

A Solid-State Nitrogen-15 NMR and Ab Initio Study of Nitrobenzenes

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Insight into the unexpectedly small range of isotropic nitrogen chemical shifts in nitrobenzene derivatives is gained through measurements of the chemical shift (CS) tensor by solid-state NMR experiments and ab initio molecular orbital (MO) and density functional theory (DFT) calculations. The principal components, δ_{ii} , of the ^{15}N CS tensors have been measured for nitrobenzene, 4-nitroaniline, 4-nitrotoluene, 4-nitroanisole, 4-nitroacetophenone, nitromesitylene, and 2,4,6-tri-*tert*-butylnitrobenzene. No obvious correlations of the δ_{ii} values with traditional reactivity parameters were observed. The CS tensor components change significantly for the para-substituted nitrobenzenes, but these variations nearly cancel to yield isotropic shifts that fall in a range of only 3 ppm. Ab initio calculations of the δ_{ii} values at the HF level are in poor agreement with the experimental values, whereas MP2 calculations and DFT calculations employing the B3LYP functional are in better agreement with experiment. The calculated (B3LYP/6-311G**) δ_{ii} values follow a trend in which δ_{11} and δ_{33} increase while δ_{22} decreases with the accepted electron withdrawing ability of the para substituent. These changes tend to cancel yielding a variation in δ_{iso} of only 4 ppm. These calculations indicate that the CS tensor has the same orientation as the carbon CS tensor in the isoelectronic benzoate anion: δ_{11} bisects the O–N–O angle, δ_{33} is perpendicular to the NO_2 plane, and δ_{22} is in the NO_2 plane and perpendicular to δ_{11} .

Introduction

NMR spectroscopy is indubitably the most widely used technique for the characterization of organic substances. Chemical shifts for ^1H , ^{13}C , and ^{15}N in organic molecules have been extensively tabulated and many empirical relationships between the chemical shift and electronic and molecular structure have been suggested.^{1a} For example, Craik and co-workers have measured the ^{15}N and ^{17}O isotropic chemical shifts in para and meta-substituted nitrobenzenes.^{1b}

With few exceptions, only the isotropic chemical shifts from solution NMR experiments have been reported and utilized. This has occasionally resulted in confusion when the isotropic chemical shift, δ_{iso} , did not correlate with well-known substituent electronic parameters or displayed little variation. One possible reason for this lies in the three-dimensional nature of the magnetic shielding experienced by the nuclei. The chemical shift (CS) tensor is characterized by its three mutually perpendicular

principal components, δ_{11} , δ_{22} , and δ_{33} , and the three Euler angles that determine its orientation within the molecular frame. These are, of course, a consequence of the electronic and geometric structure of the molecule. Solution NMR experiments measure the *isotropic* chemical shift, which is the average of the CS tensor principal components:

$$\delta_{\text{iso}} = 1/3(\delta_{11} + \delta_{22} + \delta_{33}) \quad (1)$$

Therefore, if δ_{iso} can provide insight into molecular and electronic structure, a more complete knowledge of the CS tensor should, in turn, yield a better understanding of these structures. For a powder sample there are a few approaches that one can take toward the characterization of the CS tensor. Experimentally the analysis of the NMR spectrum of a stationary powder sample will yield the three principal components of the CS tensor (δ_{ii} , $i = 1, 2$, and 3). Alternatively, an analysis of the spinning side-band intensities in a spectrum obtained with slow magic angle spinning will also provide δ_{ii} values.² Neither method will provide information about the orientation of the CS tensor. Unambiguous determination of the CS tensor orientation usually requires an oriented sample such as a large single crystal.³ If the observed nucleus is dipolar coupled with a nearby NMR-active nucleus and

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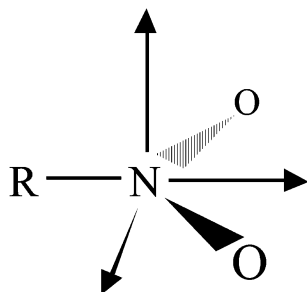
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(1) (a) For ^{13}C examples see: Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance*, 2nd ed.; Wiley: New York, 1980; Chapter 4. (b) Craik, D. J.; Levy, G. C.; Brownlee, T. C. *J. Org. Chem.* **1983**, *48*, 1601.

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SCHEME 1. Symmetry-Constrained Orientation of the Nitrogen Chemical Shift Tensor in a Nitro Compound

the spin-pair is “isolated”, analysis of the CS/dipolar powder spectrum can also provide information on the orientation of the CS tensor with respect to the internuclear vector and therefore the molecular frame.⁴ Occasionally it is possible to infer the orientation of the CS tensor from the local symmetry of the molecule at the nuclear site. For example, the C_{2v} symmetry of the nitro group in nitrobenzene dictates that the nitrogen CS tensor must have one component along the C_2 axis, one component perpendicular to the NO_2 plane, and the third component in the NO_2 plane and perpendicular to the C_2 axis (Scheme 1). One can also use molecular orbital (MO) theory or density functional theory (DFT) to calculate the δ_{ii} values and the tensor orientation. Direct comparison of the results of these calculations with observed chemical shift values requires that the absolute magnetic shielding tensor components, σ_{ii} , can be converted to the chemical shift scale. For ^{15}N such a conversion can be accomplished, and the two are related by⁵

$$\delta_{ii} \approx -135.8 - \sigma_{ii} \quad (2)$$

where δ is the chemical shift with respect to pure liquid nitromethane and σ is the absolute shielding relative to the “bare” nucleus. Even if such a relationship is not available the orientation of the CS tensor may still be predicted since the principal axes of the magnetic shielding tensor, σ , and the chemical shift tensor, δ , are coincident.

