

Theoretical Studies on Spectra & Photoreactivity of Benzaldehyde, Hydroxybenzaldehydes & Fluorobenzaldehydes

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CNDO/S CI calculations have been made on benzaldehyde; *p*- and *m*-hydroxybenzaldehydes; and *p*- and *m*-fluorobenzaldehydes. The calculated spectra are compared with the previous results, wherever available. The effect of substituents on energies of lowest $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ is considered in the light of above calculations. The photoefficiencies of substituted aromatic carbonyls towards hydrogen abstraction reaction are discussed in terms of the character of the calculated electronic states.

It is well known that the carbonyl compounds which have lowest $^3(n, \pi^*)$ state undergo photochemical hydrogen abstraction easily as compared to those having $^3(\pi, \pi^*)$ as the lowest excited state. Though in certain cases where $^3(\pi, \pi^*)$ is the lowest triplet, some n, π^* properties are exhibited through processes like spinorbit coupling, thermal equilibration before decay and vibronic mixing between the two triplets¹⁻⁷. There exists some controversy regarding the poor reactivity of OH substituted carbonyl compounds in hydrogen abstraction reaction⁸⁻¹⁰. Pitts *et al*⁸ consider that these molecules have a π, π^* lowest triplet instead of having an n, π^* lowest triplet whereas Porter and Suppan⁹ explain the anomalous behaviour by postulating a charge-transfer (CT) triplet state through which the molecule has to pass before the reactive n, π^* triplet is populated. Godfrey *et al*¹⁰ on the other hand, explain such photostability on the basis of deprotonation in excited state.

In this study an attempt has been made to rationalize the energies and characters of the lowest triplet state for benzaldehyde; *m*- and *p*-fluorobenzaldehydes; and *m*- and *p*-hydroxybenzaldehydes on the basis of MO calculations coupled with configuration interaction (CI). The results have been used to study the effect of substituents on the photoreactivity of these compounds towards hydrogen abstraction reaction.

Calculations

In view of the amount of time and effort required for ab initio calculations of these large molecules we determined the energies and wavefunctions in the CNDO/S approximations of Bene and Jaffe¹¹. Various parameters used are given in Table 1. The β° value for fluorine is the same as used by Yadav *et al*¹² to produce sufficiently accurate results on first two excitation energies of fluorobenzenes. Identical value has also been used by Salahub *et al*¹³. Small variations in these parameters however do not produce significant effects on the spectroscopic data¹¹. Due to scarcity of computer time the number of CI states has been restricted to 20 lowest singly excited states.

TABLE 1 — VARIOUS PARAMETERS USED IN THE CALCULATION
Atom

Parameter	H	C	N	O	F
β° (eV)	-12	-17	-26	-45	-60
γ_{AA} (eV)	12.85	11.11	12.01	13.00	14.10
ξ	1.20	1.625	1.95	2.275	2.60

The calculations for *p*-hydroxybenzaldehyde were repeated with 50 CI states also (Table 2, values within parentheses) and results do not differ much from those with 20 CI states.

The singlet and triplet transition energies are calculated by the well known Roothan equations¹⁴.

$$\Delta E_{\text{singlet}} = \epsilon_{f'} - \epsilon_i - (J_{if'} - K_{if'}) + K_{if'}$$

$$\Delta E_{\text{triplet}} = \epsilon_{f'} - \epsilon_i - (J_{if'} - K_{if'}) = K_{if'}$$

where $\epsilon_{f'}$ and ϵ_i are the orbital energies of the MO's whereto and wherefrom the electron has been excited; and $J_{if'}$ and $K_{if'}$ are the molecular Coulomb and exchange integrals. As in the CNDO theory $K_{if'} = 0$ for n, π^* state¹¹, the $^1(n, \pi)$ and $^3(n, \pi)$ states turn out to be degenerate.

All calculations have been carried out on the IBM-360/44 system at Delhi University, Computer Centre.

