

## A Complete Active Space Self-Consistent Field and Density Functional Theory Study of $S_0$ , $T_1$ , $S_1$ States of Five Phenol *ortho*-Derivatives

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The low-lying electronic states ( $S_0$ ,  $S_1$  and  $T_1$ ) of five phenol *ortho*-derivatives have been studied by the complete active space self-consistent field (CASSCF) and B3LYP methods. Structure optimizations indicate that the  $S_1$  structures of 2-nitrophenol, salicylaldehyde, 2-acetylphenol are H transfer structures, but those of salicylamide and salicylic acid not. The  $T_1$  structures are all H transfer structures. To these five phenol *ortho*-derivatives, all the transitions of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow T_1$  are come from the HOMO to LUMO orbital, and show  $\pi-\pi^*$  transition characters. Additionally, *ortho*-effect is also discussed.

**Keywords:** Complete active space self-consistent field, Density functional theory, Phenol *o*-derivatives.

### INTRODUCTION

The usual polar effects of substituents will operate from the *o*-position not less than from the *p*-position, but in the *o*-substituted compounds there is evidence of some additional factor which is absent in the isomeric derivatives and this additional factor is defined as *ortho*-effect. Meyer emphasized the fact that the *ortho*-effect does not depend upon the chemical nature of the substituent, but appears rather to be governed by its size (as measured, according to him, by the weights of the atoms)<sup>1</sup>. The strengths of aromatic acids and bases are also profoundly influenced by substituents in the *o*-position and analogies are found in phenomena such as the greater strength of allocinnamic acid than of cinnamic acid<sup>2</sup>. The classical dissociation constants of Ostwald and others indicate that all *o*-substituted benzoic acids are stronger than benzoic acid itself and often considerably stronger than their *m*- and *p*-isomers and this is confirmed by recently measured thermodynamic constants for benzoic acid as unity. *ortho*-Effect has not been widely investigated and used in organic synthesis, but also found important implications in photochemistry<sup>3-5</sup>.

There are some investigations of the *ortho*-effect on the photodissociation dynamics<sup>6-9</sup>. Shao and Baer found that the  $\text{NO}_2$  and  $\text{NO}$  fragment channels have been observed for three nitrotoluene isomers and significant OH production was observed in the dissociation of *o*-nitrotoluene and this was attributed by *ortho*-effect which involves a bicyclic intermediate and subsequent rearrangement to the nitrite form prior to fragmentation<sup>8</sup>. The product internal energy distributions

in the  $\text{NO}$  fragment from dissociation of *o*-nitrotoluene between 224 and 238 nm were noted to be different from those of the  $\text{NO}$  fragments produced from dissociation of nitrobenzene<sup>9</sup> or  $\text{NO}_2$ . 2-Nitrophenol, salicylaldehyde and 2-acetylphenol are the typical excited-state intramolecular proton-transfer (IESPT) molecules. Zheng *et al.* found that the IESPT bands for 2-nitrophenol, salicylaldehyde, 2-acetylphenol come from  $S_0$ - $S_1$  transition and these three electronically excited molecules are evolved rapidly in the Franck-Condon region along a large number of skeletal coordinates without involving the O-H stretching coordinate by resonance Raman spectroscopy technique. These facts indicate that the IESPT for 2-nitrophenol, salicylaldehyde and 2-acetylphenol would be barrierless processes<sup>10-15</sup>. The CASPT2 and TD-DFT energy calculations also predicted no barrier in the ESIPT reaction of 2-acetylphenol<sup>16,17</sup>.

*ortho*-Substituted phenols constitute popular model systems for the investigations of intramolecular hydrogen bonding<sup>18</sup>. In such a scenario, some molecular orbital studies on *ortho*-substituted phenol derivatives such as 2-nitrophenol, 2-nitroresorcinol, 4,6-dinitroresorcinol, 1,2-dihydroxybenzene, 2-hydroxythiophenol, salicylaldehyde and 2-mercaptobenzaldehyde have been performed<sup>19-29</sup>. However, most of studies are concentrated on ground states.

