596. *Interaction at a Distance in Conjugated Systems. Part IV.*[1] *The Ultraviolet Spectra of* 4-p-*Substituted Styryl- and Phenylethynyl-pyridines and their* 1-*Oxides and Benzenoid Analogues.*

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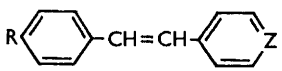
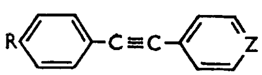
The ultraviolet spectra of the ionic and neutral species of the compounds mentioned in the title are recorded. The frequencies of the longest-wavelength band are used to obtain a measure of the influence of the substituents and heteroatoms on the energy of the transition from the ground to the first excited state. This, together with infrared and basicity data,[1,2] indicates that long-distance interaction between substituent and heteroatom is qualitatively similar but is quantitatively much greater in the excited state than in the ground state.

THE basicities of a series of 4-*trans*-styryl- and 4-phenylethynyl-pyridines (I, II; Z = N) and their 1-oxides (I, II; Z = $^+$N-O$^-$) indicate that interaction between the substituents on the benzene rings and the heteroatom is always small, but is larger for the styryl than for the phenylethynyl series.[2] The intensities of the C=C and C≡C stretching modes in the infrared spectrum show that the heteroatom and the substituent group influence the electron distribution essentially independently.[1] The foregoing work was related to the ground state of the molecules: in order to obtain information about the degree of interaction in excited states we have now studied ultraviolet spectra.

(I)





(II)

The absorption maxima are recorded in Table 1. We wished to compare the energies of the electronic transition from the ground to the first excited state in these compounds; this is proportional to the frequency of the longest-wavelength band. These frequencies are given in Table 2; where the band had vibrational fine structure the true position of the band centre was estimated by the extrapolation to the smoothed-out envelope of mid-points of lines connecting points on the envelope of equal extinction.

The effect of the substituents in the purely benzenoid compounds is measured by the differences between the values for the substituted compounds and that for stilbene or tolan. These differences are given in Table 3, cols. 1 and 6. They are all negative, showing that the introduction of the substituents lowers the energy of transition to the

TABLE 1. *Positions and absorption coefficients of light absorption maxima of substituted stilbenes and tolans.*

Compounds		$R·C_6H_4·CH=CH·C_6H_5$
R = H	*a*	228 (15,400); 294 (27,900); 307 (27,600)
NMe$_2$	*b*	234 (11,500); 330 (21,000)
	c	228 (14,000); 297 (28,700); 308 (28,400)
OMe	*a*	229 (13,000); 303 (28,100); 318 (27,500)
Me	*a*	230 (15,400); 229 (29,000); 312 (29,000)
Cl	*a*	230 (14,200); 300 (32,400); 313 (31,800)
NO$_2$	*a*	242 (10,200); 267 (8,320) *; 356 (21,400)
Compounds		$R·C_6H_4·C≡C·C_6H_5$
R = H	*a*	215 (17,200); 220 (15,400); 237 (7,800); 264 (19,100); 272 (20,900); 279 (27,000); 287 (19,600); 296 (23,800)
OMe	*a*	287 (28,400); 303 (24,400)
Me	*a*	218 (19,000) *; 223 (16,800) *; 267 (23,600); 275 (26,000) *; 282 (34,200); 291 (24,600); 300 (30,400)
Cl	*a*	223 (16,400); 269 (24,800); 277 (27,500); 285 (36,200); 293 (26,100); 302 (32,200)
NO$_2$	*a*	234 (12,000); 330 (20,100)

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[1] Part III, Katritzky, Boulton, and Short, *J.*, 1960, 1519.
[2] Part II, Katritzky, Short, and Boulton, *J.*, 1960, 1516.

TABLE 1. (*Continued.*)

