299. On the Correlation between Ionization Potentials and Excitation Energies, Part III: Pyrazine[1])

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(5. VII. 73)

Summary. A recently suggested scheme for relating ionisation potentials (IP) to excitation energies (E) has been applied to pyrazine and 2,6-dimethylpyrazine. The results indicate that in these systems the energy gap (ΔE) between the two lowest lying $^1n,\pi^*$-states is significantly smaller than that (ΔIP) between the corresponding ^2n-states of the parent radical cations. The values estimated for ΔE on the basis of ΔIP, measurable by photoelectron spectroscopy, disagree with those calculated theoretically but seem to be supported by the experimental evidence available.

Since $\Delta E = \Delta IP$ would normally be expected, the relationship $\Delta E < \Delta IP$ actually present in these systems is discussed and related to the different shape of the n-MO's involved in the ionization and excitation processes.

Introduction and previous work. – Although in aromatic heterocyclic systems the location of n, π^*-excited states is of great importance for an understanding of deactivation processes not involving radiation [2], unequivocal information is still lacking. In particular the difference (ΔE) between the lowest lying n, π^*-states $^1B_{3u}$ and $^1B_{2g}$[2]) of pyrazine (**PY**) has continued to be a matter of discussion.
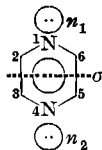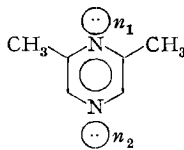
PY   DMPY

In earlier work [4] it was suggested that in view of the large spatial separation between the lone pair orbitals n_1 and n_2, assumed to be localized, the symmetry-adapted linear combinations

$$n_s = \frac{1}{\sqrt{2}} (n_1 + n_2), \quad A_g\text{-symmetry} \tag{1}$$

$$n_a = \frac{1}{\sqrt{2}} (n_1 - n_2), \quad B_{1u}\text{-symmetry} \tag{2}$$

should have roughly the same orbital energies ε, *i.e.*:

$$\varepsilon (n_s) \approx \varepsilon (n_a). \tag{3}$$

This would result in practically degenerate electron promotions to the (lowest-lying) π_s^*-MO of B_{3u}-symmetry.

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[1]) For parts I and II see [1].

[2]) For a discussion of these and similar symmetry designations see [3]. The symbols s and a refer to the symmetry behaviour of the MO's with respect to the mirror plane as represented above.

In terms of the nomenclature and definition of signs used previously [1] and assuming *Koopmans'* theorem [5] to hold in (4), it was implied in [4] cited above that, since

$$E\,(^2A_g) - E\,(^2B_{1u}) = IP\,(n_s) - IP\,(n_a) = \Delta IP \approx 0, \qquad (4)$$

then also

$$E\,(^1B_{3u}) - E\,(^1B_{2g}) = E\,(\pi_s^* \leftarrow n_s) - E\,(\pi_s^* \leftarrow n_a) = \Delta E \approx 0. \qquad (5)$$

Support for this assumption was first provided by *Robinson & El-Sayed* [6] from a study of the absorption spectrum of crystalline **PY** at 4° K. They situated the forbidden $\pi_s^* \leftarrow n_a$ transition slightly below the allowed $\pi_s^* \leftarrow n_s$ absorption ($\Delta E \approx 0.05$ eV); later, however, *Innes et al.* [3] concluded that this assignment is rather uncertain. Nevertheless, a small splitting between these two n, π^*-states of **PY** was also proposed by *Hochstrasser & Marzzacco* [7] $\{\Delta E \approx - (0.1-0.2)$ eV$\}^3)$ from a comparative study of absorption and fluorescence spectra. Similar values were found by *Li & Lim* [8].

All these assignments were thought to be reasonable on the basis of (4) and (5), but they became somewhat doubtful when photoelectron spectroscopical investigations by *Gleiter et al.* [9] revealed $\Delta IP = -1.72$ eV$^4)$. A significant splitting between the 'lone pair' MO's n_s and n_a had been predicted previously from the calculations of *Clementi* [12] and of *Hoffmann et al.* [13], and rationalized by *Hoffmann* [13–14] by introduction of the 'through bond' *vs.* 'through space' coupling concept. Indeed, as a direct consequence, *Jordan et al.* [15] pointed out that 'the $\pi^* \leftarrow n$ singlet-singlet absorption of **PY**, observable over a span of 7000 cm^{-1}, consists almost certainly of only *one* (allowed) transition'.

