Substituent Effects on Azomethine Proton Chemical Shifts and ^{13}C–H Coupling Constants in *N*-Benzylideneanilines. Generality of Inverse Substituent Effects on the Azomethine Proton Chemical Shifts

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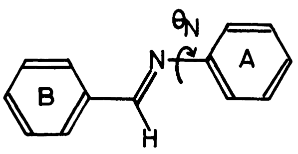
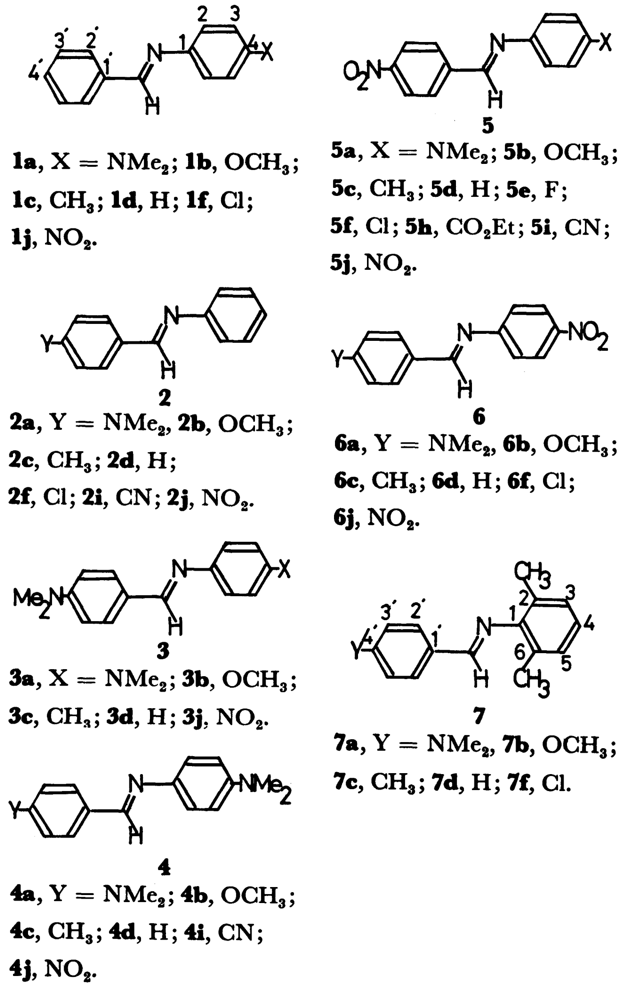
Azomethine proton chemical shifts were measured for series of *N*-benzylideneanilines; $C_6H_5CH=NC_6H_4X$-4, 4-$YC_6H_4CH=NC_6H_5$, 4-$NMe_2C_6H_4CH=NC_6H_4X$-4, 4-$YC_6H_4CH=NC_6H_4NMe_2$-4, 4-$NO_2C_6H_4CH=NC_6H_4X$-4, 4-$YC_6H_4CH=NC_6H_4NO_2$-4, and 4-$YC_6H_4CH=NC_6H_3(CH_3)_2$-2,6. It was found that for *N*-benzylideneanilines carrying the variable substituents X on the anilino benzene ring the azomethine protons undergo upfield shifts with increasing electron-withdrawing property of X, whereas those for *N*-benzylideneanilines carrying the variable substituents Y on the benzylidene benzene ring exhibited expected lowfield shifts with increasing electron-withdrawing property of Y. ^{13}C–H coupling constants for azomethine carbon-hydrogen bonds ($J(^{13}$C–H)) were also measured for several derivatives of 4-$NO_2C_6H_4CH=NC_6H_4X$-4, 4-$YC_6H_4CH=NC_6H_4NO_2$-4, and 4-$YC_6H_4CH=NC_6H_3(CH_3)_2$-2,6. In contrast with the substituent effects on the azomethine proton chemical shifts, the coupling constant increases with increasing electron-withdrawing property of the substituent X or Y, regardless of the position of the substituents, indicating that a through-bond electronic effect of the substituent is a predominant factor to determine the magnitude of the coupling constant. These results show that the anomalous substituent effects on the azomethine proton chemical shifts are a general phenomenon in *N*-benzylideneanilines which carry variable substituents on the anilino benzene ring, and support our previous proposition that the anomaly is likely to originate primarily from the change of molecular conformation of these *N*-benzylideneanilines in solution.

