

Anisotropic Chemical Shifts and Spin Rotation Constants of ^{15}N from Liquid and Solid State NMR: Nitrobenzene

D. SCHWEITZER AND H. W. SPIESS

Max Planck-Institute, Jahn-Strasse 29, 6900 Heidelberg, West Germany

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The study of the ^{15}N spin-lattice relaxation time T_1 in nitrobenzene at 14 and 32 MHz from -10 to 60°C showed that at 32 MHz relaxation due to anisotropic chemical shift is predominant. At low frequencies, the relaxation is caused mainly by spin rotation and at low temperature also by intermolecular dipole-dipole interaction. From the powder spectrum in solid nitrobenzene, the principal elements of the shielding tensor $\hat{\sigma}$ were obtained: $\sigma_{xx} = -273 \pm 10$ ppm, $\sigma_{yy} = +94 \pm 10$ ppm, and $\sigma_{zz} = +156 \pm 10$ ppm relative to liquid nitrobenzene, $\Delta\sigma = \sigma_{xx} - \frac{1}{2}(\sigma_{yy} + \sigma_{zz}) = -398 \pm 20$ ppm. From the almost axially symmetric $\hat{\sigma}$ -tensor, the spin rotation constants were calculated: $C_{\parallel} = 11.4 \pm 1.5$ kHz and $C_{\perp} = 1.35 \pm 0.5$ kHz, where C_{\parallel} is the component parallel to the twofold axis of the molecule. These values for $\Delta\sigma$ and the spin rotation constants are in excellent agreement with those obtained by analysis of the relaxation data. A comparison of anisotropic chemical shifts and spin rotation constants for ^{15}N and ^{13}C in isoelectronic compounds is given.

INTRODUCTION

In a recent NMR study (*1*) on pyridine, we were able to show that detailed information can be obtained by combining ^{15}N and ^{13}C measurements in the liquid and solid state. We found that relaxation due to anisotropic chemical shift (ACS) is an important relaxation mechanism for ^{15}N in pyridine. This is mainly due to the large value of the anisotropy of the chemical shift, $\Delta\sigma = 672 \pm 20$ ppm (*1*). In liquid azoxybenzene, Lippmaa *et al.* (*2*) observed a frequency dependence of the relaxation rate characteristic for relaxation through ACS even between 4 and 6 MHz and deduced a value of $\Delta\sigma = 570 \pm 100$ ppm. In the linear molecule NNO, $\Delta\sigma$ has recently been determined in a liquid crystal: $\Delta\sigma = 512 \pm 10$ ppm for the central ^{15}N and $\Delta\sigma = 368 \pm 10$ ppm for the end ^{15}N (*3*). It is interesting to compare the general features of ^{15}N relaxation with the similar findings for ^{13}C , where much experimental material has been collected in the last years. For ^{13}C , relaxation due to ACS is not an important mechanism except in a few cases (*4-7*). In view of the large values for $\Delta\sigma$ quoted above, one expects that relaxation through ACS might be a *generally* more important mechanism for ^{15}N .

We therefore report here frequency-dependent relaxation studies for ^{15}N in nitrobenzene at 14 and 32 MHz. Measurements of T_1 for ^{15}N in nitrobenzene at 4 MHz have been reported by Lippmaa *et al.* (*2*) with which our data can be compared. Their studies were carried out in a temperature range of $10-200^\circ\text{C}$, showing that relaxation due to spin rotation interaction (SRI) is the most important relaxation process under these conditions. Only at temperatures below 30°C does dipole-dipole interaction (DDI)

start to play a certain role, whereby the *intermolecular* DDI is more important than the *intramolecular* one.

The parameters for the spin rotational and the frequency-dependent relaxation rates, the spin rotation constants, and the elements of the shielding tensor $\hat{\sigma}$ can be determined independently from solid state measurements. This greatly simplifies the analysis (1). In the case of pyridine, we have already demonstrated that ^{15}N anisotropic chemical shifts can be determined in the solid even without proton decoupling if one works in high magnetic fields such as 75 kG. Therefore we report here the ^{15}N powder spectrum of nitrobenzene at 32 MHz.

