ANOMALOUS POLAR SUBSTITUENT EFFECT ON ^{15}N NMR CHEMICAL SHIFTS OF ANILINE DERIVATIVES. ACYLANILIDES AND RELATED COMPOUNDS

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The ^{15}N chemical shifts of various *m*- and *p*-substituted anilides and related derivatives, $ZNHC_6H_4Y$ [$Z = C_6H_5CO$, CH_3CO, CF_3CO, CH_3SO_2, $(C_6H_5O)_2PO$ and H], were correlated with σ^- constants. With all series of anilides investigated, the plotted points for the *m*- and *p*-substituted derivatives tend to be separated from each other and to lie on two different regression lines. Reinvestigation from this point of view revealed that similar separations occur generally with substituted aniline derivatives. The anomalous polar substituent effect was ascribed to the very large contribution of a resonance effect. In addition, the local π-polarization effect causes a negative slope for the *m*-substituted series in the case of carboxylic anilides.

INTRODUCTION

Structures of natural and synthetic amides have been elucidated fairly extensively by usual and temperature-dependent ^{1}H, ^{13}C and ^{15}N NMR spectroscopy[1,2] and a large collection of chemical shift and coupling constant data have been accumulated.[3,4] Among a variety of NMR studies, ^{15}N NMR provides useful information concerning the structural features of amines and amide derivatives.[5,6] ^{15}N NMR spectra of various amines and related compounds have been reviewed by Levy and Lichter,[7] who pointed out the contribution of the paramagnetic term to the chemical shifts. The δ^{15}N values of amides are considerably lower than those of corresponding amines. Aromatic amides usually have ^{15}N resonances at slightly lower fields than those of aliphatic amides.[5] Substituent effects on the ^{15}N chemical shifts of anilines were discussed in relation to polar and *ortho*-steric effects.[8,9] The δ^{15}N values of substituted benzamides were correlated with the Hammett σ[10] and other[11] substituent constants. The polar effect on δ^{15}N by the substituent on the benzoyl group was shown to be normal ($\rho > 0$).

In previous investigations,[12–15] the rotational barriers of variously substituted benz- and salicylamides were correlated with their ^{15}N chemical shifts. We also reported that the ^{1}H and ^{13}C chemical shifts of substituted benzanilides, $XC_6H_4CONHC_6H_4Y$, could be cor-

related well with σ (σ^-).[16] In contrast, the correlation between δ^{15}N and σ^- of anilino substituents was only fair.[17] We tried to use some other substituent constants in an attempt to improve the correlation, but none of them gave a better correlation with the ^{15}N chemical shifts as a whole.

In this paper, we discuss this problem further, focusing on the peculiar separation of the plotted points of *p*-substituted anilides from those of *m*-substituted anilides in their Hammett plot [equation (1)][18] and to interpret this finding in terms of an unusually large contribution of resonance effects.
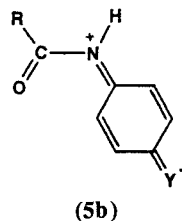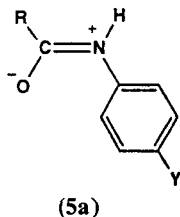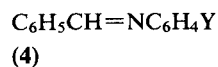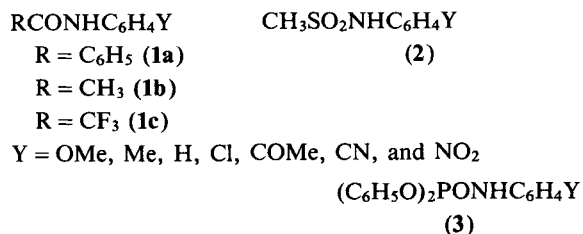
$$\delta = \rho\sigma + \delta_0 \qquad (1)$$

RESULTS AND DISCUSSION

In a search for the reason for the large dispersion of the Hammett plots concerning δ^{15}N values of anilides, we examined further the substituent effect on the ^{15}N chemical shifts (δ^{15}N) of some carboxylic anilides and related compounds (given in Table 1) by means of a correlation analytical approach using the Hammett equation [equation (1)]. As easily suspected from Figure 1, the plotted points for *m*- and *p*-substituted anilides seemed to lie on two separate straight lines. Hence the Hammett plots for the *m*- and the *p*-substituted derivatives were treated independently. The unsubstituted derivative (Y = H) was included in both plots. In order to evaluate the electronic effects due to

