

Bridge effect of the C=C, C=N and N=N bonds on the long distance electronic charge transfer of *para*-substituted stilbenoid compounds

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Dedicated to the memory of Dr. Piet Leclercq

Abstract. By means of ^{13}C -NMR spectroscopy and *ab initio* molecular orbital theory calculations, we have analyzed the bridge effect of the C=C, C=N and N=N bonds on the long distance charge transfer of 4-dimethylamino-4'-nitrostilbenoid compounds in the ground electronic state.

After a complete spectral assignment of the ^{13}C -NMR signals in these molecular compounds, we have characterized the effect of the nitrogen centres on the molecular bridge by means of the chemical shifts of the carbon centres, the theoretical charge densities and the dipolar moments.

From an electronic molecular point of view, our results describe two main properties of the double bond bridge. The first is related to the local charge accumulation capacity given by the type of the atomic centres and the structural orientation of the double bond bridge, and the second property is related to the modulation of the electronic charge distribution through the molecular system by the electrical polarization of the bridge.

Other complementary experimental evidences have permit us to establish new local molecular domains of the bridge effect in these stilbenoid compounds by means of linear correlations between ^{13}C -NMR chemical shifts of the aromatic carbon centres of the acceptor-phenyl group and the molecular polarity of the species under study.

Keywords: Stilbenoid compounds, ^{13}C -NMR, *ab initio* molecular orbital calculations

1. Introduction

Intramolecular electronic charge transfer (IECT) of electron-donor and electron-acceptor substituted aromatic compounds has been subject of our research program during the last decade [1–6]. In these works we have established the role of the olefinic bonds as a molecular conduction channel. Thus, in a novel comprehension of the role of these olefinic bridges, the π -conduction channel can be seen as one-dimensional channel of charge migration between the donor and the acceptor groups, where the linear and nonlinear electrical properties of these molecular bridges, such as the inner conductance or resistance, determine the final charge distribution in the molecular species [6,7].

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This new period, own of this emergent field of research, has been recently denominated as the birth of the molecular electronics [8], and our contributions have been particularly oriented to the studies of intramolecular electronic distribution process, where some structural arrangements can define new molecular electronic devices. In this line of research, we have now analyzed the effect of the C=C, C=N and N=N bonds on the molecular electronic charge distribution of 4-dimethylamino-4'-nitrostilbenoid compounds in the ground electronic state from an experimental and theoretical point of view.

By means of ^{13}C -NMR spectroscopy we have developed a complete spectral assignment of the carbon signals and we have analyzed the chemical shifts of the present molecular species respect to the biphenyl structure as a referential molecular model. While, from a theoretical point of view, we have analyzed the electronic molecular structures by means of *ab initio* molecular orbital calculations in a HF/6-31G* basis set [9].

The observed ^{13}C -NMR chemical shifts of some stilbenoid compounds have early been explained in terms of free energy linear relationships [10], in order to characterize the *resonance* and *inductive effects* of the electron-donor group through the molecular system. However, in this work, we have oriented our analysis to the role of the double bond bridge on the long distance charge transfer, as well as, on the electronic charge molecular distribution. Thus, two new characteristic molecular properties of these type of bridges have been explored. The first is related to the local charge accumulation capacity, given by the type of the atomic centres and the structural orientation of the double bond bridge, and the second property is related to the modulation of the electronic charge distribution through the molecular system by the electrical polarization of the bridge.

This last property induce a particular chemical shift of the aromatic carbon centres of the acceptor-phenyl group. Thus, a new complementary experimental evidence, based on linear correlations observed between ^{13}C -NMR chemical shifts and dipolar moments, have permitted us to establish new local molecular domains of the bridge effect in these stilbenoid compounds.

2. Experimental section

2.1. Materials

4'-Nitro-4-N,N-dimethylaminobiphenyle (DA), 4'-nitro-4-N,N-dimethylamino-stilbene (DCCA), N-(4-N,N-dimethylaminobenzylidene)-4-nitroaniline (DCNA) and 4'-nitro-4-N,N-dimethylaminoazobenzene (DNNA) species were obtained from TCI America Inc. However, N-(4-nitrobenzylidene)-4-N,N-dimethylaminoaniline (DNCA) was synthesised by means of a standard condensation [11] using 4-N,N-dimethylaminoaniline and 4-nitrobenzaldehyde [12]. All these compounds were recrystallized and sublimated a reduced pressure and fresh solutions were prepared in each spectroscopic measurement. The solvent of spectroscopy grade was obtained from Aldrich Chemical Co.

