January, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 301—303 (1985)* 301

# A New Aspect on the Origin of an Anomalous Substituent Effect on the Azomethine Proton Chemical Shifts in 4-Substituted *N*-Benzylideneanilines

Ryoichi Akaba, Hirochika Sakuragi, and Katsumi Tokumaru*
*Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305*

(Received July 14, 1984)

Carbon-13 chemical shifts, azomethine proton chemical shifts, and azomethine carbon-hydrogen coupling constants have been determined for *N*-benzylideneaniline and its several derivatives bearing *o*-methyl and/or *p*-nitro groups on the aromatic ring on the nitrogen atom (ring A). The anomalous upfield shift of the azomethine proton caused by introduction of a 4-nitro group on the ring A can be attributed to the increase in the twist angle $\theta_N$ of the ring A from the molecular plane containing the C=N bond.

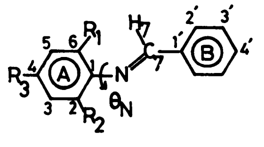
Molecular conformations of *N*-benzylideneanilines have been studied by many workers,[1] and in previous papers, the present authors have shown that introduction of a 4-nitro group as well as 2,6-dimethyl groups increases the twist angle $\theta_N$ (formula shown below) in solution by UV spectroscopy,[1] and in gas phase by photoelectron spectroscopy.[2]

Concerning NMR of *N*-benzylideneanilines, one of the present authors reported with collabolators an anomalous substituent effect on the azomethine proton ($H_7$) chemical shifts for a series of 4-substituted *N*-benzylideneanilines, $C_6H_5CH=NC_6H_4$-X-4, in which with the increase in electron-withdrawing property of the 4-substituents $H_7$ exhibited an unexpected upfield shift ($\rho$=+0.04) whereas for a series of 4'-substituted *N*-benzylideneanilines, 4-Y-$C_6H_4CH=NC_6H_5$, $H_7$ exhibited a normal downfield shift ($\rho$=−0.16) with the increase in the electron-withdrawing property of the substituents.[3] The origin of this anomalous substituent effect has been argued,[4—9] for example, in terms of a through-space field effect,[3,5,8] but still remains puzzling.

We now wish to propose that this anomalous substituent effect originates primarily from the change of molecular conformation with the substituent as previously shown by UV[1] and photoelectron spectroscopy.[2] The present proposition is based on consideration that the introduction of an electron-withdrawing nitro group on the C-4 position of the anilino benzene ring (ring A) enhances delocalization of lone-pair electrons on the nitrogen atom into the ring A accompanied by an increase in the twist angle $\theta_N$ in solution, which leads to changes of the ring current effect by the ring A exerted on $H_7$, resulting in the anomalous upfield shift of its chemical shift.

## Results and Discussion

The following six *N*-benzylideneanilines **1**—**6** have been examined for their carbon-13 chemical shifts, $H_7$ chemical shifts, and azomethine carbon ($C_7$)-hydrogen coupling constants. The results are summarized in Table 1, and schematically illustrated for the selected quantities in Fig. 1.



**1**; $R_1=R_2=R_3=H$
**2**; $R_1=H$, $R_2=CH_3$, $R_3=H$
**3**; $R_1=R_2=CH_3$, $R_3=H$
**4**: $R_1=R_2=H$, $R_3=NO_2$
**5**; $R_1=H$, $R_2=CH_3$, $R_3=NO_2$
**6**; $R_1=R_2=CH_3$, $R_3=NO_2$

Figure 1 indicates that on successive introduction of methyl groups on 2- and 2,6-positions of **1**, the chemical shift of $C_7$ shows an upfield shift from **1** to **2** by

Table 1. Chemical shifts for $^{13}$C's and azomethine protons ($CDCl_3$, ppm from TMS) and azomethine carbon-hydrogen coupling constants ($CDCl_3$, Hz) for *N*-benzylideneanilines **1**—**6**