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the *m*- and *p*-substituents separately and impartially, six each of *m*- and *p*-substituted anilides (1a–c, 2 and 3) carrying the same substituents were chosen. The selected substituents on the anilino ring (Y) are methoxy, methyl, chloro, acetyl, cyano and nitro groups. [Two *p*-substituted derivatives (*p*-NMe$_2$ and *p*-OH) were added to the plot after careful examination which showed that the added points did not affect the ρ_p values significantly.]

RCONHC$_6$H$_4$Y   CH$_3$SO$_2$NHC$_6$H$_4$Y

   R = C$_6$H$_5$ (1a)   (2)

   R = CH$_3$ (1b)

   R = CF$_3$ (1c)

Y = OMe, Me, H, Cl, COMe, CN, and NO$_2$

                 (C$_6$H$_5$O)$_2$PONHC$_6$H$_4$Y

                           (3)

C$_6$H$_5$CH=NC$_6$H$_4$Y

(4)

      (5a)   (5b)

As the anilino nitrogen can participate directly in the mesomeric electron donation to an electron-withdrawing substituent at the *para*-position (resonance contribution of 5b), the σ^- constant[16] should be the most suitable substituent constant in order to evaluate the electronic effect of Y properly. We therefore employed σ^- in place of σ for the Hammett plots of the *p*-substituted anilide series. In fact, the best results were obtained when we used σ^- as a polar substituent constant. The ^{15}N chemical shifts of these anilides and related compounds are given in Table 1. The chemical shifts of several of these anilides, mostly *p*-substituted, have been reported previously.[17,19,20] These data agreed with the present results in most cases.

The Hammett plots of the ^{15}N chemical shifts are illustrated in Figure 1. The dashed and solid lines are the regression lines for the *m*- and the *p*-substituted series, respectively. Without exception, the plotted points for *p*-substituted anilides are clearly separated from those of *m*-substituted anilides. The ρ_p values are positive and the ρ_m values are negative for all series of carboxylic anilides 1a–c. The ρ_m values for sulphonic and phosphoric anilides (2 and 3) are positive, but their magnitudes are considerably smaller than the corresponding ρ_p values. This suggests that the polar

substituent affects differently the ^{15}N chemical shifts depending on whether it is located at the *meta*- or the *para*-position.

A very significant fact is that the δ^{15}N vs σ_m plots for all *m*-substituted acylanilides 1a–c have negative slopes. Similar trends have been observed with the carbonyl δ^{13}C of substituted benzoyl[21] and substituted cinnamoyl[22] derivatives and β-furylacrylamides.[22] The apparently reversed sign of ρ values for the δ^{13}C vs σ_I plots of these compounds were rationalized by Brownlee and Craik[23] by assuming the local polarization of the carbonyl group, which was theoretically interpreted by Reynolds.[24] The slope of the δ^{15}N vs σ plots for *m*-substituted anilides can be interpreted by taking into account the local polarization in the amide group in analogy with the deductions on arylcarbonyl compounds by Brownlee and Craik.[23] The local polarization of the carboxamide group due to the effect of the dipoles in anilino groups can be described by structure 6, in which the induced charge separation is shown by $\delta\delta+$ or $\delta\delta-$. With *p*-substituted anilides, very strong conjugation of the anilino nitrogen with the *p*-substituent might overcome the local polarization.


            (6)
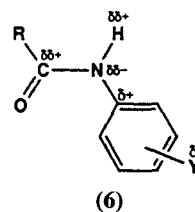
The separation of the plotted points for *m*- and *p*-substituted compounds was again observed with substituted sulphonanilides (2) and phosphoranilides (3), although the ρ_m values are positive with these amides. The nitrogen atoms of these amides must be less tightly conjugated with SO$_2$R or PO(OR)$_2$ groups than with the acyl group in acylanilides, judging from their larger ρ_p values than for acylanilides and from their positive ρ_m values. This is in accord with the fact that the N—S(P) pπ–dπ bonds in these anilides are weaker than the N—C pπ–pπ bonds in carboxamides. The δ^{15}N vs σ^- plot for benzylideneanilines 4 also showed a separation of the plotted points for *m*- and *p*-substituted compounds similar to that for sulphur and phosphorus anilides.

