J. Am. Chem. Soc. **1989**, *111*, 6082–6086

Dipolar NMR Spectra of the Oxime Moiety in (*E*)-Acetophenone Oxime. Carbon and Nitrogen Chemical Shielding Anisotropies

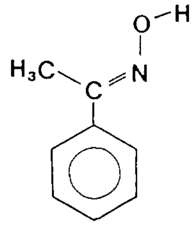
Roderick E. Wasylishen,* Glenn H. Penner, William P. Power, and Ronald D. Curtis

Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3. *Received August 10, 1988*

Abstract: Carbon-13 and nitrogen-15 dipolar NMR spectra of the oxime moiety are analyzed to obtain the principal components of the ^{13}C and ^{15}N chemical shift tensors, the orientation of the principal axis system of the shift tensor, and the carbon–nitrogen bond length. This is the first dipolar NMR investigation of a system containing a localized carbon–nitrogen double bond. Carbon and nitrogen shift anisotropies are approximately 195 and 400 ppm, respectively, with large asymmetry parameters (0.86 and 0.80). The bond length calculated from the ^{13}C, ^{14}N and ^{13}C, ^{15}N dipolar splittings, r_{CN} = 1.28 ± 0.02 Å, is in excellent agreement with the value obtained in recent X-ray diffraction experiments. For the ^{13}C, ^{14}N spin pair, our results indicate that ^{13}C dipolar spectra can be analyzed by making the high-field approximation even though $\nu_L(^{14}N)/\chi(^{14}N) = 3.0$.

NMR studies of solids provide one with the opportunity of measuring several observables that in solution are averaged to their isotropic value.[1-3] For example, one can measure the direct dipolar coupling constant between the two spins of an "isolated" spin pair.[4,5] The magnitude of this coupling is proportional to the average inverse cube of the spatial separation between the two spins, $\langle r^{-3}\rangle$. In isotropic fluids the dipolar coupling averages to zero and spatial information is lost from the NMR line shape. In the solid state one can also obtain information about the orientation dependence of the chemical shift.[1-3,6,7] Measurements on a solid powder sample yield the three principal components of the shift tensor; in isotropic media only the average of the three principal components is measured.

The chemical shielding tensor is a second-order Cartesian tensor, and in general nine independent quantities are required to completely specify this tensor for any given nucleus in a molecule.[8] However, only the symmetric part of the tensor affects the NMR spectrum in first order; hence, only six quantities are required to define the tensor.[2,8-10] In addition to the three principal values (the diagonal elements of the tensor), three angles are required to specify the orientation of the principal axis system of the tensor with respect to the molecular frame. To obtain the three angles, it is often necessary to carry out a tedious single-crystal NMR study, which involves measuring the resonance position in a single crystal as a function of its orientation in the applied magnetic field. One alternative that we use in the present study is to analyze the powder spectrum of a spin $^1/_2$ nucleus that is dipolar coupled to a neighboring spin. Such an analysis is capable of providing the dipolar coupling constant associated with the spin pair, the three principal components of the shielding tensor, and two of the angles required to specify the orientation of the shielding tensor.[11-27] The particular spin pairs examined in the present study are the $^{13}C{=}^{15}N$ and $^{13}C{=}^{14}N$ of (*E*)-acetophenone oxime (**1**). As well, ^{15}N chemical shielding anisotropies are reported for 4-methoxyacetophenone oxime (**2**) and 2,4,6-trimethoxyacetophenone oxime (**3**). Our results provide the first experimental measurement of the ^{13}C and ^{15}N chemical shielding anisotropies of the oxime moiety.



