138. Photoelectron Spectra of Unsaturated Oxides.
I. 1,4-Dioxin and Related Systems

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Summary

The He(Iα) photoelectron spectra of the four unsaturated oxides 3,4-dihydro-pyran (**6**), γ-pyran (**7**), 2,3-dihydro-1,4-dioxin (**9**) and 1,4-dioxin (**10**) are reported and analysed. Band assignments are based on *ab-initio* calculations, using the STO-3G basis set. The proposed orbital sequences (with reference to the coordinate systems given in *Table 1*) are, for the top three orbitals: **6**, π, $n\sigma$, $n\pi$; **7**, $3b_1(\pi)$, $1a_2(\pi)$, $11a_1(\sigma)$; **9**, $11b(\pi)$, $12a(\sigma)$, $11a(\pi)$; **10**, $2b_{3u}(\pi)$, $1b_{1g}(\pi)$, $6a_g(\sigma)$. Finally the (almost) localized π-orbitals have been computed by the *Foster-Boys* localization procedure.

Certainly one of the most successful techniques for assigning photoelectron spectra of organic compounds has been the empirical correlation procedure, which consists in recording the photoelectron spectra of a series of closely related compounds in which one or more structural features have been varied in a systematic fashion. The corresponding spectral changes, *e.g.* shifts in band positions and/or variations in the *Franck-Condon* contours, are then linked to the differences in structure of the individual molecules with the help of quantum-mechanical rules of thumb. It has proved convenient to derive the latter from simple equivalent orbital models [1], *i.e.* treatments which are easily parametrized [2] and thus allow the transfer of information derived from one set of spectra to those of other related systems [2] [3]. A more detailed survey of this correlation procedure has been given elsewhere [4] [5].

In connection with a detailed investigation of the photoelectron spectra of oxides, in particular of benzene oxides and their valence isomers (*e.g.* **1** → **1'**) and of

1   **1'**
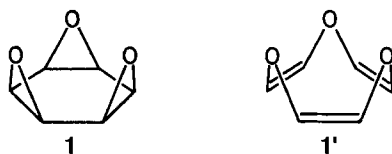
other unsaturated oxides, it was important to first derive reliable estimates for the parameters needed within an equivalent bond orbital model for such molecules. To this end it seemed particularly advantageous to base such a parametrization on the photoelectron spectra of the nine compounds 2 to 10, which form the following systematic matrix (1):

$$\tag{1}$$
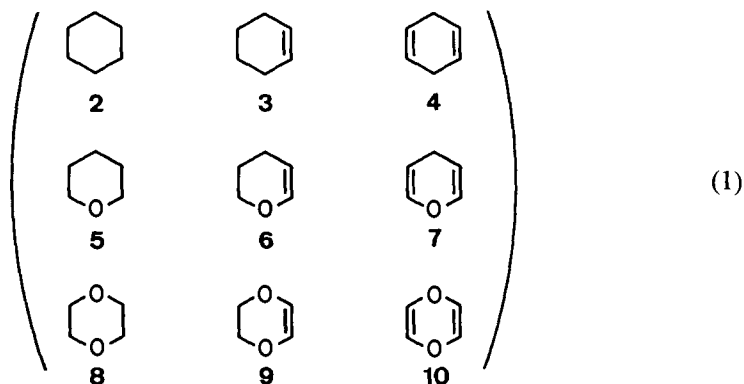
It was hoped that the six possible correlations, corresponding to the three rows and to the three columns of (1) would yield by inspection and without further difficulty the desired information, *i.e.* an unambigous assignment. In other words this 'two-dimensional' correlation was supposed to 'out-correlate' all the one-dimensional examples given previously.

However, contrary to expectation it proved singularly difficult to derive an assignment and thus an adequate set of orbital parameters without the help of *ab initio* calculations. Although unintended, the present investigation demonstrates the limitations inherent in the traditional correlation procedure. (A preliminary account has been given in [5]).

