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Electronic Spectra and Structure of p-Benzoylquinone

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Abstract

Ground and excited state electronic structure and spectra of p-benzoylquinone have been studied using the variable electronegativity SCF-MO-Cl method. The calculated values of ionization potential and excitation energies are in good agreement with experiment. It is found that the electronic structure and geometry of the molecule are appreciably different in the excited $\pi \leftarrow \pi^*$ singlet state as compared to the ground state.

Introduction:

Several experimental and theoretical studies have been carried out on the electronic spectra and structure of the para-benzoylquinone molecule (1-8). While the results of earlier

semiempirical calculations are reasonably good, the choice of parameters is somewhat arbitrary. Therefore, it is desirable to have a formalism in which this arbitrariness does not exist. Such a formalism in the frame work of electron theories was developed long ago by Brown and Hefernan (9-10) and applied recently by various workers (11-13) on various types of molecules. However, no study with this method has been made on the quinones which form an important class of molecules of biological interest. It was therefore considered desirable to study p-benzoquinone using the variable electronegativity method of Brown and Hefernan coupled with the Pariser-Parr-Pople approximation as the first step. Ab-initio molecular orbital studies have also been made recently on p-benzoquinone (8). It is generally observed in such calculations that while $\pi^* \leftarrow \pi$ transitions can be easily explained, a satisfactory study of $\pi^* \leftarrow \pi^*$ transitions requires a much larger basis set (8-14) which would eventually increase the computer time. This also shows the desirability of studying π -electronic structure and spectra of quinones by semi-empirical theories that use improved parameterization schemes.

Method:

Details of the method of calculations are available elsewhere (11-13). The atomic ionization potentials and electron affinities which appear as parameters in the calculations are considered as parabolic functions of the Slater's effective nuclear charges (Z). Next a linear relationship is assumed between Z and the number of π -electrons (q_π) on given atom, then we get

$$\begin{aligned} \text{IP} &= k_0 + k_1 q \gamma + k_2 q \gamma^2 \\ \text{EA} &= l_0 + l_1 q \gamma + l_2 q \gamma^2 \end{aligned}$$

The constants of the parabolic function are evaluated by a least squares fitting of the I.P. and E.A. values in an iso-electronic sequence. The isoelectronic sequence chosen to calculate k_0 , k_1 , k_2 and l_0 , l_1 , l_2 for carbonyl oxygen was N^- , O , F^+ , Ne^{++} and Na^{+++} . The constants for carbon were the same as in the earlier work(12). The molecular geometry was taken from the literature (15). All singly excited configurations were included in the configuration interaction (CI) treatment.

Resonance (β) integrals were calculated from the Wolfsberg-Helmholz formula (16). One-centre and two-centre repulsion integrals were calculated using the (I.R.-E.A.) approximation and the Nishimoto-Mataga formula (17) respectively. The self-consistency was tested on the bond order matrix elements. In the first SCF calculation, the limit of the self-consistency was set equal to 10^{-3} and then the I.P. and E.A. values were changed and bond orders matrix elements again calculated through various cycles. When these became self-consistent up to 5×10^{-4} , iterations were terminated.

Results and Discussion:

The ionization potentials and electron affinities of atoms in the isoelectronic sequence of oxygen are given in Table 1 and were taken from the paper by Karlsson and Martensson (11). These were employed in calculating the constants k_0 , k_1 , k_2 and l_0 , l_1 , l_2 which are given in Table 2. The starting I.P.

Table 1

Ionization potentials and electron affinities for the iso-electronic sequence of oxygen

Atom or ion and valence state *	Effective Nuclear charge (z)	I:P(ev)	E.A.(ev)
$N^- (s^2 p^2 \underline{p} \underline{p})$	3.55	0.842	-
$O (s^2 p^2 \underline{p} \underline{p})$	4.55	14.613	2.013
$F^* (s^2 p^2 \underline{p} \underline{p})$	5.55	36.213	18.109
$Ne^{++} (s^2 p^2 \underline{p} \underline{p})$	6.55	65.450	41.919
$Na^{+++} (s^2 p^2 \underline{p} \underline{p})$	7.55	-	72.675

* The orbitals under consideration are underlined and $q=1$.

