Electronic Interactions in Aromatic Compounds. Direct Electronic Interaction between Aromatic Rings in Conjugated and Non-Conjugated *cis*-Compounds

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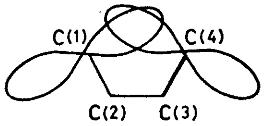
A study of charge transfer equilibria between a series of *cis*- and *trans*-4-styrylpyridines and *cis*- and *trans*-1-(4-X-phenyl)-2-(4-pyridyl)cyclopropanes with iodine has been carried out in CCl_4. Acidity constants for these heteroaromatic compounds were determined. The results obtained for the two types of measurements show that through-space conjugation, due to overlap of the non-parallel π-orbitals of the two aromatic systems, operated in both *cis*-systems.

THE hypothesis that there are factors which influence the yield of products of photocyclization in certain photochemical reactions has prompted research on the correlation of electronic populations of charge overlap and the output of photocyclization products in molecules similar to *cis*-stilbene.[1]

It was previously suggested by Simonetta and Winstein that in the synperiplanar conformation of bibenzyl the orbitals on C(1) and C(4), if properly oriented, could lead to effective overlap.[2] However we could not obtain experimental evidence to support this hypothesis.[3]

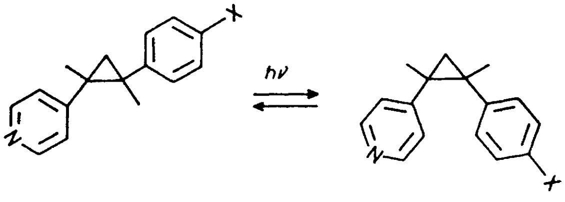


In this study we present experimental evidence for the existence of electronic charge density between the two aromatic rings of molecules similar to *cis*-stilbene. To this end, we selected compound (2) with a cyclopropane which prevents the conjugation.[4] The study was extended to include *cis*- and *trans*-styrylpyridines which have been studied from the photochemical standpoint.[5] In the *trans*-styrylpyridines there should be greater charge delocalization than in the *cis*-derivatives. But in these compounds the overall effect of electronic transmission should be almost equal if there is compensation by direct space conjugation of the π-orbitals at non-parallel axes of the two aromatic rings.

EXPERIMENTAL

Syntheses.—The *cis*-cyclopropane derivatives (2) were obtained by photoisomerization (Gallois low pressure; 1 000 W) of the corresponding *trans*-derivatives (1) prepared according to the Levine and Patrick method,[6] utilized for preparing *trans*-1-phenyl-2-(4-pyridyl)cyclopropane. New products were identified by n.m.r. The n.m.r. spectra of the *trans*-derivatives corresponds to that expected by analogy with similar products synthesized in previous work.[4] The n.m.r. spectra of the *cis*-derivatives show the characteristic chemical shifts (Table 1) of the benzene protons, no longer shielded by the aromatic rings, and the chemical shifts for auto-shielded aromatic protons.[7] The cyclopropanation reaction to obtain the *trans*-derivatives (1) led to a crude mixture of starting material [*trans*-4-(4-X-styryl)pyridine] and the corresponding cyclopropane derivative. From the n.m.r. integration curve it was possible to obtain the yields, (1b) 62.5; (1c) 63; (1d) 66.5; (1e) 72%. The yields we report were not always reproducible, and we believe this is due to the variable quality of the commercial butyl-lithium used.

Working with small quantities, we did not always manage to purify the products by simple distillation as described by Levine and Patrick.[6] Also, the reaction mixture of starting material and the corresponding cyclopropane derivative was shown to be inseparable by any chromatographic technique. In order to eliminate the residual starting material, we irradiated the binary mixtures in n-pentane with a u.v. lamp at high pressure (T.Q. 150, CGM) and then by chromathography [silica gel; ethyl ether–benzene (1 : 1)], we separated the *cis*-4-(4-X-styryl)-pyridines formed from the *trans*-cyclopropane derivatives. The *trans*-1-(4-X-phenyl)-2-(4-pyridyl)cyclopropanes were then distilled, (1b), b.p. 155—156 °C at 0.7 mmHg; (1c), b.p. 122—124 °C at 0.3 mmHg; (1d), b.p. 124—126 °C at 2 mmHg; (1e), b.p. 124—126 °C at 2 mmHg.



