183. Ionisation Energies and the Electronic Structures of the N-oxides of Azanaphthalenes and Azaanthracenes

by **John P. Maier*** and **Jean-François Muller**1)

Physikalisch-Chemisches Institut der Universität Basel, Switzerland

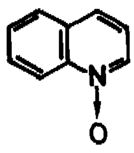
Tanekazu Kubota and **Masumi Yamakawa**

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, 553 Japan

(9. V. 75)

Summary. The HeI photoelectron spectra of the N-oxides of the azanaphthalenes **1**–**5** and of the azaanthracenes **6**, **7** were ascertained. The inferred ionisation energies, and the assignments of the spectra, are presented and are discussed in respect to the electronic structures of the N-oxides and the spectra of the azaderivatives. The data supports the description of the electronic structures of the basic heterocyclic N-oxides based on PPP SCF calculations and the electronic absorption spectroscopy.

In our preceding studies by photoelectron spectroscopy of the N-oxides of pyridines [1] and diazabenzenes [2], the ionisation energy data and the spectral detail were discussed in respect to their valence electronic structures. In this contribution we complete these investigations of the basic heterocyclic N-oxides with the presentation of the ionisation energy data and the photoelectron spectra of the N-oxides of azanaphthalenes **1–5**, and azaanthracenes **6**, **7**.



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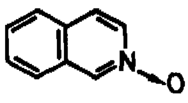

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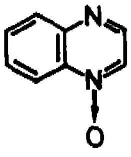

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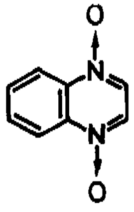

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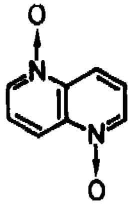

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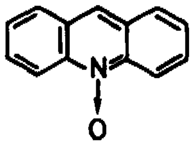

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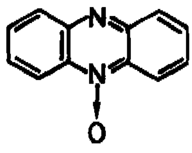

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1) Permanent address: Faculté des Sciences, Université de Metz, Ile du Saulcy, 57000 Metz, France.

Concurrently to the interpretation of the PE. spectra, the data are considered in relation to their absorption spectra [3], cathodic and anodic half-wave potentials [4], ESR. spectra of the anions [5] and the cation of **4** [6], and the theoretical predictions [3] of the electronic structures of these N-oxides.

The spectra were obtained, at elevated temperatures, with a $\pi/\sqrt{2}$ photoelectron spectrometer of the *Turner* type [7]. The spectra, shown in Fig. 1 and 2, were excited by the HeIα (21. 22 eV) photon radiation. The details and calibration procedures were hitherto described [1]. The samples of the N-oxides were those whose preparations have also been documented [5]. The high temperature necessary to obtain a sufficient vapour pressure for the PE. spectrum of phenazine di-N-oxide, resulted in its decomposition to **7**. The ionisation energies (IEs) of the N-oxides **1**–**7**, are presented in Tab. 1 where the assignments of the corresponding bands (ⓘ) are summarised. Included are the PE. spectra (Fig. 2), IEs and the interpretation (Tab. 1) of acridine and phenazine.

Discussion. – The pronounced changes in the PE. spectral pattern of the N-oxides compared to the complementary aza derivatives, are conspicuous in Fig. 2. The spectra of **2** and **5** (Fig. 1) again reveal the separation of the bands below IE ≈ 13 eV typical for the N-oxides of the azabenzenes. The assignment of the bands follows from the trends observed in the previous studies of the N-oxides [1] [2], the PE. spectra of naphthalene and anthracene [8], and comparison with calculations. The salient arguments are outlined in the following paragraphs.

