Available online at www.sciencedirect.com

Journal of Photochemistry and Photobiology A: Chemistry 170 (2005) 37–43

www.elsevier.com/locate/jphotochem

Quantum study on photophysical and photochemical process of a new photosensitizer: hypomycin B

De-Zhan Chen*, Dao-Ping Wang, De-Xin Kong, Xiao Zhang

College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, PR China

Received 11 March 2004; received in revised form 16 June 2004; accepted 14 July 2004
Available online 3 September 2004

Abstract

Ab initio and CIS theories were employed to study a new type of perylenequinonoid photosensitizer (PQP)—hypomycin B (HMB), which has only one pair of adjacent hydroxyl group and carbonyl group in its peri-region. Geometries, Mulliken charge population, energy, and photophysical and photochemical process in excited state were discussed in detail. The results indicate that HMB exhibits quite similar intramolecular proton transfer (IPT) to perylenequinone, which offers an indirect understanding that the IPT process in perylenequinonoid derivatives (PQD) is a single proton transfer process. There exists the crossing of the potential energy surface of the singlet and triplet so that the intersystem crossing (ISC) can occur. The ISC will increase triplet quantum efficiency, which is the basis for photosensitization of PQP.

Keywords: Excited state; HMB; Intramolecular proton transfer; Photophysical and photochemical process

---

1. Introduction

Perylenequinonoid photosensitizers (PQP) or perylenequinonoid derivatives (PQD) are of interest because of their light-induced antiviral and anti-tumor activity (Fig. 1) [1–6]. PQP are a novel type of photosensitizers, and have the following advantages as compared with hematoporphyrin derivatives: easy preparation and purification, high quantum yields of triplet and singlet oxygen, high phototoxicity but low dark toxicity, and rapid clearance from normal tissues [7–9]. All of these indicate that PQP are promising phototherapeutic agents. In addition, more efforts have found that PQP have potential application in the anti-oxidation and molecular probe, etc. [9].

PQP have very strong intramolecular hydrogen bonds in their molecules. This unique molecular structure enables PQP to isomerize both in ground and in excited states by means of intramolecular proton transfer (IPT)[2,10–12], which has also been called intramolecular hydrogen transfer (IHT). Previous experimental researches demonstrated that this non-radiative process played a significant role in the photosensitization of PQP [8,13]. We have found recently from the theoretical calculation that there exists the crossing of the potential energy surface in the singlet and triplet states for PQ. This is the foundation of the intersystem crossing from singlet to triplet state so that high triplet quantum yields can be achieved.

Previous reports revealed that PQ is the active center of PQD and the skeleton structure is important to reserve their photosensitive activity [3,14]. As for the PQ is concerned, relatively simple a molecule, there exists two possible IPT process in the molecule. But it is still a mystery to date whether it is a single proton transfer or two protons transfer concerted. A new compound, hypomycin B (HMB) was extracted recently from natural substances [15], which has similar structural framework with PQ but only one hydroxyl group peri to a carbonyl group. In other words, there exists only one possible intramolecular hydrogen transfer in HMB [15–19]. The IPT process of the skeleton structure of HMB is illustrated in Fig. 2. This unique structure

---

* Corresponding author. Tel.: +86 531 6182539/0304;
fax: +86 531 6180304.
E-mail address: dchen@sdnu.edu.cn (D.-Z. Chen).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.07.015

