Bridge effect in charge transfer absorption bands of *para*-substituted β -nitrostyrenes

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Abstract. Charge transfer electronic transitions in a series of *para*-substituted β -nitro-styrenes are analyzed in order to characterize the π -conduction channel between the electron-donor substituents and the NO₂ electron-acceptor group, particularly the bridge effect of the olefinic molecular structure.

Absorption bands assignment of the $\pi \rightarrow \pi^*$ electronic transitions in the near ultraviolet spectral region is carried out from an experimental and theoretical point of view. The photo-induced charge transfer spectral bands of these aromatic compounds follow the same pattern as nitrobenzene, benzaldehyde and acetophenone and the electronic transition takes place in the $\pi \rightarrow \pi^*(^1L_a)$ excited state.

Our present study based on ZINDO/S-CIS M.O. calculations permits us to analyse the role of the NO₂ electron-acceptor group, and the ethylenic group, where this last structure merges as a second electron-acceptor group. The calculated olefinic bridge molecular resistivities (ρ_o) of these β -nitrostyrenes range from 2.1 to 2.5 ($\text{\AA}/\text{quantum}$).

Keywords: Nitrostyrenes, charge transfer absorption bands, ZINDO/S-CIS M.O. calculations, molecular wires, polyene wires

1. Introduction

Recently we have started a program of research on resistivities of *molecular wires* of D–Ph–[CH=CH]_n–A type, where D = electron-donor, A = electron-acceptor and Ph = aryl group [1]. Our main interest is based on the behavior of the π -conduction channel when a photo induced charge transfer (PICT) process occurs in excited state, i.e., the *bridge effect* [1].

In the molecular electronic field, these new molecular devices, *molecular wires* as well as *molecular photodiodes*, have been defined as structurally organized and functionally integrated chemical systems built into supramolecular architectures [2]. The olefinic bridge as a particular component of *molecular wires* is analyzed in the present work.

During the last time we have been studying the aromatic carbonyl compounds as model systems of a photoinduced charge transfer process [3–5], where the aromatic group is linked to the electron-acceptor group through a *polyene molecular wire*. Now, we report in the same molecular series a stronger electron-acceptor group than the carbonyl group such as the nitro group. Thus, by means of UV-spectral absorption data and semiempirical M.O. calculations, we have characterized the π -conduction channel in excited state and the polyene bridge role after the PICT process as function of the electron-donor group strength in the *para*-substituted β -nitrostyrene molecular series (see Fig. 1).

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Fig. 1. Molecular structure of *para*-substituted β -nitrostyrenes.

2. Materials and methods

Para-substituted β -nitrostyrenes were synthesized by means of a standard condensation using *para*-substituted benzaldehydes, nitromethane and butylamine as reactants [6]. These compounds were sublimated before use, and fresh cyclohexane and ethanol solutions were prepared in the concentration range 0.01–0.1 mM. Benzaldehydes were obtained from Aldrich Chemical Co. and solvents of spectroscopic grade from Merck Chemical Co. The absorption spectra were recorded with a Lambda 11 (Perkin Elmer) spectrophotometer operating at room temperature.

By means of a HyperChem software package [7] molecular orbital calculations in the AM1 approach [8] were used to obtain the lowest energy molecular geometries. Electronic transitions energies and molecular orbital analysis of the ground and excited states were obtained by means of standardized ZINDO/S-CIS calculations [9].¹ The computational work was done on a PC network station in our Laboratory and on the RICS 6000 IBM-station at the DIC Center of the University of Chile.

