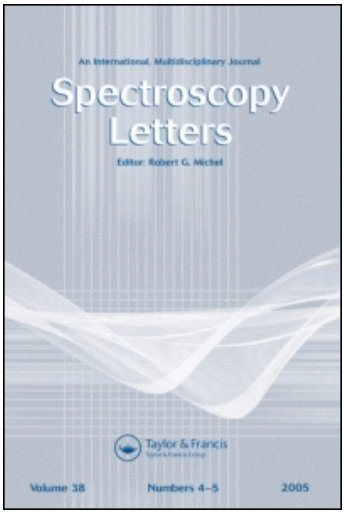

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BRIDGE EFFECT OF THE C=N BOND AND LONG DISTANCE ELECTRONIC EFFECTS OF ELECTRON-DONOR (D) SUBSTITUENTS ON N-(4-D-BENZYLIDENE)-4-NITROANILINES AND N-(4-NITROBENZYLIDENE)-4-D-ANILINE

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BRIDGE EFFECT OF THE C=N BOND AND LONG DISTANCE ELECTRONIC EFFECTS OF ELECTRON-DONOR (D) SUBSTITUENTS ON N-(4-D-BENZYLIDENE)-4-NITROANILINES AND N-(4-NITROBENZYLIDENE)-4-D-ANILINE

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ABSTRACT

By means of ^{13}C-NMR spectroscopy and ab initio molecular orbital theory calculations we have analyzed the bridge effect of the C=N bond and the long distance electronic effect of the electron-donor substituents (D: -NO_2, -Cl, -H, -CH_3, -OCH_3, and -$N(CH_3)_2$) on N-(4-D-benzylidene)-4-nitroanilines (DCNA) and N-(4-nitrobenzylidene)-4-D-ani-line (DNCA), in the ground electronic state.

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From the ^{13}C-NMR spectral assignment signals and our molecular orbital calculations on a Gaussian HF/6-31G* basis set, we have found a linear functional dependence of the chemical shifts on the electronic charge of the C_1, C_4, $C_{1'}$ and $C_{4'}$ centers. Furthermore, we have determined 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 point of view, our results permit determine in a quantitative way the local charge accumulation capacity on the C=N bond induced by the electron-donor substituent, as well as, determine the bridge effect on the dipolar moment.

Key Words: Electron-donor-benzylidenanilines; ^{13}C-NMR spectral assignments; Chemical shift calculations; HF/6-31 G* ab initio molecular orbital calculations; Bridge effect and long distance electronic effects

INTRODUCTION

Recently, we have reported the bridge effect of the C=C, C=N and N=N bonds on the para-substituted stilbenoid compounds[1] and *para*-β-*nitrostyrene* systems (D-Ph-CH=CH-NO_2)[2] as a particular cases of aromatic molecular models of long distance electronic charge transfer through a bridge bond induced by the *para*-substituent electron-donors. In a similar way, we have analyzed the electronic behavior of *para*-substituted benzylideneacetones.[3] These intramolecular electronic charge transfer (IECT) studies of polar aromatic compounds have been part of our program of research during the last years.[1–9]

Particularly, these electron-donor substituents induce a charge density perturbation through the all aromatic carbon centres of the molecular systems under study and, by following, ^{13}C-NMR spectroscopy and ab initio molecular orbital theory calculations[1,10,11] are two appropriate analytical studies to be carried out.

Therefore, in the present work we have chosen a set of polar aromatic compounds derived of the benzylideneaniline series and substituted by electron-donor groups at *para*-positions (see Fig. 1), in order to induce a systematic perturbation of the electronic charge through a C=N bridge and determine the bridge effect on the long distance electronic charge transfer.