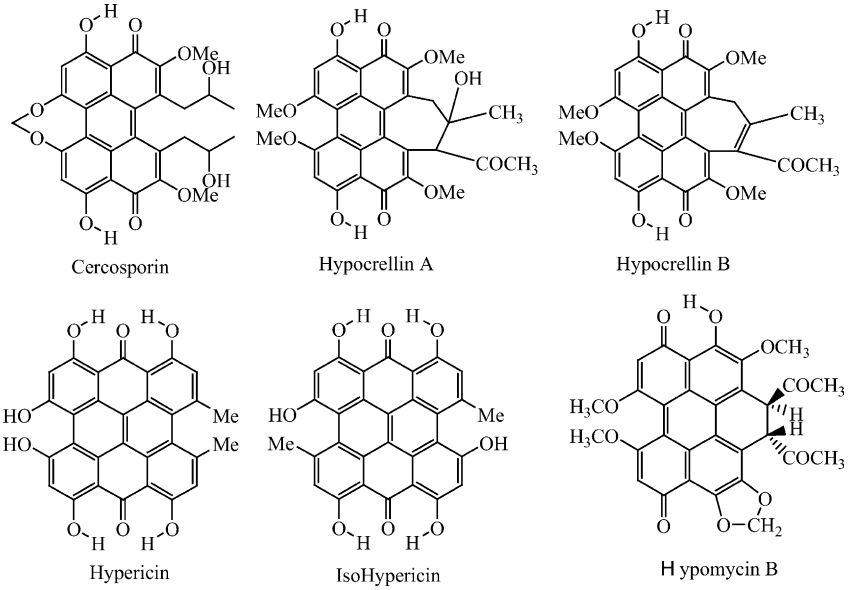

Fig. 1. Structures of several PQP.

of HMB enables us to understand IPT process of PQP easily.

In present paper, theoretical calculation on IPT process of HMB for the ground and excited states (including singlet and triplet excited state) were performed. Also, comparison of the results of HMB with those of PQ, including energy, barrier, variance of charge on the transferred hydrogen atom, and dipole moments were made. Based on all these results, possible excited-state photophysical and photochemical process of PQP was discussed. The elucidation of this primary photo-induced process will help us understand the mechanism for photosensitization of PQP. Additionally, the similar hydrogen transfer has been studied by experimental and theoretical methods [20–25], and this research also helps to understand the nature of the intramolecular proton transfer process.

2. Method of calculation

Theoretical researches have found that side chains are of minor effect on the height of the IPT barrier for these compounds [19]. So its skeleton structure may provide us a quantitative description of IPT barrier of the molecule. The geometries have been fully optimized at the restricted Hartree–Fock (RHF) level of theory with 6-31G basis set in the ground state. Previous studies demonstrated that 6-31G basis set could get the same results as 6-31G(d, p) one in principle [5]. So 6-31G basis set was used for these relatively large molecules. Configuration interaction single-excitation (CIS) method was applied to optimize molecular structure of excited states and calculate excitation energy in recent years [26–29]. The geometries in excited states were fully optimized with CIS method at the same basis set level as that in the ground state. All located transition states (TS) exhibit one expected normal imaginary frequency with a transition vector that corresponds to the motion of atom in the IPT transfer process.

The Gaussian 98 suite of programs [30] was used throughout the calculation.

3. Results and discussion

3.1. Geometries

The optimized geometries indicate that the skeleton structure of HMB is planar, as is depicted in Fig. 2, and the molecule retains plane during the process of IPT. The six-member ring containing hydrogen bond is the active center part, which is depicted in Fig. 3, because its structure alters significantly during the IPT process. The lengths of intramolecular hydrogen bond are all less than 2.0 Å, so strong hydrogen bonds exist in two isomers in the ground and excited states. For the parallel structure (*para* in brief), the length of intramolecular hydrogen bond is 1.806 Å in S_0 state, while it is 1.700 and 1.916 Å in S_1 and T_1 states, respectively. The length of carbon–oxygen of carbonyl increases regularly from S_0, S_1 to T_1. This suggests that the carbon oxygen double bond becomes weaker with the electron excited. The structures of TS change significantly. The O–O distance shrinks from 2.592 Å in the *para* structure to 2.335 Å in TS for ground state. It can be seen from Fig. 3 that the lengths of all C–O bonds tend to be averaged in TS. The position of the transferred hydrogen does not locate in the center of two oxygens. It suggests that it should be a late transition state for the reaction in S_0 and T_1, and an early transition state in S_1.

