Are protonated ortho-diazines planar in excited state?

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ARE PROTONATED ORTHO-DIAZINES PLANAR IN EXCITED STATES?†

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Photophysical kinetics of phthalazine (F, 2,3-diazanaphthalene) and conjugate acids (FH^+, FH_2^{2+}) were determined. According to CNDO/S CI calculations, first protonation only slightly changes the energy of the first (n, π^*) state. Some (σ, π^*) states are lowered upon protonation. In contrast to protonated 1,4-diazines, FH^+ and FH_2^{2+} are not distorted in excited state.

1. Introduction

1,4-diazines reveal some specific features as compared to other, "normal" diazines, containing nitrogen atoms in different aromatic rings. These include: a large increase of pK_a in the lowest excited singlet (S_1) and triplet (T_1) states and loss of radiative properties of S_1 and T_1 upon protonation. The observations were interpreted in terms of distortion from planarity of an excited protonated molecule containing two nitrogen atoms in one aromatic ring [1, 2].

In order to check whether this behaviour is characteristic of para position of nitrogen atoms we have investigated phthalazine-2,3-diazanaphthalene (F) and its protonated forms. This molecule has been chosen as an isomer of the simplest and best known 1,4-distorted structure-protonated quinoxaline QH^+.

2. Results

The following experimental and theoretical methods were applied to study phthalazine and its protonated forms: a) absorption and luminescence spectra were recorded; the results served as a basis for the evaluation of excited state kinetic parameters; b) acid-base equilibria in the S_0, S_1 and T_1 states were measured; c) CNDO/S CI method was used to locate the relative position of (n, π^*) and (σ, π^*) states of F, FH^+ and FH_2^{2+}. The results were compared with the corresponding data for quinoxaline.

2.1. Luminescence and kinetics

Luminescence quantum yields and lifetimes are collected in table 1. The remarkable increase of quantum yields of both fluorescence and phosphorescence upon protonation is observed, quite contrary to 1,4-diazines.

The kinetics of excited states, shown in table 2, has been solved only partly. Our attempts to determine intersystem crossing efficiency in FH^+ and FH_2^{2+} by the Parker method [3] failed. However, the comparison with QH^+ is possible.

The following conclusions can be drawn from table 2: a) internal conversion rate constants in the singlet manifold ($k_{S_1}^{nr}$) are comparable with the intersystem crossing rate constants in both FH^+ and FH_2^{2+}; b) T_1 radiationless depopulation rate constants ($k_{T_1}^{nr}$) decrease distinctly upon protonation; c) radiative rate constants of T_1 (k_p^r) do not undergo any substantial change upon protonation; d) the radiationless depopulation constants are much higher in the protonated quinoxaline (QH^+) than in FH^+.

2.2. Acid-base equilibria

The changes of pK_a upon excitation were determined using the Förster cycle [5]. The results are shown in fig. 1, together with the corresponding data for quinoxaline.

Also in this respect the remarkable differences between phthalazine and quinoxaline are seen: a) both pK values of Q undergo the large increase in both excited states; b) in contrast to that, the pK_a^{II} of F in the S_1 state decreases by

Table 1
Luminescence lifetimes and quantum yields of phthalazine and its protonated forms

	τ_{fl} (ns) 293 K	φ_{fl} 293 K	τ_p (s) 90 K	φ_p 90 K
F [4]	–	–	0.5	0.08
FH^+	1.0 ± 0.2	0.025 ± 0.005	1.4 ± 0.15	0.15 ± 0.05
FH_2^{2+}	5.0 ± 0.6	0.07 ± 0.02	3.8 ± 0.2	0.45 ± 0.1

Table 2
Kinetic data of the lowest excited singlet and triplet states of F, FH^+ and FH_2^{2+} compared with QH^+ at 90 K

Rate constant (s^{-1})	F	FH^+	FH_2^{2+}	QH^+ [1]
$k_f^r \times 10^{-7}$	0.25 ± 0.1	1.7 ± 0.5	3.0 ± 0.4	0.6
$k_{S_1}^{nr} \times 10^{-8}$	<50	$0.3-2.2$	$0.2-1.1$	6.0
$k_{ISC} \times 10^{-8}$	>200	$0.4-2.3$	$0.8-1.7$	6.0
k_p^r	0.16 ± 0.08	$0.12-0.7$	$0.13-0.26$	0.10
$k_{T_1}^{nr}$	1.8 ± 0.3	<0.6	<0.13	8.83

