# UPS Spectra of Cis and Trans 1-Phenyl-2-(4-Pyridyl) Cyclopropanes. A Comparison with Charge Transfer and Protonation Data

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The low ionization energy region of the USP spectra of *cis*- and *trans*-1-(4-X-phenyl)-2-(4pyridyl) cyclopropanes is assigned by analogy with those of simple related molecules. Corresponding IE values of *cis* and *trans* derivatives are equal within the limits of experimental error. This finding indicates, at variance with solution results previously obtained, that in the gas phase there is no sizeable through-space interaction between the MO's of the two *cis*-aryl groups. A possible explanation of the different conformations of the *cis* derivatives in the two phases is proposed.

The transmission of electronic effects in p-substituted *trans*-1-phenyl-2-(4-pyridyl) cyclopropanes (I) has been shown to be small by means of a kinetic approach *via* methoxydechlorination [1], determination of the charge-transfer (CT) complex constants with iodine, and acidity constants [2]. A comparison of the $\varrho$ values (both $-0.11$) obtained for CT complexation and protonation constants when plotted against the $\sigma_p$ values indicated that the conjugative effect is smaller than in *trans*-4-styrylpyridines (III) ($\varrho = -0.38$) [3], (s. Fig. A).

On the other hand, CT and protonation studies showed that in p-substituted *cis*-1-phenyl-2-(4-pyridyl) cyclopropanes (II) the conjugative effect ($\varrho_{CT} = -0.52$, $\varrho_{pKa} = -0.61$) is greater than in III [2]. This finding has been ascribed to the occurrence of direct overlap between the $\pi$ orbitals of the two aromatic rings.

As an extension of the above studies, we have analyzed I and II by means of ultraviolet photoelectron spectroscopy (UPS) in the gas phase, this technique being a sensitive tool for detecting electronic interactions.

Table 1 presents the ionization energy (IE) values below ~ 12 eV while Fig. 1 shows the UPS spectra obtained for some of the compounds studied. On the basis of the assignments of the spectra of simple related molecules we expect that the following ionizations contribute to this portion of the spectra: the outer $\pi_S$ orbitals of the aromatic rings, the outer orbitals of the cyclopropane ring with which the $\pi_S$ orbitals interact, and the almost unperturbed $\pi_A$ orbitals of the aryl groups and the nitrogen lone pair ($n_N$).

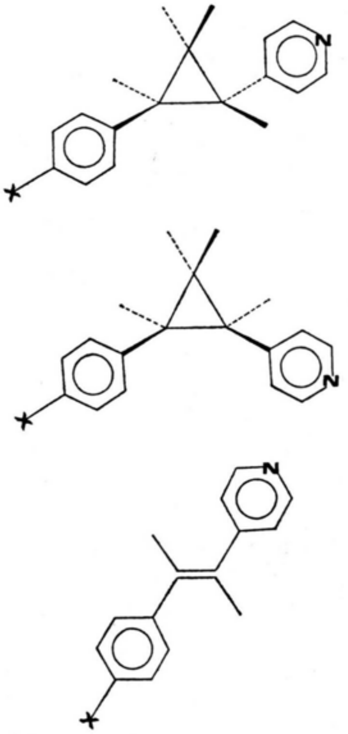

Fig. A.

Table 1. I.E. values (eV) * of I and II.

| X | IE$_1$ | IE$_2$ | IE$_3$ | IE$_4$ | IE$_1$ | IE$_2$ | IE$_3$ | IE$_4$ |
|---|---|---|---|---|---|---|---|---|
| H | 8.69 | $9.3_5$ | 10.8 | 11.5 | 8.75 | $9.3_5$ | 10.6 | 11.5 |
| p-CH$_3$ | 8.36 | $9.3_5$ | 10.5 | 11.4 | 8.44 | $9.3_5$ | 10.5 | 11.5 |
| p-OCH$_3$ | 8.13 | $9.3_5$ | 10.5 | 11.4 | 8.08 | $9.3_0$ | 10.6 | 11.5 |
| p-NO$_2$ | $9.2_5$ | $9.8_0$ | 11.1 | 11.8 | $9.3_5$ | $9.7_0$ | 11.0 | 11.7 |

* The IE data were obtained with a Perkin Elmer PS 18 photoelectron sprectrometer. The accuracy is estimated to be ± 0.05 or 0.1 eV according to the number of decimal digits reported. The samples were synthesized as previously reported [1, 2].