Experimental Results. – The photoelectron spectra of the hydrocarbons 2 (cyclohexane), 3 (cyclohexene) and 4 (1,4-cyclohexadiene) have been investigated previously [6] [7]. In particular it has been shown [7] that the electronic ground state of the radical cation 4^+ is $\tilde{X} = {}^2B_{3u}$, assuming D_{2h} symmetry, and that its first excited state is $\tilde{A} = {}^2B_{1g}$. In terms of *Koopmans'* approximation this implies that the two highest occupied molecular orbitals of 4 are $2b_{3u}(\pi)$ ($=$ HOMO) above $1b_{1g}(\pi)$, *i.e.* that this is an example of an 'inverted' sequence [8], the through-bond interaction of the basis π-orbitals dominating their through-space interaction.

The photoelectron spectra of the two oxides 5 (tetrahydropyran = oxane) and 8 (1,4-dioxane) have been recorded by *Sweigart & Turner* [9]. They have shown that there is an appreciable interaction between the lone-pair basis orbitals in 8, which is through-bond dominated. A somewhat different interpretation has been given by *Kobayashi & Nagakura* [10].

In *Figure 1* are shown the He(Iα) photoelectron spectra of 6 (3,4-dihydropyran), 7 (γ-pyran = 4H-oxin), 9 (2,3-dihydro-1,4-dioxin) and 10 (1,4-dioxin). They consist of a series of rather well resolved bands with, however, little vibrational fine-structure. The band locations have been characterized by I_j^a, the adiabatic ionization
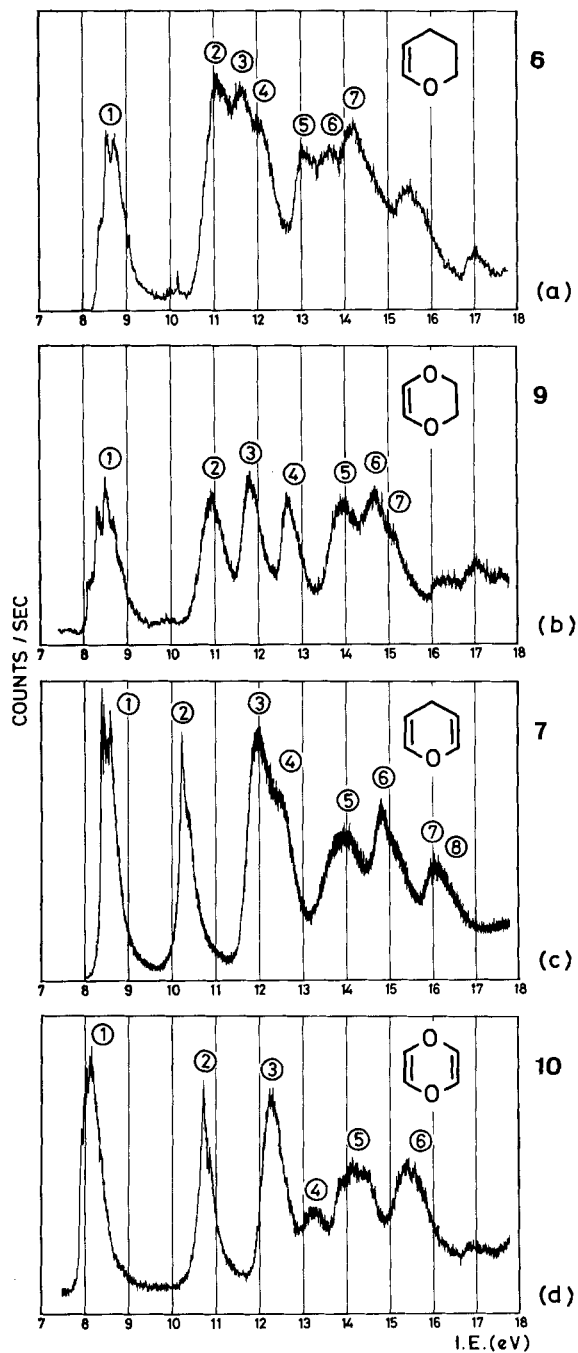
Fig. 1. *Photoelectron spectra of 3,4-dihydropyran (6), 2,3-dihydro-1,4-dioxin (9), γ-pyran (7) and 1,4-dioxin (10)*