In this paper, five *ortho*-derivatives of phenol are investigated from photochemistry view point. *ortho*-Effect of groups in the *o*-position on structures and properties of the low-lying electronic states ( $S_0$ ,  $S_1$  and  $T_1$ ) has been investigated. Combination of density functional theory (DFT) and the complete active space self-consistent field methods is used to

explore the low-lying electronic states and this researching method has been applied successfully in our group<sup>30,31</sup>. Our work will give further light on *ortho*-effect in photochemistry.

### COMPUTATIONAL STUDIES

The equilibrium structures of five *ortho*-derivatives of phenol *e.g.*, 2-nitrophenol, salicylaldehyde, 2-acetylphenol, salicylamide, salicylic acid in the  $S_0$ ,  $T_1$ ,  $S_1$  states have been optimized using the complete active space self-consistent field method. For comparison, B3LYP method was used to optimize the structures in  $S_0$ ,  $T_1$  states. TD density functional theory computations was used to obtain the vertical excitation energies. 6-311+g(d, p) basis set was combined with DFT method and cc-pVDZ was used as the CASSCF method's basis set. Once convergence reached, the harmonic frequencies were examined to confirm that the point is a true minimum.

To well describe the low-lying electronic states of five phenol *ortho*-derivatives, the three  $\pi$  and three  $\pi^*$  orbital on the ring should be used as the active orbital for the CASSCF calculation. Additionally, the two oxygen's nonbonding orbital are also included in the active space. This leads to the active space with 10 electrons in 8 orbital, referred to as CASSCF (10, 8). The CASSCF results are confirmed by comparing the results of B3LYP. All calculations were carried out in GAUSSIAN03 program package<sup>32</sup>.

### RESULTS AND DISCUSSION

**Equilibrium structures:** The selected geometry parameters of five *ortho*-derivatives of phenol in  $S_0$ ,  $T_1$ ,  $S_1$  states are shown in Fig. 1 at CASSCF and B3LYP level. Good agreements were found in the B3LYP and CASSCF (10, 8) optimized geometry results for  $S_0$ ,  $T_1$  states and these agreements confirmed that the correct active space for CASSCF method is selected in this work. All real frequencies for the optimized structures indicate that those convergence structures are true minima.

2-Nitrophenol has a planar structure with  $C_s$  symmetry in the ground state at B3LYP/6-311+g(d, p) and CASSCF(10, 8)/cc-pVDZ levels. As Fig. 1 shown, H transfer nonplanar optimized excited structures of the  $S_1$  and  $T_1$  states are found at CASSCF (10, 8)/cc-pVDZ theoretical level. Our results confirm the prediction of Zheng's resonance Raman spectroscopy experiments and Sobolewski's simple energy scan that  $S_1$  IESPT of 2-nitrophenol may be a barrierless process<sup>10,16,17</sup>. Obvious difference between  $T_1$  and  $S_1$  structures concentrates on the  $\text{ph-N=O-O}$  dihedral angle. The  $\text{ph-N=O-O}$  dihedral angles of  $T_1$  and  $S_1$  are 138.1 and 178.6°, respectively. From the viewpoint of valence theory, the interaction between the lone pair of the acceptor O atom and the  $\text{O-H } \sigma^*$  orbital is mainly responsible for the proton transfer from one oxygen to the other oxygen atom. Therefore, the  $\text{O-H}\cdots\text{O}$  angle and distance may play an important role in the proton transfer reactions. In most cases, the hydrogen bond with linear  $\text{O-H}\cdots\text{O}$  structure and short hydrogen bond distance are considered to be strong. In 2-nitrophenol, the  $\text{O-H}\cdots\text{O}$  angle of 137.7° and the  $\text{O-H}\cdots\text{O}$  distance of 2.610 Å predict that the intramolecular hydrogen bond  $\text{O-H}\cdots\text{O}$  is relatively strong in the ground state. In  $S_1$  and  $T_1$  states, the  $\text{O-H}\cdots\text{O}$  angle and distance are 144.9°,

2.575 Å and 115.0°, 2.766 Å, respectively. This result indicates that hydrogen interactions are very strong in  $S_1$  state, but relative weak in  $T_1$  state.