(1) (2)

a; X = NO_2
b; X = Cl
c; X = H
d; X = CH_3
e; X = OCH_3

Compound (1a) was obtained by nitration of (1c) and identified by n.m.r. (Table 1) and i.r. spectra, $\lambda_{max.}$ 14.5 and 9sh μm, similar to those of *p*-cyclopropylnitrobenzene. The *ortho*-isomer of (1a) showed absorptions at 15.2, 14.3, and 12.8 μm, as for *o*-cyclopropylnitrobenzene.[8]

The *trans*- and *cis*-styrylpyridines were prepared as described in the literature.[4,6,9]

General Procedure for Synthesis of cis-1-(4-*X-Phenyl-*) 2-(4-*pyridyl*)*cyclopropanes* (2).—*trans*-Cyclopropyl product (100 mg) in n-hexane (400 ml) was irradiated after deaeration with nitrogen by an unfiltered Gallois low pressure mercury lamp, using mainly the 253.7 nm line for 24 h. The *cis*-products were purified by chromatography [Chromasil MGP 800/0, 0.37—0.063 μ; light petroleum–ethyl ether (1 : 1)].

trans-1-(4-*Nitrophenyl*)-2-(4-*pyridyl*)*cyclopropane*.—*trans*-1-Phenyl-2-(4-pyridyl)cyclopropane (2 g, 0.01 mol) was added to a stirred solution of nitric acid (10.6 ml; *d* 14.4) and sulphuric acid (2.4 ml; 98%) at 0 °C. The solution was poured in ice–water and neutralized with Na_2CO_3. The mixture was extracted with $CHCl_3$ and dried (Na_2SO_4). The solvent was removed and the crude product purified by t.l.c. [silica gel; light petroleum–ethyl ether (1 : 1)]. The higher band was identified as the nitro-product (0.45 g, 20%).

TABLE 1

Chemical shifts (δ values) of *trans*- and *cis*-1-(4-X-phenyl)-2-(4-pyridyl)cyclopropanes in $CDCl_3$

	2 H, d, α-py		6 H, m, ArH		3 H, s, CH_3		2 H, t, CH		2 H, t, CH_2		2 H, d, ArH (o-NO_2)	
X	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
H	8.42	8.12	6.95 (7 H)	6.90			2.00	2.52	1.30	1.35		
CH_3	8.45	8.35	6.95	7.21	2.27	2.21	2.01	2.20	1.40	1.42		
OCH_3	8.42	8.22	6.90	6.75	3.75	3.65	2.01	2.41	1.40	1.41		
Cl	8.43	8.15	7.17	6.85			2.15	2.25	1.40	1.35		
p-NO_2	8.45	8.20	7.15 *	7.05			2.31	2.65	1.65	1.82	8.12	7.90
o-NO_2	8.47		7.25 † (5 H)				2.80 (1 H, t) 2.10 (1 H, t)		1.55		7.80 (1 H, dd)	

* Total 4 H, δ 7.22 [2 H, d, ArH(m-$NO)_2$], 7.0 [2 H, d, ArH(β-py)]. † δ 7.8 [1 H, dd, ArH(o-NO_2)].

Measurements.—*Acidity constants*. U.v. absorption spectra were measured in ethanol solution on a Optica CF4 double-beam spectrophotometer. Absorbance measurements for the determination of the acidity constants were carried out in 85 : 15 water–ethanol solution on a Unicam SP 500 single-beam spectrophotometer equipped with a thermostatted cell compartment. The acidity constants were determined spectrophotometrically as described previously.[10] The pH of the buffered solutions (Britton buffers for pH 2—7) were measured on a Sargent–Welch PBX pH meter calibrated at pH 4 and 7. All the measurements were at 298 K.

