Substituent Effects on One-Bond ^{15}N—^{13}C Couplings in *N,N*-Dimethylanilines and Nitrobenzenes

Effect of Steric Inhibition of Conjugation

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The $^1J(^{15}N^{13}C)$ values for a series of ring-substituted *N,N*-dimethylaniline-^{15}N derivatives and a series of nitrobenzene-^{15}N derivatives were measured from the ^{13}C spectra. In the nitrobenzenes, small changes in $^1J(^{15}N^{13}C)$ are attributed to the inductive effect of the substituents, since steric inhibition of conjugation has little effect on the magnitude of the coupling. In contrast, steric inhibition of nitrogen lone-pair delocalization in *N,N*-dimethylaniline derivatives markedly reduces the value of $^1J(^{15}N^{13}C)$. Theoretical calculations of $^1J(^{15}N^{13}C)$ values for the two series of compounds were made using standard INDO parameters and a 'sum-over-states' perturbation approach. Fair agreement between the calculated and experimental values is found.

INTRODUCTION

In aniline derivatives, ring substituents are known to have a profound influence on the directly bonded ^{15}N—H and ^{15}N—^{13}C spin–spin coupling interactions.[1–3] Binsch *et al.*[4] have successfully related the one-bond ^{15}N—^{13}C coupling constant to the atomic hybridizations by the empirical equation (1),

$$^1J(^{15}N^{13}C) = (80)^{-1}S_NS_C \qquad (1)$$

where S_N and S_C represent the percentage s character of the N and C contributions to the N—C bond. This relationship works reasonably well provided that the coupling interaction is dominated by the contact mechanism,[5,6] and the s electron character of the lone pairs remains unchanged.[11] Thus, in going from aniline to *p*-nitroaniline, the observed increases in $^1J(^{15}NH)$ and $^1J(^{15}N^{13}C)$ are readily explained in terms of a substituent-induced delocalization of the lone pair corresponding to a change in hybridization to give a more flattened amino-nitrogen pyramid.

Theoretical calculations in these laboratories and elsewhere[5–7] indicate that the contact term also dominates the one-bond N—C coupling mechanism in nitro compounds. It is, therefore, of interest to determine whether substituents in a series of closely related nitrobenzene-^{15}N derivatives have an effect on $^1J(^{15}N^{13}C)$ similar to that previously found in anilines.[2,3] The effect on ^{15}N and ^{13}C chemical shifts in anilines[8–10] and nitrobenzenes[11] of a reduced resonance interaction caused by *ortho* substituents which sterically twist the amino or nitro groups from coplanarity with the aryl ring has been extensively investigated and is fairly well documented. On the other hand, the effect on $^1J(^{15}N^{13}C)$ of steric inhibition of conjugation has received very little attention. Presumably, this may be attributed to the need for ^{15}N-enriched materials which facilitate the determination of $^1J(^{15}N^{13}C)$ data.

In the present investigation, a series of ^{15}N-labelled (95 % enrichment) nitrobenzenes and a series of *N,N*-dimethylanilines, each having a variety of electron-donating, electron-withdrawing and bulky *ortho* substituents, have been synthesized. To assess the role of the different substituents and their effects on the ^{15}N–^{13}C couplings and shieldings in these systems, the ^{13}C spectra have been determined. The experimental results are compared with the $^1J(^{15}N^{13}C)$ values calculated by the INDO MO approach.

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RESULTS AND DISCUSSION

Indirect isotropic nuclear spin–spin interactions arise from three types of electron coupling mechanisms.[12] Usually, the largest contribution to the coupling results from the contact term, J^C, which at the semi-empirical MO level depends upon the s-electron density, $S_x(O)^2$, at each nucleus taking part in the spin–spin interaction. The other two terms which contribute to the overall coupling are the orbital term, J^O, and the spin–dipolar term, J^D. These depend upon the expectation values of the inverse cube of the distance between the individual coupled nuclei and their respective 2p electrons, $\langle r^{-3}\rangle_x$.

