

PROTONATION EFFECTS IN N-HETEROCYCLIC SYSTEMS*

BY M. BERNDT AND W. WOŹNICKI

Institute of Physics, Nicholas Copernicus University, Toruń**

(Received April 20, 1972)

Protonation effects in the UV spectra of N-heterocyclic systems are interpreted theoretically on the basis of a modified semiempirical π -electron approach. The problem of pK_a changes under excitations is briefly discussed.

1. Introduction

The effects of protonation of N-heterocycles have been investigated by many authors [1–10], both experimentally and theoretically. The problem is interesting because of characteristic spectral shifts in the UV region recorded in the result of protonation and also because of changes in acid-base equilibria observed for these systems in excited states [15–18]. The facts mentioned above can be interpreted on the basis of a theoretical study of the electronic structures of N-heterocycles. It seems, however, that so far there is no unambiguous theoretical approach found, providing a proper understanding of the experimental facts.

The purpose of the present paper is to consider the problem in the frame of a modified semiempirical theory applied to a larger class of N-heterocyclic system.

2. Method of calculations

Mataga, Mataga and Tsuno [1, 2] have first introduced two different models in the theoretical treatment of protonation effects in N-heterocyclic systems: one based on electrostatic interaction between the bare proton and the nitrogen lone pair and the other one assuming a covalent binding between the proton and nitrogen. So far, both the electrostatic [4] and covalent [5, 6] models have been employed in different modified theoretical approaches based on π -electron methods. Some attempts have also been made providing an explicit estimation of displacement in σ -core occurring during the protonation process

* Sponsored by the Institute of Low Temperature and Structure Research, Polish Academy of Sciences (Contract No PAN — 3.1.03).

** Address: Instytut Fizyki, Uniwersytet M. Kopernika, Toruń, Grudziądzka 5, Poland.

on the basis of SCE method [6] or with the help of all valence electrons calculations [7, 8, 9]. However, the results of the calculations so far performed, being in most of the cases limited only to a few examples of protonated species, do not give an unambiguous description of the changes in electronic structures taking place in protonation.

Outline of the applied semiempirical scheme

In semiempirical LCAO π -electron methods the eigenvalue problem determining molecular orbitals is practically always formulated in some orthogonalized basis, but not in the original (non-orthogonal) atomic orbital basis χ . The Löwdin Orthogonalized Atomic Orbitals (LOAO) [12]

$$\lambda = \chi S^{-1/2}, \text{ where } S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle,$$

are most frequently (but often implicitly) used, especially in the PPP-type methods [13]. In the present calculations a modified SCF LCAO theory, formulated previously by one of us [14], has been employed. The method takes fully into account the non-orthogonality of atomic orbital basis in the form of the Fock matrix. Namely, it has been shown that the elements of this matrix in the λ basis for the closed-shell state can be reasonably approximated by the formula:

$$\begin{aligned} {}^{(\lambda)}F_{pq} &= {}^{(\lambda)}H_{pq}^C - \frac{1}{2} {}^{(\lambda)}P_{pq} {}^{(\lambda)}\gamma_{pq} + \\ &+ \delta_{pq} \sum_{r=1}^m {}^{(\lambda)}P_{rr} {}^{(\lambda)}\gamma_{pr}, \end{aligned} \quad (1)$$

where m is the number of atoms contributing π -electrons to the conjugated system, and the superscript (λ) denotes the fact that all quantities appearing in (1) are determined in the LOAO basis. The meanings of all the terms are standard ones: ${}^{(\lambda)}P_{pq}$ are the elements of the charge-bond order matrix, ${}^{(\lambda)}\gamma_{pq}$ represent Coulomb repulsion integrals and ${}^{(\lambda)}H_{pq}^C$ are the elements of ${}^{(\lambda)}H^C$ matrix being a representation of one-electron core operator \hat{H}^C in the λ basis. None of these quantities can be regarded as transferable empirical parameters due to the multicentre character of LOAO. However, it has been shown [14] that:

$${}^{(\lambda)}\gamma = T\gamma T \quad (2)$$

where $T_{pq} = (S^{-1/2})_{pq}(S^{1/2})_{pq}$; moreover

$${}^{(\lambda)}H^C = \frac{1}{2}(S^{-1/2}H_0^C S^{1/2} + S^{1/2}H_0^C S^{-1/2}) + S^{-1/2}BS^{-1/2}. \quad (3)$$

