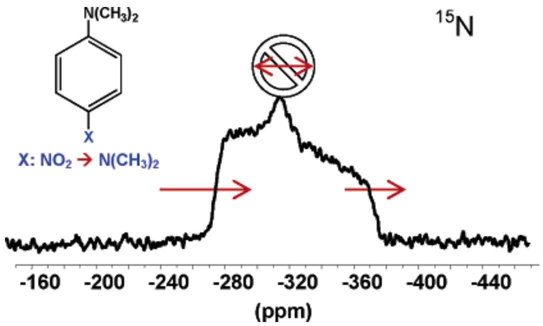
Solid-State Nitrogen-15 NMR and Quantum Chemical Study of *N*,*N*-Dimethylaniline Derivatives

Glenn H. Penner* and Andrea McCullough

Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

gpenner@uoguelph.ca

Received July 18, 2006



In this study the components of the nitrogen chemical shift (CS) tensor are examined for a series of para substituted *N*,*N*-dimethylaniline derivatives. This is done through measurement of the ^{15}N NMR spectra of powder samples and through quantum chemical calculations on the isolated molecules. Experiments and calculations show that the isotropic CS, $\delta_{\rm iso}$, decreases with increasing electron donating ability of the para substituent, in agreement with previous solution studies. More importantly, this study shows that this decrease in the isotropic (solution) CS is due to decreasing values of the CS tensor component δ_{11} and component δ_{33}. The component δ_{22} is essentially invariant to the electron donating/withdrawing ability of the para substituent. Through Ramsey's theory of nuclear magnetic shielding, it can be seen that the variation in δ_{11} and δ_{33}, and hence $\delta_{\rm iso}$, is due to changes in the n−π^* and the σ−π^* energy gaps in *N*,*N*-dimethylaniline. This, in turn, is a result of the change in the energy of the π^* molecular orbital with change in the π-electron donating ability of the para substituent. The effects of nitrogen inversion on the components of the nitrogen CS tensor components are also discussed. This study also shows the feasibility of performing ^{15}N cross-polarization experiments on nonspinning powder samples at natural isotopic abundance.

Introduction

NMR spectroscopy has become the most powerful instrumental technique employed by organic chemists. A vast arsenal of NMR experiments are now available for the characterization of new products, for structure determination, and for the investigation of molecular dynamics. NMR spectroscopy has also provided invaluable information on electronic structure via the chemical shift (CS), δ, and the indirect spin−spin coupling, J.[1]

As a general rule, chemists perform NMR spectroscopic experiments on solution samples. This has the advantage of yielding spectra with sharp resolvable lines. A disadvantage, often not realized, is that additional information is lost. This is due to the three-dimensional, *tensoral* nature of the magnetic shielding, σ, experienced by the nucleus. The chemical shift tensor is characterized by 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 the geometric structure of the molecule. Solution NMR experiments measure the isotropic CS, which is the average of the CS tensor principal components:

$$\delta_{\rm iso} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33}) \qquad (1)$$

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[1] See any good introductory organic chemistry textbook, for example: Solomons, T. W. G. *Organic Chemistry*, 7th ed.; Wiley: New York, 2000; Chapter 13. There are also many specialized NMR spectroscopy textbooks for organic chemists such as: Macomber, R. S. *A Complete Introduction to Modern NMR Spectroscopy*; Wiley: New York, 1998; or Günther, H. *NMR Spectroscopy*; Wiley: New York, 1994.

10.1021/jo061491u CCC: $33.50

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 two 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 sideband intensities in a spectrum obtained with slow magic-angle spinning (MAS) will also provide δ_{ii} values.[2]

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 CS values requires that the absolute magnetic shielding tensor components, σ_{ii}, obtained from a theoretical calculation be converted to the CS scale. For ^{15}N, such a conversion can be accomplished, and the two are related by[3]

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

where δ is the CS with respect to pure liquid nitromethane and σ is the absolute shielding relative to the "bare" nucleus.

NMR studies of organic compounds in solution have predominantly used ^{1}H and ^{13}C. Nevertheless, ^{15}N has proven to be a useful nucleus despite a receptivity that is about 1/50 that of natural abundance ^{13}C. In addition, ^{15}N usually suffers from relatively long relaxation times. Reports of the measurement of the ^{15}N CS tensor components in amines are exceedingly rare.[4]This is due to the rather small span (vide infra) of the ^{15}N powder line shape. In such cases, the line broadening obscures the details of the line shape.