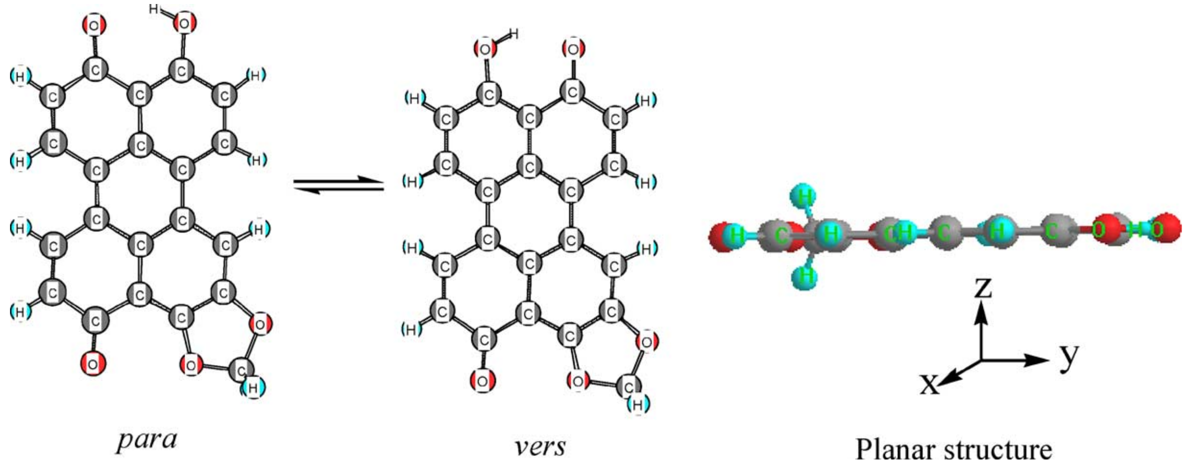

Fig. 2. Intramolecular proton transfer of HMB.

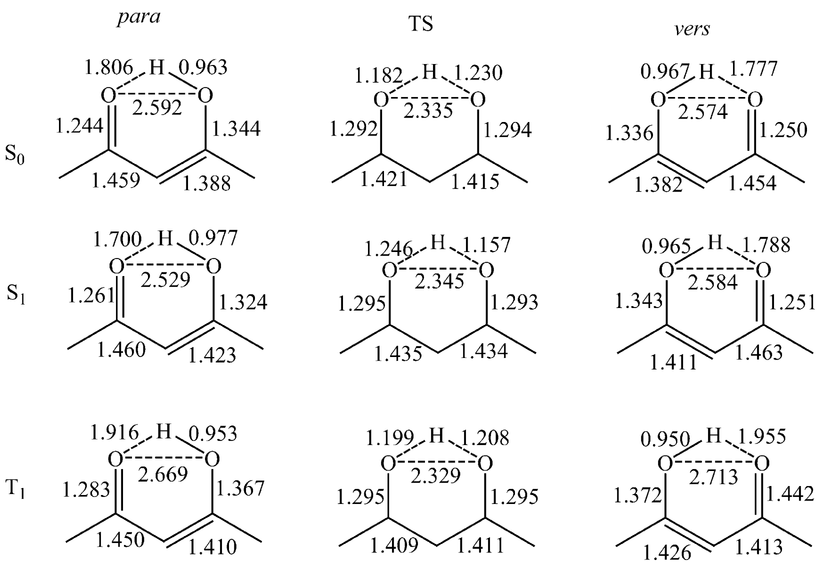

Fig. 3. Structural parameters in the active center.

It should be noted that the geometries change greatly in the triplet states. For instance, the bond length of O–H reduces to 0.953 Å and the length of intramolecular hydrogen bond elongates to 1.916 Å for *para* structure, which is much different from that in ground and singlet excited states. It means that the feature of intramolecular proton transfer in triplet state would be different from that in S_0 and S_1 states. In addition, the bond lengths of O–H and distance of O–O are all similar to other intramolecular hydrogen bond species [31,32].

3.2. Energies

The relative electronic energy (including zero-point energy) of HMB is shown in Fig. 4. In ground state, the energy of the *para* structure is lower than that of the *vers* structure. The IPT barriers of *para* and *vers* structures are 37.37 kJ/mol

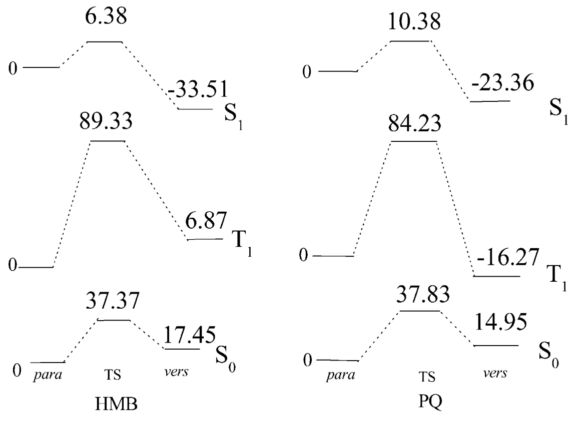

Fig. 4. Relative energy of PQ and HMB in the ground and excited states (units: kJ/mol).