Compounds		$R{\cdot}C_6H_4{\cdot}CH{=}CH{\cdot}C_5H_4N$
R = H	*d*	227 (13,700); 304 (23,600)
	c	234 (11,200); 335 (20,100)
NMe_2	*b*	250 (9,100); 374 (23,600)
	e	260 (10,700); 392 (13,700) *; 461 (17,800)
	f	230 (11,700); 325 (22,100)
OMe	*d*	231 (10,800); 322 (21,700)
	c	247 (15,800); 365 (21,000)
Me	*d*	231 (14,100); 314 (31,300)
	c	240 (13,600); 348 (22,200)
Cl	*d*	229 (14,000); 312 (30,500)
	c	238 (13,700); 339 (23,000)
NO_2	*d*	334 (22,800)
	c	338 (23,000)
Compounds		$R{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}C_5H_4N$
R = H	*d*	216 (15,800); 233 (10,300); 244 (10,300); 282 (25,700); 298 (23,300)
	c	234 (11,300); 275 (10,000); 282 (9,900); 327 (22,000)
OMe	*d*	249 (13,900); 256 (13,000); 263 (12,000); 306 (26,100)
	c	244 (15,800); 275 (8,800) *; 354 (25,600)
Me	*d*	225 (15,200); 240 (11,500); 251 (10,600); 290 (26,400); 305 (26,500)
	c	237 (14,000); 275 (9,600); 283 (8,700) *; 339 (25,600)
Cl	*d*	238 (10,600) *; 249 (12,200) *; 256 (13,400) *; 287 (31,700); 304 (29,600)
	c	234 (15,400); 251 (10,700) *; 275 (11,600); 283 (11,000) *; 331 (27,800)
NO_2	*d*	315 (23,700)
	c	326 (30,100)
Compounds		$R{\cdot}C_6H_4{\cdot}CH{=}CH{\cdot}C_5H_4NO$
R = H	*d*	213 (20,800); 239 (12,100) *; 278 (8,800); 316 (13,000)
	g	237 (12,100); 342 (11,700)
NMe_2	*b*	277 (12,500); 403 (22,500)
	h	277 (12,800); 328 (40,300)
	g	232 (18,400); 326 (17,500)
OMe	*d*	247 (18,300); 347 (36,700)
	g	248 (7,700); 374 (8,700)
Me	*d*	243 (15,600); 325 (17,400)
	g	244 (19,300); 356 (18,700)
Cl	*d*	232 (13,200); 338 (41,100)
	g	243 (12,000); 356 (33,600)
NO_2	*d*	220 (16,500) *; 352 (34,400)
	g	220 (14,000); 351 (33,800)
Compounds		$R{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}C_5H_4NO$
R = H	*d*	218 (20,500); 309 (45,100); 326 (47,600)
	g	236 (16,900); 282 (13,300); 339 (28,700)
Me	*d*	217 (14,600); 331 (35,800)
	g	240 (15,700); 289 (9,700); 347 (23,300)
Cl	*d*	217 (17,600); 313 (35,400) *; 330 (38,000)
	g	238 (23,600); 265 (25,400); 344 (24,400)
NO_2	*d*	218 (18,000); 331 (33,700)
	g	214 (32,100); 341 (61,100)

* Shoulder. Letters refer to solvent: *a*, 50% ethanol–water; *b*, 50% ethanol–aqueous sodium phosphate buffer, pH 10; *c*, 1·0N-aqueous H_2SO_4; *d*, aqueous sodium phosphate buffer, pH 10; *e*, phosphate buffer, pH 5·3; *f*, 5·0N-aqueous H_2SO_4; *g*, 20N-aqueous H_2SO_4; *h*, phosphate buffer, pH 2·2. Phosphate buffers were *ca.* 0·01M in phosphate. Positions are given in mμ, with molar absorption coefficients in parentheses.

TABLE 2. *Frequency of longest-wavelength band* (*cm.*$^{-1}$).

	1	2	3	4	5	6	7	8	9	10
	Compounds $R{\cdot}C_6H_4{\cdot}CH{=}CHAr$					Compounds $R{\cdot}C_6H_4{\cdot}C{\equiv}CAr$				
Subst.	Ph	Py	PyH^+	PyO	$PyOH^+$	Ph	Py	PyH^+	PyO	$PyOH^+$
NMe_2	30,250	26,750	21,700	24,800	—	—	—	—	—	—
OMe.........	32,500	31,200	27,400	28,800	26,760	34,100	32,700	28,250	—	—
Me	33,000	32,000	28,760	30,800	28,100	35,050	33,750	29,700	30,700	28,850
H	33,440	33,200	29,900	31,700	29,270	35,800	34,700	30,800	31,600	29,700
Cl	32,800	32,630	29,400	29,600	28,260	34,900	34,000	30,400	31,200	29,100
NO_2	28,100	29,950	29,600	28,400	28,600	30,150	31,800	30,700	30,100	29,500
NMe_2H^+ ...	33,300	—	30,800	30,500	30,750	—	—	—	—	—

TABLE 3. *Interaction between heterocyclic group and substituent* (*cm.*$^{-1}$).

	1	2	3	4	5	6	7	8	9	10
	Compounds $R\cdot C_6H_4\cdot CH=CHAr$					Compounds $R\cdot C_6H_4\cdot C\equiv CAr$				
	(See text)	Py	PyH^+	PyO	$PyOH^+$	(See text)	Py	PyH^+	PyO	$PyOH^+$
R:		(−240)	(−3540)	(−1740)	(−4170)		(−1100)	(−5000)	(−4200)	(−6100)
NMe_2 ...	(−3190)	−3260	−5010	−3710	—	(—)	—	—	—	—
OMe ...	(−940)	−1060	−1560	−1960	−1570	(−1700)	−300	−850	—	—
Me	(−440)	−760	−700	−460	−730	(−750)	−200	−350	−150	−100
Cl	(−640)	+70	+140	−1460	−370	(−900)	+200	+500	+500	+300
NO_2	(−5340)	+2090	+5040	+2040	+4670	(−5660)	+2750	+5550	+4150	+5450
NMe_2H^+	(−140)	—	+1040	−1060	+1620	(—)	—	—	—	—

excited state in all cases. For both the stilbenes and tolans the size of the effect varies with the substituent thus: $NO_2 > NMe_2 > OMe > Cl > Me > NMe_2H^+$. The effect therefore depends on the conjugation power of the substituent but not on whether it is an electron-acceptor or -donor. For the electron-donor substituents (OMe, Me, Cl) the effect is considerably greater in the tolan than in the stilbene series, probably because of the superior electron-withdrawing power of the C≡C group than of the C=C group.