TABLE 2

Equilibrium constants for the charge transfer complexes between iodine and *cis*- and *trans*-1-(4-X-phenyl)-2-(4-pyridyl)-cyclopropanes and *cis*- and *trans*-4-styrylpyridines in CCl_4 at 293 K, and pK_a values for the donors in water–ethanol (85 : 15) at 293 K

	Cyclopropanes				Styrylpyridines			
	trans		*cis*		*trans*		*cis*	
Substituent X	$K_{c.t.}$/ $dm^3\ mol^{-1}$	pK_a	$K_{c.t.}$/ $dm^3\ mol^{-1}$	pK_a	$K_{c.t.}$/ $dm^3\ mol^{-1}$	pK_a	$K_{c.t.}$/ $dm^3\ mol^{-1}$	pK_a
H	122	4.90	200	5.12	163	5.15	122	4.92
CH_3	125	4.93	238	5.20	209	5.27	175	4.94
OCH_3	109	4.88	300	5.30	248	5.40	212	5.00
Cl	96	4.85	159	4.98	130	5.05	100	4.72
NO_2	92	4.80			95	4.66	53	4.46
$NHCOCH_3$						5.10		4.92

Stability constants. The stability constants $\{K_{c.t.} = [C]/([I_2]_0 - [C])([D]_0 - [C])$, where [C] = complex concentration, $[I_2]_0$ = initial iodine concentration and $[D]_0$ = initial donor concentration$\}$ were measured spectrophotometrically with a Unicam SP 500 single-beam spectrophotometer as previously described.[11] The charge transfer (c.t.) constants are mean values of various experiments at different wavelengths and various iodine and donor concentrations. The donor concentrations were in the range 2—10 × 10^{-3} mol dm^{-3} for *cis*- and *trans*-styrylpyridines; iodine concentrations were in the range 1—2 × 10^{-3} mol dm^{-3}. The equilibrium constants exhibit maximal deviations of 5—6% from the mean values reported in Table 2.

Spectra.—I.r. spectra were taken on a Perkin-Elmer 257 spectrophotometer on films and n.m.r. spectra on a JNM-C-60 HL spectrometer. Chemical shifts are reported as δ values relative to internal tetramethylsilane.

RESULTS AND DISCUSSION

In order to study the electronic effects present in the phenyl(pyridyl)cyclopropanes, we felt it useful to study the influence that substituents on the phenyl ring had on the pyridine nitrogen of the other ring. Determination of the stability constants for the charge complexes between the derivatives under examination and iodine and of the pK_a values for the same derivatives proved to be a useful means for studying their electronic behaviour.

As shown for the pyridine [12,13] and styrylpyridine [11] complexes the iodine–phenyl(pyridyl)cyclopropanes complexes are mainly of the $n \rightarrow \sigma^*$ type, formed by interaction between a non-bonding nitrogen orbital (donor) and an iodine anti-bonding orbital (acceptor).

Table 2 shows the $K_{c.t.}$ and pK_a values for the *cis*- and *trans*-derivatives of the phenyl(pyridyl)cyclopropanes and the corresponding styrylpyridines. The data in Table 2 were correlated, using the Hammett equation, with the substituent constants σ_p and σ_I in order to rationalize and study them in an adequate way. The results of these correlations are reported in Table 3.

We point out that, although our principal interest is the study of the phenyl(pyridyl)cyclopropanes, examination and comparison of data for the styrylpyridines allows us to analyse more completely the entire problem of the transmission of the electronic effects in through-space conjugated π-systems.

