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Theoretical studies of conjugate and substituent effects on the intramolecular proton transfer: an HF/CIS study

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Abstract

To find the effect of conjugate and substituents on the intramolecular proton transfer, fourteen systems are studied using HF and CIS methods. The results indicate that the intramolecular proton transfer barrier decreases firstly, and changes a little for larger conjugate systems when the combined phenyl cycles are added from three to five. Hereby, we conjecture that the larger conjugate systems (more than three combined phenyl cycles) have little effect on the proton transfer barrier. Theoretical studies on substituents effect show that electronic donor groups enhance the H-bond and electronic acceptor groups reduce the H-bond. The position of substituents is another factor in the proton transfer reaction. The effect of all the substituents on the proton transfer barrier is small, so the character of mother molecule is crucial to the proton transfer reaction. Moreover, the linear analysis results show that the charges on the acceptor oxygen and the differences between the labile hydrogen and the acceptor oxygen have good linear relationship with the proton transfer barrier.

Keywords: Intramolecular hydrogen bond; IPT; Conjugate; Substituents; Excited state

1. Introduction

Some naturally polycyclic pigments, such as anthraquinones (AQ) and perylenequinonoid derivatives (PQD), are of the most important anti-tumor medicament [1,2]. They all possess a strong intramolecular hydrogen bond as a result that they are bearing at least one pair of carboxyl and phenolic hydroxyl that act as a proton donor and acceptor in the adjacent positions. It is widely accepted that the presence of this strong hydrogen bond is partly responsible for the characteristic photophysical properties of these compounds. Intramolecular proton transfer may occur via the intramolecular hydrogen bonds, and therefore, its characteristics should mainly influence these processes.

Petrich and co-workers have demonstrated that the excited state intramolecular proton transfer (ESIPT) exists in the PQD and has significant effect on the photo-induced activity [3–5]. There are also several reports on the intramolecular proton transfer of anthraquinones recently [1]. From a theoretical point of view, albeit an increasing number of theoretical studies of the excited state intramolecular proton transfer reactions can be found in the recent literature [6–9], the excited state intramolecular proton transfer (or hydrogen transfer) has not yet received the attention it deserves.

Most natural pigments are relatively large molecule with several combined phenyl cycles in their molecules. For example, there are eight combined phenyl cycles in hypericin. Thus theoretical studies on the natural pigments systems at high level are still very difficult by now. To further study the properties of the relative large systems, we "detach" the rings and study the smaller and simpler system, then add rings step by step [10], pictured in Fig. 1. The differences and variant tendency of the proton transfer reaction were found by comparing the different systems. Moreover, for many natural pigments, they all have different substitutents, which make the molecules not retain planar structures any more. So substitutents effect is another objects for this proton transfer process. In this paper, we studied nine anthraquinones derivatives (shown in Fig. 2) to investigate the substituents effect. We hope our work will be beneficial to study the proton transfer character of more complex systems such as hypericin and its analogues.

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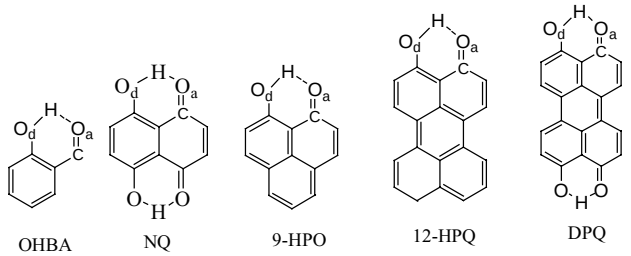
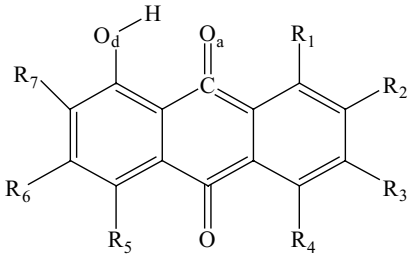


Fig. 1. Structures of several conjugate systems.



