Effect of Substituents on the ^{13}C Chemical Shifts of the Azomethine Carbon Atom of *N*-Benzylideneanilines and 2-*N*-Arylimino-2-*p*-nitrophenylethanenitriles

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The ^{13}C chemical shifts of the azomethine carbon atoms have been determined for a series of *meta*- and *para*-substituted benzylideneanilines $PhCH{=}NC_6H_4R^3$ (**1**)–(**8**), *p*-$NO_2C_6H_4CH{=}NC_6H_4R^3$ (**9**)–(**17**), $R^1C_6H_4CH{=}NPh$ (**18**)–(**26**), and *p*-$NO_2C_6H_4C(CN){=}NC_6H_4R^3$ (**27**)–(**32**) in $CDCl_3$ solution. For the compounds (**1**)–(**17**), good $\rho^+\sigma^+$ correlations are observed; the ρ^+ values are 2.73 for compounds (**1**)–(**8**) and 3.52 for the compounds (**9**)–(**17**). However, the shifts with *m*- and *p*-nitro substituents show small but appreciable lower-field deviations. For the compounds (**18**)–(**26**) plots of chemical shifts *vs.* σ^+ constants give two lines intersecting at $\sigma^+ = 0$, explicable by the overlapping effects. For the nitriles (**27**)–(**32**) the plots give two lines which do not intersect, but plots of chemical shifts *vs.* the reciprocals of the λ_{max} of the K band of the electronic spectra are found to be a straight line. This is explicable in terms of unusually strong resonance electron donation from the phenylimino system. Reaction constants (ρ^+) changed from 2.49 for (**1**)–(**3**) through 3.28 for (**9**)–(**11**) to 9.39 for (**27**)–(**29**). Apart from the dihedral angle, the sensitivities of chemical shifts to the electronic effects of the substituents in the aniline ring are affected strongly by the degree of electron demand of the carbon atom of the C=N moiety.

N-Benzylideneanilines are generally accepted to adopt *E*-non-planar or *E*-dihedral structures on the basis of their dipole moment studies,[1,*] UV spectra,[2–6] X-ray crystallography,[7,8] ^{13}C NMR spectra,[9] and molecular-orbital studies.[4,5] Since the geometry in the solid state depends on molecular packing,[10] it is not always the same as that in solutions nor in the vapour state. Because of these peculiar conformations studies of electronic substituent effects have been extensive with regard to physical and chemical properties such as IR ν_{max},[11] polarographic half-wave potential,[12] reaction rates of *N*-alkylation[13] and of *cis–trans* isomerisation,[14] base strength,[15] rate and equilibrium constants for addition reactions,[16–19] and azomethine ^{13}C chemical shifts.[9] While the effects on reaction rates depend on the reaction mechanisms,[16–19] $\rho^+\sigma^+$ correlations have been observed for the equilibrium constants[18,19] and NMR ^{13}C chemical shifts.[9] These observations seem to indicate the important role of conjugation between benzylidene and anilino groups for the stabilisation of molecules even in their non-planar conformations. However, no data for ^{13}C chemical shifts with *meta*-substituents were included,[9] hence, data which include *meta*-substituents would be essential for more clear-cut correlations and for their comparison with equilibrium data. Substituents in the benzylidene and the aniline rings can affect sterically and electronically the molecular geometry. Possible factors which can control the geometry are: (*i*) steric repulsion between hydrogen atoms in the azomethine carbon atom and aniline ring,[3,5] (*ii*) steric interaction between the anilino hydrogen atom and a substituent at the azomethine carbon atom, so increasing the dihedral angle,[20] (*iii*) steric interaction with *ortho*-substituents in the aniline ring increasing the dihedral angle,[4,21,22] (*iv*) effect of an electron-releasing group such as *p*-dimethylamino in the aniline ring decreasing the dihedral angle with increase in conjugation throughout the molecule,[8,23] (*v*) effect of an electron-withdrawing substituent such as *p*-nitro group in the aniline ring which can increase the dihedral angle with enhanced nitrogen lone pair delocalisation.[6] However, in the solid state introduction of a *p*-nitro group into the aniline ring does not increase the dihedral angle.[7]

