142. Interactions between Oxygen Lone-Pair Orbitals and Double-Bond π-Orbitals in β, γ-Unsaturated, Bicyclic Ketones; a PE-Spectroscopic Investigation

by **Pierre-Alain Carrupt, Raphy Gabioud, Albino Rubello,** and **Pierre Vogel***
Institut de chimie organique de l'Université de Lausanne, 2, rue de la Barre, CH-1005 Lausanne

and **Evi Honegger**[1]) and **Edgar Heilbronner***
Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

(7.VII.87)

The HE(Iα) photoelectron (PE) spectra of 2,3,5,6-tetramethylidene-2-bicyclo[2.2.1]heptanone (**12**), 5,6-dimethylidene-2-bicyclo[2.2.1]heptanone (**14**), 5,6-dimethylidene-2-bicyclo[2.2.2]octanone (**16**), and 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanone (**17**) have been recorded. Comparison with the PE data of other β,γ-unsaturated ketones and parent alkenes, and with the result of *ab initio* STO-3G calculations, confirm the existence of significant interactions between the oxygen lone-pair orbital n_O and the double-bond π orbital(s). It is argued that the major contributions to the basis energy shifts and to the cross term between the n_O and π orbitals are due to a 'through-bond' mechanism.

Introduction. – The assessment of the extent and of the mechanism(s) of interaction between the carbonyl-group orbitals, 2p(O) or π_{CO}, and the π orbital(s) of (a) nonconjugating double bond(s) within a (poly)cyclic molecule, seems to be, at first sight, a problem well suited for a PE-spectroscopic investigation [1–4]. However, there are some serious limitations, both from an experimental and theoretical point of view.

The basis energy $A(\pi_{CO})$ of the CO-group π orbital π_{CO} is rather low ($A(\pi_{CO}) = -10.88$ eV from the PE spectrum of H_2CO [5]), with the result that, in larger molecules, π_{CO} finds itself embedded in the closely spaced manifold of the framework σ orbitals. Symmetry permitting, π_{CO} will interact strongly with those σ orbitals lying close in energy, thus giving rise to rather diffuse MOs. This makes it difficult, if not impossible, to find a band in the PE spectrum, which could be labeled confidently as of dominant π_{CO}^{-1} origin, so that interaction cross terms involving the π_{CO} orbital (*e.g.* $\langle\pi_{CO}|\hat{H}|\pi_{CC}\rangle$ for homoconjugation) can not be derived from the PE spectra of molecules such as those investigated in this work. As far as C=C bond π orbitals π_{CC} (or their linear combinations π_j) of the molecule are concerned, the influence of a non-conjugating CO group on their orbital energies $A(\pi_{CC})$ or $\varepsilon(\pi_j)$ is best described by a negative basis-energy shift $\delta A(\pi_{CC}) < 0$, which could be called inductive. Such a shift will manifest itself in a corresponding, positive shift of the ionization energy I_j^m of the PE band, relative to its position in the spectrum of a CO-free reference molecule.

On the other hand, the interaction between (a) double-bond π orbital(s), π_{CC} π_j, and the CO-group lone-pair orbital $2p(O) \equiv n_O$ can be analyzed in more detail, because these

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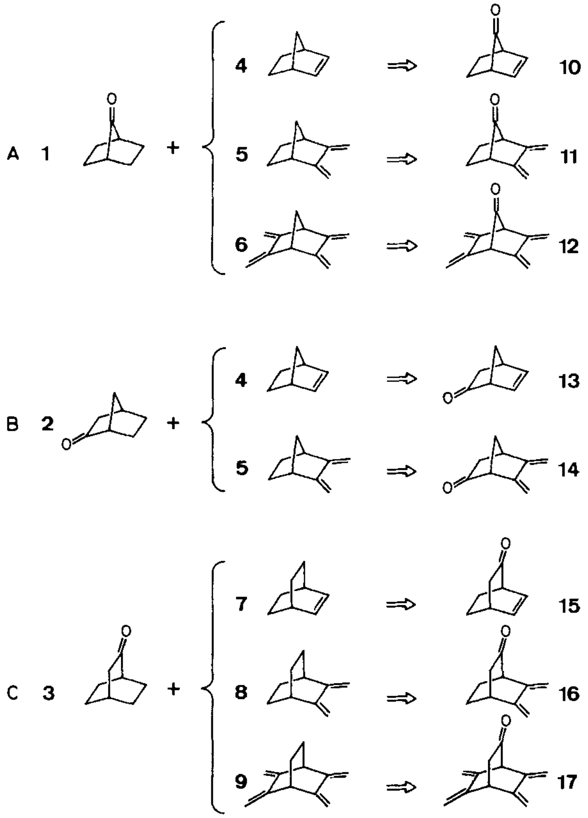
[1]) Present address: Institut für Anorganische Chemie der Universität Bern, Freiestr. 3, CH-3012 Bern.

outer shell valence orbitals give rise to well detached and easily localisable PE bands. It is convenient, and usually sufficient, to describe these interactions in terms of two types of parameters: *a*) basis-energy shifts $\delta A(\pi_{CC})$ and $\delta A(n_O)$ induced by the presence of the *other* group, and *b*) interaction cross-term $\varkappa(\pi_{CC},n_O)$, the exact meaning of which is left open for the moment.