1 R_1=OH, R_2=R_3=R_4=R_5=R_6=R_7=H
2 R_1=R_6=OH, R_2=R_4=R_5=H, R_3=CH_3, R_7=Cl
3 R_1=R_6=OH, R_2=R_4=R_5=R_7=H, R_3=CH_3
4 R_1=R_4=OH, R_2=R_5=R_7=H, R_3=CH_3, R_6=OCH_3
5 R_1=OH, R_2=R_4=R_5=R_7=H, R_3=CHO, R_6=OCH_3
6 R_1=OH, R_2=R_4=R_5=H, R_3=CH_3, R_6=OCH_3, R_7=Cl
7 R_1=OH, R_2=R_4=R_5=R_7=H, R_3=CH_3, R_6=OCH_3
8 R_1=OH, R_2=R_4=R_5=R_7=H, R_3=COOH, R_6=OCH_3
9 R_1=OH, R_2=R_4=R_5=R_7=H, R_3=CH_3, R_6=OCH_3

1 Anthraquinone, 2 Chloroemodin, 3 Emodin, 4 Erythroylancin, 5 Fallacinal, 6 Fragilin, 7 parietin, 8 Parietinacid, 9 Xanthorin

Fig. 2. Structures of anthraquinones derivatives.

2. Methods

Initial structures for all the minima and transition states have been obtained with the semiempirical AM1 molecular orbital method [11]. Using these structures as starting points, the geometries have been fully optimized at the restricted Hartree–Fock (RHF) level of theory in the ground state, while the configuration interaction all single-excitations method (CIS) [12] with the spin-restricted Hartree–Fock reference ground-state has been employed to optimize the geometries in the excited state. All located transition exhibits the expected normal imaginary frequency with a transition vector that corresponds to the motion of atoms during the proton transfer process. The CIS method has been employed because it was demonstrated that it provides a qualitatively correct characterization of the ESIPT process [13,14]. Previous studies demonstrated that 6-31g basis set could get the same results as 6-31g(d, p) basis set in principle [15], so in this paper all the structures are fully optimized with 6-31g basis set, and the energy was also calculated with 6-31g(d, p) basis set. The Gaussian 94 package of programs was used in this work.

3. Results and discussion

3.1. Effect of conjugate systems for IPT

3.1.1. Geometries

O-Hydroxybenzaldehyde (OHBA), naphthquinone (NQ), 9-hydroxyphenalenone (9-HPO), 12-hydroxyperylenequinonoid (12-HPQ) and 7, 12-dihydroxy-perylenequinone (DPQ) are studied in this article, as shown in Fig. 1. Their conjugate systems are enlarged gradually. OHBA, 9-HPO and 12-HPQ have one pair of adjacent carboxyl and phenolic hydroxyl, which makes them have only one labile hydrogen to transfer. NQ and DPQ have two pairs of carboxyl and phenolic hydroxyl in the adjacent region and have two labile hydrogens to transfer. Because of the higher barrier energy for double proton transfer, this work only involves single proton transfer. Moreover, intramolecular proton transfer and the predominant species in various states of OHBA had been investigated in several articles [16,17], but the transition state in this process was seldom involved. In this article we calculate the transition state and investigate the effect of conjugate system on proton transfer barrier without discussing the predominant species of OHBA in different electronic states.

Part of the structural parameters are filled in Table 1. Optimized results show that all the carbon atoms lie on a plane, which insures the conjugate system large enough. All the lengths of hydrogen bonds (namely, the distance between acceptor oxygen and the labile hydrogen) in the ground state (S_0) are within 2 Å, so strong hydrogen bonds exist in the ground state. The hydrogen bonds become stronger in the excited state except OHBA. The length of O_d–H becomes shorter for OHBA and NQ, while it is longer for 9-HPO, 12-HPQ and DPQ in the excited state. The distance between donor oxygen and the labile hydrogen (O_d–H) enlarged and the distance between acceptor oxygen and labile hydrogen ($H\cdots O_a$) reduced via the proton transfer. For the structure of transition state, more important is that the distance of $O_d\cdots H$ in NQ, 12-HPQ and DPQ is shorter than that of $H\cdots O_a$ in the S_0 state, whereas it is reversed in the S_1 state. That is, there will be many differences for proton transfer between the S_0 and S_1 states.