The importance of the nitrogen lone-pair electrons in the anilino group for non-planar conformations was indicated with the planarities of diarylnitrones[24] and of hydrogen bonded *o*-salicylideneanilines,[25] in which no lone-pair electrons are available. Skrabal *et al.*[23] reported that the *p*-nitro substituent in the benzylidene ring would not change the dihedral angle, but substitution of *p*-nitro group at the benzylidene ring of 2-*N*-phenylimino-2-phenylethanenitrile enhanced remarkably the K band of absorption[20] and change of benzylideneaniline by *p*-dimethylamino-*p*′-nitrobenzylideneaniline reduced greatly the dihedral angle.[8] Hence, *p*-nitro groups in R^1 as well as in R^3 may change the dihedral angle.

Since the ratios of $\varepsilon^E2/\varepsilon^K$ of the absorption spectra for 2-*N*-arylamino-2-*p*-nitrophenylethanenitriles undergo a considerable change with substituents in the aniline rings,[17] the dihedral angle also may change.

This paper is concerned with the electronic effects of *meta*- and *para*-substituents on the azomethine ^{13}C chemical shifts of *N*-benzylideneanilines (**1**)–(**26**) and 2-*N*-arylimino-2-*p*-nitrophenylethanenitriles (**27**)–(**32**), involving comparison of the ^{13}C chemical shifts with equilibrium constants for addition of nucleophiles to the benzylideneanilines and with λ_{max} of the K band of the nitriles, and dependence of reaction constants on the degree of electron demand at azomethine carbon atoms. The reasons why azomethine chemical shift has been singled out are (*i*) the azomethine carbon atom is the most important one for conjugation through the whole molecule of *N*-benzylideneanilines; (*ii*) many data are available to be compared with NMR data and the assignment of chemical shifts is made unequivocally; (*iii*) effects of both substituents in the benzylidene and the aniline rings can be observed effectively.

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[*] Though *Z–E* (or *syn–anti*) isomerism in *N*-benzylideneanilines is possible, dipole moment studies rule out a *Z* structure for benzylideneaniline. *Z*-Isomers are generally extremely unstable and exist as transient species under usual conditions. Thus, they cannot be obtained from normal syntheses and are not favoured at equilibrium in solutions. They can only be obtained on irradiation of the solutions at low temperatures. In present studies, in fact, populations of the *Z*-isomers were too small to be determined by NMR spectroscopy.

$R^1C_6H_4CR^2{=}NC_6H_4R^3$

	R^1	R^2	R^3		R^1	R^2	R^3
(1)	H	H	H	**(17)**	*p*-NO_2	H	*p*-NO_2
(2)	H	H	*p*-OMe	**(18)**	*p*-NMe_2	H	H
(3)	H	H	*p*-Me	**(19)**	*p*-OMe	H	H
(4)	H	H	*m*-OMe	**(20)**	*p*-Me	H	H
(5)	H	H	*p*-Cl	**(21)**	*m*-Me	H	H
(6)	H	H	*m*-Cl	**(22)**	*m*-OMe	H	H
(7)	H	H	*m*-NO_2	**(23)**	*p*-Cl	H	H
(8)	H	H	*p*-NO_2	**(24)**	*m*-Cl	H	H
(9)	*p*-NO_2	H	H	**(25)**	*m*-NO_2	H	H
(10)	*p*-NO_2	H	*p*-OMe	**(26)**	*p*-NO_2	H	H
(11)	*p*-NO_2	H	*p*-Me	**(27)**	*p*-NO_2	CN	H
(12)	*p*-NO_2	H	*m*-OMe	**(28)**	*p*-NO_2	CN	*p*-OMe
(13)	*p*-NO_2	H	*p*-Cl	**(29)**	*p*-NO_2	CN	*p*-Me
(14)	*p*-NO_2	H	*p*-Br	**(30)**	*p*-NO_2	CN	*p*-Cl
(15)	*p*-NO_2	H	*m*-Cl	**(31)**	*p*-NO_2	CN	*p*-Br
(16)	*p*-NO_2	H	*m*-NO_2	**(32)**	*p*-NO_2	CN	*m*-Cl

Table 1. ^{13}C Chemical shift of azomethine carbon atoms of substituted *N*-benzylideneanilines in $CDCl_3$ solution.

