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THE ELECTRONIC STRUCTURE OF POLYENES AND UNSATURATED CARBONYL COMPOUNDS[1]

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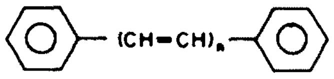
Abstract—PE spectra of polyene aldehydes are reported and discussed on the basis of a semiempirical LCFO-MO treatment within the π electron approximation. The necessary parameter values including the CC bond alternation were obtained by fitting PPP orbital and transition energies to the PE and UV data of diphenyl polyenes and polyene aldehydes. Thus, for planar systems the assignment of a PE band near 13.5 eV to the π orbital of the CO group could be given, which could be confirmed by the LCFO-MO calculations and by results from *ab initio* calculations, and which forms the basis of a discussion and comparison of π orbital interactions in planar unsaturated carbonyl compounds and hydrocarbons.

UV photoelectron (PE) spectroscopic investigations of organic molecules have produced a wealth of data supporting the molecular orbital model.[2] This is particularly true for unsaturated hydrocarbons, where, e.g. the consequences of "through space" and "through bond" interactions[3] clearly show up in the PE spectra and could be discussed in terms of semilocalized bonding orbitals[4] within the framework of an LCBO model (linear combination of bonding orbitals). This model together with the notion of correlation diagrams constructed in order to reveal the interaction of the semilocalized bonding orbitals constitutes one of the basic tools of organic photoelectron spectroscopy.[5] Apart from the π systems of hydrocarbons and their interactions with each other as well as with Walsh orbitals[6] or substituent orbitals[7] the heteroatom lone pairs have been of major interest in organic PE investigations,[8] but surprisingly little is known, e.g. about π orbital of the CO group[9,10] and its interactions with neighbouring π systems in unsaturated carbonyl compounds,[11–13] because in general it is quite difficult to assign a PE band unambigously to an ionization from this orbital, due to the fact that it is expected in a region of the spectrum where many bands overlap strongly. Furthermore, in consequence of the large difference in energy between the π orbitals of a CC bond and those of the CO group first order perturbation treatments are no longer applicable, so that in contrast to the LCBO model for hydrocarbons unoccupied orbitals have to be taken into account in discussing π orbital interactions in unsaturated carbonyl compounds.[11]

Recently we developed an LCFO-MO procedure[14] which within the Pariser–Parr–Pople (PPP) approximation[15] allows for the direct calculation of correlation diagrams in a self-consistent way, using experimental values for the ionization potentials (IP) and electron affinities (EA) of the fragments. In the present paper we will show that the electronic structure of unsaturated carbonyl compounds can be explained quite naturally by means of the LCFO-MO-model, taking into account the $\overset{*}{\pi}_{CO}$ orbital as the only unoccupied orbital. The determination of the semiempirical parameters which enter the LCFO-MO treatment will be achieved in such a way, that the orbital energies obtained by conventional PPP calculations reproduce within the framework of Koopmans' approximation[16] the experimental IP's which may be attributed to π electrons. To confirm the choice of parameters obtained by this procedure and the assignment based thereupon the LCFO-MO model is applied using theoretical as well as experimental values for the fragment orbital energies. Thus, the aim of the present paper is to discuss the different π orbital interactions in unsaturated hydrocarbons and carbonyl compounds as well as to test the validity and the applicability of the LCFO-MO method and to lay the foundations of further applications.

Photoelectron spectra. The PE spectra of the diphenyl polyenes 1 have previously been reported by Hudson *et al.*[17] Table 4 contains for comparison with calculated orbital energies the vertical IP values $I_v(i)$ for 1 (n = 1–3) obtained in the present investigation, which essentially agree with the values given in Ref. 17. Pentadienal 2 (n = 2) was obtained from crotonaldehyde by means of an aldol condensation with acetaldehyde[18] and octatrienal 2 (n = 3) was obtained from 2 (n = 2) by a Wittig reaction with formylmethylenetriphenylphosphoran.[19] The PE spectra of the polyene aldehydes 2 (n = 1–3) are given in Fig. 1 and $I_v(i)$ values are collected in Table 2. All spectra were recorded on a modified PS-16 spectrometer (Perkin–Elmer Ltd., Beaconsfield, England), the accuracy is ± 0.03 eV.