Derivatives of aniline are well suited for electronic structure studies by solid-state ^{15}N NMR spectroscopy. The partial double-bond character of the C—N bond, because of delocalization of the nitrogen lone-pair and phenyl ring π-electrons, yields ^{15}N powder spectra with larger spans. Also, as a result of the n−π conjugation, the components of the ^{15}N CS tensor, δ_{ii}, should depend on the electron donating/withdrawing ability of the para ring substituent. A serious problem in studying this effect in anilines by solid-state NMR spectroscopy is the additional complication of hydrogen bonding. The degree of H-bonding by the amino group or to the amino group will have a significant effect on the components of the CS tensor. Variations in δ_{ii} values because of this type of H-bonding can be minimized in solution by looking at very dilute solutions of the anilines in solvents that are relatively weak H-bond acceptors or donors. This is not possible in the solid state where most solid anilines are held together by networks of N−H···A or of X−H···N hydrogen bonds. Therefore, we have chosen to study a series of para substituted *N*,*N*-dimethylaniline derivatives, where variation of the para substituent should change the CS components, δ_{ii}, and the presence of the *N*-methyl groups will eliminate any complications due to hydrogen bonding.

It is useful to define the span, Ω, and the skew, κ, of a CS tensor.[5]The span is defined as

$$\Omega = \delta_{11} - \delta_{33} = \sigma_{33} - \sigma_{11} \qquad (3)$$

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

$$\kappa = \frac{3(\delta_{22} - \delta_{iso})}{\Omega} = \frac{3(\sigma_{iso} - \sigma_{22})}{\Omega} \qquad (4)$$

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

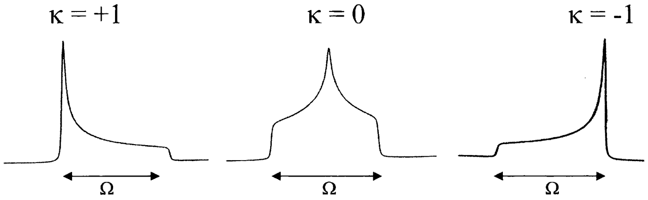

FIGURE 1. Simulated spectra of isolated spin −1/2 nuclei for different values of the skew, κ.

Experimental Section

Samples of ^{15}N aniline, 4-methoxy-*N*,*N*-dimethylaniline, 4-nitro-*N*,*N*-dimethylaniline, 4-cyano-*N*,*N*-dimethylaniline, and 4-formyl-*N*,*N*-dimethylaniline were of commercial origin. Samples of ^{15}N *N*,*N*-dimethylaniline, 4-methoxy-*N*,*N*-dimethylaniline, and ^{15}N *N*,*N*,*N′*,*N′*-tetramethyl-1,4-phenylenediamine were prepared from the corresponding anilines by the method of Giumanini et al.[6,7] Sample purities were checked by obtaining the ^{1}H and ^{15}N NMR spectra in a CDCl$_3$ solution.

Nitrogen-15 solid-state NMR spectra at room temperature were acquired on a 500 MHz spectrometer (B_0 = 11.75 T), which operated at 50.70 MHz. Spectra of the natural abundance samples were obtained with a 7 mm double resonance MAS probe (typical sample weight of 300 mg), and the spectra of the enriched samples were obtained with a 4 mm triple resonance MAS probe (typical sample weight of 70 mg) in double resonance mode. Typical spectra were acquired with proton cross-polarization (CP) 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 and CP/MAS spectra were obtained after carefully optimizing the experimental parameters with a sample of glycine (also at natural abundance) and only after an acceptable signal-to-noise ratio was obtained on the natural abundance glycine sample. The number of accumulated transients for the naturally abundant samples varied from 64 to 16 000. In some cases, 4 days of spectrometer time was required in order to obtain sufficient signal-to-noise ratios for the nonspinning samples. Samples could not be reliably spun at rates of less than 1 kHz. As a result, CP/MAS spectra contained too few spinning sidebands to reliably extract the CS tensor components from the sideband intensities.[2] Spectra were referenced to the nitrate signal of solid ^{15}NH$_4$^{15}NO$_3$ which is at 4.4 ppm with respect to pure liquid nitromethane at 20 °C.[8] Low temperature (220 K) ^{15}N CP spectra of solid stationary and MAS samples of ^{15}N *N*,*N*-dimethylaniline were obtained on the 4 mm probe.