2.2. Methods

Nuclear magnetic resonance spectra were recorded on a Bruker AMX-300 spectrometer at 300 MHz for ^{13}C , using a QNP probe. The pulse length and time delay were 7.0 μs and 3 s, respectively. The spectral band width was 25 kHz and 16000 transients were accumulated in 32 kB files, giving a resolution of 0.69 Hz/point. Apodization of the FID with an exponential multiplication (EM) was used with a line broadening of 3.0 Hz.

The recorder was releasing at room temperature and saturated solutions in deuterated chloroform with TMS as internal reference.

Quantum mechanical calculations were performed using the Gaussian[®] 98 for Windows program package [9]. The molecular orbital calculations were performed with complete molecular geometry relaxation at the HF/6-31G basis set. Good agreements between experimental and calculated ground state molecular conformations were found [13,14]. The net electronic charge distributions were performed using the HF/6-31G**/6-31G basis set [9].

3. Results and discussions

The ¹³C-NMR chemical shifts of the 4'-nitro-4-N,N-dimethylaminostilbenoid compounds in deuterated chloroform are presented in Fig. 1. On the other hand, the spectral assignment data of these carbon signals

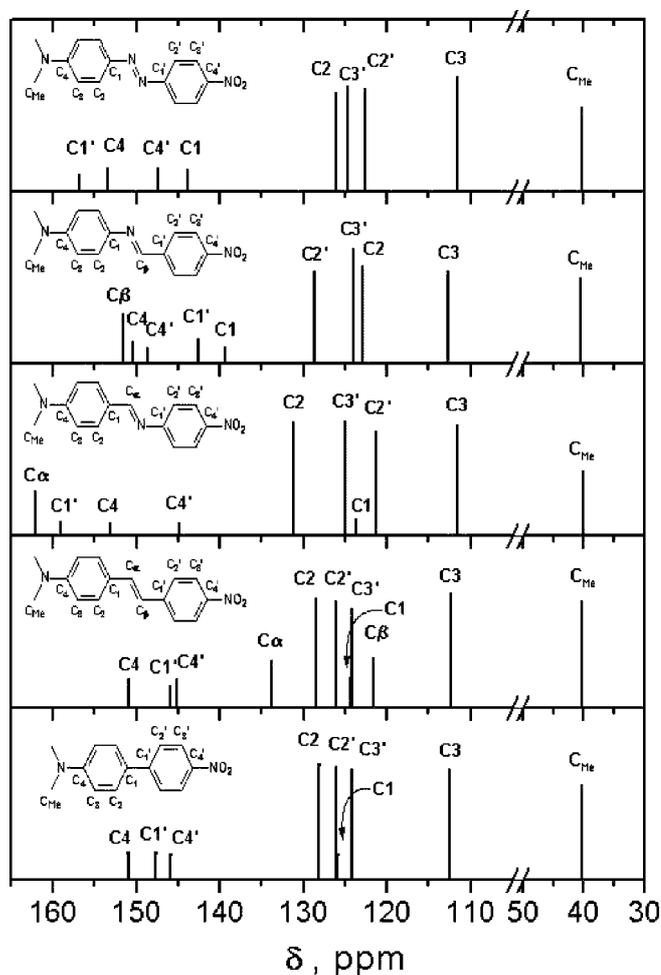


Fig. 1. ¹³C-NMR spectral signal of the 4'-nitro-4-N,N-dimethylaminobiphenyle (DA), 4'-nitro-4-N,N-dimethylaminostilbene (DCCA), N-(4-N,N-dimethylaminobenzylidene)-4-nitro-aniline (DCNA), N-(4-Nitrobenzylidene)-4-N,N-dimethylaminoaniline (DNCA) and 4'-nitro-4-N,N-dimethylaminoazobenzene (DNNA) in deuterated chloroform at room temperature.