The most complete solution NMR study of nitrobenzenes was undertaken by Craik et al., who reported ^{15}N and ^{17}O chemical shifts for 12 meta- and 12 para-substituted derivatives.^{1b} The range of ^{15}N shifts for the para-substituted derivatives is only 4.0 ppm, while that of ^{17}O is 27.1 ppm. Earlier measurements of the ipso ^{13}C chemical shifts in para-substituted nitrobenzenes yielded a range of 12.0 ppm.⁶ Whereas there are clear trends in the ^{17}O and ^{13}C chemical shifts, the ^{15}N shifts cannot be correlated with the electron withdrawing/donating ability of the para substituent or with any of the classical reactivity parameters. This conclusion was confirmed by

the more recent work of Webb et al., who also showed that the variation in ^{15}N chemical shifts due to solvent effects (5 ppm) was larger than the range due to para substitution (ca. 4 ppm).⁷

Nitrobenzenes constitute an important class of organic compounds.⁸ It is surprising, therefore, that only two nitrobenzene derivatives (or organic nitro compounds for that matter) have been investigated by solid-state ^{15}N NMR spectroscopy. More surprising is the reported observation that the δ_{ii} values for pure nitrobenzene (obtained from an analysis of the powder spectrum at -103°C without proton decoupling)⁹ and for 4-nitroaniline- $^{15}\text{N}_2$ (obtained via spinning sideband analysis of the CP/MAS spectrum)¹⁰ are very different. The assignment of the orientation of the CS tensor for nitrobenzene, which is based on the single-crystal ^{13}C tensor of the carbonyl carbon in the isoelectronic benzoate anion,¹¹ is not in agreement with a later assignment, based on ^{15}N T_1 experiments.¹² In light of these conflicting factors, and the rather small, and so far unexplained, variation of the solution chemical shift with substituent, we have undertaken a reinvestigation of the ^{15}N spectra of solid nitrobenzene and 4-nitroaniline. We further report ^{15}N δ_{ii} values for 4-nitrotoluene, nitromesitylene, 2,4,6-tri-*tert*-butylnitrobenzene, 4-nitroanisole, and 4-nitroacetophenone. In addition to experimental measurements we have also calculated δ_{ii} values in several nitrobenzene derivatives using molecular orbital and density functional theoretical methods.

Background Theory

According to Ramsey’s theory the magnetic shielding of a nucleus within a molecule can be considered as a sum of diamagnetic, σ^d , and paramagnetic, σ^p , components.¹³

$$\sigma_{ii} = \sigma_{ii}^d + \sigma_{ii}^p \quad (3)$$

The diamagnetic term depends only on the ground electronic state of the molecule. If the molecular structure is known, the approximate contribution of the diamagnetic shielding can be obtained. For example, the shielding of nucleus A in the x -direction may be approximated by¹⁴

$$\sigma_{xx}^d \approx \sigma_{av}^d(\text{fa}) + \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} \sum_{B \neq A} \frac{Z_B}{r_{AB}^3} (y_B^2 + z_B^2) \quad (4)$$

where $\sigma_{av}^d(\text{fa})$ is the shielding for the free atom. The

(3) For a recent example see: Eichele, K.; Wasylishen, R. E.; Corrigan, J. F.; Taylor, N. J.; Carty, A. J.; Feindel, K. W.; Bernard, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1541.

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summation is over all atoms, B, other than A, within the molecule, Z_B is the atomic number of atom B, y_B and z_B are the y and z coordinates of atom B, and r_{AB} is the A–B internuclear distance. The diamagnetic contribution to the total shielding is always positive.

On the other hand, the paramagnetic contribution is usually negative, resulting in a reduction of the shielding at nucleus A. Paramagnetic shielding is a second-order electronic property that depends on the ground and excited electronic states of the molecule which correspond approximately to the occupied and unoccupied MOs.¹³

$$\sigma_{ii}^p = \frac{-\mu_0}{4\pi} \frac{e^2}{2m_e} \sum_{n>0} \frac{1}{E_n - E_0} \left\{ \left\langle \Psi_0 \left| \sum_k \frac{\hat{L}_{kAi}}{r_{kA}^3} \right| \Psi_n \right\rangle \right. \\ \left. \left\langle \Psi_n \left| \sum_k \hat{L}_{kAi} \right| \Psi_0 \right\rangle + \left\langle \Psi_0 \left| \sum_k \hat{L}_{kAi} \right| \Psi_n \right\rangle \left\langle \Psi_n \left| \sum_k \frac{\hat{L}_{kAi}}{r_{kA}^3} \right| \Psi_0 \right\rangle \right\} \quad (5)$$

