JOC *Article*

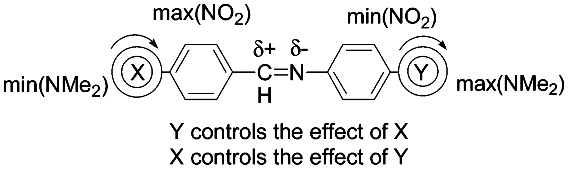
Substituent Cross-Interaction Effects on the Electronic Character of the C═N Bridging Group in Substituted Benzylidene Anilines − Models for Molecular Cores of Mesogenic Compounds. A ^{13}C NMR Study and Comparison with Theoretical Results

Helmi Neuvonen,*,† Kari Neuvonen,† and Ferenc Fülöp‡

Department of Chemistry, University of Turku, FIN-20014 Turku, Finland, and Institute of Pharmaceutical Chemistry, University of Szeged, H-6701 Szeged, POB 121, Hungary

helmi.neuvonen@utu.fi

Received January 9, 2006



^{13}C NMR chemical shifts δ_C(C═N) were measured in $CDCl_3$ for a wide set of mesogenic molecule model compounds, viz. the substituted benzylidene anilines p-X−C_6H_4CH═NC_6H_4−p-Y (X = NO_2, CN, CF_3, F, Cl, H, Me, MeO, or NMe_2; Y = NO_2, CN, F, Cl, H, Me, MeO, or NMe_2). The substituent dependence of δ_C(C═N) was used as a tool to study electronic substituent effects on the azomethine unit. The benzylidene substituents X have a reverse effect on δ_C(C═N): electron-withdrawing substituents cause shielding, while electron-donating ones behave oppositely, the inductive effects clearly predominating over the resonance effects. In contrast, the aniline substituents Y exert normal effects: electron-withdrawing substituents cause deshielding, while electron-donating ones cause shielding of the C═N carbon, the strengths of the inductive and resonance effects being closely similar. Additionally, the presence of a specific cross-interaction between X and Y could be verified. The electronic effects of the neighboring aromatic ring substituents systematically modify the sensitivity of the C═N group to the electronic effects of the benzylidene or aniline ring substituents. *Electron-withdrawing substituents on the aniline ring decrease* the sensitivity of δ_C(C═N) to the substitution on the benzylidine ring, while electron-donating substituents have the opposite effect. In contrast, *electron-withdrawing substituents on the benzylidene ring increase* the sensitivity of δ_C(C═N) to the substituent on the aniline ring, while electron-donating substituents act in the opposite way. These results can be rationalized in terms of the substituent-sensitive balance of the electron delocalization (mesomeric effects). The present NMR characteristics are discussed as regards the computational literature data. Valuable information has been obtained on the effects of the substituents on the molecular core of the mesogenic model compounds.

Introduction

The liquid-crystal and nonlinear optical properties of organic molecules with conjugated π-electron systems carrying an electron acceptor group at one end and a donor group at the opposite end have led to increasing interest in their properties. For example, both substituted phenyl benzoates and substituted benzylidene anilines are models of the molecular cores of mesogens, i.e., compounds able to form liquid crystals.[1,2] These compounds are of the general type X−C_6H_4−Z−C_6H_4−Y, where Z functions as a linking unit between two aromatic rings carrying the substituents X and Y which can act as electron donors and/or electron acceptors. The optical and electrical properties of liquid crystals have been shown to be sensitive to subtle changes in the structure of the molecule.[1−6] Changes in

---

* Corresponding author. Fax: +358-2-3336700.

† University of Turku.

‡ University of Szeged.

(1) (a) Kuze, N.; Fujiwara, H.; Takeuchi, H.; Egawa, T.; Konaka, S. *J. Phys. Chem. A* **1999**, *103*, 3054. (b) Takemasa, T.; Takeuchi, H.; Egawa, T.; Konaka, S. *J. Am. Chem. Soc.* **2001**, *123*, 6381.

(2) Wrzalik, R.; Merkel, K.; Kocot, A. *J. Mol. Model.* **2003**, *9*, 248.

(3) Qin, J.; Dai, C.; Gong, X.; Liu, D.; Chen, C.; Wu. B. *Chin. J. Chem. Phys.* **1991**, *4*, 30.

10.1021/jo0600508 CCC: $33.50 © 2006 American Chemical Society
Published on Web 03/17/2006

the substituents X and Y affect the overall electron distribution of $X-C_6H_4-Z-C_6H_4-Y$ and therefore among others the conformation of the molecule. An understanding of the mechanisms of charge generation at a molecular level is critical for an understanding of charge generation, transport, and trapping in photorefractive liquid crystals and for the design of new materials for nonlinear optical purposes.

Although NMR shielding is not determined only by the electron density, linear correlations with positive slopes between the atomic charges and the ^{13}C NMR chemical shifts for probe nuclei have been observed in several systems when the substitution is varied.[7−14] Good correlations have also been observed between the chemical shifts of the unsaturated carbons in the side chains of aromatic rings and substituent parameters.[7,8,12,15−18] Although the shift data do not usually fit the single-parameter correlation (eq 1), good to excellent correlations have been obtained with eq 2,

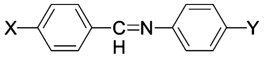
$$\mathrm{SCS} = \rho\sigma + \mathrm{constant} \tag{1}$$

$$\mathrm{SCS} = \rho_F\sigma_F + \rho_R\sigma_R \tag{2}$$

where SCS (substituent-induced change in the chemical shift) is the ^{13}C NMR shift of the side-chain carbon for a substituted compound relative to that for the unsubstituted one, and σ_F and σ_R are the inductive and resonance parameters, respectively, for the aromatic ring substituent in question.

By means of ^{13}C and ^{15}N NMR studies, together with the computational data for a set of benzaldehyde derivatives possessing a C=N double bond in the side chain, p-$X-C_6H_4-CH=N-Y$, we have recently shown that the sensitivity of the electronic character of the C=N unit to the benzylidene substituent X is dependent on the group Y (Y = Ph, CH_2Ph, C_6H_4-p-NO_2, Me, $C(Me)_3$, OMe, OH, NHPh, or NH_2). However, a detailed analysis of the origin of the phenomenon was not achieved.[8] The early NMR works of Kawasaki[19] and Akaba et al.[20] on substituted benzylidene anilines demonstrated on a qualitative level that the substituent on the benzylidene ring can influence the sensitivity of the azomethine carbon to the aniline substituent. Analogously, the aniline substituent seems to affect the sensitivity of the azomethine carbon to the benzylidene ring substituent.[20] For substituted phenyl benzoates p-$Y-C_6H_4$-$CO_2C_6H_4-p$-X, we recently observed that the electronic effects of the remote aromatic ring substituents systematically modify the sensitivity of the C=O group to the electronic effects of the phenyl or benzoyl ring substituents.[21] Liu et al. recently reported alike substituent cross-interaction effects in the theoretical bond dissociation energies concerning radical chemistry of anilines and aromatic silanes.[22] In the present study, our goal is to clarify whether the substituted benzylidene anilines, p-$X-C_6H_4-CH=N-C_6H_4-p$-Y, display a cross-interaction effect analogous to that observed for phenyl benzoates.[21] We wish especially to shed light on the substituent effects on the electronic character of the C=N bridging group in imines, an important group of mesogenic compounds.