EXPERIMENTAL

^{15}N -Nitrobenzene (95% isotopically enriched) was obtained from Isocommerz G.m.b.H., Leipzig, DDR. The sample was degassed by several freeze-pump-thaw cycles. NMR measurements (at 14 and 32 MHz for ^{15}N in the liquid, at 32 MHz and -103°C for solid nitrobenzene, and at 61 MHz for ^{13}C in the liquid) were carried out as described earlier (1).

RESULTS AND DISCUSSION

In Fig. 1 the experimental ^{15}N and ^{13}C spin-lattice relaxation rates for nitrobenzene are plotted vs temperature. Besides the data at 14 and 32 MHz for ^{15}N , values at 4 MHz, reported by Lippmaa *et al.* (2), as well as an extrapolated curve for $\nu = 0$ MHz, are also shown. This curve was obtained from the plot of the relaxation rates vs the square of the frequency, as shown in Fig. 2. The values at 4 MHz given by Lippmaa *et al.* (2) for temperatures above 10°C are in excellent agreement with the extrapolation from the higher frequencies.

At 32 MHz over the complete temperature range from -10 up to $+60^\circ\text{C}$, a large part of the total relaxation rate is due to ACS, which is predominant at low temperatures and at $+60^\circ\text{C}$ is still about half of the total rate. At temperatures below 30°C , relaxation due to DDI plays a certain role as can be seen from the relaxation rate minimum of the curve for $\nu = 0$ MHz at 0°C (see Fig. 1). For calculating an intramolecular dipolar rate ($1/T_1^{\text{DD}}$ (intra)), we have to know the correlation time for angular reorientation τ_c , which we get from the ^{13}C relaxation rates at 61 MHz for the ring carbons (Fig. 1). It has been shown (7, 8) that the ^{13}C relaxation rates for ring carbons at low temperatures are solely determined by intramolecular DDI between the carbon and the directly bound protons to a good approximation. The intramolecular dipolar relaxation rate is given by (9) [see also (8)]:

$$1/T_1^{\text{DD}}(^{13}\text{C}) = \frac{4}{3} \cdot \gamma_{^{13}\text{C}}^2 \cdot \gamma_{\text{H}}^2 \cdot \hbar^2 \cdot S(S+1) \cdot r_{\text{C-H}}^{-6} \cdot \tau_c \quad [1]$$

with $r_{\text{C-H}} = 1.085 \text{ \AA}$ and S the proton spin (extreme narrowing case).

The measured ^{13}C relaxation rates (Fig. 1) are an average over all ring carbons. Because of the relatively poor homogeneity (≈ 2 ppm) of our superconducting magnet, we are not able to distinguish between the different carbons. Levy *et al.* (6), however, have shown that the relaxation times of the *ortho* and *meta* carbons are the same and that the relaxation time of the *para* carbon differs by only 30% from this value. The carbon which is bound to the NO_2 group has a relaxation time about ten times as long. This means that the NMR signal is strongly dominated by the other five ^{13}C nuclei. The relevant directions for the DDI of these carbons as well as for the intramolecular

