Evidence of Electronic Interaction between Classically Non-conjugated Aromatic Systems

By VITTORIO MANCINI, PAOLO PASSINI, and SERGIO SANTINI
(*Dipartimento di Chimica, Università di Perugia,* 06100 *Perugia, Italy*)

Summary The occurrence of non-classic conjugation due to the overlapping of the non-parallel π-orbitals of the two aromatic systems in *cis*-1-phenyl-2-(4-pyridyl)cyclopropanes has been demonstrated by a study of charge-transfer (c.t.) complexes between iodine and a series of *cis*- and *trans*-1-(4-X-phenyl)-2-(4-pyridyl)cyclopropanes and from their acidity constants.

HOMOCONJUGATIVE interactions provide a suitable mechanism for the transmission of electronic effects in classically non-conjugated systems.[1] Here we give evidence for a direct electronic interaction between the two aromatic systems in *cis*-1-phenyl-2-(4-pyridyl)cyclopropane where it is known that the cyclopropane ring does not transmit conjugative effects.[2] We have accordingly prepared a series of *trans*-1-

(4-X-phenyl)-2-(4-pyridyl)cyclopropanes by the Levine and Patrick procedure.[3] The corresponding *cis*-derivatives were obtained from these by u.v. irradiation in n-hexane. The products of this photoisomerization were separated by chromatography and identified by n.m.r. spectroscopy.

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

Substituent	*trans*		*cis*	
X	K_{ct}/mol^{-1} l	pK_a	K_{ct}/mol^{-1} l	pK_a
H	122	4·90	200	5·12
Me	125	4·93	238	5·20
OMe	109	4·88	300	5·30
Cl	96	4·85	159	4·98
NO_2	92	4·80	—	—

In order to show the effects that the X substituents have on the electron-donor ability and the basicity of the pyridine nitrogen, we determined the values of the stability constants for the charge-transfer complexes between the *cis*- and *trans*-isomers of the cyclopropanes (n-donors) and iodine (σ-acceptor) and also the values of the acidity constants for the same donors. The c.t. constants (K_{ct}) and acidity constants were determined spectrophotometrically as described in refs. 4 and 5, respectively, and the values obtained are in Table 1. Results for the correlation of these data, using the Hammett equation, with the substituent constants σ_p[6] and σ_I[7] are in Table 2. The *trans*-derivatives give a satisfactory correlation with σ_I for both reactions. This fact indicates that only the inductive effect of the substituents is operative in the *trans*-derivatives. Furthermore the small ρ values indicate that this effect is of little importance. In contrast the data for the *cis*-derivatives correlate well with the σ_p constants, indicating that the substituents transmit their effect both inductively and conjugatively. Transmission of the effect by the conjugation mechanism must occur by the overlapping of the two π-orbitals, having non-parallel axes, of the two aromatic systems so giving rise to a non-classical conjugation. Comparison of the ρ value obtained for c.t. complexation of the *cis*-derivatives ($-0·52$) with the ρ value obtained under the same conditions for 4-*trans*-styrylpyridines ($-0·38$)[8] shows that the conjugative effect is greater in our case than in a classic conjugation through a double bond. The ρ values for the c.t. complexation and for protonation are almost the same for both the *trans*- and the *cis*-derivatives. This is to be expected when the substrates do not differ in the steric requirements for the attack by a proton and interaction with the iodine molecule. The analogy between protonation and complexation processes is also confirmed by a good linear relationship of log K_{ct} with pK_a for the two series of derivatives ($r_{trans} = 0·946$, $r_{cis} = 0·996$).

Table 2. Correlation of charge-transfer equilibrium constants and acidity constants with substituent constants.

Reaction	Substituent constants	*trans*			*cis*		
		ρ	r^a	s^b	ρ	r^a	s^b
C.t. complexation	σ_I	$-0·19$	0·992	0·02	$-0·21$	0·132	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

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

We thank the C.N.R. (Rome) for support.

(*Received*, 21*st September* 1977; *Com.* 988.)

[1] V. Mancini, G. Marino, and L. Giachetti, *Gazzetta*, 1974, **104**, 549 and references therein.
[2] V. Mancini, G. Morelli, and L. Standoli, *Gazzetta*, 1977, **107**, 47.
[3] R. Levine and G. R. Patrick, *J. Org. Chem.*, 1973, **38**, 3942.
[4] G. G. Aloisi, G. Cauzzo, G. Giacometti, and U. Mazzucato, *Trans. Faraday Soc.*, 1965, **61**, 1406.
[5] G. Cauzzo, G. Galiazzo, U. Mazzucato, and A. Mongiat, *Tetrahedron*, 1966, **22**, 589.
[6] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.
[7] P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1968, **6**, 147
[8] U. Mazzucato, G. G. Aloisi, and G. Cauzzo, *Trans. Faraday Soc.*, 1966, **62**, 2685.