Nitrogen-15 NMR spectra have been obtained for spinning and static powder samples of solid cis-azobenzene-15N2 (I). The nitrogen NMR spectra obtained with magic angle spinning exhibited spinning rate-dependent line shapes which are characteristic of dipolar coupled homonuclear spin pairs which have the same isotropic chemical shifts but different orientations of their shift tensors relative to the dipolar vector. Analysis of the 15N NMR spectrum of a static sample yielded the three principal components of the nitrogen chemical shift tensors: δ11 = 1006 ppm, δ22 = 469 ppm, and δ33 = 112 ppm. As well, comparison of observed and calculated NMR line shapes indicated that the most shielded component, δ33, is perpendicular to the CNNC plane, while the least shielded component, δ11, is in the CNNC plane and oriented approximately 15° with respect to the N=N internuclear vector. The nitrogen chemical shift tensor in I is compared with those reported in trans-azobenzene and compounds containing the X—N=N=C fragment. The nitrogen chemical shift tensors in cis- and trans-azobenzene are discussed in light of the results of ab initio shielding calculations on cis- and trans-diazene.

Introduction

The photochemical properties of the azobenzenes have been the subject of numerous investigations in the past1-4 and have provided some practical uses as dyes,5 as photochromic probes for studying motional aspects of polymers,6 and light-induced switches which can make a polymer functional.7 More recently, the reversible cis–trans isomerism of azobenzenes has been implicated in a novel "three-state" photoelectrochemical method for ultra-high-density data storage.8,9

The two geometric forms of azobenzene, cis and trans (thermodynamically stable), have been investigated by X-ray diffraction10-12 and by several solution spectroscopy techniques.13-22 For example, 15N NMR studies of the two forms of azobenzene in deuterated chloroform indicate that there is only a 17.5 ppm difference in the isotropic chemical shifts in this solvent (cis isomer at the higher frequency).13 However, IGLO calculations performed by Schindler on the related cis- and trans-diazenes, HN=NH, suggest an isotropic shift difference in excess of 70 ppm (trans isomer at the higher frequency) and that there are marked changes in the three principal components of the 15N chemical shift tensors of the two isomers.23

To help understand these differences in shielding properties, we decided to investigate the 15N NMR spectra of solid cis-azobenzene-15N2, I, which can be prepared and isolated in pure

\[
\begin{align*}
N &\equiv N \\
\text{I}
\end{align*}
\]

form from doubly enriched trans-azobenzene-15N2.24 Dipolar chemical shift NMR studies on a static powder sample of I allow us to orient the nitrogen chemical shift tensor in the molecular frame of reference and provide the three principal components of the chemical shift tensor, δij (i = 1, 2, 3).25-27 The nitrogen chemical shift parameters of I will be compared to recent solid-state 15N NMR results for trans-azobenzene-15N2 as well as with theoretical shielding calculations on two cis- and trans-diazenes.23

Theory

The influence of magic angle spinning (MAS) on the NMR spectra of homonuclear spin pairs has been the topic of several investigations in the past.25-32 For example, Maricq and Waugh suggested that the MAS NMR line shape for such a spin system can be predicted by average Hamiltonian theory.33 Later, Kubo and McDowell demonstrated that the description of the line shape proposed by Maricq and Waugh was not completely accurate, and they used Floquet Hamiltonian theory to calculate the MAS NMR line shape of a homonuclear spin system reliably at all spinning frequencies.35 Regardless, both approaches predict that if two homonuclear spins are in an environment where they are related by a 2-fold axis but do not have an inversion center, the principal components (δij) of the two chemical shift tensors will have the same magnitude but different orientations in the molecular frame of reference. Upon magic angle spinning, the distinct orientations of the two chemical shift tensors result in instantaneous differences in the chemical shifts; together with the direct homonuclear dipolar interaction, the MAS NMR line shape will be a function of the spinning speed.33-35