Although inverse substituent effects on the azomethine proton chemical shifts in *N*-benzylideneanilines (for example, 4-NO_2 substitution on the anilino benzene ring (ring A) causes an upfield shift of the azomethine proton) have been reported by several groups,[1] only a few systematic studies have been made to elucidate the anomalos substituent effects.[1e,1f,2] In a previous paper, we have suggested that the anomalous effect of the 4-NO_2 group is likely to originate primarily from the change of molecular conformation (twist angle θ_N) induced by the 4-NO_2 substitution.[3] We have also reported the ^{13}C-NMR spectra of a wide variety of *N*-benzylideneanilines, and demonstrated, on the basis of nonadditivity of the multiple substituent effects on the azomethine carbon chemical shifts, that in disubstituted derivatives such as 4-$NO_2C_6H_4$-$CH=NC_6H_4X$-4, and 4-$YC_6H_4CH=NC_6H_4NMe_2$-4 the twist angle θ_N may be a function of electronic properties of the substituents X and Y.[4] It is therefore of interest to investigate the substituent effects on the azomethine proton chemical shifts for *N*-benzylideneanilines with a variety of substituents.

In the present study, the azomethine proton chemical shifts have been measured for six series of *N*-benzylideneanilines, **1**—**6**. (Scheme 2). In order to assist understanding the nature of the substituent effects on the azomethine proton chemical shifts, ^{13}C–H coupling constants for the azomethine carbon–hydrogen bonds (J^{13}C–H)) have also been measured for the series of **5** and **6**. The coupling constants were also recorded



Scheme 1.



1

1a, X = NMe$_2$; **1b**, OCH$_3$; **1c**, CH$_3$; **1d**, H; **1f**, Cl; **1j**, NO$_2$.

2

2a, Y = NMe$_2$, **2b**, OCH$_3$; **2c**, CH$_3$; **2d**, H; **2f**, Cl; **2i**, CN; **2j**, NO$_2$.

3

3a, X = NMe$_2$; **3b**, OCH$_3$; **3c**, CH$_3$; **3d**, H; **3j**, NO$_2$.

4

4a, Y = NMe$_2$; **4b**, OCH$_3$; **4c**, CH$_3$; **4d**, H; **4i**, CN; **4j**, NO$_2$.

5

5a, X = NMe$_2$; **5b**, OCH$_3$; **5c**, CH$_3$; **5d**, H; **5e**, F; **5f**, Cl; **5h**, CO$_2$Et; **5i**, CN; **5j**, NO$_2$.

6

6a, Y = NMe$_2$, **6b**, OCH$_3$; **6c**, CH$_3$; **6d**, H; **6f**, Cl; **6j**, NO$_2$.

7

7a, Y = NMe$_2$, **7b**, OCH$_3$; **7c**, CH$_3$; **7d**, H; **7f**, Cl.

Scheme 2.

Table 1. Azomethine proton chemical shifts (δ) and ^{13}C–H coupling constants (J(^{13}C–H) of N-benzylideneanilines in $CDCl_3$

