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Comparative Study of the pK of Acridine, Thionine and Phenazine Molecules in Their First Excited Singlet and Triplet States

Raymond Constanciel and Odilon Chalvet
Centre Mechanique Ondulatoire Appliquée, Paris

Jean-Claude Rayez
Laboratoire de Chimie Physique de la Faculté des Sciences de Bordeaux

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In order to explain the differences of acido-basic reactivity of acridine and thionine in their first singlet and triplet excited states, new static indices defined from the bielectronic density matrix are used.

Key words: Acridine – Thionine – Phenazine

1. Introduction

The ground state and excited state pK's of some fifty compounds have been reported in the literature [1]. For most of these compounds the pK measured for the triplet state is close to that obtained for the ground state. However for some dyes such as thionine, azur *A*, *B* and methylene blue, the pK of the triplet state is very different from that of the ground state. This is illustrated in Table 1 for two compounds, acridine and thionine, representative of these two classes of behaviour. Due to the difficulties encountered in measuring the pK's of the excited states it may be that the numerical values are not as accurate as one might wish. Nevertheless we may consider their general pattern as qualitatively sound.

Before proceeding further, it is useful to emphasize the following points

(1) These molecules have a common basic character.

(2) For the excited states, singlet or triplet, the basic character is increased with respect to that of the ground state.

(3) For acridine the order of the excited state pK values is $pK_T < pK_S$, whereas for thionine we have $pK_S < pK_T$.

Whereas Parts (1) and (2) contain no surprise, the observations of Part (3) seem much more exciting. The pK of acridine has been extensively studied both from the experimental [1] and theoretical [4] point of view and its variation under excitation was considered typical. In contrast the acid-base properties of the thionine molecule in the first excited singlet or triplet states [2] seem puzzling and need special consideration.

Table 1

	Ground state pK_G	Singlet excited state pK_S	Triplet excited state pK_T
Acridine	5.50	10.60	5.60
Thionine	−0.33	4.50	6.30

In this paper, we are trying to determine via complementary quantum mechanical methods, the physical features that determine the particular acid-base behavior of thionine and related compounds.

2. General Considerations on the pK Calculations

2.1. The Förster Cycle Method

Although the so called Förster cycle method [5] can be somewhat criticized, it is still the most appropriate technique for the theoretical study of the pK variations when the molecule, under the influence of light, is promoted from the ground state to the first excited singlet or triplet state. This method is simple to handle and requires only the calculation of the electronic transition energies of the base and its conjugated acid.

2.2. Choice of the Calculation Method

For all the systems considered in this work, the bases as well as the conjugated acids, theory and experiment agree to impute to the π system alone the electronic transitions from which the pK's listed in Table 1 are derived. Thus, considering the great number of atoms involved in our molecules, we limit ourselves to the study of the π system by means of the SCF LCAO MO method in the Pariser Parr Pople approximation [6]. Moreover, we suppose that this technique can be reasonably applied to the case of thionine although this molecule is not quite planar. That this hypothesis is reasonable was shown in a preliminary study, when satisfactory agreement with experiment was obtained [7]. For the sake of rigor the calculations on acridine and its conjugated acid have been repeated taking into account all valence electrons by means of the SCF LCAO MO method in the CNDO/S approximation [8]. These results, obtained at the expense of considerable increase in computer time, agree quite well with those previously obtained in the PPP approximation. We thus decided to carry out all this work in the frame of the simple PPP technique.

Let us add further that, in the acridine and thionine molecules, both singlet and triplet excited states are obtained by raising an electron from the highest occupied molecular orbital of the ground state to the lowest virtual one. For various CI calculations the weight of this main configuration was always found to be greater than 90%; the remaining configurations were therefore neglected.

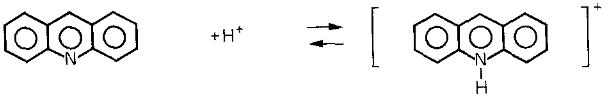

Fig. 1

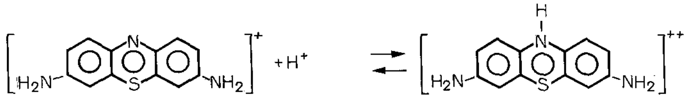

Fig. 2

2.3. *Choice of the Models*

In this work, we have examined the specific equilibria showed in Figs. 1 and 2. There is no difficulty in determining the protonation sites of the acridine molecule. The particular case of thionine needs much more attention: the problem has been already extensively discussed [7] and it has been shown that the proton is bonded to the intracyclic nitrogen atom in the states of interest at present. In the framework just defined, the theoretical treatment of the bases in the Pariser Parr Pople approximation requires no special comments.