For a static sample, the difference in the two orientations of the chemical shift tensors of the homonuclear spin pair also has a significant effect on the NMR line shape. In this case, the NMR spectrum is sensitive to the relative magnitudes of the dipolar coupling constant, R, and the chemical shift difference. For instance, if the chemical shifts of the two spins are always the same for all crystallite orientations, the homonuclear two-spin system is referred to as an A2 spin pair. The static NMR spectrum for a general A2 spin pair of I = 1/2 nuclei consists of two scaled and overlapping non-axially-symmetric shielding patterns.35-36 If, however, the chemical shift difference between the two spins is much larger than the direct dipolar coupling between them, this constitutes an AX spin pair; the static NMR spectrum for either the A or X nuclei (I = 1/2) is identical to the A2 case except for different amounts of scaling for the two subspectra. Finally, when the chemical shift difference between the two spins is not always larger than the dipolar coupling between them, this constitutes an AB spin pair. In this case, Zilm and Grant have demonstrated that the static NMR line shape is intricately related to the type of spin system (A2, AB, or AX),28 and the powder NMR line shape may be a "mixture" of all three types of spin systems. More precisely, along some directions the
cis-Azobenzene in the Solid State

homonuclear spin pair may constitute an A₂ spin system whereas along other directions it may be an AB or AX spin system.

In order to account for the powder NMR line shape of a general homonuclear spin 1/2 pair, one has to use exact expressions for the four transitions, $v_i$, and their relative intensities, $P_i$, as indicated in eqs 1:

\[
\begin{align*}
\nu_1 &= \frac{1}{2}(\nu_a + \nu_b + D - A); \quad P_1 = 1 - B/D \\
\nu_2 &= \frac{1}{2}(\nu_a + \nu_b + D + A); \quad P_2 = 1 + B/D \\
\nu_3 &= \frac{1}{2}(\nu_a + \nu_b - D + A); \quad P_3 = 1 + B/D \\
\nu_4 &= \frac{1}{2}(\nu_a + \nu_b - D - A); \quad P_4 = 1 - B/D
\end{align*}
\]

where $D = [(\nu_a - \nu_b)^2 + B^2]^{1/2}$, $A = J - R(3 \cos^2 \theta - 1)$, and $B = J + \frac{1}{2}R(3 \cos^2 \theta - 1)$. In eq 1, $\nu_a$ and $\nu_b$ describe the shielding contributions to the resonance frequencies of spin A and spin B, respectively, $J$ is the isotropic indirect spin–spin coupling in hertz, $R$ is the direct dipolar coupling constant in hertz, $(\mu_0/4\pi)(h/4\pi^2)\gamma_A\gamma_B R(\mu_B^a A^b) / (\sin \theta)^2$ (in the absence of anisotropy in $J$ and librational averaging), and $\theta$ is the angle between the applied magnetic field and the dipolar vector, $\mathbf{r}_{AB}$.

The orientations of the A and B spin chemical shielding tensors can be referenced to the dipolar interaction tensor as indicated in Figure 1. In this case, if the angles $\theta$ and $\phi$ represent the orientation of the dipolar interaction tensor relative to the applied magnetic field, $\mathbf{B}_0$, then the chemical shielding contributions to the powder NMR line shape can be evaluated from the equation

\[
\nu_i = \left(\gamma_B h_0 / 2\pi\right) \left[1 - (\sigma_1^i \cos^2 X_i + \sigma_2^i \cos^2 Y_i + \sigma_3^i \cos^2 Z_i)\right]
\]

where $\sigma_j^i$ ($j = 1, 2, 3; i = A, B$) are the principal components of the chemical shielding tensors and $X_i$, $Y_i$, and $Z_i$ are the directions cosines which orient the applied magnetic field in the principal axis system of the chemical shift tensor. These angles can be expressed by a rotational transformation as shown in eq 3. Thus, to calculate the NMR line shape for a general homonuclear spin 1/2 pair in a powder sample, the frequencies and intensities at all orientations of $\theta$ and $\phi$ relative to the magnetic field $\mathbf{B}_0$ must be calculated and summed. The two sets of independent Euler angles, $\alpha^{CS}, \beta^{CS}, \gamma^{CS}$, and $\phi^{CS}$ ($i = A, B$), are defined in Figure 1 and represent physical parameters which are characteristic for the particular molecular fragment containing the homonuclear spin pair.

It should be noted that since the dipolar interaction is axially symmetric, the overall NMR line shape for a powder sample will be invariant to any simultaneous rotation of the two chemical shift tensors about the dipolar vector. Thus, the orientations of the chemical shift tensors of a spin pair cannot be determined unambiguously from the powder NMR line shape alone. In practice, however, this uncertainty can usually be overcome by considering the local symmetry of the molecule and/or results from molecular orbital shielding calculations.