SCHEME 1



X = NO_2 (**a**), CN (**b**), CF_3 (**c**), F (**d**), Cl (**e**), H (**f**), Me (**g**), OMe (**h**) or NMe_2 (**i**)

Y = NO_2 (**1**), CN (**2**), F (**3**), Cl (**4**), H (**5**), Me (**6**), OMe (**7**) or NMe_2 (**8**)

Results

The ^{13}C NMR spectra of the benzylidene anilines shown in Scheme 1 were measured in $CDCl_3$. The measurements were performed with a low and constant sample concentration (0.1 M) with a view to diminishing intermolecular associations. The ^{13}C NMR chemical shifts for the azomethine carbon in the benzylidene anilines **1**−**8** (cf. Scheme 1) are listed in Table 1. The chemical shifts range from 151.51 to 162.71 ppm.

Discussion

Our main goals were to study the effect of the aniline substituent on the sensitivity of the electronic properties of the C=N group to the benzylidene substituent and the effect of the benzylidene substituent on the sensitivity of the electronic properties of the imine bridging group to the aniline substituent. We first investigated separately the effects of the benzylidene and aniline substituents on δ_C(C=N). Tables 2 and 3 present the substituent-induced changes in the chemical shifts, SCS [δ_C(C=N)(substituted compound) − δ_C(C=N)(unsubstituted compound)], of the C=N carbon with respect to the substituents X and Y, respectively.

Effect of the Benzylidene Substituent X on the C=N Carbon Resonance δ_C(C=N). Both electron-withdrawing (EW) and electron-donating (ED) benzylidene substituents cause shielding of the C=N carbon as compared with the unsubstituted derivative X = H (Tables 1 and 2). This is opposite to the

---

(4) Miyajima, S.; Nakazato, A.; Sakoda, N. *Liq. Cryst.* **1995**, *18*, 651.

(5) Piñol, R.; Ros, M. B.; Serrano, J. L.; Sierra, T.; De La Funte, M. R. *Liq. Cryst.* **2004**, *31*, 1293.

(6) Ajeetha, N.; Pisipati, V. G. K. M. *Z. Naturforsch., A: Phys. Sci.* **2003**, *58*, 735.

(7) Neuvonen, H.; Neuvonen, K.; Koch, A.; Kleinpeter, E.; Pasanen, P. *J. Org. Chem.* **2002**, *67*, 6995.

(8) Neuvonen, K.; Fülöp, F.; Neuvonen, H.; Koch, A.; Kleinpeter, E.; Pihlaja, K. *J. Org. Chem.* **2003**, *68*, 2151.

(9) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159.

(10) Krawczyk, H.; Szatylowicz, H.; Gryff-Keller, A. *Magn. Reson. Chem.* **1995**, *33*, 349.

(11) Lin, S.-T.; Lee, C.-C.; Liang, D. W. *Tetrahedron*, **2000**, *56*, 9619.

(12) Neuvonen, K.; Fülöp, F.; Neuvonen, H.; Koch, A.; Kleinpeter, E.; Pihlaja, K. *J. Org. Chem.* **2001**, 66, 4132.

(13) Matsumoto, K.; Katsura, H.; Uschida, T.; Aoyama, K.; Machiguchi, T. *Heterocycles* **1997**, *45*, 2443.

(14) Alvarez-Ibarra, C.; Quiroga-Feijóo, M. L.; Toledano, E. *J. Chem. Soc., Perkin Trans. 2* **1998**, 679.

(15) Craik, D. J.; Brownlee, R. T. C. *Prog. Phys. Org. Chem.* **1983**, *14*, 1.

(16) Reynolds, W. F. *Prog. Phys. Org. Chem.* **1983**, *14*, 165.

(17) (a) Halton, B.; Dixon, G. M. *Org. Biomol. Chem.* **2004**, *2*, 3139. (b) Bonesi, S. M.; Ponce, M. A.; Erra-Balsells, R. *J. Heterocycl. Chem.* **2004**, *41*, 161. (c) Mezzina, E.; Spinelli, D.; Lamartina, L.; Buscemi, S.; Frenna, V.; Macaluso, G. *Eur. J. Org. Chem.* **2002**, 203.

(18) (a) Neuvonen, K.; Fülöp, F.; Neuvonen, H.; Pihlaja, K. *J. Org. Chem.* **1994**, *59*, 5895−5900. (b) Neuvonen, K.; Fülöp, F.; Neuvonen, H.; Simeonov, M.; Pihlaja, K. *J. Phys. Org. Chem.* **1997**, *10*, 55. (c) Neuvonen, H.; Neuvonen, K. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1497.

(19) Kawasaki, A. *J. Chem. Soc., Perkin Trans. 2* **1990**, 223.

(20) Akaba, R.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1985**, 1186.

(21) Neuvonen, H.; Neuvonen, K.; Pasanen, P. *J. Org. Chem.* **2004**, *69*, 3794.

(22) (a) Cheng, Y.-H.; Zhao, X.; Song, K.-S.; Liu, L.; Guo, Q.-X. *J. Org. Chem.* **2002**, *67*, 6638. (b) Song, K.-S.; Liu, L.; Guo, Q.-X. *J. Org. Chem.* **2003**, *68*, 262.

TABLE 1. **^{13}C NMR Shifts of the C=N Carbons in Substituted Benzylidene Anilines *p*-X−C_6H_4−CH=N−C_6H_4−*p*-Y in $CDCl_3$ (TMS = 0 ppm)**

	X								
Y	**a** NO$_2$	**b** CN	**c** CF$_3$	**d** F	**e** Cl	**f** H	**g** Me	**h** OMe	**i** NMe$_2$
1 NO$_2$	160.10	160.55	*a*	161.10	161.20	162.71	162.57	161.81	162.10
2 CN	159.75	160.21	160.76	160.82	160.90	162.44	162.29	161.54	161.86
3 F	156.96	157.48	158.22	158.57	158.52	160.16	160.15	159.49	160.08
4 Cl	157.64	158.14	158.85	159.11	159.11	160.71	160.67	159.99	160.51
5 H	157.33	157.82	158.51	158.76	158.74	160.34	160.30	159.64	160.21
6 Me	156.32	156.85	157.62	158.00	157.94	159.59	159.58	158.94	159.57
7 OMe	154.76	155.35	156.24	156.81	156.68	158.41	158.46	157.88	158.65
8 NMe$_2$	151.51	152.22	153.39	154.37	154.07	155.97	156.15	155.69	156.73

[a] Data for **1c** are lacking; see Experimental Section.