Compound	Substituent Y	Substituent X	δ/(ppm/TMS)	J(^{13}C–H)/Hz	Compound	Substituent Y	Substituent X	δ/(ppm/TMS)	J(^{13}C–H)/Hz
1a	H	NMe_2	8.54		**4i**	CN	NMe_2	8.58	
1b	H	OCH_3	8.50	156.6$^{a)}$	**4j**	NO_2	NMe_2	8.64	158.8
1c	H	CH_3	8.48	156.5$^{a)}$	**5a**	NO_2	NMe_2	8.64	158.8
1d	H	H	8.49	157.3$^{a)}$	**5b**	NO_2	OCH_3	8.58	160.7
1f	H	Cl	8.51		**5c**	NO_2	CH_3	8.57	161.0
1j	H	NO_2	8.46	158.6$^{a)}$	**5d**	NO_2	H	8.56	161.0$^{a)}$
2a	NMe_2	H	8.35	154.1$^{a)}$	**5e**	NO_2	F	8.56	
2b	OCH_3	H	8.40	156.1$^{a)}$	**5f**	NO_2	Cl	8.54	
2c	CH_3	H	8.50	156.5$^{a)}$	**5h**	NO_2	CO_2Et	8.54	161.4
2d	H	H	8.49	157.3$^{a)}$	**5i**	NO_2	CN	8.54	
2f	Cl	H	8.50	158.1$^{a)}$	**5j**	NO_2	NO_2	8.55	161.8
2i	CN	H	8.58		**6a**	NMe_2	NO_2	8.31	155.9
2j	NO_2	H	8.56	161.0$^{a)}$	**6b**	OCH_3	NO_2	8.35	157.7
3a	NMe_2	NMe_2	8.40		**6c**	CH_3	NO_2	8.38	158.1
3b	NMe_2	OCH_3	8.37		**6d**	H	NO_2	8.46	158.6
3c	NMe_2	CH_3	8.34		**6f**	Cl	NO_2	8.39	159.9
3d	NMe_2	H	8.35	154.1$^{a)}$	**6i**	CN	NO_2	8.49	161.4
3j	NMe_2	NO_2	8.31	155.9	**6j**	NO_2	NO_2	8.55	161.8
4a	NMe_2	NMe_2	8.40		**7a**	NMe_2	H		153.7
4b	OCH_3	NMe_2	8.47		**7b**	CH_3	H		158.7
4c	CH_3	NMe_2	8.51		**7d**	H	H		159.6
4d	H	NMe_2	8.54		**7f**	Cl	H		160.3

a) Ref. 1d.

for some of the derivatives of **7**, which may be regarded as model compounds taking considerably twisted conformations.[5,6]

First, the results on the anomalous substituent effects on the azomethine proton chemical shifts are presented and the origin of the anomaly will be discussed. Second, efficiency of transmission of the substituent effects will also be briefly discussed on the basis of the results of the coupling constants. The present results support our previous proposition that coformational changes with substituents will be an important factor to cause the anomalous substituent effects on the azomethine proton chemical shifts in N-benzylideneanilines.

Results

Azomethine Proton Chemical Shifts. N-Benzylideneanilines, **1**—**4**, were prepared and their azomethine proton chemical shifts were measured under the conditions corresponding to infinite dilution using $CDCl_3$ as a solvent. The results are summarized in Table 1.

Examination of Table 1 indicates that for N-benzylideneanilines, **2**, **4**, and **6**, which carry the variable substituents Y on the benzylidene benzene ring (ring B), their azomethine proton chemical shifts tend to undergo downfield shifts with increasing the electron-withdrawing property of substituents Y to give normal substituent effects. In a striking contrast, those of **1**, **3**, and **5**, in which the variable substituents X are on the anilino benzene ring (ring A), exhibit anomalous upfield shifts with increasing electron-withdrawing property of the substituents X (inverse substituent effects). Careful inspection of Table 1 also reveals that the azomethine proton chemical shifts in **5** remain roughly constant independent of the electron-withdrawing groups such as CO_2Et, CN, and NO_2. These trends can well be seen in Figs. 1—3 in which the chemical shifts are plotted against Hammett σ constants.[7] The ρ values and correlation coefficients are shown in Table 2 in which a positive sign in the ρ values refers to the inverse substituent effect and a negative sign refers to the normal substituent effett. Table 3 depicts 4-NO_2 and 4-NMe_2 group-induced shifts of the azomethine proton chemical shifts in going from **2** to **6**, and to **4**, respectively.