Here E_0 , E_n , Ψ_0 , and Ψ_n represent the energies and eigenfunctions of the ground and excited states of the molecule, respectively. The angular momentum operator and position vector for electron k are given as \hat{L}_k and r_k . As can be seen from eq 5, σ^p is inversely proportional to the energy difference of the molecular orbitals being mixed. The early work of Pople and Karplus indicates that the local paramagnetic term is predominantly responsible for experimentally observed variations in ^{15}N chemical shifts.¹⁵ Of particular importance to the work being reported here is the relationship between the direction of the induced charge circulation and the direction of the corresponding component of the magnetic shielding (and hence chemical shift) tensor. For example, pictorially the operator \hat{L}_x rotates charge in the yz plane (i.e., about the x -axis). Therefore σ_{xx} (i.e., δ_{xx}) is affected by the mixing of orbitals, which causes electron circulation in the yz plane. It should be noted that the resultant mixing that occurs between occupied and unoccupied MOs must be magnetically dipole allowed. In other words, the associated electronic transition must be magnetically dipole allowed. More detailed discussions of the implications of Ramsey's theory can be found elsewhere.¹⁶

It is useful to define the span, Ω , and the skew, κ , of a CS tensor.¹⁷ The span is defined as

$$\Omega = \delta_{11} - \delta_{33} = \sigma_{33} - \sigma_{11} \quad (6)$$

and indicates the width of the NMR line shape for a nonspinning, stationary, sample. The skew is defined as

$$\kappa = \frac{3(\delta_{22} - \delta_{iso})}{\Omega} = \frac{3(\sigma_{iso} - \sigma_{22})}{\Omega} \quad (7)$$

and provides information on the symmetry of the line shape. For example, κ values of ± 1 imply axial symmetry.

Experimental Section

Samples of 4-nitrotoluene- ^{15}N , 4-nitroaniline- $^{15}\text{N}_2$, and nitrobenzene- ^{15}N were of commercial origin (CIL). 2,4,6-Tri-methylnitrobenzene- ^{15}N and 2,4,6-tri-*tert*-butylnitrobenzene-

^{15}N were prepared by the nitration of mesitylene and 1,3,5-tri-*tert*-butylnitrobenzene with $\text{Na}^{15}\text{NO}_3$ in trifluoroacetic acid.¹⁸ Sample purities were checked by obtaining the ^1H and ^{15}N NMR spectra in CDCl_3 solution.

Nitrogen-15 solid-state NMR spectra at room temperature were acquired on 200-MHz spectrometers ($B_0 = 4.7$ T), which operated at a frequency of 20.27 MHz, and a 500-MHz spectrometer ($B_0 = 11.75$ T), which operated at 50.70 MHz. Typical spectra were acquired with proton cross polarization and employed 90° pulses of about 4–6 μs and relaxation delays of 5–30 s. All spectra were acquired with high-power proton decoupling. Contact times were 3–5 ms. Natural abundance ^{15}N CP/MAS spectra of 4-nitroanisole and 4-nitroacetophenone were obtained at 11.7 T with sample spinning rates of 10 and 2.5 kHz, after carefully optimizing the experimental parameters with a sample of glycine (also at natural abundance). The number of accumulated transients were 12 000 and 30 000, respectively. Spectra were referenced to the nitrate signal of solid $^{15}\text{NH}_4^{15}\text{NO}_3$, which is at 4.4 ppm with respect to pure liquid nitromethane at 20 °C.¹⁹

Low-temperature (203 and 223 K) ^{15}N NMR spectra of solid stationary and MAS samples of nitrobenzene were obtained on a 200-MHz NMR spectrometer using variable amplitude cross polarization with proton decoupling.²⁰ Relaxation delays were 10 and 30 min for MAS and stationary samples, respectively. A contact time of 10 ms with a 90° pulse of 4.5 μs were used to acquire all spectra. The MAS spectra at 223 and 203 K were acquired with 16 and 8 scans, respectively. The spectrum of a stationary sample at 203 K was acquired with 3 scans. Spectra of the MAS samples were acquired with a 7.5 mm (o.d.) double resonance probe, at a spinning frequency of 1 kHz. Spectra of the stationary sample were acquired using a wide-line probe with a 10-mm coil. The temperatures for these experiments were calibrated via the ^{207}Pb NMR spectra of a sample of $\text{Pb}(\text{NO}_3)_2$, which were acquired under the same conditions as those for the nitrobenzene samples.²¹

The ^{15}N tensor components for all stationary samples were obtained directly from the derivatives of the spectral line shapes. All spectral simulations used the WSOLIDS program developed in this laboratory,²² which incorporates the POWDER routine of Alderman et al.²³

Calculations of nuclear magnetic shielding tensors and geometry optimizations were performed with Gaussian 98.²⁴ Previous work by Grant and co-workers shows that for many organic molecules DFT with the B3LYP functional provide good agreement with experimental carbon and nitrogen δ_{ii} values.²⁵ For that reason most of our calculations are performed at the B3LYP/6-311G** or B3LYP/6-311++G** levels (vide infra).

