182. Ionisation Energies and the Electronic Structures of the N-oxides of Diazabenzenes

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Summary. The ionisation energies and the HeI photoelectron spectra of the N-oxides of diazabenzenes are presented. The valence electronic structures of the N-oxides are discussed in view of the ionisation energies, and the profiles, of the bands. The interpreted data are compared to calculations which are in good agreement. The results are correlated to the physicochemical studies, and particularly to the electronic absorption spectroscopy, of the N-oxides. The assignment of the photoelectron spectra of the azabenzenes are considered with reference to the spectra of their N-oxides.

The electronic structure and the chemical properties of the aromatic N-oxides have attracted considerable attention in the past [1]. The recent photoelectron spectroscopic study of the pyridine-N-oxides [2] yielded the ionisation energies, and a means to discuss their electronic structure, with particular reference to the influence of the substituents on the ground and several excited states of the ions. The photoelectron spectra of the mono and di-N-oxides of the diazabenzenes **1–5** are considered in this article.

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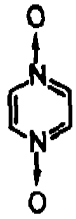

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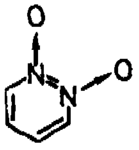

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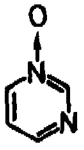

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The present data on the radical cations of the above compounds relate to the theoretical calculations [3], the ESR. studies of the cation of **2** [4], the oxidation potentials [5], and complements the studies of the anions by ESR. and polarography [6], and the absorption spectroscopy [3]. The interpreted PE. spectra allow a correlation to the PE. spectra of the diazabenzenes to be made.

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The PE. spectra were obtained with two $\pi/\sqrt{2}$ cylindrical sector (10 cm radius) condenser analyser instruments and excited by the HeIα (21.22 eV) photon radiation [7]. The ionisation energy (IE) scale was internally calibrated as described previously [2].

The samples of **1**, **2**, **3** and **5** were prepared by the method of *Ochiai* [8] and the details have been referred to in other works [6]. Pyridazine-di-N-oxide was prepared by modification of the original synthesis to improve the 1% yield [9]. This consisted of keeping pyridazine in excess H_2O_2 (90%), glacial acetic acid mixture for 24 h at 70°. Separation of the mono-N-oxide was achieved by sublimation. A yield of ≈ 15% was attained. All attempts to prepare pyrimidine-di-N-oxide (or its 2-methyl, 2-chloro derivatives), resulted only in degradation products.

In Fig. 1 are shown the HeI excited PE. spectra of the N-oxides **1–5** and that of pyridine-N-oxide (PNO). The ascertained IEs (I_i) correspond to the band number i (Fig. 1) and are presented in table 1. The values listed are the vertical IEs from the assessed band maxima, with uncertainty of ± 0.02 eV when the band is sharp, otherwise ± 0.05 eV for the separated bands. The assignment of the bands, inferred in the subsequent section are shown and for **1**, **2** and **4** the labels pertain to the symmetry of the parent diazabenzenes with the coordinate axes as depicted in Fig. 2. The IEs of PNO are included in Tab. 1 for reference in the discussion.

Discussion. – The PE. spectrum of pyridine-N-oxide (PNO) (Fig. 1) shows four distinct bands below IE of 13 eV. The ionic states represented by these were shown to be associated with electron ejection from the πO:, σO:, πa_2 and $\pi 2b_1$, MOs [2]. The IEs are given in Tab. 1. Replacement of a further CH group by N, or the NO group, leads to further stabilisation of the π MO basis energies. It then follows that in the PE. spectra of the N-oxides **1–5**, the bands below the IE of 13 eV can again be attributed to the corresponding MOs as in PNO and the additional oxygen (πO:, σO:) or nitrogen (σN:) MOs.

The increase in the IE (0.93 eV) of the πa_2 band in PNO ③, with reference to benzene, is also manifested on comparing PNO with **2** (1.0 eV), corresponding to band ⑤. The additivity of the inductive stabilization is a consequence of the node of the πa_2 MO at the points of substitution. The basis of the πb_1 component of the πe_{1g} pair of benzene is stabilized preferentially to the πa_2 and therefore, as in PNO, the ground ionic state of the N-oxides of the diazabenzenes is generated by ionisation of electrons from the MO where the electron density is concentrated around the oxygen (πO:). The narrow *Franck-Condon* profiles of the first bands of **1–5** indicate little geometry change on ionisation and are a reflection of the nonbonding nature of the πO: MO. By comparison with the IE process associated with the σO: MO in PNO (IE = 9.22 eV) the three remaining bands in the PE. spectrum of **2** (Fig. 1) are to be correlated with the MOs which comprise dominantly of the σO: linear combinations (b_{3g} and b_{1u} representations in D_{2h} symmetry) and the other πO:MO combination (b_{3u}). Only the lowest π level (IE $<$ 14 eV) is of same symmetry as the latter πO:MO and it is shown henceforth that assignment of band ④ to the πO:(b_{3u})MO is most satisfactory.

