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Molecules-in-Molecules Calculations on Some Conjugated Carbonyl Compounds

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The $\pi \rightarrow {}^1\pi^*$ and $n \rightarrow {}^{1,3}\pi^*$ transitions of some suitable conjugated carbonyl compounds have been investigated by the molecules-in-molecules method. The results are compared with experiment and previously obtained P-method results. The results for the $\pi \rightarrow {}^1\pi^*$ transitions agree well with experiment, but several unexplained features arise in the results for the $n \rightarrow {}^{1,3}\pi^*$ transitions. In particular, doubts are cast on the assignment of the glyoxal band at approximately 4.5 eV.

Die $\pi \rightarrow {}^1\pi^*$- und $\pi \rightarrow {}^{1,3}\pi^*$-Übergänge einiger substituierter Carbonylverbindungen sind mittels des Verfahren der Moleküle in Molekülen untersucht und mit früheren theoretischen sowie experimentellen Werten verglichen worden. Die Übereinstimmung ist im Fall der $\pi \rightarrow {}^1\pi^*$-Übergänge gut; bei den anderen verbleiben jedoch einige Unklarheiten, insbesondere in bezug auf die um 4,5 eV liegende Glyoxal-Bande.

Les transitions $\pi \rightarrow {}^1\pi^*$ et $n \rightarrow {}^{1,3}\pi^*$ de certains composés conjuguées carbonyles appropriés ont été étudiées par la méthode des molécules dans les molécules. Les résultats sont comparés à l'expérience et aux résultats obtenus auparavant par la méthode P. Les résultats pour les transitions $\pi \rightarrow {}^1\pi^*$ sont en accord avec l'expérience, mais plusieurs particularités non expliquées apparaissent dans les résultats relatifs aux transitions $n \rightarrow {}^{1,3}\pi^*$. En particulier, des doutes sont émis quant à l'attribution de la bande du glyoxal aux environs de 4,5 eV,

1. Introduction

If the amount of conjugation between the component systems R and S of a molecule RS is small it is usually possible to interpret its electronic spectrum in terms of the electronic spectra of the conjugated molecules RH and SH. Longuet-Higgins and Murrell [14] have developed a molecular orbital (MO) method, often called the molecules-in-molecules (MIM) method, which is specially suited for such cases. In the present work this method has been used to calculate the $\pi \rightarrow {}^1\pi^*$ and $n \rightarrow {}^{1,3}\pi^*$ transition energies of various conjugated carbonyl compounds; this is complementary to the P-method calculations carried out on these same molecules by the present authors [5]. As in this previous work the one-centre exchange repulsion term involving the lone pair and $2p_{\pi_o}$ orbitals on a given oxygen atom (γ_{on}^{ex}) was included to reproduce the $n \rightarrow \pi^*$ singlet-triplet splitting observed experimentally.

2. Theory

There are two classes of electronic transition to be considered: Charge (or electron) transfer between the occupied MOs of one component to the unoccupied

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MOs of another, and local excitation confined to one component. Formulae for the interactions between the resulting configurations are well known [14, 23].

The MOs of the component systems are taken as the π-electron self consistent field (SCF) MOs of RH and SH [5]. Where necessary the approximation is made that the states of RH and SH are fairly represented by a single configuration, or, where degeneracies occur, by an appropriate symmetry combination of configurations. The off-diagonal elements of the total configuration interaction (CI) matrix corresponding to interaction between locally excited configurations on the same component are zero, with the on-diagonal elements being given by the experimental transition energies of RH and SH. The other on-diagonal elements, corresponding to charge transfer, require the ionization potentials (I) and electron affinities (A) of RH and SH.

3. Justification for Using the MIM Method

The molecules treated in this work are given in Table 1 together with the corresponding component systems. That we may refer to a *long* bond in the composite molecule is in itself evidence of small conjugation between the components. Also, MO methods predict a smaller bond order, and hence conjugation, across the *long* bond than across the bonds in the components. Further, the π ionization potentials of the composite systems are very close to those of their component molecules, except for those of glyoxal and o-benzoquinone which are not known, and are readily interpretable in terms of ionization from localized orbitals on the components [29]. This latter observation is also true for the lone pair ionization potentials, except for that of o-benzoquinone which is not known [5, 29].