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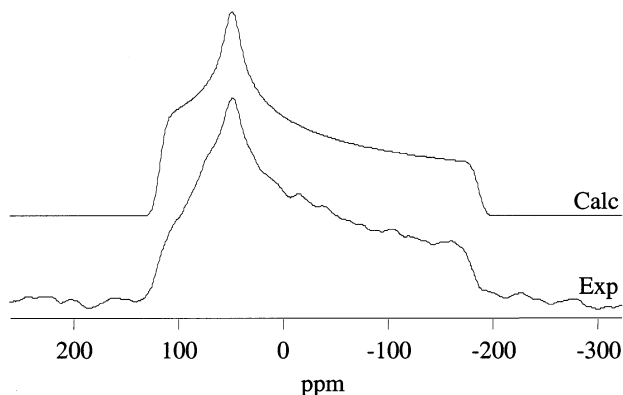


FIGURE 1. The ^{15}N NMR spectrum of a stationary sample of solid nitrobenzene at 203 K. The spectrum was obtained at 4.7 T with cross polarization and proton decoupling.

Results and Discussion

^{15}N Measurements. The observed and simulated ^{15}N CP NMR spectra of a stationary sample of solid nitrobenzene- ^{15}N at 203 K are shown in Figure 1. The CS tensor components, based on these and the MAS spectra, are $\delta_{11} = 126 \pm 6$ ppm, $\delta_{22} = 57 \pm 6$ ppm, and $\delta_{33} = -179 \pm 6$ ppm ($\delta_{\text{iso}} = -1.1 \pm 0.5$ ppm, $\Omega = 305$ ppm, and $\kappa = 0.55$). These values are significantly different from the values of $\delta_{11} = 166$, $\delta_{22} = 104$, and $\delta_{33} = -263$ ppm ($\delta_{\text{iso}} = 2$ ppm, $\Omega = 429$ ppm, and $\kappa = 0.71$) obtained some time ago by Schweitzer and Spiess.⁹ We believe that the total line shape obtained by these authors is considerably broader (i.e., larger Ω) due to the fact that high-power ^1H decoupling was not available at that time. Solum et al. have made the same observation when remeasuring the principal components of the ^{15}N CS tensor values for pyridine.^{25a} Their span of 622 ppm is significantly smaller than the earlier value of 782 ppm determined, without ^1H decoupling.

Powder ^{15}N NMR spectra for stationary samples of 4-nitrotoluene, 4-nitroaniline, 2,4,6-trimethylnitrobenzene, and 2,4,6-tri-*tert*-butylnitrobenzene are shown in Figure 2. The slow-spinning MAS spectrum of 4-nitroanisole, together with the simulation, are shown in Figure 3. Experimental values of δ_{ii} and δ_{iso} together with Ω and κ values for several nitrobenzene derivatives are provided in Table 1. For all compounds investigated, the δ_{iso} values obtained from the ^{15}N CP/MAS spectra are within 1 ppm of the average of the δ_{ii} components, in accord with eq 1. It should be noted that adding 21 ppm to the δ_{ii} values for 4-nitroaniline would bring these into excellent agreement with our values. The method of referencing used in the previous study by Taylor et al. is not specified clearly.¹⁰ Apart from 2,4,6-trimethylnitrobenzene (vide infra), the spans, Ω , of the nitrogen CS tensor for the other derivatives in Table 1 fall into the range of 300 ± 20 ppm.

An interesting feature of our results is that, although δ_{iso} changes very little with changes in the substituent, the tensor components, δ_{ii} , often show significant varia-

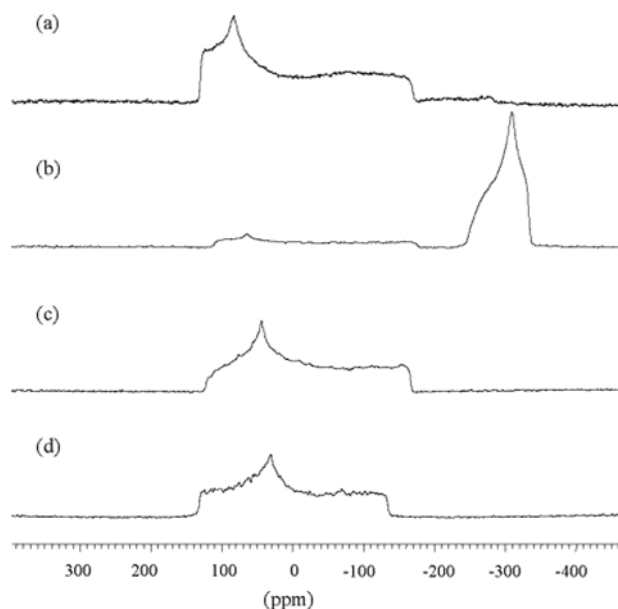


FIGURE 2. The ^{15}N CP NMR spectra of samples of (a) 4-nitrotoluene, (b) 4-nitroaniline, (c) 2,4,6-trimethylnitrobenzene, and (d) 2,4,6-tri-*tert*-butylnitrobenzene, at 11.75 T. The line shape at about -300 ppm in spectrum b is due to the $^{15}\text{NH}_2$ group.

