# MODELING SUBSTITUENT-DEPENDENCE OF THE TWIST AND SHIELDING IN A SERIES OF 4-SUBSTITUTED *N*-(4-NITROBENZYLIDENE)ANILINES

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Received February 16, 2004
Accepted July 2, 2004

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A series of 15 4-substituted *N*-(4-nitrobenzylidene)anilines was synthesized and studied by $^1$H NMR spectroscopy. Their ab initio calculated geometries and the shielding as expressed by aromatic ring currents were used in correlation analysis. The geometries were fully optimized using density functional theory B3LYP/6-311G** approaches. For the determination of the ring current contribution to the shielding of azomethine hydrogens $H_\alpha$ was used direct ab initio calculation of the chemical shielding in a model system. Experimental chemical shift values free of these contributions were successfully correlated with increments $a_p$ of chemical shift for monosubstituted benzenes. In the same manner, the contribution of the anisotropy of C=N double bond to $H_m$ hydrogen were calculated and values of the $H_m$ chemical shift free of this contribution were successfully correlated with increments of chemical shift $a_m$.

**Keywords**: Ab initio calculations; Correlation analysis; Azomethines; $^1$H NMR chemical shifts; Imines; Substituent effects; Conformation analysis; NMR spectroscopy.

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In recent years an increasing interest in polymer materials with good conducting[1–3], fiber-forming[4], liquid-crystalline[5,6], and non-linear optical[7,8] properties has been observed. Some of these materials are based on *N*-benzylideneaniline monomer units thanks to their elongated and π-conjugated structure. For better prediction of the behavior of these polymer materials, an understanding of the relationships between the chemical structure and physical properties of the monomer molecules could be useful[9,10].

The most important feature of the *N*-benzylideneaniline geometry is the twist of the aniline ring from the plane of the rest of the molecule. The

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doi:10.1135/cccc20041566

non-planar conformations and substitution dependences of the deviation of the aniline ring from the C=N plane bond were studied by spectroscopic methods[11,12], X-ray crystallography[13], and also by quantum chemical calculations[14,15].

An interesting phenomenon is related to the behavior of azomethine hydrogen $H_\alpha$ chemical shift. It was observed that when variable substituents are situated in para position of the benzylidene ring[16] (see Fig. 1, where the nitro group is placed in this particular position), the $^1H$ chemical shift of the azomethine hydrogen $H_\alpha$ can be correlated very well with the Hammett $\sigma_p$ constants[17] of the substituents and with the increments of the chemical shift $a_p$ [18] defined as a difference between $^1H$ NMR chemical shift of a hydrogen atom in benzene and in benzene substituted in para position relative to this hydrogen. They reflect electron density changes in particular position relative to the hydrogen in question. Since N=C group is bonded to the same carbon atom as the above-mentioned hydrogen, the change in electron density on $H_\alpha$ is expected to be proportional to the change in the increment $a_p$. These correlations indicate electronic effects of the substituents. In contrast, the correlation slope of the $H_\alpha$ signals in the case of 4-substituted aniline ring approaches zero[16], which could be erroneously explained by an independence of the chemical shifts on variable substituents[9,19,20].

It was shown[16,21,22] that the small range of chemical shifts can be explained by a competitive action of two effects: the electronic effect of the para substituent through bonds and the change in ring current anisotropy contribution to the shielding of the proximal $H_\alpha$ hydrogen atom. This change is again caused by the para substituent (X in Fig. 1) since the electron density redistribution on the C(aryl)–N bond changes the contribution from the conjugation of the aromatic π-electron conjugation with N=C(α) π-electron and N atom n-electrons. This affects the twist angle around the C(aryl)–N bond and, consequently, the position of the $H_\alpha$ atom with respect to the aniline ring.

