critical exponent $\gamma=1$. The specific heat $C=T^2\frac{\partial^2 f}{\partial T^2}$ can be obtained from (12) using (10), (11), and (13) in terms of the spontaneous magnetization m_0 as

$$C=\frac{m_0^2}{m_0^2+\frac{T}{T_c}-1} \tag{18}$$

This is nonzero only $T<T_c$. But from (15), the limiting value of C at $T=T_c$ is seen to be $C=D/2+1$. Therefore, the specific heat does not diverge at the critical point but has a jump discontinuity, from which we deduce the exponent $\alpha=0$.

Discussion

The generalization of the Curie-Weiss model to the D-dimensional spin system shows the critical behavior that is predicted by the phenomenological mean-field theory. This is supported by the above direct calculation of the critical exponents; $\alpha=0$, $\beta=1/2$, $\gamma=1$, and $\delta=3$. Therefore the spin dimensionality has no essential effect on the critical behavior of the model, the only difference being the critical temperature. It is worth noting that the critical temperature can be scaled to unity by assuming the length of each spin vector as $|x_i|=D^{1/2}$.

The fact that the critical temperature is inversely proportional to the spin dimension D is the manifestation of the decrease of the ordered phase stability with the incresing degree of freedom of the spin vector. As $D\to\infty$, the critical temperature approaches zero and no ordered phase exists in this limit. This infinite-dimensional spin system is closely related to the spherical model[3], in which it is shown that there is no spontaneous magnetization in the one-dimensional lattice system.

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Theoretical Studies on the Photochemical Reaction of Psoralen. Photocycloaddition of Angelicin with Thymine

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A semiempirical methods (PM3-CI-UHF. etc.) for the evaluation of ground and excited state electronic structures of psoralens are applied to angelicin with thymine. The photocycloaddition reaction of angelicin with thymine were deduced to be formed by their preferable HSOMO-LUMO interactions. The photoadduct was inferred to be a C_4-cycloaddition product with the stereochemistry of *cis-anti* formed through [2+2] addition reaction between the 3,4 double bonds of angelicin and the 5,6-double bond of thymine.

Introduction

The relative reactivity of the photoexcited states of angelicin for C_4-cycloaddition reaction is very interesting from the physical and chemical point of view on the photoexcited states. Natural products with a linear structure such as a psoralens, or with a non-linear structure, like angelicin are well known photosensitizing agent and have been used in the photochemotherapy of psoriasis and vitiligo[1,2]. Psoralens and their congeners are known to photoreact with purine and pyrimidine bases, free in DNA, upon irradiation with long wave length UV light (320-380 nm). Various physiological actions such as skin erythma on human and guinia pig skin, mutagenic and lethal effect in bacteria, in activation of DNA viruses, and inhibition of tumor transmitting capacity of various tumor cells have been attributed to this photoreaction[3].

The family of furocoumarin derivatives known as psoralen, angelicin has been actively investigated with regard to their ability of act as dermal photosensitizing agents and as probes of nucleic acid structure and fuction[4,5]. The biological activity of psoralen is primarily the result of covalent bonding with nucleic acid, especially DNA. Monoaddition at 3,4 positions results in a low-lying triplet state for the photoadduct. The low-lying triplet state is probably unreactive with respect to the second photocycloaddition because of its rapid relaxation to the ground state. On the other hand, monoaddition at 4',5'-positions yields a relatively long-lived singlet state[6]

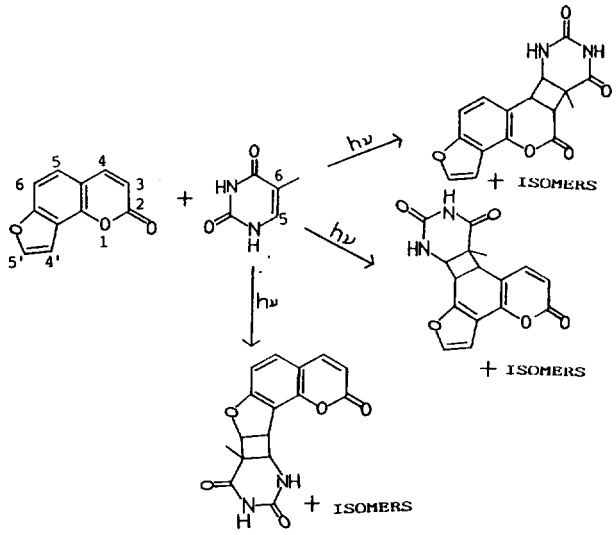

Figure 1. Photoaddition reaction of angelicin to thymine.

