# $^{14}N$ Nuclear Quadrupole Resonances of 2-Aminopyrimidine

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Four nuclear quadrupole resonance (NQR) lines due to $^{14}N$ nuclei of the ring nitrogens in 2-aminopyrimidine were paired for the powder sample by use of a frequency-modulated spectrometer and a Helmholtz coil for the Zeeman field (H). NQR parameters $e^2Qq=3707.2$ kHz and $\eta=0.0646$ were obtained for one nitrogen, and $e^2Qq=3759.6$ kHz and $\eta=0.0329$ for the other. Moreover, the frequency of the lower line of a pair of lines for the amino nitrogen was predicted from the shift of the higher line subjected to the Zeeman field in a single crystal. The region around the expected position was carefully swept and a very weak line was found at 2357.8 kHz. Thus $e^2Qq=3428.0$ kHz and $\eta=0.2488$ were deduced for the amino nitrogen. The quadrupole coupling constant for the amino nitrogen in 2-aminopyrimidine was smaller than that for the amino nitrogen in 2-aminopyridine. The asymmetry parameter for the amino nitrogen in 2-aminopyrimidine was smaller than that for the amino nitrogen in 2-aminopyridine and roughly equal to that for the amino nitrogen in aniline.

In the case of $^{14}N$ NQR, only one resonance line is found for the axially symmetric field gradient, and a pair of resonance lines are usually found for the asymmetric field gradient. However, when one of the pair, mostly the lower line, is too weak to detect, it may be difficult to determine whether the resonance is caused by a symmetric field gradient or not, as long as a frequency-modulated spectrometer is used. To overcome this difficulty, it is advantageous to inspect the line shift as well as the line broadening by applying the Zeeman field from a given direction. In the case of the axially symmetric field gradient, the line is flattened to both sides, whereas in the case of the non-axially symmetric one, the higher line shifts to the higher and *vice versa*, and the smaller the asymmetry parameter, the greater the line broadens.[1] In this way, two pairs of lines for the ring nitrogens in 2-aminopyrimidine were determined, the results being in good agreement with the assignment by Schempp.[2] As for the resonance due to the amino nitrogen in 2-aminopyrimidine, only the higher line of the pair was reported for the first time by Schempp. Thus the frequency of the lower line was calculated from its shift by the Zeeman field on a single crystal sample. A very weak line was found in the neighborhood of the calculated frequency. The resonance frequency differs from that reported recently by Schempp and Bray.[3] The derived quadrupole coupling constant and asymmetry parameter for the amino nitrogen in 2-aminopyrimidine were compared with those for the amino nitrogens in aniline and 2-aminopyridine.

## Experimental

The $^{14}N$ NQR spectra of 2-aminopyrimidine were obtained by the frequency-modulated spectrometer described previously.[4] The resonance frequencies were measured by a heterodyne-type frequency meter BC-221 whose frequency was checked by a frequency counter TR-5578 of Takeda Riken Co. The Zeeman field was supplied by a Helmholtz coil, 40 cm in diameter and 20 cm in gap-width. The exact field strength of the coil was calibrated by measuring the Zeeman shifts of a given resonance line. The crystal was mounted in a rf coil so as to rotate independently about the horizontal and vertical axes. Thus, the Zeeman field could be applied to the crystal from any direction. All the measurements were carried out at liquid nitrogen temperature.

Commercial 2-aminopyrimidine was purified by recrystallization from a solution in organic solvent. About 10 g of the sample was used. The single crystal, 15 mm in diameter and 35 mm in length, was prepared by the Bridgman-Stockbarger method.