TABLE 2. **Substituent-Induced Changes in the Chemical Shift (SCS) of the C=N Carbon (in ppm) in Substituted Benzylidene Anilines *p*-X−C_6H_4−CH=N−C_6H_4−*p*-Y in $CDCl_3$ [SCS = δ_C(C=N) for *p*-X−C_6H_4−CH=N−C_6H_4−*p*-Y − δ_C(C=N) for C_6H_5−CH=N−C_6H_4−*p*-Y]**

		X								
	Y	**a** NO$_2$	**b** CN	**c** CF$_3$	**d** F	**e** Cl	**f** H	**g** Me	**h** OMe	**i** NMe$_2$
σ(Y)[a]/σ(X)[a]		0.78	0.66	0.54	0.06	0.23	0	−0.17	−0.27	−0.83
0.78	**1** NO$_2$	−2.61	−2.16	*b*	−1.61	−1.51	0	−0.14	−0.9	−0.61
0.66	**2** CN	−2.69	−2.23	−1.68	−1.62	−1.54	0	−0.15	−0.9	−0.58
0.06	**3** F	−3.2	−2.68	−1.94	−1.59	−1.64	0	−0.01	−0.67	−0.08
0.23	**4** Cl	−3.07	−2.57	−1.86	−1.6	−1.6	0	−0.04	−0.72	−0.2
0	**5** H	−3.01	−2.52	−1.83	−1.58	−1.6	0	−0.04	−0.7	−0.13
−0.17	**6** Me	−3.27	−2.74	−1.97	−1.59	−1.65	0	−0.01	−0.65	−0.02
−0.27	**7** OMe	−3.65	−3.06	−2.17	−1.6	−1.73	0	0.05	−0.53	0.24
−0.83	**8** NMe$_2$	−4.46	−3.75	−2.58	−1.6	−1.9	0	0.18	−0.28	0.76

[a] Substituent constants from ref 23. [b] Data for **1c** are lacking; see Experimental Section.

TABLE 3. **Substituent-Induced Changes in the Chemical Shift (SCS) of the C=N Carbon (in ppm) in Substituted Benzylidene Anilines *p*-X−C_6H_4−CH=N−C_6H_4−*p*-Y in $CDCl_3$ [SCS = δ_C(C=N) for *p*-X−C_6H_4−CH=N−C_6H_4−*p*-Y − δ_C(C=N) for *p*-X−C_6H_4−CH=N−C_6H_5]**

		X								
	Y	**a** NO$_2$	**b** CN	**c** CF$_3$	**d** F	**e** Cl	**f** H	**g** Me	**h** OMe	**i** NMe$_2$
σ(Y)[a]/σ(X)[a]		0.78	0.66	0.54	0.06	0.23	0	−0.17	−0.27	−0.83
0.78	**1** NO$_2$	2.77	2.73	*b*	2.34	2.46	2.37	2.27	2.17	1.89
0.66	**2** CN	2.42	2.39	2.25	2.06	2.16	2.1	1.99	1.90	1.65
0.06	**3** F	−0.37	−0.34	−0.29	−0.19	−0.22	−0.18	−0.15	−0.15	−0.13
0.23	**4** Cl	0.31	0.32	0.34	0.35	0.37	0.37	0.37	0.35	0.3
0	**5** H	0	0	0	0	0	0	0	0	0
−0.17	**6** Me	−1.01	−0.97	−0.89	−0.76	−0.8	−0.75	−0.72	−0.7	−0.64
−0.27	**7** OMe	−2.57	−2.47	−2.27	−1.95	−2.06	−1.93	−1.84	−1.76	−1.56
−0.83	**8** NMe$_2$	−5.82	−5.60	−5.12	−4.39	−4.67	−4.37	−4.15	−3.95	−3.48

[a] Substituent constants from ref 23. [b] Data for **1c** are lacking; see Experimental Section.

general idea that ED substituents cause shielding while EW substituents cause deshielding. However, analogous results have been observed previously for the azomethine carbon of substituted benzaldehyde derivatives.[8,12,19,20,24−26] The δ_C(C=N) values were first correlated with the Hammett σ values according to eq 1. The results proved to be very poor for each of the series **1**−**8**, though the correlation improved somewhat as Y became more ED (Table 4; columns 2 and 3). This means that the ratio of the inductive and resonance factors is not correctly described by σ. Correlations with substituent parameter σ^+ were even worse than those with σ (data not shown). However, good to excellent correlations were observed when the dual substituent parameter approach (eq 2) was used (Table 4; columns 4−6).

TABLE 4. **ρ(X), ρ_F(X), and ρ_R(X) for Different Substituted Benzylidene Anilines *p*-X−C_6H_4−CH=N−C_6H_4−*p*-Y for the Correlation of δ_C(C=N) with σ(X) (eq 1) or σ_F(X) and σ_R(X) (eq 2)**

Y	ρ(X)	*r*	ρ_F(X)	ρ_R(X)	*r*	ρ_F/ρ_R
1 NO$_2$	−1.4 ± 0.5	0.7614	−3.71 ± 0.15	0.12 ± 0.20	0.9889	−31
2 CN	−1.4 ± 0.4	0.7772	−3.81 ± 0.13	0.06 ± 0.18	0.9893	−64
3 F	−2.0 ± 0.4	0.8706	−4.35 ± 0.13	−0.83 ± 0.18	0.9939	5.2
4 Cl	−1.9 ± 0.4	0.8534	−4.20 ± 0.13	−0.62 ± 0.18	0.9930	6.8
5 H	−1.9 ± 0.4	0.8609	−4.14 ± 0.11	−0.66 ± 0.15	0.9948	6.3
6 Me	−2.1 ± 0.4	0.8780	−4.42 ± 0.13	−0.94 ± 0.18	0.9940	4.7
7 OMe	−2.5 ± 0.5	0.9037	−4.82 ± 0.15	−1.46 ± 0.21	0.9943	3.3
8 NMe$_2$	−3.4 ± 0.5	0.9324	−5.68 ± 0.20	−2.54 ± 0.28	0.9939	2.2

For two aniline series, Y = NO$_2$ and Y = CN, the correlation parameter ρ_F was quite large and negative, while the correlation parameter ρ_R was small but positive. In other words, inductive effects predominate strongly. In all other cases (Y = F, Cl, H, Me, MeO, or NMe$_2$) both the inductive and the resonance parameters were negative, the predominance of the inductive effects over the resonance effects decreasing in parallel with the increasing ED ability of the aniline substituent Y. The

---

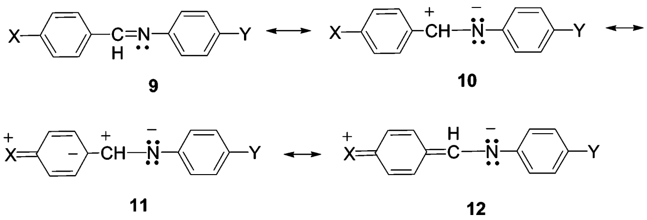
(23) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(24) Arrowsmith, J. E.; Cook, M. J.; Hardstone, D. J. *Org. Magn. Reson.* **1978**, *11*, 160.