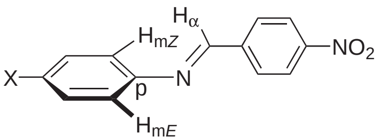

FIG. 1
4-Substituted *N*-(4-nitrobenzylidene)anilines

An alternative explanation based on the lack of the substituent effect[19] due to 90° twist in the molecule can be rejected on the basis of other successful correlations, e.g., internal chemical shift of ethyl group[16], $^{13}$C NMR chemical shift[23], and $^{19}$F NMR chemical shifts[24] in para position of the benzylidene ring or $^{1}J_{CH}$ in azomethine C(α)–$H_{\alpha}$ group[22,25] with the Hammett $\sigma_p$ of the variable para substituent X in aniline ring. These observations show that the effect of the X-substituent is transmitted throughout the whole molecule.

Since these successful correlations can be regarded only as an indirect proof of the twist in the molecule and of the ring current contribution to the chemical shielding, we have decided to reinvestigate this topic using ab initio calculations[26]. Our aim was to prove that the dihedral angle between the aniline ring and C(aryl)–N(=)–$H_{\alpha}$ plane depends on the X-substituent and that the $^{1}$H NMR chemical shifts of $H_{\alpha}$ corrected for ring current shielding correlate well with the electronic effect of the X-substituent. In particular, we evaluated the ring current chemical shielding by direct ab initio calculation[26] in the point of interest around the model system.

Of different variables characterizing the effect of the substituent in the para position we have selected $^{1}$H NMR chemical shift increments[18], $a_p$, on the basis of the highest coefficients of correlation to investigated variables[27]. Neither $^{13}$C NMR chemical shift increments[18], $z_p$, nor Hammett $\sigma_p$ or dual $\sigma_F$ and $\sigma_R$ constants describe better the transmission of the X-substituent effect to the para position of the aniline ring, to the N=CH group is concerned.

## EXPERIMENTAL

*N*-Benzylideneanilines were prepared by melting equimolar amounts of a 4-substituted aniline and 4-nitrobenzaldehyde in sand bath until the evolution of water vapor ceased. This took at 120 °C typically 30 min. The products were crystallized from ethanol. The benzylideneanilines were characterized by their melting points (Table I). All compounds gave satisfactory elemental analyses and were pure according to TLC on silica. $^{1}$H NMR spectra were recorded on a 500 MHz Bruker DRX AVANCE spectrometer in dimethyl sulfoxide (DMSO-$d_6$) under conditions of infinite dilution using tetramethylsilane (TMS) as an internal standard. Ortho and meta chemical shifts for *p*-substituted benzenes were calculated as for an AA′BB′ system.

Quantum chemical calculations were performed on an SGI Power Challenge XL supercomputer. Geometries of 4-substituted *N*-(4-nitrobenzylidene)anilines studied here were optimized using different quantum chemical methods. First, at the HF/6-31G* level, the above-mentioned dihedral angle was set to values from the interval between 0 and 180° with the increment of 45° and the full geometrical optimization was performed. For each molecule this procedure converged to the same conformer. Subsequently, the geometries of these conformers were employed as an initial guess for full geometrical optimizations using B3LYP/6-311G** approach. Moreover, the harmonic vibrational frequencies for the B3LYP/6-311G** geometries of all the compounds were calculated at this level of theory; all the frequencies were found to be real. Consequently, it was thus verified that minima were obtained. The density functional theory based B3LYP approach combines Becke's three-parameter exchange[28] and the Lee–Yang–Parr correlation[29] functionals. For NMR shielding calculation the gauge-including atomic orbital (GIAO) formalism and the B3LYP/6-311G** method were adopted. This computational strategy also provides for the current densities (Fig. 2 shows an example).

All quantum chemistry calculations were performed using the Gaussian 94 suite of programs[26], statistical calculations were carried out on PC using own scripts written in Matlab (The MathWorks, Natick (MA), U.S.A.)