To assess the several contributions to ${}^1J({}^{15}N{}^{13}C)$ in nitrobenzene derivatives, the three coupling terms have been evaluated semi-empirically by means of the 'sum-over-states' perturbation method[13] in conjunction with the standard INDO parameterization scheme. The calculations have been performed by employing standard molecular geometries.[14] In order to compare the calculated and experimental couplings, Eqn (2) is employed,

$$J^{EXP} = a_{NC}J_C' + b_{NC}(J_O' + J_D') \qquad (2)$$

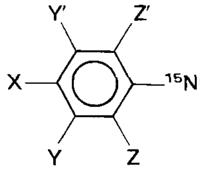
where J_C', J_O' and J_D' are the calculated values of the contact, orbital and dipolar contributions omitting a_{NC} and b_{NC}, respectively. The parameters a_{NC} and b_{NC} represent the one-center integral products $S_N(O)^2S_C(O)^2$ and $\langle r^{-3}\rangle_N \langle r^{-3}\rangle_C$, respectively, which are treated as least squares parameters as suggested elsewhere.[6,15]

For the ${}^1J({}^{15}N{}^{13}C)$ data considered in this work, values of 21.910 au^{-6} and 11.019 au^{-6} for a_{NC} and b_{NC}, respectively, are obtained. The corresponding values of these integral products are 13.199 au^{-6} and 5.247 au^{-6} when obtained from SCF atomic functions, and 15.800 au^{-6} and 3.535 au^{-6} from Slater-type atomic orbitals.[6] In Tables 1 and 2 the value of J^C is given by $a_{NC}J_C'$ and $J^O + J^D$ is similarly obtained from $b_{NC}(J_O' + J_D')$.

The experimentally determined ${}^1J({}^{15}N{}^{13}C)$ values for the nitrobenzene-${}^{15}N$ derivatives in DMSO-d_6 solution that have been examined in the present work are summarized in Table 1, and these data are compared with the MO calculated values. The calculated results show that the one-bond ${}^{15}N$—${}^{13}C$ coupling constant for the molecules considered is dominated by contributions from the contact term. In addition, it is apparent that the expected sign of ${}^1J({}^{15}N{}^{13}C)$ is negative, in agreement with conclusions reached by other workers[5–7] based on calculations involving related molecules.

The calculated results show reasonable agreement with the experimentally determined ${}^1J({}^{15}N{}^{13}C)$ values, although the overall effects of the substituents, X, Y and Z on the N—C coupling are surprisingly small. Available x-ray evidence[16] indicates that, at least in the crystalline state, the nitrobenzene molecule is planar as implied by the usual mesomeric representation

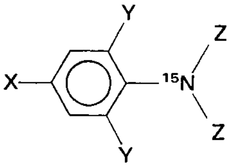
Table 1. Some calculated and experimental ${}^1J({}^{15}N{}^{13}C)$ values and related C-1 ${}^{13}C$ shifts in nitrobenzene derivatives[a]



X	Y	Y'	Z	Z'	J^C	$J^O + J^D$	J^{total}	$J^{exp\,b}$(Hz)	$\delta^{13}C$-1[c,d]
H	H	H	H	NH_2	−14.954	0.950	−14.0	(−)14.8	130.1
CH_3	NO_2	H	CH_3	NH_2	−16.860	1.080	−15.8	(−)15.8	133.0
NH_2	H	H	H	H	−16.925	0.761	−16.2	(−)16.2	135.5
NH_2	CH_3	CH_3	H	H	−15.972	0.854	−15.1	(−)15.8	135.7
CH_3	H	NO_2	CH_3	NH_2	−16.298	1.160	−15.1	(−)15.6	136.4
CH_3O	H	H	H	H	−16.325	0.652	−15.7	(−)15.9	140.6
NH_2	H	NO_2	CH_3	CH_3	−17.945	1.165	−16.8	(−)16.6	140.9
$(CH_3)_2N$	CH_3	CH_3	H	H	−18.468	0.963	−17.5	(−)14.7	142.9
t-C_4H_9	H	H	H	H	−18.142	0.924	−17.2	(−)15.0	145.3
CH_3	NO_2	NO_2	H	H	−16.218	0.843	−15.4	(−)18.0	145.4
CH_3	H	H	H	H	−16.538	0.798	−15.7	(−)14.9	145.4
t-C_4H_9	H	H	*t*-C_4H_9	*t*-C_4H_9	−20.754	1.331	−19.4	(−)13.7[e]	146.3
Cl	H	H	H	H	−19.207	0.916	−18.3	(−)15.4	146.1
H	H	H	H	H	−15.682	0.749	−14.9	(−)14.7	147.6
H	NO_2	H	H	H	−15.265	0.847	−14.4	(−)15.9	147.8
CH_3	H	H	CH_3	CH_3	−18.028	1.214	−16.8	(−)14.7	149.0
NO_2	H	H	H	H	−14.817	0.725	−14.1	(−)15.3	150.6