Table 1

Chemical shifts (ppm) of the 4'-nitro-4-N,N-dimethylaminobiphenyle (DA), 4'-nitro-4-N,N-dimethylamino-stilbene (DCCA), N-(4-N,N-dimethylamino-benzylidene)-4-nitroaniline (DCNA), N-(4-nitrobenzylidene)-4-N,N-dimethylaminoaniline (DNCA) and 4'-nitro-4-N,N-dimethylaminoazobenzene (DNNA) systems at room temperature in deuterated chloroform

Atomic centre	DA	DCCA	DCNA	DNCA	DNNA
C _{Me}	40.27	40.31	40.11	40.53	40.30
C ₄	150.97	150.94	153.23	150.38	153.40
C ₃	112.53	112.28	111.60	112.58	111.50
C ₂	128.11	128.44	131.22	122.93	126.06
C ₁	125.88	124.42	123.65	142.66	143.81
C _α	–	133.75	162.05	–	–
C _β	–	121.65	–	151.55	–
C _{1'}	147.62	146.01	159.02	139.32	156.86
C _{2'}	126.08	126.12	121.38	128.67	122.62
C _{3'}	124.17	124.20	125.02	123.97	124.70
C _{4'}	145.86	145.09	144.86	148.62	147.43

Table 2

Electronic charge densities (e) of the 4'-nitro-4-N,N-dimethylaminobiphenyle (DA), 4'-nitro-4-N,N-dimethylamino-stilbene (DCCA), N-(4-N,N-dimethylamino-benzylidene)-4-nitroaniline (DCNA), N-(4-nitrobenzylidene)-4-N,N-dimethylaminoaniline (DNCA) and 4'-nitro-4-N,N-dimethylaminoazobenzene (DNNA) systems in the HF/6-31G**/6-31G basis set

Group or atomic centre	DA	DCCA	DCNA	DNCA	DNNA
N(Me) ₂	–1.270	–1.269	–1.214	–1.269	–1.275
C ₄	+0.424	+0.423	+0.435	+0.422	+0.437
C ₃	–0.286	–0.283	–0.298	–0.287	–0.295
C ₂	–0.188	–0.195	–0.168	–0.183	–0.156
C ₁	–0.034	–0.008	–0.081	+0.221	+0.188
X _α	–	–0.161	+0.138	–0.568	–0.304
X _β	–	–0.231	–0.596	+0.100	–0.361
C _{1'}	+0.055	+0.077	+0.294	+0.003	+0.276
C _{2'}	–0.238	–0.247	–0.239	–0.220	–0.212
C _{3'}	–0.163	–0.160	–0.161	–0.198	–0.171
C _{4'}	+0.156	+0.152	+0.149	+0.165	+0.164
NO ₂	–0.464	–0.466	–0.468	–0.454	–0.456

are collected in Table 1. These results are based on a comparative spectral analysis of the compounds under study and a complete review of the spectral signals coming from published work and data base systems [10,15]. Contrarily to earlier works [10,15], we have recorded all the ¹³C-NMR signals for the series under study, including the quaternary carbons known as the lowest intensity spectral signals.

Up to date, C_α and C_β chemical shift signals have been subject of controversial assignments [15]. However, after our spectral analysis, these discrepancies have been resolved and we have incorporated a systematic theoretical study of the ¹³C-NMR chemical shifts [9]. This theoretical study is based on the net charge densities calculated from the *ab initio* molecular orbital theory in the HF/6-31 G**/6-31G basis set approach (see Table 2). Thus, we have compared the theoretical and experimental spectral assignments in Fig. 2 and we can observe a fairly well straightforward correlation between both data set.

In order to identify the effect of the double bond bridge on the molecular charge distribution of these stilbenoid compounds, we have examined the chemical shifts from an electronic and structural point of view (see Figs 3 and 4). First, we have included the corresponding *para*-substituted biphenyl compound