Table 1. Optimized Geometries for the Singlet and Triplet State of Angelicin by the PM3-UHF Calculation

Geometry	Singlet		Triplet
		Bond Length	
C3-C4	1.36		1.45
C5-C6	1.40		1.40
C4'-C5'	1.35		1.36
		Bond Angle	
C2-C3-C4	119.64		117.83
C3-C4-C10	119.19		117.78
C5-C6-C7	118.31		117.04
C10-C5-C6	121.26		121.46
C1'-C5'-C4'	116.10		111.69
C3'-C4'-C5'	104.80		106.14
		Dihedral Angle	
C2-C3-C4-C10	0.11		0.87
C10-C5-C6-C7	0.39		−0.42
C1'-C5'-C4'-C3'	0.00		−0.20

*Bond Lengths are in Å and Bond Angles in Degrees.

(Figure 1).

In this paper, we have carried out semiempirical calculations (PM3-CI-UHF methods. etc.) to give insight into molecular structure and conformational analysis of the photocycloadduct of angelicin with thymine.

Methods of Calculations

The calculations were performed using the MNDO, AM1, MINDO/3 and PM3 methods of QCPE program No. 455 (MOPAC Version 5.00)[7-10]. The optimized structures of each triplet excited states of angelicin were calculated by using an unrestricted Hartree-Fock wave function (UHF) and the energies and coefficients were estimated by the CI method. The optimized structures of the ground states of thymine was calculated by a restricted on (RHF).

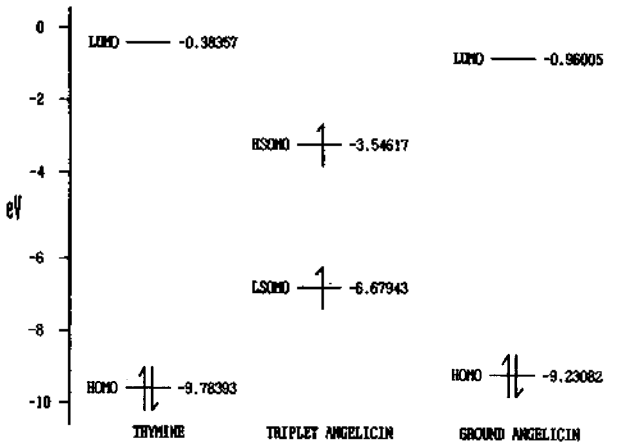

Figure 2. The energy level diagram for ground thymine and psoralen, and excited psoralen. HSOMO (Higher Singly Occupied MO), LSOMO (Lower Singly Occupied MO).

Results and Discussion

The geometries of angelicin was optimized starting from the probable bond angles, bond length and dihedral angles by the PM3-UHF calculation.

Table 1 shows optimized geometries for the singlet, triplet excited states of angelicin and the triplet excited state is predicted to be more reactive than the singlet state. The geometries of the triplet angelicin in Table 1 are thought to be reasonable, respectively. Namely, spin density accumulates at position 3 and 4 and the 3-4, 4',5' bond order changes, thus lengthening the C=C bond in triplet state. The singlet dihedral angle C2-C3-C4-C10 was obtained as 0.11° but the triplet dihedral angle was calculated to be 0.87°. Dihedral angles at the 4-positions are twisted with the pyrone rings.

Figure 2 shows energies and coefficients of higher singly occupied molecular orbitals (HSOMO) and lower ones (LSOMO) of the triplet states by means of the UHF-CI method, and those of LUMO and HOMO of the ground states of thymine by means of the RHF-CI method. As the photoadditions were sensitized by some triplet sensitizers, they were inferred to go through two-step radical paths, and that the first steps were mainly influenced by coefficients and energies of the two frontier orbitals, respectively. These additions are generally considered to proceed *via* a concerted pathway. However, the triplet state is normally involved, although the singlet state is thought to play a role for some furocoumarins[11,12]. A stepwise mechanism *via* a charge transfer has been proposed on the basis of flash photolysis experiments carried out by Bensasson *et al.*[13]. The reasonable processes *via* radical intermediates in Figure 2 are inferred from the narrow gaps (ΔE=3.1045) of the enrgies and the large coefficients between angelicin and thymine.

The first step is a cycloaddition between the 3,4 or 4',5' double bonds of angelicin and the 5,6 double bond in the thymine. Absorption of a second photon leads to a further cycloaddition between the 3,4 double bond of the 4',5' monoadduct of psoralen, and the double bond of the pyrimidine in the complementary strand of the macromolecule. 3,4-cycloadducts of psoralen are not converted into cross-linka-