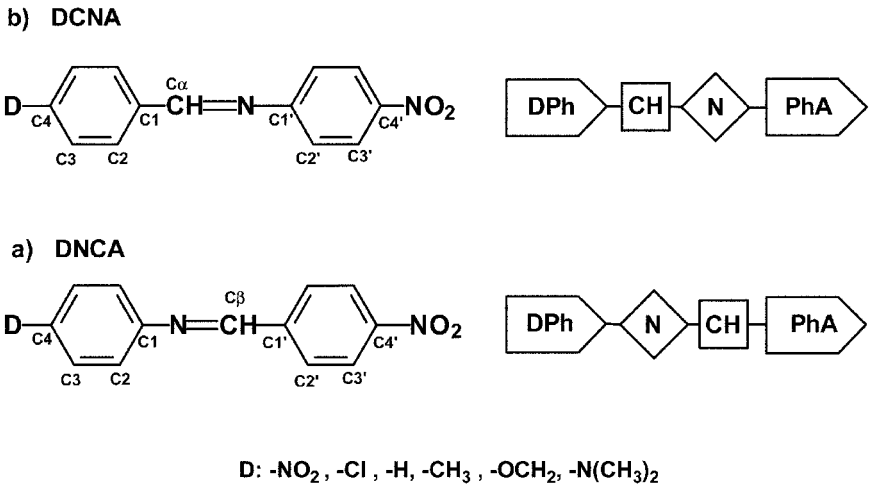

Figure 1. Molecular series derived of benzylideneanilines.

Mainly, we have analyzed the effect of the electron-donor substituents (D: $-NO_2$, -Cl, -H, $-CH_3$, $-OCH_3$, and $-N(CH_3)_2$) at the 4-position of the phenyl rings, by means of the ^{13}C-NMR chemical shifts and the theoretical electronic charge densities on the nitrogen and carbon atoms distributed through the π-molecular structure between the D-substitutents and the NO_2 acceptor group for two molecular series: (a) N-(4-D-benzylidene)-4-nitroanilines (DCNA) and (b) N-(4-nitrobenzylidene)-4-D-aniline (DNCA).

Based on the local charge accumulation capacity as well as the electrical polarization of the C=N bond, previously defined by us as two intrinsic molecular properties of these C=N bridges,[1] simples and direct experimental and theoretical evidences permit us to establish a quantitative parametrization of this long distance electronic effect, induced by the electron-donor substituent in terms of: (a) the local charge accumulation capacity at the C=N bond bridge and (b) the modulation of the electronic charge distribution determined by the electrical polarization of the same molecular bridge.

THEORETICAL SECTION

Quantum mechanical calculations were performed using the Gaussian® 98 for Windows program package.[12] The molecular orbital calculations were performed with complete molecular geometry relaxation

and the stationary structure was characterized by means of the analytical calculation of the vibrational frequencies. Good agreements between experimental and calculated ground state molecular conformations were found.[11,13–18] Geometry optimization, vibrational frequency calculation and Mullikan' Population Analysis were carried out at the restricted HF/6-31G* basis set level. Furthermore, NMR shielding tensors with Gauge-Independent Atomic Orbital (GIAO) method was used in order to obtain the calculated ^{13}C-NMR spectra.[13]

RESULTS AND DISCUSSION

The experimental ^{13}C-NMR chemical shifts of both molecular series obtained from literature, as well as the calculated values, determined in the present work, are presented in Tables 1 and 2, respectively. A good linear correlation between the experimental and calculated chemical shifts is depicted for DCNA and DNCA molecular series in Fig. 2. These results are based on a comparative spectral analysis of the compounds under study developed in our laboratory as well as, by means of a complete review of the spectral signals coming from published works and data base systems.[14–24] These fairly well straightforward relationships permit us corroborate the spectral assignment defined in previous ^{13}C-NMR studies of some molecules of these series.[1]

Up to date, C_α and C_β chemical shift signals have been subject of controversial assignments,[20] however, after our spectral analysis[1] and the present study, these discrepancies have been well resolved. Thus, we have corroborated the present spectral assignment by means of this systematic theoretical study of the ^{13}C-NMR chemical shifts (see Fig. 2).

This NMR theoretical study, based on the net charge densities calculated from the ab initio molecular orbital theory in the HF/6-31G* basis set approach, permit to analyze the role of the charge distribution in terms of the electron-donor substituent effect. Thus, from the chemical shifts dependence respect to the net charge on the atomic centers, we have compared the experimental spectral assignments depicted in Table 1 vs. the HF/6-31G* net charges for every carbon center in both aromatic series depicted in Table 3, according to the following relationship:

$$\delta = \mathbf{a}q_{6-31G^*} + \delta^\circ \tag{1}$$

In Table 4 we present the C_1, $C_{1'}$, C_4 and $C_{4'}$ carbon centre parametrizations according to the linear dependence described by Eq. (1).