Table 1. *Component and composite systems for* MIM *calculations*

Composite system	Component systems
Glyoxal	2 × Formaldehyde
Acrolein	Formaldehyde + Ethylene
Benzaldehyde	Formaldehyde + Benzene
o-Benzoquinone p-Benzoquinone	2 × Acrolein
p-Benzoquinone	2 × Formaldehyde + 2 × Ethylene

4. Ionization Potentials and Electron Affinities

The ionization potentials of benzene (I_b) and ethylene ($I_{C=C}$) and the electron affinity of ethylene ($A_{C=C}$) are given in Table 2; these values have been used successfully in MIM calculations on styrene and biphenyl [7]. $A_{C=C}$ and $A_{C=O}$ (electron affinity of formaldehyde) are almost certainly negative so that a free electron will not attach itself to these molecules, thus making difficult a direct determination by experiment. The value of $A_{C=C}$ was obtained from an expression $I+A=$ constant which has been shown, both theoretically and practically, to be valid for even alternant hydrocarbons [9]. For MIM calculations on benzaldehyde Kimura and Nagakura [11] adjusted both $A_{C=O}$ and the resonance integral across the *long* bond to give the best overall agreement between the calculated and experimental $\pi \rightarrow {}^1\pi^*$ transition energies. Their use of $A_{C=O} = -1.2$ eV was regarded as being substantiated by its previous applicability in Nagakura's MIM calculation on acrolein [18]. Unfortunately, this is not the case since Nagakura obtained this value as the result of a mis-calculation. The value given by Nagakura to the charge transfer term E_{CT}^{A} can only be arrived at by interchanging the coefficients a and b in the anti-bonding MO of formaldehyde. When the correct MO is used a value of $A_{\mathrm{C=O}} = -1.78$ eV is required to reproduce Nagakura's results. Both of the above calculations included the ground state depression, but it has been argued [17] that if it is not too large ($\ngtr 0.4$ eV say) it may be neglected since improvement of the calculation by the inclusion of doubly excited configurations would tend to depress the excited states more than the ground state. It has been demonstrated for acrolein and glyoxal in this work that with the neglect of ground state depression a value of $A_{\mathrm{C=O}} < -1.78$ eV is required for agreement between the first calculated transition energies and the experimental bands at 6.41 eV and 7.4 eV respectively. For benzaldehyde a value of $A_{\mathrm{C=O}} = -2.2$ eV gives excellent agreement between the calculated and experimental transition energies when ground state depression is neglected, but if this depression is to be included it can be shown that a value of $A_{\mathrm{C=O}} > -1.2$ eV is required for equivalent agreement. That is, inclusion of ground state depression requires markedly different values of $A_{\mathrm{C=O}}$ for acrolein (and glyoxal) and benzaldehyde, whereas the neglect of this depression necessitates an $A_{\mathrm{C=O}}$ value which is reasonable for all three molecules. For the foregoing reasons ground state depression has been neglected. For glyoxal and acrolein better agreement would be obtained using $A_{\mathrm{C=O}} < -2.2$ eV, but the value of -2.2 eV was adopted because of its applicability to benzaldehyde.

It is not known whether the P-method will afford reliable results for the electron affinities of hetero-molecules; certainly the empirical value of $A_{\mathrm{C=O}} = -2.2$ eV compares poorly with the calculated value of -0.53 eV for formaldehyde [5]. The electron affinity of acrolein (A_{acr}) was given the two empirical values of -1.2 eV and -2.2 eV, either of these values appearing to be realistic in view of the value adopted for $A_{\mathrm{C=O}}$. Since the MIM results were essentially the same for both cases only those for the former have been presented. An empirically chosen value for the second electron affinity of acrolein would introduce a further uncertainty, and in view of the high energies of the charge transfer configurations involving this parameter the error resulting from its neglect will almost certainly be small. The lone pair ionization potential (I_n) in Table 2 is that of formaldehyde.