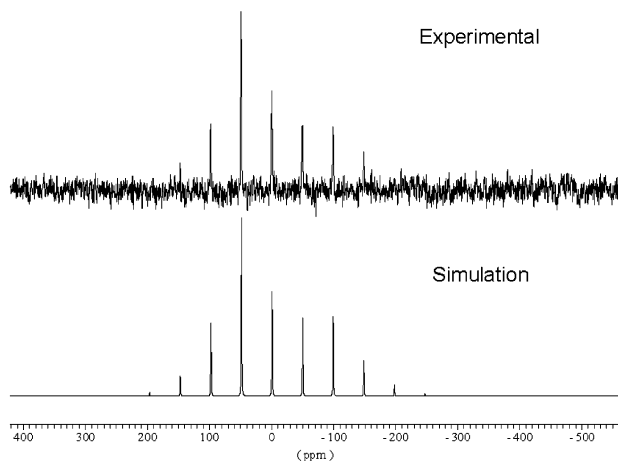


FIGURE 3. The natural abundance ^{15}N CP/MAS spectrum (upper) and simulation (lower) of 4-nitroanisole at 11.75 T, with a spinning rate of 2.5 kHz.

tion. This is particularly true for the para-substituted compounds. Such observations, where substituent effects do not perturb δ_{iso} but do change the δ_{ii} values, have been previously reported. For example, the isotropic ^{31}P chemical shift in the stabilized ylides, $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{C}(\text{O})\text{R}$, shows little variation as the substituent R is changed.^{26a} In contrast, an examination of the tensor components, as obtained from ^{31}P solid-state NMR spectra, shows that, as the R group becomes more electron donating, δ_{11} increases while δ_{22} and δ_{33} decrease in such a way that they cancel to yield nearly the same isotropic chemical

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TABLE 1. Experimental Nitrogen Chemical Shift Parameters for Several Nitrobenzene^a Derivatives

derivative	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	Ω	κ
nitrobenzene	126(6)	57(6)	−179(6)	1.1(2)	305	0.55
nitrobenzene ^b	166	104	−263	2	429	0.71
4-methyl	123(2)	44(2)	−167(2)	−0.2(2)	290	0.46
4-methoxy ^c	138(6)	40(6)	−182(3)	−0.7(2)	320	0.38
4-amino	111(2)	65(2)	−176(2)	0.6	287	0.67
4-amino ^d	91	41	−200	−21.0	291	0.64
4-acetyl ^c	130(5)	40(5)	−174(5)	−1.4(1)	304	0.41
2,4,6-tri-Me	131(3)	31(3)	−135(3)	9.5(3)	262	0.25
2,4,6-tri-t-Bu	130(3)	83(3)	−171(3)	13.7(3)	301	0.23

^a From stationary samples with CP and ¹H decoupling, unless otherwise noted. Uncertainties in the δ_{ii} and δ_{iso} values are in parentheses. Results from this work are highlighted in italics.

^b From ref 9 (static at −103°C with no decoupling). ^c From CP/MAS spectra (Herzfeld–Berger analysis of the CP/MAS spectrum). ^d From ref 10 (Herzfeld–Berger analysis of the CP/MAS spectrum)

shifts, δ_{iso} .^{26b} The range of isotropic ¹⁵N shifts for the five solid para-substituted nitrobenzenes studied here is only 2.5 ppm, whereas the ranges of δ_{11} , δ_{22} , and δ_{33} are 27, 25, and 15 ppm, respectively. For example, a comparison of nitrobenzene and 4-nitrotoluene shows that, with para substitution, δ_{11} decreases by 3 ppm, δ_{22} decreases by 17 ppm, and δ_{33} increases by 12 ppm. The resulting change in the average, isotropic, shift is only −1.3 ppm. What appears to be occurring for the para-substituted nitrobenzenes is a fortuitous near cancellation of the variations in the tensor elements to yield an almost constant isotropic chemical shift. This is quite evident when one compares the δ_{ii} values of nitrobenzene and 4-nitroaniline. Neutron diffraction studies indicate that there are head-to-tail hydrogen bonds between the NH₂ and NO₂ groups in solid 4-nitroaniline.²⁷ Presumably this hydrogen bonding is, to a large degree, responsible for a decrease in δ_{11} from 126 to 111 ppm, an increase in δ_{22} from 57 to 65 ppm, and a small increase in δ_{33} from −179 to −176 ppm. The changes in the values of tensor components δ_{22} and δ_{33} are in the opposite direction to that in component δ_{11} . The result is a change in δ_{iso} of only 0.5 ppm!

The trisubstituted derivatives 2,4,6-trimethylnitrobenzene and 2,4,6-tri-*tert*-butylnitrobenzene represent unusual cases. One would expect to observe similar changes in the ¹⁵N δ_{ii} values for these two compounds, primarily due to the effects of the NO₂ group being twisted out of the phenyl ring plane. Both compounds show a significant increase in chemical shift with respect to the parent compound. However, an examination of the data in Table 1 reveals that the increases in δ_{iso} are due to large increases in two *different* CS tensor elements. In the case of 2,4,6-trimethylnitrobenzene, it is δ_{33} that increases by 44 ppm, whereas for 2,4,6-tri-*tert*-butylnitrobenzene, it is δ_{22} that shows a significant increase of 26 ppm.

