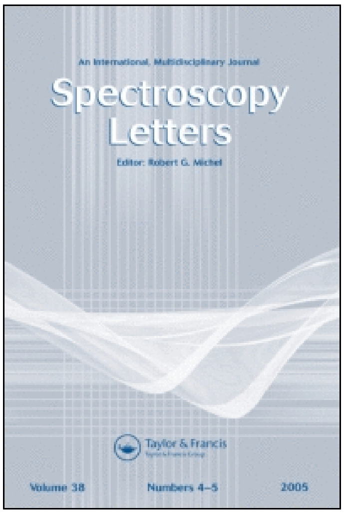

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^{13}C-Nmr Spectroscopy of β-Nitrostyrenes. II. Mono-, Bi- and Tri-Methoxy Phenyl-Substitutions and Long Distance Electronic Effects

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^{13}C-NMR SPECTROSCOPY OF β-NITROSTYRENES. II. MONO-, BI- AND TRI-METHOXY PHENYL-SUBSTITUTIONS AND LONG DISTANCE ELECTRONIC EFFECTS

Key words: poly-methoxy-β-nitrostyrenes, ^{13}C-NMR spectral assignments,
AM1 molecular orbital calculations.

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ABSTRACT

By means of ^{13}C-NMR spectroscopy and AM1 molecular orbital calculations of *mono-, bi- and tri-*methoxy-β-nitrostyrenes at the *meta* and *para* positions, we have characterized a long distance electronic charge transfer pattern on the ethylenic bridge (CH=CH) and on the aromatic ring (Ph) carbon centers, determined by the electron-donor nature of the methoxy-substituent groups.

After a complete spectral assignment of the ^{13}C-NMR signals, we have found a functional dependence of the chemical shifts on the C_1 and C_β centers respect to the C_4 and C_3 methoxy subtitution sites on the aromatic ring, while in the same molecular series C_α-chemical shifts are practically constants. On the other hand, the ^{13}C-NMR chemical shifts of the C_3 and C_4 centers plus the analysis of the AM1 electronic charge density have permitted us determine the long distance charge transfer effect induced by

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the C_4 methoxy substitutions as well as the attenuation of this effect due to the C_3 methoxy substitutions.

INTRODUCTION

Recently, we have reported the *para-β-nitrostyrene* systems (D-Ph-CH=CH-NO_2) as a particular molecular model of long distance electronic charge transfer induced by the *para*-substituent electron-donor (D) [1], in a similar behavior to *para*-substituted benzylideneacetones, reported in this journal [2]. These intramolecular electronic charge transfer (IECT) studies of polar aromatic compounds have been part of our program of research during the last years [1-6].

From our research work, *β-nitrostyrene* systems, substituted by mono- bi- and tri-methoxy groups, merge as an interesting case of long distance electronic charge transfer effect on the ethylenic bridge, due to the charge density perturbation on the aromatic carbon centers. Therefore, in the present work, we have developed an analytical study of the carbon charge densities by means of ^{13}C-NMR spectroscopy and AM1 semiempirical molecular orbital calculations [7].

Mainly, we have analyzed the effect of the mono-, bi- and tri-substitutions at the *meta* and *para* positions on the ^{13}C-NMR chemical shifts and the AM1 electronic charge densities of the carbon atoms distributed through the π-molecular structure between the methoxy-substitutents and the NO_2 acceptor group. However, we have not included the *orto*-substituents due to the steric effect introduced by the methoxy groups on the hydrogenic centers of the ethylenic bridge.

On the other hand, this kind of electronic behavior has generally been explained in terms of a qualitative *resonance effect*, but in this work, we have found a functional dependence between the carbon centers involved in the long distance electronic charge transfer process. Therefore, simple and direct experimental and theoretical evidences permit us to establish a quantitative parametrization of this long distance electronic effect.