(25) Szatmári, I.; Martinek, T.; Lázár, L.; Koch, A.; Kleinpeter, E.; Neuvonen, K.; Fülöp, F. *J. Org. Chem.* **2004**, *69*, 3645.

(26) Neuvonen, K.; Fülöp, F.; Neuvonen, H.; Koch, A.; Kleinpeter, E. *J. Org. Chem.* **2005**, *70*, 10670.

SCHEME 2



negative sign of the correlation parameters means a reverse substituent effect; i.e., *EW substituents cause shielding, while ED ones cause deshielding*.

The ^{13}C NMR chemical shift behavior described above can be understood by considering the resonance structures shown in Scheme 2. ED substituents X inductively stabilize resonance structure **10**, while EW ones have an opposite effect. The increase in the contribution of **10** caused by ED substituents affects the deshielding of the C=N carbon, with a negative value of $\rho_F(X)$ as the result. Substituents capable of ED resonance as in **11** affect the deshielding of the imine carbon. The negative $\rho_R(X)$ values reflect the contribution of this resonance-promoted inductive effect. This explanation is supported by our previous study concerning substituent dependence of the ^{15}N NMR chemical shift of the C=N nitrogen of substituted benzylidene anilines $p\text{-X}{-}C_6H_4CH{=}NC_6H_5$.[8] A positive slope of 19.6 (r = 0.9945) was observed for the correlation between $\delta_N(C{=}N)$ and $\sigma(X)$, in contrast to the negative correlation coefficients $\rho_F = -4.14$ and $\rho_R = -0.66$ observed for the dual substituent parameter correlation of $\delta_C(C{=}N)$ with $\sigma_F(X)$ and $\sigma_R(X)$ (Table 4). In the same study, the slope of -0.94 (r = 0.9992) was detected for the cross-correlation between the $q_N(C{=}N)$ and $q_C(C{=}N)$ (atomic charges on the PM3 level) for p-X-substituted benzylidene anilines.[8] Both $\rho_F(X)$ and $\rho_R(X)$ depend clearly and systematically on the aniline substituent Y (Table 4; columns 4 and 5). The numerical value for the ratio $|\rho_F/\rho_R|$ is >1 for each of the series **1**−**8**, but the value decreases as the ED ability of Y increases. In two cases, $\rho_R(X)$ is positive (Y = NO_2 or CN). This suggests that the observed $\rho_R(X)$ is a sum of the resonance-induced polar effect (**11**), for which $\rho_R(X) < 0$ and the conjugative effect (**12**), which corresponds to $\rho_R(X) > 0$. A positive or a negative $\rho_R(X)$ may be observed experimentally, depending on the relative magnitude of these two effects.

Effect of Aniline Substituent Y on ρ_F(X) and ρ_R(X). When the values of $\rho_F(X)$ and $\rho_R(X)$ were correlated with the Hammett substituent constants σ for the aniline substituent Y, satisfactory linear correlations were obtained (Figure 1). The fit of the correlations improved significantly in both cases when $\sigma^+(Y)$ was used instead of $\sigma(Y)$. Excellent correlations were observed. The goodness of the correlations verify that the effects of Y on $\rho_F(X)$ and $\rho_R(X)$ are electronic in origin. The effect of Y on $\rho_R(X)$ is ca. 1.4 times higher than that on $\rho_F(X)$. In summary, the sensitivity of the shielding of the C=N carbon and therefore the sensitivity of the electronic character of the C=N function to electron donation/electron withdrawal by the benzylidene substituent X are systematically adjusted by the electronic effects of Y: EW aniline substituents diminish, while ED aniline substituents enhance the sensitivity of the ^{13}C NMR chemical shift of the C=N carbon to substituent X.

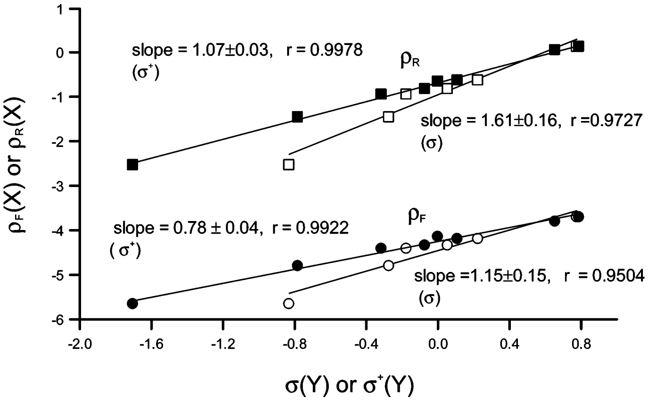
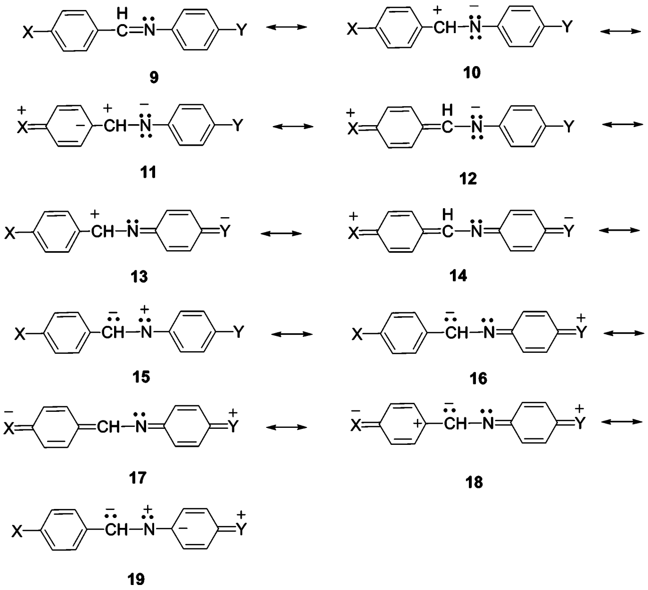


FIGURE 1. Plots of $\rho_F(X)$ and $\rho_R(X)$ for substituted benzylidene anilines $p\text{-X}{-}C_6H_4CH{=}NC_6H_4\text{-}p\text{-Y}$ vs $\sigma(Y)$ or $\sigma^+(Y)$: $\rho_F(X)$ vs $\sigma(Y)$ (○), $\rho_F(X)$ vs $\sigma^+(Y)$ (●), $\rho_R(X)$ vs $\sigma(Y)$ (□), $\rho_R(X)$ vs $\sigma^+(Y)$ (■), i.e., the effect of the aniline substituent on the sensitivity of $\delta_C(C{=}N)$ to the benzylidene substituent.