3. Results and discussion

Previously, we have developed a spectral assignment of the charge transfer electronic absorption bands in the molecular series under study. According to Platt's model [10], styrene presents two $^1(\pi \rightarrow \pi^*)$ electronic transitions in the near UV spectral region: the $^1A \rightarrow ^1L_b$ and $^1A \rightarrow ^1L_a$ transitions. The first band of styrene (1L_b) is best considered as arising from a local excitation within the benzene ring, while the second band (1L_a) involves the aryl and olefinic groups, and this band presents the highest absorption intensity [11]. Based on this band assignment of styrene spectrum we have analyzed the *para*-substituted β -nitrostyrenes spectra, in order to compare their different $\pi \rightarrow \pi^*$ spectral characteristics (Figs 2 and 3). All these aromatic systems under study, present the same spectral pattern characterized by a broad intense band corresponding to the $^1A \rightarrow ^1L_a$ transition, where this band is shifted to the red due to the effect of the electron-donor groups linked to the aromatic

¹The M.O. calculations have been developed under standard parametrization, taking into account the first 110 monoexcited configurations in the CI procedure.

Fig. 2. Electronic absorption spectra of β -nitrostyrene (A), *para*-chloro- β -nitrostyrene (B), *para*-methyl- β -nitrostyrene (C), *para*-hydroxy- β -nitrostyrene (D), and *para*-dimethylamino- β -nitrostyrene (E) in solution of cyclohexane at room temperature.

ring. Moreover, it is well known that the ${}^1A \rightarrow {}^1L_b$ transition is not significantly affected by the same substituents at the *para*-position [3,5,10,12], and therefore, both ${}^1(\pi \rightarrow \pi^*)$ electronic transitions are immersed in the same spectral region.

On the other hand, the same broad peak which for *para*-dimethylamino- β -nitrostyrene vanishes upon protonation with HCl (see Fig. 3), is assigned as the photoinduced intramolecular charge-transfer transition ${}^1A \rightarrow {}^1L_a$, involving the n lone electron pair on the amine and terminating in an empty π^* orbital on the nitro electron-acceptor group. This electronic transition, present in either the nitrobenzene and nitrostyrene precursors, is strongly affected by the donor groups linked to the aromatic ring, which enable to determine the PICT channel in the $\pi^*({}^1L_a)$ excited state. The energy and intensity of this charge-transfer band is analogous to the PICT band reported for *para*-dimethylaminobenzaldehyde [3], *para*-dimethylaminobenzalacetone [4], *para*-dimethylaminobenzonitrile and *para*-nitroaniline [13].

ZINDO/S-CIS molecular orbital calculations reported in this paper are fully congruent with the experimental spectral assignment. In Tables 1 and 2 we present the different molecular parameters involved in the ${}^1A \rightarrow {}^1L_b$ and ${}^1A \rightarrow {}^1L_a$ electronic transitions of *para*-substituted β -nitrostyrenes. Both $\pi \rightarrow \pi^*$ molecular electronic transitions are occurring within the same energy range (3.45–4.50 eV), where, according to the electron-donor group nature, the ${}^1A \rightarrow {}^1L_a$ electronic transition is systematically shifted to low energy. Furthermore, the ${}^1A \rightarrow {}^1L_a$ transition dipole moments are mainly polarized in the long molecular axis (P_x), while the ${}^1A \rightarrow {}^1L_b$ transition dipole moments are independent of the nature of the donor-substituent, being mainly polarized in the short molecular axis (P_y), according to Platt's model [10].

In addition, from these M.O. calculations we have found the 1L_a dipolar moments to be systematically higher than the ground or 1L_b excited states, in agreement with the nature of this PICT electronic state and solvent spectral shifts [14]. However, in spite of the significant enlargement of the 1L_a dipole moment as function of the electron-donor group, the charge transferred to the nitro electron-acceptor

Fig. 3. Electronic absorption spectra of *para*-dimethylamino- β -nitrostyrene (A) in solution of ethanol and *para*-dimethylammonium- β -nitrostyrene cation (B) in acid solution of ethanol, at room temperature.

Table 1
ZINDO/S-CIS $\pi-\pi^*$ ($^1A \rightarrow ^1L_b$) electronic transitions of *para*-substituted- β -nitrostyrenes (D-NS)

Compound	Transition energy (eV)	Oscillator strength (f) $f \times 100$	P_x	P_y	$\mu(D)$
β NS	4.353	0.54	0.002	0.998	10.0
Cl- β NS	4.331	0.25	0.002	0.998	6.0
Me- β NS	4.312	0.01	0.022	0.978	9.8
HO- β NS	4.230	0.01	0.564	0.434	10.3
Me ₂ N- β NS	4.120	1.31	0.040	0.960	10.7

P: Polarization axis along the transition dipole moment.