Table 1. Experimental Chemical Shifts (ppm) of the N-Benzylidenanilines

	DNCA						DCNA					
δ_{Exp}	$-NO_2$[a]	$-Cl$[a]	$-H$[a]	$-CH_3$[a]	$-OCH_3$[a]	$-N(CH_3)_2$[b]	$-NO_2$[a]	$-Cl$[a]	$-H$[a]	$-CH_3$[a]	$-OCH_3$[a]	$-N(CH_3)_2$[b]
C_4	146.35	132.64	127.26	137.11	159.33	150.30	150.09	138.51	132.25	143.05	163.10	153.23
C_3	125.06	129.36	(d)	129.88	114.62	112.58	124.09	129.27	128.88	129.60	114.40	111.60
C_2	121.20	122.30	(d)	120.98	122.57	122.93	129.90	130.36	129.27	129.27	131.90	131.22
C_1	156.21	149.33	151.06	148.46	143.69	139.32	140.58	133.88	135.53	132.88	128.49	123.65
C_i[c]	159.89	157.43	157.38	155.94	154.52	151.55	159.89	161.07	162.46	162.37	161.73	162.05
$C_{1'}$	140.58	141.32	141.78	141.95	142.03	142.66	156.21	157.45	157.82	158.02	158.21	159.02
$C_{2'}$	129.9	129.36	(d)	129.17	128.99	128.67	121.20	121.18	121.15	121.15	121.25	121.38
$C_{3'}$	124.09	123.86	(d)	123.79	123.84	123.97	125.06	124.97	124.87	124.87	124.91	125.02
$C_{4'}$	150.09	149.46	149.4	149.38	149.10	148.62	146.35	145.64	145.50	145.30	145.20	144.86

[a]Ref. [20].
[b]Ref. [1].
[c]Ci is Cβ for DNCA series and Cα for DCNA series.
[d]Not observed.

Table 2. Calculated GIAO/HF/6-31G* Chemical Shifts (ppm) of the N-Benzylidenanilines

	DNCA						DCNA					
δ_{Teo}	$-NO_2$	-Cl	-H	$-CH_3$	$-OCH_3$	$-N(CH_3)_2$	$-NO_2$	-Cl	-H	$-CH_3$	$-OCH_3$	$-N(CH_3)_2$
C_4	139.65	133.3	124.24	133.79	153.75	148.86	144.17	141.38	131.77	142.36	159.37	153.62
C_3	128.70	128.92	128.13	128.10	111.72	109.90	125.58	126.58	125.56	125.71	109.65	106.55
C_2	117.22	120.41	119.59	120.34	124.14	124.61	127.36	130.45	129.89	130.76	134.37	135.25
C_1	149.18	146.66	147.52	144.68	137.28	134.30	139.35	129.95	130.84	127.94	121.96	117.69
Ci	155.19	154.39	153.34	152.46	150.15	148.26	155.19	158.81	160.42	160.42	160.14	160.97
$C_{1'}$	139.35	140.33	141.07	141.31	141.72	142.29	156.28	157.55	158.30	158.58	158.87	159.59
$C_{2'}$	127.36	126.74	126.50	126.34	125.99	125.69	117.22	117.08	117.07	117.04	116.99	116.94
$C_{3'}$	125.58	125.59	125.59	125.60	125.66	125.68	128.70	128.67	128.65	128.64	128.66	128.66
$C_{4'}$	144.17	143.47	143.11	142.95	142.69	142.35	139.65	138.16	137.82	137.64	137.44	137.00