This conclusion is supported by theoretical calculations of ΔE by *Yonezawa et al.* [16] ($\Delta E = -1.82$ eV), by *Hackmeyer & Whitten* [17] ($\Delta E = -1.4$ eV), by *Ellis et al.* [18] ($\Delta E = -1.3$ eV) and by *Sundbom* [19] ($\Delta E = -0.76$ eV).

Recent experimental work by *Marzzacco & Zalewski* [20] led to the conclusion that the forbidden $\pi_s^* \leftarrow n_a$ transition is not situated *below* the allowed $\pi_s^* \leftarrow n_s$, i.e. $\Delta E < 0$. *Innes et al.* [21] observed electronic *Coriolis* interactions in the spectrum of **PY**. Although the perturbing electronic state could not be directly identified, it was suggested that it might well be the long sought but elusive n_a, π_s^*-state, implying again that ΔE is small and negative. Unfortunately no further apposite information could be obtained from the electron impact spectrum of **PY**, discussed by *Fridh et al.* [22]. The same is true for the threshold-electron excitation spectrum of **PY**, studied by *Pisanias et al.* [23].

A new approach to the present problem is due to *Moomaw et al.* [24]. These authors clearly recognize that the chance of locating the $\pi_s^* \leftarrow n_a$ transition forbidden in **PY** could be greatly improved by perturbing its molecular symmetry, thus weakening the selection rules. Using methyl groups as 'perturbing agents' they provided evidence that in 2,6-dimethyl-pyrazine (**DMPY**) the difference between the *0,0*-transitions of the two $\pi^* \leftarrow n$ band systems is about -0.03 eV. It was suggested that the corresponding value for **PY** would only differ slightly.

From Table 1 it can be seen that so far the experimental work for elucidation of ΔE indicates rather small values for either **PY** ($\Delta E \approx -0.2$ eV) or for its 2,6-dimethyl-substituted derivative **DMPY** ($\Delta E = -0.03$ eV). Until now however, all theoretical calculations, using the 'classical' MO–CI approach, predict a rather sizable $|\Delta E|$-value. We felt urged, therefore, to apply the recently reported ionization potential-excitation energy correlation scheme [1]. Here, in contrast to the procedures mentioned above, 'experimental' energies for the occupied orbitals (*e.g. IP*'s) are used. The difference Δ between ΔIP and ΔE is then given by

$$\Delta = \Delta E - \Delta IP = J_{n_a \pi_s^*} - J_{n_s \pi_s^*} + 2\,(K_{n_s \pi_s^*} - K_{n_a \pi_s^*}) \qquad (6)$$

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3) The definition of signs for ΔIP and ΔE in equ. (4) & (5), is based on equ. (21) in [1b].

4) From footnote 3) the negative value of ΔIP signifies that n_s– MO lies above n_a– MO, as suggested in [9] and supported in [10] and [11].

Table 1. *Previously obtained and present results for the splitting ΔE between the* n,π^*-*excited states of pyrazine* (**PY**) *and 2,6-dimethyl-pyrazine* (**DMPY**)

Approximate value for $\Delta E = E(\pi_s^* \leftarrow n_s) - E(\pi_s^* \leftarrow n_a)$ (eV)	based on	ref.
PY 0	spectra, qualitative theoretical considerations	[4]
0.05	crystal absorption spectrum	[6]
uncertain	reconsideration of work reported in [6]	[3]
-0.2	crystal absorption and emission spectrum	[7]
$> \lvert -1 \rvert$	intuitive extrapolation from measured splitting $\Delta IP = IP(n_s) - IP(n_a) = -1.72$ eV from photoelectron spectrum	[15]
small, negative	crystal absorption spectrum	[20]
small	analysis of rotational fine structure in absorption spectrum	[21]
-1.82	semi-empirical SCF-CI calculation	[16]
-1.4	*ab-initio* SCF-CI calculation	[17]
-1.3	CNDO/S-SCF-CI calculation	[18]
-0.76	semi-empirical SCF-CI calculation	[19]
-0.45	ΔIP and theoretical correction terms	present work
DMPY -0.03	absorption spectrum	[24]
-0.18	ΔIP and theoretical correction terms	present work

and is related to conceptually easily appreciated electron-repulsion terms. Thus $\Delta \neq 0$ ultimately arises from the different shapes of the occupied MO's involved in the ionization and excitation processes.

