

THEORETICAL ANALYSIS ON THE PHOTOCHEMISTRY OF COUMARIN DERIVATIVES

JA HONG KIM^{*1}, SUNG HO SOHN, and JUNG-SUNG KIM²

¹School of Chemical Science & Technology, Chonbuk National University, Chonju 561 - 756, Korea

²Department of Chemistry Education, Taegu University, Kyungsan 712-714, Korea

(Received 11 November 1995; accepted 19 December 1995)

Abstract — The photodimers with cyclobutane rings and C_2 symmetry, derived from coumarin (*syn*, head to tail and *anti*, head to head) have been calculated by PM3-UHF-CI and Molecular Mechanics force field. The photocycloaddition to coumarin and 5,7-dimethoxycoumarin(DMC) dimers were deduced to be formed by their preferable frontier orbital interactions and *via* more stable cycloaddition by the C_3 , C_4 bond. These results are consistent with the coumarin dimer model that the theoretical C_4 -photocycloaddition of coumarin is predicted much more than the experimental C_3 -photocycloaddition.

INTRODUCTION

The cycloaddition reactivity of the photoexcited state of coumarin is very interesting from the physical and chemical points of photoexcited states. Concerning which coumarin excited state is photoreactive, on the basis of molecular orbital calculations, it has been predicted that the triplet excited state is more reactive than the singlet excited state¹. This prediction is consistent with the finding that oxygen and paramagnetic ions have a quenching effect at the rate of photoreaction between psoralen and thymine. Triplet excited states are also normally longer lived than singlet excited states and so are more available for reaction, *e.g.* with oxygen².

The photodimerization of coumarin and 5,7-dimethoxycoumarin(DMC) have been the subject of interest for a long time. The triplet dimerization with benzophenone sensitization gives mainly the *anti* head-to-head dimer, and Lewis *et al*³, have shown that singlet dimerization in the presence of boron trifluoride etherate gives a high yield of the pure *syn*, head-to-tail dimer. In order to find out more about the excited state of coumarins and their possible dimer in

the photocycloaddition reactions, we have described the excited state of coumarin, 5,7-dimethoxycoumarin (DMC) the intrinsic photoreactivity of coumarin derivatives using PM3-UHF-CI and Molecular Mechanics(MM) calculations.

CALCULATIONS

The electronic transition energies were calculated by the PM3-UHF-CI calculation⁴. In the hypothetical molecular complexes, the chemical reactivity index can be used as a measure of the relative reactivity index of the various position of the photocycloaddition.

Molecular Mechanics calculations were performed by using MM2 force field and BDNR method as a minimum algorithm⁵⁻⁶. The numbering scheme for heavy atoms for coumarin and 5,7-DMC are shown in Figure 1.

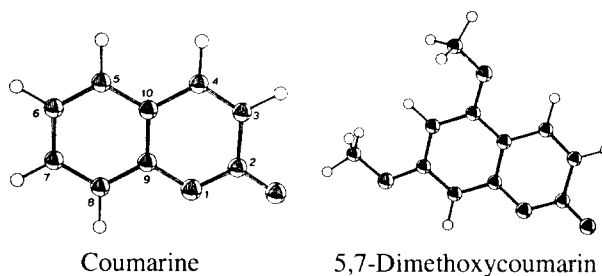


Figure 1. The molecular structure and numbering scheme for coumarin derivatives.

* To whom all correspondence should be addressed.

RESULTS AND DISCUSSION

The results of PM3-UHF-CI calculations for coumarin are summarized in Table 1. Table 1 shows optimized geometries for the ground and excited states of coumarin. It shows the carbon-carbon double bond lengthening appears to be responsible for the presence of the carbon-carbon double bond stretching mode in the phosphorescence of coumarin derivatives. And also, bond distance for the 3,4 carbon-carbon double bond and C-C singlet bonds between coumarin and 5,7-dimethoxycoumarin, as calculated from mobil bond orders(PM3-CI-UHF), increase and decrease upon excitation respectively. The singlet dihedral angle C2-C3-C4-C10 was obtained as 0.22° but the triplet dihedral angle was calculated to be 0.11° .

