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^{14}N Nuclear Quadrupole Resonances of 2,2′- and 4,4′-Dipyridyls

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^{14}N nuclear quadrupole resonances have been observed in a number of nitrogen heterocyclic compounds, such as diazines[1] and s-triazine,[2] since Guibé found the resonance of pyridine[3] in 1960. The electronic structures of these compounds have been studied by Lucken[4] recently.

In this connection, it seemed that it would be interesting to study the ^{14}N nuclear quadrupole resonances of 2,2′- and 4,4′-dipyridyls, which are considered to be as fundamentally important as pyridine, diazines and s-triazine. When 2,2′-dipyridyl is used as a chelate reagent, it attaches a cation, itself keeping the *cis*-form, whereas it is known to exist as the *trans*-form in the crystal.[5]

Experimental

Two kinds of dipyridyls obtained from commercial sources were purified by recrystallization in organic solvents; about 10-g portions of the samples were used in the experiment. 2,2′-Dipyridyl was examined in the powder state, while 4,4′-dipyridyl was examined after having once been melted.

A frequency-modulated spectrometer of the Pound-Watkins type was used to detect the resonance signals, because large asymmetry parameters were expected in both dipyridyls.[6] For the frequency modulation, the bidirectional square wave of 140 Hz was fed to an SD-111 diode, which was connected in parallel to the tank circuit of the main oscillator.

Results and Discussion

The resonance frequencies, ν, the quadrupole coupling constants, e^2Qq, and the asymmetry parameters, η, are given in Table 1.

Since ^{14}N has a nuclear spin of unity, one can usually observe a pair of resonance frequencies, ν_{I} and ν_{II}, due to a species of nitrogen atoms as follows:

$$\nu_{\mathrm{I}} = e^2Qq\,(3-\eta)/4$$
$$\nu_{\mathrm{II}} = e^2Qq\,(3+\eta)/4 \qquad (1)$$

The numbers of the resonance lines of 2,2′- and 4,4′-dipyridyls are two and six respectively. Since the six lines of the latter compound are grouped into two sets of three lines each, as is shown in Fig. 1, it seems that there are three kinds of nonequivalent nitrogen atoms, each slightly different from the others. This situation, however, gives rise to the problem on the pairing of the six lines. It can be seen from Fig. 1 that the three lines on the higher-frequency side have different intensities, while those on the lower-frequency side are so weak as to be undistinguishable. Accordingly, it is difficult to

TABLE 1. ^{14}N NUCLEAR QUADRUPOLE RESONANCE PARAMETERS OF DIPYRIDYLS AND PYRIDINE

Compounds	Resonance frequencies		Coupling constants	Asymmetry parameters	Occupation numbers	
	ν_{I} (kHz)	ν_{II} (kHz)	e^2Qq (kHz)	η (%)	a (π)	b (σ)
2,2′-Dipyridyl	3074.0±0.1	3902.5±0.1	4152.8	35.5	1.27 (1.20)*	1.38
4,4′-Dipyridyl	3001.8±0.2	3889.0±0.3				
	2996.4±0.2	3875.0±0.2	4574.2	38.1	1.27 (1.23)	1.40
	2987.4±0.2	3835.2±0.2				
Pyridine[5]	four lines	four lines				
	(2956—3001)	(3856—3919)	4584.0	39.7	1.28 (1.20)	1.40

* The values in the parentheses were calculated by the method of LCAO MO, using parameters such as $\alpha_{\mathrm{N}} = \alpha + 0.6\beta$, $\alpha_{\mathrm{adj}} = \alpha + 0.1\beta$ and $\beta_{\mathrm{C-N}} = \beta_{\mathrm{C-C}}$.