No obvious empirical relationships between δ_{iso} and δ_{ii} with reactivity parameters such as σ_{I} , σ_{R} , or σ_{p} were observed.²⁸ One must first consider the possibility that the experimental measurements are not of high enough quality to be useful in this respect. The data presented

here, in particular the δ_{ii} values obtained from the static powder spectra, are reliable and reproducible well within the quoted uncertainties. It is possible that our measurements represent too small a sampling of para-substituted nitrobenzene derivatives (five in total), but the substituents are significantly different. On the other hand, it is also possible that there are no correlations to be found. This was the conclusion of Sardashti and Maciel when they attempted to correlate the ¹⁵N δ_{ii} values of 10 para-substituted derivatives of ¹⁵N-enriched benzonitrile with reactivity parameters σ_{R} and σ_{I} .²⁹ There are no theoretical reasons for any kind of direct correlation between the CS tensor components and reactivity parameters. Reactivity parameters are based on the electronic ground states of molecules and activated complexes. Therefore they depend on first-order electronic properties. By contrast the magnetic shielding tensor, and hence the chemical shift tensor components, are second-order properties. The magnetic field, **B**₀, mixes the ground and excited states of the molecule. Therefore a knowledge of the wave functions and energies of the excited states of the molecule is required. These are the terms E_n and Ψ_n in eq 5. Kutzelnigg et al. looked at a number of cases where chemical shifts were expected to vary with electron density. Their calculations showed only one case (¹³C shift of Hückel annulenes) where the experimental relationship was theoretically confirmed. This was not true for other systems, including the ¹H chemical shifts in the same Hückel annulenes.^{15,30}

Sardashti and Maciel did, however, observe a definite trend in one component of the ¹⁵N CS tensor that followed the electron donating/withdrawing ability of the para substituent in a series of benzonitriles.²⁹ It should, in principle, be possible to qualitatively explain such trends within the framework of a perturbed MO approach, since orbital coefficients and ground and excited state energies should systematically vary as the contributions of different resonance structures change with para substituent. They were able to rationalize the changes in the observed δ_{ii} values using this approach.

The Orientation of the Nitrogen Chemical Shift Tensor. Schweitzer and Spiess proposed that the orientation of the nitrogen CS tensor for nitrobenzene is the same as that of the carbonyl carbon tensor for the isoelectronic benzoate anion.⁹ The orientation of the carbon chemical shift tensor for the benzoate ion was assumed to be the same as that for benzoic acid, which was obtained in an earlier ¹³C single-crystal study.¹¹ Our molecular orbital and DFT calculations are in agreement with this assignment. The most magnetically shielded direction is perpendicular to the NO₂ plane and the least shielded direction is along the C_{ipso}–N bond (bisecting the O–N–O angle). This arrangement is shown in Figure 4a. Stark, Vold, and Vold have suggested an orientation for the CS tensor, based on the chemical shift anisotropy (CSA) contribution to the ¹⁵N spin–lattice relaxation rate, $R_1(\text{CSA})$, in neat liquid nitrobenzene.¹² $R_1(\text{CSA})$ depends on the rotational correlation time for the tumbling motion of the nitrobenzene molecule, τ_c , the values of the CS tensor components, δ_{ii} , and the orienta-

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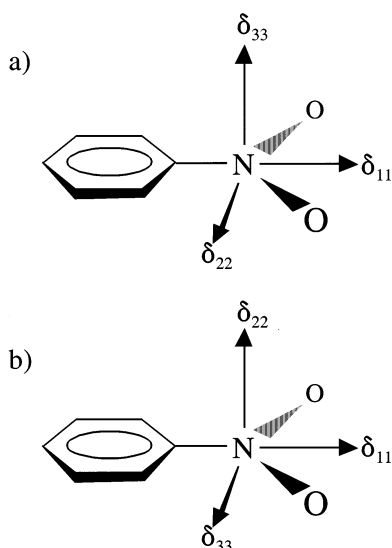


FIGURE 4. Orientation of the nitrogen CS tensor (a) based on our calculations and the carbonyl carbon CS tensor of benzoic acid and (b) based on the ^{15}N T_1 (ref 12), using the δ_{ii} values of ref 9.

tion of the CS tensor in the molecular frame. The observed value of $R_1(\text{CSA})$ at 24 °C is $4.5(\pm 0.5) \times 10^{-3} \text{ s}^{-1}$.¹² Stark, Vold, and Vold used the δ_{ii} values and orientation of Schweitzer and Spiess⁹ together with their τ_c value to obtain an $R_1(\text{CSA})$ of $9.1(\pm 1.4) \times 10^{-3} \text{ s}^{-1}$, more than twice the observed value. The best agreement was obtained with the orientation shown in Figure 4b, which yields an $R_1(\text{CSA})$ of $5.8(\pm 1.4) \times 10^{-3} \text{ s}^{-1}$. This orientation is not in agreement with that proposed by Schweitzer and Spiess and calculated by us. This is certainly due to the fact that incorrect δ_{ii} values were used. If we use our experimental shielding tensor components for nitrobenzene and the orientation shown in Figure 4a, an $R_1(\text{CSA})$ value of $4.3 \times 10^{-3} \text{ s}^{-1}$ is obtained for liquid nitrobenzene, in excellent agreement with the measured value.

Variation of δ_{ii} with Rotation of the NO_2 Group.

