1. Interaction between Oxygen Lone-Pair Orbitals of Ether and α,β-Unsaturated Ketone Functions in 3,5,6-Trimethylidene-7-oxabicyclo[2.2.1]heptan-2-one and 3,6-Dimethylidene-7-oxabicyclo[2.2.1]heptane-2,5-dione: A PE-Spectroscopic Investigation

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Controlled ozonolysis of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**1**) afforded 3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptan-2-one (**2**). Ozonolysis of **2** gave a 1:1 mixture of 3,5-dimethylidene-7-oxabicyclo[2.2.1]heptane-2,6-dione (**3**) and 3,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2,5-dione (**4**). The He(Iα) photoelectron (PE) spectra of **2** and **4** have been recorded. Comparison with the PE data of related systems, and with the result of *ab initio* STO-3G calculations, confirm the existence of significant through-bond interactions between the oxygen lone-pair orbitals n(CO) of the carbonyl functions and n(O) of the O(7) ether bridge.

Introduction. – The interpretation of PE-spectroscopic data of β,γ-unsaturated ketones suggests the presence of interactions between the oxygen lone-pair orbitals n(CO) of the carbonyl group, and the π orbital π(CC) of the C=C bond [1–4]. For bicyclo[2.2.1]heptanone, bicyclo[2.2.2]octanone, and some of their derivatives, we have shown that this interaction can be viewed as a subtle interplay between basis energy shifts $\delta A(n_p(CO))$ and $\delta A(\pi(CC))$, and the crossterm κ between these two orbitals, the latter being of both 'through-bond' and 'through-space' origin [5]. Changes in the basis energies $A(n_p(CO))$ and $A(\pi(CC))$, and in the crossterm κ, due to the interaction of the C=C function with an electrophilic reagent [6], can be invoked to explain the electron-donating ability of the homoconjugated C=O group in β,γ-unsaturated ketones [7]. 'Through-bond' interactions between the $n_p(CO)$ orbitals in 1,2-diones [8] [9], 1,3-diones [9] [10], 1,2,3-triones [9] [10a] [11], 1,4-diones [12], 1,5-diones [13], or in *p*-benzoquinone, and its derivatives [14] have also been investigated by PE spectroscopy.

We now report the synthesis of the new 7-oxanorbornanone derivatives 3,5,6-trimethylidene-7-oxabicyclo[2.2.1]heptan-2-one (**2**), 3,5-dimethylidene-7-oxabicyclo[2.2.1]heptane-2,6-dione (**3**), and 3,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2,5-dione (**4**), and the PE spectra of **2** and **4**. The assignment and interpretation of the PE spectra, based

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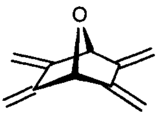

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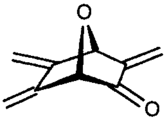

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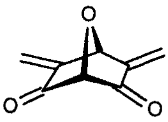

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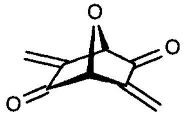

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on the correlation with orbital energies (*Koopmans'* theorem) obtained from *ab initio* STO-3G calculations, confirm the existence of a substantial interaction between the oxygen lone-pair orbitals $n_p(CO)$ of the carbonyl group(s) and the $n_p(O)$ orbital of the ether-bridge O-atom.

Experimental Results. – *Preparation of the Samples.* Ozonolysis (3% O_3 in O_2) of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**1**) [15] in toluene gave successively the corresponding trienone **2** and a 1:1 mixture of dienediones **3** and **4** (workup with Me_2S). Ozonolysis of pure **2** gave also a 1:1 mixture **3**/**4**. The lack of selectivity can be explained by the high reactivity of O_3 [16]. The selectivity could not be improved by changing the solvent (hexane, CCl_4, $CHCl_3$, CH_2Cl_2, acetone, CH_4, freon) and/or the temperature (–140° to –50°). The dienediones **3** and **4** could be readily separated by gas-phase chromatography of dilute solutions. Compounds **2** and **4** were obtained pure. They are unstable at 20° and polymerize in the condensed state. The *cis*-dione **3** is even less stable and polymerized quickly above 0°, even in dilute solution.

PE Spectra. The He(Iα) PE spectra of the trienone **2** and of the dienedione **4** are shown in *Fig. 1*. The observed band position I_j^m, which refer to the band maxima (*cf.* next paragraph), are collected in the *Table*, together with those of **1** [17], and with the orbital energies ε_j of the top seven molecular orbitals of **2** and **4**, obtained by the STO-3G procedure [18], using MNDO [19] energy-optimized geometries.