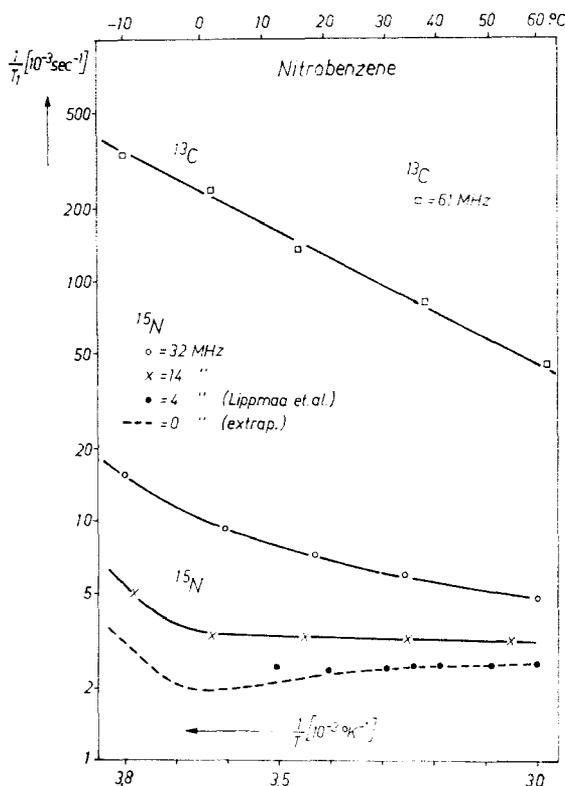


FIG. 1. Relaxation rates of ^{15}N and ^{13}C in pyridine. The dashed line was extrapolated from the frequency dependence of the ^{15}N relaxation rates (see text). Dots are experimental values taken from (2).

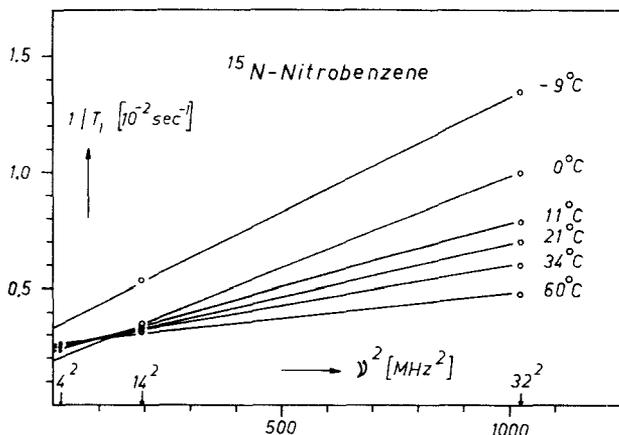


FIG. 2. Frequency dependence of experimental ^{15}N relaxation rates in nitrobenzene. Dots are experimental values taken from (2).

DDI of the nitrogen all lie in the molecular plane. Therefore the average correlation times determined from the ^{13}C measurements can also be used for ^{15}N in a first approximation. Such correlation times τ_c are given in Table 1 for some temperatures. With these

TABLE 1
CORRELATION TIMES τ_C AND SEPARATED ^{15}N RELAXATION RATES IN LIQUID NITROBENZENE

$T(^{\circ}\text{C})$	τ_C (sec)	$1/T_1^{\text{DD}}(\text{intra})(\text{sec}^{-1})$	$1/T_1^{\text{CS}}(32 \text{ MHz})(\text{sec}^{-1})$	$1/T_1^{\text{SR}}(\text{sec}^{-1})$	$(1/T_1^{\text{CS}} \cdot 1/T_1^{\text{SR}})^{1/2}(\text{sec}^{-1})$
60	$2.03 \cdot 10^{-12}$	$6.00 \cdot 10^{-5}$	$2.2 \cdot 10^{-3}$	$2.55 \cdot 10^{-3}$	$2.40 \cdot 10^{-3}$
34	$3.80 \cdot 10^{-12}$	$1.12 \cdot 10^{-4}$	$3.5 \cdot 10^{-3}$	$2.10 \cdot 10^{-3}$	$2.71 \cdot 10^{-3}$
18	$5.97 \cdot 10^{-12}$	$1.76 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$	$1.60 \cdot 10^{-3}$	$2.77 \cdot 10^{-3}$
2	$1.08 \cdot 10^{-11}$	$3.19 \cdot 10^{-4}$	$7.9 \cdot 10^{-3}$	$1.05 \cdot 10^{-3}$	$2.88 \cdot 10^{-3}$
-10	$1.51 \cdot 10^{-11}$	$4.46 \cdot 10^{-4}$	$1.16 \cdot 10^{-2}$	$7.0 \cdot 10^{-4}$	$2.84 \cdot 10^{-3}$

