^{14}N Nuclear Quadrupole Resonance of Some Heterocyclic Compounds *via* Nuclear Double Resonance

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Using proton-nitrogen double resonance in the laboratory frame, the ^{14}N nuclear quadrupole resonances (NQR) of 2,4(1*H*,3*H*)-pyrimidinedione[uracil], 2,3-dihydro-2-thioxo-4(1*H*)-pyrimidinone[2-thiouracil], 2,4-(1*H*,3*H*)-pyrimidinedithione[2,4-dithiouracil], and 1,3-dihydro-2*H*-benzimidazole-2-thione[2-mercaptobenzimidazole] have been measured at room temperature. The NQR parameters of uracil and its sulfur-substituted compounds are interpreted by using the Townes and Dailey theory.

Because of pharmacological interest, many studies of sulfur-substituted pyrimidines and purines have been performed by various spectroscopic means, but not by the nuclear quadrupole resonance (NQR). In this paper we report the observation of NQR of ^{14}N in 2,4(1*H*,3*H*)-pyrimidinedione[uracil], 2,3-dihydro-2-thioxo-4(1*H*)-pyrimidinone[2-thiouracil], 2,4(1*H*,3*H*)-pyrimidinedithione[2,4-dithiouracil], and 1,3-dihydro-2*H*-benzimidazole-2-thione[2-mercaptobenzimidazole]. These data yield information about the electron density on the nitrogen nucleus and hence about the chemical bonding of these molecules.

Spin 1 nuclei such as ^{14}N have three quadrupole states in an electric field gradient, and three transitions can occur between these three states. The frequencies are given by[1]

$$\nu_{\pm} = \frac{3}{4}e^2Qq\left(1 \pm \frac{\eta}{3}\right), \quad (1)$$

$$\nu_0 = \nu_+ - \nu_- = \frac{1}{2}\eta e^2Qq, \quad (2)$$

where e^2Qq is the ^{14}N quadrupole coupling constant and η is the asymmetry parameter.

Nuclear magnetic double resonance (NMDR) in the laboratory frame was employed to detect the NQR transitions. NMDR methods —as first introduced by Hartmann and Hahn[2] and later by Lurie and Slichter[3]— facilitate observation of ^{14}N NQR whose transition frequency often lies in the region 0.3—3 MHz and is thus not accessible by conventional continuous wave techniques.

Experimental

Samples. The samples were all polycrystalline chemicals.

NMDR in the Laboratory Frame. The details of NMDR were described by Slusher and Hahn.[4] In brief, the sample is first magnetized in a high d.c. magnetic field H_0 (about 6 kG here) for a high-field spin-lattice relaxation time and then adiabatically demagnetized to zero field [(a) to (b) in Fig. 1]. The spin order of the abundant spins [protons here] is now very high but a suitably phase or pulse modulated radio frequency field H_{1B} which resonates a rare spin [^{14}N here] quadrupole transition will continuously break the spin order of the abundant spins. The loss may be observed by adiabatically remagnetizing the sample [(c) to (d)] and observing a decrease of the majority spins' nuclear magnetic signals with the help of a 90° pulse. By sweeping the frequency ν_B of the phase or pulse modulated field [in 10 kHz steps here] the entire quadrupole resonance spectrum may be recorded. In this study ν_B was swept from 450 kHz to 4 MHz. Most parts of the NMDR apparatus built in this laboratory were based on the design of Slusher and Hahn.[4]

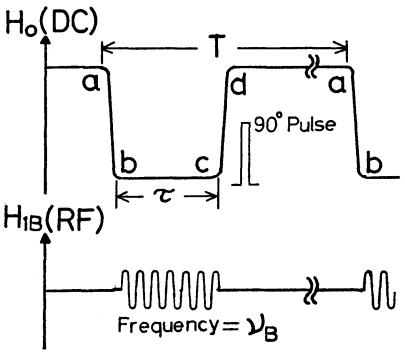

Fig. 1. Nuclear double resonance sequence.

Results and Discussion

Using the high-field and zero-field spin-lattice relaxation times for each molecule, the cycle time T [see Fig. 1] and zero field time τ were determined before performing the double resonance experiment. These data are collected in Table 1.

Table 1. High-field and zero-field spin-lattice relaxation times at room temperature and experimental conditions

Substance	T_1[a]	T_{1D}[b]	T_{1N}[c]	$[T-\tau]$[d]
Uracil	60	8	56	[90—3]
2-Thiouracil	52	3	20	[100—2]
2,4-Dithiouracil	107	8	30	[120—3]
2-Mercapto-benzimidazole	43	5	104	[60—3]

a) T_1 is the high-field spin-lattice relaxation time which is measured by 90°-τ-90° method. b) T_{1D} is the short zero-field relaxation time constant. c) T_{1N} is the long relaxation time. d) Cycle time T and zero field time τ. All the times in this table are in sec.

Figure 2 shows the zero-field proton spin-lattice relaxation, where the proton signal at first decreases quickly and later more slowly with time. This slow decay of proton magnetization is caused by the remagnetization of the proton system by cross interaction with the ^{14}N system, which has a long spin-lattice relaxation time.

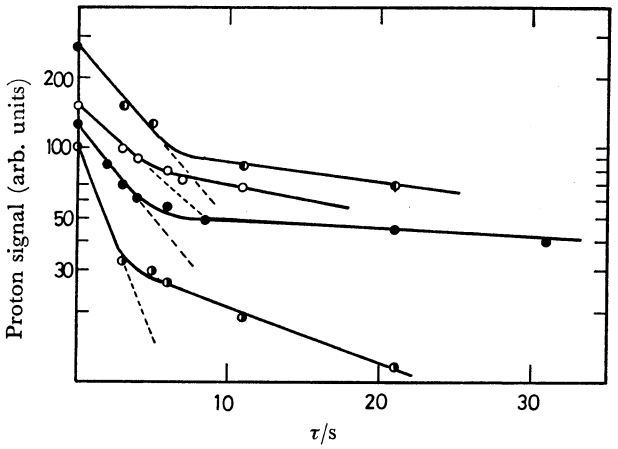

Fig. 2. Zero-field proton spin-lattice relaxation.
◐: Uracil, ◑: 2-thiouracil, ○: 2,4-dithiouracil, ●: 2-mercaptobenzimidazole.