and 19.19 kJ/mol in ground state, respectively. The IPT barriers of hydrogenoxalate anion and 9-hydroxyphenalenone are 27.16 kJ/mol [33] and 29.87 kJ/mol [5], so the larger conjugated systems increase the IPT barrier slightly. Considering the singlet excited state, the *vers* structure is more stable than the *para* structure, which is contrary to the situation in ground state, and the reaction barrier from *para* to *vers* is only 6.38 kJ/mol. It follows that the IPT is easy to take place in S_1 state, and the *vers* structure becomes the predominant component in singlet. In triplet, the energy for the *para* and *vers* structure is close to each other. The energy barrier in this state is 89.33 kJ/mol and much higher than that both in S_0 and S_1 states. So IPT is less likely to take place in triplet. Comparing the IPT barrier of HMB with PQ [5], it can be found that they exhibit little difference in ground state and a little difference in excited states. For instance, the barrier in ground state is 37.32 kJ/mol for HMB and 37.83 kJ/mol for PQ. This suggests that the IPT in PQ is also a single proton transfer process. Previous experimental studies demonstrate that hypomycin B do not execute excited state H-atom or proton transfer [15]. From our calculated results and the similarity to PQ's characteristic of intramolecular proton transfer, we can conclude that intramolecular proton transfer is also present in HMB, which is agreement with our previous conjecture [34].

As we proposed in our previous paper [19], the energy of the molecules depends on the number of molecular resonance mode. The more the resonance mode is, the lower the energy of the molecule is, vice versa [35]. It is five for the *para* structure and four for the *vers* structure in ground state, so the *para* structure is a stable one, which agrees with our calculated results. In addition, S. Nagaoka constructed a nodal-plane model in which the relative stability of molecular isomers depends on the electronic state of the molecule [36], for example, in ground state the keto form is stable, in the first excited state proton transfer takes place and yields a enol form. In S_0 state, the *para* structure is a stable one, while in S_1 state the *vers* structure becomes a stable one. Our calculated results agree well with that predicted by nodal-plane model.

3.3. Mulliken charge and dipole moments

The Mulliken charges of hydrogen atom transferred are listed in Table 1. The results indicate that charge of the hydrogen atom increases about 15% from *para* to TS and the charge on hydrogen in TS is the highest one, then the charge decreases from TS to *vers* isomer. That is, there is a charge variance during the IPT process.

Table 1
Variance of Mulliken charge population on the hydrogen in the IPT process of HMB

	para	TS	*vers*	$\Delta\varepsilon^{\mathrm{HMB}}_{para}$	$\Delta\varepsilon^{\mathrm{HMB}}_{vers}$
S_0	0.488631	0.560814	0.494687	0.07218	0.06613
S_1	0.501236	0.559595	0.494383	0.05836	0.06521
T_1	0.464178	0.479752	0.445924	0.01557	0.02048

$\Delta\varepsilon^{\mathrm{HMB}}_{para}$ represents the variance of charge on the transferred hydrogen from *para* to TS, and $\Delta\varepsilon^{\mathrm{HMB}}_{vers}$ represents that from *vers* to TS.

Table 2
Change of dipole moment in the IPT process of HMB (unit: Debye)

		X	*Y*	*Z*	Total
S_0	*para*	1.7857	−0.9240	−0.0001	2.0106
	vers	−1.9951	−0.5242	−0.0003	2.0628
	TS	3.0315	−0.3062	0.0000	3.0470
S_1	*para*	2.2660	−1.0062	0.0026	2.4794
	vers	2.1675	−0.3318	−0.0034	2.1927
	TS	3.1954	−0.4037	−0.0001	3.2208
T_1	*para*	−1.1927	1.5658	0.0003	1.9683
	vers	−0.3105	−1.6645	0.0008	1.6932
	TS	−1.0948	1.0428	−0.0002	1.5119

X, *Y* and *Z* represent the axis of coordinates.

Table 2 depicts how the dipole moments of HMB change in IPT process. When the hydrogen atom is transferred, the dipole moments increase notably in both ground state and singlet excited state, which implies that polar solutions will facilitate the IPT process. While in the triplet state, the case is quite different. The dipole moment of TS decreases compared with that of the other two isomers. So the isomerization process will be slow down by polar solution via shrinking of dipole moment.