^{13}C–H Coupling Constants. The J(^{13}C–H) values were also measured for the series of **5**, **6**, and **7**, and are also shown in Table 1 together with those of **1** and

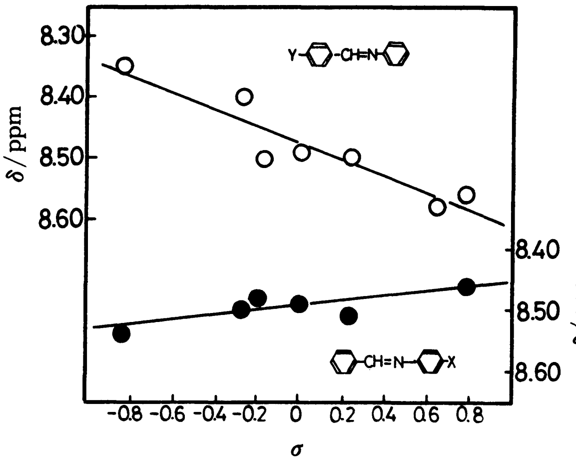


Fig. 1. Hammett Correlations of Azomethine Proton Chemical Shifts in **1** and **2**.

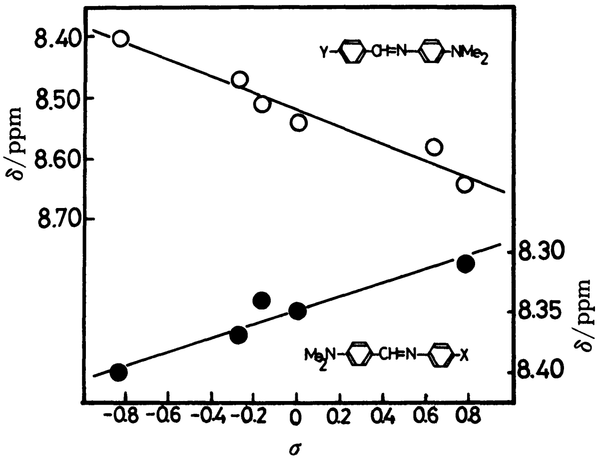


Fig. 2. Hammett Correlations of Azomethine Proton Chemical Shifts in **3** and **4**.

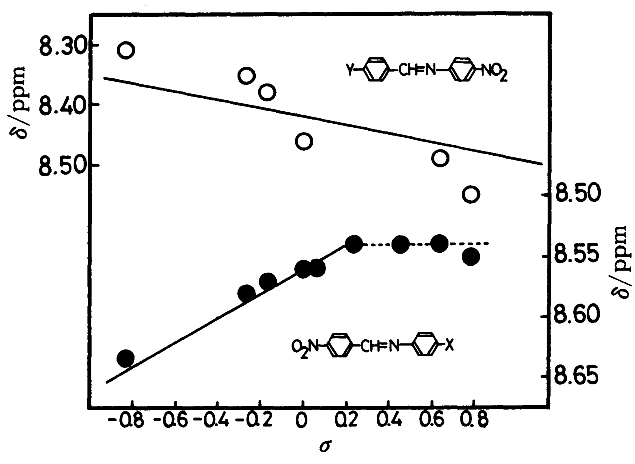


Fig. 3. Hammett Correlations of Azomethine Proton Chemical Shifts in **5** and **6**.

Table 2. Hammett Correlations of the Azomethine Proton Chemical Shifts[a]

Series	ρ Value	Correlation coefficient
1	+0.04	0.812
2	−0.14	0.937
3	+0.06	0.952
4	−0.13	0.976
5	+0.06	0.886
5[b]	+0.09	0.991
6[c]	−0.15	0.956

a) Regression analyses were carried out with relative values ($\delta_H - \delta_X$ or $\delta_H - \delta_Y$) of the chemical shifts. b) The chemical shifts of **5h**, **5i**, and **5j** were omitted in the regression analysis. c) The chemical shift of **6f** was omitted in the regression analysis.

