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Variance of charges in the process of isomerization of perylenequinone

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Abstract

AM1 method was employed to calculate the variance of charges for hydrogen and oxygen in the process of isomerization of perylenequinone (PQ) in different states. It was found that (i) charge of hydrogen increased at the beginning, and then decreased with the change of reaction coordinate. The maximum of the charge was approximately 30% higher than the initial value. (ii) There was a certain relationship between the ΔQ of hydrogen and the barrier in the process of isomerization. In the states of possessing identical charges, the larger the ΔQ, the higher the barrier; in the states of possessing different charges, the barrier also related to the charge of oxygen. (iii) While a little change occurred in the charge of hydrogen in IHT process, the molecular dipole moment varied rather remarkably. There was a discrepancy between each other. (iv) In the process of transfer of H17, the charge of H18 varied very slightly, which indicated that the transfer of two hydrogens was almost independent and exerted a weak influence on each other. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: AM1 calculation; Charge; Intramolecular hydrogen transfer; Isomerization; Perylenequinone

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1. Introduction

Perylenequinonoid derivatives (PQD) are a type of photosensitive pigments widespread in nature. Due to their excellent photosensitive properties, they have drawn more and more attention [1–3]. Moreover, they are expected to be developed as new phototherapeutic medicines. The unique structures of PQD enable them to isomerize on ground and excited states. The isomerization of the active center of PQD, perylenequinone (PQ), is indicated in Fig. 1. It has been found that this intramolecular hydrogen transfer (IHT) is critical for PQD to reserve their photosensitive activity and structural stability [4,5].

Meanwhile, this process makes PQD a good experimental material to study IHT, and to be the focus of attention [6–10]. It is more important that the barriers of IHT of PQD in excited states decrease markedly, which enhance the acidity of hydroxyls of PQD [11]. As a result, PQD obtain a new path of photosensitivity [12,13]. It is thus evident that studying the isomerization of PQD has great significance in many ways. But there are many problems to be solved in this field. For example, we know nothing about the variance of charge of hydrogen in the process of isomerization [9,10]. Apparently, it is very difficult to answer through experiments. However, it could be investigated by theoretical methods. In view of the successful calculations of barriers and dipole moments of IHT of PQD by semiempirical quantum chemistry method AM1 [14,15], we employed AM1 to calculate the charges of hydrogen and oxygen of PQ in the process of isomerization in different states, including ground state, excited states, anion, anion- and cation-free radicals. The results are expected to be helpful in solving this fundamental problem.

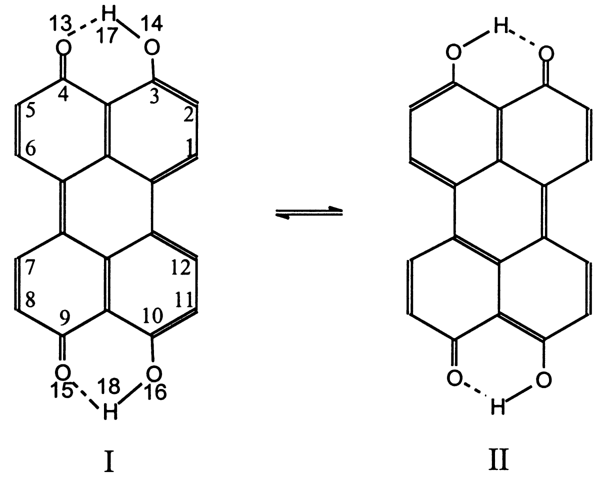

Fig. 1. Isomerization of PQ.

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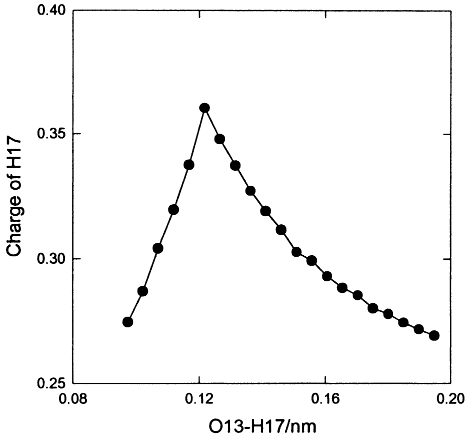

Fig. 2. Variance of charge for H17 of PQ in ground state against reaction coordinate.