In the present investigation, we first analyse the PE spectra of the unsaturated, bicyclic ketones **10**–**17** in terms of the above parameters by applying the traditional correlation procedure [6] to the sets *A*, *B*, and *C* shown in the *Correlation Schemes*. It will be found that a self-consistent set of reasonable parameters $\delta A(\pi_{CC})$, $\delta A(\pi_j)$, $\delta A(n_O)$, and $\varkappa(\pi_{CC},n_O)$ can be found, which rationalizes all of the observed data within satisfactory limits of error. In a second step, we shall try to confirm the assignments suggested by these parameters, using minimal basis set *ab initio* calculations [7], and to interpret the parameters in terms of specific electronic mechanisms.

Correlation Schemes



Experimental Results. – In *Fig. 1* are shown the He(Iα) PE spectra of the tetraenones **12** and **17**, and of the dienones **14** and **16**. The observed band positions I_j^m, *i.e.* those of the band maxima are collected in the *Table*, toghether with the literature values of the ketones **1**–**3**, the unsaturated hydrocarbons **4**–**9**, the enones **10**, **13**, **15**, and the dienone **11** (references given in the *Table*).

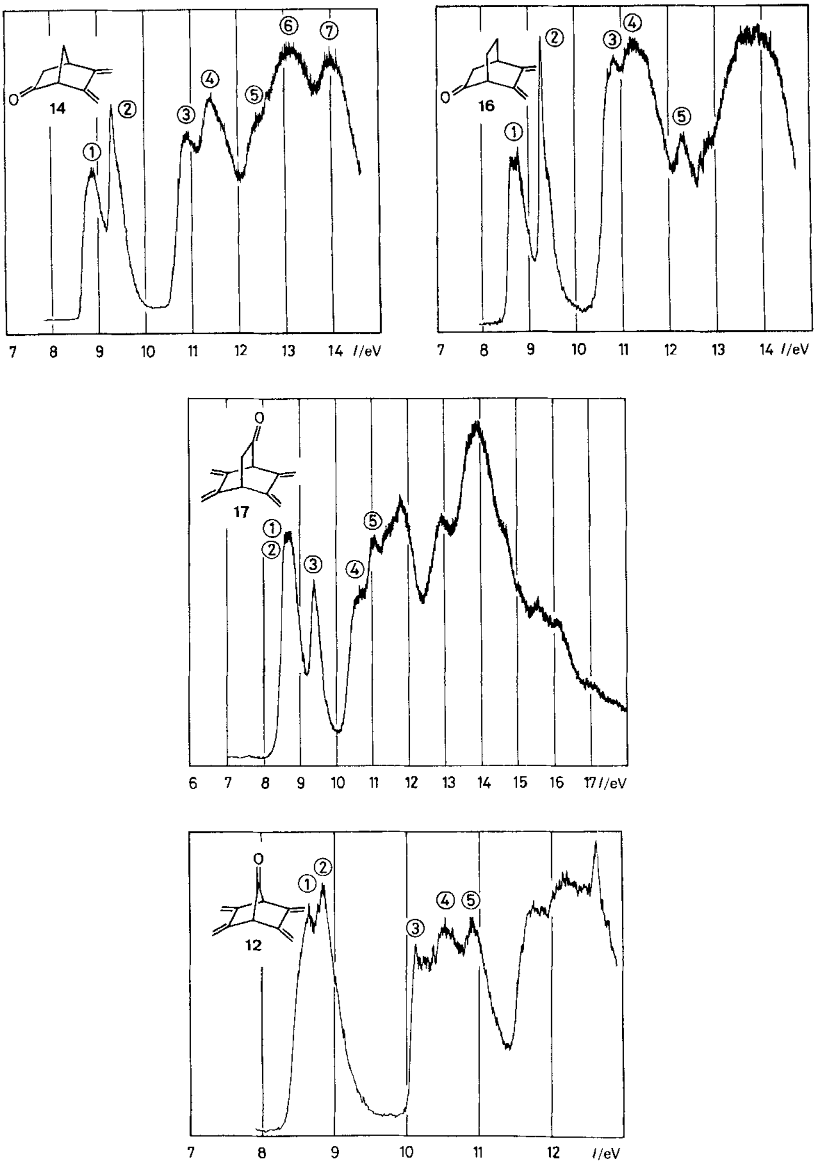


Fig. 1. *HE(Iα) PE spectra of* **12**, **14**, **16**, *and* **17**

PE-Band Correlations. – We shall now analyse the PE spectra with reference to the *Correlation Schemes*. To this end, it is of advantage to proceed in descending order of symmetry.

Correlation Set A. The correlation **1**→**6**→**12** takes place within the symmetry group C_{2v}. Thus, the relevant linear combinations π_j of the double-bond π orbitals are symmetry-conditioned, one combination per irreducible representation, as shown in *Fig. 2*, where the π_j(symm. label) are arranged in increasing order of orbital energy, from left to right.