## RESULTS AND DISCUSSION

Since the success of correlation strongly depends on the number of measurements (in the present case equal to the number of compounds), fifteen 4-substituted *N*-(4-nitrobenzylidene)anilines for substituents (see Fig. 1 and Table I) were prepared. As was observed previously[16], the correlation of the chemical shift of the $H_o$ hydrogen $\delta(H_o)$ with increments of chemical shift $a_o$ is satisfactory (cf. Eq. (*1*); $r$ is the correlation coeficient and $s_e$ is the standard error of the $\delta(H_o)$.

$$\delta(H_o) = 0.90_{(0.08)}\, a_o + 7.41_{(0.04)} \qquad (1)$$

$$r = 0.9514,\ s_e = 0.1603$$

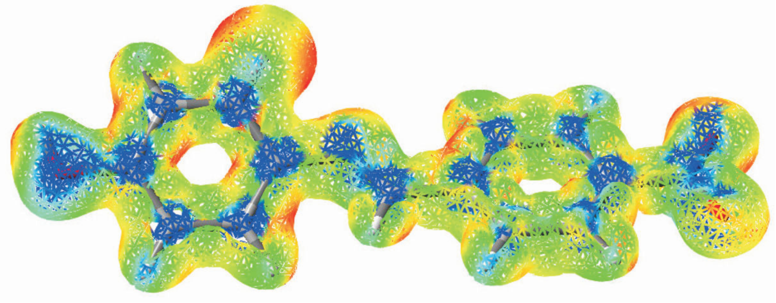

FIG. 2

The electron density distribution of 4-hydroxy-*N*-(4-nitrobenzylidene)aniline obtained from the *y*-component of the B3LYP-GIAO/6-311G**-computed current density (the *y*-axis is directed approximately parallel to the plane of the aniline ring)

In contrary to that, the correlation of the $H_\alpha$ proton with the $a_p$ chemical shift increments is unreliable. Namely, the regression slope approaches zero which could be erroneously taken as an independence of $\delta(H_\alpha)$ on $a_p$ increments of chemical shift (see Eq. (*2*) and discussion above).

$$\delta(H_\alpha) = 0.06_{(0.02)}\, a_p + 8.806_{(0.006)} \qquad (2)$$

$$r = 0.6677,\ s_e = 0.02$$

Low $s_e$ value (0.02) testifies that some degree of correlation between the chemical shifts and the $a_p$ increments exists. Moreover, the correlation coefficient of orthogonal regression[30] – the value not dependent on the slope of the regression line – is high (0.9981) due to a close proximity of the points to the regression line.

TABLE I

Characteristics of the prepared 4-substituted *N*-(4-nitrobenzylidene)anilines (increments of chemical shift $a_o$, $a_m$, and $a_p$; $^1$H NMR chemical shift of $H_\alpha$, $H_o$, and $H_m$; the experimental and published (references are given in parentheses) melting points)

| Entry | X | $a_0$ | $a_m$ | $a_p$ | $\delta(H_\alpha)$ ppm | $\delta(H_0)$ ppm | $\delta(H_m)$ ppm | M.p. °C | M.p. °C (lit.) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $NEt_2$ | –0.66 | –0.18 | –0.67 | 8.7961 | 6.7153 | 7.3603 | 142–143 | 146 (34) |
| 2 | $NH_2$ | –0.75 | –0.25 | –0.65 | 8.7721 | 6.6233 | 7.2435 | 166–167 | NA[a] |
| 3 | OMe | –0.48 | –0.09 | –0.44 | 8.8065 | 7.0059 | 7.3881 | 134–135 | 136–139 (35) |
| 4 | OH | –0.56 | –0.12 | –0.45 | 8.7246 | 6.8429 | 7.2860 | 168 | 168.5 (36) |
| 5 | NHCOMe | 0.12 | –0.07 | –0.28 | 8.7817 | 7.6585 | 7.3394 | 223–226 | 223–226 (37) |
| 6 | F | –0.26 | 0.00 | –0.20 | 8.7946 | 7.2689 | 7.4127 | 112–113 | 109–110 (38) |
| 7 | Cl | 0.03 | –0.02 | –0.09 | 8.7955 | 7.4854 | 7.3660 | 134 | 134–136 (35) |
| 8 | Br | 0.18 | –0.08 | –0.04 | 8.7918 | 7.6128 | 7.2962 | 160–161 | 166–167 (37) |
| 9 | Me | –0.14 | –0.06 | –0.17 | 8.8047 | 7.4127 | 7.2737 | 122–123 | 125–127 (35) |
| 10 | H | 0.00 | 0.00 | 0.00 | 8.8048 | 7.4548 | 7.3475 | 89–90 | 89–90.5 (39) |
| 11 | CN | 0.36 | 0.18 | 0.28 | 8.7987 | 7.9095 | 7.4574 | 190 | 172 (37) |
| 12 | COMe | 0.62 | 0.14 | 0.21 | 8.8216 | 8.0336 | 7.4112 | 143–144 | 146 (40) |
| 13 | COOEt | 0.71 | 0.11 | 0.21 | 8.8220 | 8.0319 | 7.4110 | 177–178 | 177–178 (38) |
| 14 | $CONH_2$ | 0.61 | 0.10 | 0.17 | 8.8365 | 7.4917 | 7.3781 | 187–188 | NA[a] |
| 15 | $NO_2$ | 0.95 | 0.26 | 0.38 | 8.8400 | 8.3095 | 7.5101 | 202–203 | 200 (41) |