Table 2

Values of the constants obtained from least squares fitting

Constants	k_0	k_1	k_2	l_0	l_1	l_2
Values	21.30	-7.13	0.47	0.45	-5.30	6.83

and E.A. of oxygen are 14.64 and 1.98 eV respectively, while the values obtained at the end of the last SCF cycle are 13.72 and 1.33 eV respectively. The starting I.P. and E.A. of both

the carbons i.e. atoms numbered 2 and 3 (see Fig.1) are 11.19 and 0.01 eV respectively, while the final values of I.P. for the two carbons are 11.69 and 11.31 eV and for E.A. are 0.31 and 0.08 eV respectively. The net π -charge distribution is given in Table 4 on the various atoms and we see that the net +ve charge in the ground state on atom number 2 is more than that on atom number 3. Therefore, the electron affinity of atom number 2 is expected to be more than that of atom number 3 and this is reflected in the last I.P. and E.A. values of the two carbon atoms. This also justifies the I.P. and E.A. values as empirical parameters and shows that the method is able to take care of the changes in electron environments of the various atoms.

The ionization potential of the molecule evaluated by the Koopmans theorem at the end of the first SCF cycle is 10.18 eV while its value at the end of the last SCF cycle is 9.77 eV. The experimental value obtained by Vilesov (18) by photo-ionization method is 9.68 eV. Thus we see that while the theoretical value obtained by a fixed parameter approach would be appreciably different from the experimental value, the agreement is improved as the parameters are allowed to change.

The calculated electronic singlet transition energies and oscillator strengths along with the CI composition of excited state wave functions are given in Table 3. The experimental excitation energies (3) and those calculated by Wood (8) using an ab-initio method are compared with the present results in the same table. We found that the excitation energies do not change much after CI and the excited state wave functions may be satis-

Table 3

Excitation Energies

Calculated Excitation energy. (ev.)	Observed Excitation Energy (ev.)	Excitation Energy from Ref.(8) (ev.)	Oscillator strength.	CI composition of excited state wave functions
3.98	-	-	0.0	0.9950 (3→5)
4.11	4.07	7.5	1.3023	0.9791 (4→5)
5.44	5.13	7.9	0.0	0.9947 (4→6)
5.52	-	-	0.0	0.6882 (4→7) -0.7156 (2→5)

factorily represented by only one term. The calculated values of Wood are appreciably larger than the present results which are observed to be in a satisfactory agreement with experiment. It has been clearly indicated by Wood (8) that his choice of basis set is not adequate to calculate the $\Pi^* - \Pi$ excitation energies. Therefore, the large difference between the present and his results are not surprising. A similar observation regarding the basis set has been made by Del Bene *et al.* (14). The first two calculated excitation energies are quite close together and both are comparable to the lowest observed excitation energy but as the calculated oscillator strength of the first transition is zero, we assign the observed excitation energy to the second cal-

culated transition, which corresponds to an electron jump from the highest occupied to the lowest empty molecular orbital and has an appreciable calculated oscillator strength. Though the calculated oscillator strength for the third transition is zero, it may be assigned to the second observed excitation energy, assuming that some perturbation may make it allowed. This corresponds to an electron jump the highest filled to the next to the lowest empty molecular orbital.

