Substituent Effects on the ^{1}H, ^{13}C, and ^{15}N NMR Spectra of Substituted Benzanilides

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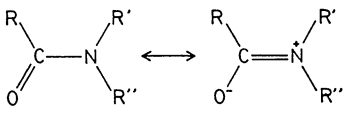
The ^{15}N, carbonyl ^{13}C, and amide ^{1}H NMR spectra of a series of substituted benzanilides, $XC_6H_4CONHC_6H_4Y$, measured in four solvents of different polarity were correlated with the electronic effects of substituents by the use of the Hammett equation. Except for the ^{13}C chemical shift vs. the σ_x plot, the ρ-values are positive, showing that the chemical shift tends to move down-field as the substituent becomes electron-withdrawing. Substituent effects could be assumed to arise from a cross conjugation of competing amide and benzoyl resonance structures perturbed via an inductive mechanism by the substituent on the anilino ring. The ^{15}N chemical shifts of $XC_6H_4CONHC_6H_5$ can be expected to be correlated with the rotational barrier, since the down-field shift of the ^{15}N chemical shift (in reference to unsubstituted) benzanilide was ascribed to a steric inhibition of the aryl-carbonyl conjugation. This trend is actually shown by a plot of the ^{15}N chemical shift vs. the rotational barrier of a similarly substituted *N,N*-dimethylbenzamide. The NH group of 2-methoxy- and 2-chlorobenzanilides was shown to be intramolecularly hydrogen bonded with the ortho substituent (CH_3O or Cl) by their ^{1}H NMR and infrared NH spectra.

Rotational barriers about the C-N bond of amides and related compounds have been studied very extensively by dynamic nuclear magnetic resonance spectroscopy.[1-7] Since the partial double bond character of the amide C-N bond is attributed by electron theory to the contribution of the mesomeric structure (**II**) which bears a positive charge on the nitrogen atom, the electron density on the nitrogen atom should be correlated with the height of the C-N rotational barrier. On the other hand, the correlations between the chemical shift and the electron density have been reported with various nuclei.[8-11] Without a few exceptions the chemical shift moves towards up-field as the electron density on the nucleus increases. The ^{15}N chemical shift was also correlated with its electron density by Mason.[12] From the view point of the polar effect by substituents, the chemical shifts of the relevant nuclei were also discussed on the basis of their Hammett plots.[13-15]



(I) (II)

We have been studying salicylanilides and related amides both in terms of theoretical interest concerning the hydrogen bonding and rotational barriers as well as in terms of pharmaceutical interests. Thus, the intramolecular hydrogen bonding of a series of salicylanilides could be correlated with their antibacterial activities.[16] On the other hand, the DNMR of a series of *N,N*-dimethylsalicylamides showed a considerable lowering of the rotational barriers in comparison with those of unsubstituted and other *o*-substituted analogs.[17,18] The rotational barriers of these amides were correlated with their ^{15}N chemical shifts.[19]

In this investigation, ^{1}H, ^{13}C, and ^{15}N chemical shifts, as well as some spin-spin coupling constants in relation, of several aroyl(X)-substituted benzanilides were measured and correlated with the rotational barriers of the corresponding *N,N*-dimethylbenzamides.[18] On the other hand, the polar substituent effect on the chemical shifts caused both by the substituent on the aroyl and on the anilino aromatic rings (X and Y, respectively) were examined by plotting them against the Hammett's σ–, or a similar substitent constant, in order to obtain further insight into the nature of the substituent effect.

Experimental

^{15}N-Labeled and other anilides were prepared by the reaction of substituted benzoyl chlorides with ^{15}N-labeled aniline. In all runs, excess benzoyl chloride was added by portions to ^{15}N-labeled aniline.

The NMR spectra were recorded on a JEOL FX-90Q spectrometer using a 10-mmϕ probe. The samples for the measurement were prepared by dissolving ca. 100 mg of ^{15}N-labeled benzanilide in ca. 1.5 ml of the solvent. The ^{15}N specta were measured at 9.04 MHz using a repetition of 18-μs pulses (flip angle 45°) and 3-s delays; 50 to 100 scans per spectrum were accumulated under broad-band irradiation for complete proton decoupling. The ^{15}N chemical shifts were given in ppm downfield from liquid NH_3 (external reference). The accuracy was ±0.7 Hz (0.02 ppm). In the case of measurements of non-enriched anilides, 1000—5000 scans were accumulated in order to obtain clear spectra.

