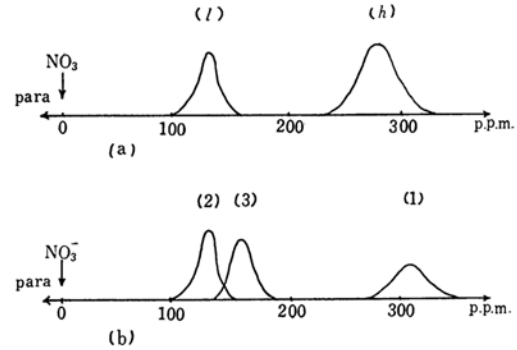

Fig. 1. NMR spectra of NaN_3 in aq. sol. (a) and $C_2H_5N_3$ (b).

Nuclear Magnetic Resonance of Azides

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We have measured, in a field of 16250 gauss, the chemical shift σ and the spin-lattice relaxation time T_1 of the N^{14} nuclear magnetic resonance (NMR) of the sodium azide in aqueous solution and of the ethyl azide.

As shown in Fig. 1 (a), NaN_3 gives two resonance lines. σ of the line of lower field side (*l*) is 130 p. p. m. and that of higher field side (*h*) is 280 p. p. m. where the origin of σ is resonance point of NO_3^-. The line width of *l* is narrower than that of *h* and the ratio of the absorption areas of *l* and *h* is equal to 1 : 2. As the atomic groups containing nitrogens which present in aqueous solution of NaN_3 we can cite three kinds, N_3^-, HN_3 and NaN_3, but the first is overwhelming in its quantity. The structure of the N_3^- is known to be linear[1] and so *l* must be the line of central nitrogen and *h* that of the both ends of the N_3^-. The origin of the line widths is mainly the spin-lattice relaxation and the T_1 values measured by the saturation method are 5.8 and 3.6 m. sec. for *l* and *h*, respectively.

Ethyl azide gives three lines, as shown in Fig. 1 (b), of equal intensity of which the σ's are 130, 160 and 310 p. p. m. respectively. The line widths increase in order from lower field one to higher one and their T_1 values are measured to be 4.5, 2.2 and 1.1 m. sec., respectively.

In methyl azide three nitrogen atoms are colinear and the angle CNN is 120° [1]. We expect that the ethyl azide might have the same structure as the methyl azide and we number the three nitrogen atoms 1, 2 and 3 from the carbon atom side.

The spectral position of the lowest line is just the same as the line *l* of the N_3^- and so this line is considered to arise from the central nitrogen (2). For the assignment of the other two lines, consider the electronic structures A and C given by Pauling[1],

$$\text{A:}\quad \mathrm{R-\ddot{N}=N^+=\underset{\cdot\cdot}{N}^-}:$$

$$\text{C:}\quad \mathrm{R-\underset{\cdot\cdot}{\ddot{N}}-N^+\equiv N}:$$

and calculate the number of unbalanced p-electron U_p by the method analogous to Townes and Dailey's[2]. As the atomic wave function of σ bonds we use the sp^2 hybridized orbital for nitrogen atom 1 and sp hybridized orbitals for 2 and 3.

1) L. Pauling, "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, p. 271.

In the Table I, the first and the second row show the U_p's of three N-atoms for the structure A and C respectively, and the last for the structure in which A and C are equally mixed.

TABLE I. NUMBER OF UNBALANCED p-ELECTRON OF NITROGEN ATOMS 1, 2 AND 3 OF AZIDE FOR THE STRUCTURES A AND C AND ALSO FOR THEIR EQUALLY MIXED STRUCTURE

	1	2	3
A	−2/3	0	0
C	−1/6	0	−1/2
	−5/12	0	−1/4

Since the spin-lattice relaxation is originated from the intramolecular quadrupole coupling, the inverse T_1 should be proportional to (e^2qQ^2) and hence to U_p^2. Therefore, we conclude that the line having the shortest T_1 is caused by the nitrogen atom 1 and the line having the medium T_1 by the atom 3. The assignment of three lines is indicated in Fig. 1 (b).

Several authors[3] have discussed on the NMR spectra of nitrogen. The spectra are separated into two groups; the first is the ammonia group distributing around the position $\sigma=300$ p. p. m. and the second is the nitro and CN-group around the position $\sigma=0$. It is remarkable that the azides have the lines belonging to each group. The diamagnetic shift due to *one* 1s electron or *one* 2s electron is calculated to be +120 and +17 p. p. m. respectively, and the paramagnetic shift due to *one* 2p electron to be −460 p. p. m. assuming the mean excitation energy of 5 eV. The chemical shift beyond 200 p. p. m. as displayed by the azides should be attributed to the paramagnetic shift of the 2p electron and so be proportional to U_p. But the experimental results are just in opposite direction; the line of the N-atom (1) having the largest U_p is the most diamagnetic. Such a contradiction was already found by Masuda[4] in the case of molecular chlorine compounds and the azides give the second example.

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2) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

3) For example, B. M. Schmidt, L. C. Brown and D. Williams, *J. Mol. Spectroscopy*, **2**, 551 (1958).

4) Y. Masuda, *J. Phys. Soc. Japan*, **11**, 670 (1956).