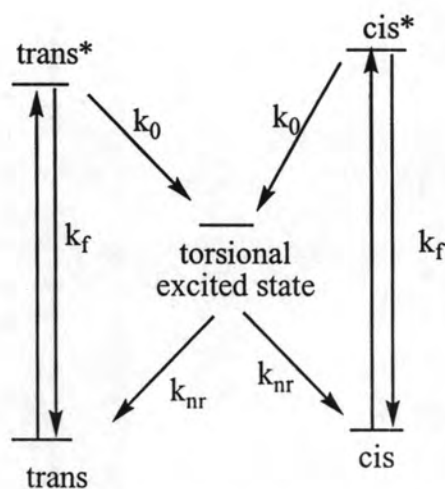


CHAPTER IV

CONCLUSIONS

During the course of this research, the syntheses of various methoxycinnamates were carried out with the aim to study the relation between the position of methoxy group and their photochemical and physical properties. All *trans*-cinnamates were synthesized by esterification between *trans*-cinnamic acid and 2-ethylhexanol. The cinnamic acid was synthesized by Knoevenagel condensation of benzaldehyde and malonic acid, and 2-ethylhexanol. As the result, cinnamate with methoxy substituted at 2,4,5 position on the aromatic ring displays the highest photostability against artificial UVA and UVB radiation whereas the 2,4,6-trimethoxy substituted cinnamate shows the less photostability. Therefore, these two trimethoxy substituted cinnamates were selected for a study of their photophysical properties mainly through fluorescence spectroscopy. The results are supported by also studying the ortho, meta and para substituted cinnamates.

The fluorescence quantum yield varies dramatically with the methoxy group position of the aromatic ring. It was found that the meta substituted cinnamate gave strong fluorescence whereas the para substituted one was quenched. This observation corresponded to the change in the UV spectrum, in which the lowest $\pi\pi^*$ states were more splitted in meta than in the para. Thus there were two absorption bands in the meta and a single band in the para. This meta effect was also observed in 2,4,5-trimethoxy substituted cinnamate in which two intense absorption bands and large fluorescence quantum yield were observed. In contrast, similar to the para-substituted one, 2,4,6-trimethoxy substituted cinnamate which showed a single absorption band and very weak fluorescence. In addition, semi empirical quantum mechanical calculations confirm the observed state ordering and furthermore supported the difference in the experimentally determined activation energies for non-radiative decay. High barrier for non-radiative decay was observed for the meta-substituted cinnamate. In contrast, a low barrier for non-radiative decay was observed for the para-substituted cinnamate, thus, para-methoxycinnamate relaxes mainly via non-radiative deactivation. The deactivation pathways have been schematically depicted in Scheme 4.1.



Scheme 4.1 Proposed excited state deactivation pathways of cinnamates.

In summary, these cinnamates are safe enough to use as UV absorption materials in sunscreen because their excited state lifetimes are not long enough to sensitize other molecules such as oxygen and form undesired chemical reactions. Moreover, this “meta-effect” is also found in other arylene system such as stilbene.^{47,48} It could be used to improve other fluorescence material applications. All parameters under the acute toxicity test not being affected by **9E** treatment may suggest that this compound is safe at the 5,000 mg/kg body weight dose used in the rat oral toxicity. Based on the clinical chemistry, hematology and pathology data, **9E** is not toxic to rats under the conditions of this investigation. Thus the compound is a promising UVA filter.⁴⁹