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Theory

For an isolated pair of unlike spins, AX, that are directly bonded, such as ^{13}C and ^{14}N or ^{13}C and ^{15}N, one has to consider the Zeeman, chemical shielding, and direct dipolar interactions. The resonance frequency for the A spins (spin $^1/_2$) depends on the orientation of the principal-axis system of the A-spin chemical

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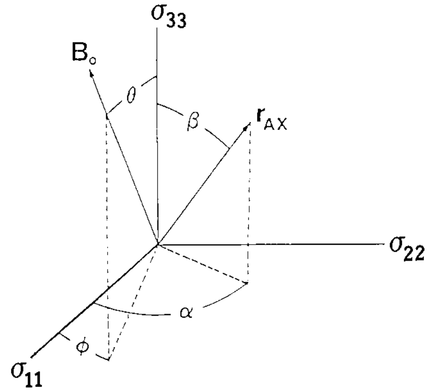

Figure 1. Angles α and β define the orientation of the dipolar vector, $\mathbf{r}_{AX}$, in the principal-axis system of the chemical shielding tensor; θ and ϕ define the orientation of the molecule in the magnetic field, B_0.

shielding tensor in the laboratory frame, defined by θ and ϕ as indicated in Figure 1 and by the Euler angles α and β required to orient the dipolar vector in the principal-axis system of the chemical shielding tensor. Specifically the resonance frequency of spin A is given by eq 1[12,16,18]

$$\nu_m(\theta,\phi) = \nu_L - \nu_{CS} - m\nu_D \qquad (1)$$

where

$$\nu_L = \gamma_A B_0/2\pi \qquad (1a)$$

$$\nu_{CS} = (\gamma_A B_0/2\pi)[\sigma_{11}\sin^2\theta\cos^2\phi + \sigma_{22}\sin^2\theta\sin^2\phi + \sigma_{33}\cos^2\theta] \qquad (1b)$$

$$\nu_D = R[1 - 3(\sin\beta\sin\theta\cos(\phi-\alpha) + \cos\beta\cos\theta)^2] \qquad (1c)$$

$$R = \frac{\gamma_A\gamma_X\hbar}{2\pi}\,\frac{\mu_0}{4\pi}\langle r_{AX}^{-3}\rangle$$

In eq 1 the allowed values of the quantum number m depend upon the spin of nucleus X, for $I = {}^1/_2$, $m = \pm{}^1/_2$, and for $I = 1$, m may assume values of +1, 0, or −1. σ_{11}, σ_{22}, and σ_{33} are the principal components of the chemical shielding tensor with the convention $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$, with θ being the polar angle between σ_{33} and B_0, and ϕ the azimuthal angle between σ_{11} and the projection of B_0 onto the σ_{11}–σ_{22} plane. In practice NMR spectroscopists generally measure chemical shifts, the differences in shielding constants between the nuclei of interest and a reference nucleus, as opposed to chemical shielding constants. In this study we will report the principal components of the chemical shift tensor using the convention $\delta_{11} > \delta_{22} > \delta_{33}$ (*note* that δ_{33} corresponds to the most shielded component of the chemical shift tensor). The chemical shielding anisotropy will simply be defined as $\delta_{11} - \delta_{33}$; this provides a direct measure of the maximum width of the spectrum in the absence of dipolar coupling.[23] More elegant definitions can be found elsewhere.[2,3] The asymmetry parameter, η, will be defined following the convention of Haeberlen[2] and Spiess;[3] it is restricted to values between 0 (axial symmetry) and 1. All other symbols have their usual meaning.

In writing eq 1, we have assumed that the axis of quantization for all nuclei is along the applied magnetic field, B_0. In typical contemporary NMR systems, B_0 is 1.5–15 T, and this assumption, known as the high-field approximation, is valid provided that both the A and X spins are spin $^1/_2$ nuclei. If the X nucleus is a quadrupolar nucleus, the high-field approximation will be valid only if the Larmor frequency of the quadrupolar nucleus, $\nu_L(X)$, is much greater than the nuclear quadrupolar coupling constant, $\chi(X)$. In systems where the magnitude of $\chi(X)$ approaches $\nu_L(X)$, the high-field approximation breaks down and eq 1 is not strictly valid. For the ^{13}C, ^{14}N spin pair of the oxime moiety one can obtain reasonable estimates of the angles α and β using eq 1 provided $B_0 \geq 4.70$ T (vide infra).