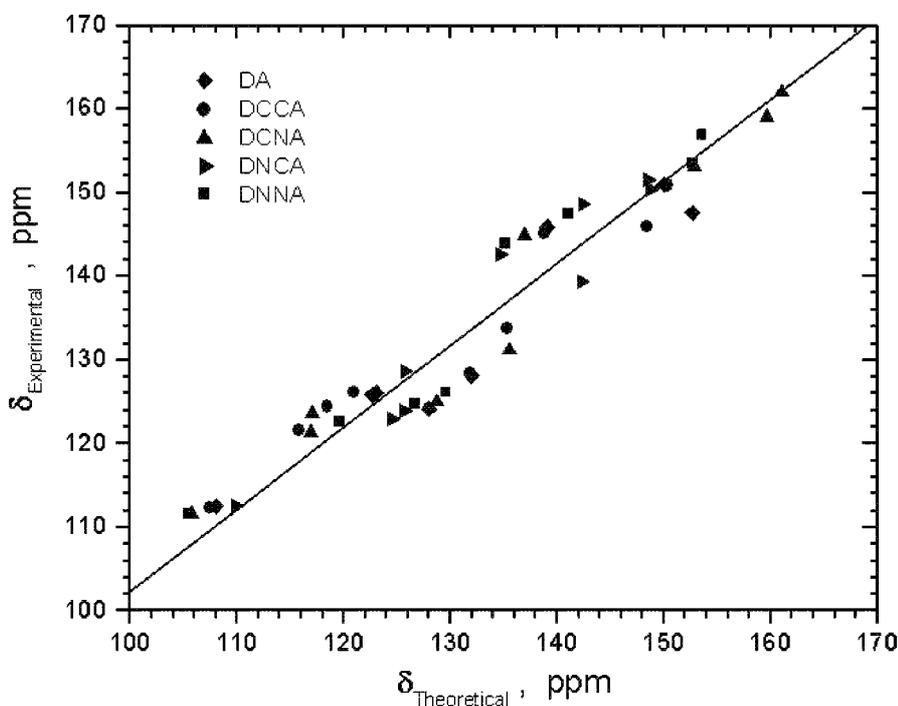


Fig. 2. Plot of the calculated HF/6-31G**/6-31G chemical shifts ($\delta_{\text{Theoretical}}$) versus the experimental chemical shifts ($\delta_{\text{Experimental}}$) of the 4'-nitro-4-N,N-dimethylaminobiphenyle (DA), 4'-nitro-4-N,N-dimethylaminostilbene (DCCA), N-(4-N,N-dimethylaminobenzylidene)-4-nitroaniline (DCNA), N-(4-nitrobenzylidene)-4-N,N-dimethylaminoaniline (DNCA) and 4'-nitro-4-N,N-dimethylaminoazobenzene (DNNA).

as a model structure without double bond molecular bridge, in order to know the effect of the C=C bridge on the aromatic carbon chemical shifts. Only slight chemical shift changes can be observed after to compare the same aromatic carbon centres of biphenyl (DA) and stilbene (DCCA) compounds (see Table 1). These similar chemical shifts determine a same kind of electronic molecular distribution as can be corroborated from Fig. 3, where the bridge effect in DCCA slightly modifies the chemical shifts of the C_1 and $C_{1'}$ centres respect to the same centres in DA. However, contrarily to the C=C bond effect before observed, the nitrogen centres on the same bridge in C=N, N=C or N=N centres, introduce a significant perturbation of the chemical shifts on the carbon centres of the aromatic systems. Particularly C_1 and $C_{1'}$ carbons, both atomic centres adjacent to the nitrogen centre on the bridge (see DCNA, DNCA and DNNA in Table 1), experiment a notorious chemical shift respect to the same centres in the stilbenic compound (DCCA), where the C_α and C_β centres in DCNA and DNCA, respectively, present the extreme cases of high chemical shifts (see Figs 3 and 4). Furthermore, we can observe that the N=C bridge in the DNCA system, induces an inversion of the chemical shift order in the C_1 and $C_{1'}$ respect to the same carbons in the remainder compounds (see Table 1). Obviously, this fact would involve a diminution of the charge migration through the bridge toward the acceptor group and thus, effectively, we could explain the diminution of the dipolar moment (see Table 3). Therefore, this bridge effect can be considered determinant in the control of the charge transfer electronic transport toward the NO_2 acceptor group after modify the π -conduction molecular channel.

Furthermore, after to analyze the chemical shift sensitivity respect to the atomic nature of the molecular bridge in Figs 3 and 4, we have found a singular effect on the chemical shifts of the carbon centres of