Previous MIM calculations on carbonyl compounds [11, 18] neglected charge transfer configurations involving $I_{\mathrm{C=O}}$, the assumption being that these con-

Table 2. *Ionization potentials* (I) *and electron affinities* (A) *of the component systems* (eV)

$I_{\mathrm{C=C}}$ [7]	I_b [19]	$I_{\mathrm{C=O}}$ [29]
10.45	9.52	14.4
$I_{1\mathrm{acr}}$ [29]	$I_{2\mathrm{acr}}$ [29]	$A_{\mathrm{C=C}}$ [7]
11.07	14.87	-1.54
$A_{\mathrm{C=O}}$	A_{acr}	I_n [29]
-2.2	-1.2	10.86

figurations would be of too high an energy to mix in appreciably with the other configurations. This assumption has been shown to be valid for all the molecules in this work except glyoxal, but it is to be remarked that this is largely due to the use of a more recent experimental value of $I_{C=O}$ [29] which is 2.6 eV larger than that previously reported [28]. Thus, charge transfer configurations involving $I_{C=O}$ were considered for glyoxal only.

5. $\pi \rightarrow {}^1\pi^*$ Transitions

It should be noted that in the subsequent presentation of data and results that E (calc.) and E (expt.) are the calculated and experimental transition energies in eV; M_x and M_y are the transition dipole moments and f is the oscillator strength.

The SCFMOs of the component molecules are given in Table 3; the experimental transition energies of the component molecules and the configurations to which they are assigned are given in Table 4.

It will be seen later that the p-benzoquinone (2 × ethylene + 2 × formaldehyde) calculation was in no way successful, and consequently the analogous treatment of o-benzoquinone was not carried out.

The MOs and locally excited configurations of acrolein need special attention for the following reasons. a) The lowest state energies and the contribution of the main configuration to these states obtained from P-method calculations [5] are 5.51 eV (98% ${}^1\Psi_2^3$) and 6.79 eV (83% ${}^1\Psi_1^3$). The interconfigurational energies differ by less than 0.3 eV from the state energies, thus justifying the simplification

Table 3. SCFMOs *of the component molecules*

Ethylene	$\theta_1 = (\phi_1 + \phi_2)/\sqrt{2} \quad \theta_2 = (\phi_1 - \phi_2)/\sqrt{2}$
Formaldehyde	$\omega_1 = a\phi_1 + b\phi_2 \quad \omega_2 = b\phi_1 - a\phi_2$
	$a = 0.4858, \quad b = 0.8741$
Benzene[a]	$\psi_2 = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$
	$\psi_3 = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2$
	$\psi_4 = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2$
	$\psi_5 = (-2\phi_1 + \phi_2 + \phi_3 - 2\phi_4 + \phi_5 + \phi_6)/\sqrt{12}$
Acrolein	$\theta_1 = 0.2882\,\phi_1 + 0.4163\,\phi_2 + 0.5169\,\phi_3 + 0.6903\,\phi_4$
	$\theta_2 = 0.6039\,\phi_1 + 0.5823\,\phi_2 - 0.0886\,\phi_3 - 0.5370\,\phi_4$
	$\theta_3 = -0.6174\,\phi_1 + 0.3652\,\phi_2 + 0.5752\,\phi_3 - 0.3932\,\phi_4$
	$\theta_4 = 0.4136\,\phi_1 - 0.5951\,\phi_2 + 0.6278\,\phi_3 - 0.2838\,\phi_4$

[a] ψ_1 and ψ_6 are not given since they are not necessary to afford a good interpretation of the benzene electronic spectrum [3].

Table 4. *The experimental* $\pi \rightarrow {}^1\pi^*$ *transition energies of the component molecules and the configurations to which they are assigned*

	Configuration	E (expt.)	f
Benzene [12]	$\Psi_{B_{2u}} = (\psi_3^{-1}\psi_5 - \psi_2^{-1}\psi_4)/\sqrt{2}$	$E_\alpha = 4.71$	0.002
	$\Psi_{B_{1u}} = (\psi_3^{-1}\psi_4 + \psi_2^{-1}\psi_5)/\sqrt{2}$	$E_p = 5.96$	0.10
	$\Psi_{E_{1u}} = (\psi_3^{-1}\psi_5 + \psi_2^{-1}\psi_4)/\sqrt{2}$	$E_\beta = 6.76$	0.69
	$\Psi_{E'_{1u}} = (\psi_3^{-1}\psi_4 - \psi_2^{-1}\psi_5)/\sqrt{2}$	$E_{\beta'} = 6.76$	
Ethylene [22]	$\theta_1^{-1}\theta_2$	7.60	
Formaldehyde [34]	$\omega_1^{-1}\omega_2$	7,92	
Acrolein [30]	$\theta_2^{-1}\theta_3$	6.41	
	$\theta_1^{-1}\theta_3$	8.49	