## Results and Discussion

Since $^{14}N$ has a nuclear spin of unity, we can usually obtain a pair of resonance frequencies, $\nu_I$ and $\nu_{II}$, as follows:

$$\nu_I = K(3-\eta), \quad (1)$$

$$\nu_{II} = K(3+\eta), \quad (2)$$

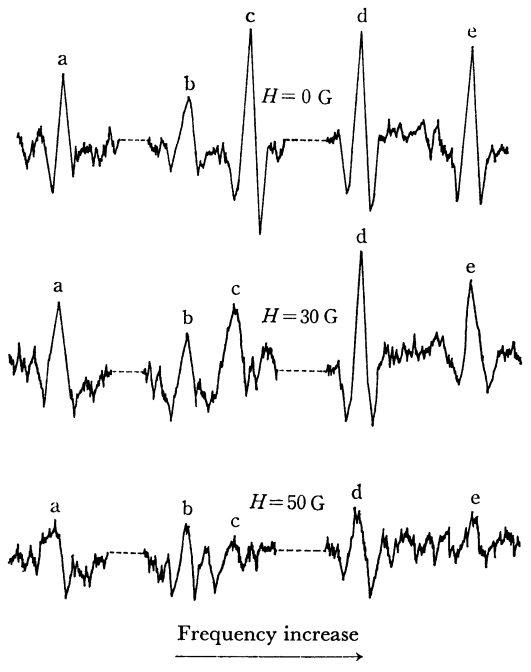


Fig. 1. Line shapes of $^{14}N$ NQR in the powder sample of 2-aminopyrimidine under the Zeeman field.

1) H. Negita, *J. Chem. Phys.*, **44**, 1734 (1966).
2) E. Schempp, Ph. D. Thesis, Brown University (1968).
3) E. Schempp and P. J. Bray, *J. Magn. Resonance*, **5**, 78 (1971).
4) H. Negita, M. Hayashi, and T. Okada, *J. Sci. Hiroshima Univ., Ser. A*, **35**, 85 (1971).

where $K=e^2Qq/4$, and $e^2$Qq and $\eta$ are the quadrupole coupling constant and asymmetry parameter, respectively.

*Determination of two Pairs of Resonance Lines for the Ring Nitrogens.* Figure 1 shows how the shapes of five resonance lines of the powder sample, denoted by *a*, *b*, *c*, *d*, and *e* in the order of increasing frequency, change with the increase in strength of the Zeeman field. We see that resonance lines *c* and *e* become broader than *a* and *d*, with the increase in field strength. Therefore, *c* and *e* are paired together and they have a considerably smaller $\eta$ value than *a* and *d*. From Eqs. (1) and (2), $e^2Qq=3759.6$ kHz and $\eta=0.0329$ were obtained for *c* and *e*, whereas the corresponding values for *a* and *d* are 3707.2 kHz and 0.0646, respectively. The results are consistent with those of Schempp[2] within experimental error.

On the other hand, as line *b* scarcely broadens even when $H=50$ G, it must have a large $\eta$ value.

*Detection of the Lower Line for the Amino Nitrogen.*

The frequency of the higher resonance line for the amino nitrogen in 2-aminopyrimidine was reported by Schempp to be 2784.2 kHz.[2]

When $H\neq 0$ and $\eta$ is small, the first-order perturbation method can be used, and the resonance frequencies are as follows:[5]

$$\nu_I' = 3K - (\eta^2K^2+D^2\cdot\cos^2\theta)^{1/2}, \quad (3)$$

$$\nu_{II}' = 3K + (\eta^2K^2+D^2\cdot\cos^2\theta)^{1/2}, \quad (4)$$

where $D=g\mu_0H$, and $\theta$ is the polar angle of the direction of the Zeeman field in the coordinates of the principal field gradients. The subscripts refer to the resonance lines corresponding to those in Eqs. (1) and (2) when $D=0$. When $H\neq 0$ and $\eta$ is large, the second-order perturbation method has to be used. The resonance frequencies are as follows:[5]

$$\nu_I'' = K(3-\eta)+D^2(A+2B-C)/K, \quad (5)$$

$$\nu_{II}'' = K(3+\eta)+D^2(2A+B+C)/K, \quad (6)$$

where

$$A = \sin^2\theta\cdot\cos^2\varphi/(3+\eta), \quad (7)$$

$$B = \sin^2\theta\cdot\sin^2\varphi/(3-\eta), \quad (8)$$

$$C = \cos^2\theta/(2\eta), \quad (9)$$

and $\varphi$ is the azimuthal angle of the direction of the Zeeman field in the coordinates of the principal field gradients.