The ^{15}N tensor components for all stationary samples were obtained via spectral simulations using the WSOLIDS program,[9]

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developed in the laboratory of R. E. Wasylishen, which incorporates the POWDER routine of Alderman et al.[10]

Calculations of nuclear magnetic shielding tensors and geometry optimizations were performed with Gaussian 03.[11] 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.[12] For that reason, most of our calculations are performed at the B3LYP/6-311++G** levels. It should be pointed out that good agreement or better agreement with experimental values is not critical to this study since the solid-state structures and nitrogen inversion potential energy curves for most of the compounds are not known (vide infra).

Results and Discussion

NMR Spectra. Figures 2−4 show the ^{15}N CP spectra of six para substituted *N*,*N*-dimethylaniline derivatives, together with simulations. The components of the nitrogen CS tensors for each compound, as obtained from the spectral simulations, are provided in Table 1. The ^{15}N CP/MAS spectrum of each sample gave a narrow single peak, with the exception of 4-formyl-*N*,*N*-dimethylaniline which gave two peaks of approximately equal intensity. The likely reason for this observation is that there are two chemically inequivalent molecules per asymmetric unit in the crystal structure. Since there is no crystal structure available for 4-formyl-*N*,*N*-dimethylaniline, we cannot confirm this. If the data for these para substituted *N*,*N*-dimethylanilines are arranged according to the electron donating/withdrawing ability of the para substituent (as they are in Table 1), obvious trends can be seen. The isotropic CSs, as obtained from the CP/MAS spectra, decrease with an increase in the electron donating ability of the para substituent. This is consistent with the solution values; however, the ^{15}N shifts in solution are consistently lower than those in the solid state. This difference reflects the difference in average geometry and intermolecular interactions between the molecules in the solid state and those in DMSO solution. It is interesting to note that this difference decreases significantly with increase in the electron donating ability of the para substituent. In the solid state, the change in δ_{iso} between $\mathrm{X} = \mathrm{NO_2}$ and $\mathrm{X} = \mathrm{NMe_2}$ is −34.4 ppm, whereas the change in δ_{soln} is −26.0 ppm.

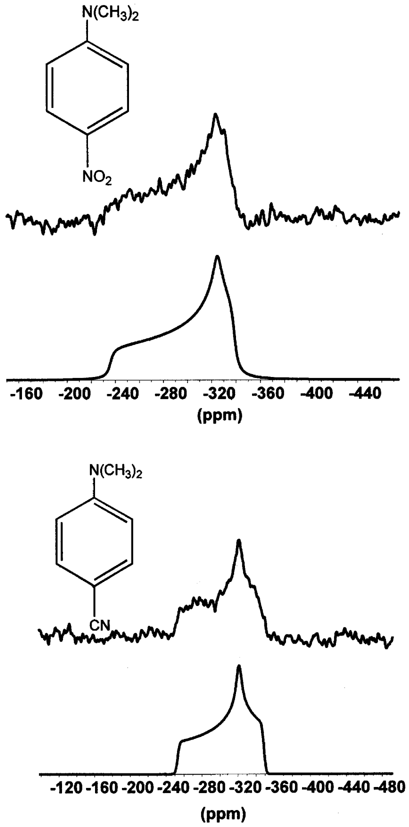

FIGURE 2. Experimental and simulated ^{15}N powder line shapes for solid *N*,*N*-dimethyl-4-nitroaniline and *N*,*N*-dimethyl-4-cyanoaniline.

Turning to the CS tensor components, one can see that the values of δ_{11} decrease with the increase in the electron donating ability of the para substituent. This decrease, in going from $\mathrm{X} = \mathrm{NO_2}$ to $\mathrm{X} = \mathrm{NMe_2}$, is −61.5 ppm. The component δ_{22}, on the other hand, changes very little, and all values lie in the range of -323.0 ± 2.0 ppm. The component δ_{33} also decreases in going from $\mathrm{X} = \mathrm{NO_2}$ to $\mathrm{X} = \mathrm{NMe_2}$, with a total change of −42.2 ppm. Since the solution (isotropic) CS is the average of δ_{11}, δ_{22}, and δ_{33} (see eq 1), the decrease in the observed solution ^{15}N CS, δ_{soln}, can be attributed to a decrease in the CS tensor components δ_{11} and δ_{33}.