Optimized results show that the distance between the donor oxygen and the acceptor oxygen reduced for the normal molecule (marked as I in tables) with the enlarging of the conjugate system and the difference decrease gradually for the anterior four systems. The $O_d\cdots O_a$ in the S_1 state is a little shorter than that in the S_0 state except OHBA. For transition states of the five systems, the difference of $O_d\cdots O_a$ is no more than 0.003 Å in the S_0 state and 0.007 Å in the S_1 state, although it has many differences in the normal molecules. But the distance of $O_d\cdots O_a$ in TS for the 12-HPQ and DPQ is much shorter than that for the preceding three ones. The change of $O_d\cdots O_a$ during the IPT process becomes smaller with the enlarging of the conjugate system for the preceding four systems. Moreover, the length

Table 1
Intramolecular hydrogen bond and distance (Å) between the donor oxygen and the acceptor oxygen

		O_d–H···O_a[a]		O_d···O_a[b]		O_a–C[c]	
		S_0	S_1	S_0	S_1	S_0	S_1
OHBA	I	0.958, 1.926	0.950, 2.071	2.692	2.785	1.227	1.283
	TS	1.315, 1.117	1.156, 1.275	2.345	2.361	1.283	1.297
NQ	I	0.958, 1.899	0.955, 1.890	2.646	2.634	1.233	1.254
	TS	1.152, 1.271	1.221, 1.206	2.342	2.353	1.288	1.291
9-HPO	I	0.965, 1.812	0.971, 1.769	2.606	2.586	1.247	1.264
	TS	1.208	1.214	2.342	2.359	1.294	1.299
12-HPQ	I	0.964, 1.793	0.972, 1.726	2.587	2.550	1.246	1.266
	TS	1.169, 1.244	1.286, 1.135	2.337	2.347	1.294	1.305
DPQ	I	0.963, 1.814	0.975, 1.714	2.597	2.537	1.243	1.258
	TS	1.185, 1.227	1.243, 1.173	2.335	2.342	1.292	1.294

[a] I represents the normal molecule, and TS represents the transition state. The first datum in O_d–H···O_a column is the length of O_d···H, and the second one is for H···O_a.
[b] O_d···O_a represents the distance between donor oxygen and acceptor oxygen.
[c] O_a–C represents the length of acceptor oxygen and carbon double bond.

of bond O_a–C becomes much longer in the S_1 state for the five systems.

3.1.2. Mulliken charge population

A way to analyze the theoretical results is to compare the evolution of charge separation along the reaction path. Table 2 shows part of the Mulliken charge population in the five systems in the S_0 and S_1 electronic states. This article only includes the charges on labile hydrogen and its neighboring oxygen atoms in the proton transfer active part. The results indicate that the charge of labile hydrogen increase greatly during the reaction, and it is the largest in TS, which is about 20% higher than the initial molecule and agreement with the previous studies on PQD [18]. It can also be found that the labile hydrogen charge of TS has slight difference in the ground and excited states for the five systems. The variance of charge on the hydrogen for OHBA and NQ is much larger than the other three. The charge on the labile hydrogen increases a little in the S_1 excited state for the normal conformation except OHBA. The general trend is the Mulliken population increases with the enlarging of the conjugate system. The variance of charge on the hydrogen for OHBA and NQ in the S_1 state is larger than that in the S_0 state, whereas it is the reverse for the other three systems.

For the acceptor oxygen, the Mulliken charge population also increases greatly during the reaction. And the change of charge on the acceptor oxygen in the S_1 state is larger than that in the S_0 state except 9-HPO, which has a little decrease in the S_1 state. But the variance of the charge on the acceptor oxygen in the S_0 state is much larger than that in the S_1 excited state. So the variance trend of charge on the acceptor oxygen is the same to the labile hydrogen. In this way, the interaction of charges on labile hydrogen and acceptor oxygen enhances during the reaction

Table 2
Mulliken charge population of the oxygen and the labile hydrogen

		Q_H[a]		Q_{O_d}[b]		Q_{O_a}[b]	
		S_0	S_1	S_0	S_1	S_0	S_1
OHBA	I	0.4740	0.4679	−0.799	−0.804	−0.588	−0.609
	TS	0.5611	0.5605	−0.825	−0.835	−0.729	−0.723
NQ	I	0.4794	0.4804	−0.794	−0.799	−0.605	−0.617
	TS	0.5631	0.5670	−0.809	−0.823	−0.772	−0.765
9-HPO	I	0.4891	0.4962	−0.791	−0.789	−0.677	−0.708
	TS	0.5601	0.5616	−0.810	−0.815	−0.810	−0.815
12-HPQ	I	0.4866	0.4928	−0.797	−0.797	−0.676	−0.707
	TS	0.5572	0.5521	−0.802	−0.805	−0.825	−0.822
DPQ	I	0.4883	0.5025	−0.790	−0.788	−0.656	−0.688
	TS	0.5616	0.5619	−0.809	−0.810	−0.796	−0.797

[a] Q_H represents the Mulliken charge on the labile hydrogen. ΔQ_H represents the variance of Q_H during the proton transfer.
[b] Q_{O_d} and Q_{O_a} represent the charge on the donor oxygen and acceptor oxygen.