The separation of the plotted points for the *m*- and *p*-substituted aniline derivatives in the Hammett plots of δ^{15}N was revealed to be general. The δ^{15}N vs σ^- plots for anilines and anilinium chlorides also showed similar separation of the plotted points for the *m*- and *p*-substituted compounds [Figure 1(d)], although ρ_m did not become negative in any instance. Hence the fact

that the ρ_m values for sulphonanilides (**2**), phosphoranilides (**3**) and benzylideneanilines (**4**) are apparently smaller than the ρ_p values for the same series is not evidence for the local polarization of the sulphonamido, phosphoramido and azomethine groups in these compounds. Our recent studies on $\delta^{31}P$ of *m*- and *p*-substituted phosphoranilides (**3**) showed that the $\delta^{31}P$ vs σ plot has a negative slope ($\rho = -1\cdot92$), indicating that local polarization of the phosphoric ester group [$(C_6H_5O)_2PO$] induced by the field effect due to the YC_6H_4NH group predominantly occurs. This localization can be described by structure **7a**. Hence the alternative local polarization **7b** of the phosphoramido group [$(C_6H_5O)_2PONH$] was doubtful.

As indicated above, the substituent effect on $\delta^{15}N$ is irregular; *m*- and *p*-substituted aniline derivatives have considerably different ρ values. In previous studies on similar Hammett plots,[16] the plotted points related mainly to *p*-substituted derivatives, with only a few

7a   **7b**
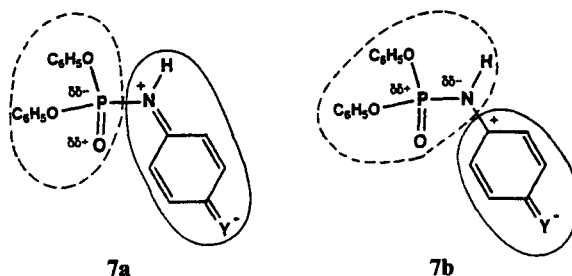
m-substituted derivatives. Probably for this reason the different behaviour of the ^{15}N chemical shifts of *m*- and *p*-substituted anilides was overlooked.

We examined further this peculiar substituent effect. With the aim of evaluating quantitatively the contributions of inductive and resonance effects to $\delta^{15}N$, the chemical shift values were regressed to the Taft's dual

Table 1. ^{15}N chemical shifts[a] of various *m*- and *p*-substituted anilides, $ZNHC_6H_4Y$, in DMSO-d_6[b]