Quantum Chemical Calculations. Quantum chemical calculations of the nuclear magnetic shielding have been performed on the para substituted *N*,*N*-dimethylaniline derivatives. The CS components, δ_{ii}, the span of the CS tensor, $\Omega = \delta_{11} - \delta_{33}$, and the isotropic CS, δ_{iso}, are given in Table 2.

The values in this table follow the same trends as those obtained from the solid-state NMR experiment in that the values of δ_{11} and δ_{33} decrease with the increasing electron donating ability of the para substituent, whereas the δ_{22} values show only small changes (range of -311.5 ± 2 ppm). The observed range in δ_{11} values, however, is about 1.5 times larger than the calculated range. The experiments and calculations show that Ω decreases with the increase in the electron donating ability of the para substituent. This is consistent with the expected decrease in the $\mathrm{C_{ipso}}$−N bond order and increase in bond length. Table 4 provides the optimized bond lengths for the molecules in this study.

Calculations of δ_{ii} values using the optimized structures and the optimized TZPV basis set of Ahlrichs and co-workers[14,15]

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(13) See ref 6, page 305 (Table 34).

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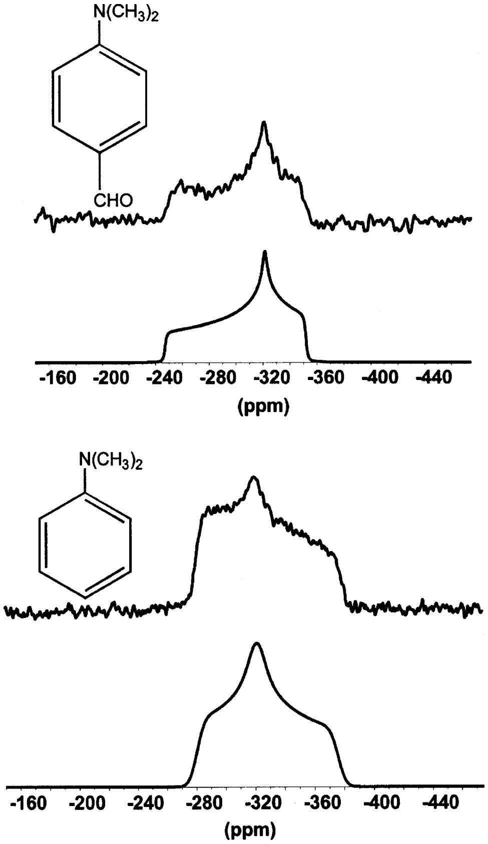

FIGURE 3. Experimental and simulated ^{15}N powder line shapes for solid *N*,*N*-dimethyl-4-formylaniline and *N*,*N*-dimethylaniline.

for *N*,*N*-dimethylaniline and the NO_2 and CH_3O derivatives gave numbers that were all within 2 ppm of those calculated with the 6-311++G** basis. Performing Hartee−Fock calculations (6-311++G**) yielded results that were in much poorer agreement with the experiment.

Ideally, it is desirable to use accurate crystal structures for quantum chemical calculations of molecular properties in the solid state. Crystal structures, as obtained from X-ray diffraction studies, are only available for two of the compounds studied here: 4-nitro-*N*,*N*-dimethylaniline and 4-cyano-*N*,*N*-dimethylaniline.[16,17] Table 3 shows the ^{15}N CS tensor components, as well as the isotropic shift, for 4-nitro-*N*,*N*-dimethylaniline and 4-cyano-*N*,*N*-dimethylaniline when the X-ray structures are used. These values are relatively close to the calculated values when fully optimized structures of the individual (isolated) molecules are used, with the exception that δ_{22} for 4-cyano-*N*,*N*-dimethylaniline differs by 7.6 ppm between the two structures.

Orientation of the CS Tensor. In order to relate the CS tensor components to molecular electronic structure, it is important to know the orientation of the CS tensor. Unfortunately, spectra of powder samples do not provide this information. In some cases, the orientation of the CS tensor with respect to the molecular frame can be inferred from the local molecular symmetry around the nucleus of interest. For example, if the amine nitrogen in the *N*,*N*′-dimethylaniline derivatives is planar (as it is for several of the compounds studied here) then one component of the CS tensor will point perpendicular to the molecular plane, the second component bisects the $C_{Me}-N-C_{Me}$ bond angle (and is parallel to the $C_{ipso}-N$ bond), and the third component is in the molecular plane and perpendicular to the other two components (see Figure 5). In such cases, the