Table 3
Proton transfer barrier and its related factor

	H-bond[a]	$O_d\cdots O_a$[b]	Q_H[c]	ΔQ_H[c]	Q_{O_a}[c]	$Q_H - Q_{O_a}$[c]	$\Delta E_{6\text{-}31g}$[d]	$\Delta E_{6\text{-}31g(d,p)}$[d]
S_0								
OHBA	1.9261	2.692	0.4740	0.0871	−0.588	1.062	87.64	81.03
NQ	1.899	2.646	0.4794	0.0837	−0.605	1.0844	78.66	72.14
9-HPO	1.8124	2.606	0.4891	0.0710	−0.677	1.1661	42.93	38.39
12-HPQ	1.793	2.587	0.4866	0.0706	−0.676	1.1626	51.44	46.99
DPQ	1.814	2.597	0.4883	0.0733	−0.656	1.1443	51.06	45.78
S_1								
OHBA	2.0713	2.785	0.4679	0.0926	−0.609	1.0769	80.44	62.78
NQ	1.890	2.634	0.4804	0.0856	−0.617	1.0974	63.22	58.36
9-HPO	1.7692	2.586	0.4962	0.0654	−0.708	1.2042	35.18	29.41
12-HPQ	1.7258	2.550	0.4928	0.0593	−0.707	1.1998	40.71	36.29
DPQ	1.7135	2.537	0.5025	0.0594	−0.688	1.1905	43.92	39.30

[a] H-bond represents the length of intramolecular hydrogen bond by unit Å.
[b] $O_a\cdots O_d$ denotes the distance between donor oxygen and acceptor oxygen by unit Å.
[c] Q_H and Q_{O_a} denote the Mulliken charge population on the labile hydrogen and acceptor oxygen, $Q_H - Q_{O_a}$ represents the difference between Q_H and Q_{O_a}. ΔQ_H denotes the variance of charge on the labile hydrogen during the proto transfer, that is, the difference of charge on the labile hydrogen between transition state and normal molecule.
[d] $\Delta E_{6\text{-}31g}$ and $\Delta E_{6\text{-}31g(d,p)}$ are the proton transfer barrier with 6–31g basis set and 6–31g (d, p) basis set by unit kJ/mol.

process and favors the reaction. For the donor oxygen, the Mulliken charge population also increases a little during the reaction.

3.1.3. Reaction barrier and its related factors

All the reaction barriers in the S_0 and S_1 states are filled in Table 3. The results indicate that the barriers decrease, considering the former three systems both in the S_0 and S_1 states. However, the difference of barrier for the latter two systems is very small. That is, another pair of adjacent carboxyl and phenolic hydroxyl has little effect on the first intramolecular proton transfer.

To find the essence of the hydrogen transfer, we further studied the pertinent factor of the proton transfer barrier. Six factors were taken into account, as shown in Table 3. Linearity analysis shows that the charge on acceptor oxygen (Q_{O_a}), the difference between charge on labile hydrogen and acceptor oxygen ($Q_H - Q_{O_a}$) are linear with the barriers. The pertinent coefficients are 0.971 and 0.966, respectively, shown in Fig. 3. We fit linear with parameters in the S_0 and S_1 states separately, and find new results. In the S_0 state, the barrier is linear with the H-bond length, $O\cdots O$ distance, Q_H, ΔQ_H, Q_{O_a} and $Q_H - Q_{O_a}$. The pertinent coefficients are 0.964, 0.925, 0.985, 0.984, 0.982 and 0.988, respectively, which shows that good linearity relationship appeared in the same electronic state.

3.2. Effect of substitutents

3.2.1. Geometries

In this part, we studied anthraquinone and its eight derivatives to understand the effect of substituents on the intramolecular proton transfer reaction. Taking anthraquinone as mother molecule, we add electronic donor groups –CH_3, –OCH_3, –OH, –Cl and electronic acceptor groups –CHO and –COOH in the different position. The substituted positions are mainly in R3, R6 and R7 position, as shown in Fig. 2.

