167. On the Correlation between Photoelectron and Electronic Spectra in *trans*-Azomethane

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Summary. A possibility of correlating electronic and photoelectron spectra is discussed, using *trans*-azomethane as an example. The *Coulomb* and exchange integrals required were obtained by three semi-empirical SCF-methods: MINDO/2, CNDO/2, and a modified CNDO method. The orbital energies were taken as minus the corresponding experimental ionization potentials. The sequence of the transition energies $\Delta E(n_s \to \pi^*) < \Delta E(n_a \to \pi^*) < \Delta E(\pi \to \pi^*)$ is found to be different from the ionization potential sequence $\mathrm{IP}(n_s) < \mathrm{IP}(\pi) < \mathrm{IP}(n_a)$, in agreement with previous spectroscopic studies; the results support the latest view that the $\pi \to \pi^*$ transition of the azo group occurs at around 12 eV.

Introduction. Photoelectron spectroscopy (PE.-spectroscopy) has become a powerful tool for studying the electronic structure of molecular systems [1]. However, little progress has been made towards a quantitative correlation between photoelectron and electronic spectral data. In this communication we discuss a possible correlating procedure using *trans*-azomethane as an example.

Theoretical procedure. Consider the electronic transition from the ground-state configuration (${}^1\chi_0$) to the excited singlet configuration (${}^1\chi_{i\to k}$). The transition energy $\Delta E(i \to k)$ is given by [2]

$$\Delta E(i \to k) = E({}^1\chi_{i\to k}) - E({}^1\chi_0) = F_{kk} - F_{ii} - J_{ik} + 2K_{ik}\,. \tag{1}$$

J_{ik}, K_{ik} are the *Coulomb* and exchange integrals for the molecular orbitals (MO) ψ_i, ψ_k, and F_{kk}, F_{ii} are defined as

$$F_{zz} = H_{zz}^{\mathrm{core}} + \sum_{j=1}^{\mathrm{occupied}} (2J_{jz} - K_{jz}). \tag{2}$$

If ψ_i, ψ_k are self-consistent field (SCF) MO's, then the corresponding F-matrix is diagonal and the terms F_{kk}, F_{ii} in (1) are equal to the SCF-orbital energies $\varepsilon_k, \varepsilon_i$:

$$F_{kk} = \varepsilon_k;\quad F_{ii} = \varepsilon_i\,. \tag{3}$$

Inserting (3) into (1) leads to

$$\Delta E(i \to k) = \varepsilon_k - \varepsilon_i - J_{ik} + 2K_{ik}\,. \tag{4}$$

The term ε_k in (4) is a little troublesome since it is the energy of a virtual MO. To get rid of it we consider a second transition leading from ${}^1\chi_0$ to ${}^1\chi_{j\to k}$. The corresponding transition energy $\Delta E(j \to k)$ is:

$$\Delta E(j \to k) = \varepsilon_k - \varepsilon_j - J_{jk} + 2K_{jk}\,. \tag{5}$$

Subtracting (4) from (5) leads to

$$\Delta E(j \to k) - \Delta E(i \to k) = \varepsilon_i - \varepsilon_j + J_{ik} - J_{jk} + 2(K_{jk} - K_{ik})\,. \tag{6}$$

Assuming the validity of *Koopmans'* theorem [3], we equate ε_i, ε_j to the negative vertical ionization potentials IP(i), IP(j), *e.g.* the energies required for ejecting an electron from ψ_i or ψ_j, respectively.

$$\varepsilon_i = -\mathrm{IP}(i)\,; \quad \varepsilon_j = -\mathrm{IP}(j). \tag{7}$$

Combining (6) and (7) leads to

$$(\Delta E(j \to k) - \Delta E(i \to k)) - (\mathrm{IP}(j) - \mathrm{IP}(i)) = J_{ik} - J_{jk} + 2(K_{jk} - K_{ik}). \tag{8}$$

Note that equ. (8) equates the differences of two experimentally accessible terms to a sum of J- and K-terms which can readily be calculated from the MO's ψ_i, ψ_j, ψ_k.

This simple procedure depends on the following assumptions: (1) *Koopmans'* theorem is valid [3] [4]. (2) The excited state under consideration is adequately described by a single configuration.

In assuming (1), we neglect any reorganization of ground state SCF-wavefunctions in the positive ion. As a result, the computed IP's turn out to be systematically too high. However, for differences between pairs of IP's, as shown in (8), this type of error should largely cancel out. Indeed, *Basch, Robin, Kuebler, Baker & Turner* [5] found that the differences between measured IP's and the corresponding SCF-orbital energies are approximately constant in a number of cases. Assumption (2) is perhaps more questionable since there is no easy way of verifying its validity. Presumably it will be valid if the following conditions are met:

(a) The molecule has high symmetry, leading to factorization of the CI-matrix (configuration interaction) into sub-matrices of different symmetry.