μ : Dipolar moments in excited state.

group does not follow the same trend. In Table 3 we present the ZINDO/S-CIS net charge density distribution in the main fragments of the molecular array after the PICT $^1A \rightarrow ^1L_a$ electronic transition. From these results the net charge change on the nitro group due to the substituents decreases slightly along to the *para*-substituted molecular series.

In Fig. 4 we present the net charge change of the nitro group and the ethylenic carbon centers in the $^1A \rightarrow ^1L_a$ excited state, as function of the spectral shift of the same $^1A \rightarrow ^1L_a$ electronic transition. From this figure we can observe the amazing behavior of the olefinic bridge carbon centers, which present an electron-acceptor trend respect to the migration charge coming-out from the aryl and the electron-donor groups.

Recently we have shown that the π -conduction channel presents its own resistance to the photoconduction charge migration (*the bridge effect*) [1], and we have defined a theoretical concept of *molecular resistance by quantum absorption* [1] ($\rho_a(l)$) as:

$$\rho_a(l) = 1/Q_r(l),$$

Fig. 4. ($^1A \rightarrow ^1L_a$) net charge density (Q) distribution in the main electron-acceptor fragments of *para*-substituted β -nitrostyrenes by means of ZINDO/S-CIS calculations as function of the ($^1A \rightarrow ^1L_a$) spectral shift energy relative to nitrostyrene.

Table 2
ZINDO/S-CIS $\pi-\pi^*$ ($^1A \rightarrow ^1L_a$) electronic transitions of *para*-substituted- β -nitrostyrenes (D-NS)

Compound	Transition energy (eV)	Oscillator strength (f) $f \times 100$	P_x	P_y	$\mu(D)$
β NS	3.961	70.93	0.925	0.075	17.9
Cl- β NS	3.992	74.21	0.982	0.018	14.8
Me- β NS	3.827	0.01	0.980	0.020	19.3
HO- β NS	3.547	0.01	0.889	0.111	18.3
Me ₂ N- β NS	3.463	1.31	0.792	0.208	22.7

P: Polarization axis along the transition dipole moment.

μ : Dipolar moments in excited state.

Table 3

($^1A \rightarrow ^1L_a$) net charge density distribution in the main fragments of the nitrobenzene (NB) and *para*-substituted β -nitrostyrenes (β NS) by means of ZINDO/S-CIS calculations

Compound	Q_{NO_2}	$Q_{C=C}$	Q_D	Q_{Ph}	Q_r
NB	-0.732	—	—	0.732	1.000
β NS	-0.562	0.174	0.000	0.387	0.768
Cl- β NS	-0.540	0.164	0.014	0.363	0.738
Me- β NS	-0.542	0.121	0.017	0.404	0.740
HO- β NS	-0.519	0.087	0.035	0.399	0.709
Me ₂ N- β NS	-0.469	-0.006	0.149	0.326	0.641

where Q_r is the net charge transferred to the nitro-acceptor group (Q_{NO_2}) in each molecular species relative to nitrobenzene (see Table 3). From this table we noted that the Q_{NO_2} of nitrobenzene is 30% bigger than β -nitrostyrene.

Based on the metal wires behavior, we have carried out the molecular resistivity (ρ_o) calculation of 2.1 ($\text{\AA}/\text{quantum}$) according to

$$\rho_a(l) = \{\rho_o/S\}l$$

where we have assumed a typical mean cross section (S) of $4.5 \text{ \AA}^2$ for these π -orbitals centered on the alkene carbons [1] and a (C=C–N) molecular length (l) of $2.81 \text{ (\AA)}$.

The olefinic bridge molecular resistivities due to the substituent effect range from 2.1 to 2.5 ($\text{\AA}/\text{quantum}$), a similar magnitude order found in benzalketones [15].

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