

## Theoretical Study on Intramolecular Proton Transfer of Perylenequinonoid Derivatives

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**Abstract:** Intramolecular proton transfer of hypomycin A in the ground state  $S_0$  and singlet excited state  $S_1$  were calculated by high level quantum chemical method in this letter. It was found that the IPT barriers for  $I \rightarrow TS_1$  are 38.56 kJ/mol in  $S_0$  and 8.19 kJ/mol in  $S_1$ , while those for  $I \rightarrow TS_4$  get approximately 17 kJ/mol higher in  $S_0$  and 28 kJ/mol higher in  $S_1$ . The calculation of IPT rate constants suggests that the experiment observed process of PQD is in  $S_1$ . The height of the IPT barriers correlate not only with the variance of charge for labile hydrogen, the change of H-bond's length, the change of O-H bond's length and the change of O-O distance, but also with the reactant molecular H-bond's length. Moreover, the correlations are the same for  $S_0$  and  $S_1$ .

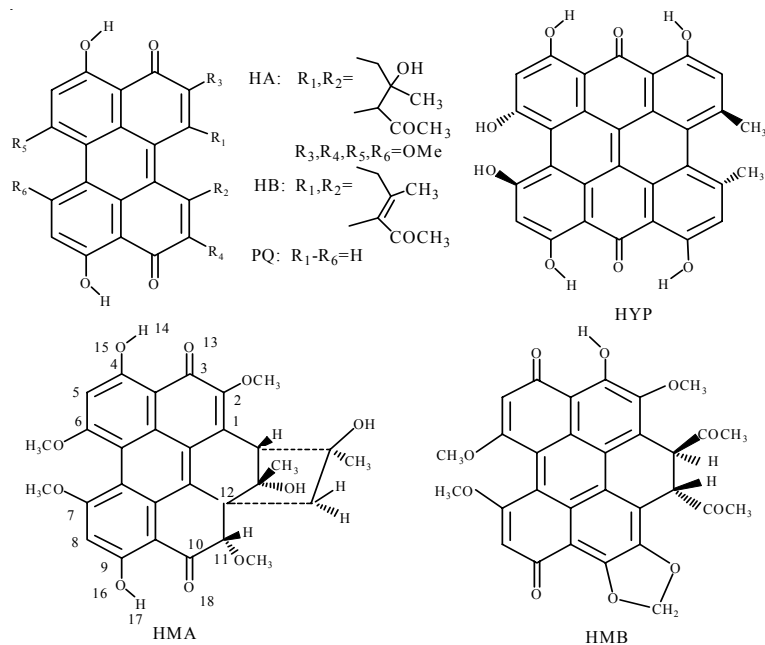
**Keywords:** Perylenequinonoid derivatives, hypomycin A, intramolecular proton transfer, quantum chemical calculation.

In the past two decades, perylenequinonoid derivatives (PQD), such as hypocrellin A (HA), hypocrellin B (HB) and hypericin (HYP) have attracted considerable attention owing to their excellent properties of photosensitization and great advantages over the investigation of intramolecular proton transfer (IPT)<sup>1-5</sup>. Previous researches demonstrated that IPT both in the ground state and excited states exists in PQD and is critical for PQD to reserve their photosensitive activity<sup>3,6</sup>. Although much work has been done on PQD's IPT, some fundamental questions still remain. For instance, due to the molecular skeleton's good symmetry, it is still uncertain which proton is transferred during the IPT processes; it has been found that IPT barriers are associated with the variance of charge for labile hydrogen and the change of H-bond's length, *etc.*<sup>7,8</sup>, however, there is not systematic comparative study between the height of IPT barrier and related parameters of the reactive region up to now. In addition, if certain relationships existed among them, it is still uncertain whether they are the same for  $S_0$  and  $S_1$ .

