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Solid-State ^{15}N NMR Studies of the Nitroso Group in the Nitrosobenzene Dimer and *p*-Nitroso-*N*,*N*-dimethylaniline

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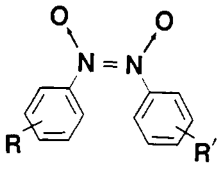
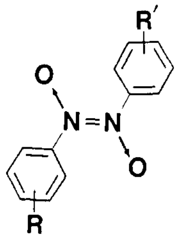
Abstract: The three principal components of the nitrogen chemical shift (CS) tensor have been measured for the nitrosobenzene-$^{15}N_2$ dimer (**1**) and (*p*-[^{15}N]nitroso)-*N*,*N*-dimethylaniline (**2**) using solid-state ^{15}N NMR spectroscopy. Nitrosobenzene exists as a colorless dimer in the solid state, while **2** is a green monomeric nitroso species. This structural difference leads to very different ^{15}N shielding tensors for these two compounds. For example, the ^{15}N chemical shift anisotropy (CSA) for compound **1** is 285 ppm, whereas for **2** the corresponding value is 1479 ppm. This latter value is the largest nitrogen CSA reported to date. Analysis of the dipolar chemical shift NMR spectrum of **1** yields two possible orientations of the nitrogen CS tensor in the molecular frame; results from ab initio localized orbital/local origin chemical shielding calculations on a simple model compound indicate that the actual orientation has the most shielded component of the CS tensor δ_{33} perpendicular to the molecular plane, while the intermediate component δ_{22} makes an angle of 23° with respect to the N–N bond and is approximately perpendicular to the N–C_{ipso} bond. On the basis of shielding calculations and dipolar NMR studies on related molecules, the most shielded component of the nitrogen CS tensor of **2** is perpendicular to the CNO plane, while the intermediate component lies in the molecular plane and approximately along the bisector of the CNO bond angle. The experimental results obtained in this study are compared to those of earlier studies where nitrogen is part of a planar π system.

Introduction

It is well known that aromatic C–nitroso compounds exist as colorless cis or trans dimers, exhibiting an azodioxy structure, or as colored monomeric species.[1-4] In the solid state, the majority of these compounds exist as dimers, although exceptions do exist, with a monomer–dimer equilibrium normally occurring in solution. Numerous studies involving X-ray diffraction, IR, UV-visible, and NMR spectroscopy have been performed to elucidate the structures of many of these species and also to characterize the monomer–dimer equilibrium.[5-17]



cis dimer



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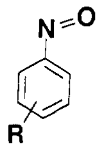

monomer

Orrell et al. have carried out a multinuclear NMR study of nitrosobenzene in order to characterize the structure of this species in solution.[17] Their results showed that decreasing temperature favors the cis dimeric azodioxy isomer. Interestingly, the reported difference in ^{15}N chemical shifts in chloroform solution at 0 °C between the monomer and the cis dimer was nearly 600 ppm, with the nitrogen atom in the dimer being more shielded than in the monomer. Such a shift difference is substantial when compared with the known range of nitrogen chemical shifts in organic nitrogen compounds (approximately 1100 ppm).[18] Large differences in the ^{13}C chemical shifts were also reported for the carbon atom ipso to the nitrogen. Clearly, this indicates dramatic differences in the electronic framework of these two species, and it was speculated that the deshielding in the monomer may be due to low-lying $n_N \rightarrow \pi^*$ circulations which enhance the paramagnetic shielding term. Unfortunately, the study of isotropic chemical shifts provides no definitive evidence on the origin of such a dramatic shielding difference.

Given the greater sensitivity of the chemical shift (CS) tensor to the nature of the local bonding environment, we have decided to use ^{15}N solid-state NMR spectroscopy to study the nitrogen chemical shielding in the nitrosobenzene-$^{15}N_2$ dimer (**1**) and (*p*-[^{15}N]nitroso)-*N*,*N*-dimethylaniline (**2**). X-ray diffraction studies on **1** have shown it to exist exclusively as the cis dimer in the solid.[6] The unit cell is orthorhombic and contains eight equivalent molecules (space group *Pbcn*). Also, due to the presence of the ^{15}N–^{15}N homonuclear spin pair in **1**, it is possible to orient the nitrogen chemical shift tensor with respect to the ^{15}N–^{15}N bond vector r_{NN} due to the fact that these two nuclei are directly dipolar

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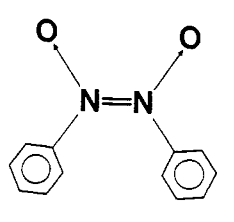

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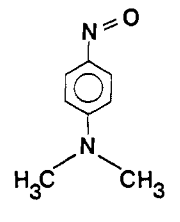
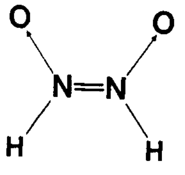


2

coupled to one another.[19-23] X-ray investigations on **2** have shown the unit cell to be triclinic, containing two independent monomeric molecules (space group $P\bar{1}$).[5] By studying the nitrogen CS tensors in both an azodioxy structure and a monomeric nitroso species, differences in the electronic structure of these two related systems can be probed.