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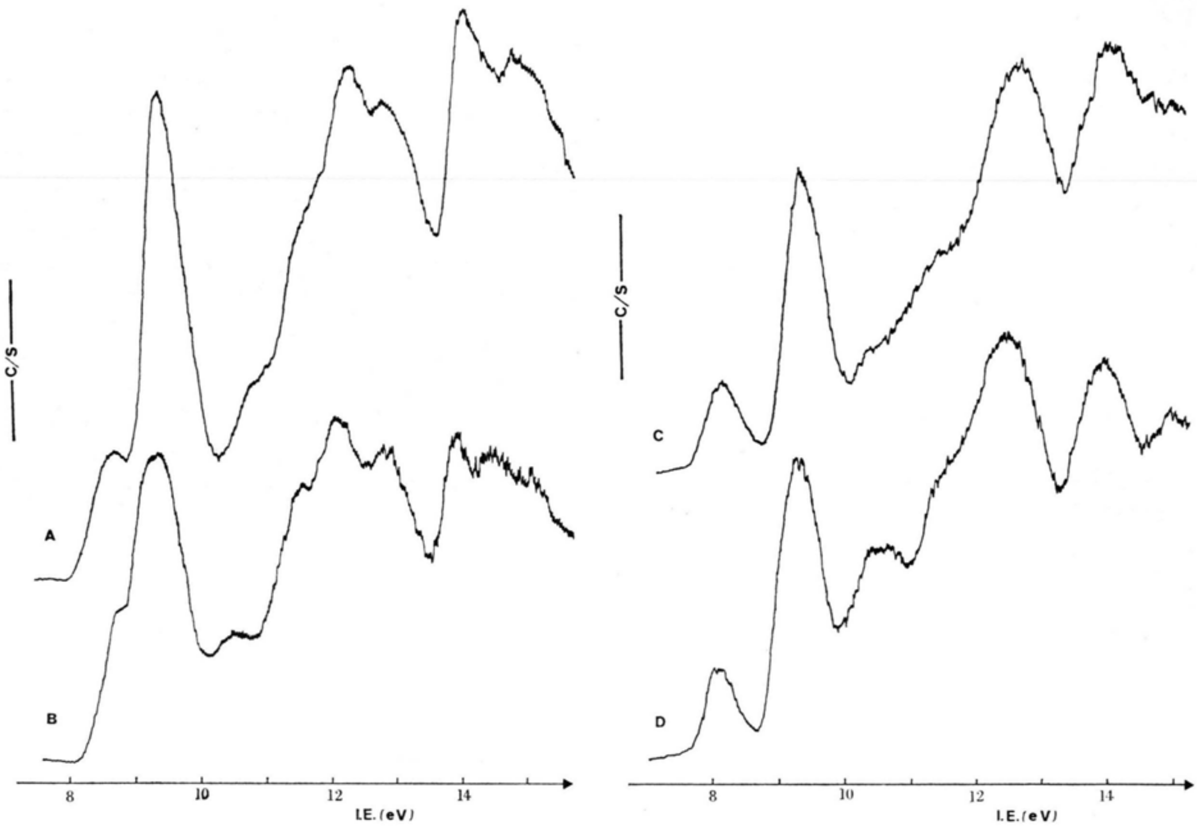

Fig. 1. He(I) photoelectron spectra of I ($X = H$:A, $X = OCH_3$:C) and II ($X = H$:B, $X = OCH_3$:D).