Finally note that the angles α and β are a property of the molecule under consideration and that for any given molecule the experimentalist cannot control these angles.

The powder spectrum was calculated by integration over all orientations in 1° steps of θ and ϕ and by the summation over all the allowed transitions. The A spins will have $2I + 1$ transitions, where I is the spin of X:

$$I(\nu) = \sum_{m=-I}^{+I}\int_0^{\pi/2}\int_0^{2\pi} g(\nu_m(\theta,\phi) - \nu)\sin\theta\,d\theta\,d\phi$$

The resulting theoretical spectrum was convoluted with a Gaussian function, $g(\nu)$, introducing some line broadening to better fit the experimental spectrum.

Our program can include the effects of indirect spin–spin coupling, J, and anisotropy in J;[11a] however, this was ignored as such effects are probably negligible for this spin pair in oximes since $|J_{iso}| \leq 5$ Hz.[28-30]

Experimental Section

The acetophenone oximes were prepared by reaction of the acetophenones with hydroxylamine hydrochloride.[29] Acetophenone-$^{13}C_\alpha$ (99%) and hydroxylamine hydrochloride-^{15}N (99%) were obtained from MSD Isotopes. Compound **1** was 99% enriched in both ^{13}C and ^{15}N, whereas **2** and **3** were 30% enriched in ^{15}N.

Carbon-13 and nitrogen-15 NMR spectra were obtained at 50.323 and 20.300 MHz, respectively, by using a Bruker MSL-200 spectrometer (B_0 = 4.70 T). Powder samples (0.3 g) were packed into aluminum oxide rotors, and all spectra were recorded at 21 °C with high-powered proton decoupling and cross polarization using the Hartmann–Hahn match. The 90° pulse widths were 4.8 μs for ^{13}C experiments and were 5.5 μs for ^{15}N experiments. All spectra were acquired by using the FLIPBACK pulse sequence[31] with delay times of 60 s for **1** and 5 and 10 s for **2** and **3**, respectively. Contact times were optimized and were typically 5 ms.

Static spectra had acquisition times of 50–102 ms, and sensitivity enhancements corresponding to 150–400-Hz line broadening were applied before Fourier transformation. In some cases base-line corrections using a spline interpolation were employed to compensate for any rolling base line.

Magic-angle-spinning spectra were obtained with acquisition times of 205 ms. The FIDs were zero filled to twice their original size, and the signal-to-noise was enhanced with 5–10 Hz line broadening before Fourier transformation.

Carbon-13 chemical shifts were referenced with respect to external adamantane, which has shifts of 38.56 ppm (CH_2) and 29.50 ppm (CH) with respect to TMS.[32] Nitrogen-15 chemical shifts were referenced with respect to the ammonium-^{15}N signal of external ammonium nitrate, which has a shift of 23.8 ppm with respect to liquid ammonia at 20 °C.

Spectral simulations were performed as described in the previous section using the programs DIPCSA and DIPSPIN1, which were written in this laboratory. Computations were performed on both a VAX 8800 and a Perkin-Elmer 3230 computer.

Results and Discussion

1. Carbon-13 NMR Spectra. The ^{13}C NMR spectrum of a powdered sample of solid ^{13}C-enriched (*E*)-acetophenone oxime (oxime carbon) is shown in Figure 2a. Since the natural abundance of ^{14}N ($I = 1$) is 99.635%, the spectrum arises almost exclusively from the $^{13}C{=}^{14}N$ spin pair. One important feature of this spin pair is that the spin $^1/_2$ powder pattern will consist of a component, the $m(^{14}N) = 0$, which is unperturbed by the ^{13}C, ^{14}N dipolar interaction (see eq 1). For the spin $^1/_2$, spin 1 pair the integrated intensity of this component is one-third of the total intensity of the powder pattern, and the discontinuity and shoulders occur at δ_{22} and at δ_{11} and δ_{33}, respectively, as indicated in Figure 2. Knowledge of these three variables greatly facilitates the determination of the other three variables: α, β, and r_{CN}. Initial simulations of the spectrum in Figure 2a were carried out using the C,N bond length, 1.278 Å, recently determined in an X-ray diffraction experiment.[33] After optimizing the angles α and β by a trial and error procedure, attempts were made to optimize

