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Electron Spin Resonance of Oriented Solid of Isocyanic Acid Irradiated with γ-Rays

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Free radicals in the γ-irradiated solid of isocyanic acid at -196 °C have been studied by electron spin resonance (ESR) spectroscopy at -196—-100 °C. An oriented solid of isocyanic acid was prepared by solidification of isocyanic acid around an aluminum rod with cooling for the measurement. The ESR spectra consisted of a pair of triplets and a pair of sextets, when the longitudinal axes of the oriented solid were parallel and perpendicular, respectively, to the dc magnetic field. The absorptions were assigned to an anion radical ($HNCO^-$) by analysis of anisotropy of the spectrum and by deuteration of isocyanic acid. The observed constants were: $g_\perp=2.0025$, $g_{//}=1.9985$; $A_x(N)=21.2$ G, $A_y(N)=24.8$ G, $A_z(N)=21.8$ G. The anion radical was assumed to be preferentially oriented in the oriented solid, taking two orientations whose $g_{//}$ axes were perpendicular both to each other and to the longitudinal axis of the oriented solid.

On the flash photolysis of isocyanic acid vapor, NH, NH_2 and NCO radicals were detected by absorption spectroscopy.[1,2] They were also postulated to account for the result of gas chromatography on the photolysis of vapor.[3] Radicals formed on the γ-irradiation of isocyanic acid solid at low temperatures, however, have not been studied.

In the present work, ESR measurements on isocyanic acid solid irradiated with γ-rays have been carried out. An attempt was made to prepare an oriented solid of isocyanic acid which can be used instead of a single crystal of the acid, since the melting point of the acid, -86 °C,[4] is too low to prepare a single crystal without special apparatus. In addition, deuteration of isocyanic acid was performed for identification of the radicals. Changes in the ESR spectra with light irradiation and with elevation of temperature were also examined.

Experimental

Materials. Isocyanic acid was prepared by the pyrolysis of cyanuric acid vapor in a stream of dry nitrogen at 600 °C according to reported method.[1] Further purification of the resulting isocyanic acid was carried out by distillation under reduced pressure of 5 mmHg. Deuterated isocyanic acid was prepared by the pyrolysis of deuterated cyanuric acid with a 33% yield. The deuterated cyanuric acid was prepared by dissolving cyanuric acid (3.0 g, 0.07 mol) in deuterium oxide (100 g, 5.56 mol) with heating under reflux for 6 hr. The degree of deuteration determined by mass spectrometry was 88%.

Preparation of Oriented Solid of Isocyanic Acid. Oriented solid of isocyanic acid was prepared in the following way. Isocyanic acid was solidified around an aluminum rod (1 mm diameter) in a glass tube (8 mm diameter) by cooling with liquid nitrogen (Fig. 1a), and the resulting oriented solid was sealed in another sample tube (10 mm diameter) in nitrogen atmosphere, as shown in Fig. 1b. After γ-ray irradiation at -196 °C, the solidified isocyanic acid was dislodged from the surface of the aluminum rod. It was then divided radially into several wedge-formed pieces (Fig. 1c), one of which was inserted into a crack in a Teflon tube so as to have the longitudinal axis of the piece, *i.e.* the axis of the mark of aluminum rod, held horizontally (Fig. 1d). The angle between the longitudinal axis of the piece and the direction of the dc magnetic field is referred to as orientation-angle, orientation-angles 0° and 90° indicating the axes parallel and perpendicular, respectively, to the dc magnetic field. The wedge-formed piece was inserted into the Teflon tube crack in order to keep the longitudinal axis parallel to the vertical tube axis and was rotated around its longitudinal axis.