In treating the conjugated acid, however, we have supposed that the proton approach changes essentialy the electronegativity [9] of the nitrogen atom: this model is particularly suited to the qualitative study of the pK variations under excitation and it has been already successfully applied in much previous work [10]. In other respects, some calculations using the CNDO/S approximation [11] show that this method implicitly takes into account the electronegativity effect, at least for these kinds of molecules.

3. Results of Calculations

In Diagrams 1 and 2 (refering respectively to acridine and thionine), we have plotted the transition energies $\varDelta E_S$ and $\varDelta E_T$, from the ground state to the first singlet and triplet excited states against the $|W_{2p}(N)|$ parameter corresponding to the protonated nitrogen atom [Let us recall that $|W_{2p}(N)|$ increases with the approach of the proton.]

At first sight, we see that, with the exception of the acridine triplet state[1], the slopes of all the curves are negative and then $pK_G < pK$, in accordance with the general rules stated by J. Bertran *et al.* for electron acceptor heteroatoms [10]. Moreover, as is shown in the Diagram 1, considering the variations of the transition energies $\varDelta E_S$ and $\varDelta E_T$, we obtain from the application of the Förster cycle method the sequence $pK_T < pK_S$ which agrees with the experimental facts.

On the other hand, in Diagram 2, we have a situation which leads to the result $pK_S < pK_T$ again in agreement with experience.

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[1] This disagreement, which is maintained in a rather large configuration interaction calculation, does not exceed the commonly estimated error in the theoretical determination of pK [12].

Diagram. I

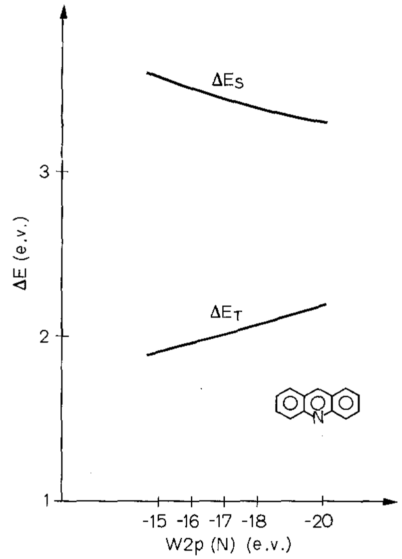
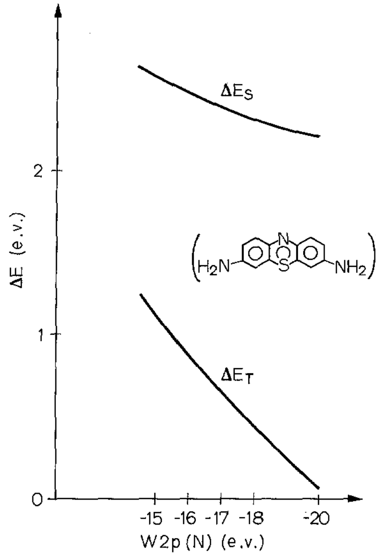


Diagram. II



4. Discussion

If we consider acridine as a classical example of the type of molecule studies so far [10], this one of thionine appears to be very particular. The use of the so called "limiting-case" model [13], allows us to account qualitatively for this divergence from an energetic viewpoint. By "limiting-case" model we mean the parent molecule obtained by allowing to the ionisation potential of the protonated heteroatom either the value $-11.22\,\mathrm{eV}$ which characterises a carbon atom or a negative infinite value which characterizes an isolated center retaining two electrons.

Then, when $|W_{2p}|$ increases from 11.22 eV to an infinite value, the π system changes, in the first case, from anthracene, passes through acridine and tends to the positive ion of the diphenylmethyl radical with two electrons fully localized in the nitrogen atom (Fig. 3).

In the second case, the π system pratically changes from the positive ion of a diphenylmethyl like radical [14], passes through thionine and tends to a bipositive ion formed by two benzene-like core systems, containing ten electrons only, with two electrons fully localized on the nitrogen atom (Fig. 4).

5. Interpretation Using Static Indices

In the preceeding sections, we have shown that the energy calculation leads to a satisfactory interpretation of the experimental data which, let us recall this important fact, always consists in measuring energy differences like transition energies. In other hand, we have noted that the qualitative conclusions obtained do not depend on the particular method (PPC + IC, CNDO/S...) used.