In Eq. (2) γ is the $m \times m$ matrix formed by the Coulomb repulsion integrals γ_{pq} determined in the "true" atomic orbital basis χ . The diagonal matrix H_0^C appearing in (3) has the elements:

$$H_{pp}^C = \langle \chi_p | \hat{H}^C | \chi_p \rangle = -I_p^{\text{eff}} - (Z_p - 1)\gamma_{pp} - \sum_{\substack{r=1 \\ (r \neq p)}}^m Z_r \gamma_{rp}, \quad (4)$$

where Z_r is the number of π -electrons contributed by an atom r to the conjugated system, and I_p^{eff} is the effective ionization potential for the $2p\pi$ electron of the atom p belonging to some definite surrounding in a molecule. Finally, the elements of the B matrix:

$$B_{pq} = H_{pq}^C - \frac{1}{2}S_{pq}(H_{pp}^C + H_{qq}^C)$$

can be approximated in the following way:

$$B_{pq} \simeq \frac{1}{2}(I_p^{\text{eff}} + I_q^{\text{eff}})(S_{pq} - 1)S_{pq}. \quad (5)$$

It is evident from the above that the overlap matrix S plays a very important role in the formulation of the theory. In the adapted form of the theory the overlap integrals are calculated theoretically assuming the atomic orbitals χ_i to be simple Slater-type orbitals. However, the exponents ζ appearing in these orbitals are treated as empirical parameters characterizing each type of atom, occurring in the conjugated system. Such a procedure cannot be applied for calculations of Coulomb integrals since they have to include some correlation corrections and, therefore, for each pair of different types of atoms (*e. g.* NN, CN, CC) an empirical curve $\gamma = \gamma(R)$ has to be determined (here R denotes the distance).

In order to reduce the number of parameters, involved in the calculations, for each particular pair of atoms the curve $\gamma(R)$ has been determined as it follows:

- a) the values of γ in several chosen points (for definite distances R) have been treated as empirical parameters,
- b) the values of γ for distances R lying in between the chosen points have been determined with the help of linear interpolation,
- c) for distance $R > 7 \text{ \AA}$ the following relation has been used:

$$\gamma = \frac{k}{\epsilon} \frac{e^2}{R}.$$

The above theoretical approach implies, therefore, the use of the following empirical parameters:

- 1) one-centre type: ζ and I^{eff} (characterizing particular types of atoms of the conjugated system),
- 2) two-centre type: $\gamma(R)$ for definite chosen R distances (characterizing each pair of particular types of atoms).

In our calculations after the SCF procedure the standard configuration interaction treatment including all singly excited configurations has been employed.

On the choice of the values of empirical parameters

With respect to the concept of covalent and electrostatic models being employed in the treatment of protonation process by several authors, it seems to us that within the frame of a π -electron semiempirical scheme of calculations such a division of approaches is not justified. In practice, in both of these models, regardless of their physical meanings, the effects of protonation are taken into account by an appropriate choice of

empirical parameters. Therefore, in our scheme of calculations we have assumed that the protonation process affects the parameters characterizing protonated nitrogen atoms and their adjacent carbon atoms. Since it is difficult to estimate *a priori* values of the parameters, we have applied the least squares method¹ for determining the values of the necessary parameters, which reproduce the spectral data for both the neutral and protonated forms of simple azacompounds (*i. e.* pyridine, pyrimidine, and pyrazine) in an optimized way. In the procedure, however, we took advantage only of the experimental absorption maxima values and it seems probable that the results could be improved, if we included the experimental values of oscillator strengths as well, since they provide a rather important information, when considering the protonation effects. The optimum parameters for the neutral nitrogen atoms N, protonated ones N⁺ and adjacent carbon atoms C' are given in Table I. The remaining parameters for carbon atoms have been taken from the previous paper on hydrocarbon [14].