1

$CH_3-(CH=CH)_n-CHO$

2

PPP calculations. In order to determine the parameters which enter the LCFO-MO calculations described in the following section, we use the PPP method in the standard form[21] with core integrals given by the Goeppert-Mayer and Sklar approximation

$$h_{\mu\mu} = \alpha_\mu = U_\mu - \sum_{\nu \neq \mu} Z_\nu \gamma_{\mu\nu} \quad \text{and} \quad h_{\mu\nu} = \beta_{\mu\nu} \text{ or } 0. \qquad (1)$$

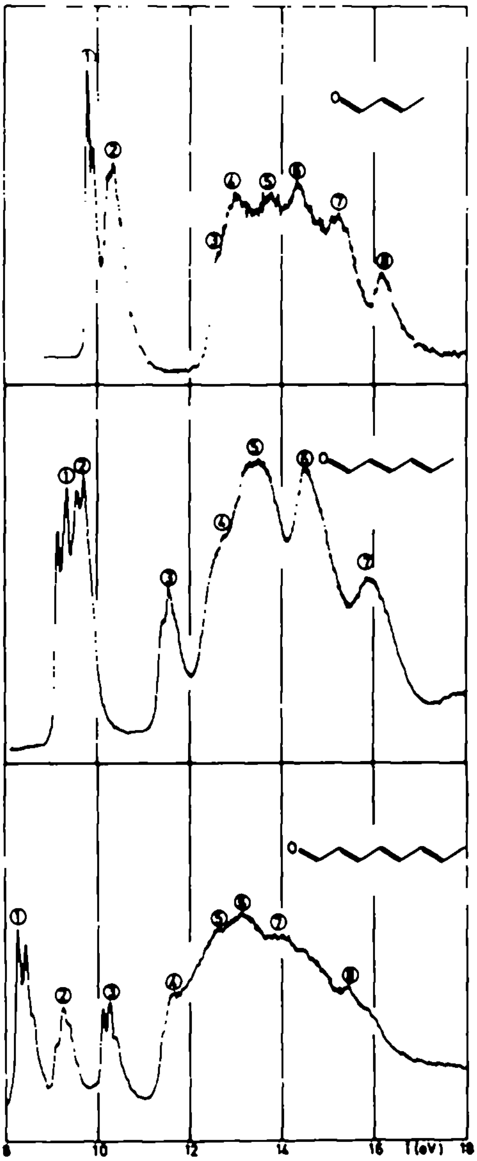


Fig. 1. He(I) photoelectron spectra of crotonaldehyde, pentadienal and octatrienal.

Electron interaction integrals are calculated from Mataga formula[22]

$$\gamma_{\mu\nu}^{(XY)} = 1/(a_{XY} + r_{\mu\nu}) \quad \text{with} \quad 1/a_{XY} = (\gamma_{\mu\mu}^{(X)} + \gamma_{\mu\mu}^{(Y)})/2, \qquad (2)$$

with one-center $\gamma_{\mu\mu}^{(X)}$ values given by the Pariser relation.[23] Thus for hydrocarbons only β_{CC} remains to be fixed, U_C being an additive constant which is entirely determined by the choice of the zero of energy. From the difference of the UV spectra of polyenes and cyanines it is known[24] that bond alternation may be rather important in determining the electronic structure of polyenes. We therefore set the length of the formal single and double bonds in the polyenes equal to:

$$r = 140 \pm \Delta r \qquad (3)$$

and take for the r dependence of β_{CC} the formula:

$$\beta_{CC}(r) = -17.464 \times 10^{12}/r^6 \text{ eV} \qquad (4)$$

Table 1. Parameter values for π electron calculations on unsaturated carbonyl compounds

	[eV]		[pm]
U_C	− 9.85	$r_{CC}(ar)$	140
U_O	−18.25	$r_{C=C}$	137.5
γ_{CC}	11.08	r_{C-C}	142.5
γ_{OO}	14.52	r_{CO}	121.4

$\beta_{CC} = -17.464 \cdot 10^{12}/r^6$ [eV]

$\beta_{CO} = -8.8086 \cdot 10^{12}/r^6$ [eV]

proposed by Kon,[25] which corresponds to $\beta_{CC} = -2.32$ eV for the benzene CC bond with $r = 140$ pm.