[a] Samples were measured as 1 M solutions in DMSO-d_6.
[b,c] ${}^1J({}^{15}N{}^{13}C)$ values and ${}^{13}C$ chemical shifts were measured at 5000 Hz/16 K real points.
[d] ${}^{13}C$ chemical shifts are expressed in ppm relative to internal tetramethylsilane.
[e] Measured at 70 °C.

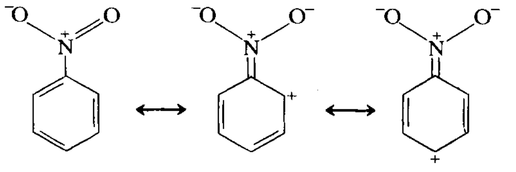
Table 2. Some calculated and experimental $^1J(^{15}N^{13}C)$ values and related C-1 ^{13}C shifts in aniline derivatives[a]



X	Y	Z	J^C	J^O+J^D	J^{total}	$J^{exp\,b}$(Hz)	δC-1[c,d]
H	H	H	−18.629	1.896	−16.7	(−)12.1	148.1
NO_2	H	H	−18.860	21.45	−16.7	(−)14.7	155.5
H	H	CH_3	−12.493	1.785	−10.7	(−)13.2	150.5
NO_2	H	CH_3	−11.821	2.028	−9.8	(−)15.6	153.3
H	CH_3	CH_3	−14.446	1.616	−12.8	(−)12.9	148.9
NO_2	CH_3	CH_3	−14.626	1.928	−12.7	(−)14.2	156.4
H	CH_3	H	−20.597	1.874	−18.7	(−)11.9	143.4
NO_2	CH_3	H	−18.296	2.249	−16.0	(−)14.8	152.0
Br	Br	H	—	—	—	(−)17.6	142.3
Br	Br	CH_3	—	—	—	(−)16.3	146.6

[a] Samples were measured as 1 M solutions in DMSO-d_6.
[b,c] $^1J(^{15}N^{13}C)$ values and ^{13}C chemical shifts were measured at 5000 Hz/16 K real points.
[d] ^{13}C Chemical shifts are expressed in ppm relative to internal tetramethylsilane.

of the conjugative effect of the nitro group:

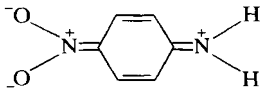


The electronic interaction between ring substituents and the nitro group is expected to influence the π-bond order in the N—C bond, as is also the presence of bulky groups *ortho* to the nitro group which sterically interfere with the coplanarity of the nitro group and the aryl ring. It has been shown that steric inhibition of conjugation leads to marked increases in the *para* carbon shieldings in nitrobenzenes.[17] An estimate of the range of $^1J(^{15}N^{13}C)$ values to be expected from hybridization changes may be deduced from the literature[18] values reported for nitromethane (−10.5 Hz) and nitrobenzene (−14.5 Hz). The latter values, incidentally, are in excellent agreement with the predictions of Eqn (1) for bonding of a nitro group to sp^3 and sp^2 hybridized carbon atoms, respectively.

The narrow range of observed $^1J(^{15}N^{13}C)$ values reported in Table 1, approximately 2 Hz, despite the substantial changes in the electronic character of the substituents involved, suggests that the N—C π-bond order is probably very small and is not of primary importance in determining the coupling in these systems. Even in nitromesitylene,[19] where the nitro group is twisted by 66° from the plane of the benzene ring, or in the more extreme case of tri-*t*-butylnitrobenzene where the resonance interaction is expected to be even further reduced, there are no appreciable effects on $^1J(^{15}N^{13}C)$.