The results indicate that all the frameworks are almost planar structures. Table 4 lists the length of H-bond and the $O\cdots O$ distance. The lengths of hydrogen bonds in the ground states and the excited states are within 2 Å, so strong hydrogen bonds exist in all these anthraquinone derivatives. Substituted by different groups, the anthraquinone derivatives change their hydrogen bonds a little. The general trend is electronic donor groups increase the H-bond and electronic acceptor groups decrease the H-bond. With the proton transfer, the distance between donor oxygen and labile hydrogen (O_d–H) enlarged and the distance between acceptor oxygen and labile hydrogen ($H\cdots O_a$) reduced. For the transition states, the distance of $O_d\cdots H$ in the nine derivatives of anthraquinone is shorter than that of $H\cdots O_a$ in S_0 state, whereas it is reversed in the S_1 state except erythroylancin.

Calculation results indicate that the distance between donor oxygen and acceptor oxygen ($O_d\cdots O_a$) in the S_1 state is a little shorter than that in the S_0 state. The distance of $O_d\cdots O_a$ for chloroemodin and fragilin is shorter than that in the other seven derivatives of anthraquinone, which changes little in these systems. The changes of $O_d\cdots O_a$ distance in chloroemodin and fragilin are the biggest among the nine derivatives of anthraquinone. Thus it can be seen that the chloric group has much effect on the system. Moreover, the length of C–O_a double bond is a little shorter in fragilin and parietin-acid than that in other anthraquinones derivatives both in the S_0 and S_1 states. That is, electronic acceptor groups are influential to the C–O_a double bond.

3.2.2. Mulliken charge population

Table 5 shows part of the Mulliken charge population in the nine systems in S_0 and S_1 electronic states. The results

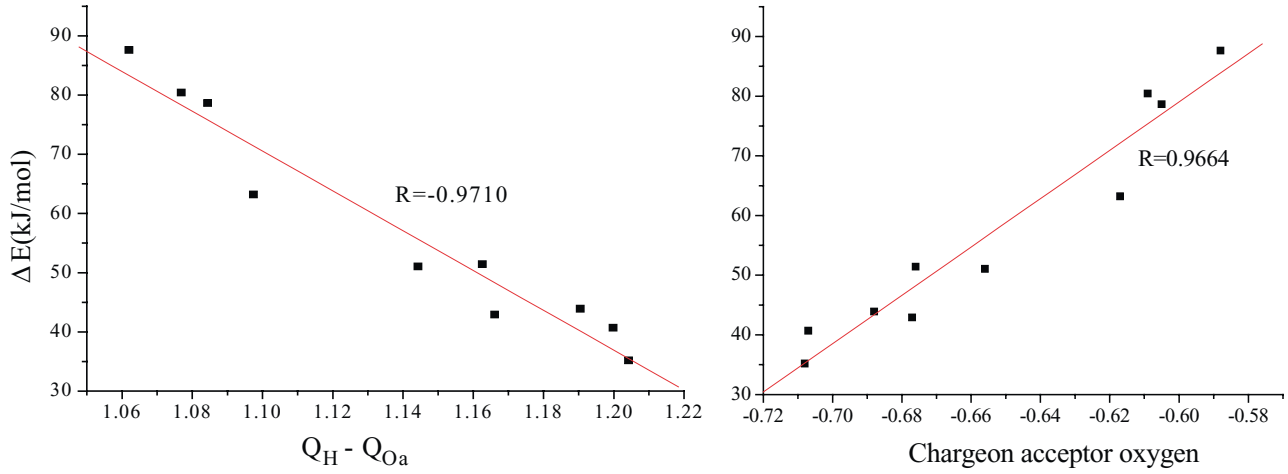


Fig. 3. Fit linear with barrier and Q_{O_a}, $Q_H - Q_{O_a}$.

indicate that the charges of labile hydrogen increase greatly during the reaction, and it is the largest in TS, which is about 20% higher than the initial molecule and agrees with that for PQ [18]. The charge of labile hydrogen increases a little in the S_1 state. Among them, the variance of charge on labile hydrogen is the largest for chloroemodin and fragilin. The differences for the other seven systems are small.