[a] NA, not available.

Clearly, there are several different contributions to the chemical shift of $H_\alpha$ in the investigated systems. In 1997 Wawer et al.[15] prepared nine 4-substituted *N*-[4-(dimethylamino)benzylidene]anilines and calculated by the semiempirical AM1 method[38] their geometries. Dihedral angles between the aniline ring and the N=C–$H_\alpha$ plane were found in the range from 28° (X = OMe) to 35.6° (X = $NO_2$). The correlation with $a_p$ increments was rather good ($r = 0.9650$; our result).

The resulting dihedral angles are shown in Table II and regression parameters with $a_p$ variable are in the upper part of Table III. It can be seen that all parameters are statistically significant – their ratio to corresponding standard deviation ($sb_0$ and $sb_1$, respectively) is always larger than the critical value of Student's t-distribution.

The next step was the determination of the anisotropy contribution due to the aniline ring current to the shielding of the $H_\alpha$ atom. Three different

TABLE II
Dihedral angles (in °) between aniline ring and the rest of the molecule in 4-substituted *N*-(4-nitrobenzylidene)aniline series as obtained by the DFT geometrical optimizations, values of the benzene ring current anisotropy contribution $\Delta\sigma(H_\alpha)$ to the chemical shift of $H_\alpha$ the absolute chemical shielding in $HN{=}CH_2$ model system at the positions corresponding to the $H_m$, and the average value $\Delta\sigma(H_m)$. See the text for details

| Entry | Substituent | γ | $\Delta\sigma(H_\alpha)$ ppm | $\Delta\sigma(H_{mZ})$ ppm | $\Delta\sigma(H_{mE})$ ppm | $\Delta\sigma(H_m)$ ppm |
|---|---|---|---|---|---|---|
| 1 | $NEt_2$ | 21.272 | –0.4984 | –0.1032 | –0.4827 | –0.2929 |
| 2 | $NH_2$ | 26.828 | –0.4855 | –0.0918 | –0.4594 | –0.2756 |
| 3 | $OCH_3$ | 30.256 | –0.4553 | –0.0716 | –0.4271 | –0.2494 |
| 4 | OH | 30.568 | –0.4472 | –0.0655 | –0.4159 | –0.2407 |
| 5 | $NHCOCH_3$ | 33.290 | –0.4150 | –0.0418 | –0.3771 | –0.2095 |
| 6 | F | 36.812 | –0.3804 | –0.0160 | –0.3362 | –0.1761 |
| 7 | Cl | 37.799 | –0.3488 | –0.0430 | –0.3084 | –0.1757 |
| 8 | Br | 40.170 | –0.3435 | 0.0063 | –0.3040 | –0.1489 |
| 9 | $CH_3$ | 36.986 | –0.3770 | –0.0133 | –0.3306 | –0.1720 |
| 10 | H | 39.550 | –0.3400 | 0.0106 | –0.2952 | –0.1423 |
| 11 | CN | 42.117 | –0.2919 | 0.0468 | –0.2448 | –0.0991 |
| 12 | $COCH_3$ | 43.179 | –0.2974 | 0.0456 | –0.2485 | –0.1015 |
| 13 | COOEt | 42.178 | –0.3134 | 0.0317 | –0.2674 | –0.1179 |
| 14 | $CONH_2$ | 40.321 | –0.3303 | 0.0180 | –0.2988 | –0.1404 |
| 15 | $NO_2$ | 45.409 | –0.2759 | 0.0606 | –0.2263 | –0.0828 |