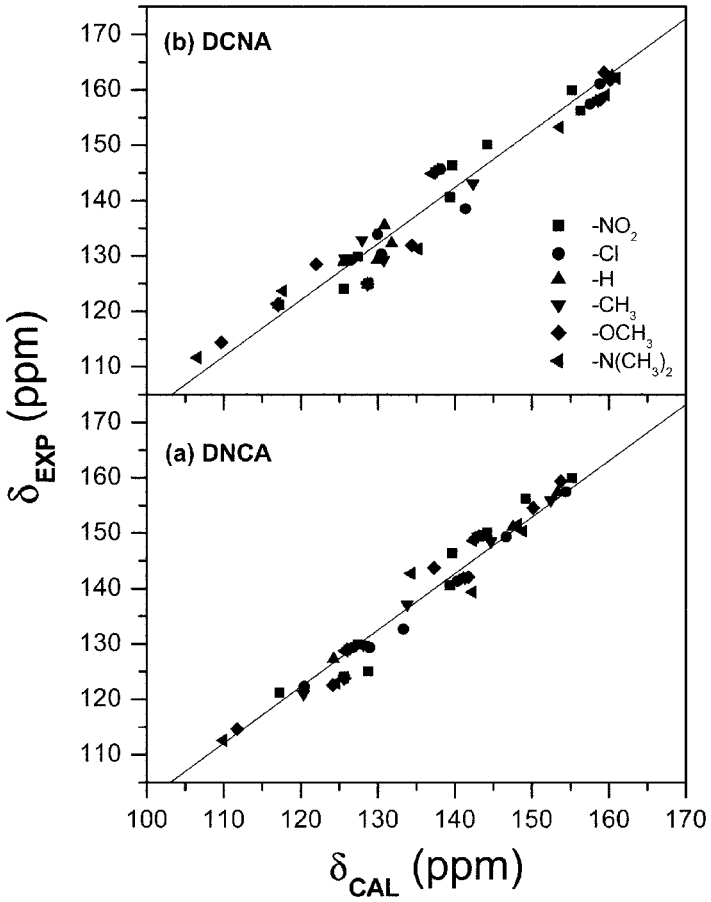

Figure 2. ^{13}C-NMR chemical shifts for benzylideneaniline molecular series under study substituted by electron-donar groups.

Contrarily to these carbon centres, C_2, $C_{2'}$, C_3 and $C_{3'}$ were found to be practically independent of the net charge parameter, while C_α and C_β do not follow a linear correlation.

From all these carbon centres, the $C_{4'}$ centre merge as the best parameter for long distance electronic effect analysis due to the electron-donor substituents. In Fig. 3 we can observe a well straightforward linear correlation of the chemical shifts of the $C_{4'}$ centre in terms of the net charge modulated by the electron-donor strength of the substituent groups in a quantitative description of the molecular series

Table 3. Mullikan Population Analysis (e.) by Centre (HF/6-31G* Basis Set Level)

	DNCA						DCNA					
q	$-NO_2$	-Cl	-H	$-CH_3$	$-OCH_3$	$-N(CH_3)_2$	$-NO_2$	-Cl	-H	$-CH_3$	$-OCH_3$	$-N(CH_3)_2$
D	−0.422	0.000	0.205	0.022	−0.319	−0.221	−0.407	0.013	0.212	0.037	−0.304	−0.203
C_4	0.143	−0.142	−0.205	0.039	0.435	0.392	0.160	−0.126	−0.186	0.054	0.453	0.423
C_3	−0.165	−0.179	−0.198	−0.225	−0.269	−0.277	−0.174	−0.187	−0.207	−0.232	−0.276	−0.287
C_2	−0.232	−0.209	−0.217	−0.209	−0.200	−0.194	−0.215	−0.191	−0.197	−0.190	−0.180	−0.175
C_1	0.266	0.239	0.240	0.232	0.220	0.216	−0.018	−0.044	−0.041	−0.052	−0.066	−0.078
X[a]	−0.540	−0.539	−0.537	−0.539	−0.544	−0.545	0.122	0.125	0.124	0.126	0.130	0.132
Y[b]	0.122	0.114	0.111	0.110	0.107	0.103	−0.540	−0.550	−0.552	−0.555	−0.563	−0.572
$C_{1'}$	−0.018	−0.013	−0.01	−0.009	−0.007	−0.004	0.266	0.270	0.272	0.273	0.275	0.279
$C_{2'}$	−0.215	−0.218	−0.219	−0.219	−0.220	−0.221	−0.232	−0.235	−0.235	−0.236	−0.237	−0.239
$C_{3'}$	−0.174	−0.173	−0.173	−0.173	−0.173	−0.173	−0.165	−0.165	−0.165	−0.164	−0.164	−0.164
$C_{4'}$	0.160	0.157	0.156	0.156	0.155	0.154	0.143	0.141	0.140	0.139	0.138	0.137
A	−0.407	−0.412	−0.417	−0.417	−0.419	−0.421	−0.422	−0.428	−0.430	−0.433	−0.433	−0.437

[a]X is a nitrogen atom for DNCA series and Cα for DCNA series.
[b]Y is Cβ for DNCA series and nitrogen atom for DCNA series.