In the study of the PE. of the *para*-substituted pyridine-N-oxides, the first three IEs were found to give a good linear correlation with the dipole moments of the molecules [2]. Using these regressions the dipole moments of **1** and **2** [10] (μ = 1.66 D and 0.0 D respectively) yield the IEs of the σO: and πa_2 bands as 9.61 eV, 10.67 eV and 9.94 eV, 10.95 eV respectively. Within the errors involved, these values have their counterparts in the PE. spectra (Fig. 1): bands ②, ④ in **1**, ② or ③ and ⑤ in **2**. In the latter molecule, the σO:MOs differ in energy due to their interactions with the σ framework. The MINDO/2 and CNDO/2 calculations prophesy separations of

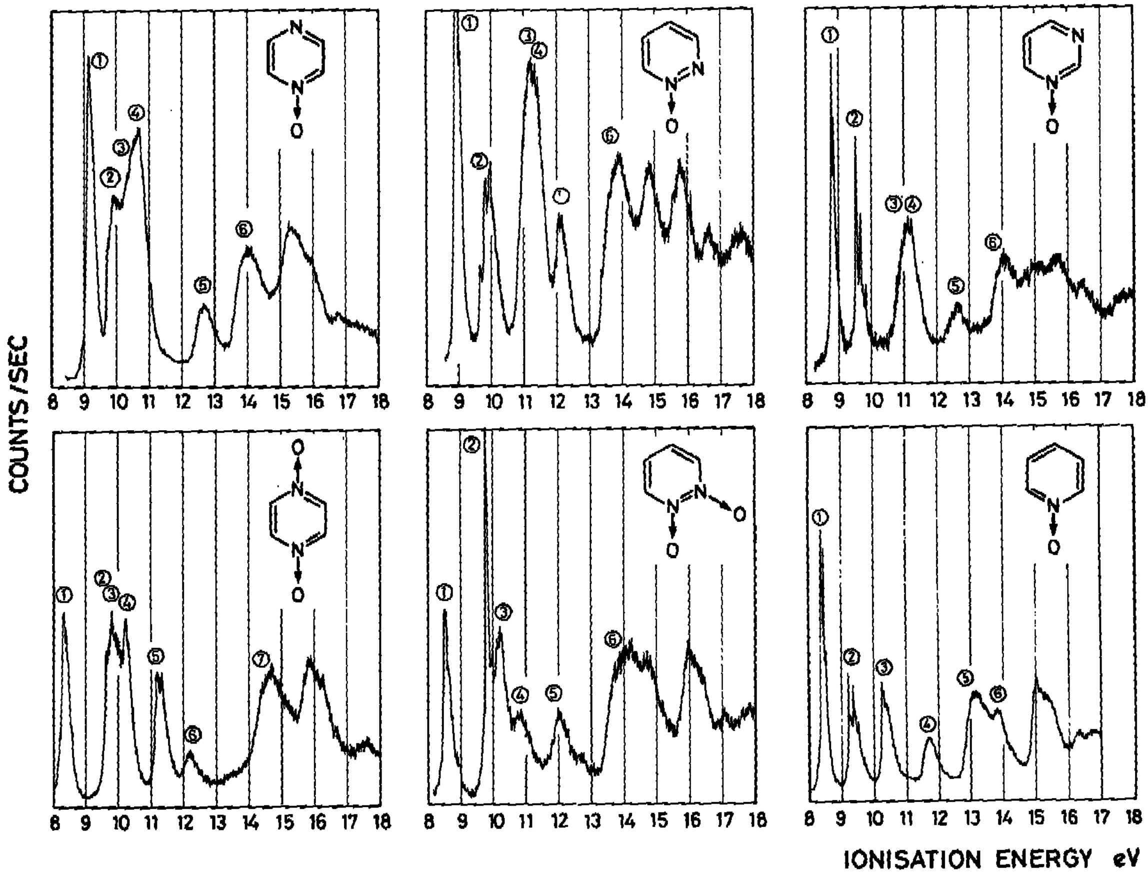

Fig. 1. *HeI photoelectron spectra of the N-oxides of the diazabenzenes,* **1–5** *and of pyridine-N-oxide*
Abscissa – Ionisation Energy/eV. Ordinate – Counts/sec