Recently, a novel perylenequinone named hypomycin A (HMA) (**Scheme 1**) has been isolated<sup>9</sup>. The C11-C12 of HMA is a single bond instead of a double bond for other PQD. As the result, the molecular conjugated system is disrupted. The IPT processes of H14 and H17 should be distinguishable, which makes it much easier to determine the

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**Scheme 1** Chemical structures of PQD

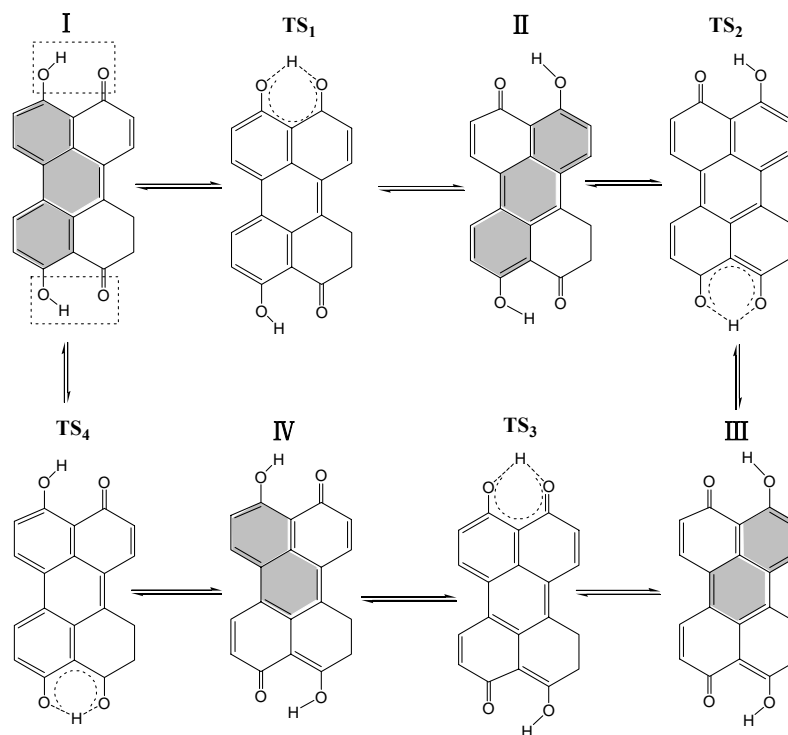
PQD's IPT mechanisms. Moreover, as shown in **Scheme 2**, the various IPT modes of HMA facilitate the comparative study between the IPT barrier and related parameters. The characters mentioned above show HMA has special advantage over the study of PQD's IPT. This stimulated us to take the advantage of quantum chemical calculation for further study. Since it has been reported that the side chains have little effect on the PQD's IPT<sup>8</sup>, we prefer to calculate the active center of HMA firstly in this letter.

## Methods

The molecular geometries were fully optimized at the restricted Hartree-Fock (RHF) level of theory with the 6-31G basis set in  $S_0$ , while the configuration interaction single-excitations (CIS) method with the spin-restricted Hartree-Fock reference ground state has been employed to optimize the excited state geometries at the same basis set level. The GAUSSIAN 98 package of programs was used in this work.