Since in our opinion the strongest evidence for the approximate magnitudes of ΔE in **PY** was provided by the study of **DMPY** (*vide supra*) [24], we also applied the above procedure to **DMPY**. This required an interpretation of its photoelectron spectrum in order to establish ΔIP^{DMPY}. From this and the known ΔIP^{PY} [9], estimates of ΔE^{DMPY} and ΔE^{PY} were made as outlined in [1]. The necessary Coulomb ($J_{n_s \pi_s^*}$, $J_{n_a \pi_s^*}$) – and exchange-integrals ($K_{n_s \pi_s^*}$, $K_{n_a \pi_s^*}$) were calculated, using the CNDO/2 – method [25] which proved most satisfactory in previous work [1].

Comparison between the PE-spectra of PY and DMPY. – Fig. 1 shows the photoelectron spectra of **PY** [9] and **DMPY**. We restrict the discussion to the band systems observed up to $\sim$12 eV. Following the interpretation for **PY** given in [9], this part of the spectrum involves four distinct bands, arising from the removal of an electron from the n_s-, the π_a-, the n_a- and the π_s-MO (the numerical values are given in Table 2). Unfortunately, for **DMPY** the situation is not so clear-cut due to overlapping bands. The assignment proposed is based on the following:

1) In **PY**, the most intense vibrational component of the first band is the $5' \leftarrow 0$ transition, leading to $IP_v(n_s) = 9.63$ eV [9]. The onset of the first band in **DMPY** exhibits roughly the same vibrational fine structure ($\tilde{\nu} \approx 680$ cm^{-1}) as **PY** ($\tilde{\nu} = 605$ cm^{-1}
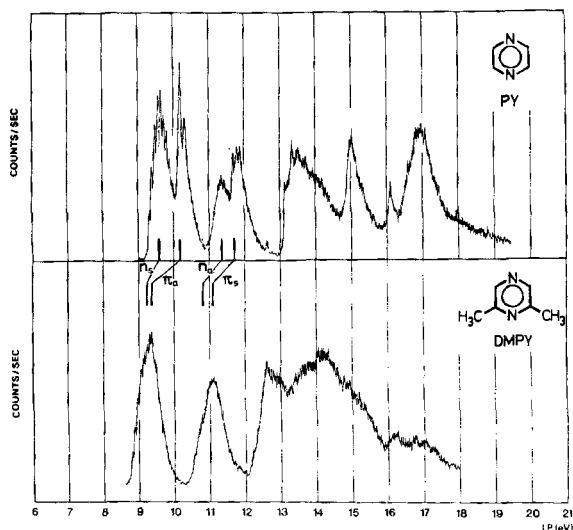
Fig. 1. *Photoelectron spectra of* **PY** *and* **DMPY**. *Correlation of vertical* n- *and* π-*ionization potentials*
(see text)

ν_{6a} [22]), suggesting its assignment to the ionization of an *n*-electron. In view of the structural similarity of the two molecules, it would be reasonable to assume that $IP_v(n_s)$ [5]) of **DMPY** is also associated with the $5' \leftarrow 0$ transition. This would give $IP_v(n_s) = 9.15$ eV. However, point 2) below leads us to favor the $6' \leftarrow 0$ transition, yielding $IP_v(n_s) = 9.24$ eV.

2) For **PY**, $IP_v(\pi_a)$ and $IP_a(\pi_a)$ coincide in the sharp peak at 10.18 eV. [9]. For **DMPY** we therefore took $IP_a(\pi_a) = IP_v(\pi_a) = 9.32$ eV, this being the highest intensity component of the 9 eV-band system.