Results and Discussion

All the molecules (benzaldehyde, *p*- and *m*- fluorobenzaldehydes, *p*- and *m*-hydroxybenzaldehydes and anion of *p*-hydroxybenzaldehyde were assigned a planar configuration extended in the *X-Z* plane. The ring dimensions were taken as those of the benzene ring ($C-C_{\text{benzene}} = 1.39\text{\AA}$). Other bond distances and bond angles used are given below :

C = O	1.22 Å	C—F	1.33 Å
(O=)C—H	1.09 Å	O—H	0.196 Å
C—O(—H)	1.36 Å	<C—O—H	105°

TABLE 2 — EXPERIMENTAL AND THEORETICAL TRANSITION ENERGIES (TE) [BEFORE CONFIGURATION INTERACTION (CI), AFTER CI AND MODIFIED VALUES] AND OSCILLATOR STRENGTHS OF BENZALDEHYDE AND DERIVATIVES

State	TE(without CI)		TE(after CI)		Lowest ³ (n, π*) modified, final ordering				
	Symm.	TE(eV)	Symm.	TE(eV)	Symm.	TE(eV) calcd.	TE(eV) obsd.	<i>f</i> _{calc}	<i>f</i> _{obs}
C₆H₅CHO									
<i>S</i> ₁	<i>n, π*</i>	4.5913	<i>n, π*</i>	3.0603	<i>n, π*</i>	3.0603	3.14 ¹⁷ 3.33 ²⁴	0.0	0.55 × 10 ⁻³
<i>S</i> ₂	<i>n, π*</i>	5.4987	<i>π, π*</i>	4.6352	<i>π, π*</i>	4.6352	4.3	0.0029	0.0026 ¹⁶
<i>S</i> ₃	<i>π, π*</i>	5.5364	<i>π, π*</i>	5.6257	<i>π, π*</i>	5.6257	5.10		
<i>T</i> ₁	<i>n, π*</i>	4.5913	<i>n, π*</i>	3.0603	<i>π, π*</i>	2.8433	3.123 ²⁵		
<i>T</i> ₂	<i>n, π*</i>	5.4987	<i>π, π*</i>	2.9425	<i>π* π*</i>	2.9425			
<i>T</i> ₃	<i>π, π*</i>	4.1672	<i>π, π*</i>	3.7368	<i>π, π*</i>	3.7368			
<i>m</i>-FC₆H₄CHO									
<i>S</i> ₁	<i>n, π*</i>	4.6220	<i>n, π*</i>	3.1414	<i>n, π*</i>	3.1414	3.319	0.0	
<i>S</i> ₂	<i>π, π*</i>	5.1942	<i>π, π*</i>	4.4797	<i>π, π*</i>	4.4797		0.014	
<i>S</i> ₃	<i>n, π*</i>	5.6614	<i>π, π*</i>	5.5132	<i>π, π*</i>	5.5132		0.077	
<i>T</i> ₁	<i>n, π*</i>	4.6220	<i>n, π*</i>	3.1414	<i>π, π*</i>	2.8624			
<i>T</i> ₂	<i>π, π*</i>	3.6383	<i>π, π*</i>	2.8624	<i>n, π*</i>	2.9244	3.099 ¹⁶	0.0	
<i>T</i> ₃	<i>n, π*</i>	5.6614	<i>π, π*</i>	3.5090	<i>π, π*</i>	3.5090			
<i>p</i>-FC₆H₄CHO									