TABLE I

The values of the optimum parameters used in the calculations

a) The values of exponents ζ and effective ionization potentials I^{eff}

	N	N ⁺	C
ζ	1.623	1.734	1.440
I^{eff} in eV	12.35	13.40	10.464

b) The values of Coulomb repulsion integrals γ^* in eV

Pair of atoms	Distance R			
	0	1.397 Å	$\sqrt{3} \times 1.397$ Å	2×1.397 Å
NN	11.78	6.5925	5.1137	4.1118
N ⁺ N ⁺	12.00	6.5925	5.1137	4.1118
CN		6.3925	5.1137	4.0118
C'C'		6.1925	4.7137	3.8118

* For $R > 2 \times 1.397$ Å we assume: $\gamma_{\text{NN}} = \gamma_{\text{N}^+\text{N}^+} = \gamma_{\text{CN}} = \gamma_{\text{C}'\text{C}'} = \gamma_{\text{CC}}$ (*cf.* the previous paper [14]).

In the case of simple azacompounds (pyridine, pyrimidine, and pyrazine) the calculations have been performed on the basis of experimental geometric configurations. Since the exact geometries of the remaining systems studied here are unknown, we assumed them tentatively to be juxtapositions of the pyridine (or pyrazine) and benzene rings, taking $r_{\text{CC}} = 1.40$ Å and $r_{\text{CN}} = 1.34$ Å.

¹ We greatly appreciate the assistance of Dr J. Budziński in performing the calculations according to his program on the computer MINSK 22.

3. Results and discussion

The reliability of experimental data is of particular importance in semiempirical methods. The first theoretical studies on protonated N-heterocycles [1, 2, 5, 7, 8] were based on erroneous experimental measurements for pyridine (which was first pointed out in the literature by Nishimoto *et al.* [6]). Before considering the effects of protonation for large N-heterocyclic system (*e. g.* mono- and diazaphenanthrenes, phenazine, quinoxaline) we decided to perform some tentative calculations on simple azacompounds: pyridine, pyrimidine, and pyrazine. Since no reliable experimental data concerning the spectra of all these systems in aqueous solutions seem to be available, we have measured² the UV spectra of the neutral and mono- and diprotonated forms, respectively, for all the compounds mentioned above. The results are presented in Figures 1, 2 and 3.

As it can be seen, it is difficult to state the general trends in the absorption spectra occurring under the influence of protonation. Although the red shifts in the result of protonation prevail for both first and second bands, this is not the case for the first band

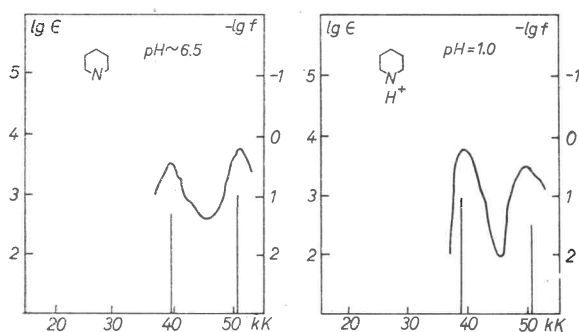


Fig. 1. Absorption spectra of neutral and monoprotonated forms of pyridine compared with the theoretical results obtained in the calculations, being represented as vertical lines

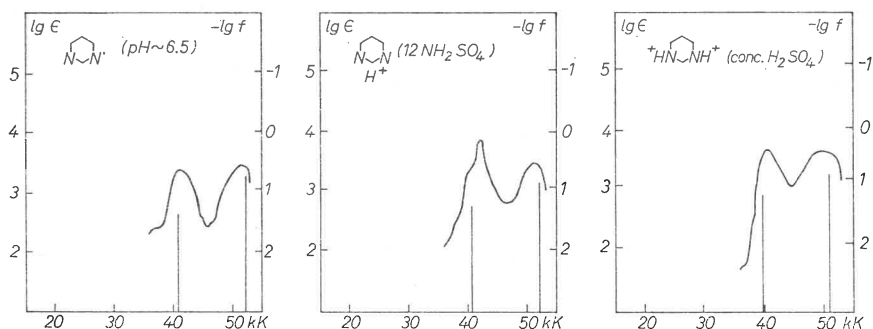


Fig. 2. Absorption spectra of neutral, mono- and diprotonated forms of pyrimidine compared with the theoretical results of the present paper (see caption to Fig. 1)

² Thanks are due to Dr A. Bączyński for his help in taking the measurements. The spectral data were recorded by means of the spectrophotometer "Unicam" SP 700.