## Results and Discussion

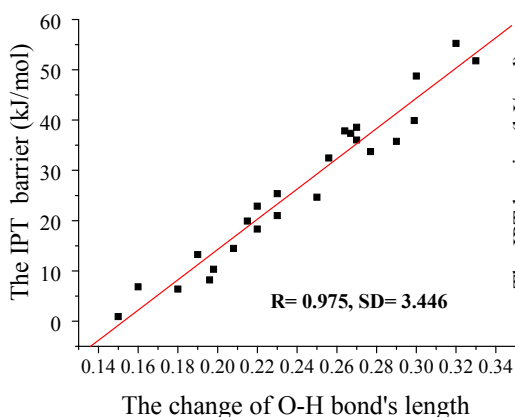
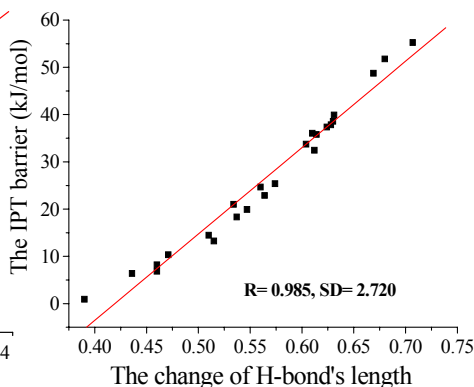
The IPT barriers in  $S_0$  and  $S_1$  have been listed in **Table 1**. The IPT barriers associated with the most stable isomer I were discussed detailed firstly and for  $I \rightarrow \text{TS}_1$  are 38.56 kJ/mol in  $S_0$  and 8.19 kJ/mol in  $S_1$ , both of which are very near to those of PQ (37.83 kJ/mol in  $S_0$  and 10.38 kJ/mol in  $S_1$ )<sup>10</sup>, while IPT barriers for  $I \rightarrow \text{TS}_4$  get approximately 17 kJ/mol higher in  $S_0$  and 28 kJ/mol higher in  $S_1$ . The theoretical results can be invoked to direct and explain the experiment to determine the IPT mechanisms of PQD.

**Scheme 2** The IPT processes for the active center of HMA**Table 1** The IPT barriers in the ground state and singlet excited state (kJ/mol)

	I→TS <sub>1</sub>	II→TS <sub>1</sub>	II→TS <sub>2</sub>	III→TS <sub>2</sub>	III→TS <sub>3</sub>	IV→TS <sub>3</sub>	IV→TS <sub>4</sub>	I→TS <sub>4</sub>
S <sub>0</sub>	38.56	18.34	48.74	13.25	25.36	32.46	6.82	55.24
S <sub>1</sub>	8.19	35.78	51.77	0.91	21.01	24.67	14.47	36.03

The IPT rate constants have also been calculated employing the RRKM theory. At 298.15K, the rate constants for I→TS<sub>1</sub> are  $3.21 \times 10^5 \text{ s}^{-1}$  in S<sub>0</sub> and  $1.06 \times 10^{11} \text{ s}^{-1}$  in S<sub>1</sub>; for I→TS<sub>4</sub>, they are  $3.62 \times 10^2 \text{ s}^{-1}$  and  $2.62 \times 10^6 \text{ s}^{-1}$ , respectively. The rate constant for I→TS<sub>1</sub> in S<sub>1</sub> is in agreement with the experiment data, which are  $(4.65 \pm 0.62) \times 10^{11} \text{ s}^{-1}$  for HA<sup>2</sup> and  $(1.89 \pm 0.06) \times 10^{11} \text{ s}^{-1}$  for HYP<sup>11</sup> in EtOH/MeOH. This offers good evidence that the experiment observed IPT processes of HA and HYP are in S<sub>1</sub>.

Comparative study for various IPT of HMA together with those for the active center of HA and HMB showed that the height of the IPT barriers in S<sub>0</sub> and S<sub>1</sub> correlated well with the variance of charge for labile hydrogen (R=0.892), the change of H-bond's length (R=0.985), the change of O-H bond's length (R=0.975) and the change of O-O distance (R=0.878). Moreover, the correlations among them are the same for S<sub>0</sub> and S<sub>1</sub>.

**Figure 1** The change of O-H bond's length against the IPT barrier**Figure 2** The change of H-bond's length against the IPT barrier

The IPT of PQD proceeds through a four-electron/three-center interaction accompanied by charge separation. The electrostatic interaction may play an important role in this process. It is also interesting to note that linear relationship was also found between the IPT barrier and the reactant molecular H-bond's length ( $R=0.901$ ), indicating the larger the reactant molecular H-bond's length, the higher the IPT barrier. This offers a simple parameter to theoretically characterize the height of IPT barrier for PQD, rather than time-consuming calculation.

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