3.4. The photophysical process of HMB in the excited state

The electronic population of the frontier orbital was sketched in Fig. 5. Only the HOMO and LUMO are considered in this paper and they are all π type bonds. Calculated results indicate that the excitation transition coefficients are all close to 0.7. So, electronic transition from HOMO to LUMO is main component in the lowest excitation. In other words, the transitions from HOMO to LUMO are all $\pi \rightarrow \pi^*$ type.

The photo-induced reactions take place in excited state, as is also the case for HMB. So it is essential to elucidate its excited state photophysical process in order to make clear the mechanism of its photosensitization. According to the Frank–Condon theory, the molecular structure changes little shortly after it is excited because the photo-induced process is quite quick. The excitation energy was calculated based on the ground state structures. The excitation energy and oscillator strength are displayed in Table 3. The data indicate

Table 3
Energy and oscillator strength of electron transition in the ground state for HMB

	para		TS		*vers*	
	E (eV)	*f*	*E* (eV)	*f*	*E* (eV)	*f*
1	4.1680	0.0000	3.6195	0.6784	3.7756	0.5050
2	4.2004	0.3851	4.1541	0.0000	4.1299	0.0000
3	4.2561	0.9946	4.3656	0.5789	4.2369	0.8885

E and *f* represent excitation energies and oscillator strengths.

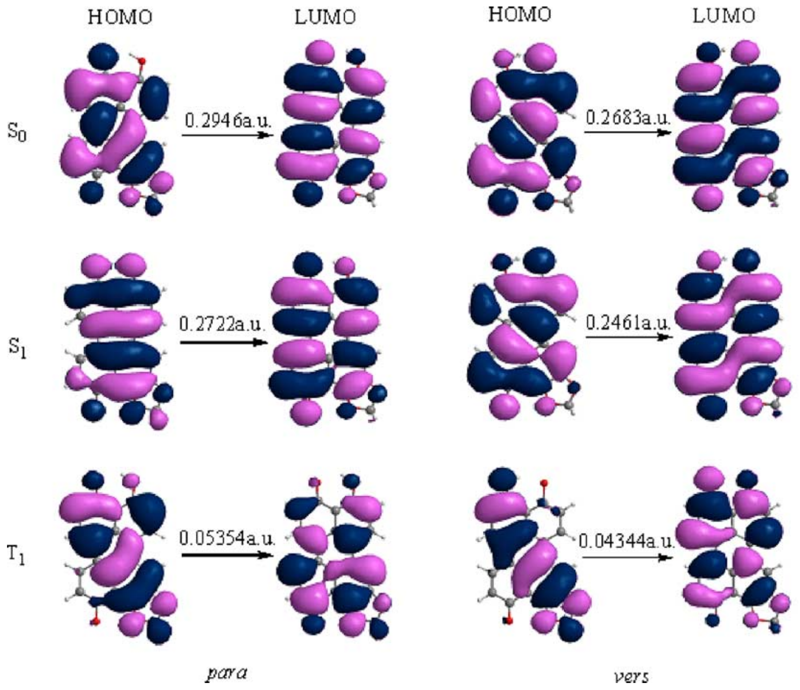

Fig. 5. HOMO and LUMO for HMB.

that vertical excitation energy is 4.2561 and 4.2369 eV for the *para* and *vers* structures, respectively.

The excited state structure and energy were determined by fully optimization. According to the equation $t = 1.499/fE^2$ [37], where E is the energy gap of different states in unit of cm^{-1}, f is oscillator strength of the electronic state and t is the life-span of this state in unit of second. The life-span of a certain state can be figured out. The results are displaced in Table 4.

According to the results, the life spans of the first three singlet excited states are about 10^{-9} s. Previous studies indicate that the CIS methods overrate the excitation energy [38], so the fluorescence emitting time is more than 10^{-9} s. So we can draw a conclusion that the excited states of HMB have long life spans. On the other hand, relaxation process is slower than intersystem crossing (ISC) and IPT process, which are in time scales of 10^{-7} to 10^{-11} s and 50–250 ps respectively [37,39]. So before fluorescence is emitted, the excited molecule can execute IPT quickly and intersystem crossing. As a result, the HMB achieve high triplet quantum yield effectively. This property attributes to the good photosensitization of HMB.