Table. *Ionization Energies* I_j^m *and PE-Band Assignments of Molecules* **1** *to* **17**. I_j^m = observed positions of PE-band maxima (experimental error of new recordings ±0.03 eV if two decimals given, ±0.05 eV if second decimal given as subscript). ε_j = orbital energies calculated by the STO-3G procedure [7], using the MNDO minimum-energy structure. The values in parentheses, given for **1**, **2**, **4**, **5**, **10**, and **13**, refer to the STO-3G minimum structure (*cf.* text). I_j^{KT} = predicted vertical ionization energy using *Koopmans'* theorem and regeression (*5*).

	I_j^m/eV	$-\varepsilon_j$/eV	I_j^{KT}/eV	Assignment	
1	9.06 [2]	8.02 (8.06)	9.26	n_O	
	11.10	10.66 (10.78)		σ	
		10.89 (10.90)		π_{CO}	
2	9.14 [2]	8.27 (8.23)	9.44	n_O	
		10.26 (10.34)		π_{CO}	
	10.70	11.02 (11.26)		σ	
3	9.10 [2]	8.23	9.41	n_O	
		9.92		π_{CO}	
	10.68	10.61		σ	
4	8.97 [2]	7.87 (7.87)	9.16	π	
	10.55	10.44 (10.42)		σ	
5	8.41 [9]	6.92 (7.21)	8.51	π_2 (a″)	
	10.20	9.54 (9.70)	10.30	π_1 (a′)	
	10.70	10.52 (10.55)		σ	
6	8.34 [10]	6.85	8.47	π_{2-} (a_2)	
	8.82	7.20	8.71	π_{2+} (b_1)	
	10.01	9.43	10.23	π_{1-} (b_2)	
	11.02	9.59	10.34	π_{1+} (a_1)	
		10.93		σ	
7	9.07 [11]	7.67	9.03	π	
	10.04	9.92		σ	
8	8.37 [9]	6.76	8.41	π_2 (a″)	
	10.14	9.75	10.44	π_1 (a′)	
	10.53	10.12		σ	
9	8.36 [10]	6.73	8.38	π_{2-} (a_2)	
	8.56	6.88	8.49	π_{2+} (b_1)	
	10.20	9.45	10.24	π_{1-} (b_2)	
	10.59	9.77	10.46	π_{1+} (a_1)	
	11.55	10.27		σ	
10	9.25 [2]	8.20 (8.29)	9.39	n_O (a″)	
	9.61	8.35 (8.35)	9.49	π_{CC} (a′)	
		11.11 (11.11)		π_{CO} (a′)	
	11.00	11.15 (11.15)		σ	
11	8.64 [2]	6.97	8.55	$\pi_2 - \lambda n_O$	
	9.58	8.57	9.74	$n_O + \lambda\pi_2$	
	10.70	9.97	10.59	π_1	
12	8.66	7.00	8.57	$\pi_{2+} - \lambda n_O$	(b_1)
	8.87	7.14	8.66	π_{2-}	(a_2)
	10.11	9.22	10.08	$n_O + \lambda\pi_{2+}$	(b_1)
	10.54	9.78	10.46	π_{1-}	(b_2)
	10.90	10.05	10.65	π_{1+}	(a_1)
		10.81		π_{CO}	
13	8.86 [2]	7.42 (7.62)	8.86	$\pi - \lambda n_O$	
	10.09	9.02 (9.18)	9.95	$n_O + \lambda\pi$	
	11.20	10.32 (10.40)		π_{CO}	
		11.76 (11.92)		σ	
14	8.90	7.12	8.65	$\pi_2 - \lambda n_O$	
	9.29	8.36	9.50	$n_O + \lambda\pi_2 - \lambda\pi$	
	10.91	10.26	10.79	$\pi_1 + \lambda n_O$	
		10.42		π_{CO}	
	11.40	10.94		σ	
15	8.96	7.63	9.00	$n_O + \lambda\pi$	
	9.92	8.82	9.81	$\pi - \lambda n_O$	
		10.00		π_{CO}	
	10.63	10.91		σ	
16	8.70	6.98	8.56	$\pi_2 - \lambda n_O$	
	9.27	8.41	9.53	$n_O + \lambda\pi_2 - \lambda\pi_1$	
	10.80	10.19	10.74	$\pi_1 + \lambda n_O$	
	11.20	10.91		σ	
		11.09		π_{CO}	
17	8.75	7.06	8.61	π_{2-}	(a″)
	8.85	7.07	8.62	$\pi_{2+} + \lambda n_O$	(a′)
	9.42	8.55	9.63	$n_O + \lambda\pi_{2+} - \upsilon\pi_{1+}$	(a′)
	10.65	9.88	10.53	π_{1-}	(a″)
		10.34		π_{CO}	
	11.10	10.44	10.92	$\pi_1 + \upsilon n_O$	(a′)
	11.50	11.50		σ	