Table 3. 4-NO_2 and 4-NMe_2 Group-Induced Shifts of the Azomethine Proton Chemical Shifts (ppm)[a]

Y	NO_2-induced shift	NMe_2-induced shift
NMe_2	+0.04	−0.05
OCH_3	+0.05	−0.07
CH_3	+0.12	−0.01
H	+0.03	−0.05
CN	+0.09	0.00
NO_2	+0.01	−0.08

a) Positive values denote upfield shifts.

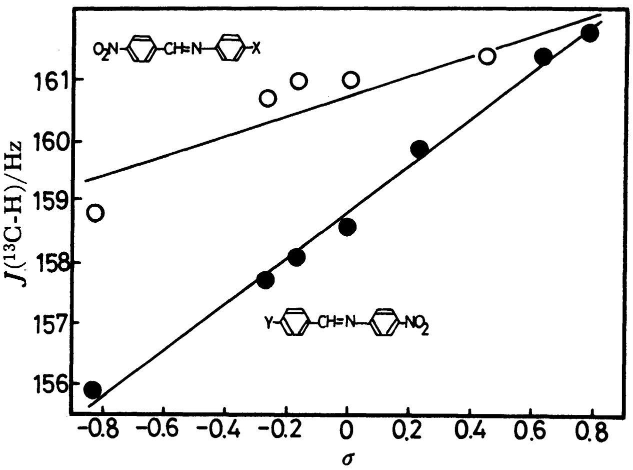


Fig. 4. Plot of $J(^{13}C-H)$ *vs.* Hammett σ Constants in **5** and **6**.

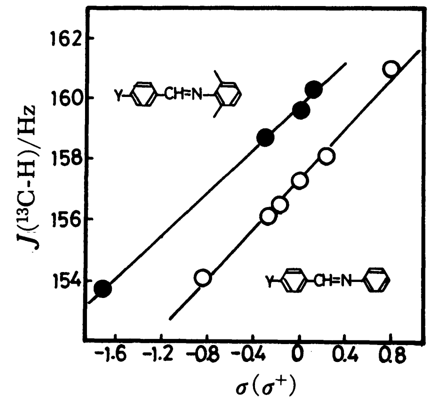


Fig. 5. Plot of $J(^{13}C-H)$ *vs.* Hammett σ^+ and σ Constants in **7** and **2**, respectively.

2 reported by Inamoto *et al.*[1d] As shown in Table 1, the $J(^{13}C-H)$ values for all the series studied increase with increasing electron-withdrawing property of the substituents X or Y regardless of the positions of the substituents, which is in sharp contrast with the results of the azomethine proton chemical shifts. It is also clear that the $J(^{13}C-H)$ values of the disubstituted derivatives **5** and **6** are greater than those of the monosubstituted derivatives **1** and **2**, respectively. Comparison of the $J(^{13}C-H)$ values between **2** and **7** indicates that replacement of two hydrogen atoms by the 2,6-dimethyl groups on the ring A usually increases the $J(^{13}C-H)$ values. Plots of the $J(^{13}C-H)$ values of **5**, **6**, and **7** against Hammett σ or σ^+ constants result in linear relationships as shown in Figs. 4 and 5. In Fig. 5, the Hammett plot is also shown for **2** for the sake of comparison. The ρ values and correlation coefficients are listed in Table 4.