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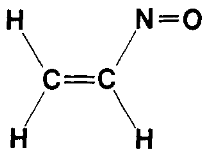

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The experimental results have been supplemented with ab initio chemical shielding calculations on both a model dimeric (**3**) and a monomeric (**4**) nitroso compound for several reasons. Firstly, ambiguities in the orientation of the CS tensor in the molecular frame of reference arise when using the dipolar chemical shift method. More specifically, this technique yields only two of the three angles required to completely characterize the chemical shift tensor in **1**. Consequently, two possible orientations will result, and a chemical shielding calculation will help to determine which is the correct orientation. Secondly, solid-state ^{15}N NMR studies on a powder sample of **2** yield no orientation information on the principal axis system (PAS) of the nitrogen CS tensor in this molecule. The alternative is to perform a single crystal NMR study, but to date attempts to isolate a large single crystal of **2** have been unsuccessful. It is anticipated that an ab initio chemical shielding study will lend insight into the PAS of the nitrogen CS tensor in these monomeric nitroso systems. Lastly, it would be interesting to determine if the shielding calculations can reproduce the trends observed for the principal components of the CS tensor in these two systems. Furthermore, the method of calculation in this study is the localized orbital/local origin (LORG) method of Bouman and Hansen,[24] which computes the shielding tensor as a sum over localized molecular orbitals in a molecule. This approach is advantageous in that the chemical shielding tensor can be readily analyzed in terms of the calculated electronic structure of the system under study. Such an approach is applicable to the present study in order to understand the extreme differences in nitrogen chemical shielding that occur in these monomeric and dimeric nitroso species.

Theory

Shielding Calculations. Using a perturbative approach to determine the electronic energy of a molecule in an external magnetic field, Ramsey[25] formulated the chemical shielding tensor of a nucleus (A) in an isolated molecule as the sum of a diamagnetic and a paramagnetic shielding term:

$$\sigma^{\text{tot}}_{\text{A}\alpha\beta} = \sigma^{d}_{\text{A}\alpha\beta} + \sigma^{p}_{\text{A}\alpha\beta} \tag{1a}$$

$$\sigma^{d}_{\text{A}\alpha\beta} = \frac{\mu_0}{4\pi}\frac{e^2}{2m}\left\langle \psi_0 \left| \sum_i \frac{(r_i r_{i\text{A}}\delta_{\alpha\beta} - r_{i\alpha} r_{i\text{A}\beta})}{r^3_{i\text{A}}} \right| \psi_0 \right\rangle \tag{1b}$$

$$\sigma^{p}_{\text{A}\alpha\beta} = -\frac{\mu_0}{4\pi}\frac{e^2}{2m^2}\sum_{k\neq 0}(E_k - E_0)^{-1}\Bigg[\langle \psi_0 | \sum_i L_{i\alpha} | \psi_k \rangle \times \left\langle \psi_k \left| \sum_i \frac{\text{L}_{i\text{A}\beta}}{r^3_{i\text{A}}} \right| \psi_0 \right\rangle + \left\langle \psi_0 \left| \sum_i \frac{L_{i\text{A}\alpha}}{r^3_{i\text{A}}} \right| \psi_k \right\rangle \langle \psi_k | \sum_i L_{i\beta} | \psi_0 \rangle \Bigg] \tag{1c}$$

These equations are valid when both the origin of the vector potential and the nucleus whose shielding is of interest are located at the coordinate origin. Raynes has previously given a more general version of these expressions, allowing for the noncoincidence of each of these factors.[26] In the above expressions, μ_0 is the permeability of free space, e and m are the electronic charge and mass, respectively, α and β refer to the Cartesian components x, y, or z, $r_{i\text{A}}$ is the distance from electron i to nucleus A, L_i is the electron orbital angular momentum operator, and $\delta_{\alpha\beta}$ is the Kronecker delta. Summations are taken over all electrons i and states k except the ground state $k = 0$. The diamagnetic term is positive and therefore leads to shielding. It is relatively easy to calculate this term accurately by ab initio methods as it depends only on the ground electronic state of the molecule. Conversely, the paramagnetic term is normally negative and therefore leads to deshielding. It is much more difficult to calculate accurately than the diamagnetic term due to a dependence on the wave functions and energies of the excited states of the molecule, including the continuum. Two points are worth mentioning at this stage concerning the paramagnetic shielding term: Firstly, it is obvious from eq 1c that the smaller the energy gap from a ground state to a virtual singlet state of the molecule, the larger the contribution from this excitation to the paramagnetic shielding term. In general, one cannot correlate the paramagnetic shielding with a single electronic transition as many can contribute appreciably to this term. However, if the molecule has a low-lying virtual state such that one excitation is much lower in energy than the remainder, correlations of this nature become possible. Secondly, only those electronic transitions that involve a rotation of charge contribute significantly to the paramagnetic shielding. For example, $\sigma \rightarrow \pi^*$, $\sigma_x \rightarrow \sigma_y^*$, $\pi \rightarrow \sigma^*$, or $n \rightarrow \pi^*$ type of mixing occurs in the presence of a magnetic field because a 90° rotation of charge occurs (in the case of p atomic orbitals). Such transitions are said to be magnetic dipole allowed on the basis of local symmetry selection rules. However, transitions such as $\sigma_x \rightarrow \sigma_x^*$ or $\pi \rightarrow \pi^*$, which involve a linear displacement of charge (electric dipole allowed), are symmetry forbidden, although such excitations can have nonvanishing transition moments due to moment of momentum angular momentum terms and consequently can contribute to the paramagnetic shielding.[27] Furthermore, it is important to keep clear that the charge circulation occurs in a direction about the magnetic field vector, and therefore the orientation of the molecule in the magnetic field dictates the nature of the induced charge circulations. The requirement of charge rotation can be related to the presence of the orbital angular momentum operator L_i in eq 1c. As a qualitative example,