values for τ_C , we get intramolecular dipole-dipole relaxation rates [$1/T_1^{\text{DD}}(\text{intra})$] for ^{15}N , if, in Eq. [1], we replace $\gamma_{^{13}\text{C}}$ by $\gamma_{^{15}\text{N}}$ and $r_{\text{C-H}}$ by $r_{\text{N-H}} = 2.71 \text{ \AA}$, the distance between the nitrogen and the nearest-neighbor proton. Moreover, there are two equivalent nearest-neighbor protons. Therefore, we have to multiply the relaxation rate by a factor of two. Because of the r^{-6} distance dependence, we can neglect the other protons. Table 1 shows the calculated rates $1/T_1^{\text{DD}}(\text{intra})$. From the comparison with the relaxation rate for $\nu = 0 \text{ MHz}$ (Fig. 1), we find that intramolecular DD relaxation gives only a minor contribution to this rate at all temperatures in agreement with Lippmaa *et al.* (2).

Relaxation rates due to ACS ($1/T_1^{\text{CS}}$) for 32 MHz are also given in Table 1, and it can be seen that for this frequency, $1/T_1^{\text{CS}}$ is at least 25 times as large as $1/T_1^{\text{DD}}(\text{intra})$ over the entire temperature range. The rate $1/T_1^{\text{CS}}$ contains information about the anisotropic chemical shift $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$. For $\Delta\sigma$, we have the expression (9) (see also (1) for further explanation):

$$\Delta\sigma = [15/(2 \cdot T_1^{\text{CS}} \cdot \omega^2 \cdot \tau_C^{\text{eff}})]^{1/2}. \quad [2]$$

Here, ω is the Larmor frequency and τ_C^{eff} the effective correlation time for angular reorientation. For simplicity, we treat nitrobenzene as a symmetric top in the following. This has some justification, because the moment of inertia tensor is almost axial with respect to the twofold axis of the molecule (see also below). Then τ_C^{eff} is given by (10-12):

$$\tau_C^{\text{eff}} = \tau_{C_{\perp}} \{1 - (3(\rho - 1)/(5 + \rho)) \sin^2 \beta \cdot (1 - (3(\rho - 1)/(2(2\rho + 1))) \cdot \sin^2 \beta)\}, \quad [3]$$

where ρ is the ratio of the correlation times of reorientation perpendicular and parallel to the symmetry axis ($\rho = \tau_{C_{\perp}}/\tau_{C_{\parallel}}$) and β is the angle between the molecular vector of interest and the symmetry axis of the rotational diffusion tensor.

If we tentatively use the effective correlation times τ_C found from the dipolar rate of the ^{13}C measurements (Table 1), we get from Eq. [2] a value $|\Delta\sigma| = 399 \text{ ppm}$. The value of $|\Delta\sigma|$ can be calculated separately for each temperature. The value given above is an average over all temperatures with an accuracy of about $\pm 45 \text{ ppm}$.

We have also measured $\Delta\sigma$ directly from the frozen solid. Figure 3 shows the powder pattern of the ^{15}N in nitrobenzene, typical for a nearly axially symmetric chemical shift tensor. Again as in the case of pyridine (1), the frequency splitting due to ACS far exceeds the dipolar line broadening. The spectrum was taken at -103°C and the central frequency was 31.9859 MHz. From a computer fit, we got $\sigma_{xx} = -273 \pm 10 \text{ ppm}$,

