UVA Chemical Filters:

A Systematic Study

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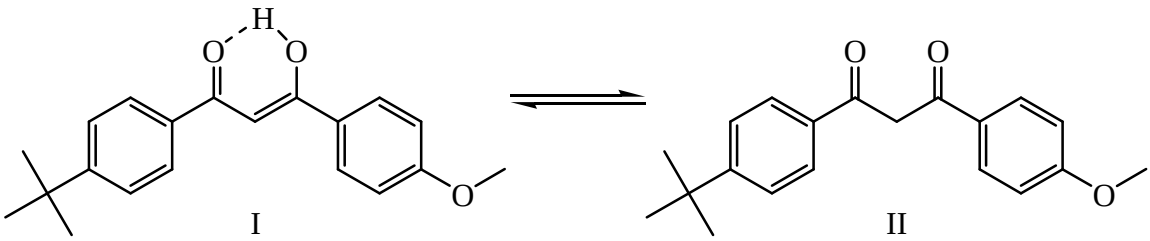
Contents

Abstract

Sunscreens are a popular and effective method of protecting against the damaging effects of solar radiation including skin cancer and immune system suppression. Chemical sunscreen filters achieve this by absorbing ultraviolet radiation and can be classified as UVB (280 – 320 nm) or UVA (320 – 400 nm) sunscreens depending on the wavelengths in which they absorb energy. An efficient sunscreen must afford protection against both UVB and UVA. The majority of chemical filters approved for use worldwide are UVB absorbers and the few UVA filters approved provide minimal UVA protection or show only moderate photostability. For example, the enol form of the β-diketone, BMDBM (I), absorbs strongly in the UVA region but is prone to photodegradation via the keto form (II).



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The purpose of the research presented has been to investigate methods aimed at improving sunscreen protection against wavelengths in the UVA region. The first approach involves adaptation of the commonly used sunscreen filter, BMDBM, to enhance its effectiveness as a UVA sunscreen filter. The emphasis has been on improving the photostability and absorption properties whilst maintaining the chemical identity of the sunscreen. This can be achieved by chelation of either Zn(II) or Al(III) by the enol form (I) of BMDBM. The results of a systematic study including potentiometric titration, spectroscopic analysis and laser flash photolysis studies are presented.

A second approach has been the encapsulation of the β-diketone, BMDBM, in cyclodextrins. Cyclodextrins are cyclic oligosaccharides having a hydrophobic central cavity. The interest in cyclodextrins comes from their ability to encapsulate other molecules (guest) within their annuli to form host-guest complexes held by non-covalent forces. The formation of such inclusion complexes often results in the modification of the guest characteristics. The inclusion complexes formed between BMDBM and either β-

cyclodextrin (βCD) or hydroxypropyl-β-cyclodextrin (HPβCD) has been characterized by ^{1}H and ^{1}H ROESY NMR spectroscopic methods.

The further method aimed at improving UVA protection has involved exploring the use of theoretical methods as a tool in the design of potentially new sunscreens. In particular, the ability of the SAC-CI method to represent the trends and properties important to the photochemistry of a series of known β-diketones has been investigated. This information can then be used to complement experimental methods in the design of candidate sunscreen filters having the desired properties.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying.

Jacqueline F. Cawthray

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Abbreviations

I	ionic strength
[ ]	concentration (mol dm^{-3})
Å	Ångström (10^{-10} m)
ACAC	2,4-pentanedione
BA	1-phenyl-1,3-butanedione
BMDBM	4-tert-butyl-4′-methoxydibenzoylmethane, tradenames: avobenzone, Parsol® 1789
$BMDBM^{-}$	β-diketonate anion of BMDBM
CD	cyclodextrin
CE	chelated enol
DBM	1,3-diphenyl-1,3-propanedione
DMSO	dimethyl sulphoxide
f	oscillator strength
HEPES	*N*-2-hydroxyethylpiperazine-*N′*-2-ethanesulphonic acid
HF	Hartree-Fock
HPβCD	2-hydroxypropyl-β-cyclodextrin
IMHB	intramolecular hydrogen bond
IMPT	intramolecular proton transfer
IndolePh	1-(1H-indol-6-yl)-3-phenyl-1,3-propanedione
K	keto
LFP	laser flash photolysis
M^{2+}	divalent metal ion
MO	molecular orbital
NapPh	1-(2-naphthyl)-3-phenyl-1,3-propanedione
NCE	non-chelated enol
OMC	2-ethylhexyl-4-methoxycinnamate, octyl methoxycinnamate, octinoxate
PES	potential energy surface
RAHB	resonance-assisted hydrogen bonding
RHF	restricted Hartree-Fock
SAC	symmetry-adapted cluster
SAC-CI	symmetry-adapted cluster-configuration interaction
TEAOH	tetraethyl ammonium hydroxide

TGA	Therapeutic Goods Administration
UVAI	ultraviolet AI radiation (340 - 400 nm)
UVAII	ultraviolet AII radiation (320 - 340 nm)
UVB	ultraviolet B radiation (280 - 320 nm)
UVC	ultraviolet C radiation (100 - 280 nm)
UVR	ultraviolet radiation
ZPE	zero point energy
βCD	β-cyclodextrin
8-oxo-dG	8-oxo-7,8-dihydro-2´-deoxyguanosine
λ_{max}	wavelength of maximum absorption