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Nitrogen 14 Nuclear Quadrupole Resonance Study of Several Condensed Ring Compounds

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The ^{14}N nuclear quadrupole resonance spectra of 2-mercaptobenzothiazole, isatin(1*H*-indole-2,3-dione), and isatoic anhydride(2*H*-3,1-benzoxazine-2,4(1*H*)-dione) have been observed at room temperature by the nuclear double resonance method. The quadrupole coupling constants and the asymmetry parameters thus obtained were interpreted by the Townes and Dailey theory.

In this paper, we wish to report the first observation of the nuclear quadrupole resonance (NQR) of the ^{14}N in several condensed ring heterocyclic compounds. The parameters thus obtained, *i.e.*, the quadrupole coupling constant (e^2Qq/h) and the asymmetry parameter (η) correspond to the electronic environment around each nitrogen atom. In the case of nitrogen, these parameters are usually dominated almost entirely by the distribution of the valence electrons in each nitrogen atom. The three frequencies$^{1)}$ of ^{14}N NQR are given by:

$$\nu_{\pm} = 3/4e^2Qq/h(1 \pm \eta/3) \qquad (1),\ (2)$$

$$\nu_0 = \nu_+ - \nu_- = 1/2\eta e^2Qq/h \qquad (3)$$

where e^2Qq/h and η are the quadrupole coupling constant and the asymmetry parameter respectively.

The frequency, ν_0, is relatively low, almost always below 1000 kHz. In this case, such conventional NQR techniques as using a regenerative spectrometer may not be accessible because of their low sensitivity. Therefore the nuclear double resonance technique$^{2)}$ in the laboratory frame (^{1}H–^{14}N cross relaxation) was employed.

Experimental

The double resonance technique will be briefly described. A single cycle in an experiment consists of three stages. In the first, the major nuclei which give strong NMR signals, such as ^{1}H, are polarized in a high magnetic field ($\simeq$1T) for two or three high-field spin-lattice relaxation times, T_1. Next, the sample demagnetization is performed adiabatically. The minor nuclei (searched for NQR signals) are irradiated with a certain RF field; intensity, H_{1B}, and frequency, ν_B, after the sample has been removed from the magnet to the region of a zero external field for a cerain time period, τ s. In the third stage, the sample is returned to the magnet. A 90° pulse is immediately applied to monitor the remaining magnetization of the major nuclei. The amplitude of the free induction decay (FID) or echo is recorded. If H_{1B} is applied at the frequency of the quadrupole resonance of the minor nuclei, the monitored magnetization, $M(\tau)$, can be expected to vary as;

$$M(\tau) = M(0) \exp\left[-(1/T_{1d} + 1/\tau_{AB})\right]. \qquad (4)$$

Here, T_{1d} is the spin-lattice relaxation time in a zero magnetic field for the major nuclei and τ_{AB} is the cross relaxation time between the major spin and the minor spin, which has a finite value if ν_B is equal to the resonance frequency. The NQR absorption line is recorded as a dip of the magnetization of the major nuclei. If T_1 is 100 s, one scanning of ν_B from 2 MHz to 3 MHz by 10 kHz steps takes 6 h.

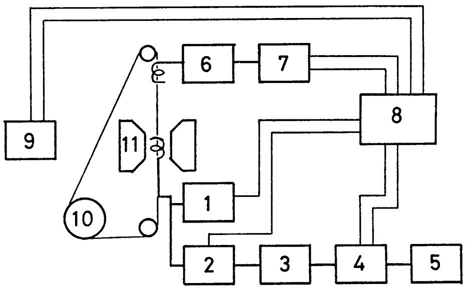


Fig. 1. Nuclear double resonance apparatus.
1) Transmitter, 2) preamplifier, 3) receiver amplifier, 4) gated integrator, 5) chart recorder, 6) wideband power amplifier, 7) PLL synthesizer, 8) pulse generator, 9) motor driver, 10) stepping motor, 11) magnet pole piece.

The double resonance apparatus was built in this laboratory$^{3)}$ (Fig. 1).

Pulsed NMR. We used a conventional, single-coil, pulsed, proton magnetic resonance spectrometer operating at 26.7 MHz (6.28×10^{-1} T). The transmitter was a modified YAESU FL-101 apparatus operating as a C-class amplifier. The pre-amplifier and receiver amplifier were hand-made. The spectrometer was constructed with care taken to insure stability of sensitivity and a short recovery time.