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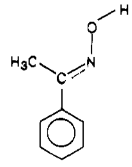
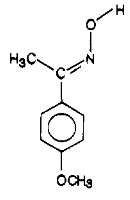
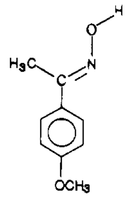
Table I. Direct Dipolar Coupling Constants, Principal Components of the Chemical Shift[a] Tensor, and the Angles α and β

compd	nucleus	R,[b] Hz	δ_{11}, ppm	δ_{22}, ppm	δ_{33}, ppm	δ_{iso},[c] ppm	α, deg	β, deg	$\Delta\sigma$	η
	$^{13}C{=}^{14}\mathrm{N}$	1041	259	150	62.5	157	80	80	196.5	0.86
	$^{13}C{=}^{15}\mathrm{N}$	1460	259	150	62.5	157	80	80	196.5	0.86
	$^{15}N{=}^{13}\mathrm{C}$	1460	560	328	160	349 (347.2, 344.9)	52	90	400	0.80
	^{15}N		555	323	158	345 (344.5, 342.6, and 340.9)			397	0.79
	^{15}N		559	323	160	347 (344.7)			399	0.77

[a] The principal components of the chemical shielding tensor can be obtained from the components of the chemical shift tensor as follows:[53,54] $\sigma_{ii}(^{13}\mathrm{C}) = 186.4 - \delta_{ii}(^{13}\mathrm{C})$ and $\sigma_{ii}(^{15}\mathrm{N}) = 244.6 - \delta_{ii}(^{15}\mathrm{N})$. These values will be uncorrected for bulk susceptibility effects. [b] The R values correspond to $r_{\mathrm{CN}} = 1.28 \pm 0.02$ Å. [c] Values in parentheses were obtained from CP/MAS experiments.

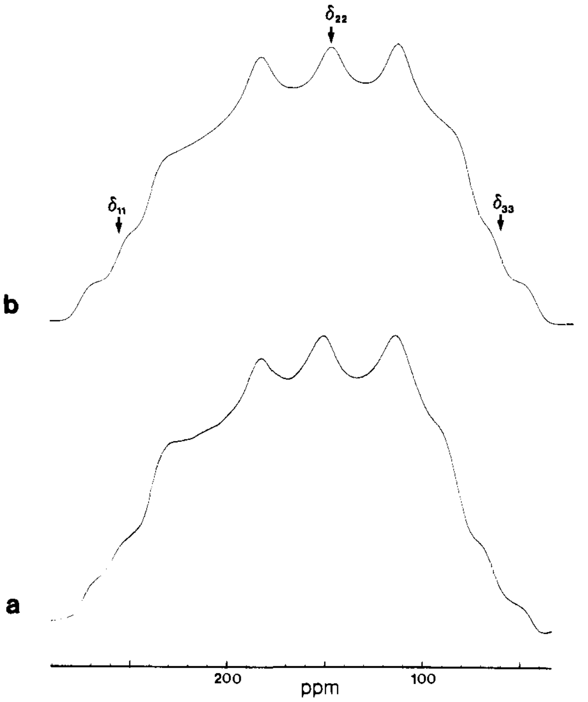


Figure 2. Observed (a) and calculated (b) carbon-13 NMR spectrum of a solid powder sample of (E)-acetophenone oxime. The oxime carbon is ^{13}C enriched; thus the spectrum results mainly from the $^{13}C{=}^{14}\mathrm{N}$ carbon.