Table 1. *Ionization energies of the compounds* **6, 7, 9** *and* **10**. All values in eV. Estimated precision: ±0.02 eV if two decimals given, otherwise ±0.05 if second decimal as subscript or ±0.1 if one decimal given. Orbital labels refer to the axes defined in the formulae.

	6 C_1 I_j^a	I_j^m	a)	Orb. b)	**7** C_{2v} I_j^a	I_j^m	a)	Orb.	**9** C_2 I_j^a	I_j^m	a)	Orb.	**10** D_{2h} I_j^a	I_j^m	a)	Orb.
①	8.37	8.56	8.84	π	(?)c)	8.38d)	8.43	$3b_1$	8.07	8.48e)	8.43	$11b$	7.75	8.13	7.72	$2b_{3u}$
②		11.1_0	11.22	$n\sigma$		10.20	10.42	$1a_2$	10.3	10.9_5	10.80	$12a$	10.3_0	10.70	10.82	$1b_{1g}$
③	11.7	12.06		$n\pi$		12.0_0	11.88	$11a_1$		11.8_0	11.76	$11a$	11.8_0	12.30	11.60	$6a_g$
④		12.1				12.5				12.6_5	12.97	$10b$		13.25		
⑤		13.1				14.0				13.9_5				14.2_0		
⑥		13.7				14.8_0				14.6_5				15.4_5		
⑦		14.2_5				15.3				15.0				17.0		
⑧						16.1				16.3				18.0		
⑨						17.7				17.0_0						
⑩										17.5_5						

a) Calculated ionization energies I_j^m from regression (2), using the STO-3G orbital energies given in *Table 3*.
b) Type of orbital: n = lone-pair dominated.
c) Ill defined band onset *(cf. Fig. 1, b)*.
d) Vibrational spacing: 1570 ± 50 cm^{-1}, 530 ± 50 cm^{-1}.
e) Vibrational spacing: 1560 ± 50 cm^{-1}, 470 ± 50 cm^{-1}.

energy and by the position I_j^m of the band maxima. For all practical purposes the I_j^m can be identified with the vertical ionization energies, $I_j^m \approx I_j^v$, the difference between these values being of the same order as the experimental errors. The band positions are listed in *Table 1* for the compounds **6, 7, 9** and **10**, together with the assignment to be derived below.

Table 2. *Assumed geometries for the four compounds* **6, 7, 9** *and* **10**. Bond lengths in pm, bond angles in degrees. The dihedral angles are defined relative to the angle zero for the syn-planar conformation
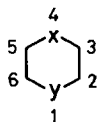
Comp.	x	y	Bond lengths					Bond angles				Dihedral Angles	
			2–3	3–x	2–y	5–x	6–y	23x	y23	3x5	2y6	23x5	32y6
6	CH_2	O	134	152	136	154	143	120.0	125.0	114.0	116.0	15	15
7	CH_2	O	134	152	136	152	136	121.6	124.4	110.0	118.0	0	0
9	O	O	134	136	136	143	143	123.0	123.0	115.3	115.3	15	15
10	O	O	134	136	136	136	136	123.0	123.0	114.0	114.0	0	0

Theoretical Results. – *Ab-initio* calculations at the STO-3G level [11] were carried out for molecules **6, 7, 9** and **10**. In all cases standard bond lengths [12] were used and, in general, standard angles. In some instances construction of rings with standard bond lengths precluded the use of standard angles, *e.g.,* **10**. Compounds **7** and **10** were assumed to be planar by analogy to **4** which has been shown to possess D_{2h} symmetry [13]. Support for this finding was obtained in these laboratories by MINDO/3 [14] geometry optimizations. Nonplanar conformations similar to the experimentally observed 'half-chair' of **3** [15] were used for **6** and **9**. A more complete description of the geometries is found in *Table 2*. The canonical molecular orbital energies, ε_j, and corresponding orbital labels are given in *Table 3*. Within the approximation of *Koopmans'* theorem ($-\varepsilon_j \approx I_j^m$) these values serve as a starting point for the discussion of the spectra.