Compd.	δ_C	$\Delta\delta_C$[a]	Compd.	δ_C	$\Delta\delta_C$[a]
(1)	160.31	0	**(17)**	160.10	2.84
(2)	158.36	−1.95	**(18)**	160.12	−0.19
(3)	159.45	−0.87	**(19)**	159.66	−0.65
(4)	160.47	0.16	**(20)**	160.15	−0.16
(5)	160.69	0.38	**(21)**	160.42	−0.11
(6)	161.23	0.92	**(22)**	160.47	0.16
(7)	162.37	2.06	**(23)**	158.63	−1.68
(8)	162.59	2.28	**(24)**	158.44	−1.87
(9)	157.25	0	**(25)**	157.09	−3.22
(10)	154.68	−2.57	**(26)**	157.25	−3.06
(11)	156.09	−1.17	**(27)**	148.18	0
(12)	157.39	0.14	**(28)**	140.92	−7.26
(13)	157.55	0.30	**(29)**	145.63	−2.55
(14)	157.60	0.35	**(30)**	146.55	−1.63
(15)	158.31	1.06	**(31)**	146.99	−1.19
(16)	159.88	2.63	**(32)**	149.42	1.25

[a] $\Delta\delta_C = \delta_C$(substituted) − δ_C(unsubstituted).

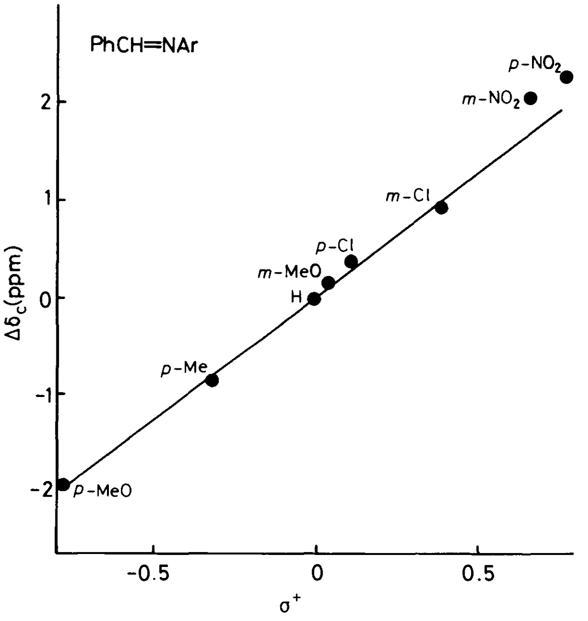


Figure 1. Plots of azomethine carbon chemical shifts of *N*-benzylidenearylamines **(1)**–**(8)** *vs.* σ^+ constants.

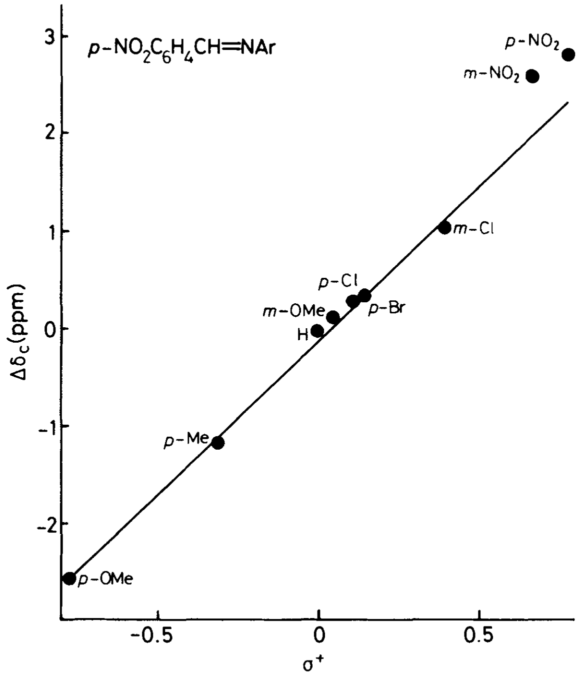


Figure 2. Plots of azomethine carbon chemical shifts of *N*-*p*-nitrobenzylidenearylamines **(9)**–**(17)** *vs.* σ^+ constants.