In Fig. 2 the orbital energies of diphenylbutadiene 1, (n = 2) and diphenylhexatriene 1, (n = 3) are given as a function of Δr. Agreement between the computed orbital energy differences with the corresponding differences of IP's as given by the PE spectra is obtained for Δr = 2.5 pm, corresponding to r = 142.5 pm and r = 137.5 pm for the single and the double bonds respectively. It should be emphasized, that according to the procedure chosen these r values have no physical meaning apart from determining the β values through eqn (4). By equating the computed orbital energies with the negative IP's the additive constant U_C is determined as $U_C = -9.85$ eV.

If the method is to be applied to unsaturated carbonyl compounds using again the Pariser relation to determine the one-center electron interaction integrals, two additional parameters U_O and β_{CO} are needed. In contrast to the hydrocarbons the assignment of the experimental IP's to π orbitals is not straightforward in the case of unsaturated carbonyl compounds, as there is the oxygen lone-pair orbital n_O which may be found among the π MO's, and the lowest π MO belonging mainly to the CO group is expected to lie among the σ ionizations.[11] Thus

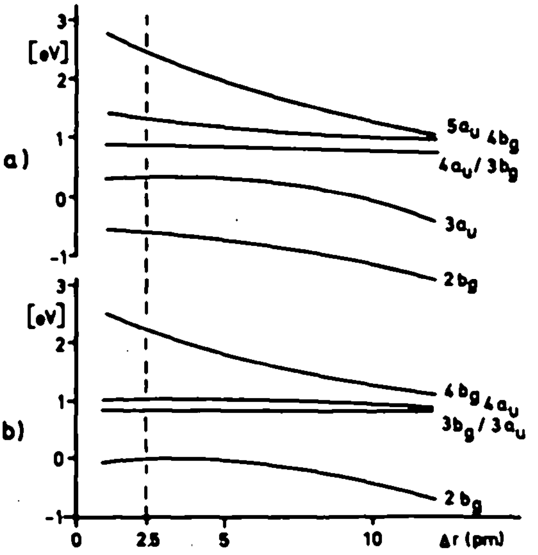


Fig. 2. Relative PPP orbital energies ϵ_i viz. bond alternation Δr for (a) diphenyl hexatriene and (b) diphenylbutadiene. Best agreement with spacing of PE bands is obtained for Δr = 2.5 pm.

the determination of suitable parameter values is slightly more involved.

From a set of trial calculations for linear polyene aldehydes it is seen that with increasing absolute value of U_O all π orbitals are stabilized, whereas β_{CO} leaves all occupied π orbitals except the lowest one more or less unaffected, so that from the first π ionizations of the polyene aldehydes U_O can be fixed. If the ionization close to 9.5 eV, i.e. the first PE band of 1, ($n = 1$), but the second band of 1, ($n = 2$) and ($n = 3$), is assigned to the n_O orbital, this leads to a value $U_O = -18.25$ eV which is well within the range of values proposed in the literature.[26] The β_{CO} cannot be fixed from the PE spectra as this would require an assignment of the lowest π MO. But if we choose β_{CO} such that the lowest calculated singlet transition energy reproduces the experimental energy of the first π–π^* transition,[18] we obtain $\beta_{CO} = -2.75$ eV.

The final parameter set is collected in Table 1, the results obtained from the PPP calculations for the polyene aldehydes are given in Table 2 together with experimental IP values of 2 ($n = 1$–3) and their assignment corresponding to the theoretical results. Before discussing this data we will report the LCFO–MO calculations.

LCFO–MO *calculations*. The LCFO–MO method is an SCF procedure based on linear combinations of fragment orbitals (FO's), which allows for the inclusion of experimental IP's and EA's of the fragments within the evaluation of the diagonal elements of the Fock matrix and for the truncation of the basis set so that only a few or even none of the unoccupied FO's may be included in the calculation. This method has been described in detail in a previous paper,[14] and here we give only the results of an application to polyenes, diphenylpolyenes and polyene aldehydes.