SCHEME 3



To couple the effect of the benzylidene substituent X on $\delta_C(C{=}N)$ and the effect of the aniline substituent Y on $\rho_F(X)$ and $\rho_R(X)$, more resonance structures (**13**−**16**, Scheme 3) than those shown in Scheme 2 have to be considered. When the aniline substituent Y is EW, it can inductively stabilize resonance structures **10**, **11**, and **12**, and the groups able to conjugate can still allow the contribution of resonance structures **13** and **14**. When Y is an EW group, the contribution of **15** cannot be significant, and **16** is reasonable only when Y is capable of conjugative electron donation. Thus, the sign and magnitude of $\rho_F(X)$ and $\rho_R(X)$ can be rationalized as discussed in the previous section. A more detailed explanation is given in the Supporting Information. The better $\sigma^+(Y)$ than $\sigma(Y)$ correlations in Figure 1 verify the significance of the conjugative effects of Y, i.e., the significance of the resonance structures **16**−**18**.

Effect of Aniline Substituent Y on the C=N Carbon Resonance δ_C(C=N). For each different benzylidene substituent X (**a**−**i**), as the aniline substituent Y (**1**−**8**) was varied, the smallest shift value (the lowest frequency) of the imine carbon was observed with the most ED substituent Y = NMe_2, and the largest shift value (the highest frequency) was observed with Y = NO_2. This is a normal effect. ED aniline substituents cause shielding of the C=N carbon as compared with the unsubstituted derivative (Y = H), while EW substituents cause deshielding. The $\delta_C(C{=}N)$ values were first correlated with the Hammett σ

TABLE 5. **ρ(Y) and ρ^+(Y) for Different Substituted Benzylidene Anilines p-X$-C_6H_4-CH{=}N-C_6H_4-$$p$-Y for the Correlation of δ_C(C=N) with σ(Y) and σ^+(Y) (eq 1)[a]**

X	ρ(Y)	r	ρ^+(Y)	r
a NO_2	5.23 ± 0.42	0.9809	3.44 ± 0.05	0.9995
b CN	5.08 ± 0.40	0.9819	3.34 ± 0.05	0.9994
c CF_3	4.96 ± 0.43	0.9820	3.07 ± 0.06	0.9991
d F	4.13 ± 0.9	0.9856	2.71 ± 0.05	0.9988
e Cl	4.37 ± 0.31	0.9851	2.86 ± 0.05	0.9990
f H	4.14 ± 0.28	0.9864	2.71 ± 0.06	0.9986
g Me	3.94 ± 0.27	0.9866	2.58 ± 0.05	0.9987
h OMe	3.76 ± 0.25	0.9870	2.46 ± 0.05	0.9986
i NMe_2	3.30 ± 0.22	0.9868	2.16 ± 0.04	0.9987

[a] Values of σ and σ^+ are from ref 23.

values according to eq 1. Satisfactory correlations were obtained for each of the series **a**−**i** (Table 5; columns 2 and 3). However, significant improvements in the correlations were observed when substituent parameter σ^+ values were used instead of those for σ, the correlations then being excellent (Table 5; columns 4 and 5). The positive values of ρ mean a normal substituent effect.

The chemical shift data were also analyzed with the dual substituent parameter in eq 2 (Table 6; columns 2−5). Again the correlation is improved significantly when substituent parameters σ_F(Y) and σ^+_R(Y) were used for eq 2 (Table 6; columns 6−9), and excellent correlations were observed. The positive values of the correlation parameters [ρ_F(Y) and ρ_R(Y)] mean a normal substituent effect, i.e., ED *substituents cause shielding while EW substituents cause deshielding*. EW substituents Y inductively stabilize resonance structures **10** and **11** (Scheme 3), decreasing the electron density on the imine carbon, while ED substituents inductively stabilize resonance structure **15**, with $\rho_F(Y) > 0$ as a consequence. Substituents Y capable of electron withdrawing via conjugation (e.g., NO_2) allow a contribution from **13**, and those capable of conjugative electron donation (e.g., NMe_2) allow a contribution from **16**. This explains $\rho^+_R(Y) > 0$. A resonance-induced polar effect (**19**) also leads to $\rho^+_R(Y) > 0$. In contrast with the situation for the benzylidene substituents, where inductive effects predominate (Table 4), $\rho_F(Y)/\rho^+_R(Y)$ is now close to 1 (Table 6; column 9). The effect of the benzylidene substitution is in line with the recent computational studies of Wiberg,[27] which showed that in disubstituted benzenes the inductive effects strongly predominate over the resonance effects in the overall effect of the substituents on the reaction center in the side chain, while the effect of the aniline substitution differs.

Effects of Benzylidene Substituent X on ρ^+(Y), ρ_F(Y), and ρ^+_R(Y). For the single-parameter correlation, the value of ρ^+(Y) decreases systematically as the benzylidene substituent X becomes more ED (Table 5; column 4); i.e., increasing electron donation by the benzylidene substituent decreases the sensitivity of the ^{13}C NMR chemical shift of the C=N carbon to the aniline substituent Y. Analogously, although the ratio $\rho_F(Y)/\rho^+_R(Y)$ varies by less than 15%, the correlation parameters ρ_F(Y) and ρ^+_R(Y) clearly change when the benzylidene substituent is changed (Table 6; columns 6 and 7; Figures 2 and 3). In both cases the correlation with σ is better than that with σ^+. In this respect, the situation is the same as that for the effect of X on δ_C(C=N). Both the inductive and the conjugative effects of Y

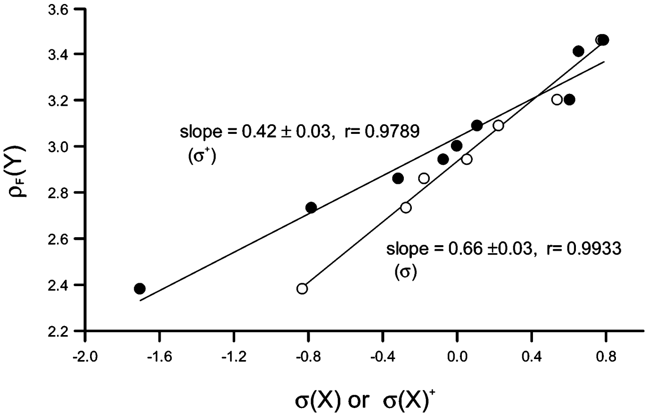


FIGURE 2. Plots of ρ_F(Y) for substituted benzylidene anilines p-X−$C_6H_4CH{=}NC_6H_4-$$p$-Y vs σ(X) or σ^+(X): ρ_F(Y) vs σ(X) (○), ρ_F(X) vs σ^+(X) (●), i.e., the effect of the benzylidene substituent on the sensitivity of δ_C(C=N) to aniline substitution.