Results

The ^{13}C chemical shifts for azomethine carbon atoms and the differences of the chemical shifts relative to those for the corresponding unsubstituted compounds are presented in Table 1. The present data for benzylideneanilines substituted in the *para*-positions are in good agreement with ones reported earlier.[9]

Benzylideneanilines **(1)**–**(8)** *and* p-*Nitrobenzylideneanilines* **(9)**–**(17)**.—The ^{13}C chemical shifts of azomethine carbon atoms for **(1)**–**(8)** (R^1 = H, R^2 = H) and **(9)**–**(17)** (R^1 = *p*-NO_2, R^2 = H) bearing *meta*- as well as *para*-substituents show good correlations with the Brown–Okamoto σ^+ constants,[26] much better than Hammett σ constants,[27] with ρ^+ values of 2.73 (correlation coefficient r = 0.996) and 3.52 (r = 0.994), respectively, as seen from Figures 1 and 2. However, the points with *m*- and *p*-nitro substituents **(7)**, **(8)**, **(16)**, and **(17)** show lower field deviations from the lines; if these points are excluded, reaction constants become 2.51 and 3.16, respectively, and the correlation coefficients for both are improved to 0.998. Similarly, good correlations were observed between the chemical shifts and the equilibrium constants for the addition of methanol (K_{MeOH})[18] and propanethiol (K_{PrSH}),[19] as shown in Figures 3 and 4. The slopes and the correlation coefficients are 2.25 and 0.991 with **(1)**–**(8)** for K_{MeOH}; 2.63 and 0.984 with **(9)**–**(17)** for K_{PrSH}, and 2.41 and 0.980 with **(9)**–**(17)** for K_{MeOH}, respectively. Also, lower field deviations from the lines were observed with an *m*-nitro substituent **(7)** and **(16)**. In spite of these deviations from the lines, however, plots of chemical shifts for **(9)**–**(13)** and **(15)**–**(17)** *vs.* those for **(1)**–**(8)** gave an excellent straight line without deviation with a slope of 1.29 (r = 1.000), and also plots of K_{PrSH} for **(9)**–**(13)** and **(15)**–**(17)** *vs.* K_{PrSH} for **(1)**–**(8)** gave similar results with a slope of 1.11 (r = 0.997). Therefore, the observed deviations with *m*- and *p*-nitro substituents in Figures 1–4 are not ascribed to experimental error.

Benzylideneanilines Substituted in the Benzylidene Ring (R^2 = R^3 = H) **(18)**–**(26)**.—For **(18)**–**(26)**, including *meta*- as well

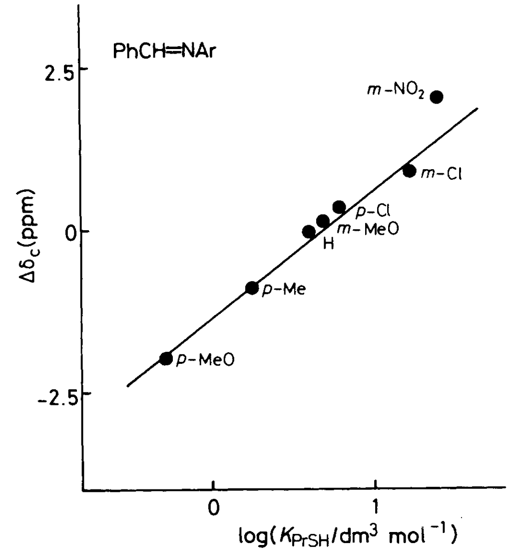


Figure 3. Plots of azomethine carbon chemical shifts *vs.* equilibrium constants K_{PrSH} for the addition of propanethiol to *N*-benzylidenearylamines (**1**)–(**8**).