2. Methods

Firstly, we used MMX method [16] in PCMODEL program to optimize the molecular structure. Then calculations were carried out with complete geometry optimization using AM1 method [17]. After obtaining the primary structure, we took the bond length between O13 and H17 as reaction coordinate and changed the bond length step by step to calculate each of them using AM1 method [14,15]. The effectiveness of this method has been verified by employing 9-HPO, an analog of PQ, as a model molecule. The calculated barriers for 9-HPO were well consistent with the experimental results, even better than those calculated by ab initio STO-3G method [14]. Keyword UHF (unrestricted Hartree-Fork) was added while calculating free radicals. And keywords Excited and Triplet were added during the calculation of singlet and triplet excited states, respectively.

3. Results and discussion

3.1. Variance of charge of hydrogen

The calculations indicate that the charge of H17 of PQ in different states increases at the beginning, and then decreases following the change of reaction coordinate. In addition, the coordinate of maximum charge is identical with that of the barrier of isomerization [14]. The variance of charge of H17 of PQ in ground state and of PQ anion-free radical ($PQ^{\bullet -}$) against reaction coordinate is shown in Figs. 2 and 3. The figures of other states are similar to them, and have thus been omitted. It can be seen from Table 1 that in the process of isomerization, the maximum charge of H17 is approximately 30% higher than the initial value. The charge of singlet excited state increases least, while that of cation-free radical increases most.

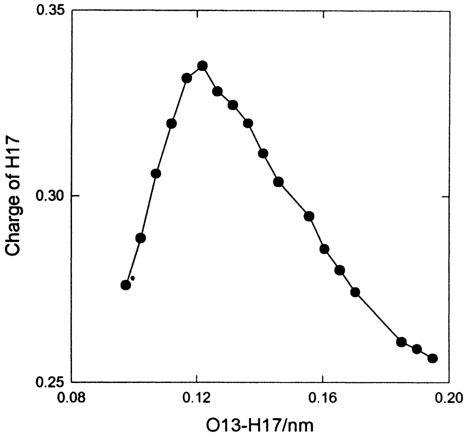

Fig. 3. Variance of charge for H17 of $PQ^{\bullet -}$ against reaction coordinate.

3.2. Relationship between charges and barriers

It is well known that the charge of oxygen of phenolic hydroxyl will decrease in singlet excited state, and, on the contrary, the charge of carbonyl oxygen will increase in singlet excited state. As a result, the IHT between hydroxyl and carbonyl will be facilitated in singlet excited state [18]. Consequently, it has been considered that the charges of oxygen and hydrogen play an important role in the IHT process.

In combination with the difference between the maximum charge and the initial value of H17 in IHT process (ΔQ) and corresponding barriers (Table 1), it can be found that there exists a certain correlationship between them. For instance, in the states of possessing no charge, ΔQ of PQ are similar in ground state and triplet excited state (PQT), and their barriers also have no marked difference; ΔQ of singlet excited state (PQS) is smaller than that of the former two states, the barrier of PQS is lower than that of the former. In the states of possessing negative charge, the ΔQ of PQ anion (PQ^-) is larger than that of PQ anion-free radical ($PQ^{\bullet -}$) and the barrier of the former is, indeed, higher than that of the latter. Besides ΔQ of hydrogen, the barriers also relate to the charge of oxygen in the states of possessing different charges, which results from the fact that H17 moves in the electric field formed by oxygen, and the barriers are inevitably influenced by oxygen. Therefore, although ΔQ of PQ cation-free radical ($PQ^{\bullet +}$) is larger than that of PQ, PQT, PQ^-, etc., the barrier of $PQ^{\bullet +}$ is much lower than that of the latter, which obviously arises from the small charge of oxygen of $PQ^{\bullet +}$ (Table 2).