Y	C_6H_5CO	CH_3CO	CF_3CO	CH_3SO_2	$(C_6H_5O)_2PO$	$PhCH=NC_6H_4Y$
p-NMe₂	127·0	137·7	132·3	122·4	74·8	322·9
	(120·7)	(132·7)	(127·1)	(117·4)	(68·4)	
p-OH	129·3	137·8	132·3	122·6	75·3	331·4
	(126·0)	(132·5)	(127·0)	(117·7)	(70·7)	
p-OMe	132·1	137·9	132·2	123·5	76·7	330·9
	(125·6)	(132·8)	(126·8)	(118·1)	(71·5)	
p-Me	133·4	139·3	133·0	125·6	79·3	332·2
	(128·6)	(133·8)	(127·7)	(120·7)	(74·6)	
m-Me	134·1	139·8	133·4	126·8	80·7	333·0
	(129·4)	(134·9)	(128·2)	(122·0)	(76·1)	
H	133·9	140·0	133·4	127·1	81·2	332·9
	(129·4)	(134·8)	(128·3)	(122·2)	(76·7)	
m-OMe	134·6	140·2	133·7	127·8	81·8	332·6
	(129·6)	(133·7)	(128·1)	(122·6)	(76·8)	
p-Cl	133·2	139·1	132·5	126·6	81·1	336·8
	(128·1)	(133·3)	(127·1)	(121·7)	(76·2)	
m-Cl	133·7	139·5	132·9	127·9	82·7	338·3
	(129·1)	(134·2)	(127·2)	(123·0)	(77·9)	
m-Ac	133·9	139·8	133·1	127·5	82·0	
	(128·9)	(134·3)	(127·9)	(122·1)	(77·5)	
p-Ac	136·1	142·1	134·4	131·2	86·6	
	(131·2)	(136·4)	(128·8)	(125·1)	(81·9)	
m-CN	133·6	139·4	132·5	128·1	83·4	339·5
	(128·4)	(133·7)	(127·3)	(123·3)	(77·0)	
p-CN	136·2	142·1	134·3	132·1	87·9	341·5
	(131·2)	(136·7)	(129·2)	(127·5)	(82·9)	
m-NO₂	133·5	139·6	132·8	128·7	83·8	334·9
	(128·3)	(132·7)	(127·5)	(124·2)	(79·3)	
p-NO₂	136·8	142·9	134·5	133·5	89·5	351·7
	(133·7)	(137·2)	(129·3)	(129·2)	(84·9)	

[a] Downfield chemical shifts (ppm) from NH_3 (external).
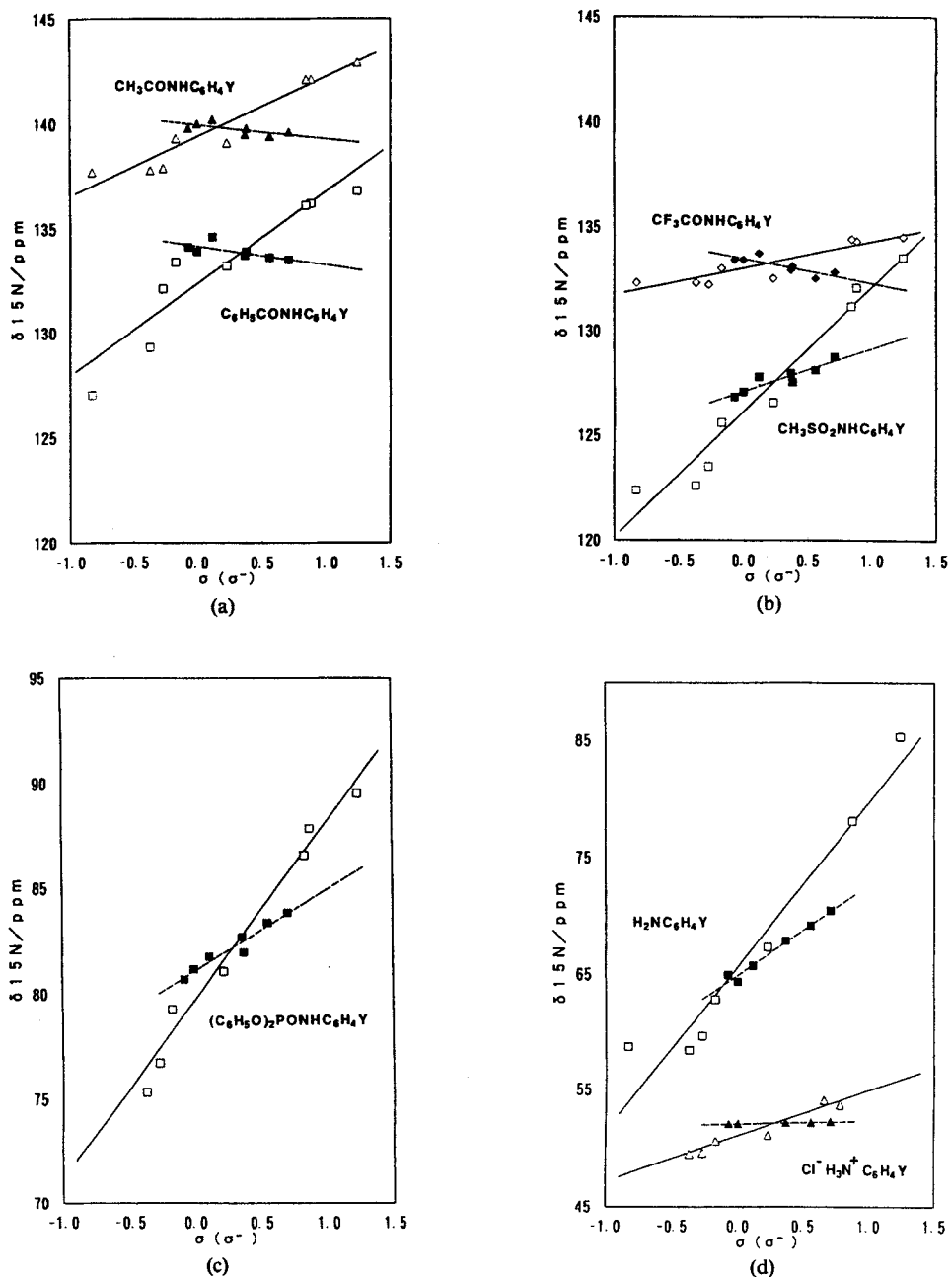[b] Chemical shifts in pyridine-d_5 are given in parentheses.