Before comparing the data obtained for the two series of compounds [styrylpyridines and phenyl(pyridyl)-cyclopropanes], it is useful to analyse each series separately. Examination of the data for the cyclopropane derivatives has been already studied by us previously,[14] and in this paper we presumed that direct electronic effects are present. Similar considerations can also be applied to the styrylpyridines. From the data in Table 2 one can see how both *trans*- and *cis*-styrylpyridines correlate with σ_P and not with σ_I, which indicates that in both series of derivatives the effects of the substituents are transmitted to the reaction centre principally by conjugation. However, in the *trans*-cyclopropane derivatives the correlation is better with σ_I than with the σ_P, showing the absence of conjugated electronic effects in these derivatives. This result appears obvious for the *trans*-styrylpyridines in which the two aromatic rings, which are in the same plane as a double bond, can interact conjugatively in the classical way. For the *cis*-styrylpyridines, which are not planar; the result must be explained by assuming the presence of direct electronic effects between the two rings. In fact, if the values for the *cis*- and *trans*-derivatives are compared, it can be seen that $\rho_{pK_a}(cis) = \rho_{pK_a}(trans)$, and that $\rho_{K_{c.t.}}(cis) > \rho_{pK_{c.t.}}(trans)$, noting that in both the *cis*- and *trans*-compounds there is a quantitatively equivalent substituent effect on the reaction centre, and in the c.t. complex there is an even greater effect of the substituents in the *cis*- than in the *trans*-series. It is known that the partial loss of conjugation in the *cis*-derivatives, owing to a loss of planarity, should lower the effect of the substituents. The fact that this does not occur signifies that in the *cis*-derivatives direct electronic interaction between the two rings is present, as was previously observed. This fact is also confirmed by the distances observed, from molecular models, between the corresponding $2p$ orbitals in the *cis*-aligned phenyl rings that imply overlap integrals of 0.05—0.15, *i.e.* of appreciable magnitude.*

TABLE 3

Correlation of charge-transfer equilibrium constants and acidity constants of derivatives of Table 1 with substituent constants

Donors	Reaction	Substituent constant	*trans*			*cis*		
			ρ	r [a]	s [b]	ρ	r [a]	s [b]
Cyclopropanes	C.t. complexation	σ_I	−0.19	0.992	0.02	−0.21	0.137	0.07
		σ_p	−0.11	0.780	0.05	−0.52	0.984	0.03
	Protonation	σ_I	−0.16	0.982	0.02	−0.28	0.157	0.08
		σ_p	−0.11	0.910	0.04	−0.61	0.991	0.03
Styrylpyridines	C.t. complexation	σ_I	−0.41	0.737	0.10	−0.57	0.730	0.15
		σ_p	−0.39	0.987	0.04	−0.55	0.989	0.04
	Protonation	σ_I	−0.69	0.735	0.12	−0.63	0.820	0.10
		σ_p	−0.56	0.986	0.04	−0.54	0.985	0.03

[a] Correlation coefficient. [b] Standard deviation.

In the *trans*-styrylpyridines the complexation reaction is less sensitive to the effect of substituents with respect to protonation ($\rho_{K_{c.t.}}$ −0.39, ρ_{pK_a} −0.56). Similar results have been observed in the case of the pyridines ($\rho_{K_{c.t.}}$ 2.34, ρ_{pK_a} 6.01)[15] and can be explained by the fact that the charge transferred in the complexation process is less than that transferred in the protonation process.[12] To this, there should also be added another consideration regarding the effect of the solvent used (CCl_4 in complexation and H_2O–EtOH in protonation), such that in water the effect of the substituents is increased as the ionic and dipolar forms are stabilized by solvation.[16]

However, in the *cis*-styrylpyridines, the effect of the substituents is quantitatively equivalent for the two reactions, complexation and protonation. This result leads us to suppose a type of complexation in which the iodine molecule, given its size, interacts simultaneously with the pyridine nitrogen and with the π-electron system of the two aromatic rings which, because of direct electronic interaction, have a certain degree of electron overlap.

An interesting comparison can be seen from the data reported in Table 3 between the values for the styrylpyridines and those obtained for the corresponding cyclopropane derivatives. The absence of conjugative effects in the *trans*-cyclopropane derivatives makes the reaction centre less sensitive to substituent effects than in the corresponding styrylpyridines. In the *cis*-derivatives, instead, the ρ values are equivalent for the cyclopropane derivatives and for the corresponding styrylpyridines. This again proves the presence in the latter derivatives of a conjugative interaction between the two π-electron systems.

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