A computational study of the photodimerisation of 2-ethylhexyl-*p*-methoxycinnamate

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Abstract

Theoretical studies using computational methods have been carried out to determine the lowest energy geometrical structures of some of the photoproducts generated via the photodimerisation of 2-ethylhexyl-*p*-methoxycinnamate and hence their relative stabilities. *Ab initio* molecular orbital calculations have been used to investigate the structures and the transition states of the various dimers resulting from the cycloaddition reactions. Geometry optimizations and energy calculations were performed with the Gaussian 98 program, using the B3LYP density functional and 6-31+G(d) basis set. GaussView was used to visualize the transition state structures. The results show that the process of ultraviolet light-induced cyclodimerisation is through a stepwise mechanism via diradical intermediates. The photochemical reaction pathway involves the lowest excited singlet state of the different ethylene-ethylene molecular arrangements along the reaction coordinate. Due to spin inversion, a triplet radical is formed. The theoretical calculations predicted the most stable dimer forms result from isomers with a *trans-trans* configuration along the cyclobutane ring. These dimers are the most likely that were identified by HPLC analysis where only seven out of a possible thirteen dimers could be separated.

References;

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