ESR Measurement. The solid of isocyanic acid was irradiated with ^{60}Co γ-rays to a dose of $8\times10^5\sim8\times10^6$ rad at -196 °C. The ESR measurement was run using a Varian V-4502 X-band spectrometer with a cylindrical cavity in the TE_{110} mode and with 100 kHz field modulation at several different temperatures between -196 °C and -100 °C. The oriented solid could be rotated in the cavity so that ESR spectrum was obtained at any desired orientation-angle. The γ-irradiated solids of isocyanic acid were subsequently exposed to light from an Ushio Denki HB 500/B high pressure mercury lamp (500W; wavelengths>2800 Å) in a transparent quartz Dewar vessel at -196 °C.

Mass Spectrometry. Mass spectra of deuterated isocyanic acid vapor were analyzed with a Hitachi RMU-6 mass spectrometer.

Results

Oriented Solid of Isocyanic Acid. On cooling with liquid nitrogen, solidification of isocyanic acid proceeded from the wall of the glass sample tube to the

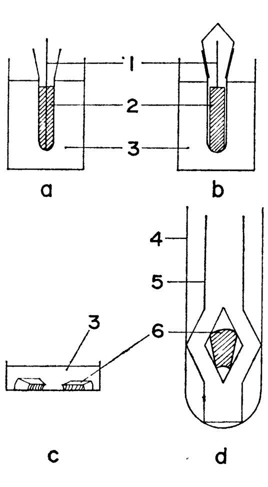


Fig. 1. Preparation of oriented solid of isocyanic acid; aluminum rod (1), isocyanic acid (2), liquid nitrogen (3), ESR sample tube (4), Teflon tube (5) and γ-irradiated isocyanic acid (6).

surface of the aluminum rod. The gradient of temperature of the isocyanic acid turned out to have a cylindrical symmetry around the axis of the aluminum rod. The resulting solid of isocyanic acid was a polycrystal made of needle-like crystallite preferentially oriented with the cylindrical symmetry, since any piece of oriented solid exhibited the same anisotropic spectrum. The narrower wedge-angle of the piece (Fig. 1d) gave a sharper and more symmetric spectrum. It was found that the use of a Teflon rod for solidification of isocyanic acid yielded a broader and less anisotropic spectrum than that obtained with an aluminum rod.

ESR Spectrum of Isocyanic Acid. The above procedure for preparing the oriented solid is hereafter referred to as the oriented solid method. The experimental rectangular coordinate system of the oriented solid, X, Y and Z, was defined as shown in Fig. 2. The Z axis corresponds to the longitudinal axis of the aluminum rod and the Y axis coincides with the bisector of the wedge-angle of the wedge-formed piece. The X axis is perpendicular to both the Y axis and Z axis.

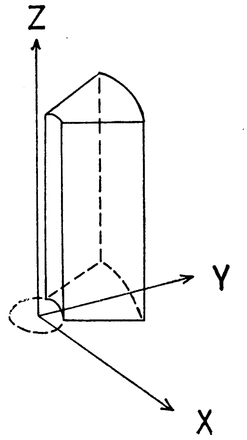


Fig. 2. Experimental rectangular coordinate system of oriented solid.

The γ-irradiated oriented solid prepared by the oriented solid method gave the spectra as shown in Fig. 3 when the solid was rotated around the Y axis keeping the Y axis perpendicular to the dc magnetic field. Remarkable changes in the pattern occurred with change in the orientation-angle from 0° to 90°. The spectrum at 0° consisted of six strong lines with equal intensity, though the lines in higher field became broader (Fig. 3a). At 90 ° ten lines were observed with relative intensity ratios of about 1 : 1 : 1 : 2 : 1 : 1 : 2 : 1 : 1 : 1 (Fig. 3d). A slight change in pattern can be seen on variation from 0° to 60° (Figs. 3b and 3c).