The polar angle $\theta$ is related to the Eulerian angles $\psi_1$, $\psi_2$, and $\psi_3$ as shown in Fig. 2 by the equation:

$$\cos\theta = \sin\psi_2\cdot\sin\psi_3\cdot\sin\alpha\cdot\cos\beta + \cos\psi_2\cdot\sin\psi_3\cdot\sin\alpha\cdot\sin\beta + \cos\psi_3\cdot\cos\alpha, \quad (10)$$

where $\alpha$ and $\beta$ are the polar and azimuthal angles of the direction of the Zeeman field in the coordinates fixed to the sample, respectively. The exact value of *D* is determined from the Zeeman shifts of line *c*, which has $e^2Qq=3759.6$ kHz and $\eta=0.0329$, in the single crystal. That is, Eqs. (3) and (10) can be used in order to obtain the value of *D*, since line *c* has a small $\eta$. From

5) P. A. Casabella and P. J. Bray, *J. Chem. Phys.*, **28**, 1182 (1958).

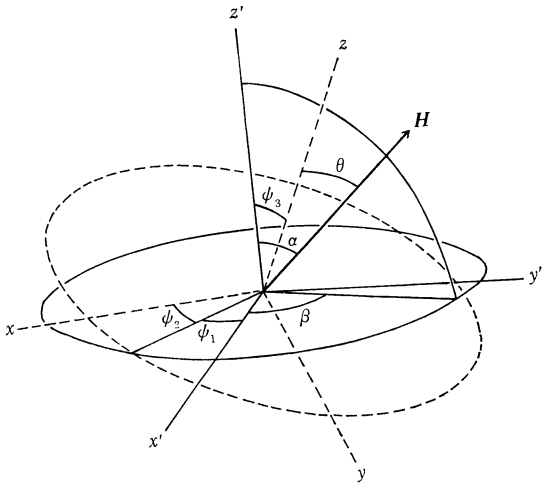


Fig. 2. Eulerian angles $\psi_1$, $\psi_2$, and $\psi_3$.
*x*, *y*, and *z*: the coordinates of the principal field gradients.
*x'*, *y'*, and *z'*: the coordinates fixed to the sample.

the Zeeman study of line *c* in the single crystal, it is found that $\nu_I'$ takes 2785.5, 2786.0, and 2783.1 kHz for the cases ($\alpha=0°$, $\beta=180°$), ($\alpha=90°$, $\beta=180°$), and ($\alpha=90°$, $\beta=200°$), respectively. From these values, the value of $D^2$ was determined to be 807.8 kHz.[2]

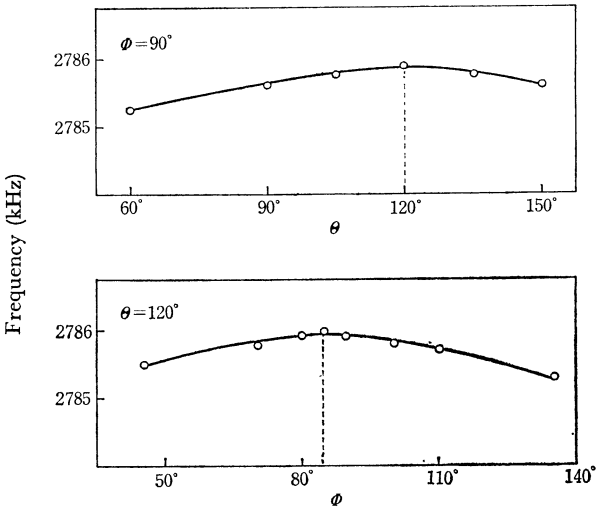


Fig. 3. The angular dependence of the Zeeman shifts of line *b*.