Figure 1. $\delta^{15}N$ vs σ^- (Y) plots for (dashed lines) m- and (solid lines) p-substituted anilides, $ZNHC_6H_4Y$, measured in DMSO-d_6: (a) actanilides (Z = CH_3CO) and benzanilides (Z = C_6H_5CO); (b) trifluoroacetanilides (Z = CF_3CO) and methanesulphonanilides (Z = CH_3SO_2); (c) diphenylphosporanilides [Z = $(C_6H_5O)_2PO$]; (d) anilines (Z = H) and anilinium chlorides (ZNH = $NH_3^+Cl^-$)

substituent parameter (DSP) equation:[25,26]

$$\delta = \rho_I \sigma_I + \rho_R \sigma_R + \delta_0 \qquad (2)$$

The results are given in Table 2. As can be seen from its percentage contributions, the contribution of the resonance effect to the ^{15}N chemical shifts is very large and the electronic effect on $\delta^{15}N$ of the p-substituent Y originates largely from the resonance contribution, which can be described by the canonical formula **5b**. Simultaneously, the correlation coefficient r_c for the combined assembly of m- and p-substituted derivatives is considerably lower than r_c for the partial assembly consisting of m- or p-derivatives. This implies that the separation of the plotted points is statistically meaningful.

In order to compare this feature with the cases of the chemical shifts of other nuclei, the results of similar analyses of ^1H and ^{13}C chemical shifts of benzanilide, for example, are also given in Table 2. In general, the separations of the plotted points for the m- and p-substituted compounds are slight and barely exceed the limit of experimental error for the ^{13}C chemical shifts. For the ^1H chemical shifts, the separation becomes slightly larger but not so obvious as for the ^{15}N chemical shifts. As expected, the correlation coefficient for the whole assembly is nearly the same as those for the local m- and p-assemblies.

The very predominant contribution of the resonance effect to $\delta^{15}N$ was supported by the analysis using the Yukawa–Tsuno equation [equation (3)],[27] in which r is a measure of the resonance demand:

$$\delta_p = \rho_m(\sigma_p^\circ + r\,\Delta\sigma_R) + \delta_{0m} \qquad (3)$$

In accord with the results of DSP analysis, the resonance demand r is fairly large for all series of anilides (Table 3).

As revealed by the two DSP analyses, the contribution of the resonance term is overwhelming in the $\delta^{15}N$ of substituted anilines and even in those of substituted anilinium ions. Thus, in the $\delta^{15}N$ vs σ^- plots, the very large contribution of the resonance effect must be responsible, at least partly, for the upward deviation of the plotted points for p-substituted derivatives from the regression line for m-substituted derivatives.