In Table 3 the results for some simple polyenes are collected. They were obtained by using as FO's ϕ_I the occupied and the unoccupied π MO of the ethylene fragment and the occupied π MO's and the lowest unoccupied one of the butadiene fragment respectively. The orbital energies e_I of the occupied FO's ϕ_I were taken to be:

$$e_I = -I_v(I) + 0.4/n_{occ}, \qquad (5)$$

with n_{occ} being the number of occupied FO's (OFO) of the fragment under consideration; the $I_v(I)$ values were taken from PE data[29] and the second term takes into account the σ inductive perturbation associated with the combination of the fragments.[14] For the lowest unoccupied fragment orbital (LUFO) e_I was set equal to $-EA$,[30] which was left uncorrected since varying e_I of the LUFO by ±1 eV influences the energies of the occupied orbitals of the combined system by less than 0.05 eV.

If instead of the $I_v(I)$ values of ethylene those of Me substituted derivatives[29] are used in the calculation, the PE spectra of the corresponding Me substituted butadienes[29] are well reproduced. This demonstrated the wide range of applications for the LCFO–MO method.

The results for the α,ω-diphenylpolyenes which are collected in Table 4 show that the PE spectra are very well reproduced if we choose the polyene unit and the two benzene rings as fragments and include all OFO's and the LUFO of the polyene unit as the only unoccupied FO. This means that in the case of 1 ($n = 3$) we had to solve an 10 × 10 SCF problem instead of the 18 × 18 PPP-SCF problem so that for molecules of this size the LCFO–MO procedure becomes computationally faster than the conventional SCF method in spite of the integral transformation to the FO basis. But as pointed out previously,[14] the method was not developed in order to save computer time, but rather for a pictorial interpretation of the PE spectra of complex molecules. This is demonstrated by the wave functions also given in Table 4 which show, e.g. that the lowest π MO's ($1a_u$ and $1b_g$) are mainly given by the combinations of the totally symmetric benzene orbitals, whereas the next one ($2a_u$) as well as the HOMO are mixtures of polyene and benzene orbitals increasingly localized in the polyene fragment as one proceeds along the series from 1 ($n = 1$) to 1 ($n = 3$).

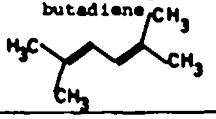
In Table 5 results of different sets of LCFO–MO calculations for pentadienal are listed. The data in column I–III, which were obtained by using as FO's ϕ_I the occupied butadiene and carbonyl π MO's together with the unoccupied butadiene and carbonyl MO's, only the unoccupied carbonyl MO and no unoccupied MO's respectively, demonstrate that it is necessary but also sufficient to include just one occupied FO for the whole system. As experimental values are used for e_I in evaluating the Fock matrix elements the results depend on the oxygen parameters U_O and β_{CO} only through the ϕ_I so

Table 2. Vertical ionization potentials $I_v(i)$ and negative orbital energies ($-\epsilon_i$) from PPP calculations for polyene aldehydes 2[a]

	2(n=1)			2(n=2)			2(n=3)		
i	$I_v(i)$	MO	$-\epsilon_i$(PPP)	$I_v(i)$	MO	$-\epsilon_i$(PPP)	$I_v(i)$	MO	$-\epsilon_i$(PPP)
1	9.86(1050)	n_O	-	9.22(1540)	π_{CC}	9.10	8.42(1290,1370)	π_{CC}	8.46
2	10.35	π_{CC}	10.29	9.56	n_O	-	9.30(1130)	n_O	-
3	12.8	?	-	11.44	π_{CC}	11.45	10.32(1290)	π_{CC}	10.39
4	13.8	π_{CO}	13.36	12.7	?	-	11.7	π_{CC}	11.82
5	14.3	?		13.4	π_{CO}	13.26	12.7	?	-
6				14.4	?	-	13.6	π_{CO}	13.21
7							14.0	?	-

[a] Energies in eV, vibrational fine structure (cm^{-1}) in brackets.

Table 3. LCFO-MO results (negative orbital energies $-\varepsilon_i$) for simple polyenes together with PPP results and experimental $I_v(i)$ and EA values[a]