Table 1. *Ionisation Energies (eV) of the N-oxides* **1–5**[a])

Compound	I_1	I_2	I_3	I_4	I_5	I_6
1	9.17 (πO:)	(9.9, 10.3 ; σO: , σN:)		10.68 (πb_{2g})	12.72 (πb_{1g})	13.85
2	8.33 (πO: b_{1g})	(9.78, 9.86; σO: b_{3g} σO:b_{1u})		10.22 (πO:b_{3u})	11.18 (πb_{2g})	12.2
3	8.89 (πO:)	9.95 (σO:/N:)	(11.05, 11.2 ; σN:/O:, π)		12.0 (π)	13.8
4	8.51 (πO: b_1)	9.76 (πO:a_2)	10.18 (σO: a_1)	10.73 (σO:b_2)	11.92 (πb_1)	13.6
5	8.80 (πO:)	9.52 (σO:/N:)	(11.1, 11.2 ; σN:/O:, π)		12.60 (π)	14.0
PNO	8.38 (πO:)	9.22 (σO:)	10.18 (πa_2)	11.59 (πb_1)	13.0	13.8

a) The band symmetry shown in parentheses for **1**, **2** and **4** is that corresponding to the parent diazabenzenes. See Fig. 2 and text.

0.1 eV and 0.4 eV respectively; with the σO:b_{3g} lying above σO:b_{1u} in energy. In the PE. spectrum of **1**, the additional band (③) that is present in the low IE region corresponds to the nitrogen lone-pair (σN:). In contrast to the situation in **3** and **5**, no mixing between the σO: and σN: lone pairs is possible in **1**. The calculations disagree on the order of the two MOs.

The changes in the energy of the πb_{2g} ionisation process on comparison of the spectra of **2** and **1** (0.5 eV) can be extrapolated to pyrazine. The IE of 10.1 eV so acquired is in accord with this assignment of the 10.18 eV band in pyrazine [11]. Such a correlation starting with PNO yields an IE of 9.7 eV for the πa_2 band in pyridine. This also supports previous results which assigned the lower IE component of the double band (adiabatic IE = 9.3 eV) to the σN: process [11] [12]. The σO:IE in **1** is also by ≈ 0.7 eV to higher energy than in PNO. These trends can be clearly seen in the correlation diagram (Fig. 2).

As in pyridazine and pyrimidine where the π-band IEs are much alike [11], the PE. spectra of **3** and **5** also bear a good deal of resemblance. Variations are expected for the bands associated with the σO:, σN:MOs which mix with each other and with the deeper σ levels to a different extent. The three residual bands, ③, ④, ⑤ in the PE. spectra of **3**, **5** (Fig. 1) stem from the πe_{1g} pair in benzene and the second σO:/σN:MO (bands ③ or ④). The positions of the π bands are deduced from the change in the *Coulomb* integral, at the point of substitution of the additional nitrogen, $\delta\alpha^N = -3.29$ eV, and in the ortho position $\delta\alpha^N_o = -1.03$ eV. The latter parameters were inferred from the PE. spectra of azanaphthalenes [13], whose assignments have been substantiated [14]. The first-order perturbation treatment on the πMOs of PNO obtained by the PPP SCF (or MINDO/2) procedure yields the π IEs for **1**, **3** and **5** as follows:

N-oxide	**1**	**3**	**5**
IE (πO:)	9.0 (9.17) ①	8.9 (8.89) ①	8.7 (8.80) ①
IE (πa_2)	10.7 (10.68) ④	11.3 (≈11.2) ③	11.3 (≈11.2) ③
IE ($\pi 2b_1$)	12.8 (12.72) ⑤	11.9 (12.0) ⑤	12.4 (12.6) ⑤

The experimental IE of the numbered band are given in parentheses. Bands ⑤, which are clearly separated in the spectra (Fig. 1) illustrate the good agreement attained. In the case of **1**, the same assignment is obtained, as deduced above by alternative reasoning. The correlation diagram (Fig. 2) is congruous with the assignments of the π bands in the PE. spectra of pyrimidine and pyridazine proposed [11] and supported by the PE. spectra of their fluoro derivatives [15], angular distribution studies [16] and recent calculations [17]. The interpretations based on CNDO calculations [18] are, however, in discord with the other works.