3) The band system at 11 eV in **DMPY** consists of two bands arising from the n_a- and π_s-ionization, by analogy to **PY** where these bands are well separated. The inflection point at 10.76 eV and the maximum at 11.11 eV might well be the corresponding IP_v's, but in order to get more reliable values for these quantities, we have resolved this band system into its two components, using a procedure proposed by *Fraser & Suzuki* [26]. In a first step, the corresponding band system of **PY** was approximated by two skewed *Gaussian* functions, each characterized by position of maximum (X_0), maximum intensity (Y_0), full width at half maximum (DX) and asymmetry parameter (B). The synthesis of the envelope was carried out iteratively, the convergence criterion being the root mean square difference between experimental and theoretical areas under the curves. Assuming similar band shapes for **DMPY**, the procedure was applied to its 11 eV band system, the B- and DX-values being those of **PY**. The position of the maxima as well as of the onsets of the two curves led to the vertical and adiabatic IP's, resp., given in Table 2. The resolved band systems of **PY** and **DMPY** are shown in Fig. 2. Attention is drawn to the al-

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[5])   For convenience we use the symmetry designations s and a also for the MO's in **DMPY**, although this molecule lacks the corresponding mirror plane.

Table 2. *Ionization potentials, Coulomb- and Exchange-terms and predicted splitting between n,π^*-states of* **PY** *and* **DMPY** (all values in eV)

| | $J_{n_S\pi_S^*}$ | $J_{n_a\pi_S^*}$ | $K_{n_S\pi_S^*}$ | $K_{n_a\pi_S^*}$ | adiabatic IP's / vertical IP's from orbitals | | | | ΔIP_a^f | ΔIP_v^f | $\Delta E_a = \Delta E^g$ | ΔE_v^g |
					n_S	π_a	n_a	π_S				
PY[a]	9.49	10.55	–	–	9.29	10.18	10.80[b]	11.66	-1.51		-0.45	
					9.63	10.18	11.35	11.77		-1.72		-0.66
DMPY	9.03	10.30	~0	~0	8.80[d]	9.32[e]	10.25[b]	10.80[b]	-1.45		-0.18	
					9.24[c]	9.32[e]	10.78[b]	11.12[e]		-1.54		-0.27

[a]) *I P*'s from [9].
[b]) From deconvolution (Fig. 2).
[c]) For assignment see text.
[g]) Difference between $\pi^* \leftarrow n$ transition energies; see equ. (6), (7), footnote 3) and text.

[d]) First vibrational component (Fig. 1).
[e]) Highest intensity component (Fig. 1).
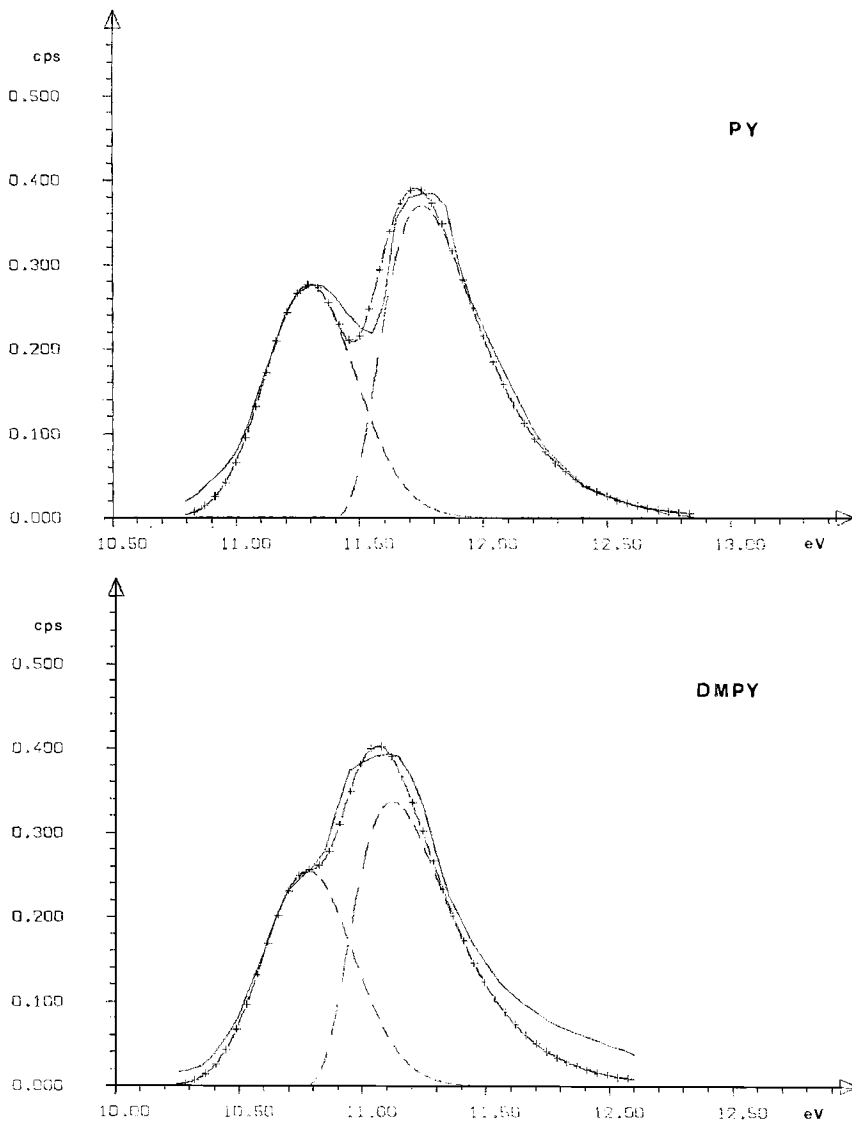[f]) Difference between n-*I P*'s; see equ. (5), footnote 3) and text.