$\sigma_{yy} = 94 \pm 10$ ppm, $\sigma_{zz} = 156 \pm 10$ ppm, and $\sigma_{AV}(\text{solid}) = +7.7$ ppm relative to liquid nitrobenzene¹ (dipolar linewidth ≈ 2.5 kHz). If we define

$$\Delta\sigma = \sigma_{ii} - \frac{1}{2}(\sigma_{jj} + \sigma_{kk}) \quad [4]$$

with $\sigma_{ii} = \sigma_{\parallel}$ in the direction of the unique axis of the $\hat{\sigma}$ tensor, we can compare this with the value we derived from the relaxation rates $1/T_1^{\text{CS}}$. With the definition [4] we get $\Delta\sigma = -398 \pm 20$ ppm from the solid, giving the same absolute value as we got from the relaxation rates in Eq. [2], showing that the effective correlation times τ_c^{eff} for the intramolecular dipolar rate and for the chemical shift relaxation are essentially the same.

The elements of the chemical shift tensor $\hat{\sigma}$ are connected with the elements of the spin rotational tensor \hat{C} . Although nitrobenzene is an asymmetric rotor, the principal axis systems of $\hat{\sigma}$ and \hat{C} coincide by symmetry and also coincide with the moment of

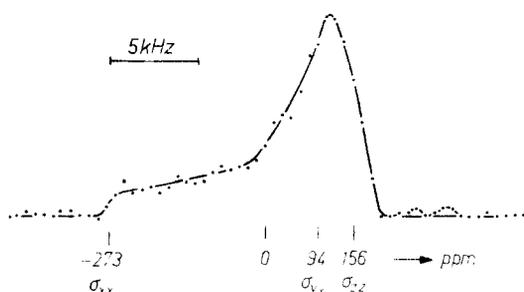


FIG. 3. Powder spectrum of ^{15}N in nitrobenzene at 32 MHz and -103°C , reference liquid nitrobenzene.

inertia tensor $\hat{\Theta}$. For this case we can express (I) the individual elements of the spin rotation tensor C_{ii} , using the expressions of Flygare *et al.* (14, 15) (for details see (I)), by²

$$C_{ii} = \frac{2}{3\Theta_i} \left(\Theta_{N_2} C_{N_2} - \frac{3\delta_i m c \mu_0 g_K}{|e|} \right) \quad [5]$$

with $\Theta_{N_2} \cdot C_{N_2} = 2.07 \cdot 10^{-34}$ g cm² sec⁻¹ being the product of the moment of inertia and the spin rotation constant of the reference compound $^{15}\text{N}_2$ (16), Θ_i the moment of inertia of the molecule which we want to consider in the direction of the principal inertia axis i , δ_i the individual component of $\hat{\sigma}$ relative to the reference compound $^{15}\text{N}_2$, μ_0 and g_K are the nuclear magneton and the nuclear g -factor of the K -nucleus ($g_K(^{15}\text{N}) = -0.567$), e and m the electronic charge and mass, and c the velocity of light. For calculating the elements of the spin rotation tensor C_{ii} from Eq. [5], we have to know the assignment of the principal axes of $\hat{\sigma}$ to the molecular axes. From the powder spectrum we have only determined the principal elements of $\hat{\sigma}$ and not the assignment. By symmetry, one principal axis must be perpendicular to the molecular plane and the other two in the plane, one bisecting the ONO angle and the other perpendicular to it.

In order to make an assignment despite the lack of complete information, we compare our ^{15}N results with the ^{13}C $\hat{\sigma}$ tensor in the isoelectronic benzoate ion (17). In this case

¹ We have used the convention $\sigma_{xx} \leq \sigma_{yy} \leq \sigma_{zz}$ for the principal axis system (13).

