

Solvent *versus* Substituent Effects on the Nitrogen NMR Shielding of the Nitro-Group in Substituted Benzenes

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Intermolecular effects are shown to induce a variation of about 5 ppm in the nitrogen NMR shieldings of aromatic nitro groups. The latter turn out to be comparable to those exerted by substituents in nitrobenzene derivatives in solutions in a given solvent. Substituent effects on the NO₂ nitrogen shielding in nitrobenzenes, in a given solvent, seem to reflect contributions from the so-called field-inductive effects on the electron charge distribution in such systems, and are insensitive to the resonance effects concerned with the delocalized π -electron systems involved.

KEY WORDS ¹⁴N shielding Solvent and substituent effects Substituted nitrobenzenes

INTRODUCTION

The problem of substituent effects in aromatic systems, particularly in benzene derivatives, has long been a subject of interest.¹ While the classical form of the Hammett equation involves *para*- and *meta*-substituent parameters, σ_p and σ_m , respectively, there has been an everlasting discussion about a further separation of the effects into the so-called field-inductive contributions (those transmitted through space and via the σ -bond system concerned), and the resonance or mesomeric contributions which should represent effects from π -electron conjugation.¹⁻⁴

There have been attempts galore at correlating NMR chemical shifts of various nuclei, including those of nitrogen,⁵⁻⁶ with the substituent parameters σ_m and σ_p , or their modifications which are also supposed to account for the corresponding field-inductive contributions F and resonance contributions R¹. Nitrogen NMR, in view of its large range of chemical shifts^{5,6} seems to be a potentially attractive tool for such purposes, but there is a problem which has generally been overlooked, that of the remarkable sensitivity of nitrogen chemical shifts to effects of molecular interactions in solutions.⁵⁻¹⁰ The nitrogen chemical shifts of aromatic nitro groups seem potentially to be a measure of field-inductive effects of substituents. In the conventional representation of resonance structures (Fig. 1), the electron charge distribution in the vicinity of the nitrogen nucleus involved does not appear to be significantly

affected by the π -electron conjugation with a substituted phenyl ring, since the nitrogen atom retains a formal positive charge.

RESULTS AND DISCUSSION

The results of high-precision ¹⁴N measurements on nitrobenzene are presented in Table 1. The data indicate that there is a solvent-induced variation in the shielding within a range of about 6 ppm, throughout the set of 13 solvents employed which represents a large variety of solvent properties. This range of variation does not depart significantly from those observed for the nitro group nitrogen shielding in nitroalkanes, about 10 ppm in nitromethane¹¹ and about 5-6 ppm in its higher alkane homologues,¹² it is also about the same as in the case of the O-nitro moiety in methyl nitrate, MeONO₂.¹³

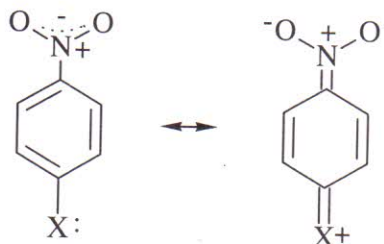


Figure 1. A schematic representation of resonance structures depicting the π -electron conjugation in a *para*-substituted nitrobenzene.

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In order to gain a more detailed insight into the observed solvent-induced variation in the nitrogen shielding of nitrobenzene, we have employed the empirical scheme¹⁴⁻¹⁷ of solvent and solute properties which can be expressed by master Eqn (1):

$$\sigma_{(i,j)} = \sigma_{0(i)} + a_{(i)}\alpha_{(j)} + b_{(i)}\beta_{(j)} + s_{(i)}[\pi_{(j)}^* + d_{(i)}\delta_{(j)}] \quad (1)$$

where i and j stand for solute and solvent, respectively; σ is the relevant solute property (the nitrogen shielding, in the present case), α represents hydrogen-bond donor strength of the solvent, β represents its hydrogen-bond acceptor strength, π^* is its polarity-polarizability, and δ is a correction for polychlorinated solvents ($\delta = 0.5$) and aromatic solvents ($\delta = 1$). The solute terms, a , b , s and d , represent the corresponding responses of the nitrogen shielding to a given property of the solvent employed, and σ_0 is the nitrogen shielding in the reference state which is approximated by a solution in cyclohexane. The solvent parameter set employed in the present work is given in Table 2, together with the least-squares fitted estimates of the solute nitrogen shielding responses. Linear correlation coefficients for the experimental values with respect to those retrieved by means of Eqn (1) are given in Table 2.