Salicylaldehyde and 2-acetylphenol show similar photochemical behaviour from the computation results. The skeleton of salicylaldehyde and 2-acetylphenol at  $S_0$  and  $T_1$  are planar, while their  $S_1$  structures are non planar. Additionally, similar to 2-nitrophenol, all their  $T_1$  and  $S_1$  structures are H transfer geometries. Zheng *et al.*<sup>11</sup> and Peteanu & Mathies<sup>12</sup> studied the  $S_0 \rightarrow S_1$  resonance Raman spectroscopy of salicylaldehyde and 2-acetylphenol and their results indicate in the Franck-Condon region the proton-transfer dynamics of salicylaldehyde are similar to that of 2-acetylphenol and all their short-time proton-transfer dynamics being distributed over a wide range of vibrational modes without involving the O-H stretching coordinate. That's to say,  $S_1$  IESPT processes of salicylaldehyde and 2-acetylphenol are barrierless too. However, there is difference in their geometry, for example, the  $\text{ph-C=O-H}$  and  $\text{ph-C=O-CH}_3$  dihedral angle are 177.6 and 170.0°, respectively in their  $S_1$  structures. The  $\text{O-H}\cdots\text{O}$  angle and distance of the salicylaldehyde  $S_0$ ,  $S_1$ ,  $T_1$  states are 141.5°, 2.719 Å, 145.7°, 2.622 Å and 140.3°, 2.698 Å. To 2-acetylphenol, the  $\text{O-H}\cdots\text{O}$  angle and the  $\text{O-H}\cdots\text{O}$  distance are 141.9°, 2.640 Å for  $S_0$ , 145.1°, 2.581 Å for  $S_1$ , 142.6°, 2.654 Å for  $T_1$ , respectively. Above analysis indicates that the hydrogen interactions in  $S_1$  are most strong in the  $S_0$ ,  $S_1$ ,  $T_1$  three states of salicylaldehyde and 2-acetylphenol.

Different properties are found in excited geometry optimization of salicylamide (Fig. 1). To the ground structure, the  $\text{NH}_2$  with the  $\text{C=O}$  forms a conical shape. The  $S_1$  structure isn't an H transfer structure, but  $T_1$  structure is. More similarity between  $S_0$  and  $S_1$  structures may indicates that the  $S_1$  state of salicylamide may have longer life time than those of 2-nitrophenol, salicylaldehyde, 2-acetylphenol. That's to say, fluorescence of salicylamide may stronger than that of 2-nitrophenol, salicylaldehyde and 2-acetylphenol. These results are corresponding to our resonance spectroscopy experiments of salicylamide's  $S_0 \rightarrow S_1$  absorption band can't be carried out effectively for its overwhelming fluorescence. The  $\text{ph-C=O-N}$  dihedrals of the  $S_0$ ,  $S_1$ ,  $T_1$  states are 178.3, 178.4 and 178.5°, respectively. That's to say, in  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow T_1$  transition processes, salicylamide skeleton keeps nearly planar. Hydrogen interactions were found more strong in  $T_1$ ,  $S_1$  than that in  $S_0$ , for the  $\text{O-H}\cdots\text{O}$  angle and distance are 141.9°, 2.652 Å, 145.8°, 2.605 Å and 143.7°, 2.618 Å for  $S_0$ ,  $S_1$ ,  $T_1$  states.

Salicylic acid has several stable isomers in ground state. In this paper, the most stable structure of salicylic acid is studied, as Fig. 1 shown. At CASSCF (10, 8)/cc-pVDZ level, all the  $S_0$ ,  $S_1$ ,  $T_1$  structures are planar. The  $S_1$  structure is similar to that of the  $S_0$  state, that is to say, the  $S_1$  state would have long life time and strong fluorescence radiation when excited. This results lead to reasonable agreements with fact, for it's well known that salicylic acid is strong fluorescence species. Comparing the  $S_0$ ,  $S_1$ ,  $T_1$  structures of salicylic acid with those of salicylamide, similar behavior was found. Both of their  $S_1$  structures aren't H transfer structures and  $T_1$  structures are. The  $\text{O-H}\cdots\text{O}$  angle and distance are 141.3°, 2.675 Å for  $S_0$ , 144.5°, 2.649 Å for  $S_1$ , 142.3°, 2.626 Å for  $T_1$ , respectively.