| Compound No. | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_{1'}$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ | $C_7$ | $H_7$ | $J(^{13}C\text{-}H)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 151.95 | 120.76 | 128.97 | 125.79 | 128.97 | 120.76 | 136.11 | 128.68 | 128.58 | 131.17 | 160.07 | 8.49 | 157.3[a] |
| **2** | 150.92 | 131.71 | 130.97 | 125.50 | 126.58 | 117.44 | 136.36 | 128.53 | 128.53 | 130.97 | 159.00 | 8.40 | 158.5 |
| **3** | 151.12 | 126.87 | 127.95 | 123.60 | 127.95 | 126.87 | 136.01 | 128.63 | 128.34 | 131.27 | 162.37 | 8.25 | 159.6 |
| **4** | 157.82 | 121.15 | 124.87 | 145.50 | 124.87 | 121.15 | 135.53 | 129.97 | 128.88 | 132.25 | 162.46 | 8.46 | 158.6[a] |
| **5** | 156.84 | 132.59 | 125.26 | 145.11 | 122.57 | 118.17 | 135.53 | 129.12 | 128.82 | 132.15 | 161.39 | 8.37 | 159.3 |
| **6** | 156.89 | 128.09 | 123.25 | 143.49 | 123.25 | 128.09 | 135.14 | 128.88 | 128.73 | 132.20 | 162.76 | 8.23 | 160.3 |

a) Ref. 3.

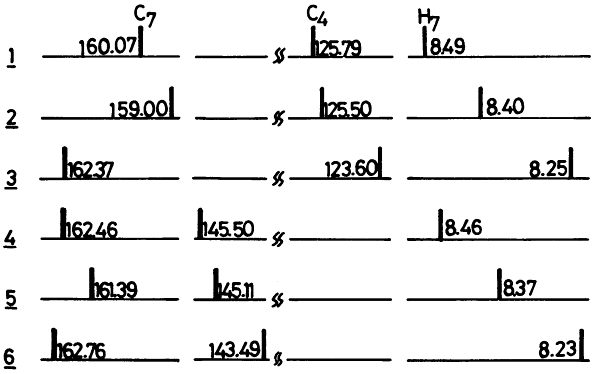


Fig. 1. Schematic illustration of the chemical shifts for $C_4$, $C_7$, and $H_7$ ($CDCl_3$, ppm downfield from TMS).

1.07 ppm, then a remarkable downfield shift from **2** to **3** by 3.37 ppm, $C_7$ of *3* resonating at much lower field than that of **1**. The chemical shift of $C_4$, as has already been reported by Kobayashi's group,[10] shows a slight upfield shift from **1** to **2** by 0.29 ppm, then a larger upfield shift from **2** to **3** by 1.90 ppm. The upfield shifts of $C_4$ and $C_7$ from **1** to **2** can be understood in terms of an inductive effect of the methyl group. However, the remarkable downfield shift of $C_7$ and the larger upfield shift of $C_4$ between **1** and **3** cannot be explained simply in terms of the inductive effect of the two methyl groups. These changes observed between **1** and **3** can be reasonably interpreted in terms that the introduction of the bulky 2,6-dimethyl groups forces the ring A to be highly twisted from the imino molecular plane. This distortion will cause the nitrogen lone pair to interact effectively with the aromatic $\pi$-system ($n$-$\pi$ conjugation) to increase the electron density on $C_4$ leading to its upfield shift, as proposed previously.[11] The *N*-lone pair delocalization will succesively lead to the shift of electrons on $C_7$ to the nitrogen atom to decrease the electron density on $C_7$. The effect of the decrease in electron density on $C_7$ caused by the *N*-lone pair delocalization is predominant to the inductive effects of the two methyl groups finally giving the downfield shift of the $C_7$ chemical shift. The downfield shift of $C_7$ from **1** to **3** could also be explained in terms of a decrease of $\pi$-$\pi$ conjugation throughout the $\pi$-system accompanied by the increase of the $n$-$\pi$ conjugation. For example, $\beta$-vinyl carbon of 2,6-dimethylstyrene is reported to resonate at 6.2 ppm lower field than that of styrene, and this lower field shift was explained in terms of steric inhibition of resonance between the vinyl group and the phenyl group.[12] By analogy, the decrease of the $\pi$-$\pi$ conjugation from **1** to **3** by the 2,6-dimethyl substitution may also cause a lowfield shift of $C_7$, which is in the same direction as predicted by the consideration on the increase of the $n$-$\pi$ conjugation.

The above explanation that the twisting of the ring A from the molecular plane induces the significant lowfield shift of the $C_7$ carbon is supported by $^{13}C$–H coupling constants. It is well known that the carbon-hydrogen coupling constant depends on the s character of the C–H bond,[13] and the larger s character is caused by the decrease of $\pi$ electron density on the carbon atom. The $^{13}C$–H coupling constant is increased from 157.3 (Hz) from **1** to 158.5 for **2**, then to 159.6 for **3**, which indicates that on successive introduction of the *o*-methyl groups on **1** the $C_7$–H bond increases in the s character possibly through the decrease in the $\pi$ electron density on $C_7$.