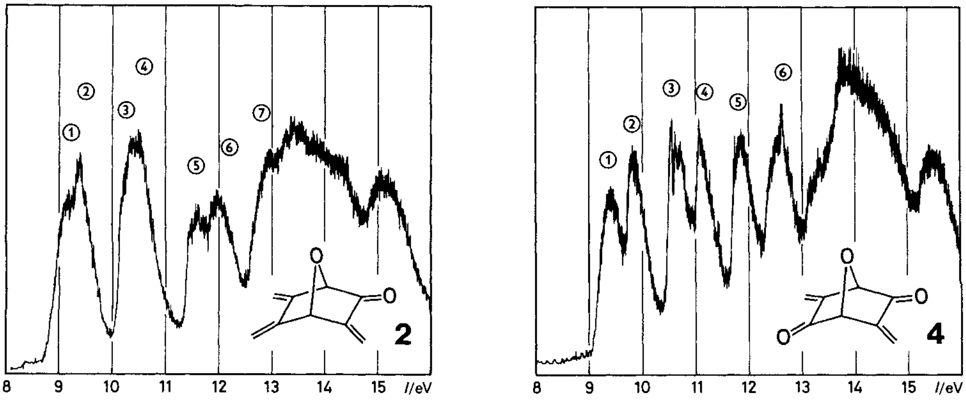


Fig. 1. *PE Spectra of* **2** *and* **4**

Assignment. – Our first task consists in assigning the observed bands in the PE spectra of **2** and **4** to radical cation states, *i.e.* to *Koopmans* states [20]. In the absence of ancillary experimental information (*e.g.* vibrational fine-structure, energy dependence of band

Table. *Position* I_j^m *and Assignment of the Bands in the PE Spectra of Compounds* **1**, **2**, *and* **4**. The band numbers refer to those given in *Fig. 1*.

Molecule **1**

Band	I_j^m/eV	ε_j	Orbital	Type
①	8.60	−7.08	$5a_2$	π(AA)
②	9.22	−7.56	$7b_1$	π(SA)
③	9.62	−8.81	$7b_2$	p(O)
④	10.40	−9.50	$6b_2$	π(AS)
⑤	10.65	−9.78	$9a_1$	π(SS)
⑥	12.1	−11.92	?	σ

Molecule **2**

Band	I_j^m/eV	ε_j	Orbital	Type
①	9.20	7.42	28a	$\pi(\leftarrow a_2$; AA)
②	9.42	8.09	27a	p(O); p(CO)
③	10.25	8.65	26a	$\pi(\leftarrow b_1$; SA)
④	10.55	9.59	25a	p(O)
⑤	11.65	10.96	24a	$\pi(\leftarrow b_2$; AS)
⑥	12.05	11.11	23a	s(O); π(CO)
⑦	13.0	12.49	22a	σ

Molecule **4**

Band	I_j^m/eV	ε_j	Orbital	Type
①	9.40	7.96	14b	p(O); p(CO; b)
②	9.85	8.27	14a	$\pi(\leftarrow a_2$; AA)
③	10.52	9.02	13b	$\pi(\leftarrow b_1$; SA)
④	11.08	9.60	13a	p(CO; a)
⑤	11.85	11.32	12b	p(O); p(CO; b)
⑥	12.55	11.44	12a	s(O);σ
⑦	13.3	12.33	11b	π(CO)

intensitities, *etc.*), we rely on the correlation of observed band positions I_j^m (= position of band maximum) with the computed *ab initio* STO-3G orbital energies ε_j (*cf.* the *Table*), assuming that $I_j^m \approx I_j^v$ (= vertical ionization energy), and that $I_j^v = a + b\varepsilon_j$.

Although integrated intensities of PE band are not always a safe guide, one can not neglect them for closely related molecules, such as **1**, **2**, and **4**. Comparing their PE spectra, one notices that the second band in the spectrum of **2** (labeled ③④ in *Fig. 1*) has an integrated intensity equal to the sum of the intensities of the slightly split bands ① and ②. It must, therefore, be composed of two partial bands. From both the *Franck-Condon* envelope and the half-width of the double band ③④ at $I_{3,4}^m = 10.4$ eV, we deduce that the positions of the partial bands are $I_3^m \approx 10.25$ eV and $I_4^m \approx 10.55$ eV, as listed in the *Table*. (On the other hand, the first four bands in the PE spectrum of **4** are all single.)

The linear regression of the I_j^m on the ε_j, based on the seven first bands in the PE spectra of **2** and **4**, is – relative to the means $\overline{I_j^m} = 11.048$ eV and $\overline{\varepsilon_j} = 9.875$ eV – given by:

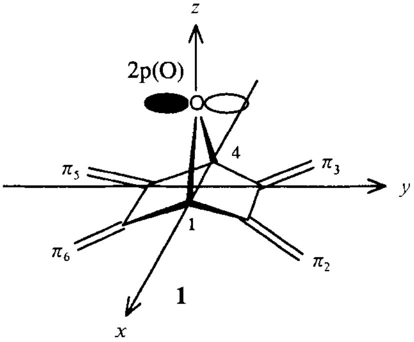
$$I_j^m/\text{eV} = (11.048 \pm 0.061) - (0.794 \pm 0.037)(\varepsilon_j/\text{eV} + 9.875) \qquad (1)$$

This regression, which includes the standard deviations of the mean I_j^m and of the slope, is based on 12 degrees of freedom, and is characterized by a residual variance about the regression of $V(I_j^m) = 0.052$ eV^2 (standard error SE(I_j^m) = 0.228 eV).