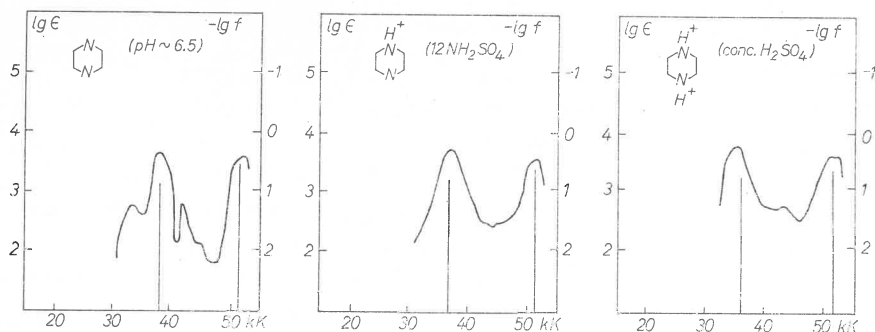


Fig. 3. Absorption spectra of neutral, mono- and diprotonated forms of pyrazine compared with the theoretical results (see caption to Fig. 1)

of pyridine. However, the experimental data indicate evidently that the effects of protonation cannot be considered properly without taking into account the changes of the values of oscillator strengths, which can be sometimes the only changing factors in the course of protonation (*e. g.* for the first bands of pyrimidine and its monoprotonated form the positions of absorption maxima are the same, while the oscillator strength values are rather greatly changed).

These conclusions seem to be confirmed, when considering the experimental results for other N-heterocycles and their corresponding protonated forms [10, 11]. In the case of the compounds being studied here, namely 1- and 4-azaphenanthrenes, 1,7-, 1,10-, and 4,7-diazaphenanthrenes, quinoxaline and phenazine, the effects of protonation are usually connected with red shifts of absorption maxima and increases of extinction coefficients values, but here again these features cannot be treated as a rule since there are exceptions from these.

Since it is very difficult to correlate distinct theoretical transition energies with appropriate experimental absorption maxima positions for systems as large as these considered here, particularly when there is no information on polarizations available, all the calculated results are presented in figures, where the theoretical values are given as vertical lines superimposed on experimental spectra. The following relation between the values of the oscillator strength f and the extinction coefficient ε has been assumed [24]:

$$\lg f = \lg \varepsilon - 4.$$

When considering the agreement between the experimental and theoretical results it should be remembered that the results for simple azines (Fig. 1, 2, 3) must be treated separately since the experimental positions of absorption maxima for these systems (both, the neutral and protonated ones) were taken as reference data in our calculations. However, we did not take advantage of the experimental values of oscillator strengths (being estimated in our measurements), when determining the optimum parameters with the least squares procedure, and therefore it is worth noting that in the case of simple azines the changes in the theoretical values of the oscillator strengths when passing from the neutral forms to mono- and diprotonated ones seem to be correct.

In the case of quinoxaline the experimental measurements indicate red shifts for the first and second bands under the influence of protonation and this is quite well reproduced in the theoretical results (Fig. 4).

Also the theoretical values of the oscillator strengths seem to illustrate the experimental ratios fairly well — both theory and experiment reveal slight changes in the oscillator

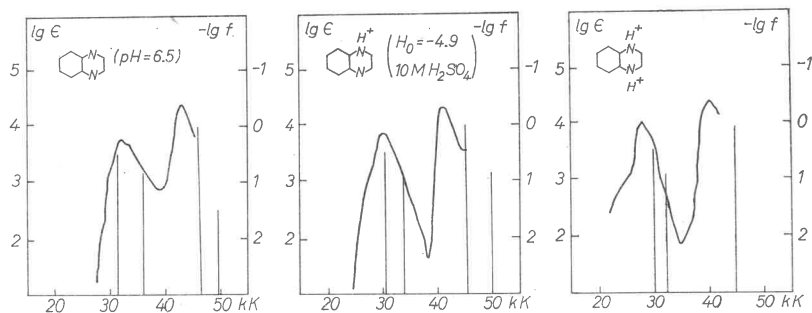


Fig. 4. Absorption spectra of neutral, mono- and diprotonated forms of quinoxaline, reproduced after UV Atlas [11] and Grabowska (private communication), compared with the theoretical results (see caption to Fig. 1)

strength values under the protonation. According to the theoretical results for phenazine (Fig. 5) the sequence of the components of the first band (in the region 20–30 kK) seems to be inverted for the diprotonated form with respect to the monoprotonated and neutral ones, but because of the lack of information concerning the experimental polarizations