^{15}N chemical shifts are considered to be most significantly influenced by the local paramagnetic term, which increases when the molecule has a low-energy excited state which is localized considerably on the nitrogen atom, when the orbitals on the nitrogen are closer to the nucleus, and when the nitrogen atom is multiply bonded.[7] The contribution of the local paramagnetic term has been correlated with the electronic transition energies in several cases.[28,29] The $\delta^{15}N$ values of N-substituted anilines could also be correlated

Table 2. Dual substituent parameter (DSP) Analysis [using equation (2)] of the polar substituent effect on the ^{15}N NMR chemical shifts of various substituted anilides, $RNHC_6H_4Y$

RNH		ρ_I[a]	ρ_R[a]	δ_0[a]	$I(\%)$	$R(\%)$	r_c
C_6H_5CONH	All	+1·09(2·35)	+7·99 (2·72)	134·1 (1·02)	12·0	88·0	0·748
	m	−0·52(0·34)	−1·56 (0·51)	133·9 (0·14)	25·0	75·0	0·917
	p	+2·71(1·78)	+11·52 (1·92)	134·1 (0·73)	19·0	81·0	0·958
CF_3CONH	All	−0·31(0·83)	+1·91 (0·83)	133·4 (0·69)	14·0	86·0	0·572
	m	−1·04(0·37)	−0·94 (0·48)	133·4 (0·23)	52·5	47·5	0·888
	p	+0·64(0·59)	+3·28 (0·56)	133·5 (0·38)	16·3	83·7	0·941
CH_3SO_2NH	All	+4·64(2·29)	+8·57 (2·31)	126·9 (1·92)	35·1	64·9	0·833
	m	+2·35(0·32)	−0·24 (0·41)	127·0 (0·20)	90·8	9·2	0·966
	p	+6·36(1·56)	+12·72 (1·48)	127·3 (1·00)	33·3	66·7	0·978
$(PhO)_2PONH$	All	+6·73(2·76)	+11·54 (2·79)	81·0 (2·32)	36·8	63·2	0·864
	m	+4·11(0·28)	+0·62 (0·37)	81·0 (0·18)	86·9	13·1	0·992
	p	+8·02(1·79)	+16·68 (1·70)	81·4 (1·15)	32·5	67·5	0·983
NH_2	All	+13·69(5·56)	+18·00 (6·45)	65·6 (4·46)	43·2	56·8	0·847
	m	+7·65(0·85)	+2·73 (1·20)	64·9 (0·53)	73·7	26·3	0·986
	p	+20·50(5·51)	+24·14 (5·94)	65·6 (3·47)	45·9	54·1	0·955
$NH_3^+Cl^-$	All	+1·69(1·32)	+4·95 (1·68)	52·0 (1·01)	25·4	74·6	0·790
	m	+0·30(0·07)	+0·029(0·096)	52·1 (0·04)	91·1	8·9	0·950
	p	+2·29(0·67)	+7·36 (0·85)	51·8 (0·42)	23·7	76·3	0·983
^{13}C (carbonyl) C_6H_5CO	All	+0·61(0·23)	+1·28 (0·27)	165·63(0·10)	32·3	67·7	0·914
	m	+0·57(0·13)	+0·27 (0·20)	165·63(0·05)	68·2	31·8	0·946
	p	+0·70(0·11)	+1·54 (0·11)	165·59(0·04)	31·3	68·7	0·993
^1H (amide NH) C_6H_5CO	All	+0·59(0·03)	+0·70 (0·10)	10·30(0·04)	45·5	54·5	0·973
	m	+0·57(0·03)	+0·42 (0·05)	10·28(0·01)	57·8	42·2	0·997
	p	+0·63(0·11)	+0·81 (0·12)	10·31(0·05)	43·7	56·3	0·982

[a] Standard deviations are given in parentheses.