The first bands in the spectra are correlated with a MO, where the πO: contribution prevails. This follows from the composite representation of the N-oxide where the IEs of the separate moieties, azaaromatics and the oxygen p-basis are known [1]. Indeed the first IE of all the N-oxides **1**–**7**, is smaller than of its parent azaderivative, albeit the inductive effect of the NO group has been shown to be comparable to the CN group [1]. However, the πO: contribution is expected to be less pronounced as the size of π system grows as a result of the decrease in the IEs of the ring π electrons and the increasing number of π MOs of low IEs. This has been noted from the absorption spectra of the N-oxides [3] where it was remarked that the band characteristics of the basic heterocyclic compounds are retained when more than two rings are present. The analyses of the ESR. spectra of the cations of the di-N-oxides of pyrazine, quinoxaline and phenazine [6] indicate a decrease in the spin density on the oxygen of the NO group for the sequence given. The coefficients of the O p-basis in the highest occupied MO are given as 0.83, 0.70, and 0.60 for PNO, **1** and **6** respectively by the PPP SCF calculations [3]. The *Franck-Condon* profiles of the first bands in the PE. spectra of the N-oxides (Fig. 1, 2) are narrow as is the case in the smaller N-oxides. This feature supports the assignments and the implication of the similarity of the geometries of the ground states of the molecule and the cation is as expected for ionisation of an electron from a MO where the density is to a large extent around the oxygen. This observation supports the assumption, made in the interpretation of the ESR. data of the cations [6], of little geometry change, but a large decrease in the π electron density at the oxygen of the NO group on formation of the cation.

The bands ② generated as a consequence of the ionising process when the electrons are expelled from the MO localised as the σO: lone-pair are identified from the IE of 9.22 eV of this process in PNO and their relative positions in the PE. spectra of **1**, **2** and **6** (Fig. 1, 2). As in the N-oxides of diazabenzenes, introduction of a further N into the ring ensues in the IEs of the σO: band to be shifted to around 10 eV in