For the acceptor oxygen, the Mulliken charge population also increases greatly during the reaction. And the change of charge on the acceptor oxygen in the S_1 state is smaller than that in the S_0 state except chloroemodin and fragilin, which is a little increase in the S_1 state. But the variance of the charge on the acceptor oxygen in the S_0 state is much larger than that in the S_1 excited state. For the donor oxygen, the Mulliken charge population also increases a little during the reaction.

3.2.3. *Effect of substituents on IPT barrier*

All the reaction barriers and some related factors in the S_0 and S_1 states are filled in Table 6. Because of the similar structure, their reaction characters are similar. But there are still differences among them. The order of H-bond length is: chloroemodin, fragilin < erythroylancin, xanthorin < parietin, emodin < AQ < fallacinal, parietin-acid. That

Table 4
Intramolecular hydrogen bond and distance between the donor oxygen and the acceptor oxygen (Å)

		O_d–H···O_a*		O_d···O_a		O_a–C	
		S_0	S_1	S_0	S_1	S_0	S_1
AQ	I	0.959, 1.832	0.961, 1.791	2.603	2.579	1.250	1.258
	TS	1.338, 1.096	1.164, 1.250	2.352	2.343	1.309	1.320
Chloroemodin	I	0.962, 1.797	0.964, 1.759	2.583	2.560	1.252	1.261
	TS	1.316, 1.110	1.168, 1.239	2.346	2.336	1.307	1.325
Emodin	I	0.959, 1.830	0.962, 1.791	2.605	2.581	1.252	1.261
	TS	1.336, 1.099	1.176, 1.233	2.354	2.339	1.311	1.324
Erythroylancin	I	0.959, 1.827	0.964, 1.783	2.605	2.591	1.253	1.284
	TS	1.324, 1.156	1.214, 1.192	2.369	2.337	1.313	1.329
Fallacinal	I	0.959, 1.836	0.961, 1.794	2.604	2.578	1.249	1.258
	TS	1.354, 1.088	1.168, 1.244	2.358	2.340	1.308	1.321
Fragilin	I	0.961, 1.802	0.963, 1.762	2.588	2.564	1.251	1.260
	TS	1.342, 1.094	1.180, 1.225	2.353	2.335	1.311	1.324
Parietin	I	0.959, 1.830	0.962, 1.791	2.606	2.582	1.252	1.261
	TS	1.336, 1.099	1.177, 1.231	2.354	2.339	1.311	1.325
Parietin-acid	I	0.958, 1.839	0.961, 1.797	2.611	2.585	1.249	1.258
	TS	1.346, 1.093	1.192, 1.218	2.356	2.340	1.311	1.320
Xanthorin	I	0.959, 1.827	0.962, 1.786	2.605	2.580	1.252	1.261
	TS	1.357, 1.086	1.197, 1.209	2.361	2.337	1.312	1.326

Table 5
Mulliken charge population of oxygen and labile hydrogen

		Q_H		Q_{O_d}		Q_{O_a}	
		S_0	S_1	S_0	S_1	S_0	S_1
AQ	I	0.4859	0.4896	−0.793	−0.794	−0.721	−0.735
	TS	0.5637	0.5712	−0.810	−0.830	−0.870	−0.875
Chloroemodin	I	0.4960	0.4994	−0.773	−0.774	−0.734	−0.748
	TS	0.5689	0.5758	−0.797	−0.813	−0.870	−0.886
Emodin	I	0.4867	0.4902	−0.795	−0.795	−0.730	−0.745
	TS	0.5634	0.5725	−0.816	−0.835	−0.876	−0.886
Erythroylancin	I	0.4870	0.4942	−0.794	−0.795	−0.731	−0.782
	TS	0.5612	0.5737	−0.819	−0.841	−0.874	−0.895
Fallacinal	I	0.4871	0.4908	−0.790	−0.791	−0.715	−0.730
	TS	0.5633	0.5731	−0.807	−0.830	−0.865	−0.875
Fragilin	I	0.4927	0.4963	−0.772	−0.773	−0.729	−0.743
	TS	0.5654	0.5755	−0.795	−0.816	−0.867	−0.883
Parietin	I	0.4860	0.4896	−0.796	−0.797	−0.729	−0.744
	TS	0.5629	0.5721	−0.817	−0.836	−0.875	−0.888
Parietin-acid	I	0.4860	0.4897	−0.792	−0.793	−0.718	−0.732
	TS	0.5636	0.5741	−0.813	−0.837	−0.871	−0.877
Xanthorin	I	0.4864	0.4900	−0.795	−0.796	−0.731	−0.745
	TS	0.5603	0.5730	−0.819	−0.843	−0.873	−0.887