EXPERIMENTAL SECTION

Materials

β-nitrostyrene (NE), *3*-methoxy-*β-nitrostyrene* (3-OMeNE), *4*-methoxy-*β*-

nitrostyrene (4-OMeNE), 3,4-dimethoxy-*β-nitrostyrene* (3,4-OMeNE), *3,5*-dimethoxy-*β-nitrostyrene* (3,5-OMeNE), *3,4,5*-trimethoxy-*β-nitrostyrene* (3,4,5-OMeNE) were synthesized by means of a standard condensation using methoxy-substituted benzaldehydes, nitromethane, and butylamine as reactants [8]. These compounds were recrystallized before use and fresh solutions were prepared in each spectroscopic measurement. Benzaldehydes were obtained from Aldrich Chemical Co. and solvents of spectroscopic grade were obtained from Merck.

Methods

Nuclear magnetic resonance spectra were recorded on a Bruker AC-P 200 spectrometer at 50.3 MHz for ^{13}C, using a QNP probe. The pulse length and time delay were 2.0 μs and 2.62 s, respectively. The spectral band width was 25 kHz and 250 transients were accumulated in 65 kB files, giving a resolution of 0.381 Hz/point. Apodization of the FID with an exponential multiplication (EM) was used with a line broadening of 1.0 Hz. The concentration range of the samples dissolved in 0.5 mL of deuterated acetone was 15 to 25 mg.

The molecular orbital calculations used the AM1 semiempirical approach [7] on a PC network station in our Laboratory. The AM1 calculations were performed with complete molecular geometry relaxation. Good agreement between experimental and AM1 bond lengths and bond angles were found for the set of molecular species under study [9].

RESULTS AND DISCUSSION

In Figure 1 we present a ^{13}C-NMR spectral assignment of these *β-nitrostyrenes* based on a comparative analysis of previous spectral data of *para*-substituted *β-nitrostyrenes* [1], *para*-substituted benzylideneacetones [2], and poly-methoxy-benzaldehydes [10], since these compounds present a similar spectral pattern to our

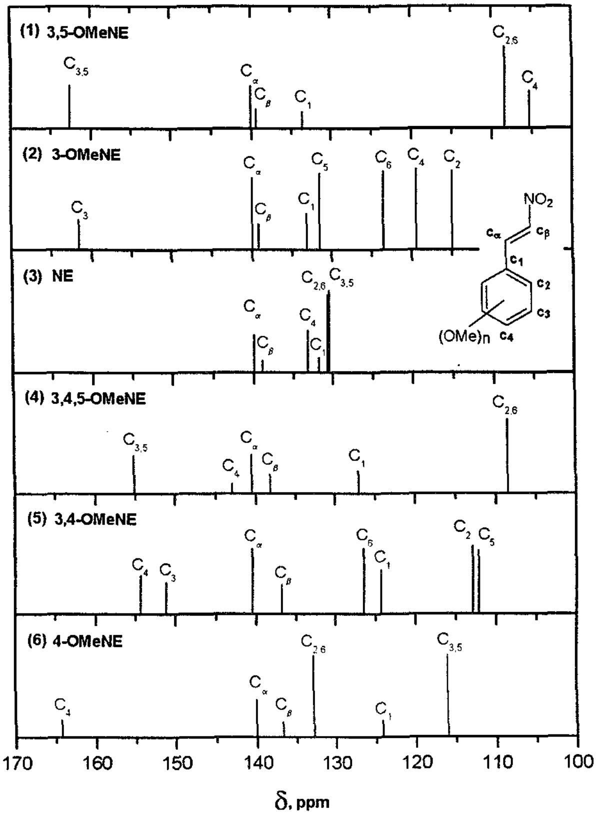

FIG. 1. ^{13}C-NMR spectral signal assignments of the methoxy-substituted nitrostyrenes in deuterated acetone at room temperature.

molecular series. In Table 1 we present the ^{13}C-NMR spectral chemical shifts of all compounds under study.

From these results, we can observe how the different methoxy substituents induce a characteristic ^{13}C-NMR spectral chemical shift range on the carbon centers given by: 59 ppm in C_4, 50 ppm in C_3 and C_5, 24 ppm in C_2 and C_6, 10 ppm in C_1, 3 ppm in C_β, and lower than 1 ppm in C_α. But, the observed substituent effect, in terms of the long distance electronic charge transfer distribution, induce different behaviors on the

TABLE 1

^{13}C-NMR Spectral band assignment of the methoxy substituted nitrostyrenes (ppm).