The insensitivity of $^1J(^{15}N^{13}C)$ to structural changes, particularly those expected to alter the N—C double bond character, suggests that the minor changes that are observed stem principally from the inductive effects of the substituents, an explanation which has previously been advanced to account for the order of observed ^{15}N shifts in nitrobenzenes.[20,21] This conclusion indicates that the nominally sp^2 hybridizations of the nitro group nitrogen and the aryl carbon to which it is coupled remain essentially unchanged in this series. This is in agreement with both the relatively constant s-characters, reflected in the contributions to the overall coupling mechanism from the contact term, and the rather small contributions of the orbital and dipolar terms which depend upon the p-electron distribution in the molecules concerned.

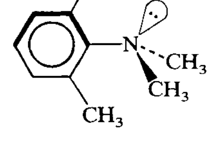
The experimentally measured and calculated $^1J(^{15}N^{13}C)$ values for several aniline derivatives are given in Table 2. Several points are noteworthy in the data presented. In considering the effect of substituents on $^1J(^{15}N^{13}C)$ in aniline, it may be seen that enhanced coupling results from both methylation at nitrogen (1.1 Hz) and the introduction of a nitro group at the *para* position (2.6 Hz), whereas methylation at the *ortho* positions causes a small decrease (0.2 Hz). The enhancement due to the nitro group has been previously interpreted[2,3] in terms of delocalization of the nitrogen lone-pair over the aryl system and conversion of the amino group to a more planar geometry.



In the case of 2,6-dimethylaniline, increases in $^1J(^{15}N^{13}C)$ arising individually from *N*-methylation (1.0 Hz) and *para* nitration (2.9 Hz) are similar to those found in aniline. In marked contrast, however, is the observation that in going from aniline to 4-nitro-*N,N*-dimethylaniline $^1J(^{15}N^{13}C)$ increases by 3.5 Hz, whereas the comparable change in going from 2,6-dimethylaniline to 4-nitro-2,6-dimethyl-*N,N*-dimethylaniline is only 2.3 Hz.

The decrease in $^1J(^{15}N^{13}C)$ brought about by the *ortho* methyl substitution in *N,N*-dimethylaniline is most readily explained in terms of the well-established inhibition of the resonance interaction resulting from sterically induced twisting of the dimethylamino group from coplanarity with the aryl ring. Similarly, examination of the $^1J(^{15}N^{13}C)$ data for 2,4,6-tribromoaniline and its *N,N*-dimethyl derivatives suggests that the decrease in coupling observed in the latter compound also has its origin in a comparable steric effect. In *N,N*-dimethylanilines, steric inhibition of resonance has been widely investigated through its effect on basicity,[22] photoelectron[23,24] and ultraviolet[25] spectra, ^{13}C[8] and ^{15}N[9] chemical shifts, and ^{13}C—H coupling constants.[26,27]

A consequence of a twisted conformation in which the dihedral angle between the lone-pair orbital and



the plane of the ring approaches 0° is the more pyramidal arrangement of the amino group with greater localization of s-electron density at nitrogen. This is consistent with the observed low and high frequency shifts in the nitrogen[9] and *para* carbon[8] signal positions, respectively, as well as with a decrease in the N—C π-bond character and, now, with reduced coupling between the directly bonded nuclei. The barrier to C—N rotation in anilines is a measure of the interaction of the nitrogen lone-pair with the conjugated π-electrons, and a fairly good Hammett correlation is observed.[28,29] It is also found that the barrier decreases with an increase in the size of the alkyl substituents attached to the nitrogen atom.[29]

In the present work, it is instructive to examine the effect of substituents on $^1J(^{15}N^{13}C)$ in both anilines and nitrobenzenes in terms of the mono substituent parameter (MSP) and dual substituent parameter (DSP) Hammett relationship:

$$\text{MSP};\ \Delta J = J\sigma + C \tag{3}$$

$$\text{DSP};\ \Delta J = J^{I}\sigma^{I} + J^{R}\sigma^{R} + C' \tag{4}$$

where ΔJ is the difference in couplings between compounds with X and H substituents, σ, σ^I and σ^R are the Hammett substituent constants, and J, J^I and J^R are the coupling constant parameters which reflect the σ, inductive and resonance contributions of the substituents, respectively, in a given series.

Using σ, σ^I and σ^R values[30a,b] and ΔJ from the experimental data for *meta*- and *para*-substituted anilines and nitrobenzenes, best fitted values for J, J^I and J^R were obtained by regression analysis. The results of these fits are summarized in Table 3.