	MO	$-\varepsilon_i$(LCFO)[b]	$-\varepsilon_i$(PPP)	Exptl. $I_v(i)$ or EA
Butadiene	$2b_g$	- 0.70	0.13	- 0.62[c]
	$1a_u$	9.03	8.49	9.03[d]
	$1b_g$	11.42	10.95	11.42
Hexatriene	$2b_g$	- 0.75	0.67	>0[e]
	$2a_u$	8.50	7.95	8.29[d]
	$1b_g$	9.94	9.95	10.26
	$1a_u$	11.81	11.40	(11.9)
1-Methylbutadiene	$4a''$	- 0.69	-	-
	$3a''$	8.58	-	8.61[d]
	$2a''$	11.10	-	11.10
1,4-Dimethylbutadiene	$3a_u$	- 0.69	-	-
	$2b_g$	8.24	-	8.09[d]
	$2a_u$	10.67	-	10.6
1,1,4,4-Tetramethyl-butadiene	$4a_u$	- 0.69	-	-
	$3b_g$	7.74	-	7.83[d]
	$3a_u$	10.19	-	10.12

[a] All energies in eV

[b] The following ε_I values for the fragments were used: ethylene -10.11, 1.78; butadiene -11.26, -8.83, 0.62; propene -9.33, 1.78, 1.1-dimethyl ethylene -8.83, 1.78 eV, see equ.(5) and Ref.29.

[c] Ref.30

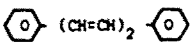
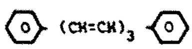
[d] Ref.29

[e] Ref.31

that the final results are not very sensitive to the values chosen for these parameters as may be seen from columns II, IV and V. Thus, one would expect that the orbital energies of the combined system are essentially determined by the value of β_{CC} for the bond uniting the fragments which could therefore be chosen such as to reproduce the experimental IP's as closely as possible in order to obtain some quantitative information about the extent of the conjugative interaction between the π systems of the polyene and the carbonyl fragments. But as is seen from columns VI and VII, only the energy of the highest occupied MO depends appreciably on this parameter; the corresponding IP is expected to increase with increasing interaction.

In Table 6 the LCFO-MO results for the polyene aldehydes are collected. Values obtained by using the PPP orbital energies of the fragments are given in the columns labelled "theoretical e_I". Also given are the lone-pair energies calculated from the corresponding IP of acetaldehyde ($I_v(n_O) = 10.21$ eV[10]) and the destabilization of the n_O orbital due to the redistribution of the π electrons in the combined system, which according to the general product approach[14,32] amounts to 0.65 eV for acrolein and to 0.8 and 0.9 eV for pentadienal and heptatrienal respectively. This confirms the assignment of the first band of 2 (n = 1) and the second band of 2 (n = 2, 3) to the n_O ionization and thus also confirms the assignment of the π_{CC} MO's. For calculations with "experimental e_I" IP values of ethylene, butadiene and hexatriene corrected according to eqn (5) were chosen using 0.9 instead of 0.4 to account for the greater σ inductive perturbation due to the CO group, together with IP = 13.5 eV and EA = −0.86 eV for the carbonyl fragment, i.e. the σ inductive perturbation of the CO group due to polyene fragment was taken into account by choosing an IP close to that of acetaldehyde instead of the IP of formaldehyde. The "theoretical" and "experimental" e_I values differ mainly in $e(\pi^*_{CO})$ which affects the wave functions but has little influence on the calculated orbital energies of the combined system. Using the higher $e(\pi^*_{CO})$ value reduces the charge redistribution during the union of the fragments and therefore leads to lone-pair orbital energies nearly constant within the series of polyene aldehydes.

Table 4. LCFO–MO results (negative orbital energies $-\epsilon_i$ and LCFO–MO's) for α,ω-diphenylpolyenes, together with PPP results and experimental $I_v(i)$ values[a]