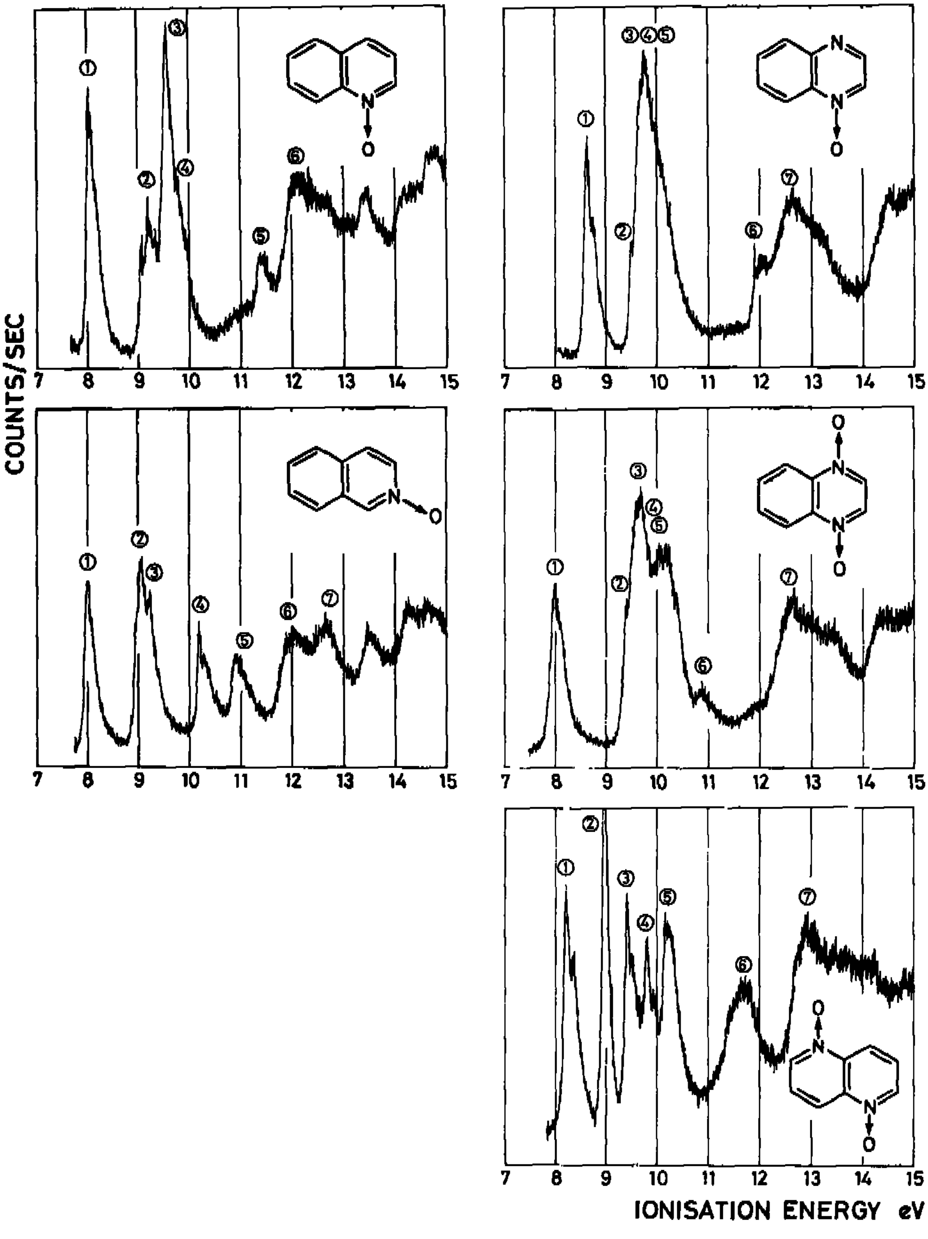


Fig. 1. *HeI photoelectron spectra of the N-oxides of azanaphthalenes* **1–5**. Abscissa: Ionisation Energy [eV]. Ordinate: Counts/sec

pyrazine-mono-N-oxide, where the σN: band is also located. The PE. spectra of **3** and **7** show that this tendency is also apparent here. In the di-N-oxides, two bands of the σO: combinations are anticipated in this region (cf. spectra of **4**, **5**), as well as the other πO: band.

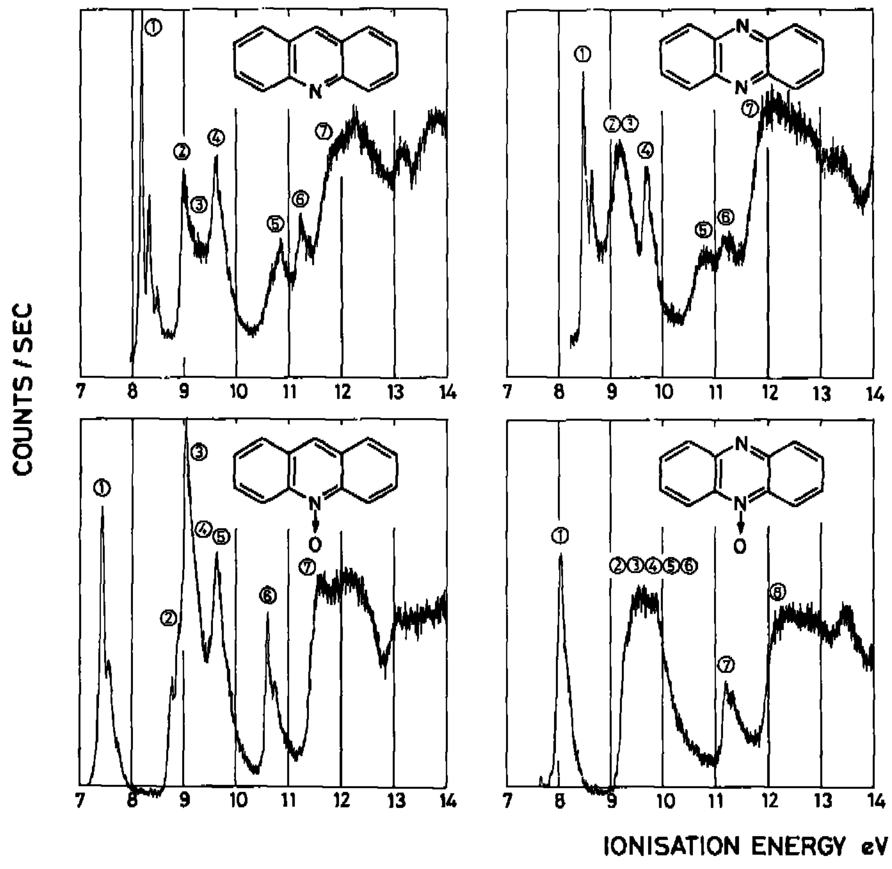


Fig. 2. *HeI photoelectron spectra of acridine, phenazine and their mono-N-oxides* **6** *and* **7**. Abscissa: Ionisation Energy [eV]. Ordinate: Counts/sec