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consider a monomeric nitroso compound in a Cartesian coordinate system with the N–O bonding axis along the x axis and situated in the xy plane. Consider first the magnetic field perpendicular to the molecular plane (σ_{zz}). According to eq 1c, we have to operate with L_z. Jameson and Gutowsky have previously given the results of operating with the orbital angular momentum operators on the p- and d-type atomic orbitals,[28] and we will make use of these results here: $L_z|p_x\rangle = -p_y$; $L_z|p_y\rangle = p_x$; $L_z|p_z\rangle = 0$. Immediately, one can see that this operator corresponds to a rotation of the atomic orbital about the z axis. Therefore, it is clear that transitions involving π molecular orbitals will not occur in this orientation since the L_z operator annihilates the p_z atomic orbital (i.e., the p_z atomic orbital is collinear with the magnetic field vector). However, mixing of σ_x and σ_y orbitals can occur as this involves a rotation about the z axis. Next, consider the magnetic field vector along the N–O bond axis (σ_{xx}). We have the following: $L_x|p_x\rangle = 0$; $L_x|p_y\rangle = -p_z$; $L_x|p_z\rangle = p_y$. Again, it should be clear that any MO corresponding to the N–O σ bond will not be affected by the magnetic field in this orientation, whereas a transition such as $n \rightarrow \pi^*$, which mixes p_y and p_z atomic orbitals, will occur. Arguments of this nature will be used extensively throughout this article.

Modern day ab initio calculations of the shielding tensor have been predominantly performed at the SCF level and are based on coupled Hartree–Fock perturbation theory (CHF).[29] A major limitation of this method is related to the fact that the SCF wave functions do not guarantee gauge invariance, and one is often forced to implement very large basis sets to eliminate this problem. Consequently, earlier shielding calculations were practical only for first-row atoms. However, in the last decade, significant improvements have been made with the advent of several variant schemes of the CHF method which apply gauge factors to localized atomic (GIAO)[30] or molecular orbitals (IGLO, LORG).[24,31] Combined with the advances in computational power, it has now become possible to calculate reliable shielding tensors for atoms of the first and second rows of the periodic table, provided that the atom of interest does not have a formal double bond with a neighboring atom and that it does not have a localized lone pair. The progress being made in this area is covered by C. J. Jameson in the *Specialist Periodical Reports on Nuclear Magnetic Resonance*[32] as well as in several other excellent recent review articles.[33,34]

Solid-State NMR. The CS tensor is a second-rank Cartesian tensor which, in general, can be quantified by nine independent components. However, to first order, only the symmetric part of the CS tensor contributes to the NMR spectrum, and therefore six independent quantities need be defined: three principal components (the diagonal elements) and three Euler angles orienting the PAS of the CS tensor in the molecular frame of reference.[35] The traditional way of obtaining such information has been single crystal experiments in which the crystal is rotated about three orthogonal axes in the magnetic field and the chemical shift is studied as a function of crystal orientation. Unfortunately, such experiments are time-consuming, and single crystals of sufficient quality and size are often unavailable. Consequently, one is often forced to study powder samples from which the three principal components of the CS tensor can still be extracted, but information on the orientation of the PAS of the CS tensor in the molecular frame is usually unavailable. However, if the observed spin is directly dipolar coupled to an adjacent spin, it becomes possible to use the resulting dipolar splittings in the powder line shape to obtain two of the three Euler angles as well as the three principal components of the CS tensor. This very useful technique is referred to as the dipolar chemical shift method.[19,23]

For an "isolated" homonuclear spin pair ($I = {}^1/_2$), such as the two directly bonded ^{15}N spins in the nitrosobenzene-^{15}N (**1**) dimer, one has to consider the Zeeman, chemical shielding, direct dipolar, and indirect spin–spin (J) interactions. In principle, all of these interactions except the Zeeman interaction are dependent upon crystal orientation with respect to the applied magnetic field. Since the two ^{15}N nuclei in **1** are related by an approximate C_2 symmetry axis, their CS tensors will have the same principal components but different tensorial orientations in the molecular frame of reference. In such a case, there will inevitably be some orientations in which the chemical shift difference between the two ^{15}N nuclei becomes comparable to or even smaller than the dipolar coupling between them. Consequently, a general expression for the transition frequencies and relative intensities has to be used to account for the ^{15}N NMR powder line shape. The transition frequencies ν_i and relative intensities P_i for the four transitions of a two-spin-$^1/_2$ system can be written as:[20,36]

$$\nu_1 = {}^1/_2(\nu_A + \nu_B + D + A); \quad P_1 = 1 - B/D \qquad (2a)$$

$$\nu_2 = {}^1/_2(\nu_A + \nu_B + D - A); \quad P_2 = 1 + B/D \qquad (2b)$$

$$\nu_3 = {}^1/_2(\nu_A + \nu_B - D + A); \quad P_3 = 1 + B/D \qquad (2c)$$

$$\nu_4 = {}^1/_2(\nu_A + \nu_B - D - A); \quad P_4 = 1 - B/D \qquad (2d)$$

where

$$D = [(\nu_A - \nu_B)^2 + B^2]^{1/2}$$

$$A = J_{iso} - R_{eff}(3\cos^2\Omega - 1)$$

$$B = J_{iso} + {}^1/_2 R_{eff}(3\cos^2\Omega - 1)$$

In eqs 2, ν_A and ν_B describe the shielding contributions to the resonance frequencies of spin A and spin B, respectively, J_{iso} is the isotropic value of the indirect spin–spin coupling in hertz, $R_{eff} = \langle R\rangle - \langle \Delta J/3\rangle$, R is the dipolar coupling constant $(\mu_0/4\pi)(h/4\pi^2)\gamma_A\gamma_B\langle r_{AB}\rangle^{-3}$, ΔJ is the anisotropy in the indirect spin–spin coupling $J_\parallel - J_\perp$, Ω is the angle between the applied magnetic field and the dipolar vector $\mathbf{r}_{AB}$. The angular brackets indicate that the quantities are subject to motional averaging. Both ν_A and ν_B are dependent upon the orientation of the CS tensor with respect to the external magnetic field. In the present case, it is convenient to express the two CS tensors in the PAS of the dipolar interaction where powder averaging is performed. However, after the relative orientation between the two CS tensors and the dipolar tensor is obtained, one only needs to examine one of the two CS tensors since the other can be readily obtained by performing a C_2 rotation in the molecular frame. Therefore, the orientation of the dipolar vector can be defined with respect to one of the two CS tensors which is depicted in Figure 1. From eqs 2, it is clear that the powder line shape for a static sample contains information on both the magnitude and relative orientation of the CS and dipolar tensors. Consequently, by simulating the powder line shape, the PAS of the CS tensor can be defined with respect to the dipolar vector in the molecular frame.