Table 2. Estimated Energies and Coefficients of the Triplet of Angelicin

	PM3	AM1	MINDO/3	MNDO
HSOMO C3	0.0140	0.4937	0.0347	0.5055
C4	0.0831	0.4262	0.0170	0.3917
C5	−0.4008	−0.2963	−0.2790	−0.2827
C6	0.4377	0.0519	0.1849	0.0964
C4′	−0.2528	−0.1256	−0.0675	−0.1242
C5′	0.3987	0.0104	−0.1626	0.0189
LSOMO C3	0.5155	0.5125	0.0198	0.5328
C4	0.4961	0.1819	0.0300	0.2002
C5	−0.3047	−0.0830	−0.2402	−0.0994
C6	0.0151	0.3113	0.1834	0.2919
C4′	−0.1015	−0.1796	−0.7521	−0.1691
C5′	0.0005	0.0680	−0.0264	0.0590
State Energy/eV	3.2809	3.2580	4.0176	3.2927

Table 3. The Interaction Energy and Heats of Formation for Angelicin < >Thymine (in kcal/mol)

Formation	E_{total}	$E_{torsion}$	E_{strain}	ΔH_f
Angelicine(3,4)				
cis-syn	30.839	23.104	24.509	−193.323
cis-anti	28.104	22.985	21.774	−196.036
trans-syn	29.809	23.441	23.479	−194.460
trans-anti	28.421	22.950	22.091	−195.055
Angelicine(4′,5′)				
cis-syn	30.964	27.601	22.374	−192.234
cis-anti	29.095	27.710	20.504	−193.979
trans-syn	31.678	28.212	23.088	−191.538
trans-anti	31.031	27.656	22.441	−192.108
Angelicine(5,6)				
cis-syn	26.408	23.456	20.078	−168.517
cis-anti	26.271	23.719	19.941	−168.546
trans-syn	26.408	23.456	20.078	−168.517
trans-anti	26.698	23.320	20.368	−168.157

ges by further irradiation at 365 nm as they do not absorb at this wavelength[14].

We have carried out the semiempirical calculation to give insight into the excited triplet state of angelicin by means of PM3, AM1, MINDO/3, and MNDO methods, also. The results of the frontier orbitals, the orbital functions and energies, are shown in Table 2.

As the latest and most refined of these procedures, AM1 was employed as the preferred computational tool with PM3, MNDO and MINDO/3 included primarily for purposes of comparison. The three methods gave almost the similar results in the points of the coefficient sizes and orders, and the energy values and the gaps except for a few data of MNDO/3.

Compared with UHF energy differences between the S_0 and S_1 states, energy separations between the singlet and the triplet states are smaller by about 3 Kcal/mole, mainly because energies for triplet states are lowered in CI calculations.

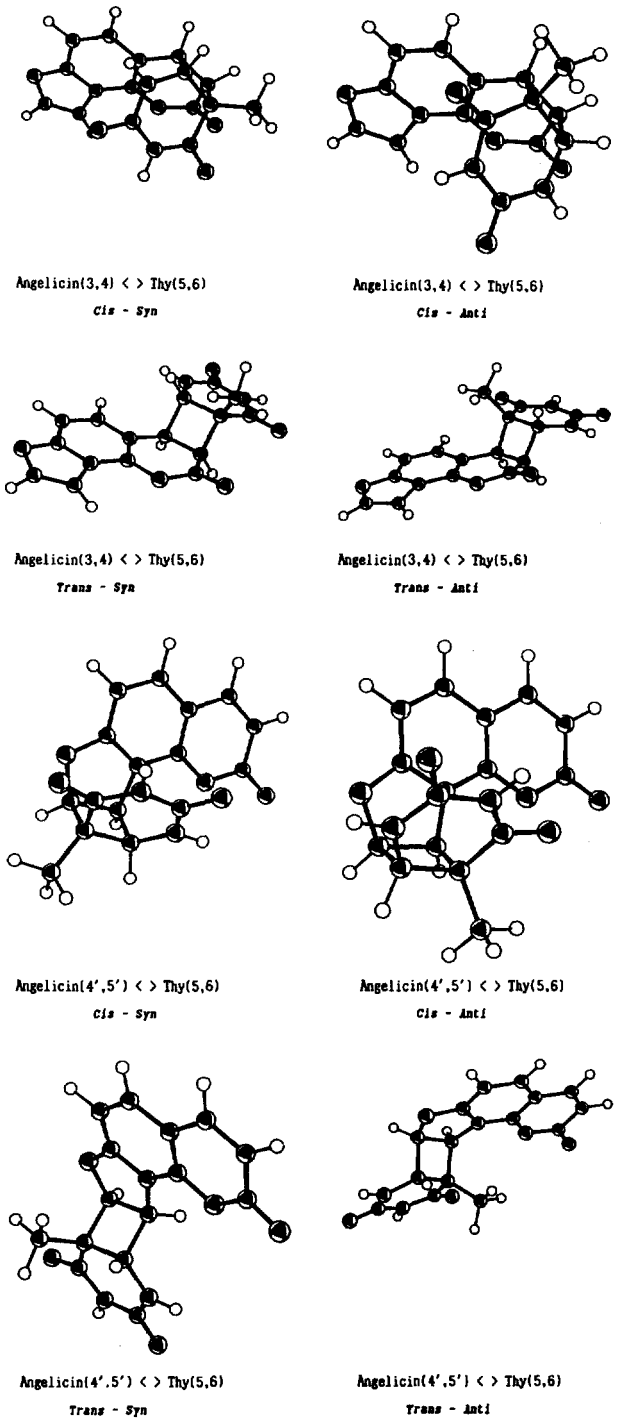

Figure 3. Stereo ORTEP drawing for possible photocycloadducts.