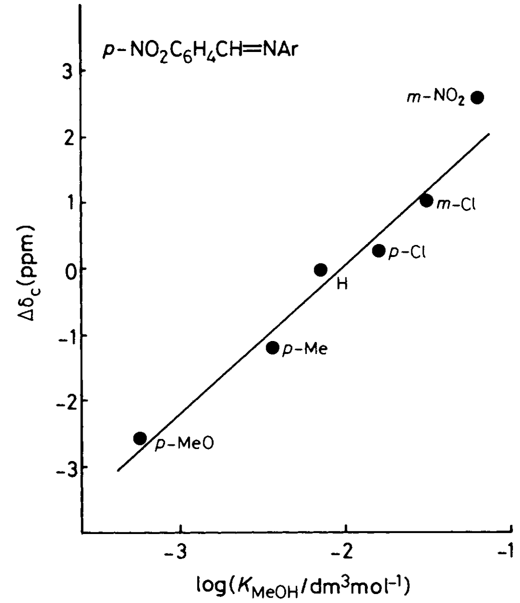


Figure 4. Plots of azomethine carbon chemical shifts *vs.* equilibrium constants K_{MeOH} for the addition of methanol to *N*-*p*-nitrobenzylidenearylamines (**9**)–(**17**).

as *para*-substituents, plots of azomethine chemical shifts *vs.* σ^+ constants, shown in Figure 5, gave two lines broken at $\sigma^+ = 0$. With electron-attracting groups except for *p*-chloro, a fairly good straight line with a ρ^+ value of -4.35 ($r = 0.987$) and with electron-releasing groups except for *p*-dimethylamino group (**18**) a straight line with a ρ^+ value of 1.01 ($r = 0.998$) were obtained. Though similar trends were reported earlier with benzylideneanilines bearing para-substituents alone,[9] the correlation with σ^+ constants observed here is much better than with σ constants. The points with *p*-chloro and *p*-dimethylamino groups (**18**) and (**23**) show significant deviations from the lines.

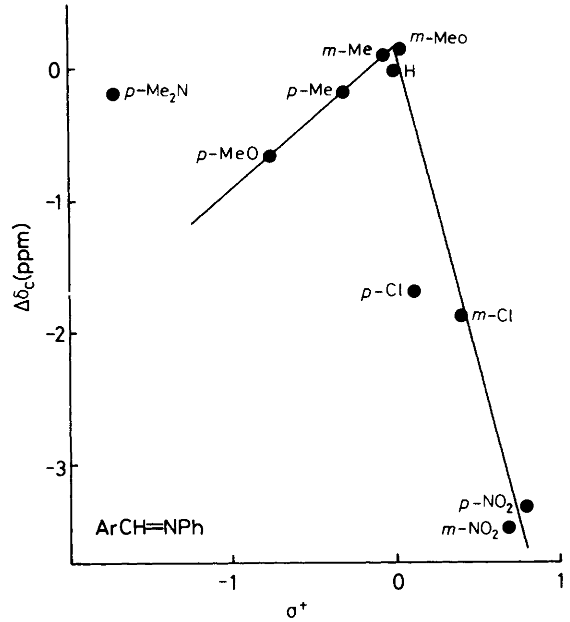


Figure 5. Plots of azomethine carbon chemical shifts of *N*-benzylideneanilines (**1**) and (**18**)–(**26**) *vs.* σ^+ constants.

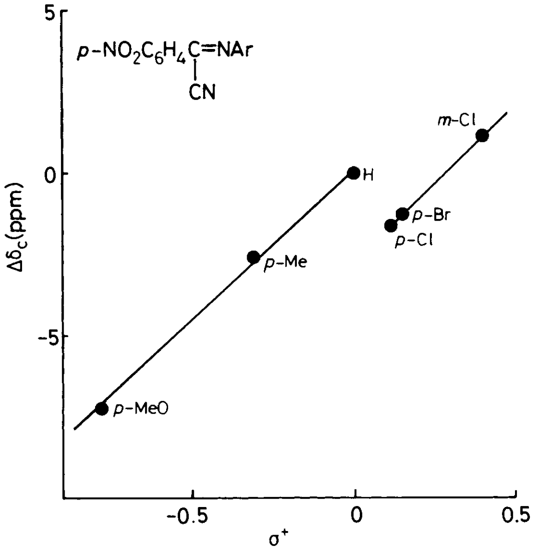


Figure 6. Plots of azomethine carbon chemical shifts of 2-*N*-arylimino-2-*p*-nitrophenylethanenitriles (**27**)–(**32**) *vs.* σ^+ constants.