Table 4. Parametrizations of the Experimental Chemical Shifts vs. the Theoretical Net Charge ($\delta = aq + \delta^{\circ}$)

	DNCA				DCNA			
Parameter	C_4	C_1	$C_{1'}$	$C_{4'}$	C_4	C_1	$C_{1'}$	$C_{4'}$
Slope (ppm e^{-1})	43.7 ± 5.4	315.4 ± 46.7	144.0 ± 7.9	224.8 ± 30.5	39.3 ± 6.0	277.1 ± 19.2	207.8 ± 19.2	229.7 ± 22.4
Intercept (ppm)	137.3 ± 1.4	73.7 ± 11.0	143.2 ± 0.1	114.2 ± 4.8	141.6 ± 1.7	146.3 ± 1.0	101.2 ± 5.2	113.4 ± 3.1
R^2	0.97	0.95	0.99	0.96	0.95	0.99	0.98	0.98
SD	3.2	1.9	0.1	0.14	3.6	0.9	0.2	0.1

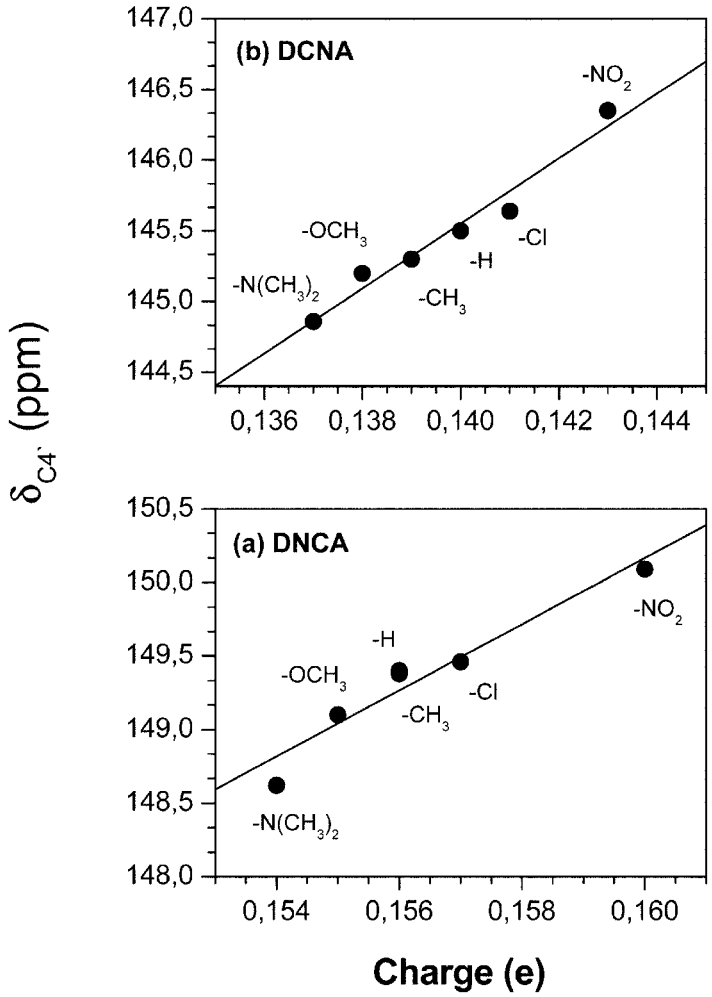

Figure 3. ^{13}C-NMR chemical shifts for $C_{4'}$ atomic centre vs. HF/6-31G* theoretical net charge.

(D:-NO_2 < -Cl < -H < -CH_3 < -OCH_3 < -$N(CH_3)_2$). In both molecular systems, DNCA and DCNA, the charge transfer trends is the same, whenever, the long distance electronic charge transfer observed on the DCNA system is larger than the DNCA system.