Experimental Section

The general procedure used to prepare pure cis-azobenzene-15N₂ (1) was described by Hartley.24 trans-Azobenzene-15N₂ was procured from MSD Isotopes, Montreal. This sample (0.8 g) was dissolved in 40 mL of distilled acetone, and the solution was put into two water jacketed photolysis tubes. After irradiation with a Hanovia 200-W medium-pressure mercury lamp for 8–12 h, the acetone solution was diluted with 60 mL of distilled water, cooled in an ice–water bath for 10 min, and then filtered. The filtrate was washed with 6.5 mL of light petroleum ether. The remaining aqueous acetone filtrate was extracted several times with distilled chloroform. The combined chloroform extracts were dried with MgSO₄, filtered, and then evaporated in vacuo. This mixture was then separated on a preparative silica gel TLC plate (Fisher) by elution with light petroleum ether; the top band contains residual trans-azobenzene-15N₂ whereas the lower band is cis-azobenzene-15N₂. The lower band was removed and extracted with cold chloroform (0 °C). The extract was dried with MgSO₄ and filtered, and the chloroform was removed in vacuo to yield pure cis-azobenzene-15N₂ (vide infra). This procedure was repeated three times to yield approximately 280 mg of pure cis-azobenzene-15N₂. The purity of the final sample was confirmed by 13C NMR in deuterated chloroform. In a freezer, the cis-azobenzene-15N₂ sample was then loaded into a 7-mm zirconium oxide rotor for solid-state NMR studies. Between solid-state NMR experiments, the sample was stored in a freezer to minimize thermal isomerization to the trans form.

Nitrogen-15 and carbon-13 solid-state NMR spectra were obtained at 20.3 and 50.23 MHz, respectively, on a Bruker MSL-200 NMR spectrometer. All NMR spectra were acquired with proton cross polarization (CP) and high-power proton decoupling. Typical τ/2 pulse widths for 1H, 15N, and 13C were between 4.5 and 6.5 μs. Contact times were typically 10–12 ms. The FLIPBACK pulse sequence was used to acquire all NMR spectra with recycle times of 3–5 min between the acquisition of successive transients. Spinning frequencies for the CP/MAS NMR experiments were 1.5–4.0 kHz. The spectral width for all 15N NMR experiments was 62.5 kHz with data file sizes of 4096 points. Sensitivity enhancements of 5 and 200 Hz were applied to the free induction decays (FIDs) prior to Fourier transformation. The 15N NMR spectra were referenced to liquid NH₃ (20 °C) at 0 ppm by setting the observed ammonium signal of solid NH₄NO₃ at 23.8 ppm. The 13C NMR spectra were referenced with respect to TMS at 0 ppm by setting the observed methylene carbon signal of solid adamantane at 38.57 ppm. The 13C NMR spectrum of a static sample of I was simulated using a program which carries out calculations based on eq 1–3 (J = 0). All calculations were performed on a 80386/387 microcomputer with a Fortran algorithm which incorporates the extrapolation scheme of Alderman et al.25 The resulting calculated MR spectra were convoluted with a Gaussian line broadening function.

Self-consistent-field (SCF) and nitrogen chemical shielding calculations on cis- and trans-diazene were performed on a Stellar
NMR spectra of each molecule retain a four equivalent molecules per unit cell, each molecule is gets smaller, being approximately of the spinning frequency. For instance, at a spinning frequency used for several NMR experiments but could always be completely removed by preparative TLC. Immediately obvious from the \( ^{15}N \) NMR spectra in Figures 2 and 3. The spectra in Figure 3 are the expanded isotropic regions of the \( ^{15}N \) NMR spectra shown in Figure 2. The \( ^{15}N \) NMR spectrum in Figure 2b corresponds to that of a freshly prepared sample of cis-azobenzene-\( ^{15}N_2 \), \( \delta_\text{iso} = 511 \text{ ppm} \) as is apparent in Figure 2a,c. The trans-azobenzene-\( ^{15}N_2 \) NMR signals appeared in the samples only after the rotors had been used for several NMR experiments but could always be completely removed by preparative TLC. Immediately obvious from the \( ^{15}N \) NMR spectra in Figures 2 and 3 is a splitting of the \( ^{15}N \) resonance lines of 1. From Figure 3 it is clear that the shape and splitting of the isotropic \( ^{15}N \) NMR signal of 1 vary as a function of the spinning frequency. For instance, at a spinning frequency of 2035 Hz, the splitting of the isotropic \( ^{15}N \) peaks is in excess of 100 Hz. As the spinning frequency is increased, the splitting gets smaller, being approximately 65 Hz at 3374 Hz. Also, from Figure 2a, it is clear that the line shape of the different order sidebands varies.