Figure 3 shows the anglar dependence of the Zeeman shifts of line *b* when the sample is rotated about a given axis. The Zeeman field was applied along the *Y*-axis of the laboratory frame as shown in Fig. 4, and the frequencies of line *b* were measured at various rotating angles ($\Theta$) about the *X*-axis for a constant rotating angle ($\Phi=90°$) about the *Z*-axis. The maximum frequency or shift was found for $\Theta=120°$. Next, the frequencies were measured at various rotating angles ($\Phi$) about the *Z*-axis for $\Theta=120°$. The shift was maximum at $\Phi=85°$ and $\nu_{II}''$ was estimated to be 2786.0 kHz. It is thus concluded that the principal *z*-axis of the field gradient lies in the *XY* plane when $\Theta=120°$ and $\Phi=90°$, and coincides with the direction of the Zeeman field when

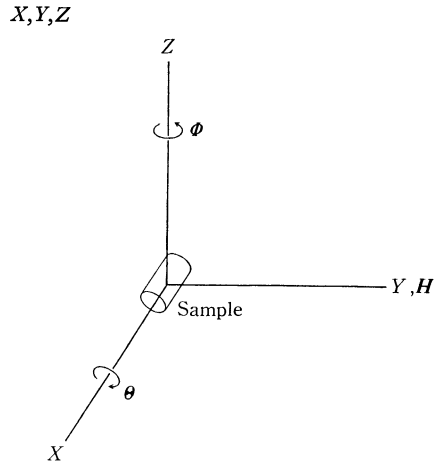


Fig. 4. The rotating angles $\Theta$ and $\Phi$ in the laboratory frame.

$\Theta=120°$ and $\Phi=85°$. Under the latter conditions, the relations $A=B=0$ and $C=1/(2\eta)$ are obtained from Eqs. (7), (8), and (9). Hence the following equation for $\nu_{II}''$ is derived from Eq. (6): $2786.0=K(3+\eta)+807.8/(2\eta K)$. On the other hand, the higher line for the non-Zeeman field is expressed by $2784.2=K(3+\eta)$. Thus the NQR parameters for the amino nitrogen are calculated as $e^2Qq=3414.0\pm17.6$ kHz and $\eta=0.2630\pm0.0179$. Substituing these values into Eq. (1), the frequency of the lower line for the amino nitrogen is obtained to be $2335.4\pm26.4$ kHz for the non-Zeeman field. The neighborhood of this frequency was carefully swept again, and a very weak line was observed at 2357.8 kHz. These results are summarized in Table 1.

TABLE 1. $^{14}$N NQR PARAMETERS IN 2-AMINOPYRIMIDINE

| | $\nu_I$ (kHz) | $\nu_{II}$ (kHz) | $\lvert e^2Qq\rvert/h$ (kHz) | $\eta$ (%) |
|---|---|---|---|---|
| Ring $N_1$ | 2720.5 | 2840.3 | 3707.2 | 6.46 |
| Ring $N_2$ | 2788.8 | 2850.7 | 3759.6 | 3.29 |
| $NH_2$ | 2357.8 | 2784.2 | 3428.0 | 24.88 |

In general, we can not always attain the condition $\theta=0°$ by the consecutive procedures stated above. Accordingly, it is recommended to repeat the procedures until the self-consistent maximum shift is obtained, especially when the angle $\Phi$ for the maximum shift in the second procedure differs much from that fixed in the first procedure.

TABLE 2. $^{14}$N NQR PARAMETERS FOR THE AMINO NITROGENS

| Compound | $\lvert e^2Qq\rvert/h$ (kHz) | $\eta$ (%) |
|---|---|---|
| Aniline[6] | 3933 | 26.9 |
| 2-Aminopyridine[7] | 3550.3 | 34.65 |
| 2-Aminopyrimidine | 3428.0 | 24.88 |

Table 2 shows the quadrupole coupling constants and asymmetry parameters for the amino nitrogens in several similar compounds. The quadrupole coupling constant for the amino nitrogen in aniline is the largest,

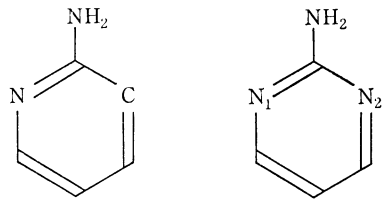


Fig. 5. The molecular frames of 2-aminopyridine and 2-aminopyrimidine.

while that for the amino nitrogen in 2-aminopyrimidine is the smallest. This suggests that the lone pair electrons of the amino nitrogen in aniline conjugate with $\pi$-electrons of the ring most weakly, while those of the amino nitrogen in 2-aminopyrimidine most strongly.