Discussion

Inverse Substituent Effects on the Azomethine Proton

Chemical Shifts. As previously found by other workers,1) the inverse substituent effect on the azomethine proton chemical shifts in **1** was also observed in the present study. Furthermore, the anomalous effects of the 4-substituents were shown to be a general phenomenon since the inverse substituent effects were also found for **3** and **5** which respectively carry 4′-NMe_2 and 4′-NO_2. The anomalous substituent effects in **1**, **3**, and **5** become more clear when we compare them with the substituent effects on the $J(^{13}C\text{–}H)$ values and the azomethine carbon chemical shifts. The comparison reveals that a principal controlling factor of the azomethine proton chemical shifts is different from that of the $J(^{13}C\text{–}H)$ values and the azomethine carbon chemical shifts. For example, the azomethine carbon chemical shifts of **5a**, **5d**,and **5j** are reported 151.46 (ppm/TMS in $CDCl_3$), 157.38, and 159.89, respectively, indicating that the azomethine carbon chemical shifts suffer substituent electronic effects.4) The $J(^{13}C\text{–}H)$ values for the same series are, as shown in Table 1, 158.8 (Hz), 161.0, and 161.8, respectively. It is well known that the ^{13}C–H coupling constant is a function of *s* character of the C–H bond.8) The above trend clearly indicates that the *s* character of the azomethine carbon–hydrogen bonds increases with increasing electron-withdrawing properties of the substituents X in **5**. These expected changes of the azomethine carbon chemical shifts and the $J(^{13}C\text{–}H)$ values indicate that through-bond electronic effects of the substituents X are important to determine the mode of the substituent effects on the $J(^{13}C\text{–}H)$ values and the azomethine carbon chemical shifts, whereas the azomethine proton chemical shifts will be governed by some other effects induced by the substituents. This does not mean that the through-bond electronic effect is absent as a controlling factor of the azomethine proton chemical shifts; it is hidden under the other effects. It has been once suggested9) that the anomalous substituent effect of 4-NMe_2 group, for example, could be ascribed to dominance of the inductive effect over the resonance effect because it was then thought that *N*-benzylideneanilines take generally twisted conformations in solution regardless of the substituents on them. However, the present study clearly indicates that this view is not sufficient to explain the inverse substituent effects since the azomethine carbon chemical shifts and the $J(^{13}C\text{–}H)$ values suffer the normal substituent electronic effects, which indicates that the azomethine protons must also suffer (though not observed) similar substituent effects.

The present findings are consistent with our previous proposition that the inverse substituent effect may arise primarily from the change of the twist angle θ_N which subsequently changes the contribution of the paramagnetic deshielding effect of the ring A exerted on the azomethine proton. Actually, it is strongly suggested by Zollinger10) and Kubota11) that **5a** will take a nearly planar confromation in solution. Our previous NMR study also supports the view,4) and furthermore, implies that the twist angle θ_N may decrease in going from X=NO_2 to NMe_2 in **5**. Under these circumstances, the paramagnetic deshielding effect of the ring A will greatly increase to result in the anomalous lowfield shift in **5a**, compared with, for example, **5j**. Since the azomethine carbon chemical shift as well as the $J(^{13}C\text{–}H)$ undergoes, as described above, the expected change upon the introduction of the electron-releasing groups, the electron density on the azomethine carbon must increase and the *s* character of the azomethine carbon–hydrogen bond must decrease in going from **5j** to **5a**. This should lead to upfield shift of the azomethine proton in going from **5j** to **5a**. The observed low field shift with increasing electron-donating property of the substituents X strongly suggests that change of the chemical shift caused by the paramagnetic deshielding effect (caused by the change of the twist angle θ_N) is larger than that by the through-bond electronic effect of the substituent X.

Comments should also be made on the findings that a better correlation of the azomethine proton chemical shifts with Hammett σ constants (correlation coefficient 0.991) was found when the electron-withdrawing groups (4-CO_2Et, 4-CN, and 4-NO_2) were excluded in the regression analysis, and that the chemical shifts almost remain constant for the derivatives bearing these substituents. In a previous paper,4) we reported that the correlation coefficients for the azomethine carbon chemical shifts *vs.* Hammett σ and σ^+ constants in **5** are 0.978 and 0.999, respectively. As shown in Table 4, that for the $J(^{13}C\text{–}H)$ *vs.* Hammett σ constants is 0.928. Based on these values, the linearity of the azomethine proton chemical shifts with Hammett σ constants should also be similarly good with a *negative* ρ value if they suffer only the substituent electronic effects. The good correlation with a *positive* ρ value could imply that the paramagnetic deshielding effect (and hence the twist angle θ_N) is linearly changed with the substituent electronic effects.