<i>S</i> ₁	<i>n, π*</i>	4.8743	<i>n, π*</i>	3.1804	<i>n, π*</i>	3.1804	3.381 ¹⁶		
<i>S</i> ₂	<i>π, π*</i>	5.4698	<i>π, π*</i>	4.5664	<i>π, π*</i>	4.5664		0.0006	
<i>S</i> ₃	<i>π, π*</i>	5.5479	<i>π, π*</i>	5.4246	<i>π, π*</i>	5.4246		0.197	
<i>T</i> ₁	<i>n, π*</i>	4.8743	<i>n, π*</i>	3.1804	<i>π, π*</i>	2.9342			
<i>T</i> ₂	<i>π, π*</i>	4.1102	<i>π, π*</i>	2.9342	<i>n, π*</i>	2.9634	3.164 ¹⁶	0.0	
<i>T</i> ₃	<i>π, π*</i>	3.3888	<i>π, π*</i>	3.7367	<i>π, π*</i>	3.7367			
<i>m</i>-OHC-H₄CHO									
<i>S</i> ₁	<i>n, π*</i>	4.6099	<i>n, π*</i>	3.0723	<i>n, π*</i>	3.0723			
<i>S</i> ₂	<i>π, π*</i>	4.9908	<i>π, π*</i>	4.3689	<i>π, π*</i>	4.3689			
<i>S</i> ₃	<i>n, π*</i>	5.5475	<i>π, π*</i>	5.4240	<i>π, π*</i>	5.4240			
<i>T</i> ₁	<i>n, π*</i>	4.6099	<i>n, π*</i>	3.0723	<i>π, π*</i>	2.8273			
<i>T</i> ₂	<i>π, π*</i>	3.5208	<i>π, π*</i>	2.8273	<i>n, π*</i>	2.8553			
<i>T</i> ₃	<i>n, π*</i>	5.5475	<i>π, π*</i>	3.3364	<i>π, π*</i>	3.3364			
<i>p</i>-OHC₆H₄CHO									
<i>S</i> ₁	<i>n, π*</i>	4.6565	<i>n, π*</i>	3.0300 (2.9211)	<i>n, π*</i>	3.0300		0.0	
<i>S</i> ₂	<i>π, π*</i>	5.2159	<i>π, π*</i>	4.4514 (4.4379)	<i>π, π*</i>	4.4514		0.004	
<i>S</i> ₃	<i>π, π*</i>	5.2837	<i>π, π*</i>	5.1878 (5.1591)	<i>π, π*</i>	5.1878		0.232	
<i>T</i> ₁	<i>n, π*</i>	4.6565	<i>n, π*</i>	3.0300	<i>n, π*</i>	2.8130		0.0	
<i>T</i> ₂	<i>π, π*</i>	3.8354	<i>π, π*</i>	2.8298	<i>π, π*</i>	2.8298			
<i>T</i> ₃	<i>π, π*</i>	3.3076	<i>π, π*</i>	3.6071	<i>π, π*</i>	3.6071			
<i>p</i>-OC₆H₄CHO									
<i>S</i> ₁	<i>π, π*</i>	4.0178	<i>n, π*</i>	3.4092	<i>n, π*</i>	3.4092		0.0	
<i>S</i> ₂	<i>π, π*</i>	4.4141	<i>n, π*</i>	3.4623	<i>n, π*</i>	3.4623		0.0	
<i>S</i> ₃	<i>n, π*</i>	4.5714	<i>π, π*</i>	3.8944	<i>π, π*</i>	3.8944		0.0507	
<i>T</i> ₁	<i>π, π*</i>	2.7941	<i>π, π*</i>	2.6500	<i>π, π*</i>	2.65500			
<i>T</i> ₂	<i>π, π*</i>	3.0713	<i>π, π*</i>	2.7524	<i>π, π*</i>	2.7524			
<i>T</i> ₃	<i>n, π*</i>	4.5714	<i>π, π*</i>	3.2451	<i>π, π*</i>	3.2451			