Table 3. Analysis of the polar substituent effect on the chemical shifts of various substituted anilides by using the Yukawa–Tsuno equation [equation (3)]

Nucleus	r	ρ_m	r_c
$C_6H_5CONHC_6H_4Y$:			
[15]N	−13·68	−0·93	0·934
[13]C	1·55	0·55	0·934
$CH_3CONHC_6H_4Y$:			
[15]N	−11·96	−0·71	0·904
[13]C	1·50	1·13	0·949
$CH_3SO_2NHC_6H_4Y$:			
[15]N	6·68	1·86	0·963
$(C_6H_5O)_2PONHC_6H_4Y$:			
[15]N	3·98	3·64	0·960
[31]P	1·97	−1·35	0·948
$H_2NC_6H_4Y$:			
[15]N	3·57	7·29	0·937

roughly ($r = 0·908$) with the electronic transition energies estimated from the wavelengths at the maxima of their ultraviolet absorption bands (Table 4). The fact that the ^{15}N nuclei of the anilinium salts resonate at the highest fields in spite of having the lowest electron densities could not be rationalized merely by the diamagnetic electron density effect. Moreover the anilide bearing an electron-withdrawing p-substituent showed a considerably larger bathochromic shift than the corresponding m-substituted anilide, while the shifts are much the same between the anilides bearing electron-donating m- and p-substituents (Table 4). Thus the large bathochromic shifts in the ultraviolet bands correspond well with the large downfield shifts

of δ^{15}N in anilides bearing electron-withdrawing p-substituents.

All these facts suggest that the lowering of the electronic excited-state energies should cause a downfield shift. The downfield shift due to the contribution of the excited state was also exemplified by Savitsky et al.[28] on some carbonyl ^{13}C chemical shifts. This, in turn, suggests that the increase in the polarizability must be responsible for the low-field shift of δ^{15}N, even if it can be superficially measured by the resonance term in the correlation analysis. On the other hand, the upfield shift by an electron-donating m-substituent should be ascribed to the diamagnetic electron density effect. Hence the ^{15}N chemical shift should be interpreted taking into account the two competing effects of the paramagnetic and the diamagnetic shielding terms. The above-discussed effects can by no means reverse the sign of ρ for carboxylic anilides, however. Thus, the reverse sign of ρ_m could be reasonably ascribed to the local polarization.

EXPERIMENTAL

All anilides used are known compounds and were prepared by the reaction of the corresponding acyl chloride or benzenesulphonyl chloride with substituted anilines. The crude anilides were purified by repeated recrystallization. The purity was checked by comparing their melting points with those in the literature.

^{1}H and ^{13}C NMR spectra were measured using a JEOL EX-270 spectrometer. [15]N spectra were recorded on a JEOL FX-90Q spectrometer using a 10 mm diameter probe. Samples for the measurements were

Table 4. Ultraviolet spectra of various compounds

Compounds	Substituent	λ_{max}/nm	$\varepsilon/l\ mol^{-1}\ cm^{-1}$
	NHZ:		
N-Substituted anilines, C_6H_5NHZ	$NH_3^+Cl^-$ [a]	203	7660
	NH_2 [a]	230	8200
	$NHSO_2CH_3$	235	9000
	$NHCOCH_3$	239	10400
	$N{=}CHC_6H_5$ [a]	262	17000
	Y:		
m- and p-substituted Acetanilides, $YC_6H_4NHCOCH_3$ [b]	p-NO$_2$	314	23000
	m-NO$_2$	241	12000
	p-CN	266	13900
	m-CN	248	10200
	m-Cl	245	7600
	p-Cl	249	7700
	m-OCH$_3$	245	10000
	H	242	11200
	p-CH$_3$	244	9500
	m-CH$_3$	245	7200
	p-OCH$_3$	249	9000

[a] UV data from Ref. 30.
[b] In methanol solution.

prepared by dissolving *ca* 100 mg of anilide in *ca* 1·5 ml of solvent. The ^{15}N NMR spectra were measured at 9·04 MHz using a repetition of 15–18 μs pulses (flip angle 45°) and 3 s delays; 2000–10 000 scans were accumulated per spectrum 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).