$pK^I(BH_2^{++}, BH^+)$ $pK^{II}(BH^+, B)$
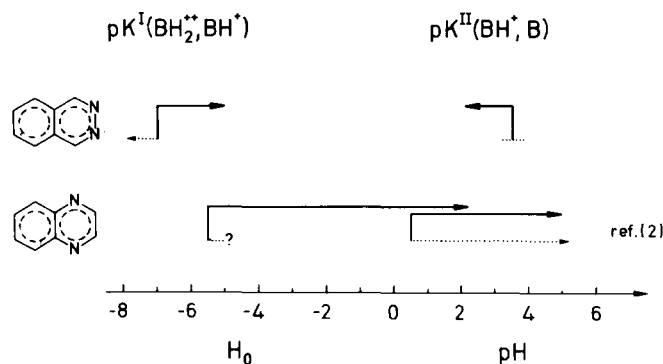

Fig. 1. Changes of pK_a values in the first excited singlet (solid line) and triplet (dotted line) states. Vertical lines mark ground state values.

1–2 pK units. This is consistent with the (n, π^*) character of excited F. c) Changes of pK_a in the triplet states of F are almost nil which is typical of many other "normal" N-heterocyclic compounds [6].

2.3. Theoretical calculations

The results of calculations up to $50\,000\,cm^{-1}$ along with the experimentally located levels are shown in fig. 2: a) in F and its protonated forms (π, π^*) states are very well reproduced, much better than in QH^+ and QH_2^{++}. In the last case the computed energies are underestimated; b) the lowest (n, π^*) states are very slightly shifted after the first protonation, so in FH^+ and QH^+ the lowest $^1(n, \pi^*)$
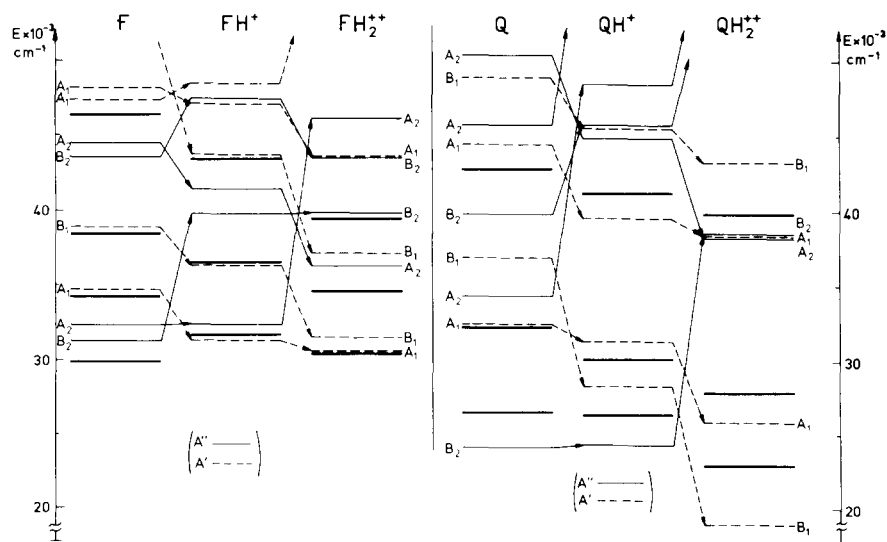

Fig. 2. Energy levels of excited singlet states of phthalazine, quinoxaline and protonated forms: ——— experimental; – – – (π, π^*) ——— (n, π^*) and (σ, π^*) states.

and $^1(\pi, \pi^*)$ states are nearby; c) as shown by the arrows, some (σ, π^*) states are considerably lowered upon protonation. The (σ, π^*) states carrying (n, π^*) character are destabilised in protonated forms; d) in doubly protonated forms the excited states are comparatively well described by single configurations.

3. Interpretation of results

On the basis of all experimental facts it seems that the model of distortion from planarity, proposed for protonated 1,4-diazines does not apply to phthalazine: a) from two (n, π^*) excited S_1 states of isomeric bases, only F undergoes a decrease of basic strength. Moreover, the first equilibrium is shifted much more in Q than in F; b) radiative properties of F increase upon protonation, what is to be expected on the basis of simple considerations of mutual positions of (n, π^*) and (π, π^*) states. This is not fulfilled in Q.

Having in mind the above results we feel that we can answer "yes" to the question posed in the title of this contribution. Why is the distortion of excited protonated forms characteristic only of 1,4-diazines? It may be that the distorted structures of 1,4-protonated forms are most easily realised from the sterical point of view. Excited state geometry optimization would be of great help here.

Our interpretation is in accord with the ab initio calculations of Del Bene [7]. She showed that from among all monocyclic diazines only pyrazine (1,4-diazine) retains its hydrogen bonding ability in the (n, π^*) state. The unusual behaviour of 1,4-diazines becomes more pronounced in larger molecules, such as 1,4-diazaphenanthrene and 1,4-diazatriphenylene.

The investigation of other orthodiazines, namely 5,6- and 2,3-diazaphenanthrenes is now under way.

Acknowledgements

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