The small variations of the chemical shifts in **5h**, **5j**, and **5i** could be interpreted in terms of combined effects of 4′-NO_2 group and minor conformational changes among these derivatives. Thus, the 4′-NO_2 group decreases electron density on the C–H bond so that the second electron-withdrawing group such as 4-CN and 4-NO_2 is not very effective to cause significant change of the chemical shift. Also if the twist angles θ_N among these derivatives are similar to each other, the ring current effects exerted on the azomethine proton may also be similar to each other to give roughly the same chemical shifts. It is not unreasonable to assume that the twist angles θ_N among **5h**, **5j**, and **5i** do not differ as much as they do among the derivatives bearing the electron-releasing groups such as 4-NMe_2 and 4-OCH_3, since through-conjugative interaction between the 4′-NO_2 and the 4-substituent, which is important to determine the twist angle θ_N for **5a** and **5b**,4,10,11) is absent in **5h**, **5j**, and **5i**. Probably, small changes of the chemical shifts caused by the 4′-NO_2 and those by the minor conformational changes will be cancelled by each other to give the observed chemical shifts.

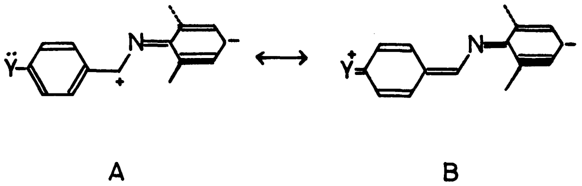
The anomalous substituent effects in **1** and **3** can also be explained similarly. As shown in the previous paper,[4)] azomethine carbon chemical shift in **3** suffers normal substituent effect. Although the $J(^{13}C\text{–}H)$ values are not available for all the compounds of **3**, those of **3d** and **3i** are 151.4 (Hz) and 155.9, respectively. These trends indicate, as discussed above, that the through-bond electronic effect of the substituents X is of primary importance for both NMR constants. On taking into account that 4-NMe_2[10)] and 4-NO_2[3–6)] substitutions tend to decrease and increase the twist angle θ_N, respectively, it is not unreasonable to consider that the inverse substituent effects in **3** may also arise primarily from the change of molecular conformation (twist angle θ_N) induced by the substituents.

The anomaly dicussed above may also be ascertained by comparison of the azomethine proton chemical shifts between **2** and **6**, and **2** and **4**. The comparison makes it clear that the 4-NO_2 and 4-NMe_2 substitution almost always generate the anomalous up- and low-field shifts, respectively, regardless of the nature of the substituents on the ring B.

Finally, it is worth noting that the anomalous substituent effect on the azomethine proton chemical shifts should not be simply ascribed to the twisted conformations of *N*-benzylideneanilines. Difference in conformation among the substituted *N*-benzylideneanilines should be taken into account to get a deeper understanding on it.[2)]

J(^{13}C-H) and Transmission of the Substituent Effects. We used in the previous section the results on the $J(^{13}C\text{–}H)$ values to get a deeper understanding on the origin of the anomalous substituent effects on the azomethine proton chemical shifts. It is also of interest to discuss the $J(^{13}C\text{–}H)$ values of **7**, and the efficiency of transmission of the substituent effects on the basis of the $J(^{13}C\text{–}H)$ values of **5**, **6**, and **7**.