It remains to understand from a physical or chemical viewpoint what factor is responsible for the differences in acid-base behavior in the various excited

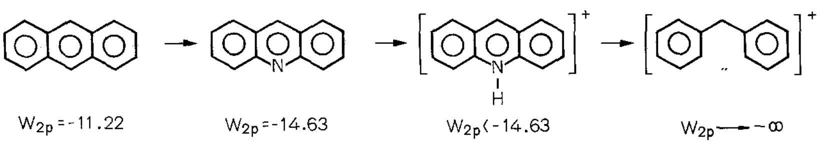


Fig. 3

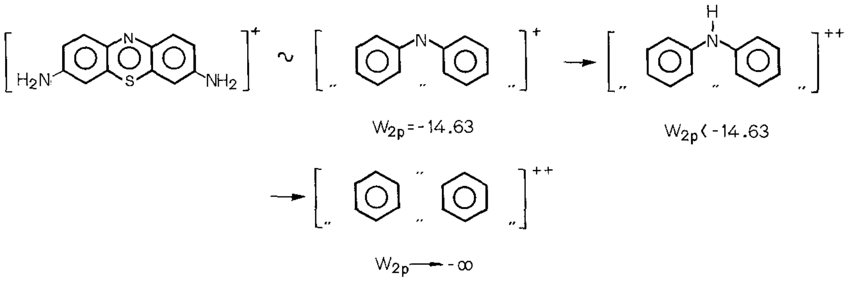


Fig. 4

states. Only after solving this problem, we can expect to be able to predict qualitatively the behavior of a new kind of molecule.

The question is now to find an index which leads to conclusions in agreement with the energetic calculations taken as reference. Let us suppose that the electronic singlet or triplet first excited states of a molecule arise from the same configuration: in this case (which corresponds to the particular molecules under study) the charges in the two excited states are rigorously equal. So it appears that, taking account of the charges alone, we are unable to understand why the pK's of singlet and triplet differ, whereas using the same approximate wave functions which serve to compute the charges, we obtain a satisfactory answer by means of the energy diagrams. Then we are led to the conclusion that, in general, there does not exist any relation between the charge and the energy variation like:

$$q_r = \left(\frac{\delta E}{\delta \alpha_r^c}\right) \tag{1}$$

as Coulson and Longuet-Higgins have shown within the restricted frame of the Hückel method [15]. That should not surprise us, if we remember that, in general, the energy is a function of not only the one electron density P_1 but also of the two electron density P_2 [16], the dependence on this second term following the explicit introduction in the hamiltonian of two particle interaction operators (electronic repulsions).

In the SCF closed shell approximation the pair density is a function of the one-electron density [17]. The energy can therefore be expressed as a function of P_1 only: so in the PPP procedure, we have [18]

$$E = \sum_r q_r \bar{\alpha}_r + 2 \sum_{r<s} p_{rs} \bar{\beta}_{rs} \tag{2}$$

with

$$\bar{\alpha}_r = \tfrac{1}{2}(\alpha_r^c + \alpha_r) \qquad \text{and} \qquad q_r = \langle r | P_1 | r \rangle$$

$$\bar{\beta}_{rs} = \tfrac{1}{2}(\beta_{rs}^c + \beta_{rs}) \qquad\qquad p_{rs} = \langle r | P_1 | s \rangle .$$

McWeeny and Diercksen have shown [19] that in this case the formula (1) is still correct and have extended the proof to the open shell systems [20].

But, when we do not determine the self-consistent set of molecular orbitals from the considered configuration (as in the CI method), the partial derivative $\delta E/\delta \alpha_r^c$ of the energy with respect to α_r^c, that we will call the reactivity index X, is a function of the charge and of the pair polarizability (first order variation of the pair density) [21]. In the particular case of two singlet and triplet electronically excited states which proceed from the same excited configuration, constructed with the self consistent set of molecular orbitals of the ground state, the entire difference of energy variations between singlet and triplet comes from the second term alone, that is from the difference of the pair polarizabilities in the two states respectively [21].

It may be that, for some choices of configuration basis, the charges in the singlet and triplet states are unable to lead to qualitative predictions about the order of pK values, this fact being due to the neglect of the pair polarizability term.

To summarize, whatever the method to determine an approximate wave function, there exists a close agreement between the results obtained by means of energy and those extracted from reactivity indices X defined as above. The differences between the reactivity indices are given either by considering the charges alone (in the case of Hückel, SCF or CCI methods) or by considering the pair polarizabilities alone (one-configuration approximation). In all other cases, e.g. for a non complete calculation with any choice of configurations in the two excited states, one needs to take account of charges and pair polarizabilities together [12], because there is no criterion which allows us to decide if the charges alone are good reactivity indices for this particular configuration basis.

6. Application

Following the discussion of the preceding section, it is possible to look at two practical solutions.

1) Perform an SCF calculation for the excited states S or T. The charges obtained differ generally and Δq may be correlated with ΔpK.