On the other hand, after to analyze the HF/6-31G* net charge density in Table 3, we have observed a particular role of the nitrogen centre on the

C=N bridge. From these net charge distributions, these nitrogen atoms merge as a new electron-acceptor centre, in a comparative way to the nitrogen centre of the nitro electron-acceptor group. In both molecular system, i.e., DCNA and DNCA (see Fig. 4), we can appreciate well three molecular zones defined by the aromatic rings, zone I and zone III, and the zone III defined by C=N bridge. According to these results, from Fig. 4 we can observe how the nitrogen centres on the bridge receive a high contribution of the electronic charge transfer. This new property define to these nitrogen atoms as true charge accumulation centres. By following, we have considered the C=N bridge bond as a new molecular device, where, based on the net charge density, we can observe two molecular behavior associated to this last property of the nitrogen center, the first one is defined by the accumulation charge on the C=N bridge, given by q(C_β+N) in DNCA and q(C_α+N) in DCNA, and the second aspect is related to the polarization

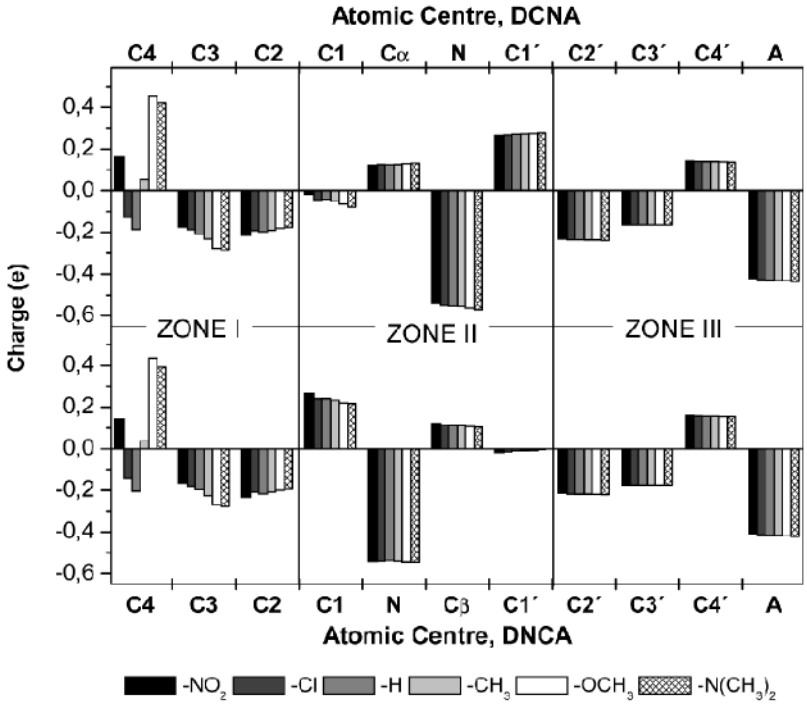

Figure 4. HF/6-31G* theoretical net charge distribution in the DNCA and DCNA molecular series.

Table 5. Electronic Charge Density of the C=N Bridge Bond and Calculated Dipolar Moment (μ) of N-Benzylidenanilines (HF/6-31G* Basis Set Level)

	DNCA			DCNA		
Subtituent	Y+X (e)[(a)]	Y−X (e)[(a)]	μ (D)	Y+X (e)[(b)]	Y−X (e)[(b)]	μ (D)
-NO_2	−0.418	0.662	1.69	−0.418	−0.662	1.69
-Cl	−0.425	0.653	3.21	−0.425	−0.675	4.81
-H	−0.426	0.648	5.48	−0.428	−0.676	7.04
-CH_3	−0.429	0.649	5.91	−0.429	−0.681	7.62
-OCH_3	−0.437	0.651	6.17	−0.433	−0.693	8.42
-$N(CH_3)_2$	−0.442	0.648	7.75	−0.440	−0.704	9.98

[(a)] X is a nitrogen atom and Y is Cβ for DNCA series.
[(b)] X is Cα and Y is a nitrogen atom for DCNA series.

of the C=N bridge, given by q(C_β-N) in DNCA and q(C_α-N) in DCNA, see Table 5.

The data presented in Table 5 show that, while the charge accumulation on the C=N bridge follows the same behavior for both DCNA and DNCA molecular systems, the position of the nitrogen center on the bridge determines the polarization magnitude of the C=N bond. Thus, we can observe that DNCA present a diminution of the long distance electronic charge transfer when we compare to DCNA, in agreement to the minor polarization of the C=N bond respect to DCNA. Therefore, the polarization parameter merge as a new paradigm in order to generate a modulation of the magnitude of the dipolar moments in these kind of molecular systems.

In spite of the charge transfer through the π-molecular conduction system determines the nature of the dipolar moment, the bond electrical polarization effects induced by the electron-donor substituent on the molecular C=N bridge control the net charge migration towards the nitro-acceptor group in these aromatic bezylideneanilines.

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