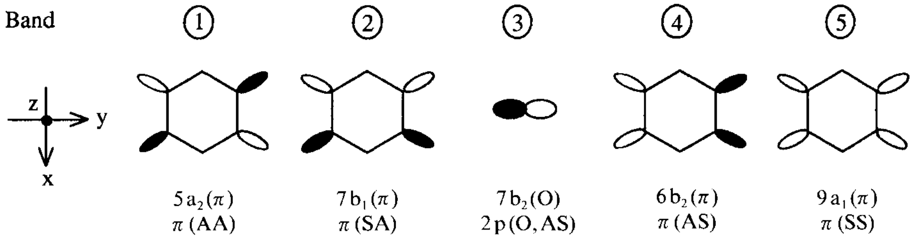
We note in passing that assigning the band at 10.4 eV in the PE spectrum of **2** to a single *Koopmans* state would yield a regression of type (*1*) with residual variance $V(I_j^m) = 0.136$ eV^2 (11 degrees of freedom). The corresponding variance ratio (with respect to that of (*1*)) is F = 0.136/0.052 = 2.61, which shows that the assignment of two *Koopmans* states to the band now labeled ③④ leads to a significant improvement of the regression on a 90% confidence level ($F_{0.9}(12,11) = 2.21$). This provides additional support for the proposed assignment. However, it must be borne in mind that the assignments given in the *Table* are nevertheless tentative ones, being tied intimately to the assumed reliability of the *ab initio* STO-3G model calculations. In the ensuing discussions, we shall use these assignments as a working hypothesis.

Band Correlation. – As usual, the correlation of the bands in the PE spectra of **1**, **2**, and **4** relies *a*) on the symmetry and nodal properties of the computed molecular orbitals of the molecules, *b*) on the orbital character, *i.e.* the dominant localised (or semi-localised) orbitals that can be recognised in the orbital diagrams of the vacated canonical orbitals *(cf. Fig. 2)*, and *c*) on the size of the observed band shifts, which occur under the influence of the replacement of the exocyclic CH_2 groups by an O-atom.

Molecule **1**. The assignment of the PE spectrum of **1** (symmetry C_{2v}) has been established in [17]. It is rather straightforward, being almost completely symmetry-conditioned. The canonical π orbitals assigned to the bands ①, ②, ④, and ⑤ are practically linear combinations of the localised two-centre π orbitals π_j in positions j = 2, 3, 5, and 6, whereas band ③ is linked to an orbital strongly localised on the atomic 2p(O) orbital of the O-atom in position 7, as shown in the following diagram:



(2)



The symbols S (= symmetric) and A (= antisymmetric) refer to the behaviour with respect to reflection in the *xz*- and the *yz*-plane (in this order).

In contrast, it is almost impossible to assign the strongly overlapping band system beginning with band ⑥ at $I \approx$ 12 eV. It is due to electron ejections from σ orbitals, *e.g.* from ribbon orbitals of the six-membered ring of C-atoms [21].

Molecule **4**. Replacement of the two exocyclic CH_2 groups in positions 2 and 5 of molecule **1** by O-atoms, to yield molecule **4**, leaves the number of electrons, and thus the number of occupied molecular orbitals, invariant. The descent in symmetry from C_{2v} to C_2 mixes the nine a_1 and the five a_2 orbitals, and the seven b_1 and seven b_2 orbitals of **1** to yield the fourteen a and the fourteen b orbitals of **4**, respectively. This introduces a modest, but important restriction for possible correlations. In addition, the following effects are expected on the basis of previous experience [22].

1) Replacement of CH_2 by O in hydrocarbons $RR'C{=}CH_2$ lowers the self-energy of the two-centre basis π orbital by roughly 3.0 eV [5] [22]. This is too large a change to allow the application of a simple first-order perturbation treatment for the correlation of the π bands in the spectra of **1** and **4**, because of the extensive orbital mixing involved (see below). The only conclusion that can be drawn is that electron ejection from orbitals strongly localised on the CO group π orbitals will yield bands imbedded in the high energy band system above 13 eV of the PE spectrum of **4**.