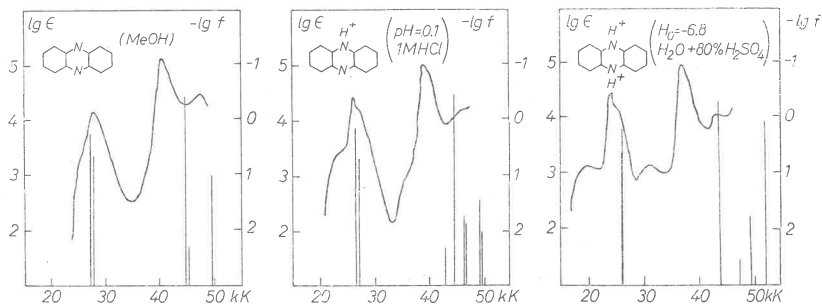


Fig. 5. Absorption spectra of neutral, mono- and diprotonated forms of phenazine (reproduced after UV Atlas [11]) compared with the theoretical results (see caption to Fig. 1)

in this case it is difficult to state whether agreement between the experiment and theory occurs.

The great number of theoretical levels for the further region (40 → 50 kK) makes an appropriate comparison of the results even more difficult. In general, however, both the theory and experiment reveal a trend towards red shifts resulting in the protonation in this case. As far as 1- and 4-azaphenanthrenes (Fig. 6 and 7, respectively) and 4,10-, 1,10-diazaphenanthrenes (Fig. 8 and 9, respectively) are concerned, the sets of the levels obtained in the calculations reproduce the shapes of the experimental spectra quite well.

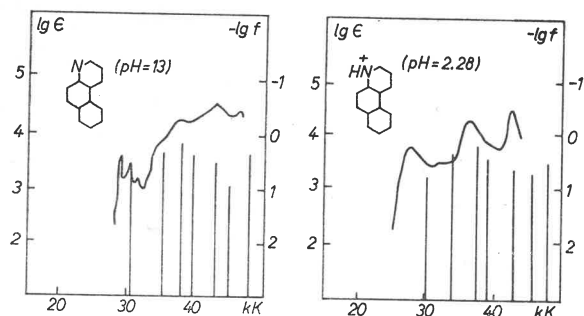


Fig. 6. Absorption spectra of neutral and monoprotonated forms of 4-azaphenanthrene (reproduced after Perkampus [10]) compared with the theoretical results (see caption to Fig. 1)

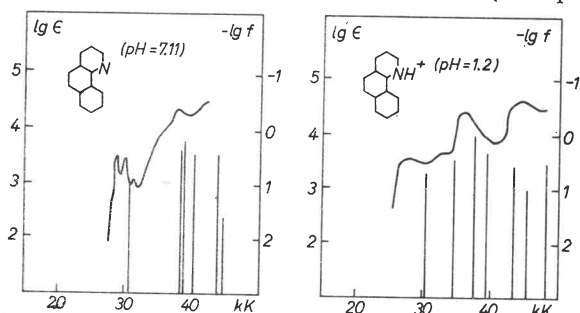


Fig. 7. Absorption spectra of neutral and monoprotonated forms of 1-azaphenanthrene (reproduced after Perkampus [10]) compared with the theoretical results (see caption to Fig. 1)