The asymmetry parameter of the amino nitrogen in 2-aminopyrimidine is nearly equal to that in aniline, but considerably smaller than that in 2-aminopyridine as shown in Table 2. This may be attributed to the molecular structure in which the nitrogen and carbon atoms in the ring are situated symmetrically or asymmetrically with respect to the C–N bond at the amino group.

Recently, $\pi$- and $\sigma$-electron densities for the ring nitrogen were derived from the following equations by Lucken:[8]

$$y - x = 2\eta e^2Qq/(3e^2Qq_p), \quad (11)$$

$$2 - y = (1-\eta/3)\cdot e^2Qq/[(1-\cot^2\gamma)\cdot e^2Qq_p], \quad (12)$$

where $x$ and $y$ are $\pi$- and $\sigma$-electron densities respectively, $2\gamma$ is the $\angle$CNC bond angle, and $e^2Qq_p$ the quadrupole coupling constant due to one $2p$-electron of nitrogen atom. If it is assumed that $2\gamma=115.2°$ [9] and $e^2Qq_p=9$ MHz in Eqs. (11) and (12), both $\pi$- and $\sigma$-electron densities can be evaluated. Table 3 lists these values obtained for the ring nitrogens in pyrimidine[10] and 2-aminopyrimidine. We see that the amino group behaves like an electron-donor to the ring nitrogens. Simple LCAO MO calculations were carried out in order to make comparison with the results of NQR. The calculated values of $\pi$-electron densities for the ring nitrogens are qualitatively in good agreement with those predicted by NQR.

TABLE 3. $\pi$- AND $\sigma$-ELECTRON DENSITIES IN PYRIMIDINE AND 2-AMINOPYRIMIDINE

| Compound | $\pi$ | | $\sigma$ |
|---|---|---|---|
| | NQR | MO[a] | |
| Pyrimidine[9] | 1.138 | 1.144 | 1.281 |
| 2-Aminopyrimidine $N_1$ | 1.308 | 1.203 | 1.325 |
| 2-Aminopyrimidine $N_2$ | 1.299 | | 1.308 |

a) The values of LCAO MO were calculated by the parameters such as $\alpha_N=\alpha+0.5\beta$, $\alpha_{C-N}=\alpha+0.1\beta$, $\alpha_{NH_2}=\alpha+0.4\beta$, $\alpha_{C-NH_2}=\alpha$, $\beta_{C-N}=\beta$, and $\beta_{C-NH_2}=0.6\beta$.

The total electron excess on the ring nitrogen can be computed from the values for the orbital occupation

6) C. T. Yim, M. A. Whitehead, and Donald H. Lo, *Can. J. Chem.*, **46**, 3595 (1968).
7) R. Ikeda, S. Onda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **72**, 2501 (1968).
8) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London and New York (1969), p. 234.
9) P. J. Wheatley, *Acta Crystallogr.*, **13**, 80 (1960).
10) E. Schempp and P. J. Bray, *J. Chem. Phys.*, **46**, 1186 (1967).

numbers as follows:

$$z = x + 2y - 3 \quad (13)$$

From Table 3 and Eq. (13), the values of $z$ are obtained to be 0.700 $e^-$ for the ring nitrogens in pyrimidine and 0.958 $e^-$ and 0.915 $e^-$ for those in 2-aminopyrimidine. Thus, it is to be noted that the magnitudes of the electron transfer from the amino group to the ring nitrogens in 2-aminopyrimidine are larger by 0.258 $e^-$ and 0.215 $e^-$ respectively than that from the hydrogen atom in pyrimidine.