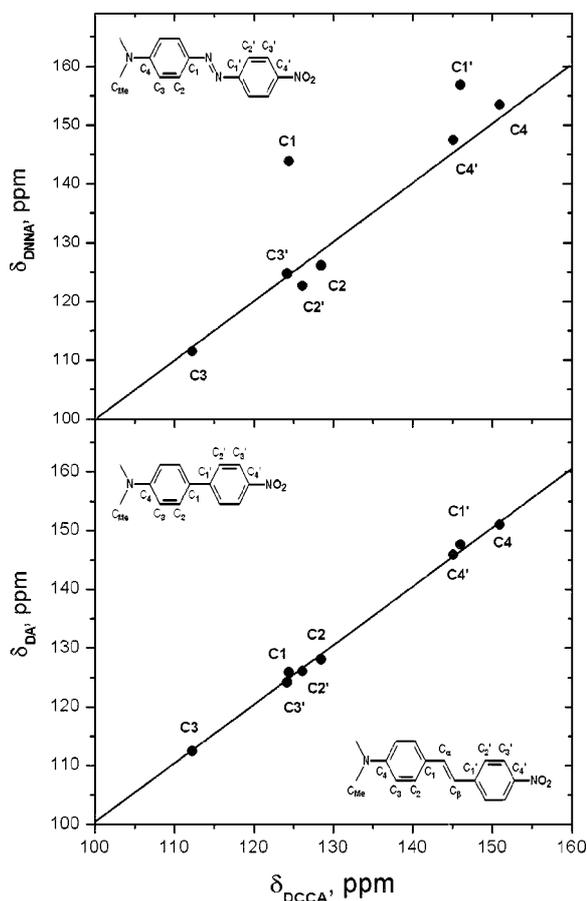


Fig. 3. Plots of linear correlations between chemical shifts of 4'-nitro-4-N,N-dimethylaminobiphenyle (DA) and 4'-nitro-4-N,N-dimethylaminoazobenzene (DNNA) versus 4'-nitro-4-N,N-dimethylaminostilbene (DCCA).

the nitro-phenyl groups. As well we known, the nitro-acceptor group, as an electronic charge withdrawal group, will induce an electronic charge migration through the molecular system from the electron-donor group by means of the resonance effect. However, after to compare the chemical shifts of the aromatic carbons of the donor-phenyl group and the acceptor-phenyl group respect to the molecular polarity, we have observed a fairly good linear correlation between every one of the chemical shifts of the $C_{1'}$, $C_{2'}$ and $C_{3'}$ carbon centres of the molecules under study and the permanent molecular dipolar moments [16] (see Fig. 5).

These results show a new property of the bridge, since the charge accumulation on the bridge (see Table 3) modulates the electronic charge transferred toward the aromatic carbons of the acceptor-phenyl group. Therefore, the aromatic carbon of the acceptor-phenyl group present a quantitative correlation of the charge migration induced by the different kinds of molecular bridges under study to be obtained from these linear correlation slopes. By following, we can ascribe an intrinsic resistivity of the conduction channel in the bridge from the chemical shifts of the $C_{1'}$, $C_{2'}$ and $C_{3'}$ atomic centres according to the following order: DNCA > DCCA > DNNA > DCNA.

Finally, the *ab initio* molecular orbital theory calculations permit to corroborate the experimental behavior before analyzed, but, in addition, these theoretical results have permitted us to characterize the

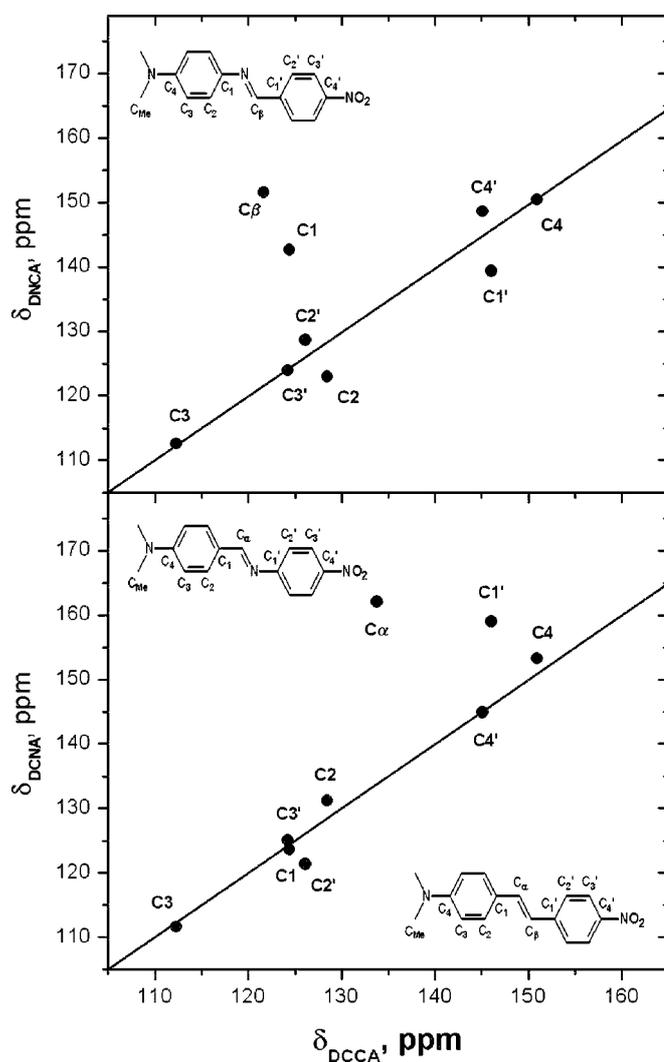


Fig. 4. Plots of linear correlations between chemical shifts of N-(4-N,N-dimethylaminobenzylidene)-4-nitroaniline (DCNA) and N-(4-nitrobenzylidene)-4-N,N-dimethylaminoaniline (DNCA) versus 4'-nitro-4-N,N-dimethylaminostilbene (DCCA).