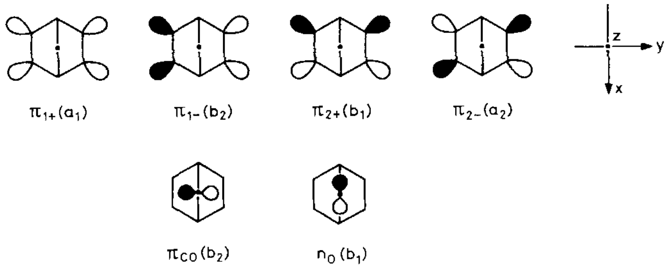


Fig. 2. *Schematic representations of the* π_j, π_{CO}, *and* n_O *orbitals of the tetraenone* **12** (C_{2v} symmetry)

Although in **12** the CO π orbital π_{CO} could interact with π_{1-}, both belonging to b_2, it is safe to assume that its low basis energy and small cross-term does not lead to significant mixing, at least on the level of our rough analysis. On the other hand, the lone-pair orbital n_O will mix with π_{2+}, whereas the orbitals π_{1+}, π_{1-}, and π_{2-} remain unaffected. For this reason, the positions of the π_{1+}^{-1}, π_{1-}^{-1}, and π_{2-}^{-1} bands in the PE spectrum of **12** will be shifted relative to their position in **6** only because of the 'inductive' effect $\delta A(\pi_{CC}) = \delta A(\pi_j)$ of the CO group, *i.e.* due to a lowering of the basis π-orbital energy $A(\pi_{CC})$. Comparison of the relevant I_j^m values yields $\delta A(\pi_{CC}) = \delta A(\pi_j) = -0.5_5$ eV. Accordingly, the basis energy of π_{2+} is expected at $A(\pi_{2+}) = -8.82\text{ eV} - 0.55\text{ eV} = -9.37$ eV. This value, together with the orbital energies $\varepsilon_{HOMO} = -8.66$ eV and $\varepsilon_{HOMO-2} = -10.11$ eV of the two mixed orbitals of **12** (obtained from the I_j^m values, using *Koopmans'* theorem in reverse) allows the straightforward computation of the basis energy $A'(n_O)$ and of the cross-term $\varkappa(\pi_{2+},n_O)$ valid for **12**, namely $A'(n_O) = -9.40$ eV and $\varkappa(\pi_{2+},n_O) = -0.72$ eV. Comparing the former value to $A(n_O) = -9.06$ eV of **1** leads to $\delta A(n_O) = -0.34$ eV, whereas the latter value yields $\varkappa(\pi_{CC},n_O) = -0.36$ eV for the interaction of the lone-pair orbital with a single π-bond basis orbital π_{CC} in the molecule **12**.

A similar treatment may now be applied to the correlation **1**→**5**→**11**, notwithstanding the fact that the symmetry is now only C_s. In this case, the in-phase linear combination of the double-bond π orbitals, $\pi_1(a')$, is orthogonal to n_O, and a comparison of the corresponding I_j^m values in the PE spectra of **5** and **11** yields $\delta A(\pi_{CC}) = -0.50$ eV, in excellent agreement with the previous shift. From it, we derive $A'(\pi_2) = -8.91$ eV, using the same arguments as above. This value, together with the 'observed' orbital energies $\varepsilon_{HOMO} = -8.64$ eV and $\varepsilon_{HOMO-1} = -9.58$ eV, leads to $A'(n_O) = -9.31$ eV and $\varkappa(\pi_1,n_O) = -0.43$ eV, both valid for the molecule **11**. In this case, the shift of the lone-pair-orbital basis energy (relative to **1**) is only $\delta A(n_O) = -0.25$ eV, *i.e.* smaller than in **12**, as one might have expected. Note that the ratio of the interaction cross-terms in **12** and **11** is $\varkappa(\pi_{2+},n_O)/\varkappa(\pi_1/n_O) = 1.67$, rather close to the theoretical value of $\sqrt{2} = 1.41$, which one would have expected, if the geometry of the norbornane skeleton were the same in **11** and **12**. It is an open question, if the slightly larger ratio observed can be interpreted by assuming that the CO group in **11** is tilted away from the butadiene moiety.

The correlation **1**→**4**→**10**, is rather simple, because the double-bond π orbital is orthogonal to the lone-pair orbital n_O. Thus, there is no interaction, and the observed I_j^m values can be taken directly as estimates of $A'(n_O) = -9.25$ eV and $A'(\pi_{CC}) = -9.61$ eV. The corresponding shift $\delta A(n_O)$ has decreased in **10** to $\delta A(n_O) = -0.19$ eV, whereas $\delta A(\pi_{CC}) = -0.64$ eV is now slightly larger than the previous values obtained from **11** and **12**, due to the endocyclic position of the double bond in **10**.

