

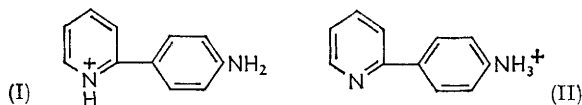
950. *Interaction at a Distance in Conjugated Systems. Part V.¹ The Ultraviolet Spectra of Phenyl-pyridines and -pyridine 1-Oxides and their 3'- and 4'-Nitro- and -Amino-derivatives.*

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The ultraviolet spectra of the ionic and neutral species of the compounds mentioned in the title are recorded. The separate and combined effects of hetero-groups and substituents on the energy of transition to the first excited state of biphenyl are discussed.

THE basicities² of phenylpyridines indicate that interaction between substituents in the phenyl rings and the heterocyclic group is small, and approximately equal to that for styrylpyridines.³ We showed that interaction in the first excited state was qualitatively similar but quantitatively stronger for the styryl- and phenylethynyl-series.¹ We now report on the ultraviolet spectra of the phenyl compounds.

Gillam, Hey, and Lambert⁴ recorded the spectra of the phenylpyridines in ethanol, and drew attention to their similarity to the spectrum of biphenyl. Krumholtz⁵ measured spectra of the phenylpyridines and their cations in aqueous solution; the present results are in good agreement with his work.



Absorption maxima are recorded in Table 1. 4'-Amino-2- and -4-phenylpyridine have two well-separated pK values;³ the spectra taken at the pH midway between these values show that the predominant mono-cations are as (I) and not as (II), because the spectra of forms of type (II) would be similar to that of 2-phenylpyridine as a free base.

The frequencies of the longest-wavelength bands are proportional to the energy of the electronic transition from the ground to the first excited state. 4-Amino- and 4-nitro-groups have large effects on the ultraviolet spectrum of biphenyl; ammonio- and 3-nitro-groups have small effects. 3-Aminobiphenyl shows two bands in the region. The effects of the hetero-groups in the unsubstituted heterocyclic compounds are indicated by the differences between their frequencies and that of biphenyl. These differences (see Table 2) are all negative (except for 3Py, which is anomalous, and 2PyO where steric hindrance occurs), showing that the introduction of the heterogroups lowers the energy of transition to the excited state. Numerically, they are much less for the 3-series than for the 2- and 4-series where direct mesomeric interaction between the phenyl and the heterogroup is possible. In each series they are in the expected¹ order, Py < PyO < PyH⁺ < PyOH⁺, except that the values for 2PyO and 2PyOH⁺ compounds are not as negative as expected (which may be explained by steric inhibition of mesomerism in these compounds) and that the value for the 4PyO-compound is somewhat more negative than expected. The relatively large value for 2-phenylpyridine may indicate greater planarity for this compound than for biphenyl.

For the substituted heterocyclic compounds, the substituent will alter the extent to which the heterogroup interacts with the rest of the system, and *vice versa*. These two effects cannot be separated; as before,¹ we have taken

$$\nu_{\text{interact.}} = \nu_{\text{subst. het.}} + \nu_{\text{benz.}} - \nu_{\text{het.}} - \nu_{\text{subst. benz.}}$$

as a measure of the interaction between the substituents and the heterogroups.

¹ Part IV, Katritzky, Boulton, and Short, *J.*, 1960, 2954.

² Part I, Katritzky and Simmons, *J.*, 1960, 1511.

³ Part II, Katritzky, Boulton, and Short, *J.*, 1960, 1516.

⁴ Gillam, Hey, and Lambert, *J.*, 1941, 364.

⁵ Krumholtz, *J. Amer. Chem. Soc.*, 1951, **73**, 3487.

TABLE 1. *Ultraviolet maxima* (10^2 cm.^{-1} ; $\log \epsilon$ in parentheses).

Subst.	2-Phenylpyridines					
	Biphenyls	(neutral molecule)		(cation)		
4'-NH ₂ ...	368 (4.29)	366* (4.04)	342 (4.21)	408 (3.79)	286 (4.12)	
3'-NH ₂ ...	{ 424 ^a (4.43) 322 (4.46)	441 (4.35)	360 (3.98)	b		
H	405 (4.21)	415 (4.09)	362 (3.99)	413 (3.89)	340 (4.07)	
3'-NH ₃ ⁺ ...	402 ^a (4.19)	b		422 (3.96)	345 (4.19)	
4'-NH ₃ ⁺ ...	403 (4.26)	b		426 (3.91)	347 (4.12)	
3'-NO ₂	400 (4.40)	422 (4.27)	366 (4.23)	429 (4.20)	356 (4.26)	
4'-NO ₂	{ 448 (4.01) 318 (4.18)	457 (4.05)	331 (4.24)	386* (3.83)	339 (4.33)	
2-Phenylpyridine 1-oxides						
	(neutral molecule)			(cation)		
4'-NH ₂	476 (4.31)	389 (4.23)	333 (3.97)	b		
3'-NH ₂	474 (4.00)	433 (4.39)	—	b		
H	—	417 (4.32)	385* (3.96)	463 (3.99)	403 (3.75)	341 (4.03)
3'-NH ₃ ⁺ ...	490 (4.31)	424 (4.30)	383* (3.86)	465* (4.11)	417* (3.79)	352 (3.97)
4'-NH ₃ ⁺ ...	488 (4.37)	424 (4.30)	388 (3.96)	465* (4.15)	415* (3.82)	352 (4.01)
3'-NO ₂	—	426 (4.39)	379 (4.15)	469 (4.27)	424* (4.06)	358 (4.13)
4'-NO ₂	457* (4.12)	380 (4.20)	348* (3.96)	—	—	344 (4.18)
3-Phenylpyridines						
	(neutral molecule)		(cation)		3-Phenylpyridine 1-oxides	
					(neutral)	(cation)
4'-NH ₂	417* (3.68)	357 (4.17)	b		c	c
H	—	{ 410 (4.12) 376* (3.86)	433 (4.10)	{ 388 (3.98) 360 (3.78)	402 (4.41)	{ 429 (4.10) 380 (4.04)
4'-NH ₃ ⁺ ...	b		429 (4.10)	{ 398 (3.93) 362* (3.84)	b	c
4'-NO ₂	459 (3.95)	337 (4.08)	472 (4.06)	340 (4.15)	{ 379 (4.30) 357* (4.22)	351 (4.25)
4-Phenylpyridines						
	(neutral)		(cation)		4-Phenylpyridine 1-oxides	
			(neutral molecule)	(cation)	(neutral)	(cation)
4'-NH ₂	337 (4.28)	277 (4.30)	{ 441* (3.79) 395* (3.60)	303 (4.20)	b	
3'-NH ₂	{ 429 (4.35) 389* (4.11)	b	c		c	
H	391 (4.21)	350 (4.24)	474 (4.20)	342 (4.35)	{ 463* (3.98) 334 (4.25)	
3'-NH ₃ ⁺ ...	b	369 (4.28)	c		c	
4'-NH ₃ ⁺ ...	b	366 (4.29)	476* (4.14)	345 (4.19)	356 (4.16)	
3'-NO ₂	408 (4.37)	373 (4.43)	469 (4.42)	351 (4.54)	362 (4.48)	
4'-NO ₂	{ 461* (3.94) 347 (4.22)	350 (4.34)	—	318 (4.34)	338 (4.35)	