For nitrobenzene the only significant term in Eqn (1) turns out to be s , the response to solvent polarity, with some corrections expressed by the product $d\delta$. The direction of the effect is a deshielding of the nitrogen nucleus with increasing polarity of the solvent used, this is reproduced neatly for nitrobenzene in the INDO/S-SOS solvaton-model MO calculations of the relevant changes in the shielding.^{18,19} We have already employed the solvaton model to address the nitrogen shieldings in a variety of nitrogenous structures,⁷⁻¹³ and it has turned out to be a useful tool for predicting solvent polarity effects on the nitrogen NMR shieldings of solutes. The results of our present calculations for nitrobenzene in solutions are presented in Table 3. Needless to say, the general direction of the changes is important, since the magnitude of the term $s[\pi^* + d\delta]$

Table 2. Solvent parameters used and least-squares fitted solute parameters for a set of master Eqns (1)

Solvent	α	β	π^*	δ	Dielectric constant ^a
cyclohexane	0	0	0	0	1.87
Et ₂ O	0	0.47	0.27	0	3.89
CCl ₄	0	0	0.29	0.5	2.21
benzene	0	0.10	0.59	1	2.25
dioxane	0	0.37	0.55	0	2.19
acetone	0.07	0.48	0.72	0	19.45
DMSO	0	0.76	1.00	0	45.80
CH ₂ Cl ₂	0.22	0	0.80	0.5	8.54
CHCl ₃	0.34	0	0.76	0.5	4.55
EtOH	0.86	0.77	0.54	0	24.20
MeOH	0.98	0.62	0.60	0	30.71
H ₂ O	1.13	0.18	1.09	0	76.70
CF ₃ CH ₂ OH	1.51	0	1.02	0	

Solute	a	b	s	d	σ_0
nitrobenzene	-0.31	-0.09	-4.53	-0.24	+12.68
	± 0.21	± 0.34	± 0.32	± 0.07	± 0.23
	ppm/unit scale			dimensionless	ppm

^a The constants were recalculated for a temperature of 35 °C from the data available in Ref. 13.

obtained from the least-squares analysis of a set of Eqns (1) is related to the empirical scale employed for solvent properties (Table 2), and the latter is not a simple function of the dielectric constant which is used in the solvation model calculations of the shieldings.

Now we turn to the effects of substituents on the nitrogen shielding of the nitro group in substituted nitrobenzenes. The relevant data are given in Table 4. Two solvents, cyclohexane and DMSO, were employed, and for a given nitrobenzene derivative, the difference in the shieldings between the corresponding solutions is fairly constant at about 4.5 ppm. Thus, there is no indication of any serious influence of substituents on the range and direction of solvent-induced variations in the shielding of the aromatic nitro group. A survey of the data in Table 4 brings some clear and important observations. If we exclude from consideration 2-substituted (ortho-) nitrobenzenes, where short range effects can take place, and if we compare only solutions in a given solvent, all of the substituents examined (Me, OMe, NMe₂, F, Cl, Br, I and NO₂), in position 3 (*meta*) as well as in position 4 (*para*), seem to invariably induce an increase in the magnetic shielding of the nitrogen nucleus, with respect to that in nitrobenzene (see Tables 4 and 5). Moreover, there is only a small difference, for

Table 1. Solvent-induced changes in the nitrogen NMR shielding of the nitro group in nitrobenzene. All data refer to 0.2 M solutions at $+35 \pm 0.2$ °C, unless stated otherwise, and are corrected for bulk susceptibility effects

Solvent	NO ₂ Nitrogen NMR shielding in ppm, referenced to external neat nitromethane	
	Experimental	Calculated ^a
cyclohexane	+12.62	+12.68
CCl ₄	+12.22	+11.92
Et ₂ O (+30 °C)	+11.31	+11.41
benzene	+10.79	+11.10
EtOH	+10.19	+9.90
dioxane	+10.01	+10.15
CHCl ₃	+9.98	+9.68
CH ₂ Cl ₂	+9.56	+9.54
MeOH	+9.38	+9.60
acetone	+9.23	+9.35
DMSO	+8.32	+8.08
CF ₃ CH ₂ OH	+7.79	+7.60
H ₂ O (0.01 M)	+7.02	+7.38

^a According to Eqn (1) and the relevant parameters from Table 2.