	MO	$-\epsilon_i$ (LCFO)[b]	LCFO-MO[c]	$-\epsilon_i$ (LCBO)[d]	$-\epsilon_i$ (PPP)	Exptl $I_v(i)$
 **1** (n=1)	$4a_u$	8.12	$0.62\phi+0.10(\phi_O+\phi_O')+0.53(\phi_S+\phi_S')$	8.27	7.82	7.93
	$3b_g$	9.17	$0.71(\phi_A-\phi_A')$	9.15	9.00	9.22
	$3a_u$	9.17	$0.71(\phi_A+\phi_A')$	9.15	9.00	9.22
	$2b_g$	9.36	$0.15\phi^*+0.70(\phi_S-\phi_S')$	9.15	9.26	(9.5)
	$2a_u$	10.60	$0.70\phi+0.25(\phi_O+\phi_O')+0.43(\phi_S+\phi_S')$	10.65	10.5	10.61
	$1b_g$	12.45	$0.09\phi^*+0.70(\phi_O-\phi_O')$	12.35	12.02	11.35 ?
	$1a_u$	12.70	$0.36\phi+0.65(\phi_O+\phi_O')$	12.68	12.35	?
 **1** (n=2)	$4b_g$	7.78	$0.79\phi_2+0.09(\phi_O-\phi_O')-0.43(\phi_S-\phi_S')$	7.93	7.57	7.54
	$4a_u$	9.07	$0.33\phi_1-0.14\phi^*+0.66(\phi_S+\phi_S')$	8.93	8.86	8.97
	$3b_g$	9.18	$0.71(\phi_A-\phi_A')$	9.15	9.00	9.14
	$3a_u$	9.18	$0.71(\phi_A+\phi_A')$	9.15	9.00	9.14
	$2b_g$	9.93	$0.52\phi_2+0.12(\phi_O-\phi_O')+0.56(\phi_S-\phi_S')$	9.90	9.92	9.94
	$2a_u$	11.17	$0.87\phi_1-0.27(\phi_O+\phi_O')+0.23(\phi_S+\phi_S')$	11.26	11.02	11.2
	$1b_g$	12.52	$-0.21\phi_2+0.69(\phi_O-\phi_O')$	12.49	12.14	?
	$1a_u$	12.64	$0.36\phi_1+0.65(\phi_O+\phi_O')$	12.57	12.29	?
 **1** (n=3)	$5a_u$	7.54	$0.87\phi_3+0.08(\phi_O+\phi_O')-0.33(\phi_S+\phi_S)$	7.65	7.42	7.27
	$4b_g$	8.57	$0.54\phi_2+0.11\phi^*-0.59(\phi_S-\phi_S')$	8.69	8.57	8.51
	$4a_u$	9.18	$0.71(\phi_A-\phi_A')$	9.15	9.03	9.07
	$3b_g$	9.18	$0.71(\phi_A+\phi_A')$	9.15	9.03	9.07
	$3a_u$	9.53	$0.18\phi_1+0.47\phi_2+0.61(\phi_S+\phi_S')$	9.50	9.55	9.51
	$2b_g$	10.44	$0.80\phi_2+0.17(\phi_O-\phi_O')+0.38(\phi_S-\phi_S')$	10.44	10.46	10.28
	$2a_u$	11.61	$0.91\phi_1+0.27(\phi_O+\phi_O')+0.12(\phi_S+\phi_S')$	11.70	11.37	?
	$1b_g$	12.56	$-0.25\phi_2+0.68(\phi_O-\phi_O')$	12.49	12.23	?
	$1a_u$	12.60	$0.37\phi_1-0.14\phi_3+0.65(\phi_C+\phi_O')$	12.57	12.30	?

[a] All energies in eV

[b] The following ϵ_I values for the fragments were used; ethylene and butadiene see Table 3, hexatriene -11.77, -10.13, -8.16, 0.2; benzene -12.35, -9.15, -9.15 eV see Equ.(5) Ref.7 and Ref.29

[c] The principal components are give: $\phi_1,\phi_2,\ldots$ denote the occupied and ϕ^* the unoccupied polyene π-orbitals and ϕ_O,ϕ_S and ϕ_A the occupied benzene π-orbitals, see Ref. 7.

[d] Same parameters as for LCFO-MO, but only OFO's were taken into account.

The good agreement of both the PPP results, based on the choice of the parameters U_O and β_{CO}, and the LCFO–MO results based on experimental IP and EA values with the PE data can be taken as further confirmation of the assignment given in Table 2.

DISCUSSION

The aim of the present investigation was to give a probable assignment of an IP from the PE spectra of planar unsaturated carbonyl compounds to the ionization from the π orbital of the CO bond and to test the applicability of the LCFO–MO method for discussing the difference in the electronic structure of unsaturated hydrocarbons and carbonyl compounds.