	Compounds	C_α	C_β	C_1	C_2	C_3	C_4	C_5	C_6
1	3,5-OMeNE	140.2	139.5	133.6	108.4	162.7	105.4	162.7	108.4
2	3-OMeNE	140.0	139.2	133.1	115.0	161.6	119.5	131.5	123.5
3	NE	140.0	139.9	131.8	130.7	130.5	133.2	130.5	130.7
4	3,4,5-OMeNE	140.5	138.2	127.0	108.5	155.1	143.0	155.1	108.5
5	3,4-OMeNE	140.5	136.9	124.3	112.9	151.2	154.4	112.2	126.5
6	4-OMeNE	140.1	136.8	124.1	132.8	116.0	164.3	116.0	132.8

before mentioned carbon centers, particularly on the C_1 and C_β centers, according to our reported data (Table 1).

Therefore, in order to characterize the nature of the spectral chemical shifts due to the C_4 and C_3 carbon centers, the net charge density on these carbons have been calculated in the AM1 approach, as can be seen in Figure 2. From this figure we can observe how the methoxy substitution effect determines the charge changes on the C_4 and C_3 centers. In addition, we have included the C_5 center due to follow the same *meta*-substitution effect as C3. In both cases, the ^{13}C-NMR chemical shifts (δ) show a linear dependence on the AM1 net charges (q_{AM1}) according to [11]:

$$\delta = a\, q_{AM1} + \delta^o,$$

where we have found the following (a, δ^o) pairs for C_4 and C_3 & C_5, respectively:

(164.3 ± 16.1, 149.0 ±2.3) and (146.4 ±11.9, 145.7 ±1.6).

However, in spite of the substituent effect on the *meta* and *para* positions, a similar slope exists for the spectral chemical shift range (105 to 165 ppm). The electronic charge transfer induced by these two carbons on the remainder carbon centers, particularly on the C_1 and C_β carbons, does not follow the same trend. Thus, it is enough to compare the chemical shifts of the C_1 and C_β observed in 4-OMeNE and 3-OMeNE (see Table 1). In both cases, the *para*-methoxy substitution induces an

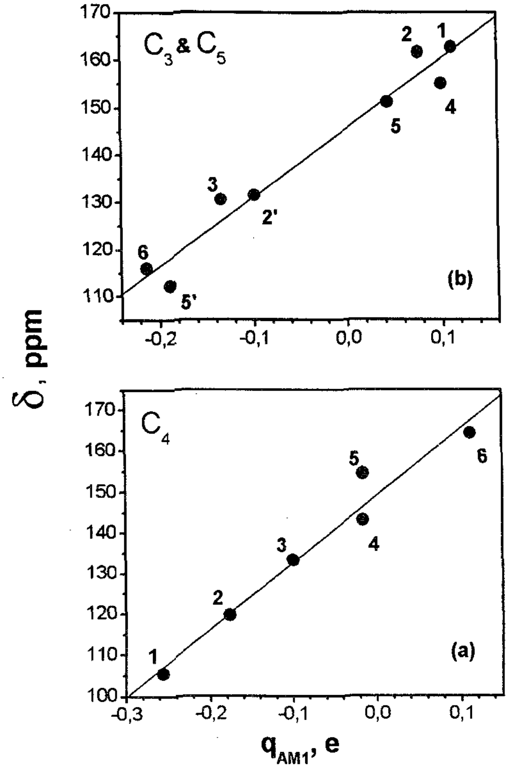

FIG. 2. Plots of the chemical shifts (δ) versus the calculated AM1 net charge (q_{AM1}) for C_4 (a) and C_3 & C_5 (b) in every methoxy-substituted nitrostyrenes according to Table 1, 2' and 5' correspond to the C_5 carbon centers.

increment of charge at a long distance, while the *meta*-methoxy substitution induces a diminution of charge on the same centers. In a percent (%) relative way, we can determine an enlargement of the net charge between 85% and 90% due to the C_4 center while, contrarily to this case, C_3 induces a charge diminution between 15% and 10% on the same C_1 and C_α centers.