² C_{ii} is an element of the spin rotation tensor defined by $\mathcal{H}_{\text{SR}} = \hbar \mathbf{I} \cdot \hat{C} \cdot \mathbf{J}$. Thus spin rotation constants obtained from molecular beam data have to be multiplied by 2π to be used in our notation.

the assignment is clear by comparison with benzoic acid, where single-crystal measurements have been done (17). Therefore we assume that the assignment of the principal axes of $\hat{\sigma}$ to the molecular axes for ^{15}N in nitrobenzene is the same as found experimentally in benzoic acid (17) as shown in Fig. 4. Using for the relative isotropic shift δ between $^{15}\text{N}_2$ and ^{15}N in liquid nitrobenzene the value $\delta = -16$ ppm (16), we get from Eq. [5]: $C_{xx} = 11.4 \pm 1.5$ kHz, $C_{yy} = 1.6 \pm 0.5$ kHz, and $C_{zz} = 1.1 \pm 0.5$ kHz.

Independently, we can deduce values for the spin rotation constants from the relaxation data. The spin rotation tensor \hat{C} obtained from the solid is almost axially symmetric.

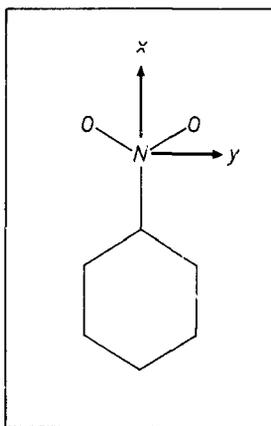


FIG. 4. Orientation of the principal axis system of $\hat{\sigma}$ for the nitrogen in nitrobenzene. For assignment see text; z-direction perpendicular to molecular plane.

Moreover, the unique axis is the same as for the axially symmetric moment of inertia tensor ($\Theta_{xx} = 204$, $\Theta_{yy} = 659$, $\Theta_{zz} = 865 \cdot 10^{-40}$ g cm² as calculated from the molecular geometry). Thus all three tensors $\hat{\sigma}$, \hat{C} , and $\hat{\Theta}$ are almost axially symmetric, the twofold axis being the common unique axis.

The two spin rotation constants are then obtained from the two equations [6] and [7] (for details see (1)):

$$\left(\frac{1}{T_1^{\text{SR}}} \cdot \frac{1}{T_1^{\text{CS}}} \right) = \frac{2(\omega \cdot \Delta\sigma)^2}{135 \cdot \hbar^2} (\rho \Theta_{\parallel}^2 C_{\parallel}^2 + 2\Theta_{\perp}^2 C_{\perp}^2) \quad [6]$$

with $\rho = \tau_{C_{\perp}}/\tau_{C_{\parallel}}$, as in Eq. [3], and

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = \frac{|e|}{2mc\mu_0 \cdot g_K} (\Theta_{\parallel} C_{\parallel} - \Theta_{\perp} C_{\perp}). \quad [7]$$

In order to make use of Eqs. [6] and [7], we have to know the ratio ρ , which is a measure of the anisotropy of the motion of the molecule in the liquid. We have already stated that the effective correlation times for relaxation due to intramolecular DDI and ACS are essentially the same, suggesting that $\rho = \tau_{C_{\perp}}/\tau_{C_{\parallel}} \approx 1$. From ^{13}C measurements of Levy *et al.* (6) in undegassed nitrobenzene at one temperature (probably 38°C), it would follow $\tau_{C_{\perp}}/\tau_{C_{\parallel}} \approx 2$. The $1/T_1$ values given in (6) are quite large compared with our data (see Fig. 1). This shows that the influence of the dissolved oxygen might be important. Nevertheless, these ^{13}C measurements suggest that ρ is not less than one. On the

other hand, from our $1/T_1^{CS}$ data presented in Table 1 and the value for $\Delta\sigma$ found in the solid, it follows that ρ should not be larger than 1.5.