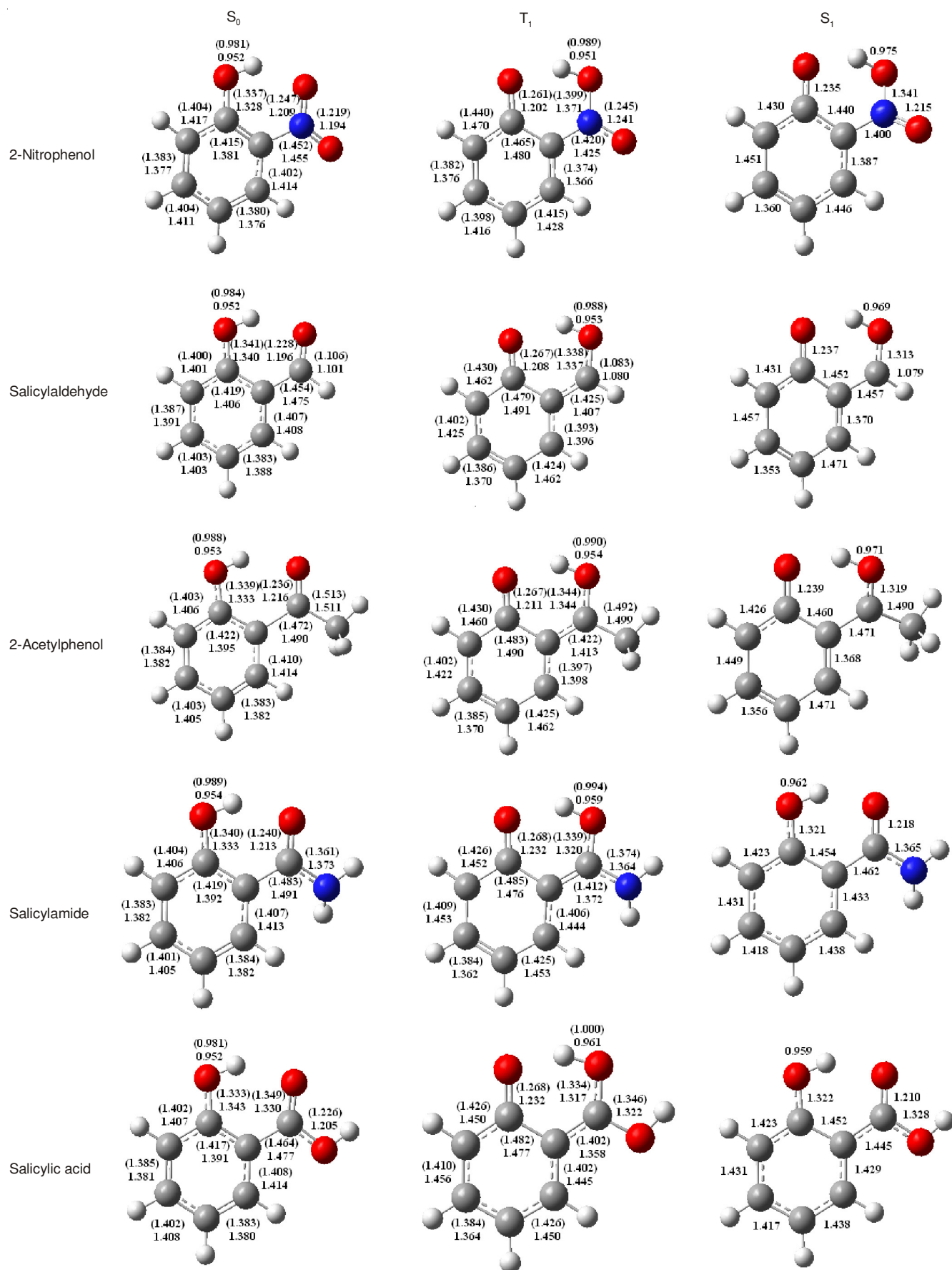


Fig. 1. Equilibrium structures of five *ortho*-derivatives of phenol (2-nitrophenol, salicylaldehyde, 2-acetylphenol, salicylamide, salicylic acid), along with the B3LYP/6-311+g(d, p) bond parameters for the  $S_0$  and  $T_1$  states (in parentheses) and CASSCF (10,8)/cc-pVDZ bond parameters for  $S_0$ ,  $T_1$  and  $S_1$  states (all values in Å)



**Excitation energies:** Table-1 lists the CASSCF/cc-pVDZ adiabatic excitation energy ( $E_a$ ) values and the TD B3LYP/6-311+g(d, p) vertical excitation energy ( $E_v$ ) values for the  $S_1$ ,  $T_1$  states and the oscillator strengths are also tabulated. The available experimental values are also given<sup>10,11</sup> in Table-1.