On introduction of a 4-nitro group in **1**, $C_7$ exhibits a downfield shift by 2.39 ppm from **1** to **4**, which is of the same magnitude as observed between **1** and **3** with 2,6-dimethyl groups. However, 2,6-dimethyl substitution on **4**, in constrast with the effect on **1**, causes a very slight downfield shift of $C_7$ by only 0.30 ppm from **4** to **6**. These results suggest that the ring A of **4**, in spite of the absence of *o*-methyl groups, may be appreciably twisted like that of **3** in which the ring A is forced to be twisted by the effect of the *o*-methyl groups. The chemical shift of $C_4$ shows an upfield shift from **4** to **5** and to **6**, and the $^{13}C$–H coupling constant for **4** is almost the same as for **2**, and then succssively increases on introduction of the *o*-methyl groups. These results suggest that, as in series of **1**, **2**, and **3**, the successive introduction of the *o*-methyl groups increases the twist angle $\theta_N$ accompanied by the decrease in the $\pi$ electron density on $C_7$.

Concerning the $H_7$ chemical shifts, introduction of a nitro group on the $C_4$ position of each of **1**, **2**, and **3** anomalously shifts the $H_7$ chemical shifts to higher field by 0.02—0.03 ppm which is reproducible and beyond the experimental error. As to methyl substitution on **1** and **4**, monomethyl substitution of their 2-positions causes an upfield shift by 0.09 ppm, but further substitution by the second methyl group at their 6-positions results in a larger upfield shift by 0.14—0.15 ppm. Thus, the effect of the methyl group is not additive, which suggests that the larger upfield shift by the second methyl substitution might be due to the further distortion of the ring A by its introduction as well as its inductive effect. The increase in the twist angle $\theta_N$ by the successive methyl substitution will reduce the paramagnetic deshielding effect of the ring A exerted on $H_7$ resulting in its upfield shift. This view is further supported by a simple calculation of the chemical shift using McConnel's equation.[14] For example, when the unsusbtituted benzene ring (ring A) increases in the twist angle $\theta_N$ from 45° to 90°, $H_7$ can be estimated to resonate at a higher field of about 0.20 ppm.[15] These results coupled with the carbon-13 chemical shifts and the $^{13}C$–H coupling constants suggest that the observed anomalous upfield shifts caused by the introduction of the 4-nitro group on **1**, **2**, and **3** could be attributed to the increase in the twist angle $\theta_N$ of the ring A from the molecular plane contaning C=N group.

Thus, introduction of the electron-withdrawing nitro group at the $C_4$ position of the ring A enhances the delocalization of the nitrogen lone pair electrons into the ring A, through so called $n$-$\pi$ conjugation, accompanied by the increase in the twist angle $\theta_N$ which in turn reduces the paramagnetic deshielding effect of the ring A on $H_7$ finally resulting in its upfield shift. The observed values for the anomalous upfield shifts remain to be slight. This can be understood by partial cancelling of the upfield shift of $H_7$ by the twisting of the ring A, because the introduction of the 4-nitro group causes the decrease in electron density of $C_7$ which would lead to the downfield shift of $H_7$.

The above estimation that the 4-nitro group enhances the twist angle $\theta_N$ in solution is supported by our recent results by UV[1] and photoelectron spectroscopy[2] which indicates that the 4-nitro derivative **4** may be more twisted than **1** in solution and in gas phase, respectively. Also in view of the recent report by UV spectroscopy that the introduction of an electron-donating 4-dimethylamino group on **1** leads to reduction of the twist angle $\theta_N$,[16] it is reasonable to consider that the introduction of an electron-withdrawing 4-nitro group tends to increase the twist angle $\theta_N$.

Finally, it is worth noting that the present study shows that apparent substituent effects in NMR may arise from the changes of molecular conformations with substituents as well as from the electronic effects of the substituents.

## Experimental

*Materials.* Preparations and characterizations of **1**—**6** are already reported.[1]

*Spectral Measurements.* *Carbon-13 NMR Spectra*: Carbon-13 NMR spectra were measured at room temperature (probe temperature 27 °C) on a JEOL FX-60 spectrometer operating in the Fourier transform mode with complete proton decoupling. The spectra were generally recorded at a pulse width of 4 μs, a pulse flip angle of 45°, and a repetition time of 5 s using $CDCl_3$ as a solvent. In some cases, single-frequency off-resonance decoupled spectra were also measured. Sample concentrations were usually 1 mol/dm$^3$ in $CDCl_3$ solutions. Digital resolution was 0.74 Hz/point. Observed chemical shifts are reported in ppm downfield from internal tetramethylsilane.