2) In addition, the above replacement introduces into **4** a pair of lone-pair atomic orbitals, which we designate by 2p(CO). Again, previous experience tells us that their basis energies must be close to −10 eV [5] [22]. Their in-phase (*a*) and out-of-phase (*b*) linear combinations (with respect to the $C_2(z)$ rotation) will interact with σ orbitals of the appropriate symmetry. In addition, the b combination interacts with the 2p(O) orbital of the O-atom in position 7.

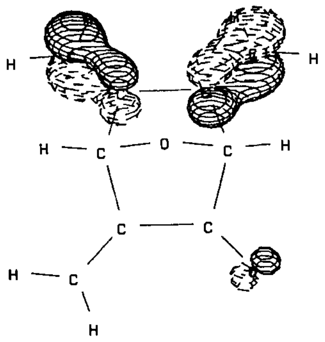
From the computed orbital diagrams presented in *Fig. 2*, it is a simple matter to assign orbital labels and orbital types to the individual canonical orbitals of **4**. These are given in the *Table*. As we shall show below, this is also the sequence expected on qualitative grounds, and there is little doubt that it is essentially the correct one, always within the *Koopmans* approximation we are using.

In *Fig. 3* is shown a bar diagram of the low energy bands in the PE spectra of **1** and **4**, including (in abreviated form) the labels of the corresponding molecular orbitals.

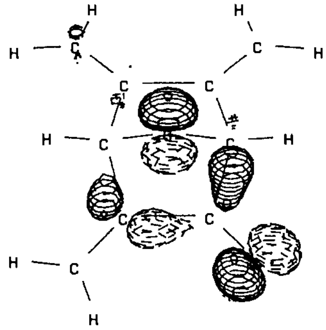
Molecule **2**. This molecule, belonging to the point group C_1, has lost all symmetry elements. However, its PE spectrum is nicely bracketed by those of the molecules **1** and **4**, so that its assignment is rather straightforward. This is indicated by the correlation lines in *Fig. 3*. Comparison with the computed molecular orbitals, presented in diagramatic form in *Fig. 2*, reveals a complete one-to-one agreement, which is a reasonably convincing indication that the proposed assignment (listed in the *Table*) is essentially correct.

We shall, therefore, accept the assignment proposed in the *Table* and in *Fig. 3* as a basis for the discussion presented in the next section.

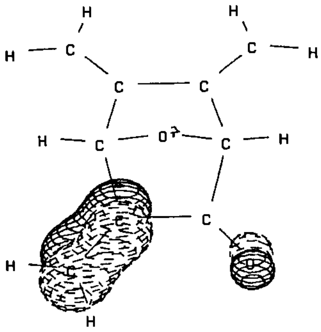
Discussion. – We discuss first the manifold of π orbitals, *i.e.* the assignments of the π bands in PE spectra of **1**, **2**, and **4**, with reference to the parent hydrocarbon **5** [17]. There, the π-orbital energies are well described in terms of a simple LCBO model (= linear combination of bond orbitals), based on the four π orbitals π_j (j = 2,3,5,6) with self-energies $A(\pi_j) = -9.4$ eV, $\beta(\pi\pi) = -0.8$ eV and a homoconjugation interaction $\kappa(\pi\pi) = -0.2$ eV [17]. The influence of the O-atom in **1** manifests itself only in a mean shift $\delta A(\pi_j) = -0.35$ eV of the π orbital energies. The parameters of this extremely crude approximation include of course 'through-space', 'through-bond', and inductive interactions between pairs of basis functions π_j in an unspecified way. The corresponding linear combinations are those shown in (*2*).



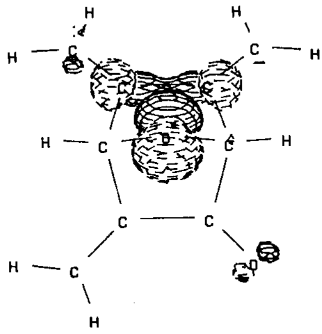
π (←a_2; AA)



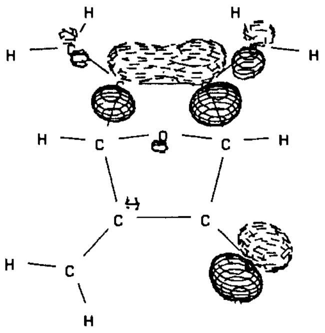
p(O); p(CO)



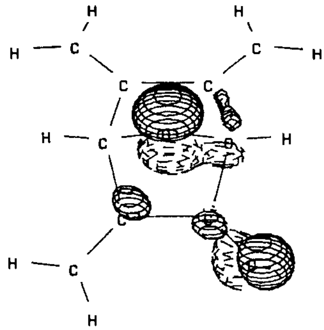
π (←b_1; SA)



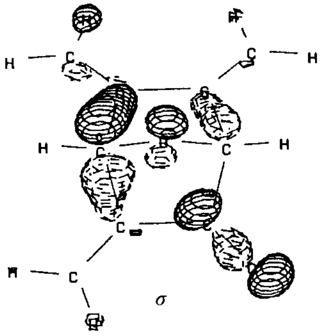
p(O)