X-ray diffraction results for cis-azobenzene indicate that crystals obtained from petroleum ether are orthorhombic with four equivalent molecules per unit cell. Each molecule is nonplanar with each phenyl ring twisted by 53° about the CN bond relative to the planar N=N-N=C-phen fragment. However, each molecule retains a \( C_2 \) symmetry axis perpendicular to the N=N bond. Thus, the splittings observed in the \( ^{15}N \) CP/MAS NMR spectra of 1 are not a result of crystallographic nonequivalence. This conclusion was supported by \( ^{13}C \) CP/MAS NMR experiments on the same sample of 1; only a single resonance line \( (\nu_1/2 = 25 \text{ Hz}) \) was observed for the ipso carbon \( (\delta_\text{iso} = 155.0 \text{ ppm}) \). However, unlike the precursor trans-azobenzene, the cis-azobenzene molecule does not have an inversion center. This is analogous to the situation reported by Kubo and McDowell for the two \( ^{11}B \) nuclei of \( \text{Na}_2\text{P}_2\text{O}_7\cdot10\text{H}_2\text{O} \) and by Challoner et al. in \( \text{cis}(2,4,6\text{-tri-tert-butylphenyl})\text{diphosphene} \). Also, Power and Wasylishen recently reported a similar effect in \( \text{cis-Pt}(\text{PEt}_3)_2\cdot\text{Cl}_2 \). From Figure 3, it is clear that the shape and splitting of the isotropic \( ^{15}N \) NMR signal of 1 vary as a function of the spinning frequency. For instance, at a spinning frequency of 2035 Hz, the splitting of the isotropic \( ^{15}N \) peaks is in excess of 100 Hz. As the spinning frequency is increased, the splitting gets smaller, being approximately 65 Hz at 3374 Hz. Also, from Figure 2a, it is clear that the line shape of the different order sidebands varies.

The isotropic chemical shift determined for the solid sample of 1, \( \delta_\text{iso} = 528.8 \text{ ppm} \), compares very well to the analogous values reported for 1 dissolved in CDCl\(_3\) and (CD\(_3\))\(_2\)SO solutions.\(^{18}\) Note that the difference observed between the \( ^{15}N \) isotropic chemical shifts for solid cis- and trans-azobenzene-\( ^{15}N_2 \) \((\sim 18 \text{ ppm})\) (Table 1) is very similar to the analogous value determined for these two isomers in CDCl\(_3\), 17.5 ppm.\(^{18}\) This observation suggests that the structural and conformational integrity of both isomers of azobenzene are maintained in CDCl\(_3\) solution. From the number of spinning sidebands in Figure 2, it is clear that the nitrogen chemical shift anisotropy of 1 is quite large. This property made the acquisition of a \( ^{15}N \) NMR spectrum of a static powder sample of 1 difficult.

The Static \( ^{15}N \) NMR Spectrum. The \( ^{15}N \) NMR spectrum observed for a freshly prepared static powder sample of 1 is shown in Figure 4a; the simulated spectrum is shown in Figure 4b. The
cis-Azobenzene in the Solid State

![Image of cis-Azobenzene structure]

Figure 4. (a) $^{13}$N NMR spectrum obtained experimentally for a static powder sample of 1. (b) Computer simulation of the powder spectrum based on eqs 1–3.

parameters used for calculating the NMR spectrum in Figure 4b are $\delta_1 = 1006$ ppm, $\delta_2 = 469$ ppm, $\delta_3 = 112$ ppm, $\alpha_1CS = \beta_1CS = 90^\circ$ (i = 1, 2), and $\gamma_1CS = -\gamma_2CS = 15^\circ$. The estimated errors in the three principal components are $\pm 2$ ppm and $\pm 4^\circ$ for the three Euler angles. The experimental parameters are summarized in Table I together with the previous solid-state NMR results for trans-azobenzene.$^{12,23}$ Also included are chemical shielding parameters obtained using ab initio shielding calculations for the cis and trans isomers of two simple model compounds.$^{23}$

