^{15}N-H Coupling Constants and Nitrogen Shifts in Some Substituted [^{15}N]Aniline Derivatives

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THE hypothesis that the magnitude of one bond ^{15}N–H coupling constants could be correlated with the stereochemistry at nitrogen and hence with bond hybridization was tested independently by two groups.[1,2] The basic hypothesis is that the coupling is dominated by the Fermi contact term and is proportional to the square of the coefficient of the 2*s* wave-function, in the LCAO treatment of the hybrid orbital. The majority of ^{15}N–H couplings correlate well, the exception being diphenylketimine The ammonium ion with a coupling of 74·5 Hz is typical of couplings for nitrogen with four neighbours, *i.e.* in molecules assumed to have sp^3 bond hybridization,[2] while amides (3 nitrogen neighbours) with couplings of *ca.* 90 Hz are typical sp^2 systems.[1,3] More recently, couplings of *ca.* 135 Hz have been found for systems of the type $RC{\equiv}\overset{+}{N}{-}H$ which are presumed to exhibit *sp* bond hybridization (two nitrogen neighbours).[4]

The coupling for [^{15}N]aniline has been determined previously[5,6] and was shown to be solvent dependent.[5] It was noted that the range of values was intermediate between the planar and tetrahedral values, an observation commensurate with some degree of p_π–p_π overlap.[6]

The situation for a series of substituted anilines is shown in the Table. The nitrogen chemical-shifts were determined both by the normal heteronuclear frequency sweep method and its INDOR version. The couplings are linearly related to the Hammet σ-factor for the substituent (see Figure).

The data for acetone solutions may be rationalized in terms of the stereochemical change expected at the nitrogen from the known electronic characters of the substituents: π-withdrawal giving a flattened pyramid at nitrogen (larger

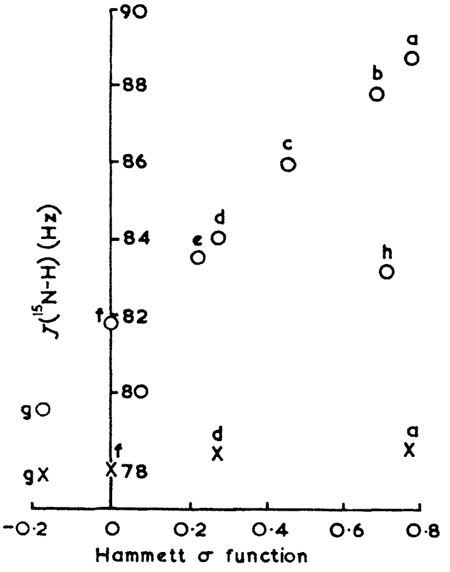

FIGURE. *A plot of* $J(^{15}$N–H) *against Hammett* σ *function in some substituted* [^{15}N]*aniline derivatives.*
a, *p*-nitroaniline; b, 2,4,6-tribromoaniline; c, 2,4-dibromoaniline; d, *p*-iodoaniline; e, *p*-bromoaniline; f, aniline; g, *p*-toluidine; h, *m*-nitroaniline; solvents, o acetone, × deuteriochloroform.

$J(^{15}N–H)$ Coupling constants and ^{15}N chemical shifts in some substituted anilines

Compound	Solvent	$J(^{15}$NH ± 0·1)Hz	^{15}N shift† (Hz; additional to 6,080,000 Hz).
p-Nitroaniline	Me_2CO	88·9	176·5 ± 0·2
	$CDCl_3$	78·7	
p-Bromoaniline	Me_2CO	83·6	89·0 ± 0·2
p-Iodoaniline	Me_2CO	84·1	110·0 ± 5·0
	$CDCl_3$	78·5	
2,4,6-Tribromoaniline	Me_2CO	87·8	
2,4-Dibromoaniline	Me_2CO	86·0	
Aniline	Me_2CO	81·9	89·9 ± 0·2
	$CDCl_3$	78·0	
p-Toluidine	Me_2CO	79·6	70·9 ± 0·2
	$CDCl_3$	76·9	70·9 ± 0·5
Anilinium	$CF_3{\cdot}CO_2H$	75·0 ± 0·3	27·0 ± 1·0
m-Nitroaniline*	Me_2CO	83·0 ± 0·3	

* Observed in natural abundance; † Measured in field at which Me_4Si resonates at 60,000,000 Hz.

coupling); π-donation giving a smaller coupling than in aniline itself.

For deuteriochloroform solutions the substituent effect is far less. This solvent effect may be due to the Lewis acid character of deuteriochloroform—a suggestion consistent with the smaller *J* values in this solvent closer to the value of 75 Hz for the anilinium ion.

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