Infrared spectra were measured with a JASCO FT-IR 5M spectrophotometer.

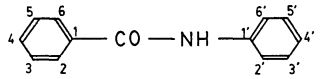
Results and Discussion

The ^{1}H, ^{13}C, and ^{15}N chemical shifts of substituted benzanilides $XC_6H_4CONHC_6H_4Y$ in four sol-

vents are given in Table 1. The substituent effect on the chemical shifts is discussed fully in the following sections. Some spin-spin coupling constants concerning ^{15}N were determined with ^{15}N-enriched anilides (**1**—**4**) and are given in Table 1.

Commenting on the coupling constants, the observed $^1J_{NH}$ and $^2J_{NC}$ values for a series of aroyl-substituted benzanilide are sometimes different from each other slightly beyond the experimental error. However, the variation is random, and no directinoal substituent effect could be deduced from the observed J values. On the other hand, the polarity of the

Table 1. The NMR Spectra of the Amide Group (-CONH-) of Substituted Benzanilides $XC_6H_4CONHC_6H_4Y$ and Related Anilides



a) $XC_6H_4CONHC_6H_5$

No.	X(or Y)	Solvent	^{15}N/ppm[a]	^{13}C/ppm[b]	^1H/ppm[b]	$^1J_{NH}$/Hz	$^3J_{NC}$/Hz
1	H	$CDCl_3$	127.1	165.9	7.87	88.8	14.6
		C_5D_5N	129.4	166.6	11.00	89.8	14.6
		CD_3OD	133.1	168.7	10.07	91.3	15.3
		$(CD_3)_2SO$	133.9	165.6	10.27	90.0	14.6
2	4-CH_3	$CDCl_3$	126.8	166.1	8.00	89.3	14.6
		C_5D_5N	128.2	166.8	10.90	89.3	14.6
		CD_3OD	132.4	168.7	9.99	90.8	16.1
		$(CD_3)_2SO$	133.0	165.3	10.19	90.8	15.6
3	4-OCH_3	$CDCl_3$	125.4	164.7	7.87	88.6	14.6
		C_5D_5N	127.3	166.4	10.69	89.3	14.6
		CD_3OD	131.7	168.2	9.96	91.8	14.6
		$(CD_3)_2SO$	132.1	164.9	10.11	90.3	15.6
4	4-Cl	$CDCl_3$	126.6	164.8	7.75	89.8	14.6
		C_5D_5N	129.0	165.9	11.11	89.3	13.6
		CD_3OD	133.2	—	10.11	91.3	16.1
		$(CD_3)_2SO$	134.6	164.4	10.32	90.8	15.5
5	4-OH	C_5D_5N	127.2	166.9	10.78		
		$(CD_3)_2SO$	131.8	165.2	10.03		
6	4-$N(CH_3)_2$	C_5D_5N	125.5	166.7	10.59		
		$(CD_3)_2SO$	130.3	165.3	9.91		
7	4-NO_2	C_5D_5N	132.2	165.0	11.36		
		$(CD_3)_2SO$	136.2	163.8	10.57		
8	3-CH_3	C_5D_5N	129.2	167.0	10.88		
		$(CD_3)_2SO$	134.1	165.5	10.30		
9	3-Cl	C_5D_5N	129.8	165.4	11.02		
		$(CD_3)_2SO$	134.6	164.2	10.41		
10	3-NO_2	C_5D_5N	130.1	164.6	11.38		
		$(CD_3)_2SO$	134.8	163.3	10.59		
11	2-CH_3	$CDCl_3$	135.0	168.4	7.53	88.3	14.6
		C_5D_5N	136.7	169.1	11.18	89.8	14.6
		CD_3OD	141.1	171.2	10.11	90.8	14.6
		$(CD_3)_2SO$	141.1	167.8	10.30	90.3	14.0
12	2-OCH_3	$CDCl_3$	134.3	167.1	9.80	88.8	16.1
		C_5D_5N	135.2	164.5	10.47	89.8	14.6
		CD_3OD	139.5	166.2	—	90.8	16.1
		$(CD_3)_2SO$	141.2	164.4	10.13	90.3	15.6
13	2-Cl	$CDCl_3$	135.8	164.8	7.99	89.8	16.1
		C_5D_5N	137.8	166.2	11.58	89.8	13.6
		CD_3OD	141.8	167.9	10.24	90.8	16.1
		$(CD_3)_2SO$	142.6	164.9	10.54	90.3	15.6
14	2-OH	$CDCl_3$	124.9	168.9	8.53	89.3	17.5
		C_5D_5N	131.3	167.2	11.18	89.8	15.6
		CD_3OD	133.5	169.7	10.24	90.8	16.1
		$(CD_3)_2SO$	136.0	166.6	10.40	90.8	15.6
15	1-Naph[c]	$CDCl_3$	135.7	167.6	8.39		
		C_5D_5N	137.0	168.5	11.44		
		$(CD_3)_2SO$	142.8	167.2	10.62		
16	2-Naph[c]	$CDCl_3$	128.7	165.8	8.36		
		C_5D_5N	128.5	166.9	11.15		
		$(CD_3)_2SO$	134.3	165.6	10.51		