2) Perform an SCF calculation for the ground state only. The excited S or T are defined on the basis of SCF molecular orbital of the ground states by means of only one configuration (when this simplification is justified by an extended CI calculation). Afterwards, we determine the reactivity indices.

The first solution involves unsolved technical difficulties, especially for the singlet state. We are then obliged to choose the second one.

The numerical determination of the reactivity indices however needs [21] the knowledge various polarizability coefficients whose exact computation is tedious [22]. Therefore, in order to compute the polarizability coefficients for the excited states [21, 23] we have made use of an approximation proposed by Coulson and Longuet-Higgins [15], and thus obtained the values listed in Table 2. These numbers give the slope of the curves which represent, according to the model we have chosen, the transition energy variations brought about by the approach of the proton.

Table 2

W_{2p} (eV)	E_S (eV)	E_T (eV)	X^S	X^T	$X^S - q^F$	$X^T - q^F$
Acridine						
−14.63	3.5794	1.8982	1.2787	1.2398	0.0173	−0.0216
−15	3.5624	1.9175	1.3160	1.2740	0.0185	−0.0235
−16	3.5105	1.9763	1.4106	1.3644	0.0195	−0.0267
−17	3.4548	2.0388	1.4954	1.4505	0.0180	−0.0269
−18	3.3999	2.0984	1.5703	1.5303	0.0152	−0.0248
−20	3.3073	2.1947	1.6915	1.6650	0.0088	−0.0177
Thionine						
−14.63	2.6177	1.2228	1.1718	1.2834	0.1247	0.2363
−15	2.5774	1.1285	1.2044	1.3164	0.1187	0.2307
−16	2.4800	0.8837	1.2929	1.4033	0.1049	0.2153
−17	2.3975	0.6552	1.3800	1.4850	0.0938	0.1988
−18	2.3269	0.4444	1.4632	1.5599	0.0846	0.1813
−20	2.2117	0.0795	1.6094	1.6849	0.0691	0.1446

Table 3

	All electron				Geminal basis			
W_{2p} (eV)	K_{78} (eV)	$\langle d^S \rangle$ (Å)	$\langle d^T \rangle$ (Å)	$\langle d^T \rangle - \langle d^S \rangle$ (Å)	$\langle d^S \rangle_g$	$\langle d^T \rangle_g$	$\langle d^T \rangle_g - \langle d^S \rangle_g$	$L^S - L^T$
Acridine								
−14.63	0.8406	3.4074	3.4162	0.0088	2.8133	3.610	0.7974	0.4322
−15	0.8224	3.4048	3.4134	0.0086	2.8258	3.6091	0.7833	0.4221
−16	0.7671	3.3980	3.4061	0.0081	2.8637	3.6035	0.7398	0.3915
−17	0.7080	3.3918	3.3994	0.0076	2.9045	3.5962	0.6917	0.3595
−18	0.6507	3.3863	3.3934	0.0071	2.9441	3.5873	0.6432	0.3292
−20	0.5563	3.3777	3.3838	0.0061	3.0097	3.5664	0.5567	0.2812
	K_{910} (eV)							
Thionine								
−14.63	0.6974	4.0940	4.1049	0.0109	2.8570	4.5306	1.6736	0.1547
−15.	0.7244	4.0937	4.1050	0.0113	2.8242	4.5575	1.7333	0.1612
−16	0.7982	4.0928	4.1051	0.0124	2.7378	4.6308	1.8930	0.1798
−17	0.8712	4.0918	4.1052	0.0134	2.6560	4.7032	2.0472	0.1990
−18	0.9412	4.0908	4.1052	0.0143	2.5800	4.7739	2.1939	0.2179
−20	1.0661	4.0887	4.1057	0.0160	2.4500	4.9020	2.4520	0.2528

We see that there exists a satisfactory agreement between the order of the energies and of the calculated reactivity indices X. Naturally the charges of the excited states, which are equal in this approximation, are perfectly inadequate quantities. The inadequacy can be removed by the use of an extended configuration basis, but some calculations have shown that a full agreement is not obtained for both base and conjugate acid [12]. This fact leads to the conclusion that a completely satisfactory treatment would imply necessarily the use of a configuration basis simultaneously adapted to the base and its conjugate acid.