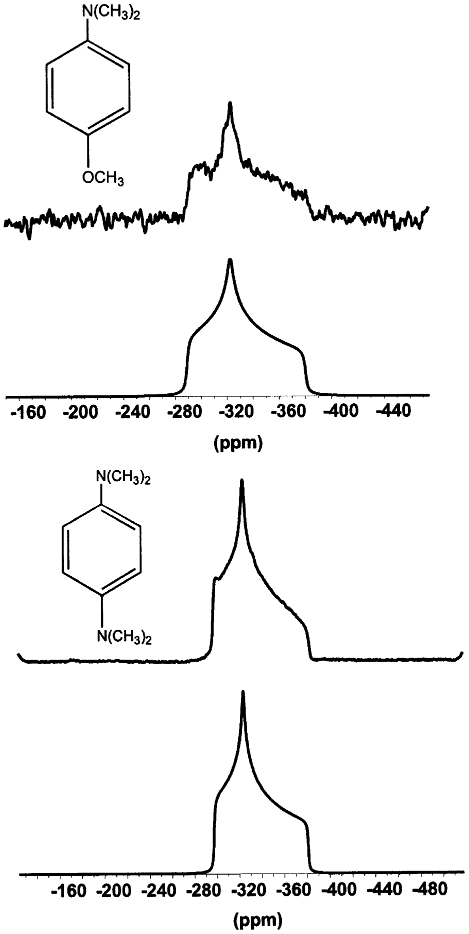

FIGURE 4. Experimental and simulated ^{15}N powder line shapes for solid *N*,*N*-dimethyl-4-methoxyaniline and *N*,*N*,*N*′,*N*′-tetramethylaniline.

TABLE 1. Experimental ^{15}N CS Values (in ppm) of *N*,*N*-Dimethylaniline Derivatives

X	δ_{11}[a]	δ_{22}[a]	δ_{33}[a]	span[b]	δ_{iso}[a]	δ_{soln}[c]
NO_2	−236.0	−325.0	−339.0	103.0	−300.7	−311.6
CN	−252.3	−321.7	−349.0	96.7	−311.0	−320.6
CHO	−253.0	−321.8	−352.0	99.0	−307.0 −310.6	−321.0
H	−280.0	−321.0	−376.0	96.0	−327.3	−335.2
OCH_3	−289.2	−323.0	−380.5	91.3	−333.2	−339.5
NMe_2	−297.5	−324.0	−381.2	83.7	−335.1	−337.6

[a] Estimated error for δ_{11}, δ_{22}, and δ_{33} is ±2.0 ppm. Estimated error for δ_{iso} is ±0.5 ppm. [b] Span: $\Omega = \delta_{11} - \delta_{33}$. [c] Sample in DMSO (see ref 13).

TABLE 2. Calculated ^{15}N CS Values (in ppm) of the *N*,*N*-Dimethylaniline Derivatives

X	δ_{11}	δ_{22}	δ_{33}	span	δ_{iso}
NO_2	−250.5	−310.8	−359.8	109.3	−307.1
CN	−262.9	−310.8	−380.0	117.1	−317.9
CHO	−259.9	−310.3	−377.9	118.0	−316.0
H	−279.2	−313.3	−388.2	109.0	−326.0
OCH_3	−286.3	−313.0	−389.3	103.0	−329.5
NMe_2	−290.7	−312.5	−391.0	100.3	−331.5

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TABLE 3. Calculated ^{15}N CS Values (in ppm) of Two *N*,*N*-Dimethylaniline Derivatives from X-ray Structures

X	δ_{11}	δ_{22}	δ_{33}	span	δ_{iso}
NO_2	−251.5	−312.3	−360.7	109.2	−308.1
CN	−260.8	−318.7	−378.8	118.0	−326.1

TABLE 4. Optimized C_{ipso}−N Bond Lengths, Nitrogen Dihedral Angles, and Relative Energies in Some *para*-X-*N*,*N*-Dimethylaniline Derivatives

X	r(CN)[a] (Å)	φ_{opt}[b] (deg)	ΔE[c] (kJ/mol)
NO_2	1.352	3.0	0.00
CN	1.376	3.9	0.00
CHO	1.374	0.0	0.10
H	1.391	11.8	0.53
OCH_3	1.401	16.4	1.31
NMe_2	1.404	16.1	4.01

[a] Bond length between the ipso carbon and the amine nitrogen. [b] Optimized dihedral angle CH_3−N−C_{ipso}−C_2. [c] ΔE is the relative energy between planar and nonplanar geometries of the $N(CH_3)_2$ group.