Table 1. (Continued)

b) $C_6H_5CONHC_6H_4Y$							
No.	X(or Y)	Solvent	^{15}N/ppm[a]	^{13}C/ppm[b]	^{1}H/ppm[b]	$^{1}J_{NH}$/Hz	$^{3}J_{NC}$/Hz
17	4′-NMe_2	C_5D_5N	120.7	166.3	10.77		
		$(CD_3)_2SO$	127.0	164.8	9.97		
18	4′-OH	C_5D_5N	126.0	166.5	10.88		
		$(CD_3)_2SO$	129.3	165.1	10.02		
19	4′-OMe	C_5D_5N	125.6	166.5	10.86		
		$(CD_3)_2SO$	132.1	165.2	10.19		
20	4′-CH_3	C_5D_5N	128.6	166.7	10.87		
		$(CD_3)_2SO$	133.4	165.5	10.23		
21	3′-CH_3	C_5D_5N	129.4	166.9	10.85		
		$(CD_3)_2SO$	134.1	165.7	10.22		
22	4′-Cl	C_5D_5N	128.1	166.9	10.95		
		$(CD_3)_2SO$	133.2	165.6	10.41		
23	3′-Cl	C_5D_5N	129.1	167.4	11.07		
		$(CD_3)_2SO$	133.7	165.9	10.45		
24	3′-NO_2	C_5D_5N	128.3	167.2	11.31		
		$(CD_3)_2SO$	133.5	166.0	10.71		
25	4′-NO_2	C_5D_5N	133.7	167.4	11.51		
		$(CD_3)_2SO$	136.8	166.2	10.83		

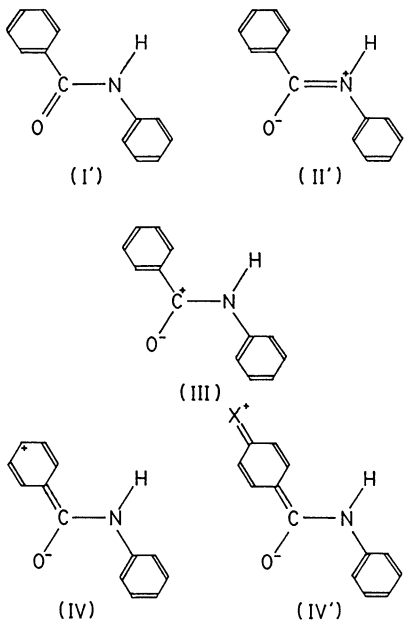
a) Downfield chemical shifts from NH_3 (external). b) Downfield chemical shifts from TMS. c) Naph=naphthanilide.

solvent was shown to cause a slight but clearly recognizable increase in the $^{1}J_{NH}$ values.

Polar Substituent Effect by the Substituent on the Aroyl and Anilino Aromatic Rings. In order to clarify the characteristic feature of the polar substituent effect on the amide moiety, the carbonyl ^{13}C and the amide ^{15}N and ^{1}H chemical shifts of several substituted anilides were plotted against the Hammett's σ-constants. The plotted diagrams are given in Figs. 1a—1f.