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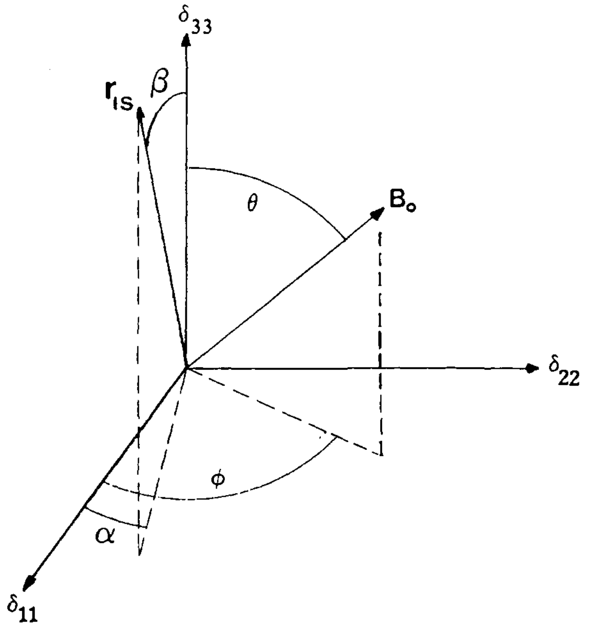

Figure 1. Angles α and β defining the orientation of the dipolar vector $\mathbf{r}_{NN}$ in the principal axis system of the chemical shift tensor. The magnetic field vector $\mathbf{B}_0$ is oriented with respect to the PAS of the chemical shift tensor by the angles θ and ϕ.

The convention used here is standard: $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$, β is the angle between $\mathbf{r}_{NN}$ and σ_{33}, and α is the angle between the projection of $\mathbf{r}_{NN}$ onto the σ_{11}–σ_{22} plane and σ_{11}, the least shielded component. In conventional NMR experiments, one measures chemical shifts δ_{ii} or differences in shielding constants with respect to some reference. The convention used is $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. Note that large chemical shifts correspond to small shielding; both δ_{11} and σ_{11} refer to the least shielded component of the chemical shift and chemical shielding tensors, respectively. The chemical shift anisotropy $\Delta\delta$ is defined as $\delta_{11} - \delta_{33}$ and simply represents the width of the nitrogen spectrum in the absence of dipolar coupling. Note that the chemical shielding anisotropy $\Delta\sigma$ is equal to $\Delta\delta$ and is defined as $\sigma_{33} - \sigma_{11}$.

Experimental Section

Both compounds **1** and **2** were prepared according to standard literature procedures,[37,38] with the exception that nitrobenzene-^{15}N and sodium nitrite-^{15}N were used as starting reagents for **1** and **2**, respectively.

All ^{15}N solid-state NMR spectra were obtained on a Bruker MSL 200 spectrometer operating at 20.3 MHz (B_0 = 4.70 T) with a Bruker double-air-bearing MAS probe. Proton–nitrogen cross polarization under the Hartmann–Hahn match was used to enhance the sensitivity of all ^{15}N NMR spectra. The proton–nitrogen contact time was 10 and 5 ms for **1** and **2**, respectively. The free-induction decay (FID) of a static sample of **1** was signal averaged for 356 transients with a recycle time of 30 s between successive transients. For a static sample of **2**, the FID was signal averaged for 4076 transients with a recycle delay of 60 s. For **1**, an acquisition time of 172 ms was used, while for **2** the acquisition time was 66 ms. In the case of **2**, a spin–echo pulse sequence was applied to improve the quality of the ^{15}N NMR spectrum.[39] All ^{15}N NMR spectra were referenced to NH_3 (*l*) by setting the observed nitrogen signal of solid $^{15}NH_4NO_3$ to 23.8 ppm.

Simulation of the ^{15}N NMR line shape of a static sample of **1** was performed with a FORTRAN-77 program that incorporates the POWDER routine of Alderman et al.[40]

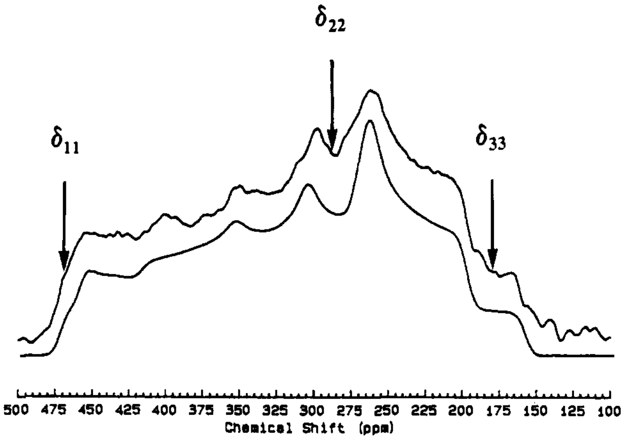

Figure 2. Nitrogen-15 NMR spectrum of a static powder sample of **1**. Upper: experimental. Lower: calculated. The three principal components of the nitrogen CS tensor are labeled.