Chemical shifts of the substituents (methyl group), which are not listed in the Table 1 are as follows; **2**: 17.79 (ppm), **3**: 18.23, **5**: 17.94, **6**: 18.33.

*$^1$H-NMR Spectra*: Azomethine proton chemical shifts were taken from a JEOL MH-100 spectrometer at room temperature in the external lock mode using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. We first examined the dilution shift for **4** as an example. The chemical shifts were as follows: 0.23 mol/dm$^3$; 845.3 (Hz), 0.10 mol/dm$^3$; 845.5, 0.08 mol/dm$^3$; 845.6, 0.03 mol/dm$^3$; 845.4. Thus, no dilution shifts were observed which allowed us to measure the chemical shifts for other componds in one concentration below *ca.* 0.1 mol/dm$^3$. The chemical shifts listed in the Table 1 are those measured in the following concentrations: **1**: 0.10 (mol/dm$^3$), **2**: 0.14, **3**: 0.11, **4**: 0.10, **5**: 0.09, **6**: 0.08.

*Azomethine Carbon-Hydrogen Coupling Constants*: The $^{13}C$–H coupling constants were taken from a JEOL FX-60 or a Varian XL-100 spectrometer in $CDCl_3$ solutions by the gated decoupling technique combined with NOE mode.

### References

1) R. Akaba, K. Tokumaru, and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **53**, 1993 (1980), and references cited therein.

2) R. Akaba, K. Tokumaru, T. Kobayashi, and C. Utsunomiya, *Bull. Chem. Soc. Jpn.*, **53**, 2002 (1980).

3) N. Inamoto, K. Kushida, S. Masuda, H. Ohta, S. Satoh, Y. Tamura, K. Tokumaru, K. Tori, and M. Yoshida, *Tetrahedron Lett.*, **1974**, 3617.

4) N. Inamoto, S. Masuda, K. Tokumaru, M. Yoshida, Y. Tamura, and K. Tori, *Tetrahedron Lett.*, **1975**, 3697.

5) N. Inamoto, S. Masuda, K. Tokumaru, K. Tori, and M. Yoshida, *Tetrahedron Lett.*, **1974**, 3701.

6) J. S. Sandhu, D. Mago, and B. J. Wakefield, *Tetrahedron Lett.*, **1975**, 1091.

7) A. S. Al-Tai, D. M. Hall,.and A. R. Mears, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 133.

8) D. Mago, J. S. Sandhu, and B. J. Wakefield, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 715.

9) M. Holík, J. Běluša, and B. Břicháček, *Collect. Czech. Chem. Commum.*, **43**, 610 (1978).

10) $^{13}C$-NMR of **1**, **2**, and **3** have been reported by Yoshida, Minato, and Kobayashi, and the discussion has been made solely on the effect of ortho-methyl susbtitution on the $C_4$ chemical shifts.[11] These compounds have been reexamined for $^{13}C$-NMR in an attepmt to get all data under the same conditions for the present purpose.

11) M. Yoshida, H. Minato, and M. Kobayashi, *Chem. Lett.*, **1976**, 1097.

12) K. S. Dahmi and J. B. Stothers, *Can. J. Chem.*, **43**, 510 (1965).

13) a) C. H. Yoder, R. H. Tuck, and R. E. Hess, *J. Am. Chem. Soc.*, **91**, 539 (1969); b) C. H. Yoder, C. D. Schaeffer, Jr., and R. E. Hess, *J. Chem. Eng. Data*, **17**, 385 (1972); c) N. Inamoto, S. Masuda, A. Terui, and K. Tori, *Chem. Lett.*, **1972**, 107.

14) H. McConnel, *J. Chem. Phys.*, **27**, 226 (1957).

15) The following bond distances were assumed for the calculation. $C_7$–H: 1.09 Å, $C_7$=N: 1.24, N–$C_1$: 1.46, $C_1$–$C_2$: 1.38, $C_2$–$C_3$: 1.40. All bond angles were assumed to be 120°.

16) J. Steiger and H. Zollinger, *Helv. Chim. Acta*, **58**, 800 (1975).