It is well known that when the following two conditions coexist, the ISC of singlet excited state may take place with high efficiency. Firstly, the potential energy surface of singlet and triplet excited states are necessary to have at least one isoenergetic point. Secondly, one microcosmic magnetic field is indispensable in order to reverse the electronic spin. According to the Frank–Condon theory, we calculate the energy of triplet excited state based on the optimized singlet excited state structure, which is illustrated in Fig. 6. It shows that energy values of *para* and *vers* structures in the triplet state are lower than that of the singlet state, while the energy of TS is much higher than that in S_1 state. Therefore, there exists a crossing of the potential energy surface for these two states. When appropriate magnetic field appends to this system, the ISC is apt to take place and the high triplet quantum state yield is achieved. As is mentioned in the preceding discussion, there is a charge variance coupling the IPT process, so the charge transfer will induce a magnetic field. As all the conditions mentioned above cooperate, the ISC will take place with high efficiency. The molecule in T_1 state has longer life-span and most photosensitive reaction occurs in this state.

Table 4
Energy, oscillator strength and life-span of electron transition in the excited state for HMB

	para			TS			*vers*		
	E (eV)	f	t (10^9 s)	E (eV)	f	t (10^9 s)	E (eV)	f	t (10^9 s)
1	3.6509	0.3113	5.5534	3.3874	0.4486	4.4766	3.1265	0.6679	3.5295
2	3.9347	1.0375	1.4346	3.9576	0.9537	1.5426	4.0254	0.0000	–
3	4.0437	0.0000	–	4.0002	0.0000	–	4.1135	0.6345	2.1463

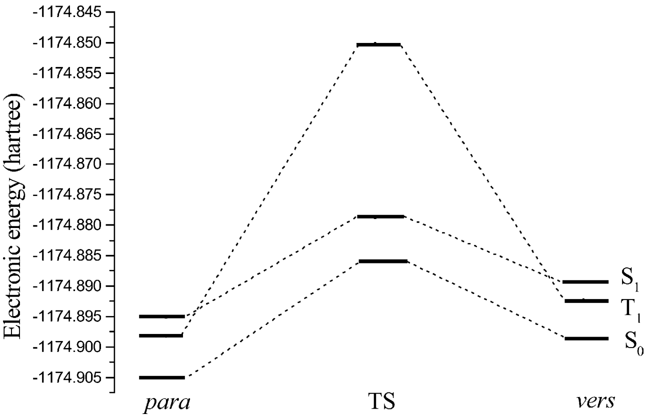

Fig. 6. Energy of HMB in the singlet and triplet excited states, where the geometries used for computing the energy in the S_0, S_1 and T_1 are that fully optimized in the S_0, S_0 and S_1 states.

4. Conclusions

A new compound, HMB, which has similar structural framework with PQ-like photosensitizers but only one hydroxyl group peri to a carbonyl group were studied theoretically. The structures of the ground and the excited states were calculated using HF and CIS theory at 6-31G basis set level. From the calculated results some conclusions can be drawn. The intramolecular proton transfer process of HMB is quite similar to PQ. Their IPT energy barriers in ground state are nearly the same, and only a little difference exists in the excited states. The change feature of the Mulliken charges and the dipole moments also shows the same similarity with that of PQ. Another important result is that there exists a crossing of the potential energy surface of the singlet and triplet so that the intersystem crossing can occur. It can also concluded that HMB is a new photosensitizer to be explored and it is a single proton transfer process in PQD, which play an important role in photosensitization of these series compounds.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 20273042) and Natural Science Foundation of Shandong Province (No. Z2002B01).

References

[1] Z. Diwu, Novel therapeutic diagnostic applications of hypocrellins and hypericins, Photochem. Photobiol. 61 (1995) 529–539.

[2] K. Das, K.D. Ashby, J. Wen, J.W. Petrich, Temperature dependence of the excited-state intramolecular proton transfer reaction in hypericin and hypocrellin A, J. Phys. Chem. B 103 (1999) 1581–1585.

[3] G.A. Kraus, W.-J. Zhang, M.J. Fehr, J.W. Petrich, Y. Wannemuehler, S. Carpenter, Research at the interface between chemistry and virology: development of a molecular flashlight, Chem. Rev. 96 (1996) 523–526.