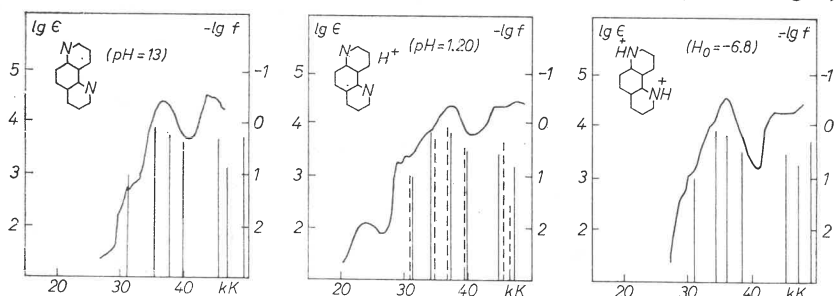


Fig. 8. Absorption spectra of neutral, mono- and diprotonated forms of 4,10-diazaphenanthrene (reproduced after Perkampus [10]) compared with the theoretical results (see caption to Fig. 1)

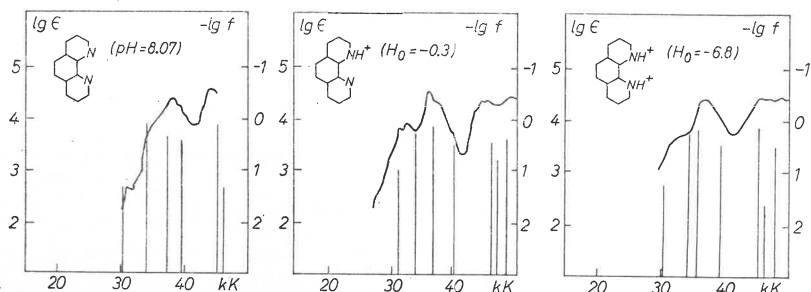


Fig. 9. Absorption spectra of neutral, mono- and diprotonated forms of 1,10-diazaphenanthrene (reproduced after Perkampus [10]) compared with the theoretical results (see caption to Fig. 1)

In the case of monoprotonated 4,10-diazaphenanthrene (Fig. 8)³ there are double vertical lines representing two sets of theoretical results. Each of the sets (dotted and continuous lines, respectively) corresponds to different position of protonation (either N-4 or N-10) being assumed in the calculations. These theoretical results, however, being very close each other do not indicate any difference between these two possible monoprotonated forms.

It is worth noting that within the frame of the present calculations we can also obtain quite reasonable results for the lowest triplet states of the systems considered here. The appropriate theoretical and experimental data are presented in Table II.

As it can be seen, in general the results of our calculations interpret the experimental spectral measurements in a proper way.

TABLE II

Locations of triplet states

System*	Theoretical results of the present paper in eV	Experimental values in eV	
		absorption ($S_0 \rightarrow T$)	emission (phosphor.)
Ph	0	1.629	1.934 [17]
	+1	1.603	1.761
	+2	1.551	
1-AP	0	2.888	2.728 [18]
	+1	2.882	2.651
4-AP	0	2.893	2.728 [18]
	+1	2.843	2.728
1,10-DAP	0	2.668	2.747 [18]
	+1	2.885	2.654
	+2	2.671	2.806
4,7-DAP	0	2.674	2.759 [18]
	+1	2.851	2.682
	+2	2.614	2.682
4,10-DAP	0	2.888	2.709 [18]
	+1	2.837, 2.894**	2.654
	+2	2.853	2.737

* Ph = Phenazine in neutral (0), mono- (+1), and diprotonated forms (+2) respectively. AP = azaphenanthrenes, DAP = diazaphenanthrenes

** In this case two theoretical results have been obtained (see text).

³ In this case the origin of the longwave band in the experimental spectrum seems rather dubious. We present it after Perkampus.

The N-heterocyclic systems considered here have been of particular importance in the investigations of acid-base equilibria in the lowest excited states [15, 16, 17, 18]. In many cases considerable changes of pK_a values under excitation have been observed experimentally. The possibility of a theoretical interpretation of pK_a values by means of the methods of quantum chemistry has been studied by several authors [17-23].

On the basis of the present calculations we tried to correlate the changes in pK_a values with the increases of the net charges on nitrogen atom under excitation, as it had been suggested previously [17, 18]. Since this correlation had failed in many cases (particularly for diazaphenanthrenes) we decided to apply the following relation:

$$pK_a = C + \sum_{B \neq N} Q_B(NN|BB),$$

where C is a constant for a family of compounds, Q_B the net charge of atom B , and $(NN|BB)$ the electron repulsion integral between the lone pair electron of the nitrogen atom N and the π -electron of atom B , according to previous suggestions of Song [20]. In the first approximation we try to estimate the contributions of the electron repulsion terms by means of the values of the π -electron repulsion integrals being used in our scheme of calculations (*cf.* the paper of Song [20]). But neither in this case, however, the correlation seems to be reasonable.