Before we can solve Eqs. [6] and [7], we have to discuss the spin rotational relaxation rates $1/T_1^{SR}$ entering Eq. [6]. Lippmaa *et al.* (2) have shown that at temperatures $T \geq 60^\circ\text{C}$, the relaxation rate at low frequencies is solely given by SRI. At 0°C , we have a relaxation rate minimum for the curve $\nu = 0$ MHz. If we assume that at this temperature the relaxation rate is given by equal amounts of relaxation due to DDI and SRI, we get $1/T_1^{SR} = 1/T_1^{DD} = 9.5 \cdot 10^{-4} \text{ sec}^{-1}$ (note that $1/T_1^{DD}(\text{intra}) = 3.3 \cdot 10^{-4} \text{ sec}^{-1}$ at this temperature). If we extrapolate these rates from 0 to 60°C , we get relaxation rates $1/T_1^{SR}$ as given in Table 1. These values agree quite well with those of Lippmaa *et al.* (2).

Now we can calculate the products $(1/T_1^{SR} \cdot 1/T_2^{CS})^{1/2}$ which are also given in Table 1, the average value being $2.72 \cdot 10^{-3} \text{ sec}^{-1}$. With this average value, we solve Eq. [6] and [7] for C_{\parallel} and C_{\perp} using values of $\rho = 1$ and $\rho = 1.5$. The results are given in Table 2. The agreement between the spin-rotation constants determined from the relaxation rates and those obtained from the solid-state measurements is remarkably good.

TABLE 2

ANISOTROPIC CHEMICAL SHIFT $\Delta\sigma$, ELEMENTS OF δ -TENSOR, AND SPIN ROTATION TENSOR IN NITROBENZENE. COMPARISON OF VALUES FOR $\Delta\sigma$, C_{\parallel} , AND C_{\perp} FROM RELAXATION RATES IN LIQUID AND FROM POWDER SPECTRUM IN SOLID NITROBENZENE

$\delta \begin{cases} xx \\ yy \text{ (ppm)} \\ zz \end{cases}$	$\begin{matrix} -273 \pm 10 \\ +94 \pm 10 \\ +156 \pm 10 \end{matrix}$	$\hat{C} \begin{cases} xx \\ yy \text{ (kHz)} \\ zz \end{cases}$	$\begin{matrix} 11.4 \pm 1.5 \\ 1.6 \pm 0.5 \\ 1.1 \pm 0.5 \end{matrix}$
$\Delta\sigma \text{ (solid)(ppm)}$	-398 ± 20	$C_{\parallel} \text{ (solid)}$	11.4 ± 1.5
		$C_{\perp} \text{ (kHz)}$	1.35 ± 0.8
$ \Delta\sigma \text{ (liquid)(ppm)}$	399 ± 45	$C_{\parallel} \text{ (liquid)}$	$\begin{matrix} \rho = 1 & \rho = 1.5 \\ 11.9 & 10.7 \end{matrix}$
		$C_{\perp} \text{ (kHz)}$	$\begin{matrix} \rho = 1 & \rho = 1.5 \\ 1.5 & 1.2 \end{matrix}$

CONCLUSIONS

The present study of nitrobenzene supports the statement given already in Ref. (1) that relaxation due to ACS is much more important for ^{15}N than for ^{13}C . For ^{13}C , most of the measurements were performed at 20–25 MHz and it is apparent that relaxation due to ACS can be neglected under these conditions in most cases (see (7)). It is clear that such a statement cannot be made for ^{15}N at the *same frequency*. On the other hand, relaxation through SRI seems to be about equally important for both nuclei.

Anisotropic chemical shifts and spin rotation constants for ^{15}N and ^{13}C can be compared in a meaningful manner for isoelectronic compounds. In Table 3 such a comparison is shown. With the exception of the linear molecules N_2 and CO , the spin rotation constants have been calculated from the experimental δ tensor elements using Eq. [5]. For N_2 and CO , on the other hand, $\Delta\sigma$ has been calculated from the observed spin rotation constants. From the limited material available now, it seems that anisotropic chemical shifts are generally substantially larger for ^{15}N compared with the correspond-