The second IE process in naphthalene, and anthracene, as well as the third in the latter, are associated with MOs which contain nodal planes which pass through the 1,4 and 5,8 and 9,10 positions in the two molecules respectively. The IEs of these MOs are 8.88 eV ($\pi 2b_{1u}$) and 8.52 eV ($\pi 2b_{3g}$), 9.16 eV ($\pi 1a_u$) in naphthalene and anthracene [8]. The changes in the IE of the corresponding bands can be correlated with the $\pi e_{1g}(A)$ band shifts in the benzene derivatives when the N or NO group is inserted at the positions where the nodal plane passes. Additivity of the IE shifts can be applied in the disubstituted molecules **3**, **4**, **5** and **7** as in the diazabenzenes and their N-oxides [2]. In PNO the shift in the IE of the $\pi e_{1g}(A)$ band is 0.93 eV [1] and thus a shift of 0.62 eV per NO group is predicted in the naphthalene system from the ratio of the *Hückel* electron densities in the *ortho* positions. This leads to the expected IEs of these bands as 9.5 eV in **1** and 10.1 eV in **4**, in good agreement with the IEs of bands ③ in **1**, and ⑤ in **4**, **5** (Fig. 1). For **6** the IEs so estimated are 9.0 eV and 9.3 eV, which would correspond to bands ③ and ④ (or ⑤) (Fig. 2). The remaining bands in the low IE region, <12 eV, are associated with the π electrons of the rings.

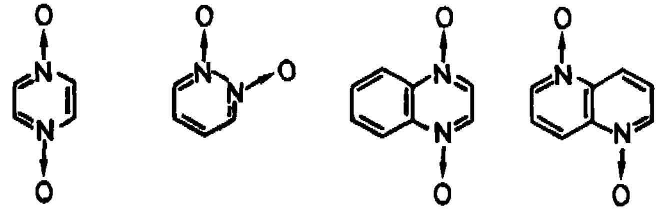
In the PE. spectra of **3** and **7**, the π bands may be identified from the perturbation of the corresponding IEs in **1** and **6** when the nitrogen is introduced. The inductive stabilisation parameters are again taken as $\delta\alpha^N = -3.29$ eV and $\delta\alpha_o^N = -1.03$ eV, for the position of introduction and *ortho* to it, from previous works [9]. This yields the following results, when the coefficients for the respective πMOs are taken from the PPP SCF calculations for **1** and **6**.

IE of π MO in **1**	expt.	8.00	9.50	9.75	11.35
IE of π MO in **3**	calc.	8.51	9.59	10.03	12.55
	expt.	8.62	≈9.6	≈10.0	12.5
Band		①	③	⑤	⑦

IE of π MO in **6**	expt.	7.45	9.04	9.3	9.63	10.6	11.5
IE of π MO in **7**	calc.	8.01	9.05	9.66	9.63	11.29	12.22
	expt.	8.0	9.3–9.8			11.13	12.2
Band		①	②–⑤			⑦	⑧

The remaining bands in the 9–10 eV IE region are the σO: and σN: bands (*vide infra*) and the corresponding IEs are given in Tab. 1.