The calculated net π -electronic charges on the various atoms, the bond orders for the different bonds for the ground and excited state are given in Table 4. The calculated net π -charges by Kuboyama (6) are compared with the present values. We find that the oxygen is negatively charged, while the two carbons are positively charged. While this is in qualitative agreement with earlier calculations, the present net charges are less than the earlier ones (6). This seems to be on account of the fixed parameter approach used in the earlier calculations. In fact in the present calculations also the net charges were appreciably larger at the end of the first SCF cycle, but when the parameters were allowed to change, the net charges decreased. The ground state bonds order for $C_1 - C_2$ and $C_2 - C_3$ bonds are compared with the values of Kuboyama (6). The two values are quite close together. We observe that the $C_1 - C_2$ and $C_2 - C_3$ bonds have single and double bond characters respectively in agreement with classical concepts.

The net π -charge distribution and bond orders are also given in Table 4 for the lowest observed singlet excited state.

Table 4
Ground and Excited state charges and Bond order*

	Bond	Bond order	Atom No.	Net charge
Ground state	1-2	0.86479	1	-0.15123(-0.500) ⁺
	2-3	0.33876(0.345) ⁺	2	+0.10136(+0.332) ⁺
	3-4	0.89268(0.873) ⁺	3	+0.2493(+0.084) ⁺
Excited State	1-2	0.62916	1	-0.11287
	2-3	0.46950	2	+0.03903
	3-4	0.71038	3	+0.03692

* The bond orders and charges for those bonds and atoms which are not included here, are to be determined from the molecular symmetry.

+ Values from A. Kuboyama, Bull. Chem. Soc. Japan 31, 752 (1958).

An examination of these reveals very interesting features. In the lowest excited state oxygen atom loses electronic charge while the carbon atom attached to it (C_1) gains the charge. There is some slight change in the charge at C_2 and it becomes more positive in the excited state as compared to the ground state.

Thus the total electronic charge on the C=O bond does not change appreciably due to the excitation but is almost localized on this bond.

We find that the bond orders for the C=O and C₂-C₃ bonds decrease as compared to the ground state values, while the C₁-C₂ bond order increases. The bond-orders are not so different together in the excited state as they are in the ground state. Thus it appears that the π -electron delocalization is increased in the excited state than in the ground state. It seems desirable to compare these features in the present results with those observed in substituted benzenes. In substituted benzenes, it is observed that all the C-C bond orders decrease and the C-X (x = substituent) bond orders increase in the excited state (12). This is known to be in agreement with experimental observations (19). Thus the peculiar observations here are the decrease in the C=O bond order and increase in the C₁-C₂ bond order. This shows that the C=O stretching frequency would decrease appreciably in the excited state as compared to the ground state. This is in agreement with experimental observations (20), the ground and excited state observed frequencies being 1667 and 1560 cm^{-1} respectively.

Hollas has carried out an extensive analysis of the electronic spectra of p-benzoquinone and he has also obtained geometry of the molecule in the $\pi^* \leftarrow \pi$ excited singlet state. He found the changes in bond lengths as $\Delta r_{\text{C}=\text{C}} = + 0.1 \text{ \AA}^\circ$, $\Delta r_{\text{C}-\text{C}} = -0.09 \text{ \AA}^\circ$ and $\Delta r_{\text{C}=\text{O}} = + 0.1 \text{ \AA}^\circ$. No experimental or theoretical analysis of this kind is available on the geometry of the molecule in the $\pi^* \leftarrow \pi$ excited states. In the present work it was thought desirable to

calculate excited state bond orders and thereby to predict the possible geometry changes in the molecule in the lowest $\pi^* \leftarrow \pi$ excited state. We find from the bond orders in the lowest excited singlet state that the C_2-C_3 bond length would increase, the C_1-C_2 bond length would decrease and the $C=O$ bond length would increase. Though we do not have any experimental value to compare with this prediction, we may compare these results qualitatively with the geometry changes given by Hollas for the singlet $\pi^* \leftarrow \pi$ state mentioned above, since the $\pi^* \leftarrow \pi$ excitation for the lowest excited state is also almost localized on the $C=O$ bond as mentioned back, like the transition of an n -electron. We find the present prediction is qualitatively in agreement with the results of Hollas.

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