Analogous to the trends observed with other arylcarbonyl compounds,[14] the slope of the ^{13}C chemical shift vs. the σ_X plot (Fig. 1a) is apparently reversed, having a negative ρ-value. The reversal had been explained by an increased contribution of the polar amide structure (**II′**) which, in turn, decreases the contribution of the locally polarized structure (**III**) of the carbonyl group.[14] In contrast to the effect of aroylsubstituent X, substituent Y on the anilino ring induces a normal substituent shift of the carbonyl ^{13}C signal with a positive ρ-value (Fig. 1b). This might be interpreted as the normal electron density effect transmitted via an inductive mechanism from the nitrogen atom which is subjected to the usual electronic effect by substituent Y.

The substituent effect on the ^{15}N chemical shifts was shown to be normal (taking positive ρ-values) when either the substituent on the aroyl ring (X) or the one on the anilino ring (Y) was altered (Figs. 1c and 1d). Since the substituent X is located on the aromatic ring farther from the nitrogen atom, through-space effects such as anisotropy and field effects cannot be expected to affect the ^{15}N chemical shift considerably. Therefore, the ^{15}N chemical shift can be assumed to be perturbed only in a through-bond manner by the



electronic (inductive and mesomeric) effect of the substituent on the aroyl moiety, which promotes or prevents the contribution of the dipolar mesomeric structure (**II**). A mesomeric contribution of the substituent X is described by **IV** (hereafter denoted as the benzoyl resonance). In short, it is a kind of so-called cross conjugation effect on the amide resonance caused by the aroyl moiety, in which the amide resonance (**II**) and the benzoyl resonance (**IV**) are in competition. The positive ρ-value of the ^{15}N chemical shift vs. the σ_X plot was interpreted as meaning that the polar mesomeric structure of amide (II) plays a less important role when the benzoyl resonance (**IV**) is expected to be strengthened by an electron-donting