For conditions of measurement see experimental. The position of the peaks treated in the text are given in *italics*. * Indicates shoulder.

^a Taken from Pestemer and Mayer-Pritsch, *Monatsh.*, 1937, **70**, 104. ^b Ionic species could not be obtained reasonably exclusively. ^c Compound not available.

For nitro-substituents, ν_{interact} values, given in Table 3, are all positive, showing that the nitro- and hetero-groups act in opposition. Values for 3'-nitro- are all considerably less than the corresponding values for 4'-nitro-groups, and values for the 3-series are less than those for the 2- and 4-series; both these observations underline the importance of mesomeric compared with inductive interaction. (The basicity measurements² show that in the ground state the inductive effect is dominant for the nitro-groups.) The cationic heterogroups cause somewhat greater values than the others.

The ammonio-groups show the ν_{interact} given in Table 4. Again the values are all positive, but they are almost identical for 3'- and 4'-groups, as is to be expected for groups which interact only by an inductive mechanism. There is no simple dependence of the magnitude of the effect on the position or nature of the heterogroup. In contrast, ν_{interact} .

TABLE 2.

	Py *	PyO	PyH ⁺	PyOH ⁺
4-Series	-14	-63	-55	-71
3-Series	+5	-3	-17	-25
2-Series	-43	+12	-65	-64

* Here and elsewhere Py indicates pyridine, PyO pyridine 1-oxide, and the cationic species are designated similarly. Differences are expressed in units of 10^{-2} cm.⁻¹.

TABLE 3.

	4'-Nitro				3'-Nitro			
	Py	PyO	PyH ⁺	PyOH ⁺	Py	PyO	PyH ⁺	PyOH ⁺
4-Series	+43	63	87	91	22	14	28	33
3-Series	14	64 *	39	58	—	—	—	—
2-Series	56	50	86	90	9	14	21	22

* This value appears anomalous; the spectrum of *p*-nitrophenylpyridine 1-oxide shows two bands (Table 1), the interpretation of which is not clear.

TABLE 4.

	4'-Ammonio			3'-Ammonio		
	PyO	PyH ⁺	PyOH ⁺	PyO	PyH ⁺	PyOH ⁺
4-Series	5	18	24	—	22	—
3-Series	—	12	—	—	—	—
2-Series	9	9	13	10	8	14

TABLE 5.

	Py	PyO	PyH ⁺
4-Series	-17	-2	-36
3-Series	-16	—	—
2-Series	+17	+9	-17

values for 4'-amino-groups (as indicated above, the simple treatment cannot be used for 3'-amino-groups) are negative (see Table 5) except in the 2-series where steric hindrance may complicate matters, although this should not occur for the neutral species of 4'-amino-2-phenylpyridine. The smallness of the effect for 4-*p*-aminophenylpyridine 1-oxide is also surprising.

These results may be compared with those obtained for the styryl and phenylethynyl compounds. For nitro- and ammonio-groups, larger positive values are found for the phenyl series; this is reasonable because the nearer the two electron-attracting groups are, the more they will compete. Larger negative values are found for dimethylamino-groups in the styryl series than for amino-groups in the phenyl series and this is less easily explained.

Experimental.—The preparation of the compounds has been described;² they were recrystallised before measurement. The spectra of the pyridines and pyridine 1-oxides, and 4-aminobiphenyl, as free bases, were measured in a phosphate buffer of pH 9.7. Biphenyl and 3- and 4-nitrobiphenyl were measured in water containing 15% of ethanol (other solutions contained up to 1% of ethanol). The spectra of the mono-cations of 2- and 4-*p*-aminophenylpyridine were obtained in an acetate buffer of pH 4.02; the corresponding di-cations, and the cations of the other pyridines were measured in *n*-sulphuric acid. The mono-cations of 2-*p*-4-*p*-, and 2-*m*-aminophenylpyridine 1-oxide were measured in phosphate buffers of pH 2.4–2.6; the corresponding di-cations, and the cations of the other pyridine 1-oxides were studied in 20*N*-sulphuric acid.