The N,N bond length reported for cis-azobenzene from X-ray diffraction experiments, $r_{NN} = 1.233 \AA$, was used to calculate the direct dipolar coupling constant, $R = 628$ Hz.$^{15}$ Including this value in the calculation of the static $^{15}$N NMR spectrum, the dipolar splitting at $\delta_1$ in the experimental $^{15}$N static NMR spectrum could only be reproduced using $\beta_1CS = 90^\circ$. Interestingly, the $\delta_3$ region of the experimental static $^{15}$N NMR spectrum could be precisely simulated as an $A_2$ spin system with $R = 628$ Hz. This result provides strong evidence that the orientation of $\delta_3$ is perpendicular to the N,N internuclear vector for both nitrogens of 1 since any deviation of $\beta_2CS$ from $90^\circ$ leads to observable effects on the $\delta_3$ region of the NMR spectrum (see eqs 1–3).

For other regions of the static $^{15}$N NMR spectrum in Figure 4a, AB character is apparent. For instance, it can be seen very clearly in Figure 4a that there are three distinct shoulders at the $\delta_1$ end of the NMR spectrum. As noted earlier, for either an $A_2$ or an AX spin pair there would only be two such shoulders at the $\delta_1$ region. In addition, there is a small peak to high frequency of the two larger peaks in the $\delta_2$ region. Again, this extra peak results from the AB character of this homonuclear spin system. The variations of the $\delta_1$ and $\delta_2$ regions of the $^{15}$N static NMR spectrum as a function of the angle $\gamma_1CS$ ($\gamma_2CS = -\gamma_2CS$) are shown for several theoretical AB NMR spectra in Figure 5 (i.e., $\gamma_1CS = \beta_2CS = 90^\circ$, i = 1, 2). Note that the line shape at $\delta_1$ is independent of the angle $\gamma_2CS$, which is consistent with eq 3 provided that $\beta_2CS = 90^\circ$. Furthermore, the theoretical NMR spectrum where $\gamma_1CS = -\gamma_2CS = 15^\circ$ represents the closest fit to the experimental $^{15}$N static NMR line shape in Figure 4a; the simulation in Figure 4b corresponds to the theoretical $^{15}$N static NMR spectrum which has been convoluted with a Gaussian line broadening to accurately represent the observed NMR line shape in Figure 4a. Thus, the two orientations of the nitrogen chemical shift tensors of 1 which are compatible with $\alpha_1CS = \alpha_2CS = 90^\circ$, $\beta_1CS = \beta_2CS = 90^\circ$, and $\gamma_1CS = -\gamma_2CS = 15^\circ$ are depicted in Figure 6.

The angle $\beta_2CS = 90 \pm 4^\circ$ determined for the nitrogens of 1 indicates that the $\delta_2$ are oriented perpendicular to the N,N dipolar vector (see Figure 1). This conclusion is consistent with previous experimental$^{30,32,43,44}$ and theoretical$^{23,44}$ results on other molecular fragments containing dicoordinate nitrogen involved in double bonds. Earlier $^{15}$N NMR experiments on trans-azobenzene-15N$^{15}$,23 benzylideneaniline,32 and several oximes$^{32,43}$ have indicated that the intermediate principal component, $\delta_{32}$, in these systems is oriented in the approximate direction bisecting the XNY angle (i.e., where a nitrogen lone pair resides). Moreover, previous theoretical shielding calculations on the geometric isomers of several diazenes$^{32,33}$ and on other similar molecules predict an orientation placing $\delta_2$ in the approximate direction of the nitrogen lone pair (i.e., $\gamma_{1CS} = 30^\circ$). Also, the LORG calculations of the nitrogen shielding tensor of cis-diazene suggest that the value for $\gamma_{1CS}$ is $24^\circ$. Thus, we conclude that the orientations of the two $^{15}$N chemical shift tensors indicated in Figure 6a are a reasonable description of the shielding environments in 1. Clearly, the two nitrogen chemical shift tensors of 1 are related by a 2-fold axis; however, as predicted from the $^{15}$N CP/MAS NMR experiments on 1, the two chemical shift tensors are obviously not related by an inversion center.

