

BASICITY OF THREE PHENYLPYRIDINES AND SIX THIENYLPYRIDINES  
IN THE  $S_1$  EXCITED STATE

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The recent synthesis of the six isomeric thienylpyridines led us to investigate the basicities of these compounds. Basicities could be determined in the  $S_1$  excited state since the compounds show fluorescence in neutral and acid media. This is a fortunate situation since many pyridine derivatives do not show fluorescence. In order to analyse the influence of the 2- and 3-thienyl groups as substituents the phenylpyridines were included in the study.

In the excited state basicities can be derived from the Förster cycle<sup>2</sup> which relates the difference between acidities (of the conjugate acids) in ground and excited state to the difference in transition energies of acid and conjugate base:

$$pK_a^* - pK_a = \Delta E / 2.3 kT \quad \text{with } \Delta E = E_B - E_{BH^+}$$

For  $E_B$  and  $E_{BH^+}$  the average values of absorption and fluorescence maxima (in frequency units) were taken as a good approximation of the 0-0 transition. Fluorescence was measured in an Aminco-Bowman spectrophotofluorometer (with Xenon source, excitation monochromator and IP 28 photomultiplier) and corrected for variable lamp intensity and photomultiplier sensitivity by the method of Melhuish.<sup>3</sup> The measured emission spectra in 0.1N  $H_2SO_4$  and in 96% ethanol were assigned to  $BH^+$  and B, respectively. This assignment is based on the fact that the excitation maxima agreed with the absorption maxima of both species and that proton transfer in the excited state does not take place in ethanol (see below).

The base strengths in the ground state were measured spectrophotometrically. The large bathochromic shifts on protonation<sup>1</sup> made it possible to obtain values of  $pK_a$  (in aqueous acetic acid/acetate buffers, ionic strength 0.01 and at 25.0°C) that were reproducible within 0.04  $pK_a$  unit (reproducibility in measurements at three buffer compositions of different pH and at two or three wavelengths).

TABLE

Acidities of phenyl- and thienyl pyridinium ions in ground and excited state and some spectral data.

Compound	$pK_a$	$pK_a^*$	$R^a$	fluorescence maxima (nm)	
				B	BH <sup>+</sup>
2-(2'-thienyl)pyridine	3.73	9.5	0	362	400
2-(3'- - ) -	4.72	11.9	0.05	355	410
2-phenylpyridine	4.55	10.0	0	328	365
3-(2'-thienyl)pyridine	4.47	12.9	0.7	368	460
3-(3'- - ) -	4.87	14.0	3.3	360	470
3-phenylpyridine	4.85	12.2	0.15	325	390
4-(2'-thienyl)pyridine	5.50	12.1	0	360	394
4-(3'- - ) -	5.65	17.4	12.5	330	420
4-phenylpyridine	5.38	14.5	10	325	380

a see text

The ground state basicities (see table) are found to be in good agreement with those determined by Katritzky<sup>4</sup> and by Sigel<sup>5</sup> under nearly identical circumstances. It is interesting that ground state and excited state basicities run roughly parallel. In both states the 4-substituted pyridines are the strongest bases, 2-(2'-thienyl)-pyridine the weakest by a large difference and in each triad the 3'-thienyl derivative is a stronger base than both the 2'-thienyl- and phenylpyridines. The main differences between ground state and excited state basicities are (i) that the latter are much larger (ii) that the structural effects in the ground state seem to be magnified in the excited state.

A discussion of basicities in terms of inductive and mesomeric effects can be made but is ambiguous. However, it is clear that the much encountered generalisation that a thienyl group is electron donating relative to a phenyl group is not of much validity (cf. also  $pK_a$  of 2-thienylcarboxylic acid 3.53, or 3-thienylcarboxylic acid 4.10, or benzoic acid 4.21).

In an attempt to correlate ground state basicities with  $\pi$ -electron energies Hückel and SCF-MO calculations were performed, but not even a qualitatively satisfactory picture emerged. An SCF-MO method with  $\sigma$ -core polarisation<sup>7</sup> could reproduce some of the trends observed but the overall picture remains poor. Apparently, for a correct interpretation neglect of  $\sigma$ -electrons is not allowed.

The much higher excited state basicities compared to the ground state values are reflected by the increased  $\pi$ -electron density on the basic centre in the excited state according to SCF-MO calculations ( $\Delta q \approx 0.1e$ ). Also here the finer details are not reflected by simple theory.

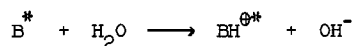
The high basicity in the excited state poses an interesting problem as to the origin of the fluorescence spectra. In solutions with pH between 6 and 9 light is absorbed by the free base but is expected to be emitted from the protonated species, provided the life time of the excited singlet state is long enough to allow the protonation equilibrium to be realised. What actually happens in aqueous borax buffers (pH 7-11) is that some compounds show two emission bands: one is identical to the band in acid, the other to the band that is exhibited in ethanol and attributed to the free base. Apparently only part of the excited molecules are protonated before they return to the ground state. The table lists values of the ratio of intensities of both bands  $R = I_{BH^+}/I_B$  (I is peak height) which is a semiquantitative measure of the degree of protonation before luminescence. Three compounds are seen to undergo no protontransfer at all ( $R = 0$ ).

The following characteristics of R are worth mentioning:

1. R becomes larger the stronger the base. This suggests increasing rate of protonation with increasing basicity.
2. R is independent of pH; apparently water is the source of the proton, and the reverse reaction between  $BH^+$  and  $OH^-$  is negligible.
3. R decreases with increasing concentration of ethanol. Either the lifetime of the  $S_1$  state decreases or (more probably) the proton exchange is slowed down. In 96% ethanol  $R = 0$ .
4. In  $D_2O$  R was measured for one compound, 3-(3'-thienyl)pyridine, and found to be 2.0. A similar decrease was found by Stryer.<sup>8</sup>

5. R is independent on temperature (between 2° and 60°C). This feature may arise from either a low energy of activation or a fortuitous cancelling of temperature effects on rate of protonation and lifetime of the excited state.

From these characteristics which partly have been found for related phenomena<sup>9</sup> it is clear that in the excited state the reaction



takes place but no equilibrium is reached and the reaction from right to left can be disregarded.

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