The number of the bands, however, is lower than that of the MO's. On energetic grounds, the first band is related to a MO mainly benzene $\pi_S$ in character, while to the second one contribute ionizations from four MO's whose prevailing character is benzene $\pi_A$, pyridine $\pi_A$, $n_N$ and pyridine $\pi_S$. The latter should contribute to the high ionization energy side of the band, considering the fact that the corresponding MO in 4-styrylpyridine gives rise to a band at 10.03 eV [4].

By analogy with the assignment of the cyclopropylbenzene spectrum [5], $IE_3$ and $IE_4$ are related to the two outermost orbitals of cyclopropane (for the nitro-derivatives, ionization from the nitro group orbitals occurs in the same energy region).

A comparison of the $IE_1$ values of the present compounds and p-X-cyclopropylbenzenes (8.66 eV and 8.05 eV [5] for $X = H$ and $OCH_3$, respectively) shows that the introduction of the pyridine ring does not destabilize the HOMO. This finding, however, does not imply that there is no transmission of conjugation through the cyclopropyl ring. In fact, on going from styrene ($IE_1 = 8.48$ eV [6]) to *trans*-4-styrylpyridine ($IE_1 = 8.34$ eV [6]), the observed destabilization is only 0.14 eV. Therefore, no sizeable variation of the $IE_1$ values for the cyclopropyl derivatives is to be expected if the conjugating ability of the cyclopropane ring is lower than that of a double bond as suggested [2, 7]. The substituent effect on the HOMO energy confirms this conclusion as well as the prevailing benzene $\pi_S$ character of the HOMO. In fact, by plotting the $IE_1$ values of I and II against those of the corresponding benzenes (9.24 [8], 8.78 [9], 8.42 [9] and 9.99 [10] for $X = H$, $CH_3$, $OCH_3$ and $NO_2$, respectively), a good straight line is obtained. In addition, the slope of the correlation line is i) lower than unity ($\sim 0.7$) indicating that the substituent effect in 1-phenyl-2-(4-pyridyl)cyclopropane spreads out over a larger system, but ii) higher than that ($\sim 0.5$) previously obtained for the plot of 3-styrylpyridines para-substituted in the benzene ring vs. benzenes, in agreement with a smaller delocalization of the HOMO in the present compounds.

The large difference found in solution for the $pK_a$ and $K_{CT}$ values between I and II has been interpreted by invoking through-space interaction in the latter compounds [2].

The occurrence of this interaction in the gas phase is expected to destabilize the out-of-phase combination of the two aromatic $\pi_S$ orbitals (HOMO) and to stabilize the corresponding in-phase combination (mainly pyridine $\pi_S$). The latter effect would lead to the appearance of a shoulder or a new peak on the high ionization energy side of the second band. However, corresponding IE values of *cis* and *trans* derivatives are equal within the limits of experimental error (see Table 1). Moreover, the second band in the spectra of the *cis* compounds does not show any shoulder on the high ionization energy side (see Figure 1).

The UPS data indicate, therefore, that in the gas phase there is no sizeable through-space interaction between the MO's of the two *cis*-aryl groups.

If the conformation involving through-space interaction were the most stable for the neutral *cis* compounds, it should have been found also in the gas phase [11]. A possible explanation of the different conformations in the two phases could reside in the peculiar processes occurring in solution. Here, the complexation produces a positive charge on the nitrogen atom (and, therefore, lowers the energy of the occupied and empty orbitals of the pyridine ring). The delocalization of this charge over the whole molecule is better achieved in a conformation allowing through-space interaction between the two aryl groups. Such a conformational change is likely to occur. In fact, theoretical calculations performed on phenylcyclopropane have shown that the energy barrier to rotation about the phenyl-three-membered ring bond is small (11.7 kJ mol$^{-1}$) [12] and that overlap between the suitable orbitals of cyclopropane with the adjacent system may still occur when the angle between the planes of the two rings is ca. 60° (the interaction is at a maximum at $\varnothing = 0°$, the bisected configuration [13]). This could explain the presence in solution of such a conformation.

Conformational variations due to a strong electron demand have been found in other cases, e.g. diphenylsulphide [14] and *p*-nitro-diphenylsulphide [15].

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