In order to have a better physical understanding of the problem, it seemed interesting to us to follow another procedure, in which the difference of pK's between the various states is qualitatively studied in two steps. Firstly, consideration of the one particle density matrix P_1 alone allows us to predict, as a rough estimate, the pK value of the excited states with respect to that of the ground state. Many previous calculations show that, for this purpose, we need only the charge on the atom to be protonated [10]. Next we introduce the pair polarizability correction in order to express more precisely the difference between the two excited states. The qualitative study of the pair polarizability difference between the singlet and triplet excited states is achieved through that P_2^S and P_2^T variations, between the base and its conjugate acid. Unlike the situation for P_1, we cannot account with a good accuracy for the influence of the whole $n^2 \times n^2$ matrix P_2, by considering only one of its elements. However using the ZDO approximation, we need only the diagonal elements of P_2 which serve to define a new $n \times n$ two particle matrix called Q. It has been shown [21] that it is possible to correlate the pair polarizability with the variation of scalar quantities, like the mean interelectronic distance $\langle d \rangle$ or the electron pair localizability L, defined by means of the matrix Q as follows

$$\langle d \rangle = \frac{1}{n(n-1)} \operatorname{Tr} Q \cdot D \tag{3}$$

and

$$L = \frac{1}{n(n-1)} \operatorname{Tr} Q \tag{4}$$

where n is the number of π electrons of the system and D is the matrix of internuclear distances.

Table 3 and the Diagrams 3, 4, 5 show the variations of the quantities $\langle d \rangle$ against W_{2p} for both singlet and triplet excited states of acridine and thionine together with $\Delta \langle d \rangle$ and ΔL.

In the case of acridine the introduction of the pair density correction leads to a destabilisation of the triplet state to a greater degree than for the singlet, when the proton is fixed [12]. This fact appears to be a consequence of the tendency, for the electrons in the singlet state, to approach one another more slowly than in triplet state; such a behavior is reflected by the variations of $\langle d \rangle$ taking account of all pairs of quasi-electrons. In the same way we observe a significant lowering of the difference between the electronic repulsion of both states, as is shown by the decrease of the exchange integral K. In short, in the approximation chosen above for the excited wave functions, the charge polarizabilities are the same in both states, only the pair polarizabilities being different. It is easy to account qualitatively for this result if, in the computation of $\Delta \langle d \rangle$, we consider the contributions of only those geminals $\{i \rightarrow m\}$ which are responsible for the difference between the two excited states [21]. Thus the results of calculations listed in Table 3 show that the triplet quasi-electrons pair is not polarizable when, for the singlet one, $\langle d^s \rangle$ increase under the influence of the proton approach. Some simple considerations using a two quasi-electron model of molecule allows us to understand why the singlet pair polarizability is greater than the triplet one. Let us consider for example the electron model of the ethylene molecule [24] and let us account for the proton approach by the variation of the charge difference Δq

Diagram. IV

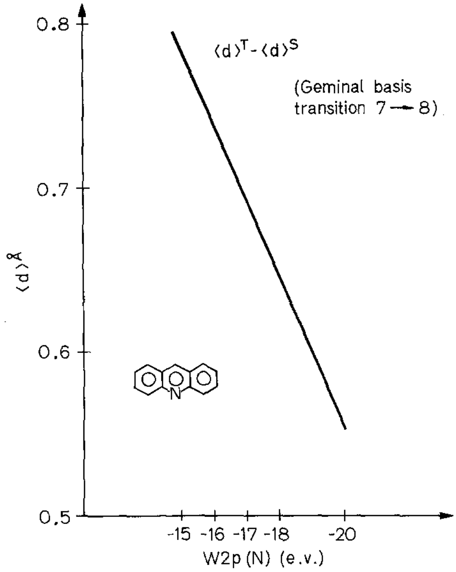
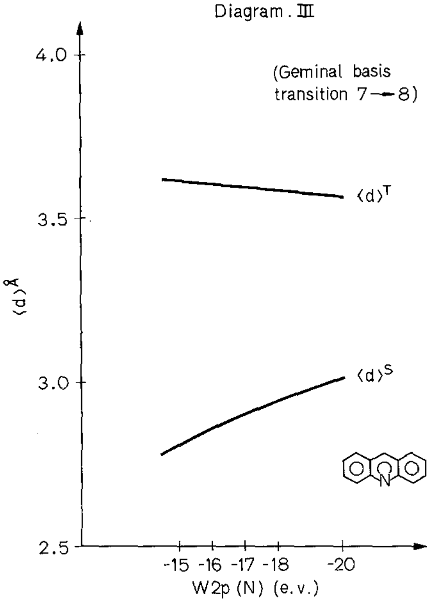
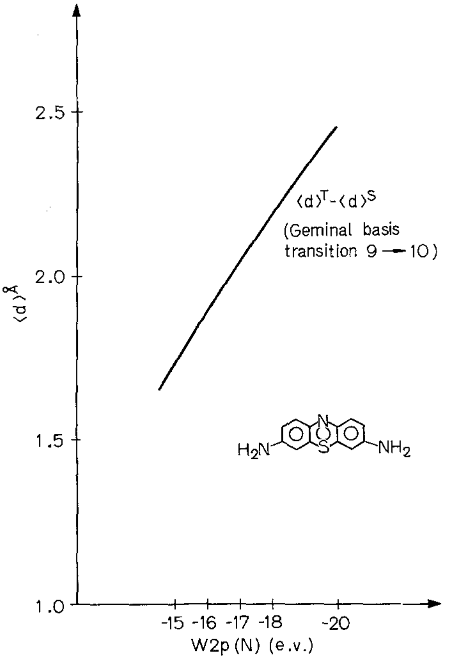
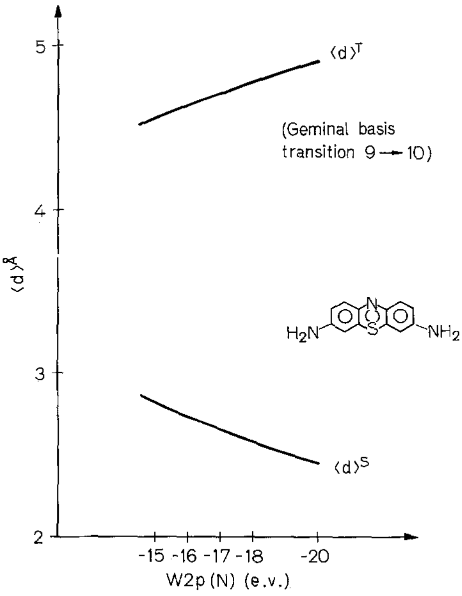