Gated Integrator. The monitored FID was stored by means of a gated integrator. We used a box-car detector as the gated integrator by inserting a reset circuit. The integrated signal was recorded on a chart recorder as one bar, whose height was proportional to the remaining magnetization $M(\tau)$.

Sample Elevator Mechanism. The sample is moved by a small elevator mechanism driven by a stepping (pulse) motor. The advantage of the stepping motor is that the velocity and the distance can be controlled electronically by means of the pulse frequency and the total number of pulses respectively. The stepping motor is ASTROSYN 34 PM-C004.

Frequency Synthesizer and Wide-band Power Amplifier. The frequency, ν_B, must be fixed during each experimental cycle. The stability required in this experiment is higher than that of a standard signal generator. Also, it is necessary to set the irradiation frequency programmably. Therefore, we employed a PLL (phase-locked loop) frequency synthesizer, whose frequency program can be set automatically. The output of the synthesizer, which is sometimes phase- or pulse- modulated, is fed to an ENI 240L wide-band power amplifier. H_{1B} is applied to the sample within a soleniod coil.

Helmholtz Coil. A small Helmholtz coil is used to cancel any remaining fields to within $\pm 10^{-4}$ T over the volume of the sample in the zero-field region. Sometimes, a pure iron magnetic shield is used in order to cancel the fairly high remaining field ($\simeq 10^{-2}$ T).

Coherent Pulse Generator. The timing of the entire experimental cycle is automatically and programmably controlled by a coherent pulse generator, which was designed and built up in our laboratory. This generator, whose components are almost all TTLs(7400 series), is composed of a quartz time base and programmable dividers.

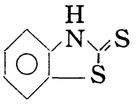
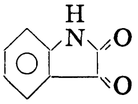
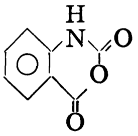
All experiments were done at room temperature. The sweeping of the minor spin irradiation (H_{1B}) was performed in 10 kHz steps from 400 kHz to 3800 kHz; therefore the total experimental error may amount to about 10 kHz.

Sample. All the samples were polycrystalline guaranteed-grade chemicals obtained from the Tokyo Kasei Kogyo Co., Ltd. Each sample volume was approximately 1 cm^3, packed in a test tube 10 mm in diameter. We tried to detect the ^{14}N NQR spectra of some other condensed ring compounds, but failed. The compounds which did not give resonances were indigo, thionine, luminol, uric acid, *N,N'*-dithiobismorpholine, and thiooxy purine. In these six compounds, the proton spin-lattice relaxation time, T_1, was too short to satisfy the adiabatic condition for the double resonance experiment.

Results

T_1, the Spin-lattice Relaxation Time in a High Magnetic Field. The T_1 of each compound was determined by the 90° pulse-t-90° pulse method. The obtained time constant of each compound is listed in the 2nd column in Table 1. For a compound with the time constant of 50 s, the experimental cycle was set at 120 s.

Table 1. Observed parameters

Compound	Resonance freq./kHz					
	T_1/s	ν_+	ν_-	ν_0	e^2Qq/h	η
2-Mercapto-benzothiazole 	50	2140	1520	620	2440	0.51
Isatin 	20	2540	2050	490	3060	0.32
Isatoic anhydride 	60	2790	—	750	3220	0.47

NQR. The observed frequencies, coupling constants, and asymmetry parameters are given also in Table 1, together with the formula of each molecule.

2-Mercaptobenzothiazole gave two strong signals, which correspond to ν_+ and ν_0 lines, and also a weak signal at 1520 kHz. This corresponds to ν_- line. The crystal and molecular structure[4] shows that there are four molecules per unit cell. However only one set of signals was obtained.

Proton relaxation time of isatin is 20 s at room temperature. For the double resonance experiment, a relaxation time constant of the major spin of about 20 or 30 s may be most favorable because of the stability of the apparatus and the lesser demands on the experimenter's patience. This chemical also gave all three lines, ν_+, ν_-, and ν_0, as is illustrated in Fig. 2. The crystal and molecular structure of isatin was elucidated by Goldschmidt and Llewellyn.[5]