is, electronic donor groups enhance the H-bond and electronic acceptor groups reduce the H-bond. The order of proton transfer barrier changes a little, and it is: chloroemodin, fragilin < parietin, emodin < erythroylancin, xanthorin < AQ < fallacinal, parietin-acid. For parietin and emodin, their electronic donor groups are at R3 positions. The electronic donor groups of erythroylancin and xanthorin are at R6 positions. We hypothesize the position is another important factor for the barrier of this reaction. Of course, further studies should be carried out when larger substitutents were added or the planar structures were changed.

We also studied the linear pertinent with the barrier, and found that H-bond is the best factor among the four factors, and the pertinent coefficient is 0.861. $Q_H - Q_{O_a}$ is another good factor with pertinent coefficient 0.859. The pertinent

Table 6
Proton transfer barrier and its related factor

	H-bond (Å)	$O_a \cdots O_d$ (Å)	Q_{O_a}	$Q_H - Q_{O_a}$	$\Delta E_{6\text{-}31g}$ (kJ/mol)	$\Delta E_{6\text{-}31g(d,p)}$ (kJ/mol)
S_0						
Chloroemodin	2.583	1.797	−0.734	1.2300	68.12	66.00
Fragilin	2.588	1.802	−0.729	1.2217	75.29	74.12
Erythroylancin	2.605	1.827	−0.731	1.2180	80.09	78.05
Xanthorin	2.605	1.827	−0.731	1.2174	81.07	79.82
Parietin	2.606	1.830	−0.729	1.2150	77.23	75.22
Emodin	2.605	1.830	−0.730	1.2167	78.67	76.59
AQ	2.603	1.832	−0.721	1.2169	81.41	79.41
Fallacinal	2.604	1.836	−0.715	1.2021	84.24	82.52
Parietin-acid	2.611	1.839	−0.718	1.2040	83.09	81.36
S_1						
Chloroemodin	2.560	1.759	−0.748	1.2474	63.63	54.43
Fragilin	2.564	1.762	−0.743	1.2393	61.72	62.40
Xanthorin	2.580	1.786	−0.745	1.2350	78.42	70.42
Erythroylancin	2.591	1.783	−0.782	1.2762	60.36	60.05
Parietin	2.582	1.791	−0.744	1.2336	70.78	62.64
Emodin	2.581	1.791	−0.745	1.2352	72.71	63.25
AQ	2.579	1.791	−0.735	1.2246	71.84	62.23
Fallacinal	2.578	1.794	−0.730	1.2208	72.36	62.76
Parietin-acid	2.585	1.797	−0.732	1.2217	77.91	68.55

coefficient of Q_a is 0.785 and $O_d \cdots O_a$ is 0.764. The pertinency agrees with the previous study [19] on hypomycin B.

4. Conclusion

Five conjugate system added combined phenyls cycles from one to five and nine anthraquinones derivatives are studied to find the effect of conjugate and substituents on the intramolecular proton transfer. Calculation results indicate that strong intramolecular hydrogen bonds exist in the fourteen systems and become stronger in the excited state except OHBA. With the enlarging of the conjugate system, the hydrogen bonds become stronger in the excited state and the intramolecular proton transfer barrier decreases firstly, and changes a little for larger conjugate systems. Hereby, we can draw a conclusion that the larger conjugate systems (more than three combined phenyl cycles) have little effect on the proton transfer barrier. Linearity analysis shows that the charge on the acceptor oxygen (Q_{O_a}) and the difference between the charge on the labile hydrogen and the acceptor oxygen ($Q_H - Q_{O_a}$) are linear with the barriers. The pertinent coefficients are 0.971 and 0.966, respectively.

Theoretical studies on substitutents effect show that electronic donor groups enhance the H-bond and electronic acceptor groups reduce the H-bond. The position of substituted groups is another factor in the proton transfer reaction. The effect of all the substituents on the proton transfer barrier is small, so the character of mother molecule is crucial to the proton transfer reaction.

On the basis of conjugate and substituents effect, we can design new type of photodynamic medicine. Enlarging the conjugate system and/or adding the appropriate substituents can augment the phototherapy window.

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