In *Figure 2* is shown a plot of calculated STO-3G orbital energies, ε_j, against the observed ionization energies, I_j^m. A linear regression by the standard least squares technique yields the relationship

$$-\varepsilon_j^{STO-3G} = -5.116 \text{ eV} + 1.357 \text{ } I_j^m \qquad (2)$$

The standard errors of the slope and of the mean orbital energy ($\overline{\varepsilon^{STO-3G}} = 9.18$ eV) are 0.076 and 0.119 eV respectively. The correlation coefficient is 0.983. One notes here a somewhat large deviation for the two points corresponding to the bands ① and ③ of **10** *(cf. Fig. 1, d)*. This may be the result of an inaccurate choice of geometry. A partial STO-3G geometry optimization of **10** resulted in a lengthening of the C–O bond from 136 pm to 141 pm with a decrease in total energy of 33 kJ mol^{-1}. The calculated STO-3G orbital energies for **10** and, in parentheses, the predicted ionization energies using regression (2) are: ① $2b_{3u}$, 5.99, (8.18); ② $1b_{1g}$, 9.50, (10.77); ③ $6a_g$, 11.12, (11.96). This seems to indicate that deviations from the relationship given in (2) could arise from a less than adequate description of ring systems that standard geometries provide. Alternatively, if the STO-3G
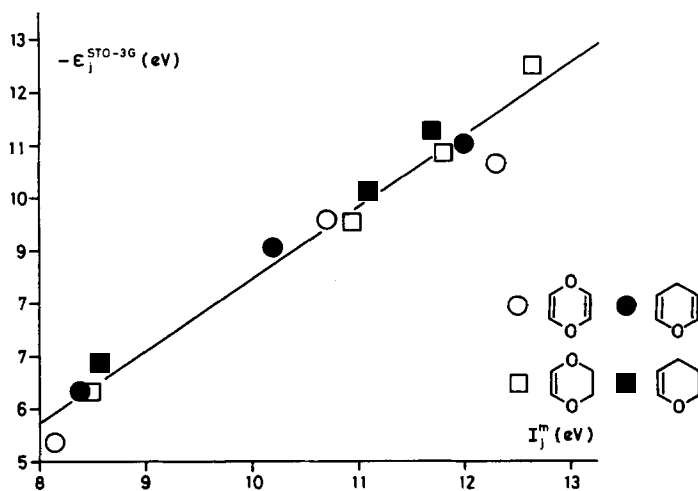

Fig. 2. *Linear regression (2) of orbital energies $-\varepsilon_j^{STO-3G}$ vs. ionization energies I_j^m for the compounds* **6, 7, 9** *and* **10**

model pictures oxygen lone pairs as being too tightly bound, this has a similar effect on the calculated orbital energies. In any case, when one considers that both σ- and π-type orbitals in molecules with and without strict σ/π-separation are being correlated, the agreement is rather satisfactory.