(b) Within one sub-matrix, the individual configurations have rather different energies and thus interact only weakly.

Thus, (b) will not be satisfied *e.g.* in cases of orbital degeneracy or of the configurational degeneracy in alternant systems. It should hold for transitions such as $n \to \pi^*$ in compounds with heteroatoms, the n-orbital being formally a σ-orbital but separated from the lower lying σ-orbital by a considerable energy gap.

Tab. 1. *Vertical ionization potentials* (IP) *for the* n_s-, π- *and* n_a-*MO's of azomethane from* [6]. *Vertical excitation energies* (ΔE) *for the transitions from each of these levels to the* π^*-*level as assigned in* [8] *for azomethane and in* [7] *and* [9] *for aliphatic azocompounds*

All energies in eV

i	IP(i) ref. [6]	ΔE(i→π^*)		
		ref. [7]	ref. [8]	ref. [9]
n_s	8.98	3.47	3.47	3.47
π	11.84	~7.60	7.60	~12
n_a	12.30	~6.30	5.29	~10.5

In this communication we have taken azomethane (I) as an example. The PE.-spectrum of I has recently been reported [6] and the first three ionization potentials have been assigned to removal of an electron from the n_s-, π- and n_a-MO (Tab. 1; for details see [6]), respectively.

The electronic spectrum of I has been recorded by *Kortüm* & *Rau* [8], and *Robin* & *Simpson* [7] have discussed the electronic spectra of several other aliphatic azo compounds. The matter was later re-examined by *Robin, Hart* & *Kuebler* [9].

For our purpose we shall consider only the electronic transitions from the MO's n_s, n_a and π to the common π^*-MO, *e.g.* the transitions $n_s \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n_a \rightarrow \pi^*$. Tab. 1 lists the associated excitation energies obtained according to the assignments made in [7], [8] and [9].

We have evaluated the J- and K-terms appearing in equ. (8) by three semi-empirical SCF-methods, namely the MINDO/2 [4] [10], the CNDO/2 [11], and a modified CNDO procedure [12].

We briefly discuss the differences in these procedures as far as they are relevant to our work: CNDO/2 has been set to mimic *ab-initio Hartree-Fock* wave functions. Following the general attitude adopted in calculations of this kind, one evaluates all repulsion integrals theoretically with parameters chosen to yield satisfactory geometries and dipole moments. In contrast, MINDO/2 has been parametrized to yield correct heats of formations, whereas the wave functions are of little concern. The various repulsion integrals are evaluated empirically, since theoretical evaluation yields too high values because of neglect of electron correlation and use of *Slater* instead of proper *Hartree-Fock* basis functions (see *e.g* [13]). The modified CNDO method has the same objective as MINDO/2 and its parametrization follows therefore a similar pattern. However, the repulsion integrals are evaluated theoretically as in CNDO/2. The success of this method in reproducing heats of atomization is an indication that an empirical evaluation of these integrals is not a necessary condition for obtaining good energy values.

Results. Tab. 2 lists the results obtained for azomethane[1]) by the three procedures described above. The orbital energies (ε_i) of the bonding n_s-, π- and n_a-MO's, the J- and K-terms for all pairs built from these three MO's and the π^*-level are presented. Fig. 1 correlates the calculated shifts according to (8) for the $\pi \rightarrow \pi^*$ and the $n_a \rightarrow \pi^*$ transitions relative to the $n_s \rightarrow \pi^*$ transition, chosen arbitrarily as reference point. (Note that equ. (8) involves only *differences* between transition energies or ionization potentials, respectively.) At the bottom of Fig. 1, the three (conflicting) assignments as quoted in [7], [8], and [9] (see also Tab. 1) are given for comparison.