The *Franck-Condon* envelopes of band ② in the PE. spectra of ③ and ⑤ are significantly different. On the band ② of **5**, as in PNO (Fig. 1) the 0–0 transition is the most intense and several vibrational excitations of the ion are discernible. These vibrational frequencies, ≈ 1200 cm^{-1} and ≈ 560 cm^{-1}, are also excited in the $\tilde{A}$ state, of PNO [2] and **3**. In the latter, however, the third vibrational component represents the vertical transition. Such a band shape is reminiscent, for example, of the bands in the PE. spectra of the diazabenzenes [11] associated with the lone-pairs (N_+, N_- Fig. 2) which are delocalised to a degree. These differences in the band profiles may be taken as an indication that σO:/σN: mixing is more important in **3** than **5**. The MINDO/2 and CNDO/2 calculations suggest that σO: and σN: are thoroughly mixed in **3** whereas in **5** the σO: is more localised.

In the PE. spectrum of **4** the first five bands are distinct. Bands ②–④ are the three remaining oxygen bands πO:(a_2), σO:(a_1) and σO:(b_2). The striking feature is

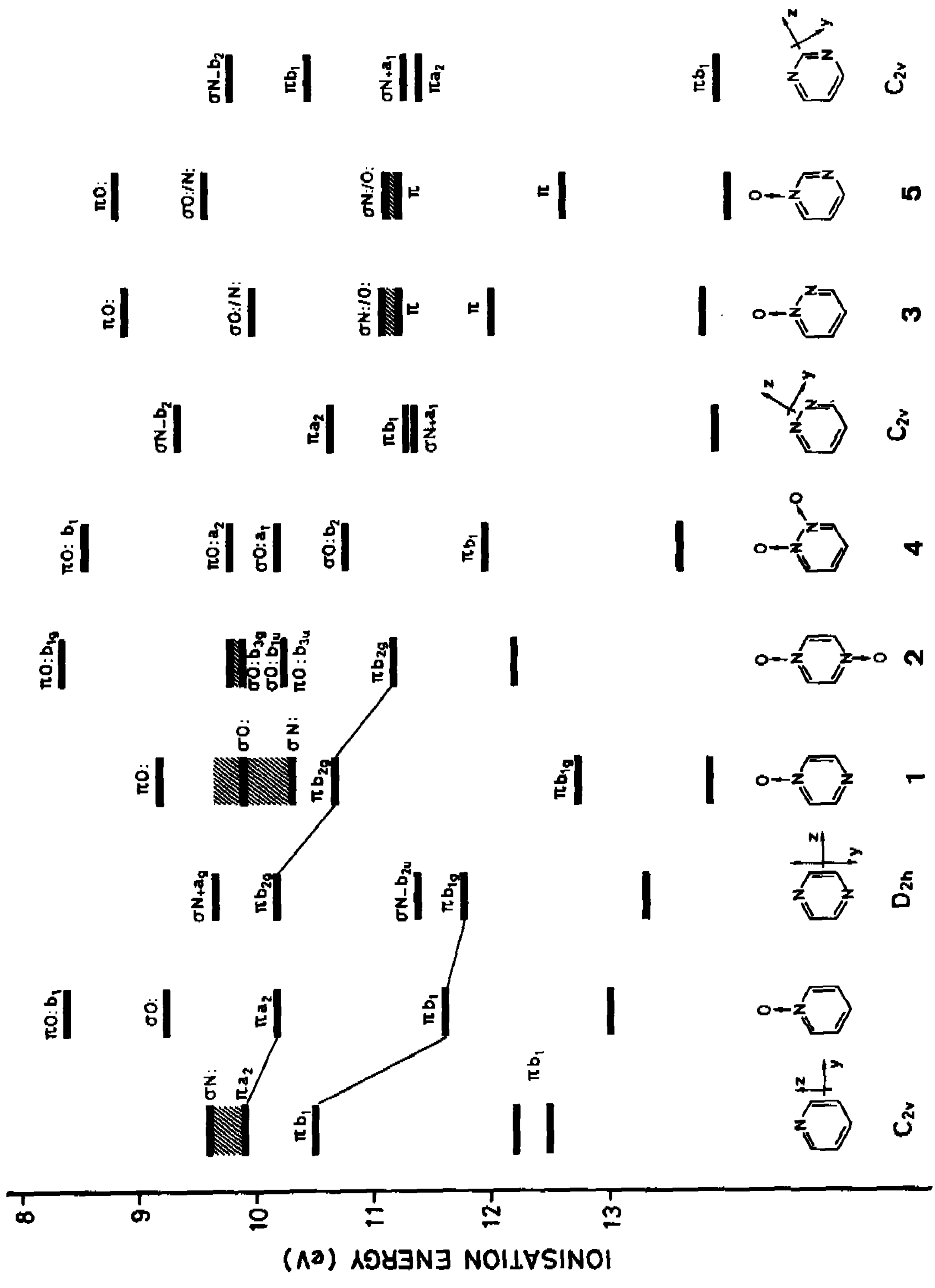

Fig. 2. *Correlation diagram of the ionisation energies of the N-oxides and of the azabenzenes*