To investigate how the CS tensor components change when the NO_2 group is twisted out of the plane of the phenyl ring, values of δ_{ii} were calculated for various NO_2 twist angles, θ , with geometry optimization at each angle. Figure 5 shows how δ_{11} , δ_{22} , δ_{33} , and δ_{iso} vary with θ . These calculations were performed at the B3LYP/6-311G** level. As the NO_2 group is twisted out of plane δ_{11} and δ_{22} increase (i.e., shielding decreases) by 15 and 53 ppm, respectively, while δ_{33} changes by less than 0.3 ppm. The principal components of the nitrogen CS tensor in nitrobenzene can be associated with magnetic dipole allowed electronic transitions between occupied and unoccupied valence MOs. The two in-plane components of the shift tensor, δ_{11} and δ_{22} , are associated with the $\sigma \rightarrow \pi^*$ electronic transition, which involves circulation of charge about an axis in the molecular plane. The CS tensor component that is perpendicular to the plane, δ_{33} , is associated with the $\sigma \rightarrow \sigma^*$ transitions, which involves in-plane electron circulation. Since twisting the nitro group out of the phenyl ring plane will have the largest effect on the π and π^* MOs of the nitro group, δ_{11} and δ_{22} are expected to have a stronger dependence on θ than δ_{33} , as is predicted by our calculations. The $\pi \rightarrow \pi^*$ transition is not magnetically dipole allowed, and there-

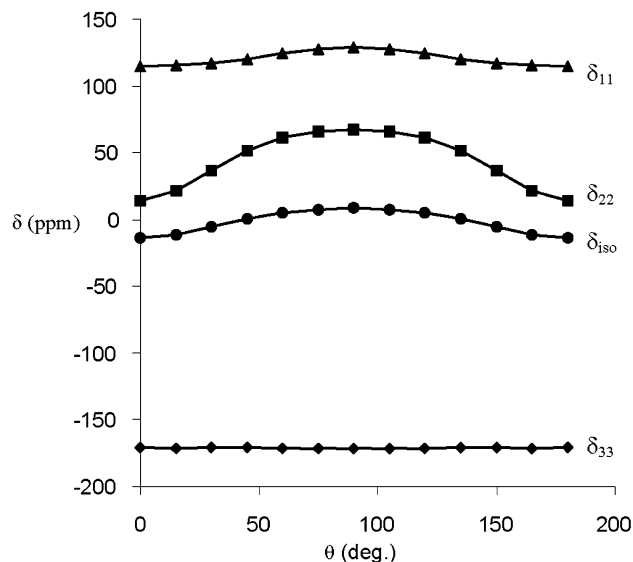


FIGURE 5. Variation of the nitrogen CS tensor components as a function of the NO_2 twist angle, θ , for nitrobenzene.

TABLE 2. Calculated Nitrogen NMR Chemical Shift Parameters for Nitrobenzene

method/basis set	structure ^a	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	Ω	κ
HF/6-31G	optimized	186	101	-250	12	436	0.61
HF/6-311++G**	X-ray	311	195	-225	94	536	0.57
B3LYP/D95**	optimized	115	14	-171	-14	286	0.29
B3LYP/D95**	X-ray	87	-4	-188	-35	275	0.33
B3LYP/6-311G**	X-ray	150	43	-181	4	331	0.35
B3LYP/6-311G**	optimized	145	38	-181	0.4	326	0.35
B3LYP/6-311++G*	X-ray	155	53	-182	9	337	0.40
B3LYP/cc-pVDZ	X-ray	126	20	-195	-16	321	0.34
B3LYP/cc-pVTZ	X-ray	153	50	-180	8	333	0.38
B3LYP/cc-pVQZ	X-ray	166	63	-175	18	340	0.40
MP2/6-311G*	optimized	151	45	-180	5	331	0.36
obsd		126	57	-179	1	305	0.55

^a X-ray structure taken from ref 32.

fore this excitation does not contribute to the magnetic shielding at the nitrogen.

Calculations on Nitrobenzene and Derivatives.

Table 2 contains the δ_{11} , δ_{22} , δ_{33} , δ_{iso} , Ω , and κ values for nitrobenzene calculated with various methods and basis sets. This table, when compared to the corresponding values for solid nitrobenzene, can be summarized as follows. HF calculations give poor agreement with experiment, while B3LYP and MP2 calculations, with triple- ζ , or better, polarization functions, are in much better agreement with our experimental values. This is not surprising since it has been shown that the effects of electron correlation need to be taken into consideration when calculating nitrogen magnetic shielding in multiply bonded systems.³³

Table 3 presents nitrogen shift tensor data calculated at the B3LYP/6-311G** level, with geometry optimization, for nitrobenzene and several derivatives. With the exception of the trimethylammonium derivative, δ_{iso} has a range of only 4.0 ppm and displays no clear trend. This

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TABLE 3. Calculated ^{15}N Chemical Shift Parameters for Various Nitrobenzene Derivatives^a

derivative ^b	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	Ω	κ
4-dimethylamino	138	47	-184	0.1	322	0.44
4-amino	138	46	-193	-3.1	331	0.45
4-methoxy	142	40	-183	-0.7	325	0.38
4-methyl	144	40	-182	0.5	326	0.36
4-fluoro	144	32	-182	-2.1	326	0.31
nitrobenzene	145	38	-181	0.4	326	0.35
4-acetyl	146	37	-188	-1.5	334	0.35
4-cyano	145	26	-178	-3.0	323	0.27
4-nitro	146	24	-180	-3.5	326	0.25
4-Me ₃ N	146	-2.6	-177	-12.4	323	0.09
range/trend ^c	+8	-23	+16	± 2	± 6	-0.2
2,6-dimethyl	166	92	-183	24.9	349	0.58
4-H ^d	158	89	-180	22.3	338	0.59