Tab. 2. *Orbital energies of the bonding n_s-, π- and n_a-MO's of azomethane; Coulomb and exchange integrals between these and the π^*-MO*

i	$-\varepsilon_i$ (eV)			$J_{i\pi^*}$ (eV)			$K_{i\pi^*}$ (eV)		
	MINDO/2	mod. CNDO	CNDO/2	MINDO/2	mod. CNDO	CNDO/2	MINDO/2	mod. CNDO	CNDO/2
n_s	9.59	9.23	12.95	9.12	11.31	12.16	0.36	0.01	0.01
π	10.55	9.84	14.14	8.87	11.23	11.02	1.67	2.36	2.42
n_a	11.47	12.40	17.27	7.85	8.84	9.22	0.28	0.02	0.04

Discussion. From Fig. 1 we see that all three theoretical procedures predict the transition energy sequence $\Delta E(n_s \rightarrow \pi^*) < \Delta E(n_a \rightarrow \pi^*) < \Delta E(\pi \rightarrow \pi^*)$ in agreement with the assignments in [7], [8], and [9]. This result is particularly gratifying since it would not have followed from a naive one-electron picture, based on the experimentally observed sequence IP(n_s) < IP(π) < IP(n_a) (see Tab. 1), or on the calculated

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[1]) The structural parameters used are those of ref. [14].

sequence of SCF-MO energies (Tab. 2). The reason for the pronounced displacement of the $\pi \rightarrow \pi^*$ transition towards higher energies is that the value of $K_{\pi\pi^*}$ ($\sim$2eV) is about an order of magnitude larger than $K_{n_s\pi^*}$ and $K_{n_a\pi^*}$ (Tab. 2). This was to be expected since the major contribution to a molecular exchange integral stems from one-center *Coulomb* repulsion integrals of the type $(\mu\mu|\mu\mu)$. However, such integrals contribute to K only if (a) the two MO's under consideration contain the same basis functions and (b) if these one-center contributions to K are large in both of them, *e.g.* if the two MO's extend over the same set of atoms. In our case these two conditions are only met by the π- and the π^*-MO.

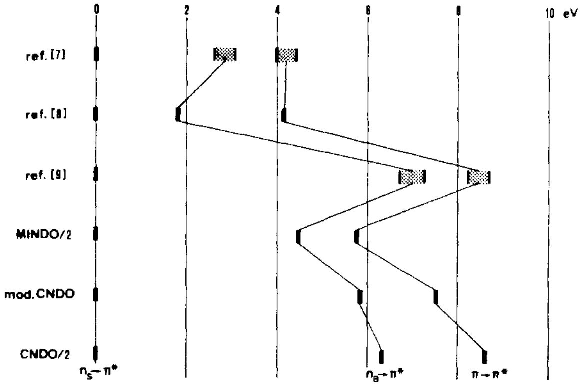

Fig. 1. *Calculated relative excitation energies of the* $n_s \rightarrow \pi^*$, *the* $n_a \rightarrow \pi^*$ *and* $\pi \rightarrow \pi^*$ *transitions of azomethane compared with the assignments of ref.* [7], [8] *and* [9] (The values from [7] and [9] denote ranges valid for aliphatic azo compounds)
The $n_s \rightarrow \pi^*$ transition is arbitrarily set at the origin of the energy scale (see text)

Note that $K_{n_s\pi^*}$ and $K_{n_a\pi^*}$ obtained from the two CNDO-methods do not vanish. Because of the incomplete σ–π separation in azomethane the two lone-pair MO's and the π^*-MO all contain small contributions from the hydrogen 1s-AO's of the CH_3-groups, leading to non-vanishing contributions of the type $(\mu\mu|\mu\mu)$. Note also that larger values for these K-terms are obtained from the MINDO/2 procedure, because of inclusion of one-center integrals of the type $(\mu\nu|\mu\nu)$ [10].

From Fig. 1 we see that all theoretical calculations predict a shift towards higher energies for both the $n_a \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ relative to the $n_s \rightarrow \pi^*$ transition, compared with the corresponding observed IP's. This is particularly striking for the two CNDO methods, where the method of evaluating the repulsion integrals leads generally to higher J- and K-terms than those obtained by MINDO/2. The increase in the difference $\Delta E(n_a \rightarrow \pi^*) - \Delta E(n_s \rightarrow \pi^*)$ relative to $\mathrm{IP}(n_a) - \mathrm{IP}(n_s)$ can be understood on a purely qualitative basis. It is essentially due to the difference $J_{n_s\pi^*} - J_{n_a\pi^*} =$ 1.2–3 eV, since the corresponding difference in the exchange terms, *e.g.* $2(K_{n_s\pi^*} - K_{n_a\pi^*})$ is negligible (compare equ. (8) and Tab. 2). The difference in J-terms indicates that an electron in the π^*-MO repels an electron in the n_s-MO more than an electron in the n_a-MO. This is reasonable, given that both 'lone pair' MO's involve some admixture of lower-lying σ-MO's, which are spread out over the whole nuclear framework. Since the n_a-MO is lower in energy than its counterpart, this mixing will be more effective, leading to less electron density for the n_a-MO, compared with the n_s-MO, in the region of the azo group where the π^*-MO is located.