Self-consistent field (SCF) and nitrogen chemical shielding calculations on **3** and **4** were performed on a Stellar GS2500 vector processing computer. The necessary SCF results were obtained with the Gaussian 90 ab initio program.[41] The molecular coordinates used were obtained from optimized geometries. All nitrogen shielding tensors were calculated using the RPAC program of Bouman and Hansen,[42,43] which uses the LORG method. The basis set used for the geometry optimizations and shielding calculations was the standard 6-311G basis supplemented with two sets of polarization functions on all heavy atoms and one set on hydrogen.

Results and Discussion

(i) Results for the Dimeric Systems. The ^{15}N NMR spectrum of a static powder sample of **1** is shown in Figure 2 along with the simulated spectrum. Spectral simulation yields the following values for the three principal components of the nitrogen CS tensor as well as the effective ^{15}N–^{15}N homonuclear dipolar coupling constant, R_{eff}: δ_{11} = 465, δ_{22} = 288, and δ_{33} = 180 ppm and R_{eff} = 540 Hz. We estimate the uncertainty in the three principal components to be ±4 ppm. Examination of the CP/MAS NMR spectrum of **1** at a rotor frequency of 6034 Hz showed two symmetrical isotropic peaks at 311.1 and 308.9 ppm, indicating that the two nitrogen atoms are slightly nonequivalent in the solid state. It is interesting that at spinning rates less than the nitrogen CSA, both the splitting of the isotropic peaks and the MAS line shape were found to be a function of the MAS rate.[44] The angles α and β were determined to be 67° and 90°, respectively, placing the most shielded direction in the molecule perpendicular to the molecular plane and the intermediate component at an angle of 23° with respect to the dipolar vector $\mathbf{r}_{NN}$. Because the dipolar interaction is axially symmetric, these findings are consistent with two possible orientations of the PAS of the nitrogen CS tensor which are related by a C_2 symmetry axis (Figure 3). It is interesting to point out that if the value of R_{eff} is taken to be equal to the direct dipolar interaction, a value of 1.32 Å is obtained for the ^{15}N–^{15}N bond length, in excellent agreement with the X-ray diffraction results ($\mathbf{r}_{NN}$ = 1.321 Å).[6] This implies that the anisotropy in the one bond *J*-coupling between the two nitrogen nuclei is small as is any librational motion about the N–N bond. Also note that the isotropic shift obtained for **1** compares well with 303 ppm obtained by Orrell et al.,[17] indicating that the structural integrity of this species is maintained in chloroform solution.

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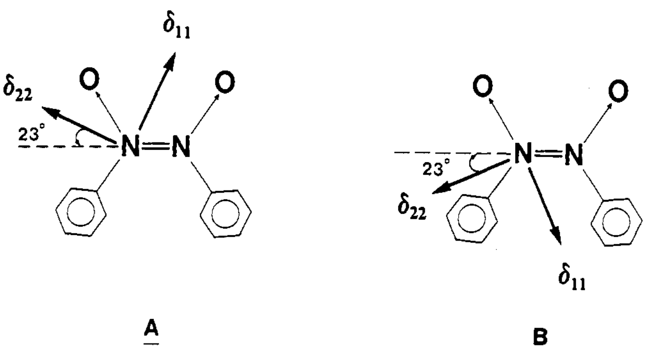

Figure 3. Two possible orientations of the principal axis system of the nitrogen CS tensor in **1**. The most shielded direction is perpendicular to the molecular plane.

Table I. Nitrogen NMR Chemical Shielding Parameters for Compounds **1–4**[a]

	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	$\Delta\sigma$	α	β
1	−220	−43	65	−66	285	67°	90°
2	−1457	−309	22	−581	1479		
3	−308	−20	118	−70	426	67°	90°
4[b]	−2621	−329	151	−933	2772	44°	90°

[a] All shielding values are in ppm. Principal components of the nitrogen chemical shift tensor of **1** and **2** have been converted to absolute shielding values by the expression:[45]

$$\sigma_{ii} = 244.6\ \text{ppm} - \delta_{ii}$$

[b] The values of α and β are referenced with respect to the C–N bond axis in **4**.

In Table I, the values of the three principal components of the nitrogen CS tensor have been converted to an absolute shielding scale on the basis of the accepted absolute nitrogen shielding in ammonia (σ = 244.6 ppm at 20 °C).[45] Also included are the values of σ_{iso}, $\Delta\sigma$, α, and β as well as the theoretical results for the model compound **3**. Given the large differences in the molecular structures of **1** and **3**, the agreement between experiment and theory is very good. The theoretical calculations determine the orientation of the nitrogen shielding tensor to be identical to that in Figure 3a, presenting strong evidence that this is the correct description of the orientation in **1**. Interestingly, although the results in Table I suggest that the isotropic shielding constants are similar in **1** and **3**, examination of the complete shielding tensor unveils differences which can be related to differences in the electronic structure of these compounds. Hence an example of one advantage of studying the complete shielding tensor rather than just its trace. Further discussion of the results in Table I will be reserved for section iii.

(ii) **Results for the Monomeric Systems.** The ^{15}N NMR spectrum of a static powder sample of **2** is shown in Figure 4. Close inspection of the line shape yields the following values for the principal components of the nitrogen CS tensor: δ_{11} = 1702, δ_{22} = 554, and δ_{33} = 223 ppm. The estimated error in the principal components is ±6 ppm. Examination of the ^{15}N CP/MAS spectrum of **2** at two different spinning rates gave the isotropic shift δ_{iso} to be 799.3 ppm. It is interesting to note that when a sample of **2** was kept for a long period of time (in excess of 6 months), the CP/MAS spectrum showed a second signal (δ_{iso} = 812 ppm) with a spinning sideband manifold similar in intensity to that of compound **2**. However, after recrystallization, the impurity disappeared. We are still uncertain at this point as to the origin of this result, but because the NMR spectra were recorded shortly after the compound was prepared, the results presented here will certainly not be affected.