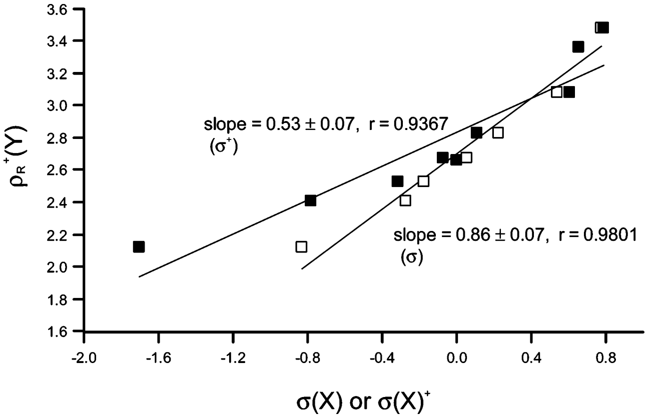


FIGURE 3. Plots of ρ^+_R(Y) for substituted benzylidene anilines p-X−$C_6H_4-CH{=}N-C_6H_4-$$p$-Y vs σ(X) or σ^+(X): ρ^+_R(Y) vs σ(X) (□), ρ^+_R(X) vs σ^+(X) (■), i.e., the effect of the benzylidene substituent on the sensitivity of δ_C(C=N) to aniline substitution.

TABLE 6. **ρ_F(Y) and ρ_R(Y) or ρ_F(Y) and ρ^+_R(Y) for Different Substituted Benzylidene Anilines p-X$-C_6H_4-CH{=}N-C_6H_4-$$p$-Y for the Correlation of δ_C(C=N) Values with σ_F(Y) and σ_R(Y) or σ_F(Y) and σ^+_R(Y) (eq 2)[a]**

X	ρ_F(Y)	ρ_R(Y)	r	ρ_F/ρ_R	ρ_F(Y)	ρ^+_R(Y)	r	ρ_F/ρ^+_R
a NO_2	2.81 ± 0.50	8.49 ± 0.65	0.9857	0.331	3.46 ± 0.10	3.48 ± 0.05	0.9994	0.994
b CN	2.79 ± 0.47	8.20 ± 0.62	0.9865	0.340	3.41 ± 0.09	3.36 ± 0.05	0.9995	1.01
c CF_3	3.17 ± 0.47	7.90 ± 0.51	0.9873	0.401	3.20 ± 0.10	3.08 ± 0.04	0.9995	1.04
d F	2.45 ± 0.35	6.53 ± 0.46	0.9886	0.375	2.94 ± 0.05	2.67 ± 0.03	0.9998	1.10
e Cl	2.57 ± 0.38	6.92 ± 0.50	0.9882	0.371	3.09 ± 0.06	2.83 ± 0.03	0.9998	1.09
f H	2.50 ± 0.35	6.52 ± 0.45	0.9890	0.383	3.00 ± 0.05	2.66 ± 0.02	0.9998	1.13
g Me	2.40 ± 0.33	6.19 ± 0.43	0.9888	0.388	2.86 ± 0.05	2.53 ± 0.03	0.9998	1.13
h OMe	2.29 ± 0.31	5.91 ± 0.41	0.9891	0.387	2.73 ± 0.05	2.41 ± 0.03	0.9997	1.13
i NMe_2	1.99 ± 0.28	5.20 ± 0.37	0.9885	0.383	2.38 ± 0.05	2.12 ± 0.03	0.9996	1.13

[a] Values of σ_F, σ_R, and σ^+_R are from ref 23.

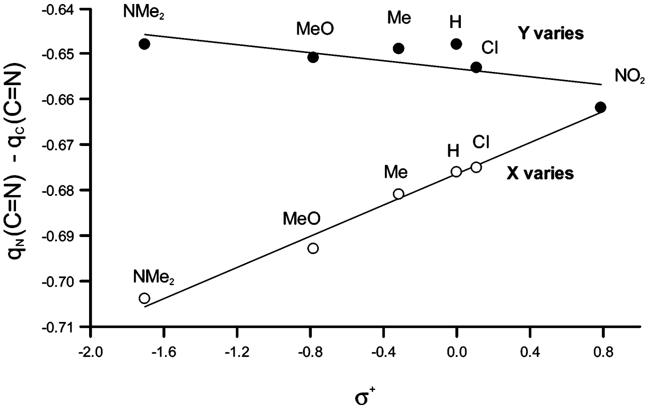


FIGURE 4. Correlation of the difference in the atomic charges (HF/6-31G*) between the C═N nitrogen and C═N carbon with substituent constant σ^+ for *N*-(*p*-X-benzylidene)-*p*-nitroanilines (○) and *N*-(*p*-nitrobenzylidene)-*p*-Y-anilines (●).

revealed the highest efficiency with the most EW benzylidene substituent (X = NO_2), while the weakest effect was observed with the most ED substituent (X = NMe_2). The effect of the benzylidene substituent X on ρ^+_R(Y) is ca. 1.3 times higher than its effect on ρ_F(Y). EW substituents X increase the contributions of resonance structures **15**, **16**, **18**, and **19** (Scheme 3) and, thereby, increase the sensitivity of the shielding of the C═N carbon to substituent Y. The higher the contributions of **15** and **16**, the more substitution Y can affect the shielding of the imine carbon by adjusting their contributions. On the other hand, EW substituents X decrease the contributions of resonance structures **10** and **13**. Accordingly, we conclude that changes in the contributions of those resonance structures which possess negative charge on the carbon affect the shielding of the C═N carbon more efficiently than do changes in the contributions of positively charged resonance structures. This result is in agreement with recent results obtained from comparisons of substituent effects on the ^{13}C NMR chemical shifts of the C═N carbon of imines and hydrazones.[8]

On the Atomic Charge Densities and the Conformations of Benzylidene Anilines. Leiva et al.[28] recently reported atomic charges (Mulliken Population Analysis, HF/6-31G*) for *N*-(*p*-nitrobenzylidenene)-*p*-Y-anilines (Y = NO_2, Cl, H, Me, MeO, or NMe_2) and for *N*-(*p*-X-benzylidene)-*p*-nitroanilines (X = NO_2, Cl, H, Me, MeO, or NMe_2). We correlated the atomic charge differences between the C═N nitrogen and the C═N carbon, q_N(C═N) − q_C(C═N), with the substituent constant σ^+ of the substituent in question for these two series (Figure 4). As the substituent on the benzylidene ring (X) becomes more electron-donating, the charge difference between the nitrogen and the carbon becomes more negative. This provides excellent support for the resonance polarization concept discussed above on the basis of the ^{13}C NMR chemical shift behavior. Nitrogen is more electronegative than carbon. Consequently, q_N(C═N) − q_C(C═N) is always < 0. The presumed increase in the contribution of **10** (Scheme 3) by ED substituents X should increase the numerical value of q_N(C═N) − q_C(C═N), as is observed (Figure 4; the lower line). On the other hand, as the substituent on the aniline ring (Y) becomes more ED, the charge difference between the nitrogen and the carbon becomes less negative (Figure 4; the upper line). This too is in accordance with our resonance polarization concept. The increase in the contribution of **15** by ED substituents Y is expected to make q_N(C═N) − q_C(C═N) less negative. Thus, the interpretation of the ^{13}C NMR results with the aid of the substituent sensitive balance of the resonance contributors as discussed above is verified by the computational data.