Diagram. III







between the ground state charges on the two centers. It is easy to verify that the two particle density matrices Q of the two excited singlet and triplet states can be expressed in term of Δq only: we find

$$Q^S = \tfrac{1}{2}\begin{pmatrix} 1-(\Delta q)^2 & (\Delta q)^2 \\ (\Delta q)^2 & 1-(\Delta q)^2 \end{pmatrix}; \; Q^T = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

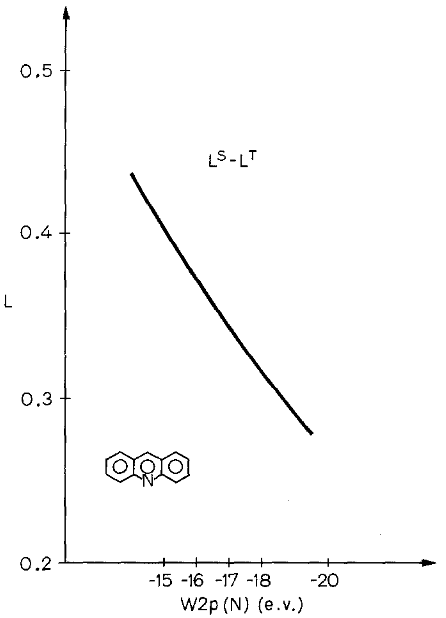
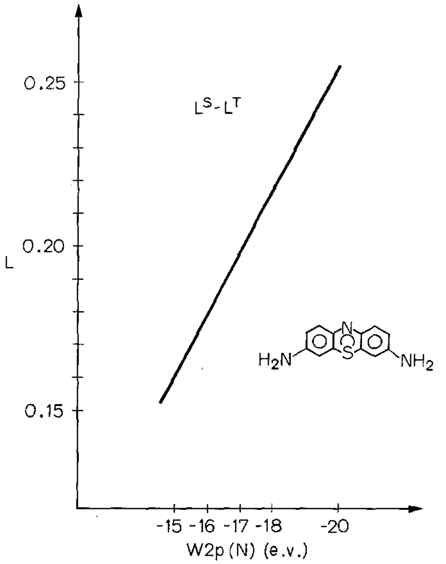


Diagram. V



where the diagonal elements give the pair density on each center and the others give the conditional pair density on the two centers simultaneously. At the first sight, we conclude that only a singlet pair polarization may be observed, since Q^S alone can change with Δq, and moreover that $\langle d\rangle^S$ increases with Δq, leading to a stabilisation of the singlet state with respect to the triplet one.

This fact, which can be provisionally accepted as a general rule, can be accounted using any kind of wave function in the framework of loge theory [25] and is sufficient to explain the major part of experimental results, that is $\mathrm{pK}_T < \mathrm{pK}_S$.

In view of the preceding discussion, the second case cannot be understood. We observe in effect a tendency for the electrons in the triplet state, to avoid one another more effectively than in singlet state and hence to produce a greater stabilization of the triplet state than of the singlet. Here, in a single geminal basis $\{i \rightarrow m\}$, the triplet pair polarizability appears to be the same magnitude as the singlet one, in contradiction with the general rule cited above. This particular behavior seems closely related to topological properties of the limiting case models associated with the molecules.