π (←b_2; AS)

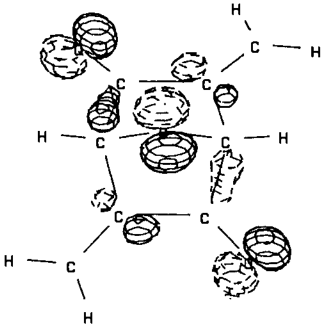


s(O); π (CO)

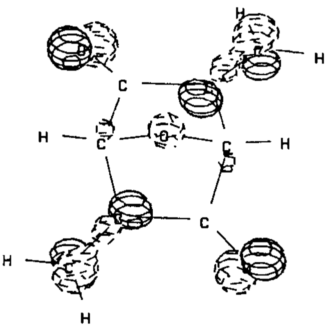


σ

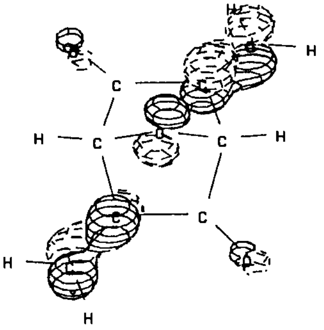
Fig. 2A. *Representation of the highest occupied MO's of* **2** *as calculated by the* ab initio *STO 3G technique* (see the *Table*)



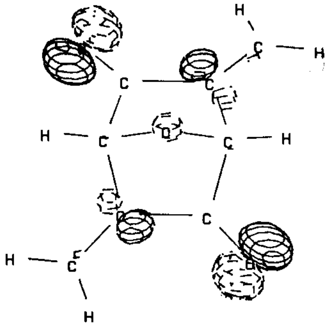
p(O); p(CO)



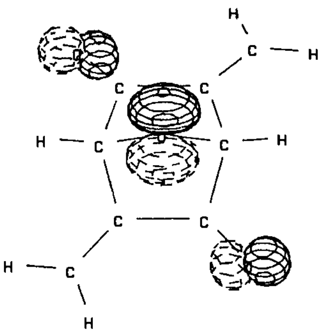
$\pi(\leftarrow a_2, AA)$



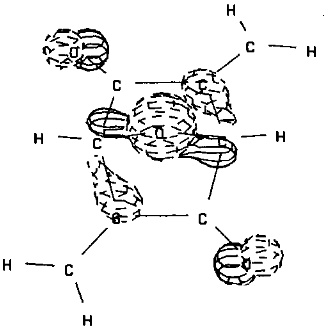
$\pi(\leftarrow b_1; SA)$



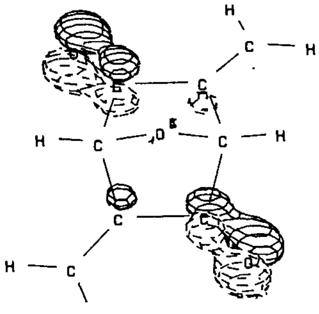
p(CO; a)



p(O); p(CO); b)



s(O); σ



π(CO)

11b

Fig. 2B. *Representation of the highest occupied MO's of* **4** *as calculated by the* ab initio *STO 3G technique* (see the *Table*)

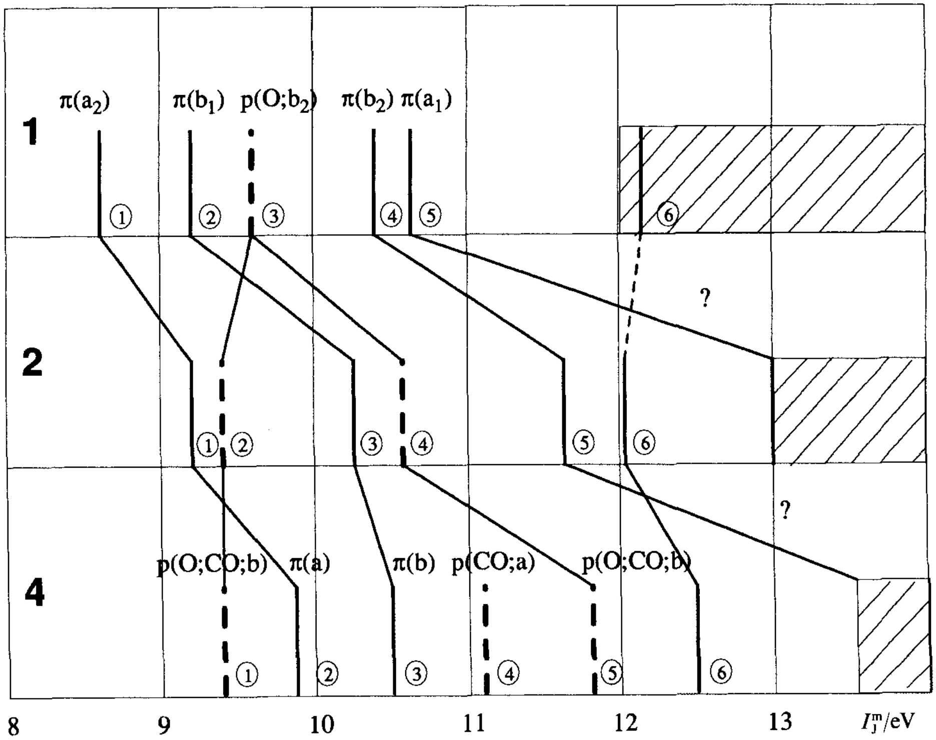
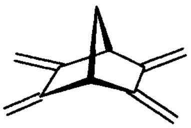