2-N-*Arylimino*-2-p-*nitrophenylethanenitriles* ($R^1 = p\text{-}NO_2$, $R^2 = CN$) (**27**)–(**32**).—For the nitriles (**27**)–(**32**) plots of chemical shifts *vs.* σ^+ constants, shown in Figure 6, gave two lines with a ρ^+ value of 9.39 ($r = 0.998$) for $\sigma^+ < 0$ and of 10.2 ($r = 1.000$) for $\sigma^+ > 0$, which is in contrast with the case for $R^2 = H$ [(**1**)–(**17**)]. For substituents of $\sigma^+ > 0$ considerably higher field deviations from the first lines with $\sigma^+ < 0$ were observed. However, as shown in Figure 7, an excellent linear relationship ($r = 0.998$) was found between chemical shifts *vs.* reciprocals[17] of the λ_{max} of the K band of their UV spectra.

Discussions

Effect of Substituents in the Aniline Ring on the Chemical Shifts for (**1**)–(**17**).—The observations of good $\rho^+\sigma^+$ correlations for [$R^1 = H$, $R^2 = H$ (**1**)–(**8**); $R^1 = p\text{-}NO_2$, $R^2 = H$ (**9**)–(**17**)] bearing *meta*- as well as *para*-substituents, seen from Figures 1 and 2, indicate that resonance electron donation (**35**) through the substituted phenylimino system should reduce the contribution of polarisation (**33**) to azomethine chemical shifts, resulting in higher field shifts. Small, but appreciable, lower-field

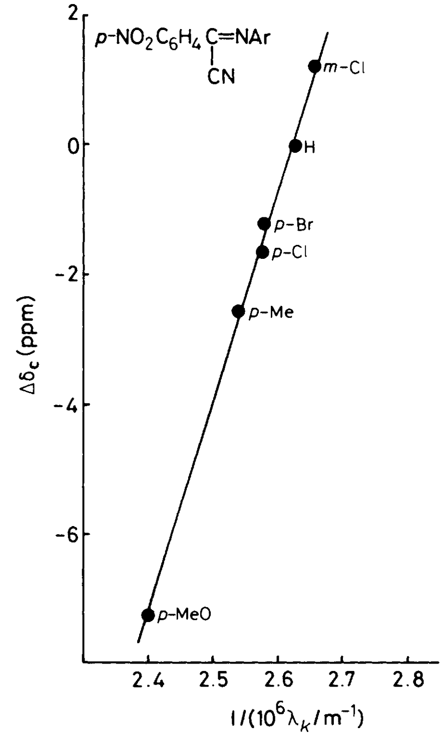
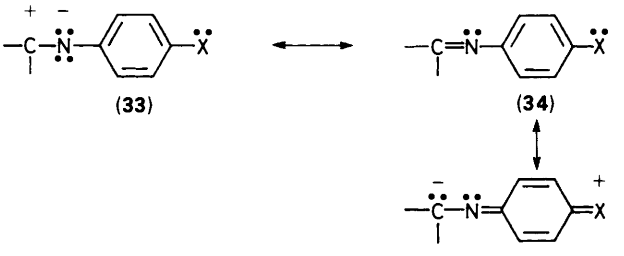
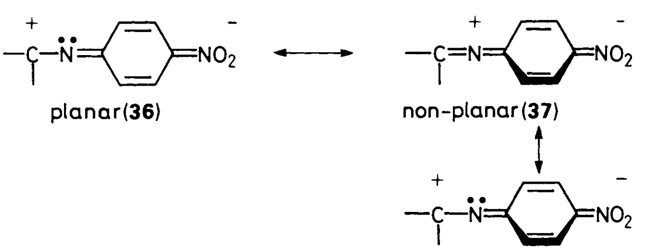


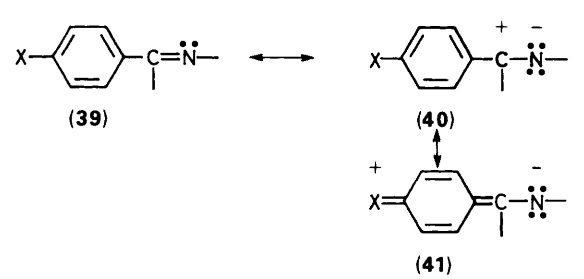
Figure 7. Plots of azomethine carbon chemical shifts *vs.* reciprocals of λ_{max} of the K band of the UV spectra for the nitriles (**27**)–(**32**).