The failure of both these attempts leads to the following alternative conclusions:

1. If we assume that at least one of the relations for pK_a values, being considered here, is reasonable, then either the electron distributions, obtained in this scheme of calculations, is uncorrect, or the estimation of the contributions of the electron repulsion terms, being performed here, is the reason of the failure in finding any correlation. In the latter case, taking into account differences in spatial orientation, when considering the repulsion integrals between the lone pair of nitrogen atom and π -electrons, may provide some better results.

2. Neither of these correlations, based on π -electron approximation, for pK_a values holds true. Considering the problem in the frame of all valence electrons methods may lead to a better understanding of the problem.

We wish to thank Dr A. Grabowska of the Institute of Physical Chemistry of the Polish Academy of Sciences for providing the material necessary in our experimental measurements, and for helpful discussions.

REFERENCES

- [1] S. Mataga, N. Mataga, *Bull.Chem. Soc. Japan*, **32**, 521 (1959); **33**, 511 (1959).
- [2] N. Mataga, S. Tsuno, *Naturwissenschaften*, **45**, 33 (1958).
- [3] K. Jankowski, *Bull. Acad. Polon. Sci. Sér. Sci. Math. Astron. Phys.*, **11**, 621 (1963).
- [4] J. S. Kwiatkowski, *Acta Phys. Polon.*, **A39**, 695 (1971).
- [5] R. D. Brown, M. L. Heffernan, *Austral. J. Chem.*, **12**, 554 (1959).
- [6] K. Nishimoto, K. Nakatsukasa, R. Fujishiro, S. Kato, *Theoret. Chim. Acta, Berlin*, **14**, 80 (1969).
- [7] A. Denis, H. Gilbert, *Theoret. Chim. Acta, Berlin*, **11**, 31 (1968).
- [8] M. L. Bailey, J. P. M. Bailey, *Theoret. Chim. Acta, Berlin*, **16**, 303 (1970).

- [9] H. Kato, H. Katô, H. Konishi, T. Yonezawa, *Bull. Chem. Soc. Japan*, **42**, 923 (1969).
- [10] H. H. Perkampus, H. Köhler, *Z. Elektrochem.*, **64**, 365 (1960).
- [11] *UV Atlas of Organic Compounds*, London and Weinheim Butterworths and Verlag Chemie.
- [12] P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).
- [13] I. Fischer-Hjalmars, *J. Chem. Phys.*, **42**, 1962 (1965).
- [14] W. Woźnicki, *New Formulation of Semiempirical Version of the SCF Theory* (in Polish), edited by N. Copernicus University Edition, Toruń 1967.
- [15] A. Grabowska, B. Pakuła, *Chem. Phys. Letters*, **1**, 369 (1967).
- [16] A. Grabowska, B. Pakuła, *Proc. Int. Conf. on Luminescence*, 1966.
- [17] A. Grabowska, B. Pakuła, *Photochem. Photobiol.*, **9**, 339 (1969).
- [18] A. Grabowska, B. Pakuła, J. Pancir, *Photochem. Photobiol.*, **10**, 415 (1969).
- [19] T. Nakajima, A. Pullman, *J. Chem. Phys.*, **55**, 793 (1958).
- [20] P. S. Song, *Photochem. Photobiol.*, **7**, 311 (1968).
- [21] J. Bertrán, J. J. Dannenberg, R. Leute, C. Ponce, O. Chalvet, R. Daudel, *Theoret. Chim. Acta Berlin*, **17**, 249 (1970).
- [22] J. Bertrán, O. Chalvet, R. Daudel, *Theoret. Chim. Acta, Berlin*, **14**, 1 (1969).
- [23] R. I. Cetine, D. U. S. Jain, F. Peradejordi, O. Chalvet, R. Daudel, *CR Acad. Sci.*, **264 C**, 874 (1967).
- [24] J. Koutecký, P. Hochman, J. Michl, *J. Chem. Phys.*, **40**, 2439 (1964).