Table 2. Observed ^{14}N NQR transition frequencies (kHz), coupling constants e^2Qq (kHz), asymmetry parameters η, and experimental temperature T (K)

Substance	[ν_+,	ν_-,	ν_0]	e^2Qq	η	T
Uracil	[2300,	1640,	660]	2630	0.502	294
2-Thiouracil	[2060,	1250,	810]	2207	0.734	300
	[2110,	1430,	680]	2360	0.580	300
2,4-Dithiouracil	[2030,	not obsd,	850]	2140	0.794	301
	[1970,	not obsd,	730]	2140	0.682	301
2-Mercapto-benzimidazole	[2340,	1790,	550]	2750	0.40	299

The observed transition frequencies, quadrupole coupling constants e^2Qq, and asymmetry parameters η are collected in Table 2. Though the two sets of lines corresponding to the two nitrogen atoms in uracil were observed at 77 K,[5] they could not be resolved at room temperature. In dithiouracil there remains some uncertainty when the ν_+ line is paired with the ν_0 line, since ν_- lines have not been observed. By comparing the absorption intensities of the two lines in each absorption band [ν_+ or ν_0], the pairing given in Table 2 was made. Figure 3 shows the chart recorder output of the ν_+ and ν_0 lines in the NQR spectrum of ^{14}N in dithiouracil. In the ν_0 [or ν_+] band, the dip of the resonance (a) [or (a')] is smaller than that of (b) [or (b')]. For the uracil group, the quadrupole coupling constant tends to decrease and the asymmetry parameter tends to increase as oxygen atoms are replaced by sulfur atoms. For uracil and its sulfur-substituted compounds it is very difficult to give the definitive assignment of one set of observed lines to one particular site within each molecule.

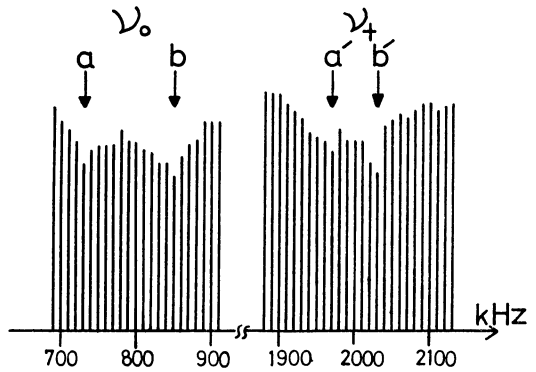

Fig. 3. Chart recorder output of the ν_+ and ν_0 lines in the NQR spectrum of ^{14}N in 2,4-dithiouracil.

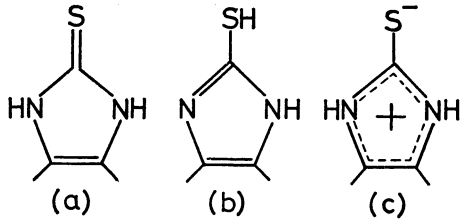

Fig. 4. Structural forms of 2-mercaptobenzimidazole.
(a) Thione, (b) thiol, (c) ionic.

Mercaptobenzimidazole can be represented by the three different structural forms illustrated in Fig. 4. When the thiol form is the predominant tautomer in the solid, we can expect two different ^{14}N NQR transitions. According to the X-ray analysis of the solid by Form *et al.*,[6] the molecule exists in the thione form with *mm* symmetry. This means the two nitrogen atoms are equivalent; our results are consistent with such a structural analysis.

The NQR parameters of uracil and its sulfur-substituted compounds are analyzed by the following formulae, (3) and (4),[1] which are used for pyrrole-type nitrogen:

$$(e^2Qq/e^2Qq_0)\left[1+\frac{\eta}{3}\right] = L - \bar{B}, \tag{3}$$

$$(e^2Qq/e^2Qq_0)\eta = \frac{3}{2}(A-\bar{B})(1-\cot^2\gamma). \tag{4}$$

Here L is the pi population, A is the N–H sigma population, $\bar{B}$ is the averaged N–C sigma population, 2γ is the CNC angle, and e^2Qq_0 is the coupling constant of an electron in a 2p orbital of nitrogen. In order to estimate L and $\bar{B}$, we assume that A is 1.33[7] and e^2Qq_0 is 7.4 MHz.[5,8] For uracil the averaged value of the two CNC angles[10] is used for 2γ. As the X-ray analysis of thiouracil has not been published, we assume 2γ is 122°. For dithiouracil the experimental values[9] are used. The results are given in Table 3. From uracil to dithiouracil, the lone pair population L is monotonically decreasing. This decrease of lone pair population suggests the increase of the ionic term $-^+NH{=}C(-S^-)-$ in the resonance structures.

Table 3. The orbital occupation numbers for nitrogen in uracil and its sulfur-substituted compounds

Substance	L (lone pair)	$\bar{B}$ (N–C)	[η][a]
Uracil	1.58	1.16	[0.502]
2-Thiouracil	1.49	1.12	[0.734]
	1.53	1.15	[0.580]
2,4-Dithiouracil	1.47	1.11	[0.794]
	1.49	1.14	[0.682]

a) The asymmetry parameters are used to distinguish the two nitrogen sites in each molecule.

References

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