The  $S_0 \rightarrow S_1$  adiabatic transition energies for 2-nitrophenol, salicylaldehyde, 2-acetylphenol, salicylamide, salicylic acid were predicted to be 352, 308, 296, 277 and 275 nm at CASSCF (10, 8)/cc-pVDZ level. At the same level, the transition adiabatic energies for  $S_0 \rightarrow T_1$  band are 578, 451, 416, 353 and 396 nm, respectively. The vertical excitation energies  $E_v$  of 2-nitrophenol, salicylaldehyde, 2-acetylphenol, salicylamide, salicylic acid by TD B3LYP/6-311+g(d,p) method are 368, 352, 345, 292 and 297 nm for  $S_0 \rightarrow S_1$  transition and 453, 416, 410, 373 and 381 nm for  $S_0 \rightarrow T_1$  transition. The experimental  $S_0 \rightarrow S_1$  transition  $E_v$  values are 347, 340 nm for 2-nitrophenol and salicylaldehyde, which are very close to those calculated values of 368, 352 nm at TD B3LYP/6-311+g(d,p) level.

The calculated results also show that the oscillator strengths ( $f$ ) are 0.0553, 0.0528, 0.0697, 0.1004 and 0.0825 for the  $S_0 \rightarrow S_1$  absorption bands of 2-nitrophenol, salicylaldehyde, 2-acetylphenol, salicylamide, salicylic acid. The experimental  $f$  values of  $S_0 \rightarrow S_1$  absorption bands of 2-nitrophenol and salicylaldehyde are 0.0689, 0.0667, respectively, which

agree with the calculated values very well. Salicylic acid and salicylamide are well-known strong fluorescence species and the calculated oscillator strengths results support the phenomena.

**Transition orbital:** Table-1 also shows the transition orbital of five *ortho*-derivatives of phenol at TD B3LYP/6-311+g (d,p) level. The transition orbital characters are also pictured as Fig. 2. From the calculated results, all the transitions of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow T_1$  come from HOMO to LUMO orbital and also show  $\pi \rightarrow \pi^*$  transition characters.

The  $S_0 \rightarrow S_1$  band absorption of 2-nitrophenol is assigned to  $\pi(\text{benzene ring}) \rightarrow \pi^*(\text{nitro group})$  transition on the basis of the TD-DFT computation, natural orbital analysis and electron loss spectroscopic results<sup>10,33</sup>. Our natural orbital analysis shows the  $\pi$  and  $\pi^*$  transition orbital of the 2-nitrophenol  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow T_1$  bands are delocalized into the benzene ring, OH and the  $\text{NO}_2$  groups. This fact indicates that there are strong intramolecular hydrogen bonding interactions in  $S_0$ ,  $S_1$ ,  $T_1$  states and our geometry optimization results confirmed this conclusion.

To salicylaldehyde, Fig. 2 shows that the orbital 32 has its electron density mostly delocalized into the benzene ring and the OH groups while orbital 33 has its electron density more delocalized into the benzene ring and the  $-\text{CHO}$  groups. This shows the  $S_0 \rightarrow S_1$  band absorption with a CT/PT character and suggests that more electron density will flow from the

TABLE 1  
ADIABATIC ( $E_a$ ) AND VERTICAL ( $E_v$ ) EXCITATION ENERGIES (IN nm) OF FOUR PHENOL *ortho*-DERIVATIVES FROM THE GROUND STATE TO THE FIRST EXCITED SINGLET STATE OSCILLATOR STRENGTH  $f$