Assignment of the Photoelectron Spectra. – We would have liked to interpret the photoelectron spectra of the nine compounds, **2** to **10**, contained in the matrix (1) by correlating band positions with the help of empirical equivalent bond models, *i.e.* choosing basis orbital energies for double bond-, lone-pair- or methylene group π-orbitals and calibrating their interaction elements, followed by solving the corresponding secular determinant. As pointed out in the introduction, this failed to provide a self-consistent explanation of the data. (We shall comment upon this later.) For this reason we decided to base the tentative assignment, presented in
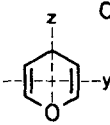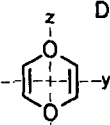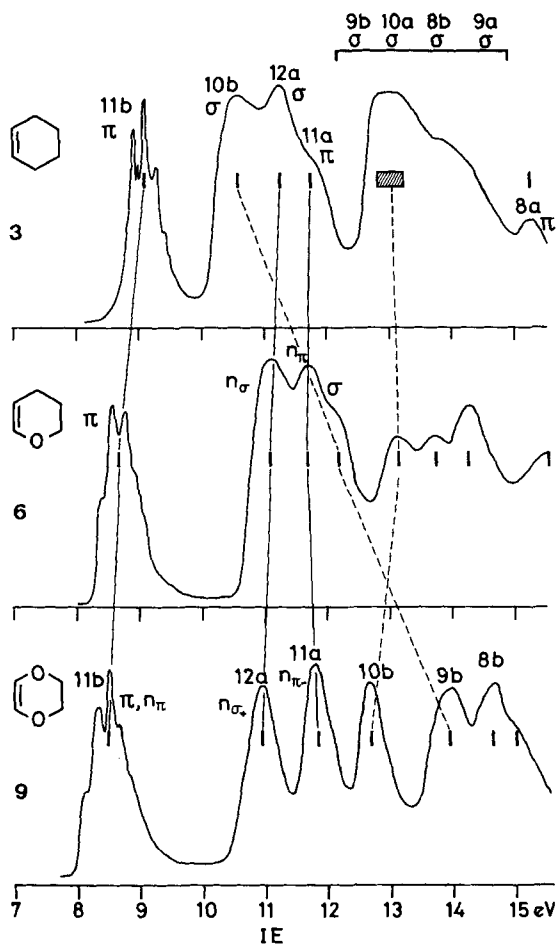

Fig. 3. *Photoelectron band assignments and correlations for compounds* **3**, **6** *and* **9**. Broken lines indicate tentative correlations

Table 3. *Orbital energies* $-\varepsilon_j^{STO-3G}$ *and orbital sequence for the four compounds* **6**, **7**, **9** *and* **10** *calculated by the* ab initio *STO-3G method, using the geometries defined in* Table 2. *All values are in eV*

6	C_1	7	C_{2v}	9	C_2	10	D_{2h}
① 6.88	23a	6.33	$3b_1$	6.32	11b	5.36	$2b_{3u}$
② 10.11	22a	9.03	$1a_2$	9.54	12a	9.57	$1b_{1g}$
③ 11.25	21a	11.01	$11a_1$	10.84	11a	10.62	$6a_g$
④ 11.67	20a	11.70	$7b_2$	12.48	10b	13.28	$1b_{2g}$
⑤ 12.86	19a	13.57	$10a_1$	12.63	9b	13.39	$5b_{1u}$
⑥ 13.44	18a	14.06	$2b_1$	13.74	8b	13.49	$3b_{3g}$
⑦ 14.34	17a	15.08	$6b_2$	14.64	10a	15.50	$4b_{2u}$
⑧ 15.14	16a	15.60	$1b_1$	15.24	9a	15.73	$1b_{3u}$
⑨ 15.40	15a	16.11	$5b_2$	16.52	8a	17.46	$4b_{1u}$
⑩ 16.22	14a	16.75	$9a_1$	16.88	7b	17.67	$3b_{2u}$

Figures 3 and *4*, on the results of the STO-3G calculations given in the previous paragraph. Such a procedure had proved to be rather reliable for hydrocarbons [16], and we expected that it applies equally well to oxygen containing systems.