None of the calculations agree with the assignments given in [7] and [8], which also imply that $\Delta E(n_a \rightarrow \pi^*) - \Delta E(n_s \rightarrow \pi^*)$ is smaller than $\mathrm{IP}(n_a)$–$\mathrm{IP}(n_s)$. In view of our analysis this does not seem reasonable. In contrast, the modified CNDO and, even better, the CNDO/2 calculations agree nicely with the most recent assignment due to *Robin, Hart & Kuebler* [9]. These authors have found that in case of the parent compound diimide (HN=NH) the splitting between the $n_s \rightarrow \pi^*$ and the $n_a \rightarrow \pi^*$ transitions is not altered by configuration interaction. We believe, therefore, that this agreement is not fortuitous. It supports *e.g.* the rather surprising prediction [9] that the $\pi \rightarrow \pi^*$ absorption of the azo group should occur around 12 eV and not, as thought earlier, at 7.6 eV [7] [8], *i.e.* near the $\pi \rightarrow \pi^*$ excitation of alkenes at 7.2 eV, as suggested by arguments based on first-order perturbation theory.

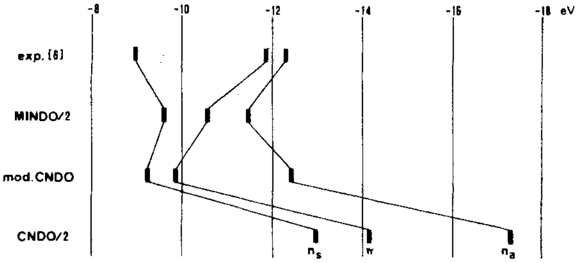

Fig. 2. *Comparison between experimental ionization potentials and computed orbital energies for azomethane*

A comment should be made about the use of calculated orbital energies from semi-empirical treatments instead of experimental IP's, *i.e.* the use of equ. (6) instead of (8). Fig. 2 indicates that the calculated values for the relevant IP's of azomethane, as obtained by the three theoretical procedures cited in this work, do not agree well with the experimental values. Thus, all these methods fail to reproduce the position of the π-IP relative to the n_s- and n_a-IP's. Furthermore, the absolute values obtained by CNDO/2 are in error by several eV's, making the procedure totally unreliable for predicting ionization potentials. It is therefore advisable to approximate the orbital energies needed in (6) by the corresponding experimental IP's, *i.e.* the use of equ. (8) as done in this work.

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168. Isomérisations en chimie des sucres. II 1)

Fermetures de cycles par attaque nucléophile intramoléculaire sur des carbones sp^2 à caractère électrophile: furannoses hybridés sp^2 en C3

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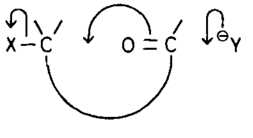
(9 VI 71)

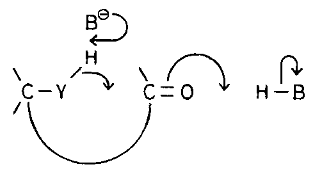
Summary. When heated with one equivalent of H_2O, the 1,2:5,6-di-O-isopropylidene-α-D-*ribo*- and -*xylo*-hexofuranos-3-uloses loose one molecule of acetone and yield the 3,6-anhydro-1,2-O-isopropylidene-α-D-*ribo*- and -*xylo*-hexofuranos-3-ulose ketohydrols. The carbonyl group of the starting material seems to provide some kind of intramolecular electrophilic assistance to the hydrolysis of the 5,6-O-isopropylidene group. When the oxygen of the carbonyl group is replaced by cyanomethylene, an analogous cyclisation takes place under base catalysis, provided that C6 bears a free hydroxyl group.

Un groupement carbonyle peut, *a priori*, participer à la fermeture d'un cycle en mettant en jeu soit le caractère nucléophile potentiel de son oxygène soit le caractère électrophile de son carbone.

Un certain nombre d'exemples de réactions du premier type ont été décrits récemment (*cf.* [2]). Elles font intervenir l'attaque du carbonyle d'un sucre par un nucléophile, ce qui crée un groupement oxido susceptible de fermer un cycle par déplacement d'un nucléofuge fixé sur un carbone de la même molécule (schéma **A**).



A



B

Les réactions du second type (schéma **B**), dans lesquelles un nucléophile de la molécule ferme un cycle par attaque du carbonyle, sont néanmoins bien plus habituelles. Ce sont elles en particulier qui conduisent à la formation des hémiacétals internes

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1) La référence [1] constitue la première communication de cette série.