Fig. 2. *Deconvolution of the second band system in the photoelectron spectra of* **PY** *and* **DMPY** (see text)
————————— experimental band
— —— —— component curves
— × —— × —— sum of component curves

most equal ratio r [$=$ area (π_8)/area (n_a)] and rr [$= Y_0(\pi_8)/Y_0(n_a)$] of the two *Gaussians* for **PY** ($r = 1.523$, $rr = 1.338$) and for **DMPY** ($r = 1.499$, $rr = 1.324$), indicating similar relative ionization cross sections for these molecules. Furthermore that the IP_v's obtained by deconvolution (Table 2) and by inspection (*vide supra*) are almost identical.

We will now discuss briefly the change of IP's on 2,6-dimethyl substitution of **PY** by qualitative application of perturbation theory arguments. The table below shows the values for $\delta IP(m) = IP(m)^{PY} - IP(m)^{DMPY}$ as well as the calculated orbital electron densities q_2 (m) at $C(2)$ for the **PY**-MO's $m = n_s, \pi_a, n_a$ and π_s, using MINDO/2-wave functions [27].

m	$-\delta IP(m)$ [eV]	$q_2(m)$ [charge units]
n_s	0.39	0.144
π_a	0.86	0.500
n_a	0.57	0.102
π_s	0.65	0.136

The relative shifts of the π_a – MO and the π_s – MO can clearly be rationalized on a purely inductive basis in view of the significant difference between q_2 (π_a) and q_2 (π_s). This, as well as the absolute magnitude of the δIP-values, is reminiscent of the behaviour of pyridine upon 2,6-dimethyl substitution, see [28]. This similarity also holds for $\delta IP(n_s)$ when compared with $\delta IP(n)$ in the case of pyridine [28], again supporting an inductive mechanism. On this basis one might predict, *e.g.* as in [24], that $|\delta IP(n_a)| < |\delta IP(n_s)|$ since $q_2(n_a) < q_2(n_s)$ [6]). However, the reverse seems to be the case, $-\delta IP(n_a)$ being significantly greater than $-\delta IP(n_s)$ (by 0.18 eV). This problem is resolved by realizing that the difference between the two lone pair charges is roughly one tenth of that of the two π-charges discussed above. Hence, second order effects (*e.g.* 'hyperconjugation') may become discernible for the n_a-MO which is nearer in energy to the CH_3-group *pseudo* π-orbitals than its n_s-counterpart [7]).

ΔE from ΔIP. For the following discussion we need the difference (ΔIP) between the n_a- and the n_s-IP in **PY** and **DMPY** as defined in (4). These values are given in Table 2.

In order to estimate ΔE, the *Coulomb*- and exchange-terms (J and K, resp.) have to be added to ΔIP according to (6). Note that the K-values for **PY** vanish within the CNDO/2-framework while those for **DMPY** do not, due to the out of plane methyl H-atoms. The associated *1s*-basis functions have non-zero coefficients in both n-MO's as well as in the π_3^*-MO, resulting in finite but negligible one- and two-center *Coulomb* contributions to the molecular exchange terms for **DMPY**. The ΔE-values are given in Table 2 and, for comparison with previous results, also in Table 1.

