that reduce the emission efficiency.

Quantum yields of photoisomerization from the E and Z-isomers of each derivative were measured and the results are summarized in Table 4. The quantum yields of photoisomerization were measured at 254, 313 and 366 nm and did not vary with wavelength. The *N,N*-dimethylthiocinnamamides with electron withdrawing and electron donating groups at the para position are

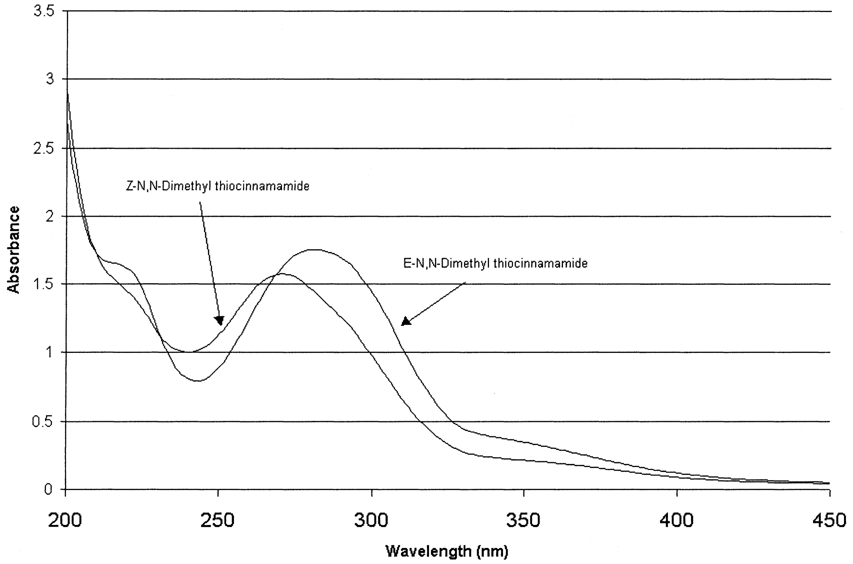


Fig. 3. Absorption spectrum of E and Z-*N*,*N*-dimethyl thiocinnamamide (1.0×10^{-4} M) in $CHCl_3$.

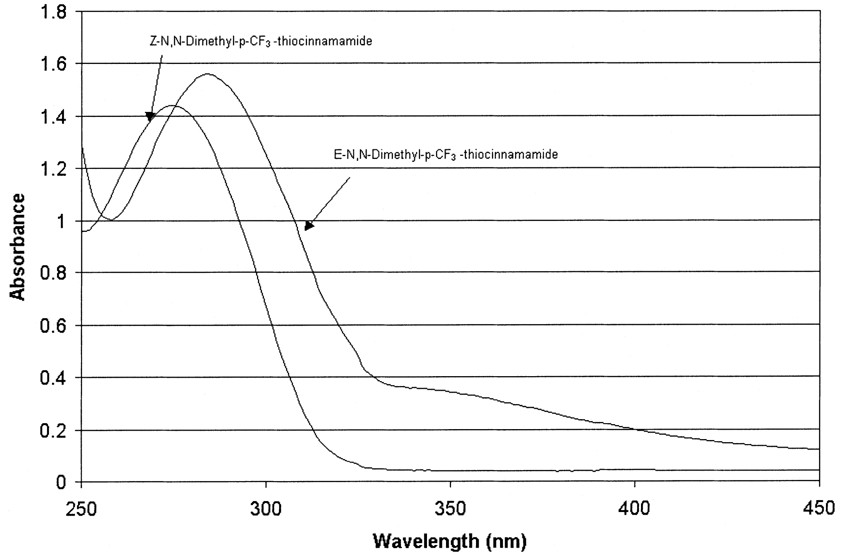


Fig. 4. Absorption spectrum of E and Z-*N*,*N*-dimethyl-*p*-trifluoromethyl thiocinnamamide (1.0×10^{-4} M) in $CHCl_3$.