Fig. 3. *Bar diagram of the low-energy bands in the PE spectra of* **1**, **2**, *and* **4**

To a first approximation, the replacement of a terminal CH_2 group in a monoene $RR'C{=}CH_2$ by an O-atom shifts the basis π_{CO} energy $A(\pi_{CO})$ by *ca.* −3 eV with respect to the basis energy $A(\pi_{CC}) = -10.2$ eV of butadiene, if R and R′ are larger alkyl moieties ($R = R' = H$: $\delta A(\pi_{CO}) = -3.99$ eV; $R = Me$, $R' = H$: $\delta A(\pi_{CO}) = -3.21$ eV; $R{=}R' = Me$: $\delta A(\pi_{CO}) = -3.14$ eV [23]). The same value ($\delta A(\pi_{CO}) = -3.25$ eV) is obtained by comparing the π-ionization energies of butadiene (9.0 eV, 11.4 eV [23]) with those of acrolein (11.0 eV, 13.8 eV [24]). In addition, the latter data yield an energy shift of $\delta A(\pi_{CC}) = -0.75$ eV for the basis orbital of the C=C bond in acrolein, due to the neighbouring CO group. Finally, as can be deduced for example from a comparison of the π-ionization energies of molecules such as **6** [25] (8.48 eV, 9.15 eV, 10.30 eV) and **7** (8.90 eV, 10.91 eV [5]), a CO group in position 2 will lower the basis energy of the π orbital in position 6 by roughly $\delta A(\pi_{homo}) = -0.5$ eV.



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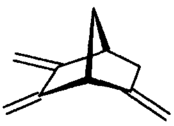

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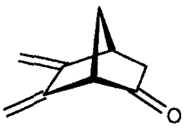

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Using all these parameters within the simple LCBO model mentioned above, yields ionization energies, which mimic reasonably well the observed π-band positions in the spectra **1**, **2**, and **4**, *i.e.*:

$$\begin{array}{llllll}
\mathbf{1} & 8.7 & 9.1 & 10.3 & 10.7 & \mathrm{eV} \\
\mathbf{2} & 9.1 & 10.2 & 10.8 & 13.2 & \mathrm{eV} \\
\mathbf{4} & 10.1 & 10.3 & 13.1 & 13.3 & \mathrm{eV}
\end{array} \tag{3}$$

This empirical result supports, therefore, the assignment derived on the basis of the *ab initio* calculation.

Once the π bands have been identified in the PE spectra, the remaining lower-energy bands must necessarily be those due to electron ejection from canonical orbitals dominated by the lone-pair basis orbitals 2p(O) of the bridging O atom, and 2p(CO) of the CO group(s). Our starting point for the basis energy A(2p(O)) of the O-atom in position 7, is given by $-I_3^m = A(2p(O)) = -9.62$ eV from the spectrum of **1**. Replacement of a C=C group in position 2 or 5 by a CO group will shift A(2p(O)) by *ca.* $\delta A(2p(O)) = -0.5$ eV. The basis energy of the CO lone-pair orbital 2p(CO) is expected to be in the range of $A(2p(CO)) = -9.5$ eV to -10 eV (in formaldehyde -10.9 eV, in acetaldehyde -10.3 eV, in acroleine -10.1 eV, in acetone -9.7 eV, in **7** -9.3 eV, all values taken from the PE spectra [5] [23], assuming that *Koopmans* theorem holds).