The effect of the hetero-groups in the unsubstituted heterocyclic compounds is indicated by the difference between their frequencies and that of stilbene or tolan. These differences are given in the first row of Table 3, and are in the order,* Py < PyO < PyH^+ < $PyOH^+$, which is that expected for increasing perturbation of the aromatic system by the heteroatom.

For the substituted heterocyclic compounds, the substituent will alter the extent to which the hetero-group interacts with the rest of the system, and the hetero-group will alter the extent to which the substituent interacts. It is impossible to separate these two effects. The object of this work was to measure the interaction between the substituents and the hetero-groups, and it is considered that a measure of this is given by subtracting from the observed frequency the quantities expected to result from the substituent, the hetero-group, and the aromatic system,† *i.e.*:

$$\begin{aligned}\nu_{\text{interact.}} &= \nu_{\text{subst. het.}} - (\nu_{\text{subst. benz.}} - \nu_{\text{benz.}}) \\ &\quad - (\nu_{\text{het.}} - \nu_{\text{benz.}}) - \nu_{\text{benz.}} \\ &= \nu_{\text{subst. het.}} + \nu_{\text{benz.}} - \nu_{\text{het.}} - \nu_{\text{subst. benz.}}\end{aligned}$$

The quantities $\nu_{\text{interact.}}$ are listed in Table **3**, cols. 2—5, 7—10.

We shall consider first the dimethylamino-, methoxy-, and methyl compounds. The quantities are all negative, *i.e.*, the interaction lowers the energy of transition to the excited state, which is as expected since these groups are electron-donors. The magnitude depends largely on the group, $NMe_2 > OMe > Me$, *i.e.*, on the electron-donor power of the substituent. It also depends on the intervening group, C=C > C≡C, which agrees with the conclusion from the basicity work that interaction through a double bond is greater than through a triple bond. The variation with the heterocyclic group is uneven and relatively small; this is rather unexpected: it indicates that for each substituent there is an increase of interaction on passing from the benzenoid to the heteroaromatic system, but that there is little variation through the various heterocyclic types.

For the chloro-ethynyl compounds the interaction is small and unfavourable, *i.e.*, the energy required for the transition to the first excited state is raised. This demonstrates that the electron-withdrawing inductive effect of chlorine is dominant. For the chloro-ethylenes, the interaction is less unfavourable, or even (in the case of the *N*-oxides) favourable: this probably indicates that the mesomeric electron-donor nature of chlorine

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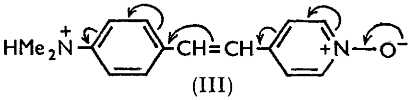
* Here and elsewhere Py indicates pyridine, PyO pyridine 1-oxides; the cationic species are designated similarly.

† This is only true if the whole molecule behaves as one single conjugated system. If the two halves of the molecule were but weakly conjugated with each other, then clearly the frequency *expected* (for no interaction) would be the same as if only the most powerful of the two substituents were present. However, we consider that the spectra of stilbene and tolan themselves show evidence of strong conjugation.

is more important, which is reasonable in view of the increased interaction through the ethylenic linkage.

For the nitro-compounds the result, Ph > Py > PyO > PyH^+ ~ $PyOH^+$, demonstrates the opposing influence of the nitro-group and the heteroatoms, which as expected is stronger for the cationic rings than for the other heterocyclics. It is of interest that this unfavourable interaction is greater for the acetylenes than for the ethylenes, which suggests that it is partly inductive in nature.

The available data for the NMe_2H^+ group indicate an opposing effect for the two cationic rings, but quite a large favourable interaction for the pyridine oxide. This may be due to back-co-ordination of type (III).



(III)

General Conclusions.—Basicity measurements [2] indicated that the interaction between substituent and hetero-group in 4-*p*-substituted styryl- and phenylethynyl-pyridines was small but measurable, and was greater in the former class of compound. The present work shows that the interaction in the first excited state, while qualitatively similar, is much greater than the interaction in the ground state.

Experimental.—Preparational details have been given before.[1,2] The spectra were measured on a Cary Model 14M-50 recording spectrophotometer in the solvents indicated in the footnotes to Table 1.

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