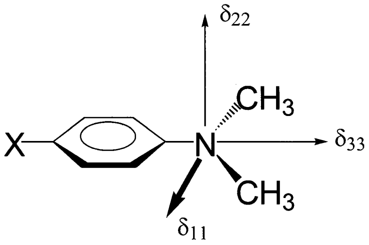

FIGURE 5. Orientation of the nitrogen CS tensor in *N*,*N*-dimethylaniline.

most straightforward method for assigning the three components is to use the results of quantum chemical calculations. The results of several calculations on *N*,*N′*-dimethylaniline unambiguously show that component δ_{11} points along the C_{ipso}−N bond, component δ_{22} is perpendicular to the molecular plane, and component δ_{33} is in the plane and perpendicular to δ_{11} and δ_{22} (see Figure 5).

Effects of Nitrogen Inversion and Nonplanarity. The effects of nonplanarity and inversion of the dimethylamino nitrogen on the CS tensor can be investigated via quantum chemical calculations. Since there is no solid-state structure for *N*,*N*-dimethylaniline, calculations must be performed on the isolated molecule, ignoring any intermolecular effects. The relative energies between the planar and the optimized structures are given in Table 4. In order to determine the effect of inversion on a particular component of the CS tensor, δ_{ii}, one must compute δ_{ii} at each angle and then calculate the average value of δ_{ii} weighted over the potential energy curve according to eq 5.

$$\langle \delta_{ii} \rangle = \frac{\sum_k^n \delta(\theta_k) \exp\left[\frac{-\Delta E(\theta_k)}{RT}\right]}{\sum_k^n \exp\left[\frac{-\Delta E(\theta_k)}{RT}\right]} \tag{5}$$

Using this method and calculating the δ_{ii} values every 5°, the average values of δ_{11}, δ_{22}, and δ_{33} are −279.4 ppm, −310.5 ppm, and −389.0 ppm, respectively. These values are very close to the values of −279.2 ppm, −313.3 ppm, and −388.2 ppm computed for a rigid molecule at the optimized geometry. These calculations predict that, for those derivatives of *N*,*N*-dimethylaniline that have planar or near-planar nitrogens in the solid state, inversion will have very little effect on the observed ^{15}N δ_{ii} values.

Relationship between the CS Tensor, δ, and the Electronic Structure. 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:[18]

$$\sigma_{ii} = \sigma^D_{II} + \sigma^P_{II} \tag{6}$$

The early work of Pople and Karplus indicates that the local paramagnetic term should be predominantly responsible for experimentally observed variations in the ^{15}N CSs.[19] Paramagnetic shielding is a second-order electronic property which depends on the ground and the excited electronic states of the molecule which correspond approximately to the occupied and unoccupied MOs.[18]

$$\sigma^P_{II} = \frac{-\mu_0}{4\pi}\frac{e^2}{2m_e}\sum_{n>0}\frac{1}{E_n - E_0}\left\{\left\langle \Psi_0 \middle| \sum_k \frac{\hat{l}_{kAi}}{r_{kA}{}^3} \middle| \Psi_n \right\rangle \times \langle \Psi_n | \sum_k \hat{l}_{ki} | \Psi_0 \rangle + \langle \Psi_0 | \sum_k \hat{l}_{ki} | \Psi_n \rangle \left\langle \Psi_n \middle| \sum_k \frac{\hat{l}_{kAi}}{r_{kA}{}^3} \middle| \Psi_0 \right\rangle \right\} \tag{7}$$

Here E_0, E_n, Ψ_0, and Ψ_n represent the energies and eigenfunctions of the ground (0) and nth 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 it can be seen from eq 7, σ^p is inversely proportional to the energy difference of the MOs being mixed. The relationship between the direction of the induced charge circulation and the direction of the corresponding component of the magnetic shielding (and hence CS) tensor is of particular importance to the work being reported here. More detailed discussions of the implications of Ramsey's theory can be found elsewhere.[20]

Ramsey's equation (eq 7) is the key to relating the components of the CS tensor to the molecular electronic structure. According to Ramsey's equation, variations in a component of the nuclear magnetic shielding tensor, say δ_{xx}, depend on the mixing of the ground-state MO, Ψ_0, and higher energy MOs, Ψ_n, by the magnetic field. For example, the angular momentum operator $\hat{l}_x$ in eq 7 indicates that the mixing must be via circular (rotational) motion of the electrons about the x axis. Hence, the transition from Ψ_0 to Ψ_n must involve rotation of charge in the y,z plane (around the x axis). This is true if the transition (mixing) is *magnetically* allowed. Since the contribution of each transition to the shielding depends on the inverse of the energy difference, $1/(E_n - E_0)$, only mixing of low-energy electronically excited states will contribute.