r_{CN}. Note that the ^{13}C NMR dipolar spectrum of (E)-acetophenone oxime ($^{13}\mathrm{C}{=}^{15}\mathrm{N}$, vide infra) was also used to help optimize all the parameters. Also, the ^{15}N NMR spectrum of the latter compound was used to obtain r_{CN}. On the basis of numerous simulations we estimate $\alpha = 80 \pm 4°$, $\beta = 80 \pm 4°$, and $r_{\mathrm{CN}} = 1.28 \pm 0.02$ Å. The simulated ^{13}C NMR dipolar spectrum of the ^{13}C, ^{14}N spin pair is shown in Figure 2b. Errors in the components of the ^{13}C chemical shift tensor (Table I) are ±2 ppm.

The ^{13}C NMR spectrum of the ^{13}C (99%) and ^{15}N (99%) doubly isotropically labeled sample of (E)-acetophenone oxime ($^{13}\mathrm{C}{=}^{15}\mathrm{N}$) is shown in Figure 3a. The simulation, Figure 3b, was carried out using the same parameters as given for the $^{13}\mathrm{C}{=}^{14}\mathrm{N}$ spin pair; however, note that the dipolar coupling is increased by a factor of 1.4027 ($\gamma(^{15}\mathrm{N})/\gamma(^{14}\mathrm{N})$) and that the spin of ^{15}N is $^1/_2$; thus the ^{13}C spectrum consists of two subspectra instead of three.

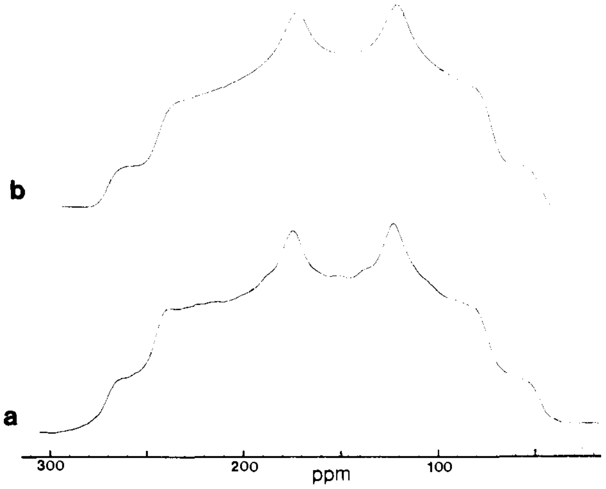


Figure 3. Observed (a) and calculated (b) carbon-13 NMR spectrum of a solid powder sample of (E)-acetophenone oxime where both the oxime carbon and nitrogen are ^{13}C and ^{15}N enriched (99%), respectively.

The carbon-13 chemical shielding anisotropy observed for the oxime group is very similar to that observed for carbons of ketones (typically 195 ppm) or olefinic carbons (typically 190 ppm).[6,7] However, the asymmetry parameter observed for the oxime carbon resembles that of an olefinic carbon much more closely than that of a ketone or aldehyde carbon.[6,7]

It is also interesting to compare the orientation that we find for the ^{13}C shift tensor with those reported for ketones[6,34,35] and olefins.[13,36] Invariably the most shielded element of the shift tensor, δ_{33}, is always perpendicular or very close to being per-

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pendicular to the $R_1R_2C{=}O$ plane or the $R_1R_2C{=}CR_3R_4$ plane. This observation is in accord with qualitative arguments[13,34,37] and theoretical calculations using semiempirical theories[38] and ab initio methods.[39-43] On the basis of the above-mentioned previous work on ketones and olefins, one would expect β to be close to 90° in (*E*)-acetophenone oxime, and indeed this is the case. The oxime moiety is not coplanar with the benzene ring but is tilted out of the plane of the benzene ring by 25° and 33°, respectively, in the two crystallographically independent molecules found in the triclinic unit cell.[33] This tilting accounts for the deviation of β from 90° (i.e., β = 80°) in **1**.