Table 3. Solvaton model calculations for medium polarity effects on nitrogen NMR shielding in nitrobenzene

Dielectric constant ϵ	Calculated variation in the shielding (ppm)
2.0	0 (arbitrary)
4.0	-2.7
8.0	-3.9
20.0	-6.0
40.0	-7.7

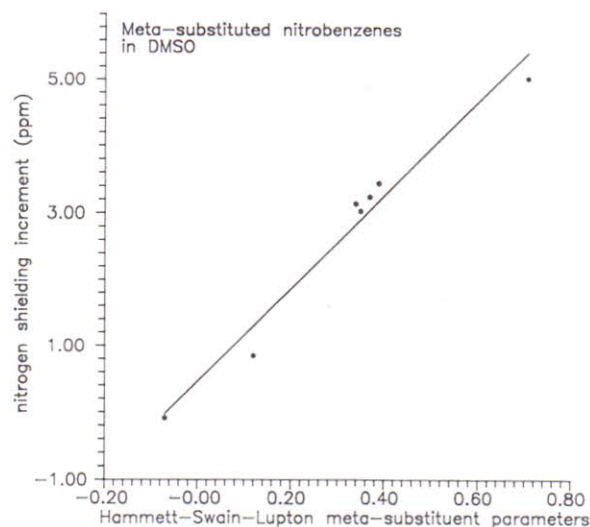
Table 4. Nitrogen NMR shieldings of nitro groups in substituted nitrobenzenes (0.25 M solutions if not stated otherwise)

Substituent	Nitrogen shielding in ppm referenced to external neat nitromethane	
	In cyclohexane	In DMSO
none	+12.62	+8.32
2-Me	+7.34	+3.26
3-Me	+12.27	+8.23
4-Me	+12.63	+8.46
2-OMe	+12.32	+7.74
3-OMe	+12.71	+9.17
4-OMe	+13.74 ^a	+9.52
4-NMe ₂	—	+10.11 ^a
2-F	+18.04	+14.30
3-F	+15.87	+11.46
4-F	+15.43	+11.21
2-Cl	+13.63 ^a	+9.21
3-Cl	+15.86 ^a	+11.56
4-Cl	+15.30 ^a	+10.74
2-Br	+12.34 ^a	+7.23
3-Br	+15.95	+11.76
4-Br	+15.23 ^a	+10.75
2-I	+10.70 ^a	+4.23
3-I	+15.93 ^a	+11.35
4-I	+14.67 ^a	+9.76
2-NO ₂	+18.49 ^a	+13.24 ^a
3-NO ₂	+18.25 ^a	+13.34
4-NO ₂	+17.65 ^a	+12.57 ^a
3,5-di-NO ₂	+22.67 ^a	+17.63 ^a

^a Saturated solutions which are less than 0.25 M.

a given substituent and solvent, between the *meta* and *para* effects on the shielding. The largest effects of this kind are exerted by an additional nitro group, about +5 ppm which is comparable to the range of solvent-induced variations in the shielding for a given substituent. Thus, solvent and substituent effects on the nitrogen shielding in nitrobenzenes are comparable in magnitude, and an important conclusion follows that there is practically no sense in considering the latter for anything else than dilute solutions in a given solvent.

An investigation of the weak solvent differentiation between substituents in *meta* and *para* positions can be

**Figure 2.** A plot of substituent-induced changes in the nitrogen shielding of *meta*-substituted nitrobenzenes, in DMSO as a solvent, against the σ_m parameters from Table 5.