Table 1. Optimized geometries for the singlet and triplet state of coumarin by PM3-UHF calculation(length: Å, angle:degree)

Geometry	Singlet	Triplet
C3-C4	1.36	1.47
C5-C6	1.40	1.40
C6-C7	1.40	1.40
C2-C3-C4	119.42	118.11
C3-C4-C10	119.20	116.63
C2-C3-C4-C10	-0.22	-0.11

The UV spectrum of the *anti*, head to head coumarin dimer has a strong maximum at 215 nm and a weaker structure band with maxima at 280 and 271 nm. A good agreement between the predicted and observed transition energies can be seen. Table 2 shows the calculated transition $^1(\pi-\pi^*)$ transition energies. If coumarin was consistent with the observed transition at 310 nm, while predicted 5,7-dimethoxycoumarin was transition at 264 nm. The lowest $\pi-\pi^*$ transition is polarized nearly along the long molecular axis in previous report.⁷ These results are consistent with the coumarin dimer model that the theoretical photocycloaddition of coumarin is

Table 2. The transition state arising from low energy configuration by PM3-UHF-CI calculations.

Molecule	Transition	Energy(nm)	
		Calcd	Obsd ^a
Coumarin	$^1(\pi, \pi^*)$	304	310
	$^3(\pi, \pi^*)$	460	457
5,7-DMC	$^1(\pi, \pi^*)$	264	-
	$^3(\pi, \pi^*)$	441	-

^aObserved value from reference 9.

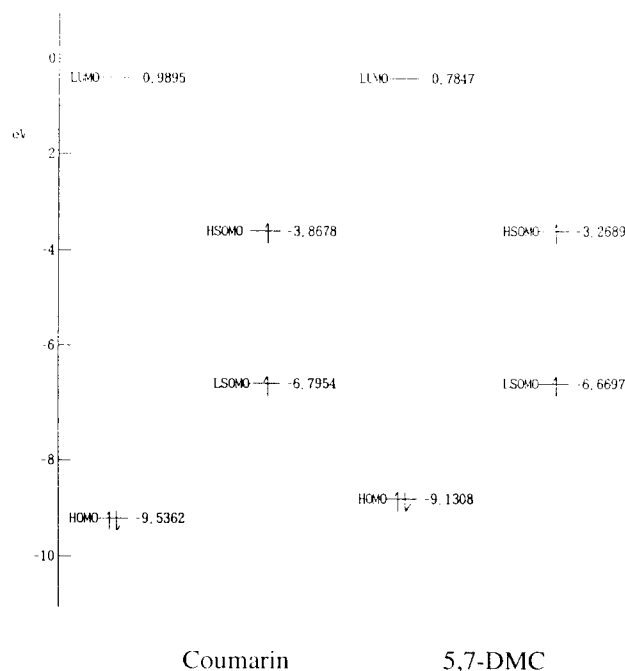


Figure 2. Estimated energies of coumarin and 5,7-dimethoxycoumarin by PM3-UHF-CI calculation.

predicted much more than is the experimental photocyclodimer.⁸

Figure 2 shows the calculated energies and patterns of coumarin and 5,7-dimethoxycoumarin. The energy differences between HSOMO(Highest Singly Occupied Molecular Orbital) and LUMO(Lowest Unoccupied Molecular Orbital) are 2.88 eV for coumarin and 2.484 eV for 5,7-DMC. The energy gap of 5,7-DMC is more narrow and it can be excited more easily.