In the PE. spectrum of **5**, the three well separated bands correspond to the two σO: and the πO: (b_g in C_{2h}) ionisation processes. The very sharp peak ② is reminiscent of the πO: (a_2) band in the PE. spectrum of pyridazine di-N-oxide [2] and is here also assigned to the πO: (b_g) MO. It is reasonable that this IE (8.92 eV) is lower than of the corresponding process in **4**, from the symmetry and sequence of the lower lying πMOs of naphthalene. This order is also predicted by the PPP and the MINDO/2 calculations as summarised for the di-N-oxides:



PPP eigenvalue (eV)	−11.18	−10.62	−11.01	−10.18
MINDO/2 eigenvalue (eV)	−11.27	−10.33	−10.54	− 9.69
Assigned IE πO: (eV)	10.22	9.76	≈10.0	8.92

The bands ③ and ④ in the PE. spectrum of **5** are assigned to the σO:MOs. In contrast, in the spectrum of **4** the bands overlap and the assignment of an IE of ≈ 10 eV to the πO: is suggested by comparison with the calculated trends. In the PE. spectrum of pyrazine di-N-oxide overlap of the πO: and σO: bands is also discernible in this energy region. The MINDO/2 calculations indicate a splitting of 0.2 eV and 0.45 eV for the two σO:MOs for **4** and **5** respectively. In **3** and **7** the energy differences of 0.58 eV and 0.5 eV respectively, are given for the σO: and σN:MOs. The rather weak band ⑥ apparent in the spectrum of **4** is also observed in its 2-methyl derivative, where it is displaced by ≈0.2 eV to lower IE [10]. The presence of another π band, near to that correlated with the πb_{1u} is predicted by the calculations. The intensity of this band is rather small relative to the preceding π bands of lower IE and this trend was also observed for the lower π bands in the PE. spectra of the N-oxides of diazabenzenes [2].

With the assignments available, extrapolation of the IEs of the bands derived from the $\pi 2b_{1u}$ band of naphthalene, to the parent azanaphthalenes can be made. The shift to higher energy of this band is 0.6 eV per NO group in **1** and **4** or **5**. From the IE of this band in **3** an IE of $\approx$ 9.0 eV is then suggested in quinoline, in agreement with the assignments of several groups [9]. Similarly the changes in IE of this band on passing from **4** or **5** to **3** lead to the value in 1,4 or 1,5 diazanaphthalene around 9.1 eV, again in the IE region where the band has been previously assigned [9] [11]. In the azanaphthalenes, there is however, always an overlap of several bands in this region. The conglomeration of the relevant bands (9–10 eV) in the PE. spectrum of **7**, allows only the energy range for the corresponding IEs in acridine and phenazine to be estimated as 9–9.6 eV, in accord with the assignments presented in Tab. 1.

Table 1. *Ionisation energies (eV) of the N-oxides* **1–7**

Compound	I_1 a)	I_2	I_3	I_4	I_5	I_6	I_7
1	8.00 (πO:)	9.01 (σO:)	9.50 (π)	9.75 (π)	11.35 (π)	12.1	12.7
2	7.98 (πO:)	9.03 (σO:)	9.21 (π)	10.18 (π)	10.88 (π)	12.0	
3	8.62 (πO:)	9.30 (σO:)	(9.60, 10.0,	10.20 ; π, π, σN:) b)		12.0	
4	7.98 (πO:)	(9.40, 9.65,	10.0 ; σO:,	σO:, π) b)	10.20 (πO:)	10.80 (π)	12.5
5	8.18 (πO:)	8.92 (πO:)	9.39 (σO:)	9.77 (σO:)	10.11 (π)	11.63 (π) c)	12.7
6	7.45 (πO:)	8.77 (σO:)	9.04 (π)	9.3 (π)	9.63 (π)	10.60 (π)	11.50
7	8.00 (πO:)	9.3 (σO:)	(9.4, 9.5,	9.7, 10.2 ; π, π, π,	σN:) b)		11.13 (π)
Acridine	8.13 (π)	8.95 (π)	9.2 (σN:)	9.56 (π)	10.79 (π)	11.17 (π)	11.8
Phenazine	8.44 (π)	(9.13, 9.15 ;	π, σN:) b)	9.65 (π)	10.76 (σN:)	11.20 (π)	11.9

The numbering of the bands (i) in Fig. 1 and 2 correspond to the index of the ionisation energies I_i.

a) The values quoted are the vertical IEs taken from the band maxima. When the bands are broad the values are taken as ± 0.05 eV, unless extensive overlap occurs in which case the values chosen are estimated from the profile of the composite band. When the band is sharp ± 0.02 eV may be assumed.

b) This order of the assignments is not implied.

c) Probably consists of two overlapping bands.