adopted in this work of approximating the acrolein states by single configurations. As will be discussed in Section 8 (*i*) *a*) the previously unassigned experimental band in the acrolein spectrum at 8.49 eV will be assigned to the configuration $^1\Psi_1^3$. b) The MO's of acrolein are taken as a good description of this molecule, although since there are no criteria for directly assessing the quality of π-electron MO's this is necessarily an assumption. Certainly, the poor agreement between the P-method results and the experimental transition energies cannot be taken as a condemnation of the MO's since this may be due to other factors. For example, if we were to change the values for the electron repulsion integrals the CI matrix elements, and hence the calculated transition energies, would be altered, but this would occur predominantly through the *actual* change in these integral-values rather than through the accompanying change in the MO's. c) That the acrolein MO's are not symmetry MO's of p-benzoquinone is a serious error since this implies that in this composite system there are three different paris of equivalent carbon atoms, a contradiction of the known geometry of p-benzoquinone. This unsatisfactory feature will be retained since there is an accompanying simplicity of calculation, and the error involved is consistent with the already qualitative nature of the calculation. With o-benzoquinone this error does not arise.

6. $n \rightarrow \pi^*$ Transitions

It is believed that MIM calculations on $n \rightarrow \pi^*$ transitions have been attempted only once previously [16].

The calculation of the $n \rightarrow \pi^*$ singlet and triplet energies has been carried out in this work for benzaldehyde, glyoxal and acrolein. Since, as will be shown later, the MIM method does not give a good description of the $\pi \rightarrow {}^1\pi^*$ electronic spectra of o- and p- benzoquinone the $n \rightarrow \pi^*$ transition energies of these molecules have not been calculated.

For acrolein, say, an $n \rightarrow \pi^*$ transition from the lone pair orbital to the unoccupied MO of the carbonyl group could be termed charge transfer, but in keeping with the spirit of the method this will be termed a local excitation since it is excitation within the carbonyl component of the system and may be equated to the formaldehyde $n \rightarrow \pi^*$ transition energy. Taking acrolein as an example $(n^{-1}\omega_2|\mathscr{H}|n^{-1}\omega_2)$ may be equated to either the experimental singlet [27] or triplet [2] $n \rightarrow \pi^*$ transition energies of formaldehyde, or it may be equated to $I_n - A_{\mathrm{C=O}} + 2(n\omega_2|n\omega_2) - (nn|\omega_2\omega_2)$ for the singlet and to $I_n - A_{\mathrm{C=O}} - (nn|\omega_2\omega_2)$ for the triplet. This double equality for the $n \rightarrow \pi^*$ singlet and triplet energies will be made in all cases. It should be noted that for a given molecule the other on-diagonal term(s) and all the off-diagonal terms are the same for both the singlet *and* triplet CI matrices in *both* equalities.

7. Method of Calculation

The one- and two-centre parameter-values and the SCFMO's of formaldehyde and acrolein were obtained as described previously [5]. A program had been written to compute all the P-method CI elements from Hückel MO's. By a suitable adjustment of data all the CI elements required for the MIM calculations of the $\pi \rightarrow {}^1\pi^*$ transition energies, and the contributions from each configuration to the transition moments were obtained. The $n \rightarrow {}^{1,3}\pi^*$ CI elements were readily calculated by hand. The $n \rightarrow {}^{1,3}\pi^*$ and $\pi \rightarrow {}^{1}\pi^*$ CI matrices were set up and diagonalized, by which procedure the state energies and the contributions of each configuration to each state were obtained. These computations were carried out on the University Elliot 503 computer. The results are given in Tables 5–8.

Table 5. $\pi \rightarrow {}^{1}\pi^*$ *transition energies of acrolein and glyoxal*

	Main configs.	E (calc.)	M_x	[a]M_y	[b]f	E (expt.)
Acrolein [30]	Ψ_0	-0.53				
	$\theta_1^{-1}\omega_2, \quad \theta_1^{-1}\theta_2$	5.91	0	0.76	0.45	6.41
	$\omega_1^{-1}\omega_2, \quad \theta_1^{-1}\theta_2$	7.82	0	-0.11	0.01	8.49
	$\theta_1^{-1}\theta_2, \quad \theta_1^{-1}\omega_2$	8.96	0	-0.94	1.05	
Glyoxal [33]	Ψ_0	-0.30				
	$\omega_1^{-1}\omega_2 - \theta_1^{-1}\theta_2$	6.82	0.90	0	0.74	~7.4
	$\omega_1^{-1}\omega_2 + \theta_1^{-1}\theta_2$	7.53	0	0	0	

[a] Axis parallel to carbonyl group.