Using for the molecule **2** $A(2p(CO)) = -9.8$ eV, and the perturbed value $A'(2p(O)) = -9.6 + (-0.5)$ eV $= -10.1$ eV, to take into account the influence of the CO group (see above), we find that we are in the presence of an almost degenerate pair of lone-pair basis orbitals with a central energy value of -9.95 eV. This agrees nicely with the value derived from the ionization energies of the lone-pair bands 2 and 4, *i.e.* $-I_{\text{lone-pair}} = -(I_2^m + I_4^m)/2 = -10.0$ eV. From the split $-(I_2^m - I_4^m)/2 = 1.13$ eV, one calculates that the cross-term between the two lone-pairs is $\kappa(2p(O), 2p(CO)) = -0.55$ eV, the negative sign being choosen in accord with the nodal properties of the linear combinations depicted in *Fig. 2*. The crudeness of such an approximation is illustrated by the fact that the lone-pair orbitals mix extensively with the $\pi_4 + \pi_5$ type linear combination of the C=C π-orbitals of b_2 parentage, as can be seen from the diagrams in *Fig. 2*.

For the molecule **4**, we make the *ad hoc* assumption that the presence of a second CO group will shift the basis energies $A(2p(CO)) = -9.8$ eV of each 2p(CO) lone-pair orbital by $\delta A(2p(CO)) = -0.5$ eV, to yield $A'(2p(CO)) = -10.3$ eV. Furthermore, the 2p(O) orbital suffers now the influence of two CO groups, which leads to a basis energy of $A'(2p(O)) = -9.6\ \mathrm{eV} + 2(-0.5\ \mathrm{eV}) = -10.6$ eV. Note that the two basis energies are again close together. Using the same cross-term as above, *i.e.* $\kappa(2p(O), 2p(CO)) = -0.55$ eV for the interaction of one of the 2p(CO) atomic orbitals with the central 2p(O) orbital, one calculates, according to this very simple model, the following positions for the lone-pair bands in the PE spectrum of **4**:

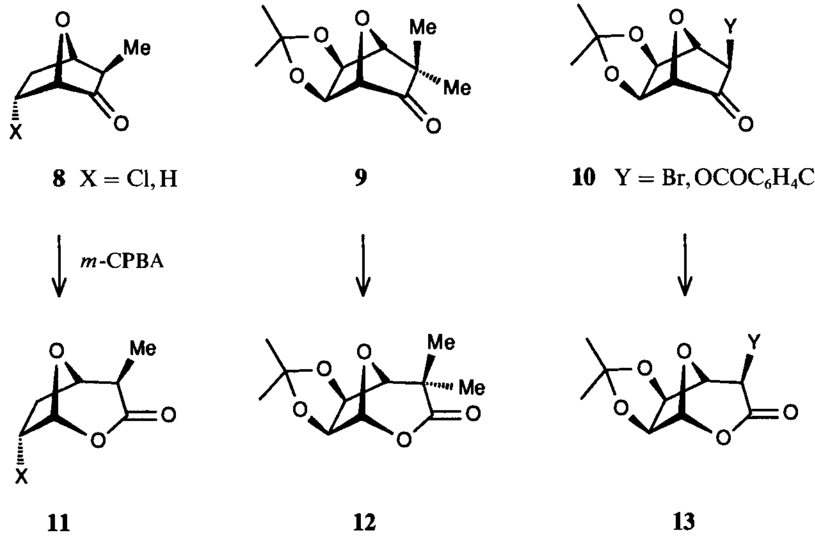
$$\begin{array}{llll}
I_j^m/\mathrm{eV\ calc} & 9.65 & 10.3 & 11.25 \\
I_j^m/\mathrm{eV\ obs} & 9.4 & 11.1 & 11.9
\end{array} \tag{4}$$

Not unexpectedly, the agreement between calculated and observed lone-pair ionization energies is not very good, because of the complete neglect of the interactions of the 2p(O) and 2p(CO) orbitals with other orbitals, but the important point is that one has to introduce again a considerable interaction between 2p(O) and the 2p(CO) to account for the wide split, observed between the corresponding PE bands, which cover a range of about 2.5 eV.

Although the results of our qualitative analysis point to sizeable interactions between the three lone-pair orbitals, we cannot distinguish at this level whether they are of 'through-space' or 'through-bond' type. However, the *ab initio* calculations, summarized in *Fig. 2,* can be interpreted to indicate that 'through-bond' interactions dominate the picture.

This interaction is expected to enhance the nucleophilicity of the σ(C(1)–C(2)) bond in 7-oxabicyclo[2.2.1]heptan-2-ones. This property is probably responsible of the high regioselectivity observed for the *Baeyer-Villiger* oxidations of ketones **8** [26], **9** [27], and **10** [28] that give exclusively the corresponding lactones **11**, **12**, and **13** *(Scheme)*. Work is underway in our laboratories to confirm this hypothesis[4])[5]).

Scheme



Conclusions. – The new trienone **2** and dienedione **4** obtained by controlled ozonolysis of tetraene **1** reveal the existence of significant through-bond interactions between the oxygen lone-pair orbitals of the ethereal (n(O)) and carbonyl (n(CO)) functions of 7-oxabicyclo[2.2.1]heptan-2-ones.