Table 3. The Results of Molecular Mechanics Calculation for Possible photocycloadducts of coumarin and 5,7-DMC dimers (in kcal/mol)

Conformation	E _{total}	E _{torsion}	E _{strain}	ΔH_f
Coumarin Dimer				
<i>Cis-Anti</i>	57.78	25.63	50.56	-104.11
<i>Cis-Syn</i>	59.94	27.72	52.72	-101.93
<i>Trans-Anti</i>	56.89	25.94	49.67	-104.97
<i>Trans-Syn</i>	57.88	27.41	50.66	-104.06
5,7-DMC Dimer				
<i>Cis-Anti</i>	87.95	42.01	71.89	-245.23
<i>Cis-Syn</i>	87.51	43.01	71.45	-245.02
<i>Trans-Anti</i>	85.33	38.61	69.27	-247.48
<i>Trans-Syn</i>	87.61	41.18	71.55	-245.69

The carbon-carbon double bond of coumarin lengthening (C3-C4 singlet state; 1.140 Å, and C3-C4 triplet state; 1.440 Å) appears to be responsible for the presence of the carbon-carbon stretching mode in the phosphorescence of coumarins and 5,7-DMC.⁹

The results of molecular mechanics calculation for possible photocycloadducts of coumarin and 5,7-DMC dimers are shown in Figure 3. In all cases, rotations about the coumarin dimer were investigated in order to locate the lowest energy conformation.

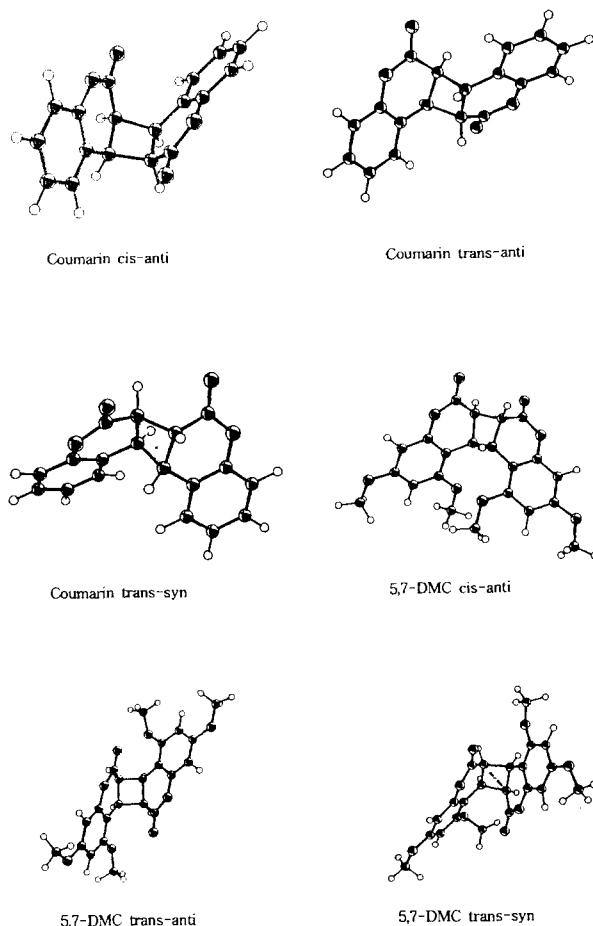


Figure 3. Stereo ORTEP drawing of molecular configuration of the possible coumarin and DMC dimers.

The calculated heats of formation and the energies given in Table 3 refer to the stable conformer for possible photocycloadducts. The heats of formation are calculated in the range -101.93 ~ -104.97 kcal/mol.

For the *anti* configuration, the *anti*-head-to-tail was found to have the lowest energy and the *anti*-head to-head form has 3.04 kcal/mol higher energy.

