BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1771—1772 (1969)

Nuclear Quadrupole Resonance of Nitrogen-14 in Some Aliphatic Nitriles[1]

Shinzaburo ONDA, Ryuichi IKEDA, Daiyu NAKAMURA and Masaji KUBO
Department of Chemistry, Nagoya University, Chikusa, Nagoya

(Received November 9, 1968)

The pure quadrupole resonance of nitrogen-14 in some aliphatic nitriles was observed by means of a modified Pound-Watkins type spectrometer previously described.[2] Frequency modulation was used for the determination of resonance frequencies, while Zeeman modulation was employed for the assignment of observed resonance absorptions to ν^{I} and ν^{II}. The samples were procured from commercial sources and purified by repeated distillation. All the compounds investigated are liquids at room temperature. Therefore, they were solidified slowly in glass tubes and cooled gradually to liquid nitrogen temperature.

Since nitrogen-14 has a nuclear spin equal to unity, one can usually observe a pair of resonance lines, ν^{I} and ν^{II}, for equivalent nitrogen nuclei when the asymmetry parameter η is finite.

$$\nu^{\mathrm{I}} = \frac{1}{4}\, eQq(3+\eta)$$

$$\nu^{\mathrm{II}} = \frac{1}{4}\, eQq(3-\eta)$$

Here eQq denotes the quadrupole coupling constant in frequency units. From the observed resonance frequencies, the quadrupole coupling constant and the asymmetry parameter were calculated with the use of these equations as shown in Table 1.

Two sets of weak ν^{I} and ν^{II} resonance lines were observed for succinonitrile. For other compounds investigated, a single set of resonance lines was observed, indicating that all atomic sites of nitrogen are equivalent in each crystal. Accordingly, quadrupole coupling constants and asymmetry parameters can be evaluated in a straightforward manner.

Quite recently, Colligiani *et al.*[3] published the results of their comprehensive study on the ^{14}N nuclear quadrupole resonance of organic nitriles. Some of their results (propio-, butyro-, amylo-, isopropio-, glutaro-, adipo- and sebaco-nitriles) are in good agreement with ours. However, resonance frequencies ($\nu^{\mathrm{I}}=2881.4$ and $\nu^{\mathrm{II}}=2824.6$ kHz) observed by them for pimelonitrile do not agree with ours ($\nu^{\mathrm{I}}=2907.7$ and $\nu^{\mathrm{II}}=2793.3$ kHz) within experimental errors. Colligiani *et al.*[3] detected only one set of resonance lines for succinonitrile at practically the same temperature, the frequencies ($\nu^{\mathrm{I}}=2995.7$ and $\nu^{\mathrm{II}}=2844.7$ kHz) being in good agreement with those (2995.2 and 2844.1 kHz) of a set observed in the present investigation.

The appearance of the two sets of ν^{I} and ν^{II} lines indicates that there are two kinds of crystallographically nonequivalent nitrogen atoms in the crystals at liquid nitrogen temperature, although the two nitrogen atoms are chemically equivalent in the molecule. Unfortunately, no X-ray crystal data are available. For this compound, one-to-one correspondence cannot be made between ν^{I} and ν^{II} owing to the proximity of doublet lines. Therefore, the frequencies of the doublet lines were averaged to evaluate eQq and η.

One is tempted to consider the existence of the trans and the gauche forms in the crystals of succinonitrile. However, we could observe only a single set of ν^{I} and ν^{II} frequencies for tetramethylsuccinonitrile having a chemical formula analogous to that of succinonitrile. On the other hand, malononitrile[4] having no rotational isomers show two sets of ν^{I} and ν^{II} at liquid nitrogen temperature. These facts suggest that the nonequivalence of nitrogen atoms is due to the difference in the crystal

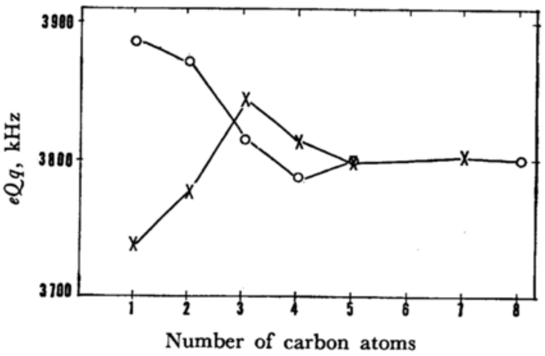

Fig. 1. The quadrupole coupling constants of ^{14}N in nitriles (cross) and dinitriles (circle).

---

[1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April 1968.

[2] R. Ikeda, D. Nakamura and M. Kubo, *J. Phys. Chem.*, **70**, 3626 (1966).

[3] A. Colligiani, L. Guibé, P. J. Haigh and E. A. C. Lucken, *Mol. Phys.*, **14**, 89 (1968).

[4] A. Sussman and S. Alexander, *Solid State Communications*, **5**, 259 (1967).

TABLE 1. NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES, ν^{I} AND ν^{II}, QUADRUPOLE COUPLING CONSTANTS, eQq, AND ASYMMETRY PARAMETERS, η, OF ^{14}N IN SOME ALIPHATIC NITRILES AT LIQUID NITROGEN TEMPERATURE

Compound	ν^{I}, kHz	ν^{II}, kHz	eQq, kHz	η, %
$CH_3(CH_2)_2CN$	2935.5±0.1	2832.1±0.1	3845.0±0.1	5.38±0.01
$CH_3(CH_2)_3CN$	2911.5±0.1	2808.6±0.2	3813.5±0.1	5.40±0.01
$CH_3(CH_2)_4CN$	2894.8±0.1	2804.2±0.1	3799.4±0.1	4.77±0.01
$CH_3(CH_2)_6CN$	2897.2±0.2	2806.9±0.2	3802.7±0.3	4.75±0.02
$(CH_3)_2CHCN$	2879.9±0.1	2830.1±0.4	3806.7±0.3	2.62±0.02
$NC(CH_2)_2CN$	2995.2±0.2 2962.5±0.2	2844.1±0.3 2816.9±0.2	3872.9	7.66
$NC(CH_2)_3CN$	2923.1±0.1	2799.5±0.1	3815.0±0.1	6.48±0.01
$NC(CH_2)_4CN$	2861.4±0.1	2818.7±0.1	3786.7±0.1	2.26±0.01
$NC(CH_2)_5CN$	2907.7±0.2	2793.3±0.2	3800.6±0.3	6.02±0.02
$NC(CH_2)_8CN$	2895.8±0.1	2805.8±0.2	3801.1±0.2	4.74±0.01
$NCC(CH_3)_2C(CH_3)_2CN$	2976.1±0.1	2903.8±0.1	3919.9±0.1	3.69±0.01

field rather than to the existence of different kinds of isomeric molecules.

As pointed out by Colligiani *et al.*,[3] long-chain nitriles and dinitriles show essentially the same quadrupole coupling constant and asymmetry parameter. The asymptotic value of eQq for large number of carbon atoms in a nitrile molecule is 3.80 rather than 3.81 MHz[3] as shown in Fig. 1. It is noteworthy that the asymmetry parameter is considerably large and varies over a fairly wide range in spite of the cylindrical symmetry of a single $-C\equiv N$ group. It is presumed that both the intramolecular charge distribution and the crystal field are responsible for this effect.