From a judicious choice of PPP parameters an assignment of the PE band near 13.5 eV to the π_{CO} is suggested. This is supported by the LCFO–MO results which show, that the IP associated with the π_{CO} is

Table 5. LCFO-MO results (negative π orbital energies $-e_I$) for pentadienal using different sets of parameter values[a,b]

MO	I full LCFO[c,d]	II LCFO[c,d]	III LCBO[c,d]	IV (ΔU_O=+2.0)	V ($\Delta\beta_{CO}$=+0.5)	VI ($\Delta\beta_{CC}$=+0.3)	VII ($\Delta\beta_{CC}$=−0.3)
$\pi_{CC}(3a'')$	9.11	9.09	8.83	8.96	9.12	9.04	9.13
$\pi_{CC}(2a'')$	11.45	11.41	11.24	11.29	11.45	11.40	11.42
$\pi_{CO}(1a'')$	13.43	13.44	13.66	13.49	13.42	13.43	13.44

[a] All energies in eV.

[b] In columns IV - VII only the changes of parameter values with respect to columns I - III are given. Results of column I - III were obtained by including all occupied FO's and all unoccupied FO's (I), only the π^*_{CO} (II) and no unoccupied FO's (III) respectively. $\Delta\beta_{CC}$ in columns VI and VII applies only to bond uniting the two fragments.

[c] For e_I values of the fragments see Table 6.

[d] e'_I values of the polyene fragment including the π inductive perturbation are - 11.32 and - 8.91 eV.

expected to be fairly constant within the series of polyene aldehydes and to differ only very little from the value of the CO fragment, thus showing that inductive and conjugative contributions more or less cancel. There is no doubt that in CH_2=O the PE band at 14.5 eV corresponds to an ionization from π_{CO} orbital $(1b_1)$[9] and that substitution of one of the hydrogens decreases the corresponding IP.[9,33] If therefore we assume that $I_v(CO) < 14$ eV for carbonyl compounds other than formaldehyde, we are left with the given assignment, which is in accord with previous suggestions[9] and theoretical calculations for acrolein,[34] which after applying a correction suggested by Wiberg *et al.*[35] predict $\epsilon(\pi_{CO}) = -13.8$ eV.

Having thus confirmed the value $e(\pi_{CO}) = -13.5$ eV as energy of the carbonyl fragment including the σ inductive perturbation due to substitution we are now in a position to apply the LCFO-MO model to an interpretation of the electronic structure of unsaturated carbonyl compounds. From Table 6 it is seen that with LCFO-MO coefficients ranging from 0.95 to 0.98 the π orbitals are very localized and little disturbed for all compounds of the series, as was already observed from the *ab initio* results for acrolein.[34] Figure 3 gives as a typical example the correlation diagram for pentadienal and shows how the orbital energies are changed by the π inductive perturbation and by conjugative interaction. This diagram stresses the importance of the π^*_{CO} orbital insofar as it shows, that both occupied orbitals of the butadiene fragment are stabilized by conjugative interaction, whereas the π_{CO} is destabilized. This is the opposite of what one would expect from the interaction of the occupied MO's alone, as may be seen from the LCBO results also given in Fig. 3. Thus, although with $P(\pi^*_{CO}) = 0.07$ the π^*_{CO} orbital is very little populated, it has an appreciable effect on the electronic structure of the unsaturated carbonyl compounds. If we use for the fragment orbital energies the PPP values instead of the experimental values (Table 6) this effect is even more pronounced due to the lower value of $e(\pi^*_{CO})(-1.5$ eV instead of $+0.86$ eV). Thus the charge redistribution on uniting the two fragments as well as the change in lone-pair energy based on this charge redistribution is much more pronounced in this case and shows better agreement with experimental lone pair IP's. This suggests that the EA of formaldehyde constitutes an upper limit of the $e(\pi^*_{CO})$ value one should use within the LCFO-MO model.

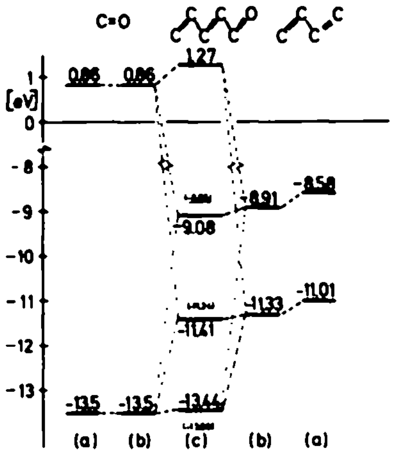


Fig. 3. Orbital correlation diagram for pentadienal, from LCFO-MO calculations. (a) FO energies e_I (cf. footnote c of Table 6), (b) FO energies including π inductive perturbation and (c) LCFO-MO energies (full lines) and LCBO-MO energies (dotted lines) of the combined system.