[b] Ground state taken as Ψ_0 (actually, acrolein 93% Ψ_0, glyoxal 97% Ψ_0).

Table 6. $\pi \rightarrow {}^{1}\pi^*$ *transition energies of benzaldehyde*

	Main configs.	E (calc.)	[a]M_x	M_y	[b]f (calc.)	E (expt.)	f (expt.)	Polar. [25]
Benzaldehyde [11]	Ψ_0	-0.34						
	$\Psi_{B_{2u}}(\alpha)$	4.48	-0.003	0.12	0.01	4.52	0.02	y
	$\Psi_{B_{1u}}(p), \theta_2^{-1}\omega_2$	5.37	0.54	0.11	0.22	5.35	0.26	x
	$\Psi_{E_{1u}}(\beta), \theta_3^{-1}\omega_2$	6.28	-0.47	0.84	0.78	6.35	1.7	
	$\Psi_{E'_{1u}}(\beta'), \Psi_{B_{1u}}(p)$	6.34	0.87	0.64	0.99	6.68		
	$\Psi_{E'_{1u}}(\beta'), \theta_2^{-1}\omega_2$	7.75	-0.63	0.16	0.45	6.97		
	$\Psi_{E_{1u}}(\beta), \theta_3^{-1}\omega_2$	7.89	-0.24	0.95	1.01	7.50		

[a] Long axis-through *long* bond. [b] Ground state taken as Ψ_0 (actually 95% Ψ_0).

Table 7. $\pi \rightarrow {}^{1}\pi^*$ *transition energies of o- and p-benzoquinone*

	2 × Acrolein E (calc.)	[a]M_x	M_y	[b]f	2 × Ethylene + 2 × Formaldehyde E (calc.)	E (expt.)	absorbance
p-Benzoquinone [24]	-0.38				-1.53		
	4.91			0	4.37	4.28	200
	5.28	1.26	0.27	1.18	4.37	5.07	24,000
	7.45						

	2 × Acrolein E (calc.)	E (expt.)
o-Benzoquinone [6]	-0.47	
	3.91	3.5
	6.59	4.9
	7.04	6.2

[a] Long axis (through carbonyl groups). [b] Ground state taken as Ψ_0 (actually 95% Ψ_0).

Table 8. *$n \rightarrow \pi^*$ transition energies with on-diagonal* CI *terms equated to* (*A*) *the experimental formaldehyde $n \rightarrow \pi^*$ transition energies, and* (*B*) *the expressions involving I_n and $A_{C=O}$*

	E (calc.)				*E* (expt.)	
	A		*B*			
	$n \rightarrow {}^1\pi^*$	$n \rightarrow {}^3\pi^*$	$n \rightarrow {}^1\pi^*$	$n \rightarrow {}^3\pi^*$	$n \rightarrow {}^1\pi^*$	$n \rightarrow {}^3\pi^*$
Glyoxal [1, 15, 20, 33]	3.63	2.48	3.26	2.88	2.7	2.4
	8.36		8.30		~4.5	
Acrolein [4, 30]	3.81	2.63	3.46	3.41	3.76	3.01[a]
	8.01		7.96		8.38	
Benzaldehyde [10]	3.96	2.75	3.65	3.25	3.41	3.17

[a] Very weak magnetic rotation band, possibly spurious (?).