carried out using some parameters which are thought of as a means of characterising substituent effects in terms of the Hammett equation or of its modifications (Table 5). The simplest form of the equation invokes the well-known *meta*- and *para*-substituent parameters, σ_m and σ_p , respectively, using numerical values reported in Ref. 1 according to the Hammett and modified Swain-Lupton scale. The data from Table 5 reveal that, for a given solvent, the nitrogen shieldings in *meta*-substituted nitrobenzenes show a decent linear correlation with the corresponding σ_m parameters (see Fig. 2). On the other hand, *para*-substituted nitrobenzenes not only fail to give an analogous correlation with the σ_p parameter set, but they also show evident discrepancies in the signs of substituent-induced changes in the nitrogen shielding with respect to the signs of the σ_p parameters involved. Since the parameters considered are collective in the sense that they try to integrate all possible effects exerted by a given substituent in a given position in the aromatic ring, the foregoing correlation in the case of *meta*-substitution and the lack of the correlation in the case of *para*-substituents provide an

Table 5. Comparison of substituent effects on the nitrogen shielding in substituted nitrobenzenes with substituent parameters^a

Substituent	Substituent-induced increment in NO ₂ nitrogen shielding							
					<i>meta</i>		<i>para</i>	
	σ_m	σ_p	F	R	C ₆ H ₁₂	DMSO	C ₆ H ₁₂	DMSO
none	0	0	0	0	0	0	0	0
Me	-0.07	-0.17	0.01	-0.18	-0.35	-0.09	0.01	0.14
OMe	0.12	-0.27	0.29	-0.56	0.09	0.85	1.10	1.20
NMe ₂	-0.16	-0.83	0.15	-0.98	—	—	—	1.79
F	0.34	0.06	0.45	-0.49	3.25	3.14	2.81	2.89
Cl	0.37	0.23	0.42	-0.19	3.24	3.24	2.68	2.42
Br	0.39	0.23	0.45	-0.22	3.33	3.44	2.61	2.47
I	0.35	0.18	0.42	-0.24	3.31	3.03	2.05	1.44
NO ₂	0.71	0.78	0.65	0.13	5.63	5.02	5.03	4.25

^a The values of the *meta*- and *para*-substituent parameters, σ_m and σ_p , respectively, as well as the field/inductive parameters F and resonance parameters R for the substituents involved are excerpted from the recently recommended set in Ref. 1.

argument that the nitrogen shieldings of the nitro groups do not respond to the resonance or conjugative effects, those which are characteristic of *para*-disubstituted benzenes (Fig. 1), and that they are sensitive primarily to the so-called field/inductive effects of substituents. This is also evident from a comparison of the field-inductive (F) and resonance (R) parameters with the relevant substituent-induced changes in the NO₂ nitrogen shieldings (Table 5).

EXPERIMENTAL

Pure samples of the compounds studied were prepared from commercially available nitrobenzenes. Special attention was paid to the use of very pure and dry solvents.⁴ All solutions were prepared and handled under a dry argon atmosphere in glove-bags. The nitrogen shieldings concerned were measured by ¹⁴N NMR at 36.14 MHz (Bruker AM-500 spectrometer) and 35 ± 0.2 °C; the temperature was maintained by a VT unit. Special precautions were taken in order to reduce the possible random and systematic errors to below 0.1 ppm upon comparing the nitrogen shieldings of the solute in different solvents. The shieldings were referenced externally to neat liquid nitromethane, using 10

mm/4 mm o.d. coaxial tubes. The inner tube contained 0.3 M nitromethane in acetone-d₆ whose nitrogen shielding is +0.77 ppm from that of neat liquid nitromethane,^{5,6} under conditions where bulk susceptibility difference effects vanish (in concentric spherical sample/reference containers); the latter value is employed as a conversion constant. Thus, the content of the inner tube serves as a precise reference to the neat nitromethane standard, and also provides a source of deuterium lock for the system. The exact resonance frequency of the ¹⁴N signal of neat nitromethane is 36.141 524 MHz, and recalculations which were carried out by method outlined in Ref. 5 yield a value of 36.136 826 MHz for a bare nitrogen nucleus. This is used in conjunction with the relevant resonance frequency differences in order to calculate the nitrogen NMR shieldings relative to that of the primary standard, neat nitromethane. The resonance frequencies of the sample and the external standard are found by Lorentzian lineshape fitting of the relevant ¹⁴N NMR signals. The nitrogen shieldings obtained are then corrected for bulk susceptibility effects, since dilute solutions were employed, their susceptibilities are assumed to be equal to those of the respective solvents at 35 °C.

The INDO/S SOS calculation within the solvaton model framework^{18,19} were carried out on the University of Surrey Primeret System using standard geometries.²¹

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