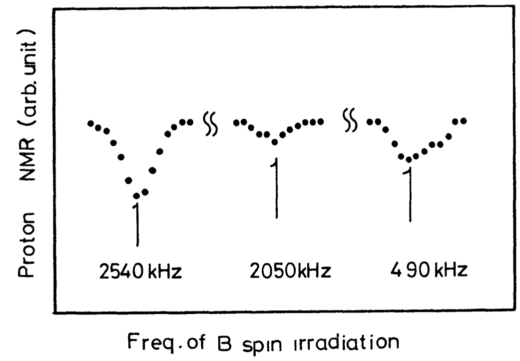
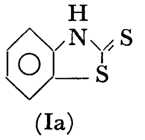


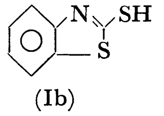
Fig. 2. Chart recorder outputs which show ^{14}N nuclear quadrupole resonance of isatin by proton-nitrogen double resonance method. B spin irradiation (searching irradiation) was performed in 10 kHz steps.

Isatoic Anhydride gave only two resonance lines, which correspond to the ν_+ line and the ν_0 line respectively. No structural data by X-ray diffraction has been reported for this compound.

Discussion

In 2-mercaptobenzothiazole(I), thione-thiol tautomerism is possible, as is illustrated below:

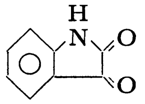

(Ia)

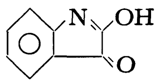

(Ib)

(I)

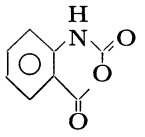
The X-ray structural study[4] supports the thione(Ia) form, while it gives no evidence for the thiol(Ib) form.

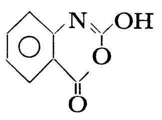
In isatin(II) and isotoic anhydride(III), lactam-lactim tautomerism can exist, as is shown below:


(IIa)


(IIb)

(II)


(IIIa)


(IIId)

(III)

The infrared results[6,7] support the lactam form(a) for both compounds.

In order to interpret the observed NQR results, the Townes and Dailey theory[1] was employed. For all three compounds, the electronic environment around each nitrogen atom may be assumed to be pyrrole-like, considering the other spectroscopic results.[4–7] The pyrrole-type formula[1] is as follows;

$$(e^2Qq/e^2Qq_0)(1+\eta/3) = L-B \tag{5}$$

$$(e^2Qq/e^2Qq_0)\eta = 3/2(A-B)(1-\cot^2\gamma). \tag{6}$$

Here, L is the pi population, A is the the N–H sigma population, B is the averaged N–C sigma population, 2γ is the CNC angle, and q_0 is the electric-field gradient caused by a 2p electron of the nitrogen atom.

For the two compounds whose molecular structures have been determined by the X-ray studies,[4,5] each bond angle, 2γ, was replaced by the corresponding value obtained from the studies. On the other hand, for isatoic anhydride, 2γ was assumed to 120°. In order to calculate the population numbers, L and A, the N–C population, B, and the atomic coupling constant, e^2Qq/h, were assumed to 1.15 and 9.1 MHz[8] respectively. Using the coupling constants and asymmetry parameters obtained at this time, the population numbers, L and A, were calculated by the above formulas [(5), (6)]; they are shown in Table 2. One may easily note that, for all the compounds, the L values are much less than 2.0, around 1.5; this fact may be explained by considering that the pi electrons take part in the conjugation of the heterocyclic ring.

TABLE 2. THE TOWNES AND DAILEY ANALYSIS BY MEANS OF A PYRROLE-TYPE FORMULA

Compound	A(N–H)	L(pi)	NET ($2.3+A+L$)
2-Mercapto-benzothiazole	1.30	1.46	5.06
Isatin	1.28	1.52	5.10
Isatoic anhydride	1.32	1.56	5.18

e^2Qq_0/h=9.1 MHz. B=1.15.

References

1) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London and New York (1969).

2) R. E. Slusher and E. L. Hahn, *Phys. Rev.*, **166**, 332 (1968).

3) Y. Hiyama, Master's Thesis, University of Tokyo (1976).

4) J. P. Chesiek and J. Donohue, *Acta Crystallogr., Sect. B*, **27**, 1441 (1971).

5) G. H. Goldschmidt and F. J. Llewellyn, *Acta Crystallogr.*, **3**, 294 (1950).

6) D. G. O'Sullivan and P. W. Sadler, *J. Chem. Soc.*, **1956**, 2202.

7) D. G. O'Sullivan and P. W. Sadler, *J. Chem. Soc.*, **1957**, 2916.

8) C. T. O'Konski and T. K. Ha, *J. Chem. Phys.*, **56**, 3169 (1972).