Table 4
Quantum yield, photostationary state, and absorption data for the three *N*,*N*-dimethyl thiocinnamamides studied

	4-H	4-OCH_3	4-CF_3
$\Phi_{E\text{-}Z}$	0.11	0.19	0.30
$\Phi_{Z\text{-}E}$	0.09	0.18	0.33
E–λ_{max}	281	281	284
E–$\varepsilon_{\lambda_{max}}$	16 800	19 400	15 000
Z–λ_{max}	271	278	274
Z–$\varepsilon_{\lambda_{max}}$	15 000	17 600	13 600
PSS (%Z) at 254 nm	50	46	49
PSS (%Z) at 254 nm calculated	50	47	52
PSS(%Z) at 313 nm	66	54	79
PSS (%Z) at 313 nm calculated	66	63	80
PSS (%Z) at 366 nm	65	90	90
PSS (%Z) at 366 nm calculated	65	87	88

larger than the quantum yields for the E and Z isomers of *N*,*N*-dimethylthiocinnamamide. This suggests that the relative energies of the frontier orbitals are not changing or are not important to the photoisomerization efficiency. The quantum yields for photoisomerization from the E and Z-isomers are nearly identical. This result is similar to the results reported by Condorelli et al. [1,2] and Ioescu et al. [5] and are consistent with photoisomerization via a common intermediate, the perpendicular intermediate of a triplet state. The photostationary state compositions (pss) of the three derivatives are wavelength dependent. The measured photostationary state compositions correlate well with pss calculated from the ratios of the absorbances of the Z and E isomers at the irradiation wavelength. Absorption spectra data for the Z isomers show that the

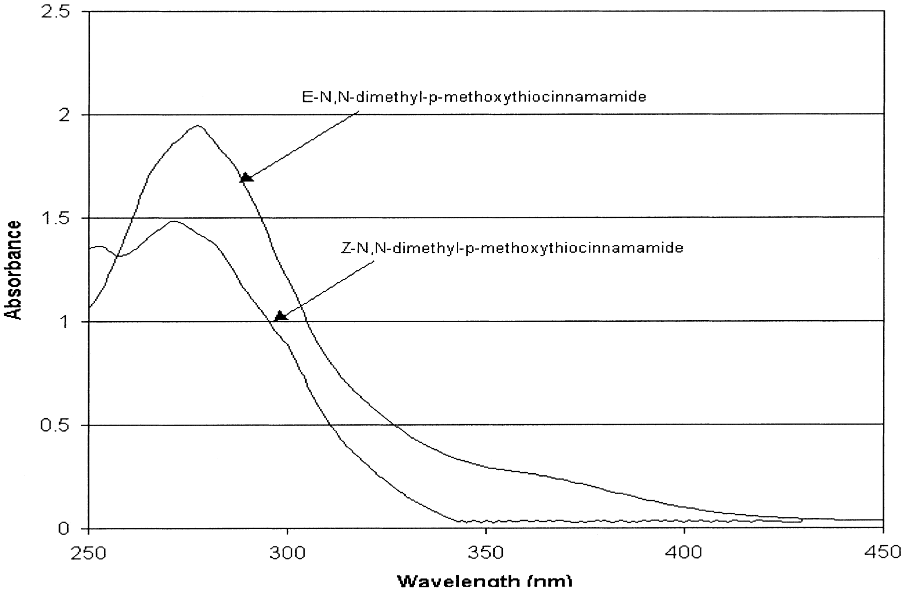


Fig. 5. Absorption spectrum of E and Z-*N*,*N*-dimethyl-*p*-methoxy thiocinnamamide (1.0×10^{-4} M) in $CHCl_3$.