(33) **(34)** **(35)**



planar(**36**) non-planar(**37**) non-planar (**38**)



(39) **(40)** **(41)**

deviations were observed with *m*- and *p*-nitro groups for (**7**), (**8**), (**16**), and (**17**) from the lines. This is probably explicable by the non-planar conformations, caused by the *n*–π conjugation of the nitroaniline type.[6] If the dihedral conformations are adopted for these benzylideneanilines, the observed lower field deviations would be ascribed to the contribution of non-planar (**37**) or (**38**), but not (**36**) to the chemical shifts. Complete parallelism (r = 1.000) between the chemical shifts for (**1**)–(**8**) and (**9**)–(**17**) implies that introduction of *p*-nitro group to benzylidene ring does not change appreciably the dihedral angle, but *p*-nitro group to benzylidene ring does not change appreciably the dihedral angle, but increases ρ^+ values from 2.73 to 3.52, resulting from the enhanced electron demand at the azomethine carbon atom, as will be discussed later.

Correlations between Equilibrium Constants for Addition Reaction and Chemical Shifts.—There are fairly good relationships (r = 0.991, 0.984, and 0.980) between the equilibrium constants for methanol or propanethiol addition and the chemical shifts for (**1**)–(**17**) (Figures 3 and 4). Equilibrium constants depend on both reactant and adduct stabilities, but azomethine chemical shifts depend on benzylideneanilines alone. Hence, the present $\rho^+\sigma^+$ correlations between the equilibrium constants and the chemical shifts support the earlier conclusion[18,19] that the change of equilibrium constants for additions are determined mainly by the change of stabilities of the reactants, benzylideneanilines. While reactivities are concerned with electron withdrawal of the C=N bond,[27] chemical shifts are concerned with the electron deficiency of the carbon atom itself, therefore, the correlations are not always good. With an *m*-nitro substituent in the aniline ring lower field deviations were also observed (Figures 3 and 4).

Benzylideneanilines (**1**) *and* (**18**)–(**26**) *Substituted in the Benzylidene Moiety.*—For benzylideneanilines bearing *para*-substituents in the benzylidene ring there has been no simple relationship between chemical shifts and σ^+ or σ constants.[9] This is also true with those bearing *meta*-substituents. However, if two points with *p*-dimethylamino and *p*-chloro groups are neglected, as seen from Figure 5, two straight lines broken at $\sigma^+ = 0$ are obtained. Situations analogous to this were reported with α-carbon atoms of *para*-substituted styrenes,[28] benzaldehydes,[29] and acetophenones,[29] and ascribed to a combination of two mechanisms, *i.e.* electron-donating conjugation and polarisation of the C=O bond.[30] By analogy, large higher field shifts ($\rho^+ = -4.35$) will be brought about by the effect of electron-withdrawing substituents (X) suppressing the contribution of polarisation (**40**) to ^{13}C chemical shifts. On the other hand, small higher field shifts ($\rho^+ = 1.01$) are explicable in terms of overlapping effects of the electron-releasing substituents: a major contribution of resonance electron donation (**41**) ($\rho^+ = 5.36$, tentatively) and a minor contribution of enhanced polarisation (**40**) ($\rho^+ = -4.35$, tentatively). The deviations with *p*-dimethylamino group (**18**) and with *p*-chloro group (**23**) are probably due to unexpectedly smaller and greater resonance electron donations (**41**), respectively.