The ab initio calculations (HF/3-21G) predict an essentially planar structure for *N*-(*p*-nitrobenzylidene)-*p*-(*N*,*N*-dimethylamino)aniline and a twisted structure for *N*-[*p*-(*N*,*N*-dimethylamino)-benzylidene]-*p*-nitroaniline, in line with the crystallographic data.[29] In the gas phase, the dihedral angle between the *p*-nitroaniline ring and the rest of the molecule, which is almost planar, is ca. 30°. In the solid state, the crystallographic data for *N*-[*p*-(*N*,*N*-dimethylamino)benzylidene]-*p*-nitroaniline show that the benzylidene ring is essentially coplanar with the C═N bond, while the aniline ring is twisted by ca. 40−50° from the plane of the rest of the molecule. Closely similar results have been obtained with *N*-(*p*-methylbenzylidene)-*p*-nitroaniline (dihedral angle 53°). On the other hand, in the solid state the molecule of *N*-(*p*-nitrobenzylidene)-*p*-(*N*,*N*-dimethylamino)-aniline is almost planar, the aniline and benzylidene rings being twisted by 9° and 4°, respectively, relative to the C−C═N−*C* axis.[29] These data, together with the crystallographic data obtained for *N*-(*p*-nitrobenzylidene)-*p*-methylaniline and *N*-(*p*-nitrobenzylidene)-*p*-methoxyaniline, suggest that the dihedral angle between the aniline ring and the rest of the molecule depends on the aniline substitution both in the solid state and in the gas phase. Koleva et al.[30] have calculated (AM1) the twist of the aniline ring for a series of *N*-[*p*-(*N*,*N*-dimethylamino)-benzylidene]-*p*-Y-anilines (28.0°−35.6°). We correlated the reported values[30] of the dihedral angle with substituent constants σ^+(Y) and observed a satisfactory correlation with a slope of 4.7 ± 0.4 ($r = 0.9756$; $n = 9$). Further, the recent work by Proks[31] reports the computed (B3LYP/6-311G**) values of the dihedral angle (τ) between the aniline ring and the rest of the molecule for *N*-(*p*-nitrobenzylidene)-*p*-Y-anilines in the gas phase and in DMSO as solvent (15 substituents Y). Despite the fact that Proks calculated the dihedral angles for the different substituents, no correlations with the substituent parameters were given. Accordingly, we have analyzed his data. Figure 5 depicts the correlations between the dihedral angle τ and substituent parameter σ^+. The statistical data for the correlations are shown in Tables S2 and S3. Satisfactory correlations between τ and substituent constant σ were found both for the gas-phase values and for the dihedral angle values observed in DMSO as solvent. The electronic effects adjust the conformation of the molecule in the gas phase and in DMSO. The larger the dihedral angle between the aniline ring and the rest of the molecule, the more EW the aniline substituent. The dihedral angle τ in DMSO solution is slightly more sensitive to the substituent than in the gas phase (cf. Tables S2 and S3). The fit of the correlations was improved when substituent parameter σ^+ was used instead of σ (Table S2; columns 4 and 5). The dual substituent parameter approach (Table S2; columns 6−9) allows an evaluation of the relative contributions of inductive and resonance effects. The values of ratio ρ_F/ρ^+_R are closely similar in the gas phase and in DMSO solution. Further, $\rho_F/\rho^+_R = 0.730$ (Table S2; IEF-PCM value) is not far from the value $\rho_F/\rho^+_R = 0.994$ observed

---

[27] Wiberg, K. B. *J. Org. Chem.* **2002**, *67*, 1613, 4787.

[28] Leiva, A. M.; Vargas, V.; Morales, R. G. E. *Spectrosc. Lett.* **2002**, *35*, 611.

[29] Morley, J. O. *J. Mol. Struct.* **1995**, *340*, 45 and references therein.

[30] Koleva, V.; Dudev, T.; Wawer, I. *J. Mol. Struct.* **1997**, *412*, 153.

[31] Proks, V. *THEOCHEM* **2005**, *725*, 69.

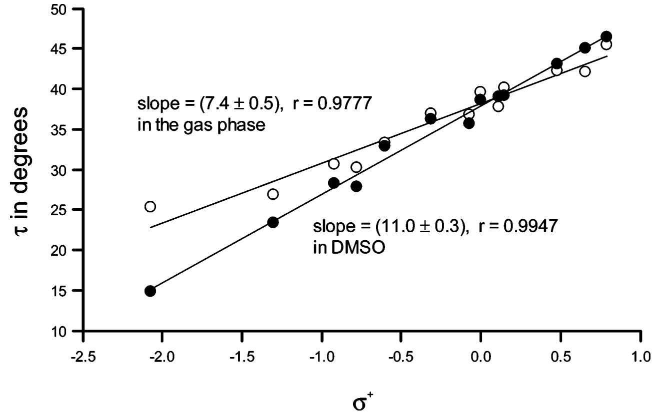


FIGURE 5. Correlation between the computed (B3LYP/6-311G**) dihedral angle τ between the aniline ring and the rest of the molecule in the gas phase (○) and in DMSO (IEF-PCM values) (●) for *p*-Y-substituted *N*-(*p*-nitrobenzylidene)anilines and substituent parameter σ^+. The values of τ are from ref 31.

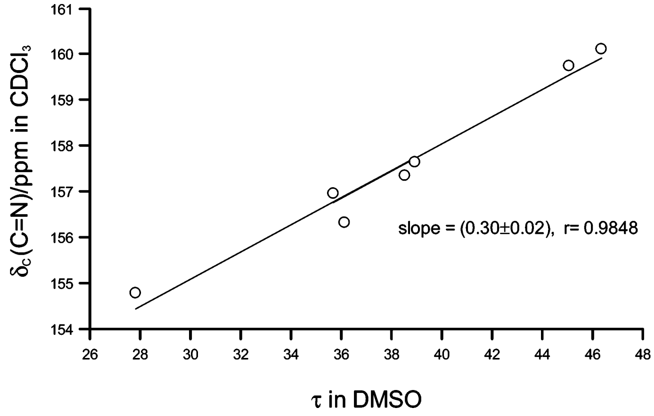


FIGURE 6. Correlation between the ^{13}C NMR shifts in CDCl$_3$ (this work) and the computed (B3LYP/6-311G**) dihedral angle τ (from ref 31) between the aniline ring and the rest of the molecule for *p*-Y-substituted *N*-(*p*-nitrobenzylidene)anilines in DMSO (IEF-PCM values).