The six lines can be interpreted by a pair of triplets due to the hyperfine interaction with ^{14}N nucleus ($I=1$) and with ^{1}H nucleus (Fig. 3a), from a consideration of both line intensities and line spacings. The ten lines can be ascribed to the twelve lines with equal intensity, four of which coalesce forming a pair of lines with relative intensity of two (Fig. 3d). The twelve lines can be divided into two groups, I and II, each of which consists of six lines similar to those observed at orientation-angle 0°. The values of nitrogen splitting change from 21.8 G to 24.8 G, while the change of proton splitting (0.8 G) is small and the proton splitting remains almost constant. The relative intensity ratios of the lines and the hyperfine structure due to N and H of Radical I are equal to those of Radical II. Consequently, Radicals I and II should have the same molecular structure and a different orientations which yield a site splitting of 6.5 G through g-anisotropy at 90°.

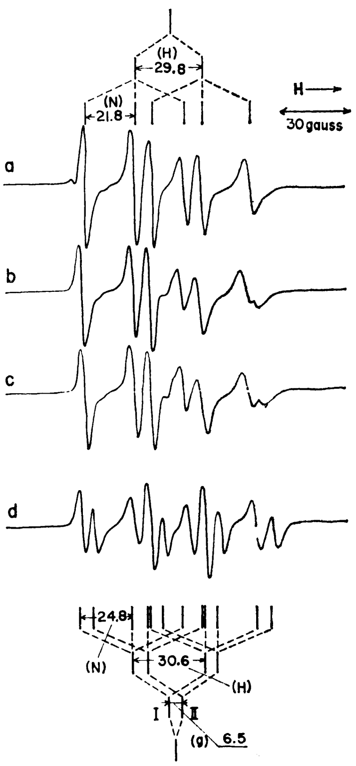


Fig. 3. ESR spectra of oriented solid of isocyanic acid irradiated with γ-rays at -196 °C with orientation-angle 0° (a), 30° (b), 60° (c) and 90° (d).

The angular dependence of the g-value around the Y axis is shown in Fig. 4, where two kinds of g-value are found, one (Radical I) remains constant throughout the angular change ($g=2.0025$), while the other (Radical II) takes the minimum value ($g=1.9985$) at orientation-angle 90°.

The oriented solid gave the spectra as shown in Fig. 5, when the solid was rotated around the Z axis keeping the Z axis perpendicular to the dc magnetic field. Spectrum 5a was obtained when the dc magnetic field was applied in a direction parallel to the Y axis. A rotation of the solid by 90° gave spectrum 5c which is similar both to 5a and 3d. The nitrogen splitting was observed to take a value 21.2 to 24.8 G on the rotation of the oriented solid, while the hydrogen splitting remained almost constant (*ca.* 30 G). The angular dependence of the g-value around the Z axis was also examined. The anisotropies of g-value are shown in Fig. 6. The observed g-values change between 2.0025 and 1.9985, corresponding to the

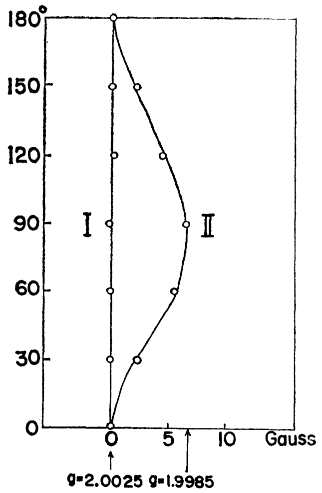


Fig. 4. Plots of the g-values of Radicals I and II for various orientations of the dc magnetic field in the XZ plane, with angles measured from the direction of the dc magnetic field in the direction of Z axis.