Let us recall that the extreme model of interest is defined as a bipositive ion formed by two benzene-like core systems. The computation of the quantities $\langle d\rangle$ in the single geminal basis $\{i \rightarrow m\}$ shows that the quasi electron pair is rather localized on a benzene like core in the S state and rather delocalized on the two benzene like cores in the T state. The contribution of this quasi electron pair to the mean interelectronic distance explains the lowering of triplet state which, contrary to singlet one, tends to have a biradicaloid character [26].

Table 4

	Triplet		Singlet	
W_{2p}	$I(G)$	$I(GG')$	$I(G)$	$I(GG')$
Thionine				
−14.63	0.1110	0.4078	0.4078	0.1110
−15	0.1065	0.4196	0.4196	0.1065
−16	0.0951	0.4516	0.4516	0.0951
−17	0.0847	0.4831	0.4831	0.0847
−18	0.0754	0.5132	0.5132	0.0754
−19	0.0671	0.5410	0.5410	0.0671
−20	0.0599	0.5660	0.5660	0.0599

A calculation by means of group indices defined as follows:

$$I(G)=\sum_{\mu}\sum_{\nu} Q_{\mu\nu} \quad \mu\nu G\,, \tag{5}$$

$$I(G,G')=\sum_{\mu}\sum_{\nu} Q_{\mu\nu} \quad \mu G,\ \nu G' \tag{6}$$

allows us to support this comparison. If we define two groups in the thionine molecule as the two benzene cores G and G', we see, in Table 4, that the intragroup localizability index $I(G)$ is more important than inter-group one $I(G,G')$ in singlet state, the reverse being true for triplet state and that these features are enhanced by the protonation. Then we observe an enhancement of the difference between the electronic repulsions of both states and an increase in the exchange integral K: it follows that $\mathrm{pK}_S < \mathrm{pK}_T$.

7. Application of the Case of Phenazine

The experimental results have been given by Grabowska [3] and are reported in Table 5. It concerns two possibilities of protonation.

	pK_G	pK_S	pK_T
1st protonation	1.21	6.00	4.00
2nd protonation	−4.30	4.10	5.70

At first sight it appears that, for the first protonation, phenazine behaves like acridine and, for the second protonation, like thionine. Unfortunately the value of pK_T for the second protonation must be considered with distrust in that it has not been determined directly but by means of an extrapolation procedure leading to the rather surprising result that the second protonation occurs more easily than the first one in the triplet state.

For the calculations in the PPP method we have assumed that in the ground state as well in the excited states, the protonation occurs in two steps leading to the equilibria showed in Figs. 5 and 6.

The energy calculations (Diagram 6) and the determination of reactivity indices X listed in Table 5 consistently show that phenazine exhibits both behaviors characterizing acridine and thionine according as the first or second

Table 5

W_{2p}	E_S	E_T	X^S	X^T	$X^S - q^F$	$X^T - q^F$
Phenazine (1ère Protonation)						
-14.63	3.4566	1.8861	1.2626	1.2499	0.0644	0.0517
-15	3.4183	1.8816	1.3002	1.2837	0.0651	0.0486
-16	3.3127	1.8759	1.3965	1.3727	0.0650	0.0412
-17	3.2084	1.8759	1.4834	1.4568	0.0617	0.0351
-18	3.1100	1.8779	1.5603	1.5344	0.0559	0.0300
-20	2.9447	1.8792	1.6843	1.6651	0.0412	0.0220
-22	2.8263	1.8720	1.7732	1.7615	0.0277	0.0160
2ème Protonation ($W_{2p}^{(1)} = -22$ eV)						
-14.63	2.8263	1.8720	1.2180	1.2863	0.1705	0.2388
-15	2.7597	1.8066	1.2599	1.3314	0.1509	0.2224
-16	2.5874	1.5712	1.3516	1.4182	0.1414	0.2080
-17	2.4267	1.3522	1.4382	1.4993	0.1310	0.1921
-18	2.2795	1.1511	1.5178	1.5733	0.1193	0.1748
-20	2.0285	0.8057	1.6514	1.6960	0.0934	0.1380
-22	1.8382	0.5373	1.7498	1.7849	0.0678	0.1029