^a Calculated at the B3LYP/6-311G** level, with geometry optimization. ^b Arranged in order of accepted electron withdrawing ability of the para substituent. ^c Excluding the 4-Me₃N derivative. ^d Calculated with the NO₂ group perpendicular to the phenyl ring plane.

parallels the solution ^{15}N NMR situation.^{1,6,7} On the other hand, trends can be clearly seen in δ_{11} , δ_{22} , and δ_{33} . In general the tensor elements δ_{11} and δ_{33} increase and δ_{22} decreases with the accepted electron withdrawing ability of the para substituent in such a way that any variations nearly cancel to yield averages, δ_{iso} , that do not show any obvious trend. Although these calculations qualitatively agree with our measurements, in that both show large variations in the δ_{ii} components of the CS tensor but small changes in δ_{iso} , they do not reproduce the observed changes in the δ_{ii} values. This is most likely due to additional intermolecular effects. These are difficult to predict and require that calculations be done on extended systems. Such calculations could, in principle, be done if accurate crystal structures and sufficient computing resources were available. Webb et al. have observed that intermolecular solvent effects induce a variation of about 5 ppm in the ^{15}N NMR spectra of nitrobenzene derivatives.⁷

A calculation of the ^{15}N CS tensor for geometry-optimized 2,6-dimethylnitrobenzene, at the B3LYP/6-311G** level, gives $\delta_{11} = 166$ ppm, $\delta_{22} = 92$ ppm, $\delta_{33} = -183$ ppm, and $\delta_{\text{iso}} = 24.9$ ppm. Compared to nitrobenzene, δ_{11} increases by 21 ppm, δ_{22} increases by 54 ppm, δ_{33} decreases by 2 ppm, and δ_{iso} increases by 24.5 ppm. These changes are similar to those calculated for nitrobenzene with the NO₂ group twisted into a position perpendicular to the phenyl ring. The additional effect of *o*-methyl groups is relatively small in that δ_{11} and δ_{22} increase by 8 and 3 ppm, respectively, while δ_{33} decreases by 3 ppm. An unusual aspect of the experimental CS tensor, which is not reproduced in these calculations, is that δ_{33} in *o*-dimethyl-substituted nitrobenzene is very different from the values we have measured (see Table 1) and calculated (see Table 3) for nitrobenzene and several derivatives. It seems improbable such a large difference is due to intermolecular interactions. One other possibility is that the structure of the nitro group in solid 2,4,6-trimethylnitrobenzene is significantly different from that for the isolated molecule. Unfortunately the only available crystal structure for this compound was ob-

tained over 4 decades ago and yields an unrealistic geometry.³⁴ We can calculate how different deformations of the nitro group will affect δ_{33} . Stretching the C₁-N bond from 1.48 Å to 1.50 Å increases δ_{33} from -182 ppm to -178 ppm, a relatively small change. Bending of the C₁-N-O bond in nitrobenzene by 5° yields a change of only 1 ppm. Stretching the N-O bond from 1.22 Å to 1.25 Å changes δ_{33} from -181 ppm to -174 ppm. All of these structural deformations are larger than would be expected, yet the resulting changes in δ_{33} fall considerably short of what is required to reproduce the experimental observations. Another possibility is that δ_{33} changes due to a large amplitude torsional motion of the nitro group. In that case δ_{11} , which is along the C₁-N bond, will be unaffected and δ_{22} must move in the opposite direction of δ_{33} . If such a motion is occurring the unaveraged value of δ_{22} would have to be about 70 ppm. This value is somewhat high but not unrealistic. Averaging due to large-amplitude torsional motion can usually be reduced by performing low-temperature experiments. A ^{15}N spectrum of stationary 2,4,6-trimethylnitrobenzene, obtained at 250 K, is nearly identical with that acquired at room temperature (295 K).

Conclusions

As expected, the measured ^{15}N δ_{ii} values for the para-substituted nitrobenzenes show no obvious correlations with the Hammett reactivity parameters. On the other hand, calculations at the B3LYP/6-311G** level show trends in the ^{15}N CS tensor components δ_{11} , δ_{22} , and δ_{33} that follow the electron donating/withdrawing ability of the para substituent.

Our calculations and solid-state ^{15}N NMR measurements show quite clearly that, even though the isotropic chemical shifts in substituted nitrobenzenes may not show much variation with substituent, the tensor components change significantly. This contrast, which has been observed in other systems, emphasizes the importance of measuring the principal components of the chemical shift tensor, not just the isotropic (solution) value.

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Supporting Information Available: Computational results (Z matrices and final energies of the optimized geometries) and ^1H NMR spectra of 2,4,6-trimethylnitrobenzene- ^{15}N and 2,4,6-tri-*tert*-butylnitrobenzene- ^{15}N . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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