For compounds **6** and **7** *Figure 3* gives the band assignments and some correlations derived (primarily) from the STO-3G calculations listed in *Table 3*. Similarly, *Figure 4* gives the corresponding information for compounds **7** and **10**. In both instances, the photoelectron spectra of the parent hydrocarbons, **3** or **4** [6], have been included. For the sake of convenience, qualitative diagrams of the relevant orbitals of the molecules **4**, **7** and **10** are displayed in *Figure 5*, together with the proposed band assignments.

In the photoelectron spectra of all six compounds band ① corresponds (within *Koopmans'* approximation) to a π-orbital (HOMO) mainly centred on the CC double bond(s). According to the STO-3G results the percentage of 'double bond character' of this orbital decreases with increasing substitution of the methylene pseudo-π orbitals by oxygen lone pair p-orbitals ($n\pi$). The phase relationship between the two double bond basis-π-orbitals in the HOMO of **7** and **10** is the same as in **4** [7] *i.e.* in-phase with respect to a reflection in the xz-plane (*cf. Table 1* for the definition of the coordinate system).

Band ② in the photoelectron spectra of **7** and **10** corresponds to the out-of-phase combination of the double bond basis-π-orbitals (relative to reflection in the xz-plane). For symmetry reasons the resulting orbitals $1a_2$ (**7**) and $1b_{1g}$ (**10**) are located exclusively on the two double bonds if strict C_{2v} (**7**) or D_{2h} (**10**) symmetry is assumed. That this assignment is presumably correct, is supported by the sharpness of the bands ② in the spectra of **7** and **10** (see *Fig. 1*), which indicates that removal of an electron from these essentially non-bonding orbitals is followed by little
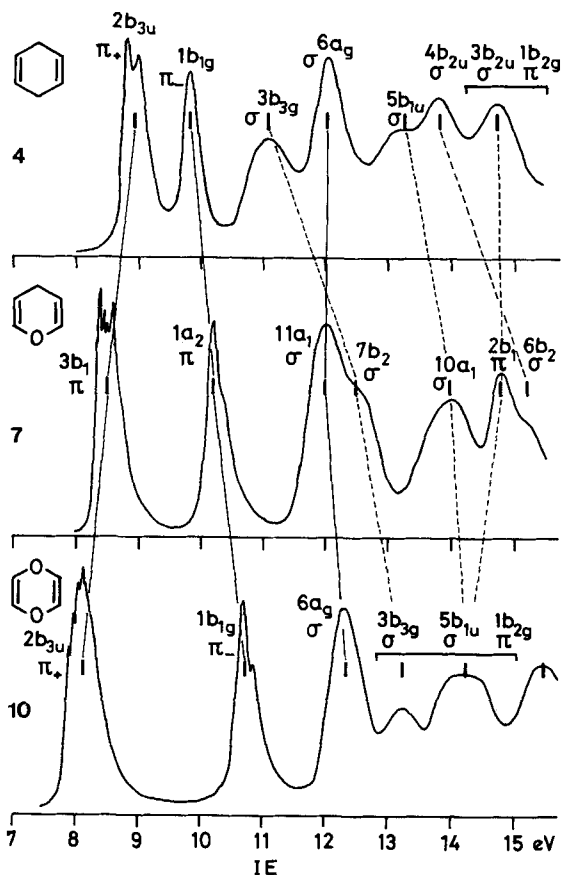
Fig. 4. *Photoelectron band assignments and correlations for compounds* **4, 7** *and* **10**. Broken lines indicate tentative correlations

reorganization of the geometry of the radical cation formed. *Figure 4* displays how the splitting between the first two bands, ① and ②, correlated with the in-phase and out-of-phase combinations of the double bond basis-π-orbitals, increases steadily on passing from **4** (1.0_0 eV) to **7** (1.8_2 eV) to **10** (2.5_2 eV). This is an indication that an oxygen $n\pi$ orbital is superior to a methylene pseudo-π-orbital as a relay orbital. In addition the bands ② in the photoelectron spectra of **4, 7** and **10** lie at increasingly higher ionization energies. Since the corresponding molecular orbitals $1b_{1g}$ (**4**), $1a_2$ (**7**) and $1b_{1g}$ (**10**) have zero coefficients on the methylene and/or oxygen centres, the stabilization of the basis-π-orbitals has to be rationalized by the change in inductive effect associated with the replacement of a methylene group by an oxygen atom, if we wish to speak in traditional chemical terms.