Table 3

HF/6-31G**/6-31G Electronic charge densities of the double bond bridge atoms (X_α and X_β as C and/or N) and experimental dipolar moments (μ) of 4'-nitro-4-N,N-dimethylamino stilbene (DCCA), N-(4-N,N-dimethyl-amino-benzylidene)-4-nitroaniline (DCNA), N-(4-nitro-benzylidene)-4-N,N-dimethyl-aminoaniline (DNCA) and 4'-nitro-4-N,N-dimethylamino-azobenzene (DNNA)

Compounds	$X_\alpha + X_\beta$ (e)	$X_\beta - X_\alpha$ (e)	μ (Debyes) ^a
DCCA	-0.392	-0.070	7.4
DCNA	-0.458	-0.734	8.6
DNCA	-0.468	+0.668	6.9
DNNA	-0.665	-0.057	8.2

^aRef. [16].

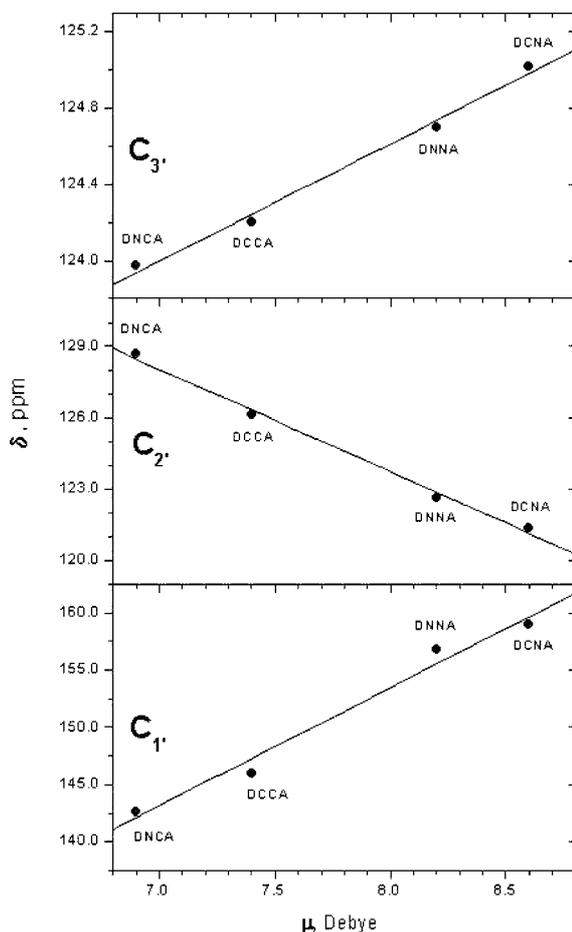


Fig. 5. Plots of linear correlations between chemical shifts of $C_{1'}$, $C_{2'}$ and $C_{3'}$ carbon centres versus the experimental dipolar moments in 4'-nitro-4-N,N-dimethylaminostilbene (DCCA), N-(4-N,N-dimethylaminobenzylidene)-4-nitroaniline (DCNA), N-(4-nitrobenzylidene)-4-N,N-dimethylaminoaniline (DNCA) and 4'-nitro-4-N,N-dimethylaminoazobenzene (DNNA).

electrical polarization of the molecular bridge. Effectively, from Table 3 we can observe two electronic properties of the molecular bridge. The first property is related to the total charge accumulated in these X_{α} and X_{β} atomic centres, i.e., $(X_{\alpha} + X_{\beta})$, which define an effective charge accumulator group or molecular device. And the second property is defined by the $(X_{\alpha} - X_{\beta})$ quantity, which determine the electrical polarization of this charge accumulator molecular device. Thus, while the C=C, C=N and N=N bonds follow a same polarization trend, the N=C bond interchange the electrical polarization of the bridge.

Acknowledgments

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