[4] U. Jozef, L. Aatto, Hypericin, an intriguing internally heterogenous molecule, forms a covalent intramolecular hydrogen bond, Chem. Phys. Lett. 319 (2000) 396–402.

[5] D.-Z. Chen, D.-P. Wang, H.-Y. Zhang, B. Tang, Theoretical study on the ground and excited state intramolecular proton transfer in perylenequinone, Chem. Phys. Lett. 353 (2002) 119–126.

[6] D.-P. Wang, D.-X. Kong, D.-Z. Chen, H.-Y. Zhang, Intramolecular H-bonding in the bay region of hypericin: an AM1 study, Dyes and Pigments 51 (2001) 71–77.

[7] Z. Diwu, J.W. Lown, Photosensitization with anticancer agents 14. Perylenequinonoid pigments as new potential photodynamic therapeutic agents: formation of tautomeric semiquinone radicals, J. Photochem. Photobiol. A: Chem. 69 (1992) 191–199.

[8] Z. Diwu, J.W. Lown, Photosensitization by anticancer agents 12. Perylene quinonoid pigments, a novel type of singlet oxygen sensitizer, J. Photochem. Photobiol. A: Chem. 64 (1992) 273–287.

[9] H.-Y. Zhang, Z.-Y. Zhang, Adv. Free Radic. Life Sci. 7 (1999) 41 (in Chinese).

[10] D.S. English, K. Das, K.D. Ashby, J. Park, J.W. Petrich, E.W. Castner Jr., Confirmation of excited-state proton transfer and ground-state heterogeneity in hypericin by fluorescence upconversion, J. Am. Chem. Soc. 119 (1997) 11585–11590.

[11] K. Das, D.S. English, J.W. Petrich, Deuterium isotope effect on the excited-state photophysics of hypocrellin: evidence for proton or hydrogen atom transfer, J. Phys. Chem. 101 (1997) 3241–3245.

[12] F. Cai, M.J. Fehr, J.W. Petrich, Observation of excited-state tautomerization in the antiviral agent hypericin and identification of its fluorescent species, J. Phys. Chem. 98 (1994) 5784–5795.

[13] F. Sureau, P. Miskovsky, L. Chinsky, P.Y. Turpin, Hypericin-induced cell photosensitization involves an intracellular pH decrease, J. Am. Chem. Soc. 118 (1996) 9484–9487.

[14] Z. Diwu, J.W. Low, Photosensitization with anticancer agents: 15. Perylenequinonoid pigments as potential photodynamic therapeutic agents: formation of semiquinone radicals and reactive oxygen species on illumination, J. Photochem. Photobiol. B 18 (1993) 131–143.

[15] P.K. Chowdhury, K. Das, A. Datta, W.Z. Liu, H.Y. Zhang, J.W. Petrich, A comparison of the excited-state processes of nearly symmetrical perylene quinones: hypocrellin A and hypomycin B, J. Photochem. Photobiol. A: Chem. 154 (2002) 107–116.

[16] H.-Y. Zhang, W. Liu, W.-Z. Liu, J.-L. Xie, Photosensitization of hypomycin B—a novel perylenequinonoid pigment with only one intramolecular hydrogen bond, Photochem. Photobiol. 74 (2001) 191–195.

[17] W.-Z. Liu, Y.-T. Chen, C. Li, N.-Y. Lin, W.-L. Li, J.-L. Xie, Studies on solid2state fermenation technology of a fungus producing perylenequinones, J. Yunnan Univ. (Nat. Sci. Ed.) 22 (2000) 389–391 (in Chinese).

[18] W.-Z. Liu, L.-Y. Ma, C. Li, Y.-T. Chen, J.-L. Xie, Structural elucidation of a new perylenequinone, Acta Pharm. Sin. 36 (2001) 313–314 (in Chinese).

[19] D.-Z. Chen, D.-X. Kong, H.-Y. Zhang, Quantum chemistry calculation research on hypomycin B'sintramolecular proton transfer on ground state, Acta Chimica Sinica. 60 (2002) 234–240 (in Chinese).

[20] A.L. Sobolewski, W. Domcke, Conical intersections induced by repulsive $^1\pi\sigma^*$ states in planar organic molecules: malonaldehyde, pyrrole and chlorobenzene as photochemical model systems, Chem. Phys. 259 (2000) 181–191.