Comparison of the $J(^{13}C\text{–}H)$ values between **2** and **7** is of particular interest. Since a methyl group is moderately electron-donating, the *s* character of the azomethine carbon–hydrogen bond would decrease from **2** to **7** to give rise to a larger $J(^{13}C\text{–}H)$ in **2** than in **7**. However, the reverse situation was found except Y=NMe_2. These results can well be explained in terms of considerably twisted conformations of **7**; introduction of the 2,6-dimethyl groups on the ring A forces the aromatic ring to be highly twisted, and the twisting is accompanied by enhancement of *N*-lone pair delocalization to the ring A, as shown in Scheme 3. Contribution of the canonical structure A must cause an increased *s* character of the azomethine carbon-hydrogen bond giving rise to the larger coupling constants in **7** than in **2**. The pronounced effect of the dimethylamino group to decrease the coupling constant indicates the efficient electron donation as shown in the canonical structure B. This finding is an alternative support for the enhanced *N*-lone pair delocalization in **7**, as shown earlier by Kobayashi.[12)] The scheme is also consistent with a more enhanced transmission of the substituent effects in **7** than in **2** (see below).



Scheme 3.

TABLE 4. HAMMETT CORREALTIONS OF THE COUPLING CONSTANTS.

Series	ρ Value/(Hz/σ)	Correlation Coefficient	Substituent Constant
1[a)]	1.99	0.980	σ
2[a)]	4.45	0.995	σ
5	1.72	0.928	σ
6	3.80	0.997	σ
7	6.48	0.988	σ
7	3.57	0.999	σ^+

a) Ref. 1d.

The efficiency of transmission of substituent effects can be evaluated by the ρ values. As shown in Table 4, the ρ value for **7** (6.48) is larger than that for **2** (4.45). This shows that substituent effect is better transmitted in **7** than in **2**, and can be explained in terms of the development of positive charge on the azomethine carbons in **7**, as shown in the Scheme 3. Better correlation of the $J(^{13}C\text{–}H)$ values with Hammett σ^+ constants than with σ constants in **7** is also consistent with the scheme.

Concerning **5** and **6**, the ρ value was found to be larger in **6** than in **5**. This can be interpreted in terms of the through-bond substituent effect on the coupling constants as discussed in the previous section; the azomethine carbon-hydrogen bond in **6** is one bond closer to the substituent Y than to X in **5**.[1d)]

Conclusion

Substituent effects on the azomethine proton chemical shifts for several series of mono- and disubstituted *N*-benzylideneanilines were examined. The inverse substituent effects were found to be a general phenomenon for *N*-benzylideneanilines carrying variable substituents at the 4-position of the anilino benzene ring regardless of the nature of the 4-substituents on the benzylidene benzene ring. On the basis of the results on similar substituent effects on the azomethine carbon chemical shifts and the ^{13}C–H coupling constants for the azomethinecarbon–hydrogen bonds together with available data on the molecular conformations of *N*-

benzylideneanilines, a concept of conformational change with substituents was invoked to account for the anomalous substituent effects.

Experimental

Materials. Most of the derivatives of **1—7** are available from a previous work.[4] Other compounds were similarly prepared, and identified by comparison of the physical and spectroscopic data with those of authentic samples.

Measurements of the Azomethine Proton Chemical Shifts. All measurements were run on a JEOL MH-100 spectrometer at room temperature (probe temperature was *ca.* 27 °C). The solvent was spectral grade $CDCl_3$. Each solution was prepared by dissolving each sample in $CDCl_3$ containing 1% tetramethylsilane as an internal reference. An aliquot of each solution was taken for further dilution. In most cases, we have examined the chemical shifts in two or three concentrations; however, no appreciable dilution shifts were observed at the concentrations below 0.07 mol dm^{-3}. The chemical shifts were obtained at each concentration as the mean of at least three scans, in most cases, four scans. Sample concentrations were *ca.* 0.03—0.07 mol dm^{-3}.

Measurements of the ^{13}C–H Coupling Constants. The ^{13}C–H coupling constants were taken from a JEOL FX-60 spectrometer in $CDCl_3$ by the gated decoupling technique. Because of low solubility, the measurements of **5b—5j** and **6b—6j** were run at 40 °C of the probe temperature. Other measurements were run at room temperature.[13]

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