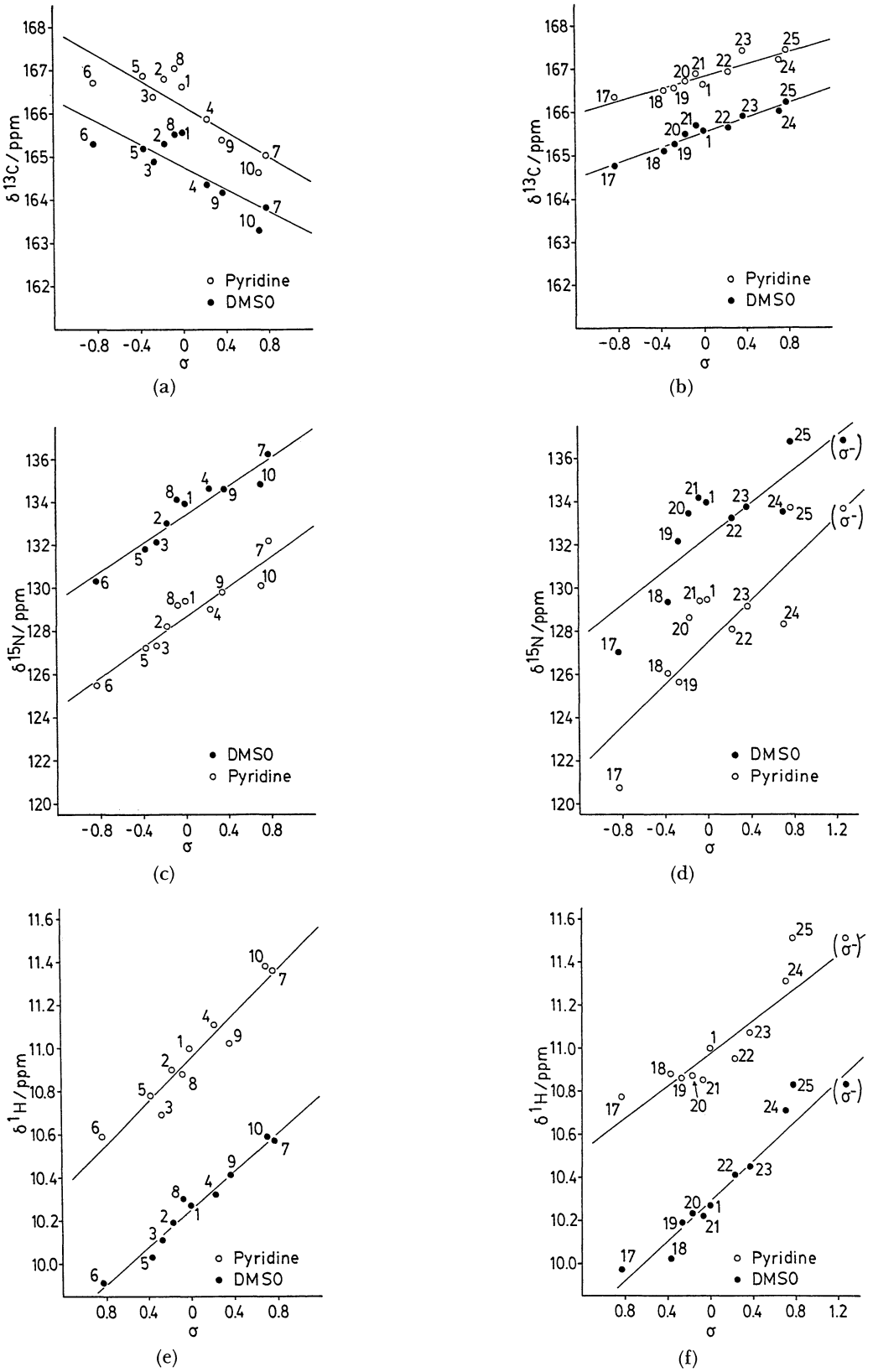


Fig. 1. The chemical shift vs. σ plot for a series of substituted benzamides.
(a) The $\delta^{13}C$ vs. σ_X plot for $XC_6H_4CONHC_6H_5$. (b) The $\delta^{13}C$ vs. σ_Y plot for $C_6H_5CONHC_6H_4Y$. (c) The $\delta^{15}N$ vs. σ_X plot for $XC_6H_4CONHC_6H_5$. (d) The $\delta^{15}N$ vs. σ_Y plot for $C_6H_5CONHC_6H_4Y$. (e) The $\delta^{1}H$ vs. σ_X plot for $XC_6H_4CONHC_6H_5$. (f) The $\delta^{1}H$ vs. σ_Y plot for $C_6H_5CONHC_6H_4Y$.

substituent X (due to the contribution of benzoyl resonance extended to the substituent X (**IV'**)), and vice versa. As remarked briefly in connection with the effect of Y on the carbonyl ^{13}C chemical shift, the effect of substituent Y on the ^{15}N chemical shift could be rationalized as a regular electronic effect which can be correlated most suitably with the Hammett's σ-constant (Fig. 1d). The deshielding effect on nitrogen becomes more significant in 2-substituted anilides **11—13** in which benzoyl resonance (**IV**) is partly prohibited by the non-coplanarity of their molecules.

Judging from the r-values for both the ^{15}N and the carbonyl ^{13}C chemical shifts vs. σ plots (Table 2), the regression to the line is better when the substituent is located on the ring farther from the observed nucleus. Therefore, the scattering of the plotted points must reflect the fact that the anisotropy or other unidentified direct effects (such as field effect) from the meta- and the para-substituents affect the chemical shift of the atoms attached nearly on the opposite side of the ring. The above trend regarding the r-values is reasonable since such effects can be expected to be considerably attenuated when the observed nucleus is separated by one more atoms from the ring bearing the substituent.

The substituent effect on the ^{1}H chemical shift of the amide NH group is analogous to that on the ^{15}N chemical shift. Again, the resonance of 2-substituted anilide (**11—14**) appears at a slightly lower field than that of unsubstituted benzanilide and that of the coressponding 4-substituted derivative. The discussion on the ^{15}N chemical shifts also applies to the ^{1}H chemical shifts, except for the effect of hydrogen bonding.

Correlation of the ^{15}N Chemical Shifts with the Rotational Barriers of the Corresponding *N,N*-Dimethylbenzamides. If the above interpretation of the substituent effect is true, an electron-donating substituent on the benzoyl aromatic ring should favor the conjugation all through the benzoyl π-system (contribution of **IV'**) and, as a result, should induce a negative charge on the carbonyl oxygen. This reasoning has been supported by the observed ^{17}O NMR chemical shifts of *N,N*-dimethylbenzamides.[18] The negative charge induced on the oxygen atom by the benzoyl resonance (**IV**), in turn, disfavors the dipolar mesomeric structure (**II'**) of the amide system which produces an additional negative charge on the oxygen. A decrease in the contribution of **II'** simultaneously causes a decrease in the positive charge on nitrogen and a lowering of the C-N bond order.