2-N-*Arylimino*-2-p-*nitrophenylethanenitriles* (**27**)–(**32**).—For the nitriles where the dihedral angles are taken to be greater than those for benzylideneanilines,[20] there is no simple correlation observed between chemical shifts and σ^+ constants. The higher field deviations with *m*-chloro, and *p*-chloro, and *p*-bromo substituents (**32**), (**30**), and (**31**), are inexplicable on the basis of an increase in dihedral angle, since anilino type *n*–π conjugation (**42**) is not important for these substituents and since an increase in the angle should cause a lower field deviation rather than higher, as discussed above. These higher-field deviations are explicable in terms of an increase in electron donation to the azomethine carbon atom from the halophenyl groups through an unusually enhanced resonance even in non-

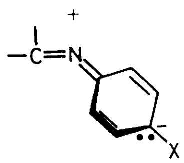


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Table 2. Variation of reaction constants for azomethine ^{13}C chemical shifts of *N*-benzylideneanilines $R^1C_6H_4CR^2 = NC_6H_4R^3$ with substituents on benzylidene group.[a]

R^1	R^2	$\rho^{+\,b}$	Ratio	r^c
H	H	2.49	1.00	0.999
p-NO_2	H	3.28	1.32	0.998
p-NO_2	CN	9.39	3.77	0.998

[a] R^3 = *p*-OMe, *p*-Me, and H for comparison. [b] Reaction constant. [c] Correlation coefficient.

planar conformations. This can be affected by a strong electron demand at the carbon atom resulting from a strong electron withdrawal by both *p*-nitrophenyl and α-cyano groups. As a result, *p*-chloro and *p*-bromo groups act as electron-releasing rather than electron-withdrawing groups as expected on consideration of their positive σ^+ values. This speculation is supported by the observation of an excellent linearity in Figure 7. This is a kind of linear free-energy relationship.

Electron Demand at Reaction Centre and Reaction Constants.—Introduction of a *p*-nitro or α-cyano group into the benzylidene group may cause a change of sensitivities or reaction constants ρ^+ for the effect of substituents in the aniline ring on ^{13}C chemical shifts of the azomethine carbon atom. The data pertinent to this are presented in Table 2. The reaction constants ρ^+ are based only on the three points with R^3 = *p*-OMe, *p*-Me, and H in each series, since the points with substituents of $\sigma^+ > 0$ for the nitriles gave another line. Introduction of *p*-NO_2 into the benzylidene ring resulted in a 1.3-fold increase in ρ^+ value from 2.49 to 3.28, and further introduction of α-CN resulted in a 3.8-fold increase in ρ^+ value from 2.49 to 9.39. Therefore, the increase in electron demand at the azomethine carbon atom results in a significant increase in ρ^+. Provided that ρ^+ is proportional to $\cos^2\theta$, where the dihedral angle θ is assumed to be constant for each series (R^3 = *p*-OMe, *p*-Me, and H), and that a molecule with R^1 = *p*-NO_2, R^2 = CN, and R^3 = OMe has a near planar conformation ($\theta = 0$) from a viewpoint of its strong K band of UV spectrum,[17,20] values of θ for (**2**) and (**10**) can be estimated to be 59 and 54°, respectively. The value for (**2**) is close to the reported value of 55° for (**1**) determined by means of crystallography.[7] However, whether an increase in ρ^+ refers or not to a decrease in dihedral angle alone is uncertain, for at least introduction of *p*-NO_2 in the benzylidene ring does not seem to change appreciably the relative dihedral angles from the observation of a complete parallelism between the chemical shifts for (**1**)–(**8**) and (**8**)–(**17**). Apart from any variation of the dihedral angle, at any rate, the increase in ρ^+ constant is ascribed to an enhanced electron-releasing resonance (**35**) through the phenylimino systems, and therefore, to a decrease in the contribution of polarisation (**33**) of the C=N bond to its ^{13}C chemical shifts.

Experimental

^{13}C NMR spectra of the samples in $CDCl_3$ solutions were recorded on a JEOL FT90Q spectrometer with $CDCl_3$ as an internal standard. The assignments of the azomethine carbon atom were made by the use of OFR or INEPT measurements together with additivity of the increments of the chemical shifts by the substituents.[31] Reproducibilities of the chemical shifts were very good and the data were precise to within 0.05 ppm for repeated measurements with changing concentrations. The differences of azomethine ^{13}C chemical shifts between those for substituted benzylideneanilines and for unsubstituted ones in each series were employed for the substituent effects.

Materials.—*meta* and *para*-substituted benzylideneanilines (**1**)–(**26**) and 2-*N*-arylimino-2-*p*-nitrophenylethanenitriles (**27**)–(**32**) were prepared by the methods described earlier.[16–19]

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