The orientation of the δ_{11} and δ_{22} axes in ketones and olefins is sensitive to the local structure; however, δ_{22} is usually close to being parallel to the C=O or C=C bonding axis.[6,36] In ethylene δ_{22} lies along the carbon–carbon bonding axis;[13] however, in acetophenone, δ_{22} deviates by 21° from the C=O axis.[35] A similar deviation of δ_{22} from the C=O axis is also observed in acetaldehyde.[13] For (*E*)-acetophenone oxime the least shielded component of the shift tensor, δ_{11}, is approximately perpendicular to the C=N bond axis while δ_{22} is close to being collinear with the C=N bond axis. Again these observations for the C=N moiety closely parallel those for the C=C and C=O fragments.

As already mentioned, there are two nonequivalent molecules in the unit cell of (*E*)-acetophenone oxime.[33] The *only* difference between these two molecules apparent in the recent X-ray diffraction study was the difference in the torsional angle between the benzene ring plane and the oxime moiety. All other bond lengths and bond angles were the same within experimental error. In magic-angle-spinning ^{13}C NMR experiments we were unable to resolve separate ^{13}C resonances for the two nonequivalent molecules; thus our results support the previous conclusion that these two molecules have very similar structures. The excellent agreement between the observed and simulated powder spectrum (Figure 3) indicates that the principal components of the shielding tensors for the two sites are the same within experimental error.

As already mentioned, by using eq 1 to simulate the ^{13}C NMR spectrum for the ^{13}C, ^{14}N spin pair, one is in effect making the high-field approximation.[44] That is, the Zeeman interaction for the quadrupolar ^{14}N nucleus is much greater than the quadrupolar interaction. At 4.7 T the ^{14}N NMR frequency, $\nu_L(^{14}N)$, is approximately 14.45 MHz and the ^{14}N nuclear quadrupole coupling constant, $\chi(^{14}N)$, 4.87 MHz; therefore, ν_L/χ = 3.0. The breakdown of the high-field approximation causes an orientation-dependent mixing of the normal ^{14}N Zeeman eigenfunctions, $|I,m\rangle$, and in principle, one should use these new "mixed" eigenfunctions to calculate the dipolar splitting of ^{13}C by ^{14}N. Although this is a straightforward problem for the case of axial symmetry where the largest component of the electric field gradient (efg) tensor is along the dipolar axis,[44,45] it is difficult if the efg tensor is not axially symmetric as in the case of **1** where η = 0.78.[46] A further problem with the oximes is that the orientation of the efg tensor is unknown.[46] Although the main features of the ^{13}C NMR spectrum of the ^{13}C, ^{14}N spin pair (Figure 2a) are accounted for by making the high-field approximation (Figure 2b) close examination of the spectra reveal some discrepancies. The most noticeable is the splitting of the δ_{22} discontinuity. Using eq 1, one predicts the splitting at δ_{22} to be equal, i.e., $|\nu_{+1}(90°,90°) - \nu_0(90°,90°)| = |\nu_0(90°,90°) - \nu_{-1}(90°,90°)|$ (see Figure 2b). Experimentally these splittings differ by approximately 200 Hz (about 10%). We attribute this difference in splitting as arising from the breakdown of the high-field approximation. We would like to point out that in spite of this breakdown one can still obtain reliable estimates of the angles α and β if an accurate value of the bond length is available. If we had only the ^{13}C NMR spectrum of the ^{13}C, ^{14}N spin pair of **1**, the estimates of these angles would be α = 76 ± 7° and β = 81 ± 5°. Errors in the principal components of the shift tensor would be less than ±2 ppm. It is of interest to mention that Doverspike et al.[47] obtained reasonable simulations of the ^{13}C dipolar spectrum of solid solutions of KCN–KBr at an applied magnetic field where the ratio of $\nu_L(^{14}N)/\chi(^{14}N)$ was only 2.