TABLE 3

ANISOTROPIC CHEMICAL SHIFTS $\Delta\sigma$ AND SPIN ROTATION CONSTANTS C_{\parallel} AND C_{\perp} FOR ^{15}N AND ^{13}C FOR ISOELECTRONIC COMPOUNDS. WITH THE EXCEPTION OF THE LINEAR MOLECULES N_2 AND CO , THE SPIN ROTATION CONSTANTS HAVE BEEN CALCULATED FROM THE EXPERIMENTAL $\hat{\sigma}$ TENSOR ELEMENTS. FOR N_2 AND CO , $\Delta\sigma$ HAS BEEN CALCULATED FROM THE OBSERVED SPIN ROTATION CONSTANTS

	Nuclei	$\Delta\sigma$ (ppm)	C_{\parallel} (kHz)	C_{\perp} (kHz)
Pyridine	^{15}N	672 ^a	-0.6	14.0
Benzene	^{13}C	180 ^b	-2.5	-15.0
Nitrobenzene	^{15}N	-398	11.4	1.35
Ag Benzoate	^{13}C	-112 ^c	-12.7	-2.2
NO_3^-	^{15}N	210 ^d	8.7	24.3
CO_3^{2-}	^{13}C	75 ^e	-11.4	-27.5
$^{15}\text{N}_2$	^{15}N	635	0	138.2 ^f
^{13}CO	^{13}C	401 ^g	0	-204.2 ^g

^a See Ref. (1); ^b see (18); ^c see (17); ^d see (19); ^e see (20); ^f see (16); ^g see (21).

ing ^{13}C . This effect is especially pronounced for the first three pairs in Table 3 where $\Delta\sigma$ is up to 3.7 times as large for ^{15}N .

On the other hand, in these cases the corresponding spin rotation constants are very similar apart from the change in sign. This seems surprising at first sight, because of the close relationship between the chemical shift and the SRI (see, e.g., (14)). Both effects arise from the interaction of the nuclear magnetic moment with magnetic fields induced by the electrons of the molecule.

One might expect that these fields should be about equal for isoelectronic compounds containing carbon and nitrogen atoms at equivalent positions. This would make $\hat{\sigma}$ equal for ^{13}C and ^{15}N , and not the spin rotation constants because $\hat{\sigma}$ is independent of the nuclear g -factor, whereas \hat{C} is proportional to it. The ratio of the g -factors is $g_{^{13}\text{C}}/g_{^{15}\text{N}} \approx -2.5$ (this also explains the sign change in C noted above). The values for $\Delta\sigma$, C_{\parallel} , and C_{\perp} for ^{15}N and ^{13}C given in Table 3 provide the basis for the statement made above about the relative importance of relaxation due to ACS and to SRI.

Finally, we want again to draw the reader's attention to the huge increase in $\Delta\sigma$ for ^{15}N compared to ^{13}C in isoelectronic compounds (see Table 3). Such a pronounced difference for the same observable for neighboring atoms as carbon and nitrogen seems to be rather unexpected. For pyridine and benzene, one would be tempted to attribute this increase to the existence of the nonbonding orbital in pyridine in contrast to benzene. The data for nitrobenzene and the nitrate ion (19) show, however, that the increase in $\Delta\sigma$ is almost as large in these cases (Table 3) where no such simple explanation is obvious.³

³ We even considered the possibility that triplet states mixed into the ground state by spin orbit coupling might give a significant contribution to the chemical shift, because it is known (22) that spin orbit coupling is much more important for nitrogen compared with carbon. An order of magnitude

On the other hand, the difference in the values for $\Delta\sigma$ in $^{15}\text{N}_2$ and ^{13}CO (21) is much smaller than for the other examples in Table 3. This shows that more experiments are needed to clarify the relationship between the anisotropic chemical shifts in carbon and nitrogen compounds.

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estimate (see also (23)) using a reasonable value for the spin orbit coupling constant (22) and the known value of the hyperfine coupling constant in azaaromatic $\pi\pi^*$ triplet states (24, 25) showed, however, that this effect would contribute not more than a few ppm, even for nitrogen.