Table 6. LCFO-MO results (negative orbital energies $-\varepsilon_i$ and LCFO-MO's as well as FO populations P_{II}) for polyene aldehydes[a]

	Theoret. e_I						Exptl. e_I^c		
	MO	$-\varepsilon_i$	φ_I^b	P_{II}	MO	$-\varepsilon_i$	LCFO - MO[d]	φ_I	P_{II}
Acrolein	n_O	9.61	π^*_{CO}	0.10	n_O	9.77		π^*_{CO}	0.06
$CH_2=CH-CH=O$	$\pi_{CC}(2a'')$	10.41	φ_1	1.90	$\pi_{CC}(2a'')$	10.24	$-0.25\pi_{CO}$ $-0.18\pi^*_{CO}$ $+0.95\varphi_1$	φ_1	1.94
	$\pi_{CO}(1a'')$	13.25	π_{CO}	2.00	$\pi_{CO}(1a'')$	13.44	$0.97\pi_{CO}$ $+0.25\varphi_1$	π_{CO}	2.00
	n_O	9.41	π^*_{CO}	0.12	n_O	9.73		π^*_{CO}	0.07
Pentadienal	$\pi_{CC}(3a'')$	9.25	φ_2	1.91	$\pi_{CC}(3a'')$	9.09	$-0.14\pi_{CO}$ $-0.15\pi^*_{CO}$ $+0.97\varphi_2$	φ_2	1.95
$H(CH=CH)_2-CHO$	$\pi_{CC}(2a'')$	11.52	φ_1	1.97	$\pi_{CC}(2a'')$	11.41	$-0.26\pi_{CO}$ $-0.10\pi^*_{CO}$ $+0.96\varphi_1$	φ_1	1.98
	$\pi_{CO}(1a'')$	13.22	π_{CO}	2.00	$\pi_{CO}(1a'')$	13.44	$0.95\pi_{CO}$ $+0.25\varphi_1$ $+0.16\varphi_2$	π_{CO}	2.00
	n_O	9.31	π^*_{CO}	0.12	n_O	9.71		π^*_{CO}	0.07
Heptatrienal	$\pi_{CC}(4a'')$	8.51	φ_3	1.93	$\pi_{CC}(4a'')$	8.38	$0.12\pi^*_{CO}$ $+0.11\varphi_2$ $+0.98\varphi_3$	φ_3	1.96
$H(CH=CH)_3-CHO$	$\pi_{CC}(3a'')$	10.44	φ_2	1.96	$\pi_{CC}(3a'')$	10.33	$-0.18\pi_{CO}$ $-0.12\pi^*_{CO}$ $+0.97\varphi_2$	φ_2	1.97
	$\pi_{CC}(2a'')$	11.99	φ_1	1.99	$\pi_{CC}(2a'')$	11.90	$-0.24\pi_{CO}$ $+0.97\varphi_1$	φ_1	1.99
	$\pi_{CO}(1a'')$	13.21	π_{CO}	2.00	$\pi_{CO}(1a'')$	13.43	$0.95\pi_{CO}$ $+0.23\varphi_1$ $+0.19\varphi_2$ $-0.11\varphi_3$	π_{CO}	2.0

[a] All energies in eV

[b] φ_1, φ_2 and φ_3 designate the occupied FO's of the polyene fragment

[c] The following e_I values for the fragments were used: CO -13.5, 0.86 (see text) and ethylene -10.11, butadiene -11.01, -8.58 and hexatriene -11.60, -9.96, -7.99 eV, obtained from $e_I = -I_v(I) + 0.9/n_{occ}$ with $I_v(I)$ values from Ref. 29

[d] Only principal components are given.

Although for the interaction of hydrocarbon fragments the inclusion of unoccupied FO's is thought to be not important and although it does not affect the qualitative appearence of the correlation diagrams, the results of Table 4 show that the spacings of the orbital energies may nevertheless change appreciably if the LUFO is taken into account. In conclusion we may therefore state that the approximations inherent to the LCBO model seem to be justified only in those cases where first order perturbation theory is applicable,[26] but that with very little additional effort one or a few unoccupied orbitals may be taken into account and the calculation may then be carried out in self-consistent manner using the LCFO-MO scheme developed recently.

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