N,*N*-dimethylthiocinnamamide isomers are shifted approximately 10 nm to shorter wavelength. The decrease in absorbance by the Z isomer at long wavelength accounts for the 366 nm photostationary state. This is similar to the results reported for the comparable cinnamamides. Irradiations were carried out in nitrogen and air saturated solution. There was no difference in quantum yield or photostationary state. Photolyses of the *p*-methoxy and *p*-CF3 were carried out at 254 nm with and without 1,3-cyclohexadiene as a triplet quencher. The concentration of the quencher was 1 M. A 15–20% decrease in quantum yield and pss are observed. This is not due to absorbance interference by the quencher, and must be due to partial quenching of the thiocinnamamide excited state. Further quenching experiments are in progress, but our initial results suggest a short lived triplet state is responsible for the photoisomerization of the tertiary thiocinnamamides. Stern–Volmer analysis of the quantum yields in the presence and absence of quencher, assuming diffusion controlled quenching, results in a triplet lifetime of less than 100 ns. This preliminary lifetime estimate correlates well with results of similar compounds [12]. Irradiation of solutions under ambient light result in identical photostationary states to the 366 nm results. The triplet sensitized photoisomerization (Michler's ketone irradiated at 366 nm) of E-*N*,*N*-dimethylcinnamamide and E-*N*,*N*-dimethyl-*p*-methoxycinnamamide result in isomerization quantum yields of 0.51 [3,4]. A shorter triplet lifetime for the thiocinnamamides compared to the cinnamamides could account for the observed differences in quantum yields.

Irradiations were carried out in several solvents, hexane, chloroform, acetonitrile, and ethanol. The quantum yield and photostationary states did not depend on the solvent. The thiocinnamamides studied are moderately stable. Prolonged irradiation results in photoproducts detected by GC and TLC. The photoproduct yield increases in hydroxylic solvents, in the presence of trace amounts of water, and under 254 nm irradiation. Photolysis of the tertiary thiocinnamamides in air results in the production of the corresponding benzaldehyde, suggesting that photo-oxidation is an important reaction. In general, tertiary thioamides are found to be inert to photo-oxidation [11]. Therefore, a triplet excited state (biradical) with significant electron density over the alkene functionality is the likely reactive excited state for this reaction. Photoproducts were also reported by Ionescu et al. [5]. Our initial determination of photoproduct yield is <25% by GC (internal standard) after long irradiation time (>48 h).

4. Summary and conclusions

The tertiary thiocinnamamides exhibit absorption spectra shifted to the visible compared to the tertiary cinnamamides as predicted on the basis of ZINDO(1) calculations. The thiocinnamamides exhibit different singlet state and triplet state frontier orbital structure than the comparable cinnamamides as calculated by semi-empirical methods. Photoisomerization is observed when the compounds are irradiated in the UV and visible. Photoisomerization quantum yields do not depend on para substitution and the tertiary thiocinnamamides photoisomerize efficiently (0.10–0.30). This contrasts the corresponding cinnamamides which are believed to photoisomerize efficiently in the singlet state only if the transition is $\pi_{\text{styryl}} \rightarrow \pi^*$. The photoisomerization quantum yields from the E and Z-tertiary thiocinnamamides are similar, as is expected for a common triplet perpendicular intermediate. Triplet quenching studies are also consistent with a triplet state. The partial quenching of photoisomerization is explained by a triplet state with a short lifetime ($<100\,\mathrm{ns}$), for which there is precedence for similar compounds [12]. A triplet state, biradical in nature, also may better explain our photoproduct results, especially our photo-oxidation and solvent incorporation results [10,12]. A triplet state is also consistent with sulfurs ability to enhance spin orbit coupling. Our preliminary conclusion of the importance of the triplet state in tertiary thiocinnamamide photochemistry does not appear to agree with conclusions of prior work. The tertiary thiocinnamamides may photoreact with a different state than the primary thiocinnamamides or the triplet state may have a short lifetime, making the triplet more difficult to characterize. We are currently expanding our investigation to repeat the primary thiocinnamamide experiments and include the secondary thiocinnamamides. The photoproducts of the thiocinnamamides studied to date are currently being isolated and characterized. The nature of the photoproducts will provide valuable data toward the determination of the mechanism of thiocinnamamide photochemistry.

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