8. Discussion of Results

(*i*) $\pi \rightarrow {}^1\pi^*$ *Transitions*

a) *Acrolein and Glyoxal.* Nagakura [18] professes to quote Walsh [30] when he says that the 1480 Å (8.38 eV) and 1460 Å (8.49 eV) bands in the acrolein spectrum arise from $\pi \rightarrow {}^1\pi^*$ transitions. However, Walsh has stated quite clearly that he believes the 8.38 eV band to arise from the second $n \rightarrow {}^1\pi^*$ transition, and although he has remarked on the correspondence of the 1460 Å band with the 1470 Å band in the acetaldehyde spectrum [31] no assignment was suggested. The $n \rightarrow {}^1\pi^*$ assignment for the 8.38 eV band is supported by both the P- and MIM calculations. It would seem reasonable to suggest the possibility of the 8.49 eV band arising from a $\pi \rightarrow {}^1\pi^*$ transition. Certainly, it does not seem reasonable to assign both these bands to $\pi \rightarrow {}^1\pi^*$ transitions since both the P-method and MIM method in the range of $A_{C=O}$ values from -1.4 eV to -2.2 eV give a separation between the second and third $\pi \rightarrow {}^1\pi^*$ transition energies of greater than 1 eV. Consequently, in the MIM calculations on o- and p-benzoquinone (2 × acrolein) the 8.49 eV band is assigned to the configuration ${}^1\Psi_1^3$. For the same reason the unassigned doublet at 1600 Å (7.75 eV) cannot be assigned to $\pi \rightarrow {}^1\pi^*$ transitions. This latter conclusion is supported by Walsh's remark that the absorption in the region 1550–1700 Å (8.0–7.3 eV) is weak, whereas the third transition may be shown, in both the P- and MIM methods, to be highly allowed.

The 7.4 eV band in the glyoxal spectrum has been assigned to the lowest $\pi \rightarrow {}^1\pi^*$ transition energy. The next $\pi \rightarrow {}^1\pi^*$ transition is predicted to be forbidden by both the MIM and P-methods, which may well be the reason why it is not observed.

b) *Benzaldehyde.* The present results for the first three bands in the benzaldehyde spectrum (other than the $n \rightarrow \pi^*$) are in excellent agreement with experimental transition energies, oscillator strengths and the limited polarization data available. Shimada and Goodman [25] have concluded that the first $\pi \rightarrow {}^1\pi^*$ band is predominantly of benzene α band character, a conclusion supported by the present calculations which give 90% α character to the lowest state. These workers also concluded that the second $\pi \rightarrow {}^1\pi^*$ transition contained much of a benzene-to-carbonyl charge transfer configuration, a conclusion partially supported by the present calculations which give 52% *p* character and 28% of the charge transfer configuration $\psi_2^{-1}\omega_2$ to the second lowest state. Further, Walsh [32] has assigned the third experimental band, which is the strongest in the spectrum, to a transition consisting mainly of benzene β character. This is in fair agreement with the intense calculated band at 6.28 eV which consists of 53% β. While the first six calculated and experimental transition energies given in Table 6 are very similar it is far from conclusive that all these experimental bands arise from $\pi \rightarrow {}^1\pi^*$ transitions, but it is interesting to note that the P-method results and the MIM method results of Kimura and Nagakura are in similar agreement with experiment.

c) p-Benzoquinone. 2 ethylene + 2 formaldehyde components: The large ground state depression of -1.53 eV will necessarily be a feature of any description of a molecule in terms of more than two components since this involves a large number of charge transfer-ground configuration interactions. The first two transition energies are accidentally degenerate (4.37 eV), a result which is retained when interactions involving the ground configuration are put to zero. Both these features have been shown to be independent of the value chosen for $A_{C=O}$ in the range -1.4 to -2.2 eV. It can only be concluded that this treatment of p-benzoquinone involving four component systems is too drastic an approach in view of the smallness of the molecule, in spite of the ease with which the p-benzoquinone ionization potentials may be equated to ionization from localized orbitals.

2 acrolein components: The cause of the present poor results is not known. However, these results do offer a qualitative interpretation of the p-benzoquinone spectrum. The first transition is predicted to be forbidden, whereas the second is predicted to be highly allowed with a large transition moment along the long axis (x) and a very small component along the short axis (y). While a small transition moment along the y axis is not observed experimentally this can be readily understood as arising from an error in the calculation in that the acrolein MO's are not symmetry MO's of p-benzoquinone.

d) o-Benzoquinone. 2 acrolein components: The results for o-benzoquinone are in very poor agreement with experiment.

It is felt that the poor results for o- and p-benzoquinone (2 × acrolein) arise from the large number of approximations involved, and that a more detailed calculation would yield much improved results. The agreement for p- benzoquinone, such as it is, is regarded as being largely fortuitous.