Band ② of the photoelectron spectra of **6** and **9** *(Fig. 3)* and band ③ in those of **7** and **10** *(Fig. 4)* are due to the ejection of an electron from a delocalized ribbon-type [17] σ-orbital involving mainly the in-plane oxygen lone-pair orbital(s) *(cf. Fig. 5)*.
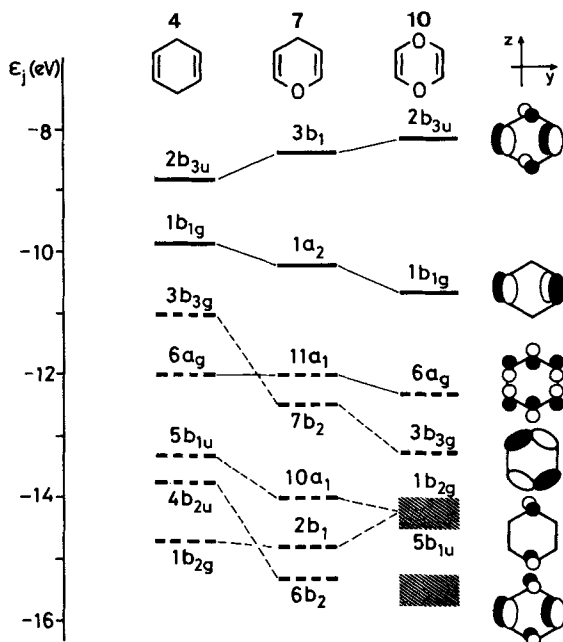
Fig. 5. *Correlation diagram of observed ionization energies for compounds* **4**, **7** *and* **10** *with schematic representation of the molecular orbitals of* **10**. Note that the drawings indicate only the phase relationship between the basis orbitals, not their contribution.

Whereas the above assignments are in all probability the correct ones, the interpretation of the remaining, higher energy part of the photoelectron spectra rests on much less secure ground due, in part, to the strong overlap of the bands, and mainly because the STO-3G orbital energies tend to cluster within small energy ranges, which renders the calculated sequence rather uncertain. Thus, the following assignments shown by broken lines in the diagrams of *Figures 3* and *4* should be taken with a grain of salt. However, we feel that notwithstanding the ambiguities involved, the proposed correlations are presumably not far off the mark.

Band ③ of **9**, and ④ or a component of ⑤ of **10** (*cf. Fig. 3, 4* and *5*) are assumed to arise from electron ejection from a molecular orbital which is essentially the out-of-phase linear combination (*i.e.* antisymmetric with respect to reflection in the xy-plane of **10**) of the two $n\pi$ basis orbitals of the oxygen atoms. Since the STO-3G orbital energies for the $1b_{2g}$, $5b_{1u}$ and $3b_{3g}$ orbitals of **10** lie so close together (see *Table 3*), all that can be said is that ionization from these three orbitals accounts for bands ④ and ⑤. The shape and width of band ⑤ suggests that it corresponds to at least two states. The third band of **6**, is also associated with a π-type orbital, largely delocalized, its largest coefficients being on oxygen and the adjacent methylene pseudo-π combination. Finally, band ④ in the spectrum of **7** is associated with another ribbon-type σ-orbital of C–C and C–H character.