Note the extreme deshielding that occurs when $\mathbf{B}_0$ is aligned in the δ_{11} direction, leading to the large magnitude of the chemical shift anisotropy in this molecule ($\Delta\delta$ = 1479 ppm). In fact, to the best of our knowledge, this is the largest nitrogen CSA yet observed. Previously, the nitrogen CSA in the bent ^{15}NO group of $[RuCl(^{14}NO)(^{15}NO)(PPh_3)_2](BF_4)$($\angle$RuNO = 138°) was determined to be 900 ppm,[46] some 579 ppm smaller than in **2**. It is interesting that when the RuNO bond angle is linear, the nitrogen CSA decreases to 442 ppm. In **2**, the CNO bond angle is approximately 116°, which is in agreement with the general trend that the nitrogen CSA in the nitroso group is a function of XNO bond angle, increasing as the angle decreases.

In Table I, the experimental results for **2** are compared with the theoretical results for the model compound **4**. Unlike the results for the dioxy species, the agreement between these two systems is rather poor. In particular, notice the large discrepancy in the least shielded component σ_{11} of 1164 ppm. Possible reasons for this discrepancy will be given in section iii. The calculated orientation of the nitrogen chemical shielding tensor in **4** is shown in Figure 5. The most shielded component σ_{33} is perpendicular to the molecular plane, while the least shielded component σ_{11} is oriented 44° off the C–N bond direction. Previous results from our laboratory involving ab initio chemical shielding calculations on nitrogen involved in planar π systems[47] have shown that although the magnitude of the principal components may be difficult to calculate, the orientation of the shielding tensor in the molecular frame is predicted quite accurately. On this basis, we anticipate that the orientation of the nitrogen CS tensor in **2** will be very similar to that depicted in Figure 5.

(iii) **Discussion.** In Figure 6, the NMR spectra for static samples of **1** and **2** are displayed on the same chemical shift scale, revealing the extraordinary differences in chemical shielding that exist between these two species. The figure also displays the fact that the largest change involves the least shielded component σ_{11} (also see Table I). Given the orientation of σ_{11} depicted in Figure 5 and for reasons outlined in the Theory section, it is reasonable to assume that the deshielding that occurs when the magnetic field is aligned parallel to the σ_{11} direction is predominantly due to the $n_N \rightarrow \pi^*$ transition. This results in a large paramagnetic shielding along the N–O bond direction. The energy gap between these orbitals is small due to the high energy of the nonbonding electrons on nitrogen and the stabilization of the π^* orbital due to the large electronegativity of nitrogen and oxygen. Consequently, due to this extremely small excitation energy, this component is highly deshielded. In **1**, the nitrogen lone pair becomes involved in bond formation, decreasing the paramagnetic shielding for axes in the plane of the molecule. In both species, the most shielded component is perpendicular to the molecular plane and is a result of high energy $\sigma \rightarrow \sigma^*$ circulations. Notice that the magnitudes of the most shielded component in **1** and **2** are very similar (Table I and Figure 6), and consequently the large difference in the CSA (and also the isotropic chemical shift) is largely due to the difference in magnitude of the least shielded component, thereby confirming the importance of the $n_N \rightarrow \pi^*$ transition in the monomeric nitroso species. This is undoubtably the origin of the relationship between the nitrogen shielding and the XNO bond angle; in the bent systems, the presence of the nitrogen lone pair results in low-lying $n \rightarrow \pi^*$ circulations which will increase the magnitude of σ_{11} and hence the nitrogen CSA. These results also provide insight on earlier related studies on C-nitroso compounds that involved correlations of the nitrogen isotropic chemical shift with the longest wavelength band in the UV or visible spectra of these species.[48] It is clear that the only correlation present is between the σ_{11} component of the shielding tensor (which will lie invariably close to the N–O bond axis) and

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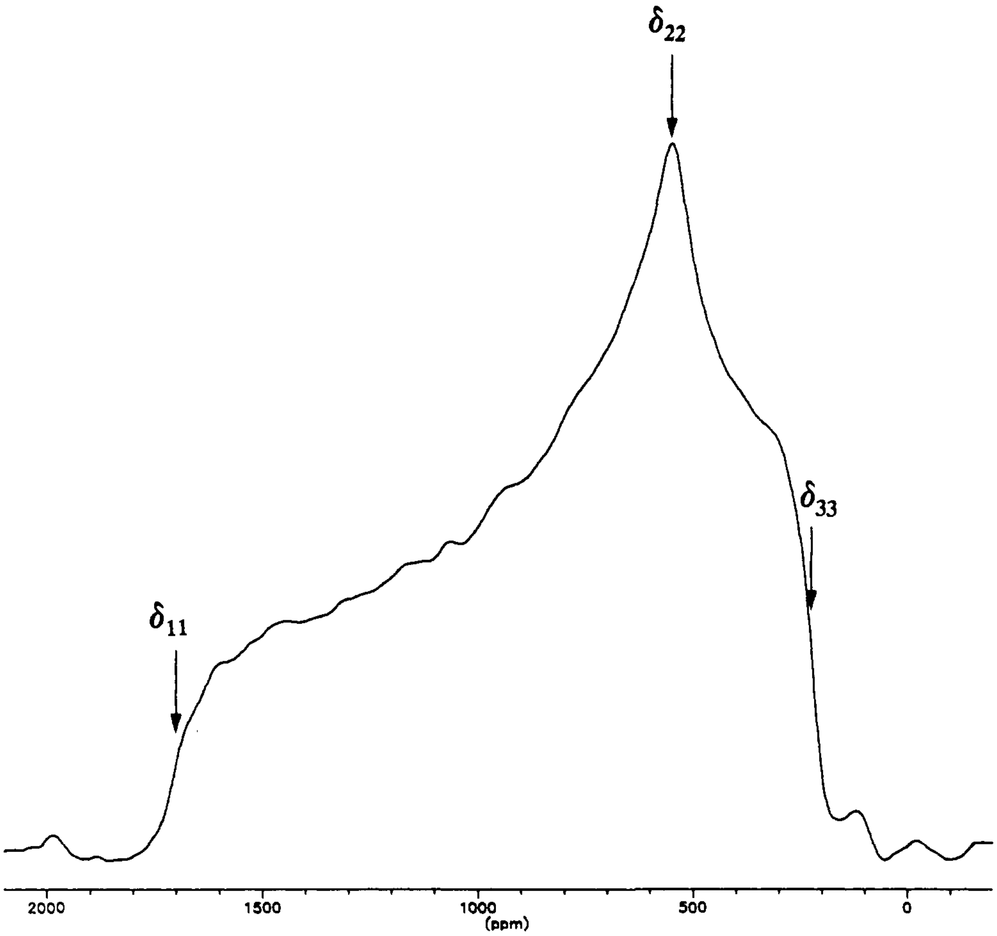