Before discussion, a further comment is necessary. As can be seen in Table 2, two values for ΔE (ΔE_a and ΔE_v) are given, calculated on the basis of the corresponding adiabatic and vertical ΔIP-values. While the estimation of ΔE_v from ΔIP_v using (6) is perfectly justifiable, the same procedure for the adiabatic values is not. Unfortunately, only ΔE_a-values are available for both **PY** and **DMPY** from experimental studies previously cited. In order to be consistent when comparing our results, we decided to use the ΔE-estimates based on ΔIP_a, justified as follows: MINDO/2-calculations for the minimum energy structure of the ^2A_g- and the $^2B_{1u}$-states of **PY**$^+$ suggest that with respect to groundstate **PY**, a significant shortening of the N $\cdots$ N internuclear distance takes place, indicating for the radical ion a slight tendency towards the formation of a 'three-electron' N—N bond [30] (*c.f.* [31] for relevant discussion). In view of the shape of the

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[6])   This sequence of charge densities is intimately related to the 'non-natural' sequence $IP(n_s) < IP(n_a)$ [9] in **PY** the importance of which will be discussed later (where pictorial representations of the n-MO's will also be found).

[7])   This argument might be weakened by the fact that, in contrast to **DMPY**, **PY** possesses two equivalent n-basis functions so that a direct comparison between the two systems is not admissible. We have localized the canonical MO's of **DMPY**, using the criterion of *Edmiston & Ruedenberg* [29] and have found that the difference between the two n-basis orbitals amounts to only 0.04 eV.

π_s^*-MO of **PY**, the same direction of nuclear displacement is expected to take place after vertical population of either n,π^*-state. Indeed, the most active mode of vibration is $\tilde{\nu}_{6a}$ for both the $\pi_s^* \leftarrow n_s$ excitation band ($\tilde{\nu}_{6a} = 582$ cm^{-1} [3]) and the n_s-ionization band ($\tilde{\nu}_{6a} = 605$ cm^{-1} [22]). If we now make the questionable assumption that

$$(IP_v(n_s) - IP_a(n_s)) - (E_v(\pi_s^* \leftarrow n_s) - E_a(\pi_s^* \leftarrow n_s)) \approx$$

$$(IP_v(n_a) - IP_a(n_a)) - (E_v(\pi_s^* \leftarrow n_a) - E_a(\pi_s^* \leftarrow n_a)), \tag{7}$$

then it follows [c.f. (6)] that:

$$\Delta E_v - \Delta IP_v = \Delta \approx \Delta E_a - \Delta IP_a. \tag{8}$$

Obviously, in view of (8) one may now use ΔIP_a as a basis for elucidation of ΔE_a, henceforth simply called ΔE. In any case, the above choice clearly does not influence our main conclusions.

Discussion. - A first glance at the data discloses that the relationship $|\Delta E| < |\Delta IP|$ holds for both **PY** and **DMPY**, suggesting a smaller splitting between the $^1n, \pi^*$-states under discussion than between the ^2n-states in these systems. This clearly supports the available experimental evidence discussed above. Furthermore, taking for granted $sgn \Delta IP$ as negative from the PE-studies, then $sgn \Delta E$ also turns out to be negative, the calculated Δ-term in (6) not being large enough to invert the sign on passing from ΔIP to ΔE. So this supports, for example, the conclusion made in [20] that the forbidden $\pi_s^* \leftarrow n_a$ transition does not lie energetically *below* the allowed $\pi_s^* \leftarrow n_s$ transition, as originally proposed in [6]. On the other hand $\Delta E^{\mathbf{PY}} = $ -0.45 eV suggests that the longest wave length $\pi^* \leftarrow n$ transition, observable over a span of 7000 cm^{-1}, in fact consists of *two* transitions.