In Fig. 3 is shown a least-square linear regression of the PPP predicted IEs (on *Koopmans'* level [12]) of the π MOs *vs.* the IEs discernible from the PE. spectra and whose allotments are compiled in Tab. 1. The data includes the parent mono and di-N-oxides of the azabenzene:

$$\varepsilon_i^{PPP}\,(\mathrm{eV}) = (0.95 \pm 0.03)\ \mathrm{IE}\ (\mathrm{eV}) + (1.66 \pm 0.25)$$

correlation coefficient = 0.984 (45 degrees of freedom). It is seen that the PPP SCF calculations give good agreement with the proposed order of the ionic electronic states, when this is represented by the MO sequence. Thus the PE. spectral assignments support the descriptions of the electronic structure of the N-oxides based on the PPP calculations and absorption spectroscopy [3].

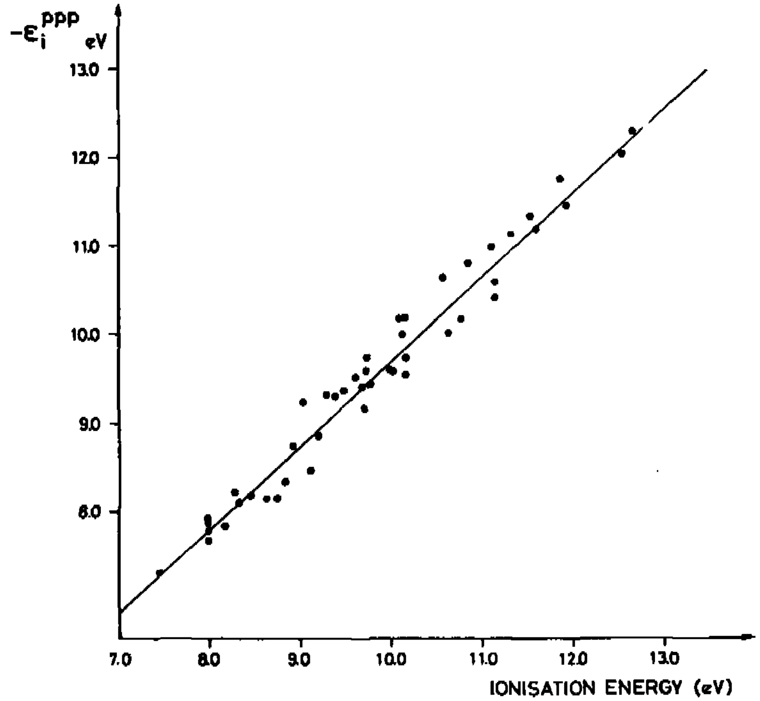


Fig. 3. *Linear correlation between the PPP SCF eigenvalues of π MOs and the PE. spectroscopic IEs of the π bands of the N-oxides* **1–7** *and of pyridine and diazabenzenes.* Abscissa: Experimental Ionisation Energy [eV]. Ordinate: PPP SCF Eigenvalues [eV]

The nature of the excited singlet [3] and triplet states [13] of the basic heterocyclic N-oxides have been discussed. The ^1L_a band in the absorption spectra has been shown to have the character of a charge transfer band from the oxygen to the π ring-system and to be comprised of one configuration by and large [3]. The latter involves electron transfer from the HOMO to the LUMO. The nature of the LUMO in question has been characterised by the ESR. studies [5] of the anions and the polarographic reduction potentials [4] and that of the HOMO is also supported by the present PE. spectroscopic studies. The changes in the IEs determined (Tab. 1) parallel the shifts in the energy of the ^1L_a transition [3] and of the T_1 energy transition which is also smoothly red-shifted and as the ring size increase the S-T gap decreases [13]. The changes in the oxidation and reduction potentials have been related to the changes of the ^1L_a transition, assuming a proportionality of the potentials to the energies of the HOMO and LUMOs [4]. The least-squares linear fit of the $\varepsilon_{1/2}^{OX}$ potentials *vs* the first IEs for the parent N-oxides obtained in this work, yields a correlation coefficient of 0.956 for 8 degrees of freedom. In conclusion it should again be emphasised that the PE. data supports the conclusions drawn previously regarding the π nature of the ground ionic state in the basic heterocyclic N-oxides and of the large contributions of the oxygen π-orbital basis to the MO associated with this transition.