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1) E. Schempp and P. J. Bray, *J. Chem. Phys.*, **46**, 1186 (1967).
2) L. Guibé and E. A. C. Lucken, *Mol. Phys.*, **10**, 273 (1966).
3) L. Guibé, *Compt. Rend.*, **250**, 3014 (1960).
4) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London and New York (1969), p. 235.
5) F. WM. Cagle, *Acta Crystallogr.*, **1**, 158 (1948).
6) H. Negita, *J. Chem. Phys.*, **44**, 1734 (1966).

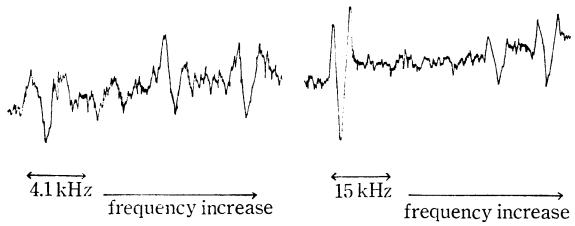

Fig. 1. ^{14}N nuclear quadrupole resonance absorption lines in 4,4′-dipyridyl.

determine which two are to be paired. The coupling constant and the asymmetry parameter of 4,4′-dipyridyl in Table 1 were derived from the two averaged values, $\nu_I(av)$ and $\nu_{II}(av)$, of three resonance frequencies grouped in the same sets.

The nitrogen atoms in dipyridyls are assumed to be in the sp^2-hybridized state and to have the maximum field gradient, q_Z, approximately in the direction of the bisector of the ∠CNC angle. The asymmetry parameter, η, is defined as $\eta=(q_x-q_y)/q_Z$ under the condition that $|q_y|>|q_x|$. In view of the ^{14}N nuclear quadrupole resonances of pyridine, hexamethylenetetramine, and γ-picoline,[7] it is preferable to choose the X- and Y-axes shown in Fig. 2.

From the bonding orbitals and the occupation numbers of these electrons, a, b_1, and b_2, at the nitrogen atom, the following expressions[4] are obtained:

$$U_p = [a+(b_1+b_2)/2]/2+[2-(b_1+b_2)/2]\cot^2\gamma - 2$$
$$\eta = -3[a-(b_1+b_2)/2]/(2U_p) \qquad (2)$$

7) E. A. C. Lucken, *Trans. Faraday Soc.*, **57**, 731 (1969).

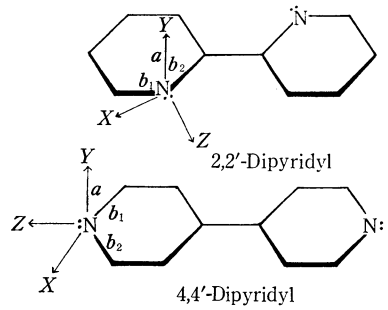

Fig. 2. Cartesian-coordinate systems at the nitrogen atoms of dipyridyls. a is the occupation number of π-orbital at the nitrogen atom, whereas b_1 and b_2 are those of σ-orbitals.

where $U_p=-e^2Qq_z/e^2Qq_p$. In Eq. (2) it is assumed that $2\gamma=\angle CNC=120°$ and that $e^2Qq_p=10$ MHz.

In 4,4′-dipyridyl, it is evident that $b_1=b_2=b$. Therefore, the values of a and b are calculated from e^2Qq and η. On the other hand, $b_1\neq b_2$ in 2,2′-dipyridyl; hence a, b_1, and b_2 cannot be calculated from Eq. (2). Therefore, the value of b in 2,2′-dipyridyl is obtained by averaging b_1 and b_2. As is shown in Table 1, the π- and σ- charge excesses in both dipyridyls are about 0.27 and 0.40 respectively, nearly equal to those of pyridine.

Simple LCAO MO calculations were carried out in order to compare the results with one another and also with those of NQR. The occupation numbers of the electrons calculated at the nitrogen atoms are almost all the same, as is to be expected from the experimental values, although calculated values are generally lower than experimental values. This discrepancy can be improved if a slightly smaller value than 10 MHz is adopted for e^2Qq_p.