The fact that we can calculate a static $^{15}$N NMR spectrum of 1 in close agreement with the experimental NMR spectrum (Figure 4) by using a value for the dipolar coupling constant based on the X-ray derived N,N bond length ($R = 628$ Hz) provides two fundamental pieces of information. First, the contributions of anisotopic indirect spin–spin interactions, $\Delta J$, to the $^{15}$N NMR spectrum of 1 are negligible, as the effect of $\Delta J$ is to modify the effective dipolar interaction according to the expression $R_{eff} = R - \Delta J/3$. Given that the absolute value of $J(15N,15N)$ is typically $10-20$ Hz for the N,N fragment, any anisotropy in the indirect spin–spin coupling tensor is expected to be small. Second, the two $^{15}$N nuclei of 1 must be relatively free of librational motions since any motion will average the direct dipolar interaction and lead to smaller values of $R_{eff}$.47,48 This is in contrast to trans-azobenzene which, according to X-ray diffraction experiments, has two different sites for the trans-azobenzene molecule within the lattice, one of which is significantly disordered (site II).17 This disorder was reflected in the reported nitrogen chemical shift parameters of trans-azobenzene as indicated in Table I.23 Thus, the nitrogen chemical shift parameters for site 1 of trans-azobenzene-15N$_2$ will be used for further comparison with the corresponding values determined for the nitrogen nuclei of 1.

Discussion. A comparison between the experimental nitrogen shielding tensors of cis- and trans-azobenzene and the theoretical shielding calculations on the diazenes shows several interesting features. First, the most shielded principal components, $\delta_{31}$, of cis- and trans-azobenzene-15N$_2$ are very similar, 112 and 109 ppm, respectively. This result was reproduced by the theoretical calculations, although the calculated magnitudes are slightly smaller. As well, both experiment and theory predict the orientation of $\delta_{31}$ to be perpendicular to the N,N double bond. Because paramagnetic shielding results from induced electronic circulations in a plane perpendicular to the applied magnetic field,49 this component should be related to $\sigma \rightarrow \pi^*$ type mixing. Furthermore, because the paramagnetic shielding is inversely related to the excitation energy of the field-induced transitions, it is clear that given the large energy separations involved in a transition such as $\sigma \rightarrow \pi^*$, small paramagnetic shielding will result, hence explaining the orientation of $\delta_{31}$. Second, the magnitudes of $\delta_1$ in cis- and trans-azobenzene, 1006 and 1034 ppm, respectively, are very similar whereas they differ by over 400 ppm in the diazene systems. Also, the magnitudes of $\delta_1$ calculated for the diazenes are consistently greater than in the azobenzene system. Given that $\delta_1$ is oriented perpendicular to both the $\pi$ electron manifold and the location of the nitrogen lone pair, it is reasonable to conclude that this component will be correlated with the $\pi \rightarrow \pi^*$ transition in these species, which is low lying in energy due to the nonbonding nature of the nitrogen lone pair electrons. Since $\Delta E_{\pi\pi}$ was reported to be 22 500 cm$^{-1}$ for trans-azobenzene and 22 900 cm$^{-1}$ for cis-azobenzene,21
to accurately calculate nitrogen shielding tensors when the reported that electron correlation effects need to be considered in the experimental results. Furthermore, it has been previously molecular interactions and/or motional averaging will be reflected to a rigid, isolated molecule in the gas phase, whereas intermolecular effects. Our optimized N–N bond lengths (trans, 1.210 Å; cis, 1.212 Å) differ from those used by Schindler on average by ~0.04 Å.23 As the shielding derivative with respect to the N–N bond length in diazene was previously calculated by Chesnut and Wright to be quite large, ~1593 ppm Å⁻¹,54 differences between the two calculations are expected.