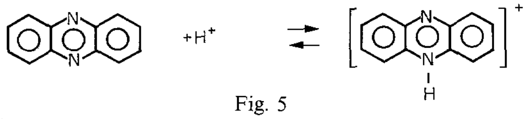


Fig. 5

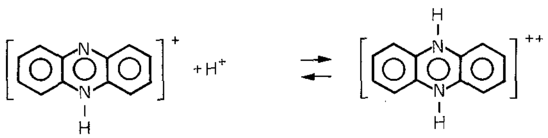


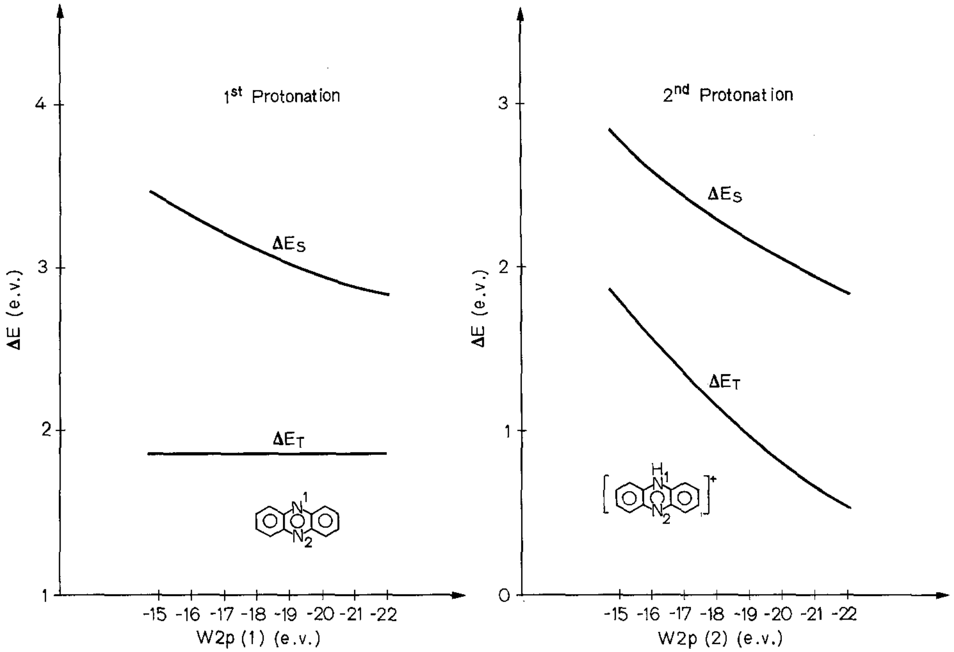
Fig. 6

protonation is involved. This fact can be easily understood in terms of limiting case models, if we assume that (Fig. 7) the monoprotonated form is an intermediate between ($|W_{2p}| = 14.63$ eV) and the positive ion of the diphenyl amine radical ($|W_{2p}| \to \infty$) and that (Fig. 8) the biprotonated form ($|W_{2p}| = 22$ eV) behaves like the bipositive ion ($|W_{2p}| \to \infty$). On the other hand, the qualitative explanation of the difference between the singlet and triplet excited states by the study of the excitation localization is clearly the same as that previously involved for acridine and thionine, despite the fact the excited state wave function must be developed in an extended three configuration basis. So phenazine alone appears to exhibit two radically different behaviors with respect to the proton approach.

8. Conclusion

We have shown in particular examples the importance of the consideration of the pair polarizabilities to explain the difference of pK of excited singlet and triplet states, the wave function of which is developed in a minimal configuration basis. The definition of quantities like the mean interelectronic distance $\langle d \rangle$ and the pair localizability L has provided very useful numerical bases for the discussion.

Diagram. VI



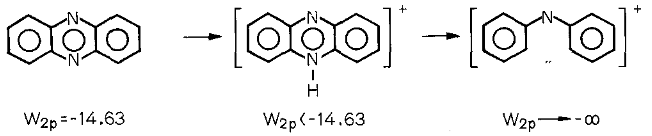


Fig. 7

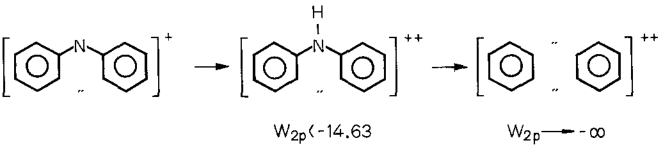


Fig. 8

The physical origin of the difference of the behavior of the molecules under a protonation in their first excited states thus appears to be a topological one in connection with the excitation localization properties.

This paper has been mainly devoted to a qualitative explanation of the experimental facts; the direct calculation of the energies, including solvation effects, remains naturally the best method for a quantitative study. In this field, our work emphasizes the necessity of a careful choice of the configuration basis, adapted to both base and conjugate acid, for which the relation

$$q_r = \frac{\delta E}{\delta \alpha_r^c}$$

is satisfied with a sufficient degree of accuracy.

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Dr. R. Constanciel
Centre de Mecanique
Ondulatoire Appliquée
23, rue du Maroc
Paris XIX, France