Accurate numerical agreement, however, is not obtained when our values are compared with the earlier cited experimental evidence ($\Delta E^{\mathbf{PY}} \approx$ -(0.1–0.2) eV, $\Delta E^{\mathbf{DMPY}} = -0.03$ eV), our predicted splitting between the n, π^*-states being too great (by $\sim$0.2 eV for **DPMY**, $\sim$0.3 eV for **PY**). In view of the agreement in the comparable case of p-benzoquinone [16], revision of the spectroscopical data might seem desirable. We believe, however, that our procedure – in view of the limitations pointed out in [1a] as well as of the approximate nature of *Koopmans'* theorem [5] involved in it – is not sufficiently reliable to challenge good spectroscopical work. For instance, configuration interaction might play a more important role for the n_a, π_s^* - with respect to the n_s, π_s^*-configuration, the former being nearer in energy to higher lying configurations of appropriate symmetry. This would then result in a further decrease of ΔE. In this respect it is interesting to note that in the *ab-initio* work of [17], ΔE changes from –2.4 eV to –1.4 before and after inclusion of configuration interaction. Nevertheless it is gratifying to note that our estimate of ΔE, based on the PE-measurement of ΔIP and the calculation of some «bridging» theoretical terms is apparently nearer to the truth than that from an elaborate *ab-initio* calculation.

Why is $|\Delta E| < |\Delta IP|$? - It was demonstrated above that for the pyrazines $|\Delta E| < |\Delta IP|$, both quantities of negative sign. Recourse to Table 1, ref. [1b], discloses that these properties are the result of the greater «lone pair» character of the lower lying n_a-MO with respect to its higher lying more diffuse n_s-partner[8]). This situation,

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[8]) This is true provided that the π^*-'target' MO has its greatest density at the hetero-atoms [1b]. Qualitative perturbation arguments as well as the pictorial representation of the calculated wavefunction (*vide supra*) show that **PY** and **DMPY** behave in this way.

pictorially represented in Fig. 3 using MINDO/2-wavefunctions and the MOPLOT-program described in [32], is a necessary consequence of the «through bond» interaction [13–14] between the two N-lone-pairs. This case is analogous to that largely discussed for the two O-lone-pairs of p-benzoquinone, see [1b]. On this basis, the sequence $J_{n_a \pi_s^*} > J_{n_s \pi_s^*}$ (Table 2) is immediately obvious and can be visualized from fig. 3, the promoted electron, which moves in the π_s^*-MO, having more space in common with the positive hole left in the n_a-MO than with that in the n_s-MO. Consequently, the $Coulomb$-attraction is larger in the former case, resulting in a larger stabilization of the n_a, π_s^*-with respect to the n_s, π_s^*-state. This, together with $IP(n_a) > IP(n_s)$ ($i.e.$ $\varepsilon(n_a) < \varepsilon(n_s)$) leads to $|\Delta E| < |\Delta IP|$.
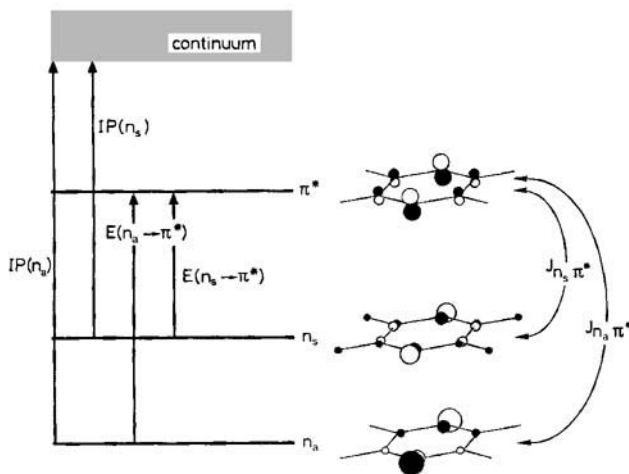

Fig. 3. *Pictorial representation of the n_s-, the n_a- and the π_s^*-MO's of* **PY**