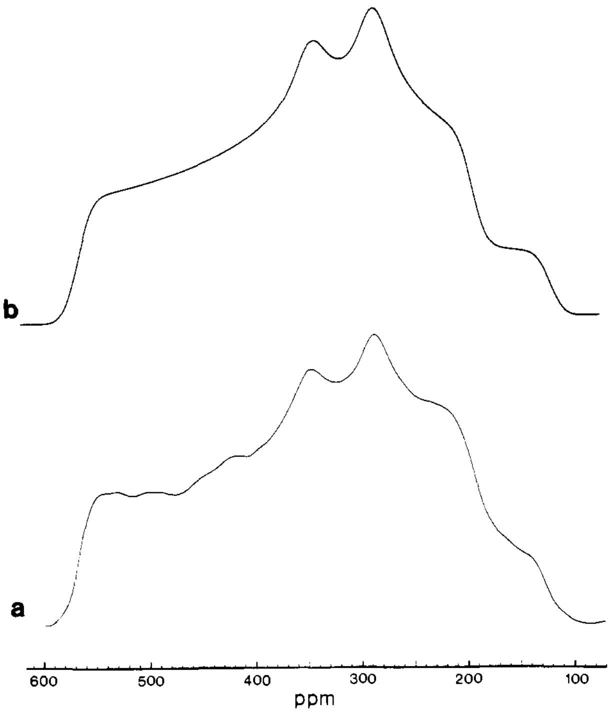

Figure 4. Observed (a) and calculated (b) nitrogen-15 NMR spectrum of a solid powder sample of (*E*)-acetophenone oxime where both the oxime carbon and nitrogen are ^{13}C and ^{15}N enriched (99%), respectively.

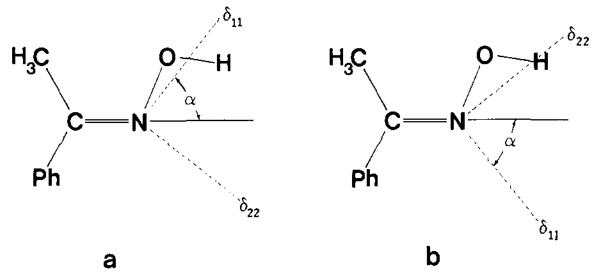

Figure 5. Possible orientations of the principal axis system for the ^{15}N shielding tensor in **1**. δ_{33} is perpendicular to the CNO plane. (a) Assuming the least shielded component, δ_{11} is approximately along the N–O bond direction; deviation 15°. (b) Assuming δ_{22} is approximately along the N–O bond direction; deviation 29°.

2. Nitrogen-15 NMR Spectra. The ^{15}N NMR spectrum of (*E*)-acetophenone oxime (^{15}N,^{13}C) is shown in Figure 4 together with the simulated spectrum. The parameters required to simulate the observed spectrum are given in Table I, as are the principal components of the ^{15}N chemical shift tensor of 4-methoxyacetophenone oxime and 2,4,6-trimethoxyacetophenone oxime. The estimated error in the shielding parameters are ±2 ppm for **1** and ±3 ppm for **2** and **3**. The errors in the angles α and β are estimated to be ±2°.