In view of our calculations, a [2+2] photocycloaddition can occur between either the 4′,5′(furan) or 3,4(pyrone) double bonds of a angelicin and the 5,6 double bond of a thymine. Also, this reaction can occur in either a syn or anti orientation. The cyclobutane ring of each of these photoadducts has four chiral centers so that for each of the four regioselectivity there are formally 12 possible photoadducts. No trans fused rings involving the furan, pyrone of the angelicin appear possible in the present photoadducts because

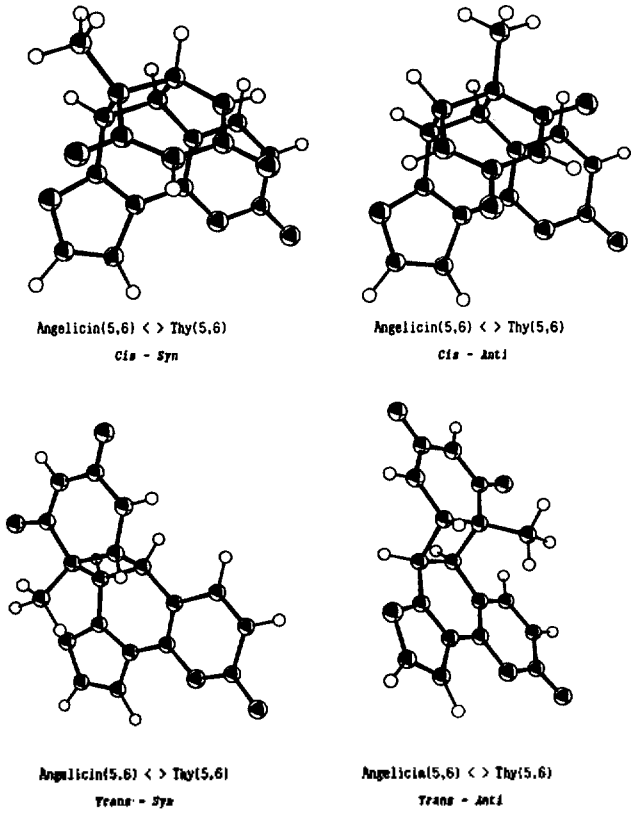

Figure 3. Continue.

of the steric constraints present in a bicyclophotadduct.

The results of semiempirical calculation for possible photocycloadducts of angelicin with thymine are shown in Table 3 and Figure 3. In all cases, rotations about the photocycloadducts were investigated in order to locate the lowest energy conformation.

Three Types of photoisomer have been proposed; (1) Angelicin(3,4)< >Thymine(5,6), (2) Angelicin(4',5')< >Thymine(5,6), (3) Angelicin(5,6)< >Thymine(5,6). The calculated heats of formation and the interaction energies in Table 3 refer to the stable conformer for possible photocycloadducts. The photochemical interaction energies are calculated from the angelicin of triplet state and thymine of ground state. The photoadduct was inferred to be a C_4-cycloaddition product with the stereochemistry of *cis-anti* formed through [2+2] addition reaction between the 3,4 double bonds of angelicin and the 5,6-double bond of thymine. The heats of formation for angelicin(3,4)< >thymine(4,5) are shown in the range −193 kcal/mol~196 kcal/mol.

The high reactivities support the suggestion that the photosensitizing properties of furocoumarines are mediated by the corresponding furocoumarin triplet states. The similary high $S \rightarrow T$ quantum yields, and triplet reactivities with pyrimidines of psoralen support the suggestion that the observed differences in photosensitizing properties of psoralens may be due to their differing geometries, which allow psoralen itself to intercalculate DNA[13].

In the similar experiments where photocycloaddition reaction of 4',5'-dihydropsoralen with thymine was carried out in solution and in the frozen state. The photoadduct was proven to be a 1 : 1 C_4-cycloaddition product, an analogue of furocoumarin-DNA bisadduct, with the stereochemistry of anti-head-to head foremed through [2+2] addition reaction between the pyrone double bond of 4',5'-dihydropsoralen and the 5,6-double bond of thymine[15].

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