Conclusion. - The results presented suggest that for **PY** (**DMPY**) the lowest excited $^1n, \pi^*$-state corresponds to the promotion $\pi_s^* \leftarrow n_s$ ($^1B_{3u}$ ($^1B_1$)), followed, within an energy range not larger than 0.45 eV (0.18 eV), by the $\pi_s^* \leftarrow n_a$ transition ($^1B_{2g}$ ($^1B_1$)). These conclusions, although differing from the results of theoretical calculations, are supported by the available experimental evidence. They were obtained, starting from an experimental basis (ΔIP) and applying a theoretically calculated but non-critical correction term (Δ, (6)), which leads to ΔE. The relative magnitude of these terms, in particular $|\Delta E| < |\Delta IP|$, is reminiscent of that already observed for p-benzoquinone [1b]. There, the comdarison between ΔE and ΔIP at once revealed the relative shape of «lone pair» orbitals, thus providing further support for the usefulness of the «through bond» $vs.$ «through space» interaction concept, popularized by $Hoffmann$ [13–14]. Specifically, for **PY** the results yield «experimental» support for the idea that the highest occupied n_s-MO (the HOMO) is appreciably delocalized as a result of «through bond» interaction. Evidence for this has also been obtained by $Wilson$ [33] from magnetic susceptibility measurements. On the other hand no chemical manifestation of this feature has been noted by $Zoltewicz$ & $Jacobson$ [34] for a **PY**-catalized ester hydrolysis or by $Zoltewicz$ & $Deady$ [35] for N-alky-

lations. This is surprising, in view of the «unexpected» shape of the HOMO of **PY**. Apparently more chemical work is needed to elucidate the ramifications of «through bond» interaction in view of the considerable existing work which clearly reveals interaction of lone pairs «through space» («α-effect») [35–36].

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300. Absolute Konfiguration von β,ε-Carotin-2-ol, β,β-Carotin-2-ol und β,β-Carotin-2,2'-diol[1])

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(5. XI. 73)

Summary. By chemical degradation and application of the modified *Horeau* method the xanthophylls of *Trentepohlia iolithus*, namely **1a**, **2a** and **3a**, have been shown to possess the $(2R,6'R)$-, $(2R)$-, and $(2R,2'R)$-configurations respectively.

Die von der Grünalge *Trentepohlia iolithus* synthetisierten Xanthophylle (als Ester) sind bisher für normale, d.h. an C(3) bzw. C(3') hydroxylierte Carotinoide gehalten worden [1]. Vor kurzem wurde jedoch erkannt, dass sie in Wirklichkeit neuartige, an C(2) bzw. C(2') hydroxylierte β,β- und β,ε-Carotine darstellen [2]. Die volle spektrale [2] und chemische [3] Charakterisierung führte zu den Konstitutionen **1a** (β,ε-Carotin-2-ol), **2a** (β,β-Carotin-2-ol) und **3a** (β,β-Carotin-2,2'-diol). Auf die *R*-Chiralität von C(6') in **1a** liess sich durch Vergleich seiner CD.-Kurve mit derjenigen von β,ε-Carotin [4–5] schliessen. Mit Hilfe der *Mills*'schen Regel [6] konnte zudem auf $(2R)$-Chiralität für **2a** und $(2R,2'R)$-Chiralität für **3a** geschlossen werden [2] [7]. Da die Anwendung dieser Regel auf Carotinoide oder verwandte Verbindungen nur mit wenigen Beispielen (z.B $(-)$-(R)-3-Methoxy-β-ionon [8]) belegt ist und zudem Ausnahmen für ihre Gültigkeit bekannt sind (vgl. [9]), haben wir die Chiralität von **1**, **2** und **3** auf unabhängige Weise überprüft und sichergestellt.

Oxydativer Abbau der O-Acetylverbindungen eines Gemisches von **1a** und **2a** mit NiO_2, analog dem bei Xanthophyll (β,ε-Carotin-3,3'-diol) angewandten Verfahren [8], lieferte zahlreiche Produkte, von denen die folgenden, für die Chiralität von **1**, **2** und **3** wesentlichen Verbindungen erwähnt werden:

$(+)$-(R)-*α-Ionon* (**4**) mit übereinstimmenden UV.[4])- und Massenspektren, GC.-Retentionszeiten, jedoch enantiomerem CD. zu $(-)$-(S)-α-Ionon [8] [10].

ε-apo-*11-Carotinal* (**5**). MS.: m/e 218 (M^+). – UV.: 286 nm. – CD.: 298 (+), 273 (+), 205 nm (+, Endabsorption), Kurve analog der von **4**, jedoch bathochrom verschoben.