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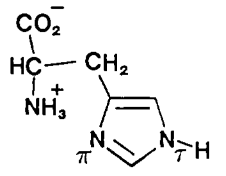
All three oximes, **1–3**, have essentially identical ^{15}N shielding parameters with $\Delta\sigma = 400$ ppm and $\eta = 0.8$. There are very few examples where ^{15}N shielding anisotropies have been measured,[1,3,48] so it is difficult to make many comparisons with structurally related compounds. The only compound that we are aware of with a "localized" C,N double bond where the principal components of the ^{15}N shielding tensor have been measured is the C_2N_π fragment of neutral histidine (**4**).[49] By analysis of the intensities of the ^{15}N spinning sidebands using the Herzfeld-Berger method,[50] a shielding anisotropy of 380 ppm was determined for the N_π nitrogen. The asymmetry parameter, η, was 0.45; however, the orientation of the shielding tensor is not known. Early calculations[40] on imidazole indicate δ_{33} is perpendicular to the ring plane; δ_{22} is in the ring plane and bisects the CNC bond angle (i.e., it lies along the orientation of the nitrogen "lone pair"). The orientation of the principal axis system of the shielding tensor determined in this theoretical study are in qualitative agreement with the one determined in recent calculations of Schindler which uses an individual gauge for localized molecular orbital (IGLO) method.[51,52] In diazenes (RN=NR), the most shielded principal component is perpendicular to the molecular plane while the least shielded component is approximately along the N–R bond (R= H,CH$_3$).[51] Our simulations on the oxime moiety of **1** indicate δ_{33} is perpendicular to the CNO plane. On the basis of the calculations, one would expect δ_{11} to be close to the N–O bond. Our spectral simulations yield $\alpha = 52°$; thus we assign the orientation of δ_{11} and δ_{22} as shown in Figure 5a. A second possible orientation of the ^{15}N shift tensor which would be consistent with the observed spectrum is indicated in Figure 5b. The latter assignment would require δ_{22} to be directed in the same general direction as the N–O bond; however, on the basis of the available theoretical calculations on imidazole[40,52] and diazene,[51] δ_{11} probably lies along the N–O bond direction in oximes.



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The fact that the torsional angles for the two nonequivalent molecules of **1** are slightly different is apparent in the CP/MAS ^{15}N spectrum where two equally intense lines separated by 2.3 ppm are observed. Analogous experiments indicate that at least three nonequivalent molecules are present in the unit cell of **2** while only a single type of molecule is present in the unit cell of **3**. The static ^{15}N NMR spectra of **1** and **2** show no evidence for two or more nonequivalent shielding components for the nonequivalent sites; therefore, we have assumed that they do not differ appreciably. For **1** this assumption is supported by the good fit of the simulated spectrum to the experimental spectrum (Figure 4), the similarity in the nitrogen-15 shielding parameters observed for the oximes **1** and **3**, and the known structure of **1**.

The very similar ^{15}N shift tensor components for **1**, **2**, and **3** indicate the nitrogen shielding in acetophenone oximes is rather insensitive to substituent effects on the benzene ring as well as the orientation of the oxime moiety with respect to the benzene ring.

Conclusion

Carbon-13 and nitrogen-15 dipolar spectra of (*E*)-acetophenone oxime provide a bond length, r_{CN}, which is in excellent agreement with a recent X-ray diffraction result. As well, the spectra provide information on the magnitude and orientation of the ^{13}C and ^{15}N shielding tensors. It is hoped that these experimental results will stimulate further theoretical calculations of shielding tensors in systems containing carbon–nitrogen "double" bonds.

Finally, our results indicate that in favorable cases one can obtain useful information from ^{13}C dipolar spectra involving the ^{13}C, ^{14}N spin pair even though the high-field approximation is not completely satisfied (e.g., $\nu_L/\chi = 3$). This is an important result because ^{15}N enrichment is generally expensive and often impractical.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support in the form of equipment, operating grants (R.E.W.), and postgraduate scholarships (W.P.P. and R.D.C.). G.H.P. acknowledges Dalhousie University for the Killam postdoctoral fellowship. R.D.C. and W.P.P. are the holders of Killam postgraduate and Sumner fellowships. We thank Dr. M. Schindler for a preprint of ref 52, Brian Millier for his assistance in maintaining the NMR spectrometer, and Annette Salsman for her help in preparing the manuscript.

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