The above results may now be summarized as follows:

Molecule	$\delta A(\pi_{CC})$/eV	$\delta A(n_O)$/eV	$\varkappa(\pi_{CC},n_O)$/eV	
10	–0.64(*endo*)	–0.19	–	
11	–0.50(*exo*)	–0.25	–0.30	(1)
12	–0.55(*exo*)	–0.34	–0.36	

Correlation Set B. The two correlations **2**→**4**→**13** and **2**→**5**→**14** are no longer as simple as those of the previous *Set A*, because of lack of symmetry. However, it can be shown that they lead to unique assignments and that the parameters involved are fully compatible with those given in (*1*).

Assuming that the basis energy shifts $\delta A(\pi_{CC}) = -0.64$ eV and $\delta A(n_O) = -0.19$ eV, derived from the correlation **1**→**4**→**10**, are valid for **2**→**4**→**13**, leads to $A'(\pi_{CC}) = -9.61$ eV and $A'(n_O) = -9.33$ eV for molecule **13**. The validity of our assumption is verified by the fact that the sum $A'(\pi_{CC}) + A'(n_O) = -18.94$ eV is identical to the sum of the first two ionization energies of **13**, *i.e.* $-(I_1^m + I_2^m) = -18.95$ eV, within 0.01 eV. From the differences $A(n_O) - A(\pi_{CC})$ and $I_2^m - I_1^m$, we compute the cross therm $\varkappa(\pi_{CC},n_O) = -0.60$ eV.

Using the $\delta A(\pi_{CC})$ and $\delta A(n_O)$ values listed for **11** and **12** in (*1*) yields for the basis energies of **14** $\varepsilon(\pi_2) = -8.91$ to -8.96 eV, $\varepsilon(\pi_1) = -10.70$ to -10.75 eV, and $A(n_O) = -9.39$ to -9.48 eV. The sum of the basis energies is, thus, -29.0 eV to -29.19 eV, a value which is in perfect agreement with $-(I_1^m + I_2^m + I_3^m) = -29.10$ eV, obtained from the PE spectrum of **14**. This proves again, that our set of $\delta A(\pi_{CC})$ and $\delta A(n_O)$ parameters (*1*) exhibits a high degree of transferability, if judged by the criterion of the sum-rule [6]. Comparison of the basis-orbital energies with the $-I_j^m$ values of **14** shows that the matched pairs differ very little from each other, which, at first sight, suggests that $\varkappa(\pi_{CC},n_O)$ must be rather small. It is easy to show that any value of $\varkappa(\pi_{CC},n_O)$ in the range of $0 \text{ eV} < |\varkappa(\pi_{CC},n_O)| < \sim 0.4$ eV would not lead to significant differences in agreement. Unfortunately, this means that no conclusions can be drawn concerning the size of the cross term $\varkappa(\pi_{CC},n_O)$ in **14** on the basis of the observed PE-spectroscopic data alone. (A comparison with the result for **13** suggests $\varkappa(\pi_{CC},n_O) \approx -0.3$ eV for **14**.)

Correlation Set C. We begin again by analyzing the last correlation **3**→**9**→**17** of the set, where we can make use of the C_{2v} or C_s symmetry of the molecules **9** or **3**, and **17**, respectively. Lowering the symmetry from C_{2v} to C_s yields $a_2, b_2 \rightarrow a''$ and $a_1, b_1 \rightarrow a'$, so that the orbitals π_{2-} (a″) and π_{1-} (a″) of **17** can not interact with n_O (a′). Accordingly, a comparison of the I_j^m values of the PE bands assigned to π_{2-} and π_{1-} in **9** and **17** directly yields the $\delta A(\pi_{CC})$ value induced by the presence of the CO group in **17**. One finds $\delta A(\pi_{CC}) = -0.39$ eV and -0.45 eV, respectively, or a mean value of $\delta A(\pi_{CC}) = -0.42$ eV, which is of the same magnitude as those listed in (*1*), but slightly smaller, because of the larger σ frame. If the same $\delta A(\pi_{CC})$ value is applied to the orbital energies of π_{2+} (a′) and π_{1+}(a′) of **9**, and if the sum of the four basis energies is now subtracted from the negative sum of the first five ionization energies of **17**, we obtain $A'(n_O) = -9.38$ eV for the basis energy of the lone-pair orbital n_O in **17**. This is lower by $\delta A(n_O) = -0.28$ eV than the corresponding energy in **3**, a value in excellent agreement with those derived for **11** ($\delta A(n_O) = -0.25$ eV) and **12** ($\delta A(n_O) = -0.34$ eV) (*cf.* (*3*)). As was already observed for **14**, the basis energies of the orbitals π_{2+}(a′), π_{1+}(a′), and n_O(a′) derived in this way are so close to the corresponding, negative ionization energies of **17**, that the influence of $\varkappa(\pi_{CC},n_O)$ must be very small. Because of the relatively large differences in the energies of these orbitals belonging to the same irreducible representation, all values of $\varkappa(\pi_{CC},n_O)$ in the approximate range $0 < |\varkappa(\pi_{CI},n_O)| < \sim 0.4$ eV are again compatible with the observed spectrum of **17**, certainly within the limits imposed by our crude treatment.