Benzanilides (**11—13**) bearing a substituent on the orthoposition of benzoyl ring, except for salicylanilide, have their ^{15}N signals at significantly lower fields than those of unsubstituted, 3-, and 4-substituted benzanilides (**2—10**). The resonance frequencies of *o*-aroyl substituted benzanilides coincide approximately with those of formanilides (138.4 and 141.9 ppm in $CDCl_3$).[20] Since the non-coplanarity of *o*-substituted benzoyl compounds have been proven by a vast amount of both experimental and theoretical studies,[21] the down field shifts observed with 2-aroyl substituted benzanilides are very probably caused by the steric hindrance to the conjugation between the aryl and carbonyl groups.

Consequently, the partial double-bond character and the amount of formal positive charge on the nitrogen atom are expected to come from the same origin, viz. the contribution of the amide resonance **II**. The amount of positive charge (or the electron density) on the nitrogen should be linear with the ^{15}N chemical shift, on one hand, while the partial double-bond character (or the bond order) of the C-N bond should be correlated with the rotational barrier, on the other hand. By combining these correlations, a linear relationship can be expected between the ^{15}N chemical shift and the rotational barrier. Unfortunately, the equilibrium between the two conformers (*s*-cis (**V**) and *s*-trans (**VI**)) about the C-N bond of benzanilide is far more favorable to the *s*-trans con-

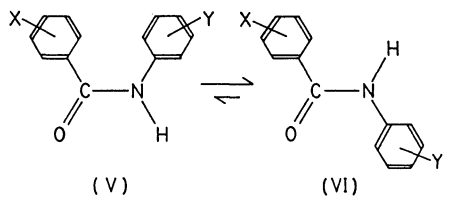
Table 2. The r-Values of the Hammett Plots in Figs. 2a—2f.

Nucleus	Solvent[a]	$KC_6H_4CONHC_6H_5$			$C_6H_5CONHC_6H_4Y$			Reference
		0	ρ	r	0	ρ	r	
^{15}N	Pyridine	128.7	3.515	0.943	127.5	4.865	0.851	This work
	DMSO	133.4	3.324	0.949	132.4	3.902	0.838	This work
^{1}H	Pyridine	10.95	0.507	0.963	10.98	0.377	0.948	This work
	DMSO	10.25	0.435	0.984	10.29	0.462	0.981	This work
^{13}C	Pyridine	166.18	−1.455	0.855	166.82	0.710	0.920	This work
	DMSO	164.78	−1.282	0.815	165.51	0.858	0.970	This work
					$NH_2C_6H_4Y$			
^{15}N	DMSO				55.03	−25.25	0.948	15
		$XC_6H_4CON(CH_3)_2$						
^{13}C	$CDCl_3$	171.05	−2.424	0.968				13

a) Perdeutrated solvents.

former (**VI**), making any estimation of the rotational barrier by DNMR extremely difficult and inaccurate. With the expectation that substituent X on the aroyl moiety should influence the rotational barrier, quite similarly in the two series of the amides (viz., $XC_6H_4CONHC_6H_5$ and $XC_6H_4CON(CH_3)_2$), the rotational barriers of the corresponding *N,N*-dimethylbenzamides were used as substitutes for those of benzanilides in the ^{15}N chemical shift vs. the rotational barrier plot shown in Fig. 2. When the 2-hydroxy derivative (**14**), capable of forming a chelate ring by a strong OH/O hydrogen bond, was excluded from the plot, the correlation became excellent, giving r=0.975. Figure 2 allowed us to conclude that the steric hindrance to the aryl-carbonyl conjugation results in a simultaneous down-field shift of the ^{15}N chemical shift and an increase in the rotational barrier.

The ^{15}N signals of salicylanilide (**14**) appear at an anomalously higher field than those of other 2-substituted benzanilides (**11**—**13**). A similar anomalous behavior was observed regarding the rotational barrier of *N,N*-dimethylsalicylamide, and has been interpreted as being the effect of chelation which induces a lowering of the partial double-bond character of the C-N bond.[18]



Solvent Effect. Solvent induced shifts of the ^{15}N spectra are also in line with an interpretation based on the mesomerism of amide, if we believe the generally accepted hypothesis that the molecular polarity tends to be augumented in polar solvents.