strategies for the determination of the ring current contribution to the shielding of azomethine hydrogen $H_\alpha$ were used, namely, the McConnell[31] approach, Haigh–Mallion[32] model, and direct ab initio calculation of the chemical shielding in a model system. However, the semiempirical methods by McConnell and Haigh–Mallion did not yield satisfactory results (data not shown). In the ab initio approach, the absolute chemical shielding ($\Delta\sigma$) was calculated for the position in space corresponding to the position of $H_\alpha$ in the compounds investigated. Thus, the system was approximated by benzene and the chemical shielding was calculated at the point in space originally occupied by the $H_\alpha$ hydrogen of a given *N*-(4-nitrobenzylidene)aniline. The B3LYP/6-311G** geometries were used. The chemical shielding data thus obtained can be used as an approximation of the ring-current contribution of the benzene ring to $H_\alpha$ hydrogen. Resulting $\Delta\sigma(H_\alpha)$ values are given in Table II. These calculated values of the diamagnetic anisotropy depend on the dihedral angle.

$$\Delta\sigma(H_\alpha) = 0.0104_{(0.0006)}\,\gamma - 0.75_{(0.02)} \qquad (3)$$

$$r = 0.9809,\ s_e = 0.0144$$

Moreover, the diamagnetic anisotropy data can be successfully correlated with increments of chemical shift $a_p$ (see Table III).

TABLE III

Results of linear regressions between a given dependent variable and the $a_p$ chemical shift increments; symbols $b_0$, $b_1$, $r$, and $s_e$ stand for the intercept, slope, correlation coefficient, and standard error of estimate, respectively. In the upper part the regressions of dihedral angles vs $a_p$ increments are given, in the lower part the results according to Eq. (*4*) are summarized (see the text for details)[a]

| Dependent variable | $b_0$ | $sb_0$ | $b_1$ | $sb_1$ | $r$ | $s_e$ | Number of the outlier |
|---|---|---|---|---|---|---|---|
| $\gamma$ | 38.7140 | 0.4891 | 19.5259 | 1.4259 | 0.9671 | 1.1858 | 1 |
| $\Delta\sigma$ | –0.3487 | 0.0030 | 0.2125 | 0.0088 | 0.9888 | 0.0111 | NA[b] |
| $H_\alpha$ | 8.8059 | 0.0059 | 0.0558 | 0.0172 | 0.6677 | 0.0216 | 4 |
| $H_\alpha + \Delta\sigma$ | 8.4572 | 0.0058 | 0.2682 | 0.0168 | 0.9754 | 0.0210 | 4 |
| $H_\alpha + \Delta\sigma$ (–4) | 8.4601 | 0.0033 | 0.2536 | 0.0099 | 0.9910 | 0.0119 | 11 |

[a] $\gamma$ values from Table I; $\Delta\sigma$ values from Table II; (–4) = point 4 left out from the regression.
[b] NA, not available.

After addition of the calculated shielding $\Delta\sigma(H_\alpha)$ (Table II) to the experimental chemical shifts (i.e., subtraction of the contribution to the shielding), the chemical shifts free of the benzene ring current contribution were obtained. These shift data were correlated with increments of chemical shift $a_p$ according to Eq. (*4*).

$$\delta(H_\alpha) + \Delta\sigma = b_0 + b_1 * a_p + \varepsilon \,, \tag{4}$$

where ε is the residual.