Figure 4. Nitrogen-15 NMR spectrum of a static powder sample of **2**. The three principal components of the nitrogen CS tensor are labeled.

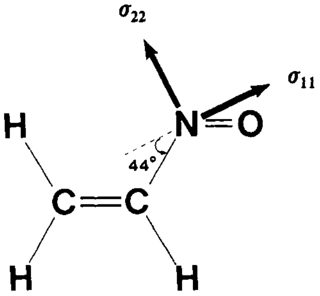

Figure 5. Calculated orientation of the principal axis system of the nitrogen CS tensor in **4**. The most shielded direction is perpendicular to the molecular plane.

the n→π* transition energy. Only because of the small excitation energy involved in this transition does the correlation with σ_{iso} exist.

These conclusions are in agreement with the ab initio chemical shielding calculations. As mentioned, the LORG formalism involves the computation of the chemical shielding tensor as a sum over localized molecular orbitals, hence facilitating the interpretation of the chemical shielding in molecular systems. In both **3** and **4**, the diamagnetic shielding is calculated to be nearly isotropic. Thus, differences in the total shielding are a result of differences in the paramagnetic term, which will be the focus of the remainder of this discussion. In **4**, the results show a large paramagnetic shielding from the nitrogen lone pair, as anticipated, in a direction along the N–O bond (approximately 62% of the total paramagnetic shielding in this direction) as well as a large contribution from the C–N bond. There exist smaller but significant paramagnetic contributions from these and other bonding orbitals in the molecular plane but perpendicular to the N–O bond axis, explaining the deviation of the least shielded component from the N–O bond direction (Figure 5). In compound **3**, none of the localized orbitals are calculated to contribute significantly to the paramagnetic shielding term. The largest contributions are from the N–N bonding orbitals and are in a direction perpendicular to this axis and in the molecular plane ($\sigma \rightarrow \pi^*$ transitions). However, the magnitudes of these contributions are small in comparison with the dominant terms in **4**. In both **3** and **4**, contributions from all localized molecular orbitals are minimal perpendicular to the molecular plane, explaining the origin of the orientation of σ_{33}.

A comparison of the experimental and theoretical results in Table I shows that in both the monomeric and dimeric systems, the largest discrepancy is in the least shielded component σ_{11}. As mentioned already, notice the large difference in σ_{11} for **2** and **4** of 1164 ppm. Due to the nature of the electronic structure of monomeric nitroso compounds, there exists an inherent danger of instability in the wave function at the Hartree–Fock level. This would give rise to a meaningless computation of the chemical shielding tensors in these systems. Given the large deshielding calculated for **4**, we are reporting, as a wave function stability test, the lowest eigenvalue of the A–B matrix[24] used for the calculation of the paramagnetic shielding in this system, 1.36 eV. The fact that this excitation energy is positive indicates that the Hartree–Fock ground state calculated for **4** is free of singlet instabilities,[49] and we can eliminate this as a possible source of experimental–computational discrepancy. Therefore, one possible origin of this deviation is undoubtably associated with the model systems used in the calculations. It appears that in compound **2**, conjugation with the aromatic ring stabilizes the nitrogen lone pair electrons with respect to the π bonding orbitals, thereby lowering the magnitude of σ_{11}. However, it is difficult to envisage that replacing the ethylene fragment with an aromatic ring will