Applying the increments $\delta A(\pi_{CC}) = -0.42$ eV and $\delta A(n_O) = -0.28$, deduced above from the correlation **3**→**9**→**17**, to the 'observed' basis energies $A(\pi_2) = -8.37$ eV and $A(\pi_1) = -10.14$ eV of **8**, and to $A(n_O) = -9.10$ eV of **3**, respectively, yields $A'(\pi_2) = -8.79$ eV, $A'(\pi_1) = -10.56$ eV, $A'(n_O) = -9.38$ eV, the sum of which is -28.73 eV, in excellent agreement with $-(I_1^m + I_2^m + I_3^m) = -28.77$ eV, observed for **16**. From the rather close agreement of the shifted basis energies $A'(\pi_2)$, $A'(\pi_1)$, $A'(n_O)$ of **16** with the corresponding, negative ionization energies, one deduces, in analogy to the conclusions reached for **17**, that the influence of the cross-terms $\varkappa(\pi_{CC},n_O)$ must be small. Any value of $\varkappa(\pi_{CC},n_O)$ in the interval from 0 to ~ -0.4 eV would be compatible with the observed PE spectrum.

Finally, the correlation **3**→**7**→**15** yields $\varkappa(\pi_{CC},n_O) = -0.48$ eV, based on the ionization energies $I_1^m = 8.96$ eV and $I_2^m = 9.92$ eV of **15** and on the basis energies $A'(\pi_{CC}) = -9.07$ eV $-$ 0.4 eV (from **7** and $\delta A(\pi_{CC})$) and $A'(n_O) = -9.10$ eV$-$ 0.3 eV (from **3** and $\delta A(n_O)$). This cross-term is of the same magnitude, but slightly smaller, than that observed for **13**.

Summarizing the results of the latter two correlation sets, wie find:

Molecule	$\delta A(\pi_{CC})$/eV	$\delta A(n_O)$/eV	$\varkappa(\pi_{CC},n_O)$/eV	
13	–0.64a)	–0.19a)	–0.60	
14	–0.50b)	–0.25b)	0 to –0.4	
15	–0.4c)	–0.3c)	–0.48	(2)
16	–0.42d)	–0.28d)	0 to –0.4	
17	–0.42	–0.28	0 to –0.4	

a) Carried over from **10** (*cf.* (*1*))

b) Carried over from **11** (*cf.* (*1*))

c) Estimated on the basis of the data in (*1*) and those of **17**.

d) Carried over from **17**.

It should be mentioned again that the cross-terms $\varkappa(\pi_{CC},n_O)$ given for **14**, **16**, and **17** are completely undefined within the range given. A value close to -0.2 eV or -0.3 eV would correspond to expectation, but can neither be proved, nor disproved on the basis of the observed PE spectra.

Assignment of the PE Spectra. – A complete assignment of the PE spectra under discussion is, for the time being, nearly impossible and even a partial assignment is less than straightforward. Some of the reasons are: *a*) Only the first few bands in the PE spectra are well detached from the strongly overlapping band systems at higher ionization energies, yielding reliable I_j^m values. *b*) The bands lack resolved vibrational fine structure, due to the large size and complexity of the molecules. *c*) Reliable calculations of ionization energies I_j^v are not possible by either SCF semi-empirical or by *ab initio* models using minimal basis sets (*e.g.* STO-3G) [7] even within the limitations of *Koopmans'* theorem, and *ab initio* calculations with extended basis sets are still prohibitive for larger molecules.

For all molecules **1** to **17**, valence-shell orbital energies ε_j have been calculated by the STO-3G procedure [7] using the minimum-energy structure derived from a MNDO treatment [8]. This could produce noticeable errors in the absolute values of the computed ε_j values, because orbital-energy calculations should be carried out at the minimum-energy structure yielded by the *same* theoretical model. However, to evaluate that risk, we have calculated the minimum-energy structures of **1**, **2** [12], **4**, **5**, **10**, and **13** [13] with the minimal basis set STO-3G *ab initio* method [7], and have found the orbital energies ε_j shown in parentheses in the *Table*. The latter do not differ dramatically from those obtained by the STO-3G procedure applied on MNDO-optimized geometries. Furthermore, the shape and symmetry of the corresponding orbitals were quite similar. On the other hand, the relative ordering of the individual orbitals, especially of the highest filled ones, will presumably be correct. These orbitals, characterized by the dominating basis orbitals, and their orbital energies are given in the *Table*.

The outer orbitals are, by necessity, those dominated by the double-bond π orbitals, π_{CC}, or their appropriate linear combinations π_j, and by the oxygen lone-pair orbital n_O. Comparing the orbital energies ε_j of the 31 π-dominated and of the 11 n_O-dominated orbitals to the observed ionization energies I_j^m, yields the following regressions, in which I_j^{KT} stands for the predicted ionization energies derived from the scaled ε_j values, assuming the validity of *Koopmans'* theorem.