As an example, consider the two important transitions in the carbonyl moiety: the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Both mix ground-state MOs with the π^* MO, but only the $n \rightarrow \pi^*$ transition is magnetically allowed. The $n \rightarrow \pi^*$ transition

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involves rotation of charge around the C═O bond. This is in the direction of the δ_{22} component of the ^{13}C CS tensor, and it is this component that varies most strongly with the substituents on the carbon.[21]

In *N*,*N*-dimethylanilines, the transitions of interest are the $n-\pi^*$ and $\sigma-\pi^*$ transitions, which are magnetically allowed. These transitions involve rotation of electrons about axes that are in the molecular plane (assuming that *N*,*N*-dimethylaniline is planar). As explained above, the δ_{11} components and δ_{33} components of the CS tensor are in the molecular plane, whereas the δ_{22} component is perpendicular to the plane. Therefore, we predict that any variations in the $n-\pi^*$ and $\sigma-\pi^*$ energy gaps should cause changes in δ_{11} and δ_{33}, while δ_{22} should remain essentially invariant. This is indeed what is experimentally observed; component δ_{11} and component δ_{33} change with the para substituent, whereas component δ_{22} does not. Since it is unlikely that changing the para substituent will have a significant effect on the *n* orbital, which is localized on the nitrogen, or the rather localized N−C σ bonds, it is most likely that the energies of the π and π^* MOs are changing with the para substituent, and this is affecting the $n-\pi^*$ and $\sigma-\pi^*$ energy gaps. It should be noted that this is a somewhat simplistic approach in that we are assuming that the variation in the energy gaps, $E_n - E_0$, is the dominant factor affecting the magnetic shielding at the nucleus. This is not always the case.[20] On the other hand, plots of the solution CS as a function of the transition wavelength, as obtained from UV−vis spectroscopic measurements, have often yielded straight lines.[22−28] Unfortunately, experimental measurements of the $n-\pi^*$ and $\sigma-\pi^*$ wavelengths for para substituted *N*,*N*-dimethylaniline derivatives are not available.

Conclusions

In contrast to a previous study of nitrobenzene derivatives,[29] this work shows a clear correlation between the components of the ^{15}N CS tensor in a series of solid *N*,*N*-dimethylaniline derivatives and the electronic properties of the para substituents. The variation in the solution CS can be explained as being due to changes in the δ_{11} and δ_{33} components, the δ_{22} component being essentially invariant. The changes in δ_{11} and δ_{33} are likely the result of the variation in the $n-\pi^*$ and $\sigma-\pi^*$ energy gaps in these molecules which, in turn, are likely a consequence of the changing $\pi-\pi^*$ energy gap resulting from the change in the electron withdrawing/donating ability of the para substituent. Although quantum chemical calculations do not quantitatively match the experimental δ_{ii} values, they clearly reproduce the trend in δ_{ii} with respect to the electron withdrawing/donating ability of the para substituent. In addition, we have shown, using quantum chemical calculations, that the values of δ_{ii} for the dimethylamino nitrogen should not change significantly during the nitrogen inversion in *N*,*N*-dimethylaniline.

This study is an excellent example of how the use of a higher field solid-state NMR spectrometer spreads out the powder spectrum of a nucleus enabling one to pick out the components of the CS tensor while, at the same time, increasing the signal-to-noise ratio to the point where ^{15}N powder spectra can be obtained without expensive isotopic enrichment.

Acknowledgment. G.H.P. would like to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support. The spectrometer used for this study was purchased with funds from the Canadian Foundation for Innovation (CFI) and the Ontario Research and Development Challenge Fund (ORDCF).

Supporting Information Available: **Z** matrices of optimized structures for all of the compounds in this study (these are the input files for the NMR calculation). The ^{1}H spectra of the compounds synthesized in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061491U

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