Species	$E_a^a$ (nm)		$E_v^b$ (nm)		$f$	Transition orbital	
	$S_0 \rightarrow S_1$	$S_0 \rightarrow T_1$	$S_0 \rightarrow S_1$	$S_0 \rightarrow T_1$		$S_0 \rightarrow S_1$	$S_0 \rightarrow T_1$
2-Nitrophenol	352	578	368 (347)	453	0.0553 (0.0689)	36-37	36-37
Salicylaldehyde	308	451	352 (330)	416	0.0528 (0.0667)	32-33	32-33
2-Acetylphenol	296	416	345	410	0.0697	36-37	36-37
Salicylamide	277	353	292	373	0.1004	36-37	36-37
Salicylic acid	275	396	297	381	0.0825	36-37	36-37

<sup>a</sup> $E_a$  was calculated at CASSCF(10,8)/cc-pVDZ level; <sup>b</sup> $E_v$  and  $f$  was calculated at TD B3LYP/6-311+g(d, p) level; <sup>c</sup>Values in parenthesis are experimental value which come from Ref. 10,11

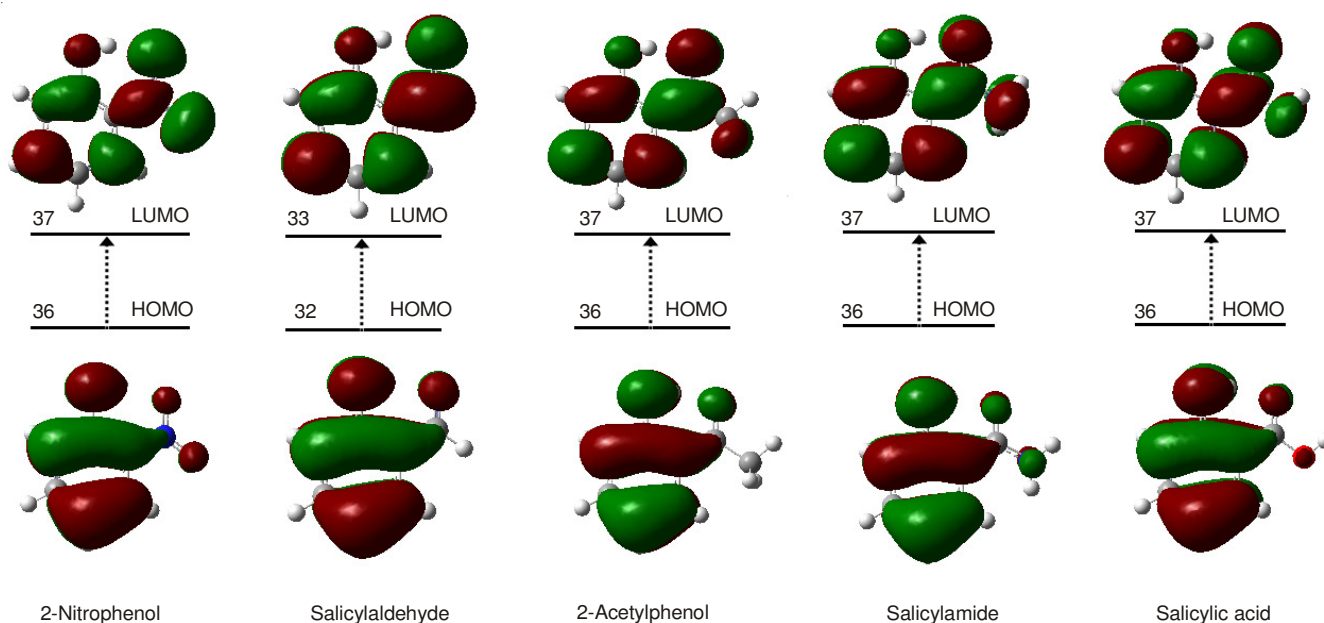


Fig. 2. Diagram of the molecular orbital involved in the  $S_0 \rightarrow S_1$  and  $T_0 \rightarrow T_1$  electronic transitions of five phenol *ortho*-derivatives

OH moiety into the -CHO moiety upon photo excitation. To 2-acetylphenol, the  $S_0 \rightarrow S_1$  band absorption shows a CT/PT character too. Fig. 2 displays that there is an excited state super conjugation interaction between the benzene ring and the  $CH_2$  groups comparing with that of salicylaldehyde. This super conjugation interaction may leads to the reorganization energy differences in their  $S_0 \rightarrow S_1$  Franck-Condon dynamics between 2-acetylphenol and salicylaldehyde in Zheng's work<sup>11</sup>. The  $S_0 \rightarrow S_1$  band absorption of salicylic acid and salicylamide shows a CT/PT character too and the  $-NH_2$  group are more conjugation with benzene ring than -OH of salicylic acid. -OH and  $-NH_2$  are isoelectronic groups, which shows obvious isoelectronic effects for their similar  $S_0 \rightarrow S_1$  band absorption characters.