π-dominated orbitals:

$$\left(\frac{I_j^{KT}}{\text{eV}}\right) = (0.678 \pm 0.019)\left(\frac{-\varepsilon_j}{\text{eV}}\right) + (3.881 \pm 0.159) \tag{3}$$

$$\text{Std. err.} = 0.141;\ r^2 = 0.978$$

n_O-dominated orbitals:

$$\left(\frac{I_j^{KT}}{\text{eV}}\right) = (0.671 \pm 0.083)\left(\frac{-\varepsilon_j}{\text{eV}}\right) + (3.731 \pm 0.688) \tag{4}$$

$$\text{Std. err.} = 0.126;\ r^2 = 0.879$$

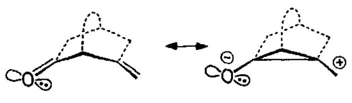
(The ranges of the slopes and intercepts correspond to their standard errors; Std. err. = residual standard error; r^2 = square of the correlation coefficient.) It is immediately obvious that the two regressions (*3*) and (*4*) do not differ significantly, which means that the particular choice of STO-3G basis functions does not produce a systematic discrimination of π_{CC}- or n_O-dominated orbitals, as far as their energy is concerned. Therefore, we are allowed to merge the regressions (*3*) and (*4*) into a single one, based on 42 data points:

$$\left(\frac{I_j^{KT}}{\text{eV}}\right) = (0.682 \pm 0.021)\left(\frac{-\varepsilon_j}{\text{eV}}\right) + (3.795 \pm 0.179) \tag{5}$$

$$\text{Std. err.} = 0.163;\ r^2 = 0.963$$

The predicted ionization energies obtained according to (*5*) are given in the *Table*, as well as the assignments corresponding to these energies. Note that these assignments agree with those underlying our correlation analysis.

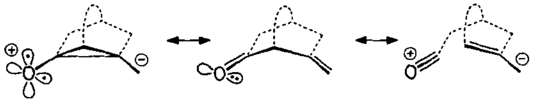
Discussion. – Our analysis of the PE spectra of the β,γ-unsaturated ketones **10** to **17** confirms the existence of significant interactions between the homoconjugated double bonds and CO groups. Such interactions had already been observed and discussed by *Houk* and coworkers [14], in particular in the molecules **10** and **13**. These interactions have been characterized by the parameters $\delta A(\pi_{CC})$, $\delta A(n_O)$, and $\varkappa(\pi_{CC}, n_O)$ collected in (*1*) and (*2*), with reference to a MO model using essentially only two basis functions, namely the π orbital π_{CC} of a double bond (or the symmetry-adapted linear combination π_j) and the lone-pair orbital n_O of the CO O-atom. Within such a model, the δA shifts can be regarded as being due to an 'inductive effect' of one of the functions onto the other, transmitted *via* the σ frame of the molecule. Thus, $\delta A(n_O)$ is mainly due to the replacement of (an) sp^3-hybridized C-atom(s) of the saturated bicyclic ketone (*e.g.* **1**, **2**, or **3**) by sp^2-hybridized C-atoms. The same mechanism contributes towards $\delta A(\pi_{CC})$, *i.e.* the replacement of an sp^3-C-atom in the molecules **4** to **9** by an sp^2-C-atom. However, as shown in (*1*) and (*2*), $\delta A(\pi_{CC})$ is significantly larger (in absolute value) than $\delta A(n_O)$. This is due to the well known electron-withdrawing ability of the CO group, which could be represented in a first, crude approximation by the limiting structures **18**↔**19**:



18 **19**

The drawback of this rationalization is that it assumes only charge transmission by homoconjugation, *i.e.* a typical overlap-controlled 'through-space' interaction [15] between the homoconjugated sp^2 centres, neglecting the 'through-bond' interaction *via* the σ relay-orbitals, which is at least as important. (A more classical description of the latter mechanism would be with reference to the polarizability of the whole σ frame.) If the 'through-space' mechanism depicted by **18↔19** were the leading contribution, one would expect much larger differences in the $\delta A(\pi_{CC})$ values given in (*1*) and (*2*), as suggested by the extensive work of *Grob* [16].

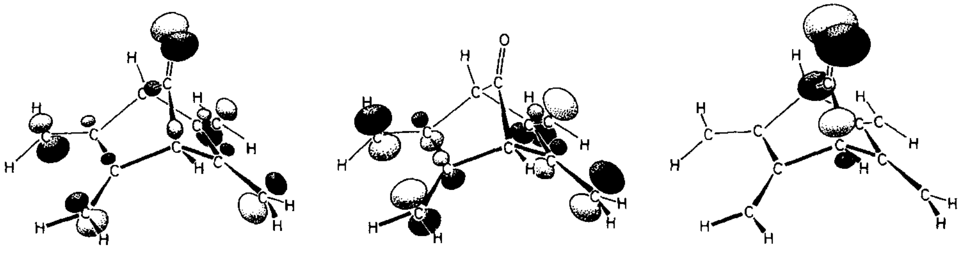
The interaction cross-term $\varkappa(\pi_{CC},n_O)$ is more difficult to rationalize, being a 'catch-all' for the competing 'through-space' and 'through-bond' interaction of the π_{CC} (or π_j) and n_O orbitals, their relative contribution depending on the relative positions and orientations of these orbitals. A resonance description could be attempted in terms of **20↔18↔21**, notwithstanding their stereoelectronic infelicity.