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REFERENCES

[1] *J. P. Maier & J.-F. Muller,* J. chem. Soc. Faraday II, *70,* 1991 (1974).

[2] *J. P. Maier, J.-F. Muller & T. Kubota,* Helv. *58,* 1634 (1975).

[3] *M. Yamakawa, T. Kubota & H. Akazawa,* Theoret. chim. Acta *15,* 244 (1969) and references therein.

[4] *H. Miyazaki, T. Kubota & M. Yamakawa,* Bull. chem. Soc. Japan *45,* 780 (1972).

[5] *T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani & Y. Oishi,* J. Amer. chem. Soc. *90,* 5080 (1968).

[6] *K. Nishikida, T. Kubota, H. Miyazaki & S. Sakata,* J. magn. Resonance *7,* 260 (1972).

[7] *D. W. Turner,* Proc. Roy. Soc. *A307,* 15 (1968).

[8] *P. A. Clark, F. Brogli & E. Heilbronner,* Helv. *55,* 1415 (1972).

[9] *F. Brogli, E. Heilbronner & T. Kobayashi,* Helv. *55,* 274 (1972) and references therein.

[10] *R. DeKock,* private communication.

[11] *D. M. W. van den Ham & D. van der Meer,* Chem. Physics Letters *12,* 447 (1972).

[12] *T. Koopmans,* Physica *1,* 104 (1934).

[13] *T. Kubota, M. Yamakawa & Y. Mizuno,* Bull. chem. Soc. Japan *45,* 3282 (1972).

184. Total Synthesis of Indole and Dihydroindole Alkaloids. VI[1][2]). The Total Synthesis of Some Monomeric Vinca Alkaloids: dl-Vincadine, dl-Vincaminoreine, dl-Vincaminorine, dl-Vincadifformine, dl-Minovine and dl-Vincaminoridine

by **James P. Kutney, Ka Kong Chan, Amedeo Failli, John M. Fromson, Constantine Gletsos, Albert Leutwiler, Vern R. Nelson** and **Joao Pedro de Souza**

Contribution from Department of Chemistry
University of British Columbia, 2075 Wesbrook Place, Vancouver, Canada V6T 1W5

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Summary. A synthetic approach to a variety of monomeric *Vinca* alkaloids is described. The sequence involves, among its crucial phases, the generation of appropriate nine-membered ring intermediates which are then elaborated *via* a transannular cyclization approach to the desired natural products.

In a previous publication in this series [2] we described in detail a general synthetic entry into the *Aspidosperma* alkaloid family. Among the various reactions employed in the sequence, perhaps the most crucial steps concern a reductive ring cleavage of an appropriate pentacyclic ammonium system (I) to the tetracyclic nine-membered structure of quebrachamine (II, R = R′= H) and the subsequent cyclization of the latter to the pentacyclic aspidospermidine skeleton (III, R = R′= H). The already demonstrated extension [3] [4] of the cyclization approach to the ester bearing alkaloids, prevalent in a variety of *Vinca* plants[3]) (for example III, R = $COOCH_3$; R′= H; 2,3-double bond)[4]) provided an obvious requirement for the total

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[1]) For a preliminary report on a portion of this work, see [1].

[2]) Part V, see [2].

[3]) For a general survey see [5].

[4]) For the sake of clarity and facile comparisons with previous publications, the more recent proposals for numbering and nomenclature of indole alkaloids (*J. Le Men & W. I. Taylor,* Experientia *21,* 508 (1965); *J. Trojanek* and *K. Blaha,* Lloydia *29,* 149 (1966)) have not been adopted in this or succeeding papers.