the sharpness of the second band and it is attributed to the a_2 combination of πO: lone-pairs which is, by and large, non-bonding. A vibrational frequency of ≈ 1300 cm^{-1} is discernible. The overlap between the σO: lone-pairs is estimated to cause a splitting of the order of 0.2 eV. However, the difference in IEs of bands ③, ④, ascribed to the two σO:MOs, is 0.65 eV and is taken to indicate that the interactions with the σ framework are important. This can be compared to the calculated energy differences of 1.05 eV and 1.4 eV by MINDO/2 and CNDO/2 respectively. Furthermore, both calculations predict the in-phase combination (σO:a_1) to lie above in energy. The remaining band ⑤ is to be attributed to the ring πb_1 MO (axes Fig. 2). It is apparent from the correlation of the IEs (Fig. 2) that extrapolation of the IE data of **4** to **3** to pyridazine follows as indicated. The splittings predicted between the energies of the σO:, σN: and σO: σO: MOs by MINDO/2 compared to the differences in the IEs, according to the assignments given (Tab. 1) are as follows:

N-oxide	**1**	**2**	**3**	**4**	**5**
MINDO/2 (eV)	0.33	0.10	1.05	1.05	0.94
Δ(IE) (eV)	0.4	0.1	1.1	0.65	0.6

Though the evaluation of the Δ(IE) values, in some cases is limited by the overlap of the bands (Fig. 1), the trends are reproduced.

Linear regression of the PPP SCF, and MINDO/2 IEs (on *Koopmans'* level [19]) and the π IEs have been found. The correlation coefficients of the least-squares fit are 0.987 for the PPP regression, and 0.970 for the MINDO/2. The IE of the πO:(a_2) band of **4** is predicted as 9.9 and 9.7 eV by the two MO procedures. Both sets of correlations support the present interpretation of the PE. spectra.

The parameters used for the PPP SCF calculations have been described in connection with the absorption spectra analyses of the N-oxides [3]. The PPP SCF CI calculations gave good agreement with the UV. excitations and have indicated that the strongly allowed ^1L_a band of the N-oxides is described predominantly by one configuration. The latter is considered to be of intramolecular charge transfer character from the oxygen in the HOMO to the π residue in the LUMO. The assignment of the ^1L_a transition has been corroborated by the correlation of the polarographic cathodic and anodic half-wave potentials with the energy of the transition [5]. The variation of the first IE of the N-oxides (Tab. 1) parallel the changes in the oxidation potentials [5]. The nature of the LUMO has been confirmed from the ESR. studies of the anions [6], whereas the HOMO characteristics have been suggested by the calculations [3] and in the case of **2** confirmed by the ESR. study of its cation, electrochemically generated [4]. The analysis of the ESR. data was indicative of a large spin density in the N-oxide group oxygen atom from the observed hyperfine coupling constants and the *g* value was attributed to the contribution from the oxygen lone pair orbitals and a large spin density in the N-oxide group oxygen atom. The PE. spectra of the N-oxides confirm the characteristics of the ground state of the cations, in its generation by electron ejection from the HOMO in which the oxygen basis contribution is dominant.

The longest wavelength bands in the absorption spectra are those of the ^1L_b transitions. The n → π^* transition, of even smaller oscillator strength, has been assumed to be buried beneath the first band in PNO [3]. From the correlation diagram (Fig. 2) it can be seen that provided the two electron term contributions and effects of configuration interaction are approximately constant within this series, as was suggested by the polarographic potentials correlation [5], the n $\rightarrow \pi^*$ transitions are probably also obscured under the other bands of the N-oxides **1–5**. It can also be noted that the large change in the ^1L_a transition energy in **2** in respect to PNO, parallels the change in the reduction potentials [5], whereas the first IEs are very similar.

In conclusion it may be remarked that the PE. spectroscopic studies of the N-oxides of the diazabenzenes confirm the conclusions drawn in the interpretation of the UV. spectra regarding the nature of the HOMO and the description of their electronic structure by means of the PPP SCF calculations. The comparison of the PE. spectra of the N-oxides with their parent nitrogen heterocycles manifest the influence of the NO group on the aromatic system. The perturbation of the π-system results in the separation of the lower excited states of the ions of the N-oxides and this can be of help in the assignment of the PE. spectra of the azaderivatives.

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