From the results in Table 3, it can be seen that the DSP treatment ($R = 0{\cdot}913$) is undoubtedly superior to the MSP fit ($r = 0.010$) in the nitrobenzene series. The close values of J^I and J^R in the nitrobenzene series, together with their opposite signs, suggest that the inductive and resonance effects tend to cancel each other, in agreement with the rather narrow range of couplings observed for the different substituents. The failure of the MSP correlation in the nitrobenzene series is apparently due to cancellation of the inductive and resonance effects whose sum, not difference, is usually denoted as σ. In the aniline series, the inductive and resonance contributions complement one another, resulting in a significantly greater substituent effect on $^1J(^{15}N^{13}C)$. Observation of a good MSP correlation is simply due to the complementary effect of J^I and J^R coefficients in the DSP regression.

Finally, from the results in Table 2, it can be seen that the contact term makes the largest contribution to the overall coupling mechanism, and that the calculations correctly predict the known negative signs of $^1J(^{15}N^{13}C)$ in these anilines. There is also fair agreement between experimental and values calculated by the INDO procedure, although the relative order is not always reproduced. Since it is well known that the calculated values are strongly influenced by the extent of nitrogen planarity and other small changes in molecular geometry, the discrepancies probably reflect the molecular geometry chosen for the calculations, as well as shortcomings inherent in the theory employed.

Table 3. Fitting results for nitrobenzene and aniline series

Molecule	Equation	r or R[a]	f[b]
Nitrobenzene	MSP: $\Delta J = 0.01\sigma + 0.69$	0.010	0.61
	DSP: $\Delta J = 1.69\sigma^I - 1.86\sigma^R + 0.10$	0.913	0.23
Aniline	MSP: $\Delta J = 3.29\sigma - 0.24$	0.976	0.20
	DSP: $\Delta J = 2.51\sigma^I + 4.15\sigma^R + 0.06$	0.995	0.09

[a] r (or R) Is the linear (or multiple) regression coefficient in the mono (or dual) substituent parameter fit.

[b] f Is an estimate of the dispersion in the interbasis comparison within a given series of molecules.

EXPERIMENTAL

Nitrobenzenes

The following nitrobenzenes were prepared by standard nitration procedures using 37.7 % w/w nitric-^{15}N acid (95 % enriched): 4-nitro-^{15}N-aniline,[31] 4-chloronitrobenzene-^{15}N,[32] 4-nitroanisole-^{15}N,[33] 2-nitromesitylene-^{15}N,[34] 1,4-dinitrobenzene-^{15}N$_2$,[35] 2,4,6-tri-*t*-butylnitrobenzene-^{15}N,[34] 4-nitro-*t*-butylbenzene-^{15}N,[36] 2-nitro-^{15}N-aniline,[31] 1,3-dinitrobenzene-^{15}N$_2$;[37] 4-nitrotoluene-^{15}N was obtained commercially.

Anilines

Aniline-^{15}N, *p*-nitroaniline-^{15}N, and *N,N*-dimethylaniline-^{15}N are commercially available.

2,6-Dimethylaniline-^{15}N was prepared by the Hofmann rearrangement of the corresponding ^{15}N-enriched benzamide. The benzamide was synthesized by generating the stoichiometric amount of ^{15}NH$_3$ from ammonium chloride (95 % enriched) and allowing it to react with the benzoyl chloride[38] prepared from commercial 2,6-dimethylbenzoic acid.

2,6-Dimethyl-4-nitroaniline-^{15}N$_2$[39] was prepared by the acid hydrolysis of doubly labeled 1-(*p*-toluenesulfonylamino)-2,6-dimethyl-4-nitrobenzene.

2,6,*N,N*-Tetramethylaniline-^{15}N was prepared by the methylation of the corresponding amine with trimethyl phosphate.[40] 2,6,*N,N*-Tetramethyl-4-nitroaniline-^{15}N$_2$[41a] and *N,N*-dimethyl-2,4,6-tribromoaniline-^{15}N[41b] were prepared by the reaction of 4-nitroaniline-^{15}N$_2$ and 2,4,6-tribromoaniline-^{15}N,[1] respectively, with formaldehyde and formic acid.

Computations

The INDO calculations were performed on the CDC 7600 systems of the Universities of London and Manchester.

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