**Discussions for *ortho*-effect:** Five *ortho*-derivatives of phenol show obvious *ortho*-effect in our calculations. First of all, *ortho*-effect appears in their excited structures. To 2-nitrophenol, salicylaldehyde and 2-acetylphenol, all their  $S_1$  and  $T_1$  structures are H transfer geometries, which shows  $S_1$  and  $T_1$  IESPT of them may be barrierless processes. To salicylic acid and salicylamide, the  $S_1$  structures are similar to their ground states. This property may leads to the intense oscillator strengths and strong fluorescence radiation and both of their  $T_1$  states are H transfer structures. All of this five molecules show intramolecular hydrogen bonding interactions in their  $S_0$ ,  $S_1$ ,  $T_1$  states. There is significant character for 2-nitrophenol, for its  $T_1$  state hydrogen bonding interaction is much weaker than that of  $S_0$ ,  $S_1$ . To the hydrogen bonding interactions of other four *ortho*-derivatives, a little difference of  $S_0$ ,  $S_1$ ,  $T_1$  states were found, though the  $S_1$  hydrogen bonding interactions is relative strong. All the transitions of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow T_1$  of these five *ortho*-derivatives of phenol come from the HOMO to LUMO orbital and also show  $\pi-\pi^*$  transition and CT/PT characters.

The similarity and difference of these five *ortho*-derivatives of phenol enclose the substitution effect in *ortho*-position of phenol.  $-NO_2$ , -CHO,  $COCH_3$ , -COOH and -CONH<sub>2</sub> are electron withdrawing groups. The excited structure optimization suggests that the  $-NO_2$ , -CHO,  $COCH_3$  appears to operate the *ortho*-effect more strong than that of -COOH and -CONH<sub>2</sub>. Namely, the rate of the photo-rearrangement, *i.e.*, the nature of the excited states, is probably controlled by the conformation of the molecules at their excited states and when the molecules are excited to the higher energy excited states, the *ortho*-derivatives of phenol can exhibit a different isomerization pathway and the exact molecular geometry depends on the substituent.

## Conclusion

In this paper, CASSCF and B3LYP calculations were performed to explore the equilibrium structures, adiabatic excitation energies, vertical excitation energies, molecular orbital of the low-lying electronic states ( $S_0$ ,  $T_1$  and  $S_1$ ) for five *ortho*-derivatives of phenol and the *ortho*-effect are also discussed.

Structure optimizations indicate that the  $S_1$  structures of 2-nitrophenol, salicylaldehyde, 2-acetylphenol are H transfer structures, but those of salicylamide and salicylic acid not. The  $T_1$  structures are all H transfer structures. The results support the experiments that the EISPT for 2-nitrophenol, salicylaldehyde, 2-acetylphenol are barrierless processes and

the strong fluorescence properties of salicylamide and salicylic acid. In their  $S_0$ ,  $S_1$ ,  $T_1$  states, all shows intramolecular hydrogen bonding interactions. There is a significant character for 2-nitrophenol, for hydrogen bonding interaction in its  $T_1$  state is much weaker than those in  $S_0$ ,  $S_1$  states.

The adiabatic excitation energies, vertical excitation energies and oscillator strengths for the  $S_1$ ,  $T_1$  states are calculated. The calculated values give reasonable agreements with available experimental results. All the transitions of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow T_1$  of the five phenol *ortho*-derivatives come from the HOMO to LUMO orbital and also show  $\pi-\pi^*$  transition and CT/PT characters. Obvious *ortho*-effect in the five *ortho*-derivatives of phenol indicates that the rate of the photo-rearrangement is probably controlled by the conformation of the excited molecules and the *ortho*-derivatives of phenol can exhibit a different isomerization pathway when excited.

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