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[4]) Through-bond interactions of type n(N:), $\sigma \leftrightarrow \pi$(CO) and n(N:), $\sigma \leftrightarrow$n(CO) have already been evidenced in 3-ketopiperidines [29]. Through-space interactions between n(N:) and n(CO) lone-pairs have been discussed in relation with the PE spectra of 2-ethoxycarbonyl-2-azabicyclo[2.2.2]octan-5-one [30].

[5]) Through-bond interactions between n(O) and π levels in allylic ethers have been evidenced by PE spectroscopy [31]. Through-bond interactions between the nonbonded electron pairs n(O), n(N), and n(S) in 1,4-dioxane, piperazine, and 1,4-dithiane, respectively, have also been discussed [32].

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Experimental Part

General. See [33].

3,5,6-Trimethylidene-7-oxabicyclo[2.2.1]heptan-2-one (**2**). A 97:3 mixture of O_2/O_3 (0.5 dm^3/min) was bubbled through a soln. of **1** (0.6 g) [15] in anh. toluene (50 ml) cooled to −90°. After disappearance of *ca.* 60% of **1** (TLC or ^{1}H-NMR), Me_2S (0.2 ml) was added and the mixture allowed to warm to 20° (1 h). The soln. was concentrated to *ca.* 1 ml by evaporation *in vacuo* and purified by column chromatography on silica gel (30 g, petroleum ether (350 ml), then petroleum ether/Et_2O 95:5). The first fraction gave 200 mg (33%) of **1**, the second fraction yielded 220 mg (55%) of **2**, yellowish oil that polymerized quickly at 5°. It can be stored under N_2 atm at −40°. UV ($CHCl_3$): λ_{max}: 248, 272, 365. IR (film): 3120, 3020, 2950, 1770, 1675, 1665, 1440, 1410, 1280, 1270, 1235, 1210, 1185, 1100, 980, 955, 935, 910. ^{1}H-NMR (CCl_4): 5.92, 5.59, 5.44 (3 *s*, 3 H); 5.39 (*s*, 2 H); 5.29, 5.22, 4.65 (3 *s*, 3 H). ^{13}C-NMR ($CDCl_3/CCl_4$ 1:1): 195.1, 145.1, 144.2, 140.6 (4 *s*, 4 C); 113.6, 107.6, 103.7 (3 *t*, 3 $CH_2{=}C$); 85.5, 84.1 (2 *d*, C(1), C(4)). MS (70 eV): 148 (8, $M^{+\cdot}$), 120 (7), 119 (9), 92 (15), 91 (100), 85 (6), 83 (9), 66 (8), 65 (32), 64 (5), 63 (11), 62 (6), 53 (7).

3,5-Dimethylidene-7-oxabicyclo[2.2.1]heptane-2,6-dione (**3**) *and 3,6-Dimethylidene-7-oxabicyclo[2.2.1]heptane-2,5-dione* (**4**). 3% O_2 in O_2 (1 dm^3/min) was bubbled through a soln. of **1** (50 mg, 0.34 mmol) in anh. toluene (5 ml) cooled to −75° for 3 min. Me_2S (0.07 ml) was added and the mixture allowed to warm to 20° (3 h). The solvent was evaporated and the residue extracted with petroleum ether. The extract was purified by prep. GC (*OV 17*, T=100–160°, 4°/min, He, 40 ml/min). The first fraction (t_R 10.7 min) gave **4**, (10–20%, internal standard) yellow oil that polymerized at 20°. The second fraction afforded **3** (10–30%, internal standard: toluene), yellow oil that polymerized quickly at 0°, even in dilute soln.

Data of **3**. UV ($CHCl_3$): $\lambda_{max.}$: 256, 336, 354, 408. ^{1}H-NMR ($CDCl_3$): 6.1 (*m*, 2 H of $CH_2{=}C(3)$ and $CH_2{=}C(5)$ *syn* to CO); 5.8 (br. *dt*, ^4J=1.5, 1.0, H−C(4)); 5.6 (br. *d*, ^4J=1.0, 2 H of $CH_2{=}C(3)$ and $CH_2{=}C(5)$ *anti* to CO); 4.5 (*d*, ^4J=1.5, H−C(1)).

Data of **4**. UV ($CHCl_3$): λ_{max}: 248, 340, 355, 392, 410. ^{1}H-NMR ($CDCl_3$): 6.3 (*d*, ^4J=0.7, 2 H of $CH_2{=}C(3)$ and $CH_2{=}C(6)$ *syn* to CO); 5.72 (*d*, ^4J=1, 2 H of $CH_2{=}C(3)$ and $CH_2{=}C(6)$ *anti* to CO); 5.0 (*m*, H−C(1), H−C(4)). MS (70 eV): 150 (19, $M^{+\cdot}$), 122 (15), 121 (2), 94 (14), 83 (100), 67 (19), 66 (43), 55 (59).

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