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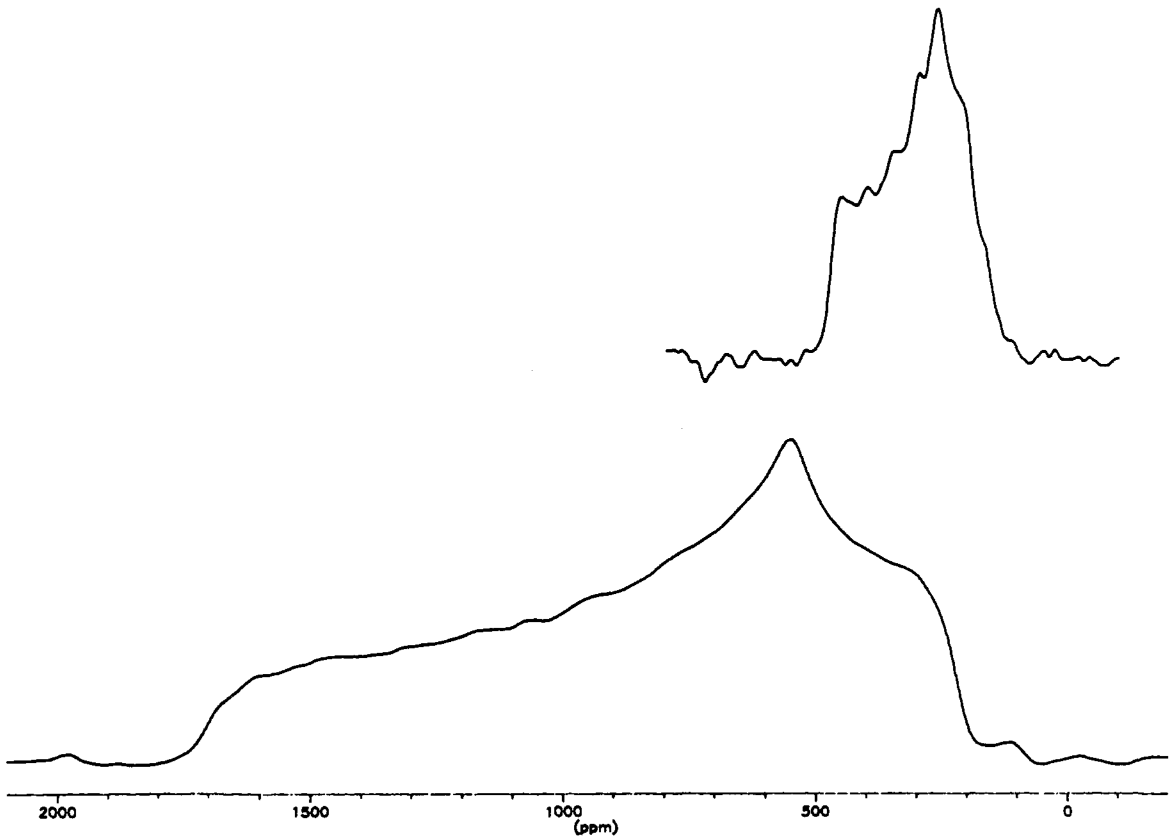

Figure 6. ^{15}N NMR spectra of **1** (top) and **2** (bottom) on the same horizontal axis, demonstrating the large difference in chemical shielding.

Table II. Nitrogen NMR Chemical Shift Parameters for Several Compounds Containing an RN=X Fragment

compd	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	$\Delta\delta$	α	β	ref
2[a]	1702	554	223	826	1479	44°	90°	this work
trans-azobenzene[b]	1034	391	109	511	925	37°	83°	56
pyridine[c]	633	414	149	399	484			54
imine	610	321	65	332	545	42°	78°	57
oxime	560	328	160	349	400	52°	90°	55
1	465	288	180	311	285	67°	90°	this work

[a] The values of α and β are defined with respect to the C–N bond axis and are based on the ab initio shielding calculations for **4**. [b] Chemical shift parameters for one of the two distinct sites in the unit cell of *trans*-azobenzene. [c] The principal components of the chemical shift tensor have been converted to a scale with respect to NH$_3$ (*l*).

lower the magnitude of σ_{11} by more than 1000 ppm. Therefore, we conclude that for **4**, despite the large basis set used in the calculations, the magnitude of the paramagnetic shielding has been overestimated. Previously, it has been suggested that second- and higher-order electron correlation effects need to be considered to accurately calculate the nitrogen[50-52] or phosphorus[43,53] chemical shielding tensor when these atoms are involved in an unsaturated bonding arrangement. Inclusion of higher-order electron correlation results in an increased shielding, and it is highly probable that this is a source of deviation in the nitrogen shielding calculation on **4**.

Finally, it is interesting to compare the results obtained here with those of other systems containing a nitrogen atom involved in p–π bonding where the nitrogen shielding tensor has been experimentally characterized. In Table II, the nitrogen shift tensors in **1** and **2** are compared with those in pyridine,[54] (*E*)-acetophenone oxime,[55] *trans*-azobenzene,[56] and benzylideneaniline.[57] Examination of the deviation in each of the three principal components shows that the largest variation is in δ_{11}. In all cases, it appears that the orientation of this component is in the R—N=X plane and approximately perpendicular to the direction bisecting the R—N=X fragment (where the nitrogen lone pair would reside). Therefore, the magnitude of this component should be related to the $n_N \rightarrow \pi^*$ transition energies in these compounds. It is also interesting that the orientation of the most shielded component is approximately perpendicular to the R—N=X plane and shows the least variation of the three principal components in the compounds studied. Again, this can be related to the fact that the paramagnetic shielding is small in this direction, resulting from high-energy in-plane circulations ($\sigma \rightarrow \sigma^*$). Lastly, the orientation of the intermediate component lies necessarily in the R—N=X plane and approximately along the direction of the nonbonding electrons associated with the nitrogen lone pair. This appears to be a general observation for nitrogen when part of a planar π system and is supported by ab initio calculations.[50] These results lend further support that the orientation of the PAS of the nitrogen CS tensor in **2** will be similar to that depicted for **4** in Figure 5.

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Conclusion

The nitrogen chemical shielding has been studied in a monomeric and a dimeric nitroso compound using both solid-state NMR and ab initio chemical shielding calculations. Both the experimental and theoretical results show a large change in chemical shielding upon moving from the dimeric to the monomeric species, due mainly to the formation of a nitrogen lone pair. In the monomer, low-lying $n_N \rightarrow \pi^*$ circulations generate large paramagnetic currents that result in a large CSA. In *p*-nitroso-*N*,*N*-dimethylaniline, the CSA is 1479 ppm, the largest anisotropy yet measured for nitrogen. In the nitrosobenzene dimer, the nitrogen CSA is 285 ppm. Overall, the ab initio chemical shielding calculations agree well with experiment. The largest discrepancy is in the least shielded component σ_{11}, and it appears that higher-order electron correlation has to be considered in order to calculate accurately the nitrogen shielding for these systems. The results obtained here are consistent with previous nitrogen shielding studies for systems containing the R—N═X moiety.

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