3.3. The discrepancy between the variance of charges and dipole moments

The variance of charge certainly will induce the change of dipole moment in the process of isomerization of PQ, which has been verified by former studies [15]. However, it can be found by comparing the data of charges and dipole moments that the change of dipole moment is weakly influenced by

Table 1
Variance of charges of hydrogens in the process of isomerization of PQ[a]

	I		IHT		II			
	H17	H18	H17	H18	H17	H18	ΔQ	Barrier(kJ/mol)[b]
PQ	0.2693	0.2691	0.3604	0.2704	0.2747	0.2734	0.0911	89.75
PQS	0.2829	0.2835	0.3558	0.2789	0.2760	0.2719	0.0729	55.40
PQT	0.2689	0.2669	0.3617	0.2745	0.2742	0.2718	0.0928	83.97
PQ$^-$	0.2555	–	0.3413	–	0.2704	–	0.0858	80.12
PQ$^{\bullet-}$	0.2565	0.2584	0.3350	0.2513	0.2761	0.2515	0.0785	59.29
PQ$^{\bullet+}$	0.2802	0.2817	0.3910	0.2877	0.3015	0.2900	0.1108	65.94

[a] PQ: ground state of PQ, PQS: singlet excited state of PQ, PQT: triplet excited state of PQ, PQ$^-$: anion of PQ removing H18, PQ$^{\bullet-}$: anion-free radical of PQ, PQ$^{\bullet+}$: cation-free radical of PQ, I: isomer I of PQ, IHT: maximum charge in IHT process of PQ, II: isomer II of PQ, ΔQ: difference between the maximum charge and the initial value of H17 in IHT process.

[b] The data are from ref [14].

Table 2
Variance of charges of oxygens in the process of isomerization of PQ

	I		IHT		II	
	O13	O14	O13	O14	O13	O14
PQ	−0.3406	−0.2501	−0.3424	−0.3776	−0.2442	−0.3595
PQS	−0.3674	−0.2210	−0.3362	−0.3577	−0.2322	−0.3551
PQT	−0.3385	−0.2570	−0.3397	−0.3447	−0.2390	−0.3446
PQ$^-$	−0.3944	−0.2764	−0.3790	−0.4079	−0.2715	−0.4116
PQ$^{\bullet-}$	−0.4051	−0.2785	−0.4252	−0.4528	−0.2873	−0.4852
PQ$^{\bullet+}$	−0.2382	−0.2116	−0.2484	−0.2888	−0.1768	−0.2688

the variance of the charge of hydrogen. For instance, ΔQ of H17 of PQ is higher than that of PQS in IHT, but the increase of dipole moment of PQS, from 0.902 D to 2.709 D, is much higher than the corresponding increase of PQ, from 0.583 D to 0.744 D [15]. Similar phenomena can be observed in other states of PQ. This is attributed to the fact that dipole moment is a property relating to the whole molecule, and is not determined only by the charge of hydrogen.

The discrepancy between variance of charges and dipole moments is very significant to reduce the barrier of IHT of PQS, because although the barrier is determined essentially by ΔQ, polar solvents have stabilizing effect on IHT process in which dipole moment varies notably, and thus reduce the barrier. So, the lower ΔQ of PQS makes its barrier lower than that of PQ, and the higher change of dipole moment of PQS makes the barrier reduce further in strong polar solvents. In fact, a strong dependence of barrier on solvent polarity for PQD has been observed [8,19].

3.4. *Influence of transfer of H17 on H18*

It can be seen from Table 1 that the charge of H18 varies slightly in the process of H17 transfer. Accordingly, we suggest the two hydrogens are almost independent in the IHT process and have a weak influence on each other, which is in agreement with the conclusion drawn by the calculations of barriers that there was only a weak cooperative effect in the double hydrogen transfer of PQ [14].

Acknowledgements

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