In order to find a functional dependence of the electronic charge transfer effect between C_4, C_1 and C_β centers, we have analyzed two different behaviors in Figure 3. This figure, part (a), illustrates the functional dependence observed between C_4 and C_1,

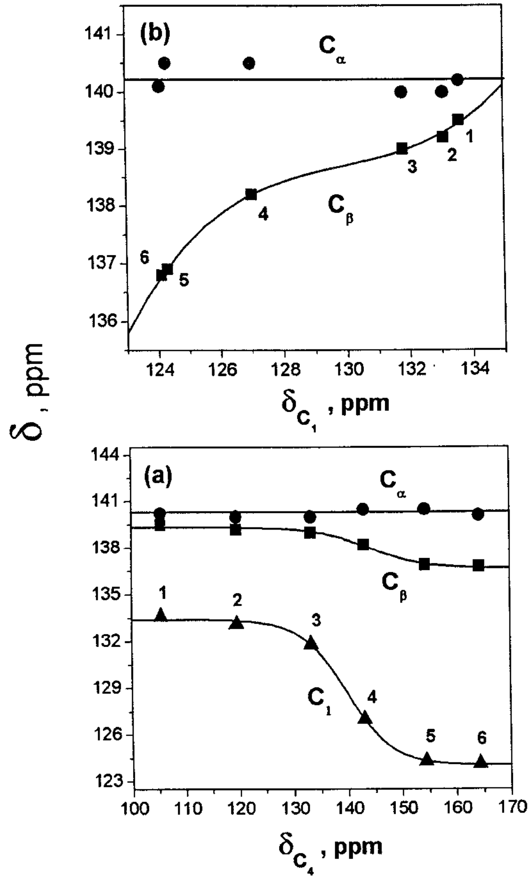

FIG. 3. Functional dependence of the C_1, C_β and C_α spectral shifts respect to C_4 center in the methoxy-substituted nitrostyrene series.

C_4 and C_β, and C_4 and C_α. While C_1 and C_β present a sigmoidal functional dependence of C_4, C_α, following a constant behavior with respect to C_4, where C_α is practically invariant to the ring-substitutions (see Table 2).

It is interesting to observe how the net charge density of the C_4 aromatic carbon center, induced by the methoxy substituents, follows an inverse behavior with respect to the C_1 and C_β centers, i.e., in the C_4 carbon experiment, a diminution of the net charge

TABLE 2

Functional dependence [a] of the C_1 and C_β spectral shifts with respect to the C_4 center in the methoxy-substituted nitrostyrene series.

δC_i	A_1	A_2	δ_0	δx
δC_1	133.4 ±0.2	124.1±0.2	139.8±0.5	4.201±0.397
δC_β	139.4 ±0.1	136.7±0.2	143.9±1.7	5.045±1.660

[a] $\delta C_4 = (A_1 - A_2) / \{1 + \exp(\delta C_i - \delta_0 / \delta x)\} + A_2$

simultaneously induced an incremental net charge on C_1. A similar behavior can be observed between C_4 and C_β (see Figure 3(a)). In Figure 3(b) we observe a direct functional dependence between C_1 and C_β, compared to the invariant behavior of C_α.

The observed functional dependence between carbons centers of both plots in Figure 3(a) and (b), permit us to corroborate the expected qualitative trend, where the electronic charge distribution through these carbon centers determine a typical resonance pattern given by: $D^{\delta+}$-C_4-C_3-C_2-C_1-C_α-C_β-$NO_2^{\delta-}$. However, an attenuation of the charge transfer effect is experimented along to the π-electronic structure according to the nature of the molecular resistance observed in the electronic conduction channel [6].

Therefore, this aromatic series merges as a good example of the long distance electronic charge transfer process, since the electron-donor perturbations through the *para-* and *meta*-substituents, establishes two different effects. The first being an incremental process of long distance charge transfer, while the second determines a contrary effect, but one lower than the first using the same relative scale. Therefore, both effects permit us to generate a modulated control mechanism for a long distance electronic charge transfer process.

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