Spectra — Characters and energies for singlets and triplets corresponding to the three lowest energy transitions are given in Table 2. The characters of these transitions have been assigned on the basis of the nature of the filled and unfilled molecular orbitals involved in the particular transition. In all the molecules studied, except the anion of *p*-OHC₆H₄CHO,

the transition with minimum energy has been assigned *n, π** character because the filled MO involved in this transition has almost entire contribution (~0.8) from the atomic orbital corresponding to lone pair on the carbonyl oxygen and the antibonding MO involved in this transition has a shared contribution from the π atomic orbitals on the carbon atoms and

the carbonyl oxygen of the molecule. However, in the case of anion of p -OH C_6H_4CHO the p , coefficient of O^- in the bonding orbital involved in the lowest energy transition is very high (~ 0.617) while in the antibonding MO of the same transition this coefficient is very small (0.016). This situation is equivalent to intramolecular charge-transfer (CT). Consequently the lowest energy transition has been assigned a CT character in this case.

Due to inherent assumptions in the CNDO method, S-T split exists only for π, π^* transitions whereas $^1n, \pi^*$ and $^3n, \pi$ states are degenerate. It can be seen from Table 2 that the calculated transition energies differ on the average by about ≥ 1.3 eV from the experimental values. These energy values were modified by configuration interaction (CI)¹⁵ and are given in column 6 of Table 2. Since all states lose their individuality in CI technique the ordering is reestablished on the basis of oscillator strength. However, it has been observed experimentally¹⁶ that S-T split for n, π^* states of a variety of substituted benzaldehydes varies from 1720 to 1780 cm^{-1} with an average of 1750 ± 30 cm^{-1} . In view of the S-T degeneracy in our calculations we have made use of the above experimental generalization to modify the theoretically calculated $^3(n, \pi^*)$ energy values for C_6H_5CHO and its derivatives. This is achieved by subtracting 1750 cm^{-1} ($=0.217$ eV) from the degenerate energy value calculated for singlet and triplet n, π^* levels after CI. This modification results in change of order of energy levels. The modified ordering of triplet levels and modified energies of these levels are also given in Table 2.

Finally ordered S-T energies are comparable with the results wherever available. The calculated results can be seen in fair agreement with the reported data. The experimentally obtained 0-0 bands¹⁶ for C_6H_5CHO , p - FC_6H_4CHO and m - FC_6H_4CHO are somewhat higher (~ 2000 cm^{-1} , 0.25 eV) than the calculated values. As the theoretically calculated transition energies correspond to 0-0 transition in isolated gaseous state, these differences can be due to solvent effect and/or due to uncertainty in the assignment of O-O band. The transition energies of benzaldehyde as calculated by Gacoin and Leclercq¹⁷ are somewhat higher (0.1 eV) than the values obtained by us. These small differences may be due to the different number of states used in CI and due to small differences in geometry and symmetry considered by Gacoin and Leclercq for C_6H_5CHO . The transition energies for various states for benzaldehyde given by Aussems *et al.*¹⁸ are also in agreement with our calculated values.

So far the authors know, the data on 0-0 bands of hydroxybenzaldehydes are available neither in the gaseous state nor in the solution phase. However, the spectra of these molecules has been studied in 0.1N HCl by Lemon¹⁹ and the long wave UV absorption bands obtained by him bear correct order of magnitude agreement with our theoretical values (λ_{max} : p -OHC $_6H_4CHO$ — exptl 280 nm, our value 238 nm; m -OHC $_6H_4CHO$ —exptl, 317 nm, our value 298 nm).

The predicted n, π^* character for the lowest triplet of benzaldehyde is in agreement with various reported

results^{8,16,17}. However, the predicted character for lowest triplets of p - FC_6H_4CHO and m - FC_6H_4CHO is in conflict with that reported in literature¹⁶. As can be seen, our calculated $^3(n, \pi^*)$ level is higher than the lowest π, π^* triplet by only 0.03 eV in p - FC_6H_4CHO and by 0.06 eV in m - FC_6H_4CHO . These small differences between $^3(\pi, \pi^*)$ and $^3(n, \pi^*)$ are of the order of kT at room temperature. Consequently, thermal equilibration of the two states is facile and hence, both the states are likely to be populated. However, the photoreactivity of p - FC_6H_4CHO and m - FC_6H_4CHO is rationalized correctly (*vide infra*) on the basis of assignments that have been made by us. Regarding the character of the lowest state of hydroxy derivatives of aromatic carbonyls there is some controversy^{9,10,20}. Porter and Suppan⁹ and Godfrey *et al.*¹⁰ have suggested n, π^* lowest triplet for hydroxybenzophenones whereas Beckett and Porter²⁰ have reported π, π^* lowest triplet for p -OHC $_6H_4COC_6H_5$. We have predicted the same order of energy levels for p -OHC $_6H_4CHO$ as reported by Porter and Suppan⁹ for p -OHC $_6H_4COC_6H_5$. However, we predict a CT lowest triplet in the case of m -OHC $_6H_4CHO$.

Recent results of Wagner *et al.*,¹ on effect of substituents on $^3(n, \pi^*)$ and $^3(o, \pi^*)$ levels, are supported by our theoretical results. The n, π^* and π, π^* transition energies are affected to varying extents by substituents from *meta* and *para* positions. The substituents in *meta* position produce negligible effect on n, π energies, as shown below.