According to the calculations, the 10b and 9b orbitals of **9** are nearly accidentally degenerate with an energy difference of 0.15 eV, whereas bands ④ and ⑤ are separated by 1.3 eV. This ambiguity is not too serious; the orbitals are both σ-type

with their main contributions ($\sim 50\%$) from the oxygen lone pairs. Band ④ of **6** is predicted to correspond to a σ-type ring orbital; band ⑤, a σ-type orbital with contributions from the oxygen lone pair and the methylene group adjacent to the double bond. The broken lines in *Figures 3* and *5* indicate our tentative correlations. The 13 to 15 eV region of **10** contains, in addition to the band due to ionization from the $1b_{2g}$ orbital, the bands associated with the $5b_{1u}$ and $3b_{3g}$ orbitals. These two orbitals are the antisymmetric combination of the σ lone pairs and a combination of ring and CH-orbitals, respectively. Band ⑤ in the spectrum of **7** can tentatively be assigned to the $10a_1$ orbital.

Table 4. *Matrix elements between π-type combinations of* STO-3G *localized orbitals for compounds* **6, 7, 9** *and* **10**. A = self energies; B = cross terms between two adjacent orbitals; Γ = cross terms between transannular orbitals. All values in eV. (The subscripts π, O, Me refer to the C,C double bond π-orbital, the π-type oxygen lone pair and the π-type combination of the C–H bond orbitals of the methylene group, respectively.)

	A	B	Γ
3 a)	$A_\pi = -8.56$ $A_{Me} = -14.21$	$B_{\pi,Me} = -1.46$	$\Gamma_{Me,Me} = +0.12$
4	$A_\pi = -8.63$ $A_{Me} = -14.37$	$B_{\pi,Me} = -1.52$	$\Gamma_{\pi,\pi} = -0.66$ $\Gamma_{Me,Me} = +0.27$
6 a)	$A_\pi = -8.67$ $A_O = -11.82$ $A_{Me} = -14.32$	$B_{\pi,O} = -2.35$ $B_{\pi,Me} = -1.53$	$\Gamma_{O,Me} = +0.20$
7	$A_\pi = -8.97$ $A_O = -12.16$ $A_{Me} = -14.40$	$B_{\pi,O} = -2.37$ $B_{\pi,Me} = -1.63$	$\Gamma_{\pi,\pi} = +0.06$ $\Gamma_{O,Me} = +0.46$
9 a)	$A_\pi = -8.89$ $A_O = -11.92$	$B_{\pi,O} = -2.40$	$\Gamma_{O,O} = +0.27$
10	$A_\pi = -9.31$ $A_O = -12.66$	$B_{\pi,O} = -2.48$	$\Gamma_{\pi,\pi} = +0.26$ $\Gamma_{O,O} = +0.62$

a)   Compounds **3, 6** and **9** are not planar, and, strictly speaking, σ-π symmetry does not exist. In these cases the 2×2 submatrices corresponding to the localized C,C banana orbitals, the two oxygen 'rabbit ear' lone pair orbitals, or the two methylene C–H bond orbitals were diagonalized to yield two orbitals which are (almost) symmetrical and antisymmetrical, respectively, with respect to the plane of the double bond. The subscripts π, O, Me refer to these (almost) antisymmetrical orbitals.

Localized Molecular Orbitals. – In view of the applications to be described in the subsequent contributions (*e.g.* [18]) it seemed appropriate to subject the STO-3G results summarized in *Table 3* to the *Foster-Boys* localization procedure [19]. As usual, one obtains for each double bond two localized banana orbitals which have to be transformed into (almost) localized σ- and π-orbitals (see footnote to *Table 4*). The self-energies A_π of these localized π-orbitals span a 1 eV range (-8.3 to -9.3 eV). Similarly the oxygen π-type orbital self energies A_O range from -11.8 eV to -12.7 eV whereas the self energies A_{Me} of the methylene pseudo-π combinations exhibit a relatively consistent value of *ca.* -14.3 eV. The observed changes in A_π, A_O and A_{Me} as well as in the cross-terms (see *Table 4*) are due to the 'delocalized' tails of the localized orbitals. They can therefore serve as a measure for the deviation due to the overall π-delocalization in the π-system of the particular molecule.

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