The correlations were much better than in the case without the correction for diamagnetic anisotropy contribution (Table III, $H_\alpha$ row).

In all these regressions the point 4 (X = OH) was classified as an outlier[27]. This can be caused by solvent effect: our spectra were measured in DMSO-$d_6$, while the increments[18] of chemical shifts, $a_p$, were obtained from $^1$H NMR experiments in $CDCl_3$. Probably, the substituent group OH interacts with solvent more strongly than the others, therefore, the $a_p$ value for OH group is biased. When this point was left out (last row in Table III), the value of correlation coefficient significantly increased. Another contribution related to the solvent effect is caused by the absence of solvent molecules in the performed quantum chemical calculations. In particular, an inclusion of explicit solvent molecules in the calculation leads to a small change of the dihedral angle γ as compared with in vacuo results[33]. The quality of correlations is also affected by the fact that all models employed are restricted to benzene molecule and do not explicitly consider the effect of the X-substituent on the electron density in the ring. Understanding the relationship between the degree of conjugation, dihedral angle and X-substituent can be further used in a study of solvent-dependent benzylideneaniline geometries, which in progress[33].

Similarly to the case of $H_\alpha$ hydrogen, correlation of $H_m$ with increments of chemical shift is not optimal (Eq. (*5*)).

$$\delta(H_m) = 0.43_{(0.08)}\, a_m + 7.37_{(0.01)} \tag{5}$$

$$r = 0.8452,\ s_e = 0.04$$

Thus, in the same way as in the case of $H_\alpha$ proton, an attempt was made to estimate the combined influence of diamagnetic anisotropies of C=N double bond and of the lone pair of nitrogen to the chemical shifts of $H_m$'s. Subsequently, the $H_m$ proton chemical shifts free of this combined contribution were correlated with $a_m$ increments of chemical shift for monosubstituted benzenes. Namely, the diamagnetic anisotropy contributions were computed for the model system $H_2C{=}NH$ in the same geometry as obtained from the B3LYP/6-311G** optimizations of the compounds from our set. Thus, the absolute chemical shielding in the positions corresponding to $H_m$ protons was calculated by the same B3LYP-GIAO approach as in the case of $H_\alpha$ (vide supra). As was the case with $H_\alpha$ protons, the McConnell and Haigh–Mallion models were not able to provide for satisfactory correlations (data not shown). Clearly, the $H_Z$ and $H_E$ protons differ in their position with respect to the C=N bond. As a consequence, the absolute chemical shielding at the corresponding points around the $H_2C{=}NH$ model is markedly different (cf. Table II). However, due to a practically free rotation around the C–N bond (for example, the B3LYP/6-311G**-calculated rotation barrier for 4-nitro-*N*-(4-nitrobenzylidene)aniline is 1.302 kcal/mol [33]), the average of the $\Delta\sigma(H_{mZ})$ and $\Delta\sigma(H_{mE})$ values can be taken as the chemical shielding of the $\Delta\sigma(H_m)$. The resulting correlation is summarized by Eq. (*6*).

$$\delta(H_m) + \Delta\sigma(H_m) = 0.87_{(0.05)}\, a_m + 7.195_{(0.007)} \qquad (6)$$

$$r = 0.9770,\ s_e = 0.03$$

The correlation is now markedly improved when compared to the results obtained for data which are not corrected for the effect of diamagnetic anisotropy.

## CONCLUSIONS

By using quantum chemical calculations of the 4-substituted *N*-(4-nitrobenzylidene)anilines, the twist of aniline ring, γ, from the rest of the molecule was shown. The ability to predict γ values could be employed in modeling work on the properties of polyazomethines. Both frequently used models of the shielding exerted by the aromatic ring current, i.e., McConnell's and Haigh–Mallion's, were found inadequate for this system; only the ab initio calculated chemical shielding based on the geometries optimized by the DFT B3LYP/6-311G** method was found satisfactory for linear regressions between the variable electronic effect of X-substituent and the chemical shift increments.

*Time allocation in the Czech Academic Supercomputer Center is gratefully acknowledged.*

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