REFERENCES

1. W. E. Stewart and T. H. Siddall, III, *Chem. Rev.* **70**, 517 (1970).
2. D. E. Wemmer and B. R. Reid, *Annu. Rev. Phys. Chem.* **36**, 105 (1985).
3. (a) I. I. Schuster, S. H. Doss and D. J. Roberts, *J. Org. Chem.* **43**, 4693 (1976); (b) G. Binsch, J. B. Lambert, B. W. Roberts and J. D. Roberts, *J. Am. Chem. Soc.* **86**, 5564 (1964); (c) A. J. Bennet, V. Somayaji, R. S. Brown and B. D. Santarsierino, *J. Am. Chem. Soc.* **113**, 7563 (1991).
4. L. M. Jackman, in *Dynamic Nuclear Magnetic Resonance Spectroscopy*, edited by L. M. Jackman and F. A. Cotton, p. 208. Academic Press, New York (1975).
5. P. W. Westerman and J. D. Roberts, *J. Org. Chem.* **43**, 1177 (1978).
6. (a) G. J. Martin, J. P. Gouesnard, J. Dorie, C. Rabiller and M. L. Martin, *J. Am. Chem. Soc.* **99**, 1381 (1977); (b) J. Dorie, J. P. Gouesnard, C. Rabiller, B. Mechin, N. Naulet and G. J. Martin, *Org. Magn. Reson.* **13**, 126 (1980).
7. G. C. Levy and R. L. Lichter, *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*. Wiley, New York (1979).
8. T. Axenrod, P. S. Pregosin, M. J. Wieder, E. D. Becker, R. B. Bradley and G. W. A. Milne, *J. Am. Chem. Soc.* **93**, 6536 (1970).
9. T. Axenrod and M. J. Wieder, *Org. Magn. Reson.* **8**, 350 (1976).
10. P. S. Pregosin, E. W. Randall and A. I. White, *J. Chem. Soc., Perkin Trans. 2* 513, (1972).
11. R. G. Jones and J. M. Wilkins, *Org. Magn. Reson.* **11**, 20 (1978).
12. H. Endo, M. Hirota, Y. Ito, I. Takeuchi and Y. Hamada, *Bull. Chem. Soc. Jpn.* **55**, 1564 (1982).
13. H. Suezawa, K. Tsuchiya, E. Tahara and M. Hirota, *Bull. Chem. Soc. Jpn.* **60**, 3973 (1987).
14. H. Suezawa, K. Tsuchiya, E. Tahara and M. Hirota, *Bull. Chem. Soc. Jpn.* **61**, 4057 (1988).
15. H. Suezawa, T. Yuzuri and M. Hirota, *Bull. Chem. Soc. Jpn.* **63**, 328 (1990).
16. H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953).
17. T. Yuzuri, T. Masubuchi, H. Suezawa and M. Hirota, *Chem. Lett.* 871 (1992).
18. L. P. Hazmmett, *J. Am. Chem. Soc.*, **59**, 96 (1937).
19. M. I. M. Wazeer and Sk. Asrof Ali, *Magn. Reson. Chem.* **28**, 601 (1990).
20. M. Fujio, Y. Tsuno, Y. Yukawa and Y. Takai, *Bull. Chem. Soc. Jpn.* **48**, 3330 (1975).
21. J. Bromilow, R. T. C. Brownlee, D. J. Craik, P. R. Friske, J. E. Rowe and M. Sadek, *J. Chem. Soc., Perkin Trans. 2* 753 (1981).
22. Z. Friedel, S. Bohm, I. Goljer, A. Piklerova, D. Poorova, A. Rickova and J. Kovac, *Collect. Czech. Chem. Commun.* **52**, 409 (1987).
23. R. T. C. Brownlee and D. J. Craik, *J. Chem. Soc., Perkin Trans. 2* 760 (1981).
24. W. F. Reynolds, *Prog. Phys. Org. Chem.* **14**, 165 (1983).
25. R. W. Taft, *J. Am. Chem. Soc.* **75**, 4231 (1953).
25. R. W. Taft, in *Steric Effects in Organic Chemistry*, edited by M. S. Newman, Chapt. 13. Wiley, New York (1956).
27. Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.* **32**, 971 (1959).
28. G. B. Savitsky, K. Namikawa and G. Zweifel, *J. Phys. Chem.* **69**, 3105 (1965).
29. K. A. Jorgensen, *J. Chem. Soc., Perkin Trans. 2*, 885 (1987).
30. *DMS UV Atlas of Organic Compounds*. Butterworths, London (1966).