Finally, Figure 4 illustrates two possible Jablonski diagrams which accommodate the luminescence and

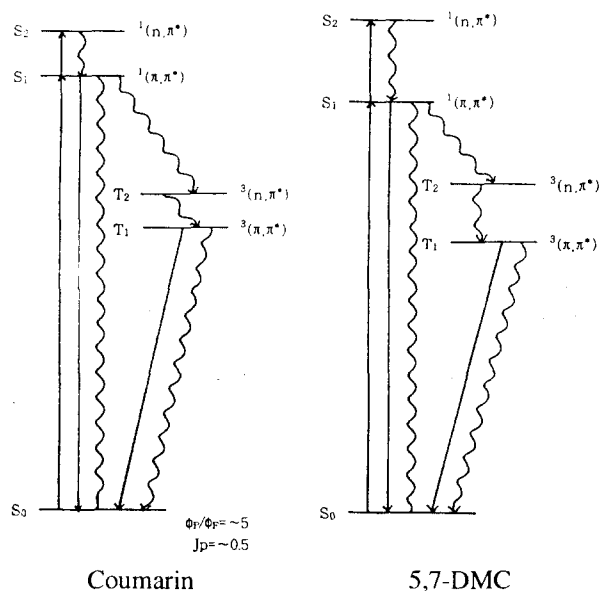


Figure 4. Approximate Jablonski diagrams of coumarin and 5,7-DMC.

calculated energy. These diagrams are presented only as a qualitative guide for interpretation of the spectroscopic behavior of coumarins and 5,7-DMC and more definite diagrams will not be possible until the locations of singlet state $^1(n, \pi)$ states are determined by FT Raman spectroscopic method.

The C₄-photocycloadducts of DMC-thymidine in methanol undergoes reversible photosplitting, yielding DMC and thymidine on irradiation with 254 nm UV light for one minutes, as is the case with the photosplitting of Py < > DMC, DMC < > DMC, and DMC < > Thy.¹⁰

If the charge transfer interaction in hypothetical photoadducts between the coumarins and the purine bases is the first step of the photocycloaddition reaction, the most probable orientation between the coumarin and purine bases can be derived from the quantum mechanics calculations.

Acknowledgment — The financial support for this work from the BSRI (Grant No. BSRI 95-3431) is gratefully acknowledged.

REFERENCES

1. Mantulin W. W. and Song P. S. (1973) Excited State of Skin-Sensitizing Coumarin and Psoralens. Spectroscopic Studies. *J. Am. Chem. Soc.*, **95**, 5122-5129.
2. Bordin, F. F., Carlassare, M. T. Conconi, A. Capozzi, F. Majone, A. Guiotto and F. Baccichetti (1991) Biological Properties of Some Benzopsoralen

- Derivatives. *Photochem. Photobiol.* **55**, 221-228.
- Lewis, F. D., Howard D. K. and Oxman J. D. (1983) Lewis Acid Catalysis of Coumarin Photodimerization. *J. Am. Chem. Soc.*, **105**, 3344-3345.
 - Stewart, J. P. MOPAC MANUAL 67th edition, Frank J. Seiler Research Laboratory, United State Air Force Academy, 1-1(1990).
 - Allinger, N. L. and Bukent U. (1982) *Molecular Mechanics*, ACS Monograph, Am. Chem. Soc., Washington D.C., 177.
 - Clark, T. A. (1985) *A Handbook of Computational Chemistry*, John Wiley and Sons, New York.
 - Kim, J. H. and Sohn S. H. (1992) Theoretical Studies on the Photochemical Reaction of Psoralen with Purine and Pyrimidine Bases. *Bull. Kor. Chem. Soc.*, **13**, 172-176.
 - Shim, S. C., Choi K. Y. and Song P. -S. (1978) Studies on the Phototoxicity of Coumarin Derivatives I; Photocyclodimerization of 5,7-DMC. *Photochem. Photobiol.*, **27**, 25-31.
 - Song, P. S. and Gordon W. H. (1970) A Spectroscopic Study of the Excited States of Coumarin, *J. Phys. Chem.*, **74**, 4234-4240.
 - Shim, S.C. (1982) Topics in Photobiology, Photochemistry of Psoralens, Proceedings of International Workshop on Photobiology, 77-81, Jeju Nat'l Univ.