[21] K. Stock, T. Bizjak, S. Lochbrunner, Proton transfer and internal conversion of *o*-hydroxybenzaldehyde: coherent versus statistical excited-state dynamics, Chem. Phys. Lett. 354 (2002) 409–416.

[22] A.L. Sobolewski, W. Domcke, Ab initio study of the excited-state coupled electron–proton-transfer process in the 2-aminopyridine dimer, Chem. Phys. 294 (2003) 73–83.

[23] W.-S. Yu, C.-C. Cheng, Y.-M. Cheng, P.-C. Wu, Y.-H. Song, Y. Chi, P.-T. Chou, Excited-state intramolecular proton transfer in

five-membered hydrogen-bonding systems: 2-pyridyl pyrazoles, J. Am. Chem. Soc. 125 (2003) 10800–10801.

[24] A.L. Sobolewski, W. Domcke, Photoinduced electron and proton transfer in phenol and its clusters with water and ammonia, J. Phys. Chem. A. 105 (2001) 9275–9283.

[25] S. Scheiner, M. Yi, Proton transfer properties of imidazole, J. Phys. Chem. 100 (1996) 9235–9241.

[26] J.B. Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch, Toward a systematic molecular orbital theory for excited states, J. Phys. Chem. 96 (1992) 135–149.

[27] M.A. Ríos, M.C. Ríos, Ab initio study of the hydrogen bond and proton transfer in 2-(2′-hydroxyphenyl)benzothiazole and 2-(2′-hydroxyphenyl)bezimidazole, J. Phys. Chem. A. 102 (1998) 1560–1567.

[28] M. Head-Gordon, D. Maurice, M. Oumi, A perturbative correction to restricted open shell configuration interaction with single substitutions for excited states of radicals, Chem. Phys. Lett. 246 (1995) 114–121.

[29] F. Zhang, G.B. Bacskay, S.H. Kable, Quantum chemical determination of the equilibrium geometries and harmonic vibrational frequencies of 1,1′-, 1,2′- and 2,2′-binaphthyl in their ground and excited (^1L_a) electronic states, J. Phys. Chem. A 108 (2004) 172–184.

[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M. W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. BaKer, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94, revision E.1, Gaussian, Inc., Pittsburgh, PA, 1995.

[31] S. Scheiner, T. Kar, M. Cÿuma, Excited state intramolecular proton transfer in anionic analogues of malonaldehyde, J. Phys. Chem. A 101 (1997) 5901–5909.

[32] D.-P. Wang, S.-G. Chen, D.-Z. Chen, Theoretical studies of conjugate and substituent effects on the intramolecular proton transfer: an HF/CIS study, J. Photochem. Photobiol. A: chem. 162 (2004) 407–414.

[33] A. Fernandez-Ramos, J. Rodriguez-Otero, M.A. Rios, High level dual level direct dynamics in the intramolecular proton transfer of hydrogenoxalate anion. Influence of tunneling and isotopic effect, J. Phys. Chem. A (1998) 102.

[34] D.-P. Wang, S.-G. Chen, D.-Z. Chen, Theoretical study on the trihydroxy-anthraquinone tautomerism in the ground and excited states, J. Mol. Struc. (Theochem.) 673 (2003) 129–136.

[35] I. Gutman, Z. Markovic, L. Marjanovic, On factors influencing the geometry of hypericin and its tautomers, Indian J. Chem. 37A (1998) 856–864 (and references cited therein).

[36] S. Nagaoka, A. Nakamura, U. Nagashima, Nodal-plane model for excited-state intramolecular proton transfer of *o*-hydroxybenzaldehyde: substituent effect, J. Photochem. Photobiol. A: Chem. 154 (2002) 23–32.

[37] N.J. Turro, Modern Molecular Photochemistry, Benjiamin/Cummings Publishing Co., Inc., 1978.

[38] C. Neiss, P. Saalfrank, M. Parac, S. Grimme, Quantum chemical calculation of excited states of Flavin-related molecules, J. Phys. Chem. A 107 (2003) 140–147.

[39] K. Das, D.S. English, M.J. Fehr, A.V. Smirnov, J.W. Petrich, Excited-state processes in polycyclic quinones: the light-induced antiviral agent, hypocrellin, and a comparison with hypericin, J. Phys. Chem. 100 (1996) 18275–18281.