(ii) $n \rightarrow \pi^*$ *Transitions*

The agreement between experiment and both calculations A and B is generally poor. Let us firstly consider the lowest $n \rightarrow {}^1\pi^*$ and $n \rightarrow {}^3\pi^*$ transitions. That calculations A give $n \rightarrow \pi^*$ singlet-triplet splittings larger than observed is readily understood. The experimental energies given in Table 8 are for the vertical transitions (band envelope maxima) since it is generally believed that it is these transitions which should be compared with calculation. However, the 3.0 eV band of formaldehyde does not correspond to such a transition, whereas the 4.3 eV band does. In formaldehyde the shapes of the two excited states are very similar [17], so there should be little difference between the singlet-triplet splittings of the

0–0 bands and of the envelope maxima. Since the singlet-triplet splitting of the 0–0 bands is 0.37 eV [8] we might "deduce" that the *vertical* $n \rightarrow {}^3\pi^*$ transition energy is 3.93 eV. If this latter value were adopted the calculated singlet-triplet splittings from *A* would be in closer agreement with experiment. At the same time, however, the agreement between the calculated and experimental transition energies of glyoxal would be worsened, for which feature no explanation is offered. Calculations *B* give singlet-triplet splittings in fair agreement with calculation, although the magnitude of the $n \rightarrow \pi^*$ transition energies is hardly improved.

Let us now consider the second $n \rightarrow {}^1\pi^*$ transitions of glyoxal and acrolein. For glyoxal both calculations *A* and *B*, like the P-method calculation, give an energy some 4 eV greater than observed. This compares with calculations *A* and *B* giving an energy for the corresponding transition in acrolein which is in excellent agreement with experiment, and while the P-method does not give such good agreement the sense of the deviation is the same as for the first $n \rightarrow {}^1\pi^*$ transition. Also, it was found in the P-method calculations on a wide range of conjugated carbonyl compounds that all the first $n \rightarrow {}^1\pi^*$ transition energies were improved by making reasonable changes in the values of two quite different parameters. While the second $n \rightarrow {}^1\pi^*$ transition energy of acrolein was also improved, in both cases the energy of the corresponding transition in glyoxal was worsened. Further, all the parameter values used in the MIM method have been reasonably successful in the P-method calculations, except, of course, $A_{C=O}$. However, it is quite clear that to predict the second $n \rightarrow {}^1\pi^*$ transition of glyoxal to be in the region of 4.5 eV would require an unreasonably large change in the value of $A_{C=O}$. It is quite apparent that the poor agreement between experiment and calculation for the second $n \rightarrow {}^1\pi^*$ transition in glyoxal is not readily explained. In view of the good agreement between experiment and calculation for the corresponding transition in acrolein, and the excellence of the agreement between the P- and MIM-method results for glyoxal one is inclined to look more closely at this 4.5 eV band in the glyoxal spectrum. That this band arises from an impurity is not considered seriously since the corresponding band has been observed for a number of cyclic α, β-diketones [13]. It is interesting that for biacetyl [26] this band does not show the characteristic shift of $n \rightarrow \pi^*$ transitions as the polarity of the solvent is changed; this result has not, as yet, been demonstrated for glyoxal or the above cyclic α, β-diketones. It is felt that the lack of agreement between the experimental band at 4.5 eV in the glyoxal spectrum and the calculated second $n \rightarrow {}^1\pi^*$ transition energy may be due to a wrong assignment but that any attempt at re-assignment on the basis of the results presented here is unjustifiable.

9. Conclusions

The results for the $\pi \rightarrow {}^1\pi^*$ transition energies are in fair agreement with experiment, except for those of o- and p-benzoquinone. The causes of these latter poor results have not been firmly established.

For the $n \rightarrow \pi^*$ transitions two interesting features emerge. One is that there appear to be no values for the vertical $n \rightarrow {}^{1,3}\pi^*$ transition energies of formaldehyde which will give good results for acrolein, benzaldehyde *and* glyoxal, at least to the level of sophistication at which we have carried out the calculations. The other is that the 4.5 eV band of glyoxal is not predictable as arising from the second $n \rightarrow {}^1\pi^*$ transition. An experimental verification of this assignment would be of interest, especially as this band appears to have been assigned solely on the basis of its low intensity.

Further calculations on the more suitable condensed ring carbonyl compounds are in progress.

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