20 **18** **21**

They describe the electron-donating ability of the homoconjugated CO group [illegible] **18↔20** would correspond to a 'through-space' mechanism, whereas **18↔21** w [illegible] associated with a 'through-bond' (hyperconjugative) mechanism related t [illegible] *G* [illegible] fragmentation and the frangomeric effect [18].

In orbital language, the 'through-space' interaction would involve the overl [illegible] trolled interaction of the lone-pair orbital n_O with π_{CC} and the corresponding an [illegible] π^*_{CC} orbitals (or the linear, symmetry-adapted π_j and π_j^*). Whereas the interac [illegible] with the antibonding π^* orbitals are relevant for the electronically excited states o[illegible]moconjugated β,γ-unsaturated aldehydes and ketones [14], their contribution in the electronic ground state can safely be neglected. In fact, even the 'through-space' interaction between



$\pi_{2+} - \lambda n_O$ b_1

π_{2-} a_2

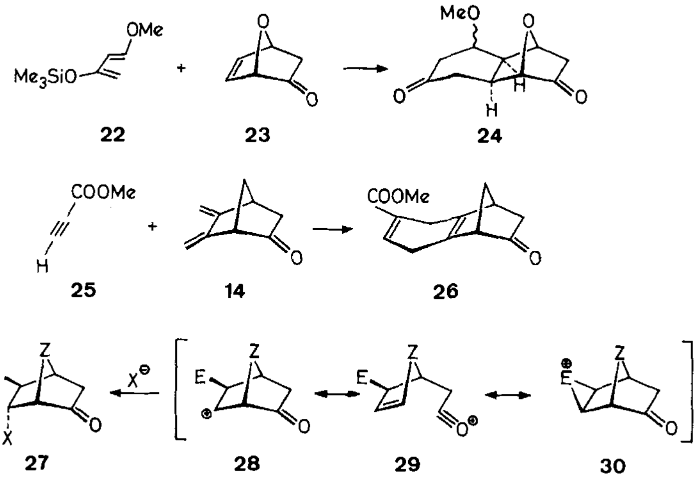
$n_O + \lambda\pi_{2+}$ b_1

Fig. 3. *Representation of the three highest occupied MOs of* **12** (*ab initio* STO-3G wave functions for MNDO-optimized geometry)

n_O and π_{CC} (or π_j) is presumably small, compared to the 'through-bond' interaction *via* the framework σ orbitals. This is strongly suggested, *e.g.* in the case of the tetraenone **12** by the shape of its HOMO, $\pi_{2+} - \lambda n_O$, represented in *Fig. 3*.

Reactions of the olefinic moiety in β,γ-unsaturated ketones have suggested that, depending on the electron demand, the CO group can behave either as an electron-withdrawing or as an electron-releasing substituent. This is illustrated by the following examples. The *Diels-Alder* addition of the *Danishefsky* diene **22** to 7-oxabicyclo[2.2.1]hept-5-en-2-one (**23**) yielded **24** as major adduct (*Scheme*). The olefinic moiety in **23** plays the role of an electron-poor dienophile in this reaction due to the electron-withdrawing effect of the homoconjugated CO group [19]. In contrast, in the case of the *Diels-Alder* addition of methyl propynoate (**25**) to 5,6-dimethylidene-2-norbornanone (**14**), the CO group in **14** acts as an electron-donating substituent leading to the major regioisomer **26** [20]. In the case of the electrophilic additions of the alkene moieties in enones **13** and **23**, the corresponding adducts **27** were formed nearly quantitatively under conditions of kinetic control [19][21]. The high stereo- und regioselectivity observed was interpreted in terms of the intermediacy of cation **30** in which the centre C(6) is preferred for the trapping of counter-ion X^-. This was attributed to the electron-donating ability of the CO group, as rationalized in terms of the limiting structures **28**↔**29**↔**30**.

Scheme



The *Lausanne* group thanks *F. Hoffmann-La Roche & Co. AG*, Basel, The *Fonds Herbette*, Lausanne, and the *Swiss National Science Foundation* for generous financial support. We are grateful to the *Ecole Polytechnique Fédérale de Lausanne* (Mr. *Santschi*) for computing time.

This work is part No. 171 of project No. 2.429-0.84 of the *Swiss National Science Foundation* (part No. 170, *cf.* [22]). Support of the work in Basel by *Ciba-Geigy AG*, *Sandoz AG*, and *F. Hoffmann-La Roche & Co. AG.*, Basel, is gratefully acknoledged.

Experimental. – Dienones **14** [23] and **16** [24], and tetraenones **12** [25] and **17** [26] were prepared according to known procedures. Wave functions and corresponding eigenvalues were obtained (for MNDO [8] optimized geometries) by the *ab initio* STO-3G technique (minimal basis set) [7], using the *MONSTERGAUSS 81* program [27] on a *CYBER 170-855 CDC* computer (*Ecole Polytechnique Fédérale de Lausanne*).

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