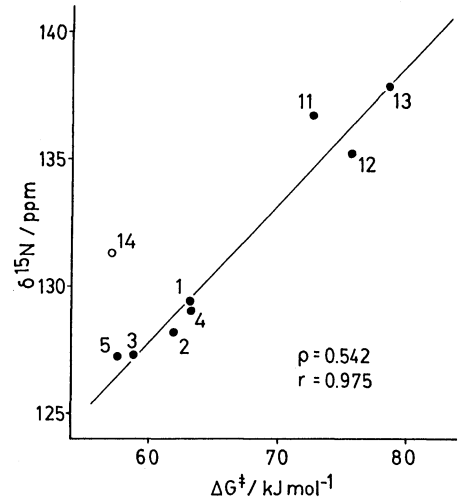
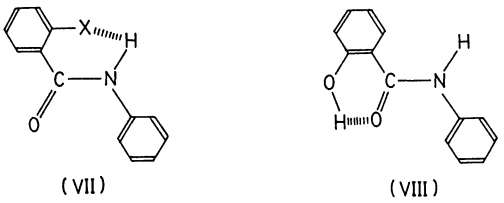


Fig. 2. The $\delta^{15}N(XC_6H_4CONHC_6H_5)$ vs. $\Delta G^{\ddagger}[XC_6H_4CON(CH_3)_2]$ plot in pyridine-d_5.

The spectra were measured in four solvents of various dielectric constants (4.8 for chloroform, 12.0 for pyridine, 32.6 for methanol, and 47.0 for dimethyl sulfoxide).[22] In addition, these solvents can be expected to interact with hydrogen-bond-forming solutes quite differently. The ^{15}N chemical shifts (Table 1) move regularly to lower fields in increasing order of the polarity of the solvent. The down-field shift is reasonable since it implies an increase in the contribution of the polar mesomeric structure (**II**) when the solvent becomes polar.

Effect of Intramolecular Hydrogen Bonding on ^1H Chemical Shifts—Evidence from Infrared Spectra. The NH signal in $CDCl_3$ of 2-methoxybenzanilide (**12**) was observed at an anomalously low field (δ; 9.80). This tendency could be seen with 2-chlorobenzanilides (**13**) to a much lesser extent. These anilides can form intramolecular NH/X hydrogen bonds in such a way as illustrated by **VII**, while keeping the most stable *s*-trans conformation of the CONH group. Therefore, the low field NH signal is suggestive of the presence of such an intramolecular hydrogen bond.



In order to prove the presence of an NH/X hydrogen bond, infrared NH stretching absorptions of several aroyl-substituted benzanilides were measured and are given in Table 3. 2-Methoxybenzanilide (**12**) absorbs at a considerably lower frequency than the normal secondary amide of the trans conformation (which usually absorbs at ca. 3640 cm^{-1} in chloroform),[23] giving an additional evidence for the intramolecular hydrogen bond. It is doubtful whether the hydrogen bond is sufficiently strong to maintain a completely planar conformation of the hydrogen-bonded chelate ring of **VII** or not. However, the

Table 3. NH and C=O Stretching Frequencies of Substituted Benzanilides $XC_6H_4CONHC_6H_5$ in CCl_4

No.	X	ν_{NH}/cm^{-1}	$\nu_{C=O}/cm^{-1}$
1	H	3445	1689
2	4-CH_3	3442	1691
3	4-OCH_3	3445	1688
4	4-Cl	3441	1692
5	4-OH	3452	—
11	2-CH_3	3437	1691
12	2-OCH_3	3376	1682
13	2-Cl	3422	1684
14	2-OH	3450	1657

attractive interaction between NH and the ortho-substituent should flatten the molecule to a considerable extent. The low-frequency shift of the NH band of 2-chlorobenzanilide (**13**) is rather small, but still suggests the presence of such an intramolecular hydrogen bond.

Since the chelation by the OH/O=C intramolecular hydrogen bond in salicylanilide (**14**) prevents such an NH/O intramolecular hydrogen bond as observed with 2-methoxybenzanilide (**12**) by taking the chelated *s*-trans conformation (**VIII**), salicylanilide (**14**) absorbs at a higher frequency (3449 cm^{-1}) in the NH stretching region.

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