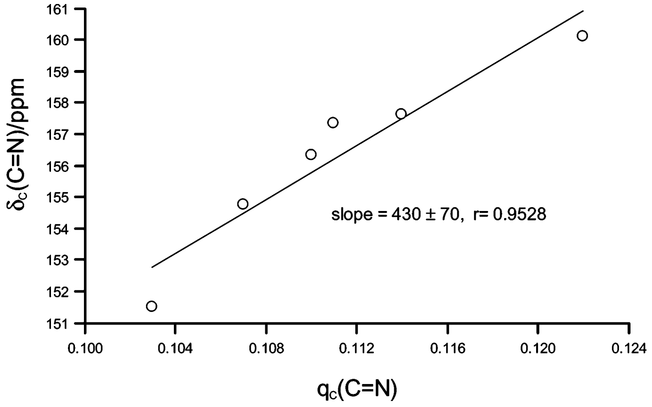


FIGURE 7. Correlation between the ^{13}C NMR shifts in CDCl$_3$ (this work) and the computed atomic charges (Mulliken Population Analysis, HF/6-31G* from ref 28) for *p*-Y-substituted *N*-(*p*-nitrobenzylidene)-anilines.

in the present study for the effect of substituent Y on the shielding of the C═N carbon for *N*-(*p*-nitrobenzylidene)-*p*-Y-anilines (Table 6). A good correlation was observed between the δ_C(C═N) values of *p*-Y-substituted *N*-(*p*-nitrobenzylidene)-anilines (this work) and the dihedral angle under discussion (Figure 6). A satisfactory correlation was likewise observed between the δ_C(C═N) values of these derivatives (this work) and the atomic charges of the imine carbon[28] (Figure 7). The more ED the aniline substituent, the greater the amount of electron density transferred from the aniline ring to the carbon of the C═N unit. At the same time, the dihedral angle between the plane of the aniline ring and that defined by the benzylidene ring and the C═N unit (if we consider them to be coplanar) decreases. The same electronic substituent effects adjust both the atomic charge on the C═N carbon and the planarity/nonplanarity of the benzylidene aniline molecular core. This is valuable information in view of the design of liquid-crystal molecules. A perpendicular arrangement ($\tau = 90°$) of the two planes (that of the aniline ring and that of the rest of the molecule) is the most favorable for the n-π conjugation involving the nitrogen lone pair and the π-electrons of the aniline ring. Increase in the EW ability of the aniline ring substituent obviously increases this electronic interaction and leads to a more positive charge of the imine carbon in parallel with an increase in the dihedral angle τ. We recently reported a corresponding substituent-dependent change in the dihedral angle between the phenyl ring and the rest of the molecule for phenyl acetates and trifluoroacetates. In those cases, the conjugative interaction between the lone pair of the ether oxygen and the π-electrons of the phenyl ring increases as the ED ability of the phenyl substituent increases.[32] Hence, the dihedral angle increases in parallel with the ED ability of the phenyl ring substituent. In light of the present results, it is obvious that the extent of the effect of the aniline substituent on the charge generation at the C═N bridging group in the benzylidene aniline system is systematically adjusted by the electronic character of the benzylidene substituent. A similar type of substituent cross-interaction has recently been observed in benzhydryl cation and anion formation.[33]

Conclusions

Both the benzylidene substituents and the aniline substituents in derivatives **1**−**8** (Scheme 1), X and Y, respectively, have been seen to have a systematic electronic effect on the shielding of the imine carbon in these substituted benzylidene anilines. The benzylidene substituents display an effect opposite to the normal one, whereas the aniline substituents exhibit a normal effect. The variations in the donor and acceptor properties of the benzylidene or aniline substituents lead to characteristic changes in the polarity of the C═N group. The inductive effects of the substituents on the benzylidene ring predominate over the resonance effects. In contrast, for substituents on the aniline ring, the contributions of the inductive and resonance effects are closely similar. Furthermore, the substituents on the neighboring aromatic ring systematically attenuate or enhance the effect of the substituent on the other ring. A subtle adjustment of the electron distribution is achieved on variation of the substituents X and Y, its extent correlating with substituent parameters. The zwitterionic nature of the resonance structures **14**, **17**, and **18** in Scheme 3 describes the polar character of the whole molecule. Comparison of the literature values of the atomic charges of the imine group and the dihedral

---

(32) Neuvonen, H.; Neuvonen, K.; Koch, A.; Kleinpeter, E. *J. Phys. Chem. A* **2005**, *109*, 6279.

(33) Kim, C. K.; Lee, K. A.; Sohn, C. K.; Sung, D. D.; Oh, H. K.; Lee, I. *J. Phys. Chem. A* **2005**, *109*, 2978.

angle characterizing the twist of the aniline ring revealed that substituent-induced changes in the conformation of the molecule and in the shielding of the imine carbon occur in parallel. The optimal use of the nonlinear optical materials and the design of new candidates for that purpose necessitate a deep understanding of the molecular origin of the macroscopic characteristics of the liquid-crystal systems. The information collected in the present work is valuable when the specific properties of mesogenic molecules are tailored.

Experimental Section

Materials. Series **5** was prepared as previously described.[8] The other syntheses were performed by means of a standard procedure: Freshly distilled or crystallized amine (1 mmol) was dissolved in 5 mL of methanol, and 1 mmol of freshly distilled or crystallized aldehyde was added. After the mixture stood at room temperature for 1 h, the solvent was evaporated off, and the products were recrystallized. The analytical data are given in Table S1 (Supporting Information). Preparation of **1c** was not successful.

Spectroscopic Measurements. ^{13}C NMR spectra (125.78 MHz) were recorded in $CDCl_3$ at 25 °C at a concentration of 0.1 mol dm^{-3}. This low and constant sample concentration was used to avoid any disturbances from intermolecular associations. The deuterium of the solvent was used as a lock signal. The spectra were measured with a ^{1}H broad-band decoupling technique. The chemical shifts are expressed in ppm relative to TMS (0 ppm) applied as an internal reference.

Supporting Information Available: A more detailed explanation of the effect of aniline substituent Y on $\rho_F(X)$ and $\rho_R(X)$. Analytical data for the prepared compounds. Statistical data for the correlation of the literature values of the dihedral angle τ between the aniline ring and the rest of the molecule in *p*-substituted *N*-(*p*-nitrobenzylidene)-anilines with different substituent parameters. Statistical data for the cross-correlations of the literature values of the dihedral angle τ between the aniline ring and the rest of the molecule in *p*-substituted *N*-(*p*-nitrobenzylidene)anilines in DMSO vs the values in the gas phase. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0600508