Conclusions

Nitrogen-15 CP/MAS and static solid-state NMR spectra of thermally unstable cis-azobenzene-¹⁵N₂ have been examined. The MAS ¹⁵N NMR spectra exhibit spinning rate-dependent line shapes which are analogous to those observed for other homonuclear dipolar coupled spin pairs. In general, such systems consist of two spins which have the same average chemical shift; however, at some orientations in the magnetic field their resonance frequencies differ. In the case of ¹⁵N, the resonance frequencies of the two dipolar coupled nitrogen nuclei will differ for all orientations of the molecule in the magnetic field except when the CNNC fragment is perpendicular to the applied magnetic field. As an aside, it should be emphasized that the observation of a doublet in MAS spectra of “equivalent” spin pairs could be interpreted erroneously as arising from crystallographic non-equivalence if spectra are not carefully examined as a function

**Table I: Experimental and Theoretical ¹⁵N Chemical Shift Parameters for Several Compounds Containing Either a Cis or Trans N,N Double Bond**

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ₁₁</th>
<th>δ₁₂</th>
<th>δ₁₃</th>
<th>δ₂₀</th>
<th>β&lt;sup&gt;CS&lt;/sup&gt;, deg</th>
<th>γ&lt;sup&gt;CS&lt;/sup&gt;, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-azobenzene (I)</td>
<td>1006</td>
<td>469</td>
<td>112</td>
<td>528.8</td>
<td>90</td>
<td>15</td>
</tr>
<tr>
<td>cis-azobenzene (II)</td>
<td>1005</td>
<td>400</td>
<td>109</td>
<td>511.0</td>
<td>83</td>
<td>37</td>
</tr>
<tr>
<td>cis-diazene</td>
<td>1171</td>
<td>665</td>
<td>70</td>
<td>634.6</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td>trans-diazene</td>
<td>1221</td>
<td>556</td>
<td>64</td>
<td>580.3</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td>cis-diazene&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1555</td>
<td>515</td>
<td>57</td>
<td>708.6</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td>trans-diazene&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1421</td>
<td>450</td>
<td>52</td>
<td>641.3</td>
<td>90</td>
<td>40</td>
</tr>
<tr>
<td>cis-dimethylidiazene</td>
<td>1197</td>
<td>651</td>
<td>53</td>
<td>633.7</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td>trans-dimethylidiazene</td>
<td>1597</td>
<td>506</td>
<td>60</td>
<td>721.0</td>
<td>e</td>
<td>e</td>
</tr>
</tbody>
</table>

*Errors in the three principal components are ±2 ppm and ±4° for the three Euler angles. * Values for trans-azobenzene-¹⁵N₂ are from ref 32. *Values taken from ref 23. Converted to chemical shifts according to the expression<sup>25</sup> δ<sub>ii</sub> = 244.6 – α<sub>ii</sub>. *Calculated in this lab. *Not specified precisely; however, ref 23 suggests that β<sup>CS</sup> is 90° and γ<sup>CS</sup> is approximately 30°.

![Figure 5](image-url) Calculated static NMR spectra showing the variation of the AB line shape at the δ₁₁ and δ₁₂ regions of the NMR spectrum as a function of the angle γ<sup>CS</sup> (γ<sup>CS</sup> = 60°, i = 1, 2).

![Figure 6](image-url) Two possible orientations of δ₁₁ and δ₁₂ for ¹⁵N. Note that γ<sup>CS</sup> (15°) corresponds to the angle between δ₁₁ and the N,N internuclear vector; δ₁₃ is perpendicular to the N,N internuclear vector and is not shown.

the small change in δ₁₁ observed experimentally is not surprising. The large differences predicted for δ₁₁ of cis- and trans-diazene are in agreement with theoretical calculations reported by Galasso which showed that ΔEₚ = 0 for cis- and trans-diazene differs by more than 2000 cm⁻¹.51 The fact that the least shielded component in the diazenes is calculated to be greater than that in the respective azobenzenes can, in part, be related to differences in the electronic structure of these two systems. Also, the calculations correspond to a rigid, isolated molecule in the gas phase, whereas intermolecular interactions and/or motional averaging will be reflected in the experimental results. Furthermore, it has been previously reported that electron correlation effects need to be considered to accurately calculate nitrogen shielding tensors when the nitrogen atom is in an unsaturated bonding environment.23,32 Since
of spinning rate. The low-frequency edge of the line shape for a static powder sample of 1 exhibits A2 character while other regions show features characteristic of AB spectra. Analysis of the dipolar chemical shift spectrum yields the principal components of the shift tensor and its orientation in the molecular axis system.

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References and Notes

(51) Ibid. 1952, 86, 243.