	$^1(n, \pi^*)$ transi- tion/eV	$^3(n, \pi^*)$ transi- tion/eV
C_6H_5CHO	3.06	2.84
m - FC_6H_4CHO	3.14	2.91
m -OHC $_6H_4CHO$	3.07	2.85

However the effect produced on π, π^* states is rather large as compared to that from the *para* position as shown below :

	$^3(\pi, \pi^*)$ transi- tion/eV	$^3(\pi, \pi^*)$ transi- tion/eV
C_6H_5CHO	3.74	
p - FC_6H_4CHO	3.74	m - FC_6H_4CHO 3.51
p -OHC $_6H_4CHO$	3.61	m -OHC $_6H_4CHO$ 3.30

Photoreactivity—This has been well established and understandable too, that the molecules with lowest $^3(n, \pi^*)$ are reactive towards photoreduction affecting inter-molecular or intramolecular hydrogen abstraction whereas those having lowest $^3(\pi, \pi^*)$ are comparatively photostable. On the basis of character of the lowest state only, our results predict that C_6H_5CHO should abstract hydrogen and it has been observed experimentally that it does so with sufficient quantum yield. However, experimental results on substituted benzaldehydes indicate that fluoro-substituted benzaldehydes show n, π^* reactivity which is contrary to our prediction. In fact, the nature of the lowest triplet is not the only deciding factor for photoreactivity. Many examples of n, π^* reactivity exhibited by molecules with lowest $^3(\pi, \pi^*)$ have been quoted in literature^{2,5,8,21-23}. In our results the energy gap between $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ is small enough to populate the higher lying $^3(n, \pi^*)$ from $^3(\pi, \pi^*)$. Consequently n, π^* reactivity is induced to the π, π^* state;

the extent of induction depending upon the energy gap between the two triplets. On these grounds our results predict that *p*-FC₆H₄CHO is more reactive than *m*-FC₆H₄CHO towards hydrogen abstraction. We have tried to explain the reactivity trends on the basis of energy difference between the low lying ³(π, π*) and the ³(n, π*) lying above in its vicinity. The Boltzmann factor, *Z*, defined as

$$Z = \exp - (E_{3n,\pi^*} - E_{3\pi,\pi^*})/kT \\ = \exp - [\Delta E_{trip}/RT]$$

has been considered as the measure of population of ³(n, π*) in the cases where it lies above the lowest lying ³(π, π*). For *m*-FC₆H₄CHO and *p*-FC₆H₄CHO the calculated *Z* values are respectively 0.0906 and 0.3227. This clearly implies that the magnitude of population of ³(n, π*) in *p*-FC₆H₄CHO is about 33% more than that in *m*-FC₆H₄CHO and hence the former is reactive. Indeed, the effect of substituent from the *meta* position has been reported to be considerable. If the electron withdrawing groups are to stabilize *n*, π* level and destabilize π, π* level as is generally believed, the fluoro derivatives should abstract hydrogen with higher quantum yield as compared to that of the parent molecule. But photo-yields of hydrogen abstraction in fluoro-derivatives of aromatic carbonyls are always found less or at the most comparable with that of the parent molecule. These observations can be fully explained on the basis of ordering of triplet levels predicted by our results.

Though a comparison of the characters of the lowest states of *p*-OHC₆H₄CHO and *m*-OHC₆H₄CHO correctly predicts latter to be less reactive in hydrogen abstraction reaction because it has CT type of lowest triplet, extremely low photoreactivity of *para* hydroxy carbonyl compounds is at complete variance with that expected on the basis of nature of the lowest state. This can be explained only if an alternate path is available to the excited singlet and ³(n, π*) remains unpopulated. On the basis of *pK* value of *p*-OHC₆H₄COC₆H₅ in the excited singlet Godfrey *et al*¹⁰ have shown that the lowest *n*, π* is in fact unpopulated and, hence, the hydroxy derivative lacks photoreactivity. Using Foster cycle and the calculated singlet energy values of *p*-OHC₆H₄CHO and its anion we have calculated the *pK** in the

excited singlet. It has been found that *pK** differs from *pK* in the ground state by 9.23 which indicates immediate deprotonation, even in the solutions of very low pH (<1). Once the excited molecule is deprotonated the population of the lowest³ (n, π*) is unlikely and hence the low reactivity in hydrogen abstraction reaction.

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