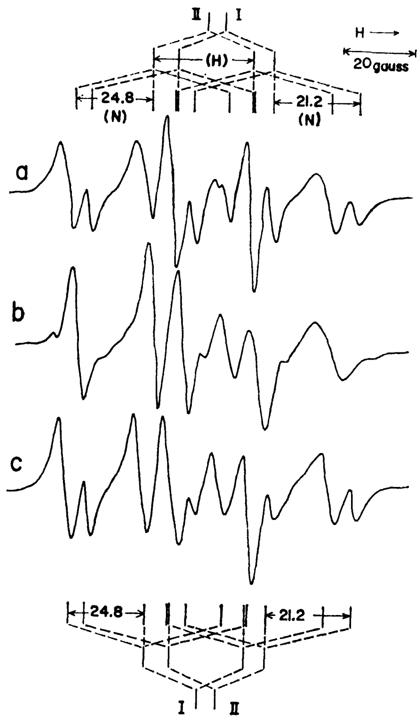


Fig. 5. ESR spectra of oriented solid of isocyanic acid irradiated with γ-rays at -196 °C. The specimen was rotated in the XY plane around the Z axis. Spectrum a was obtained, when the dc magnetic field was parallel to the Y axis. Spectra b and c correspond to a rotation of the sample tube by 45° and 90°, respectively, from the position for Spectrum a around the Z axis.

maximum g-value of Radical I and the minimum value of Radical II, respectively.

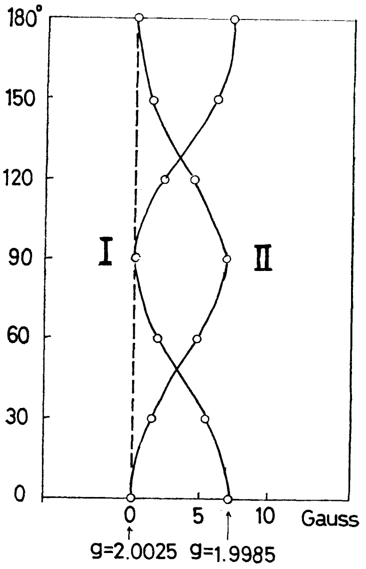


Fig. 6. Plots of the g-value of Radicals I and II for various orientations of the dc magnetic field in the XY plane, with angles measured from the direction of the dc magnetic field in the direction of the Y axis.

When the oriented solid is rotated about the Y axis, one of the triplet patterns (Radical I) remains fixed in position, while the others (Radical II) change (Fig. 3). The oriented solid is considered to be symmetric about the Z axis. Accordingly, the g-tensor of the radical produced in γ-irradiated oriented solid is axially symmetric. Both Radicals I and II seem to align to keep the $g_{//}$ axis in the XY plane (Fig. 7). The $g_{//}$ axis of Radical I is parallel to the Y axis, that of Radical II to the X axis. Both the $g_{//}$ axes of Radicals I and II are perpendicular to the Z axis. These orientation states of Radicals I and II can reasonably explain the results shown in Figs. 4 and 6. Both the molecular planes of Radicals I and II are expected to be perpendicular to the Z axis. The observed maximum and minimum values (24.8 and 21.2 G) of nitrogen splitting are considered to be the principal values of nitrogen hyperfine tensor, since the two principal axes of nitrogen hyperfine tensor can be expected to be in the molecular plane (XY plane) of

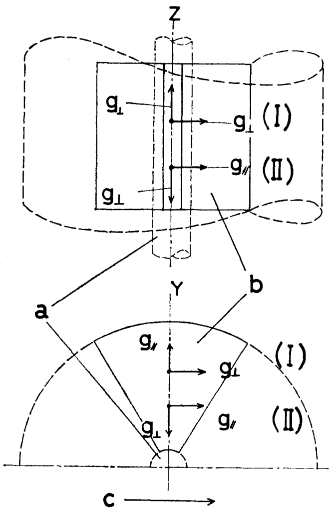
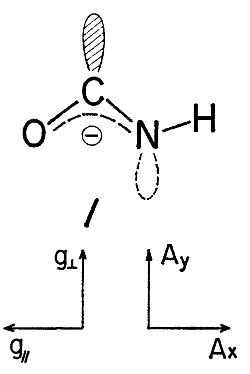


Fig. 7. The orientation state of the radicals in the oriented solid; aluminum rod (a), isocyanic acid solid (b) and the direction of the dc magnetic field at orientation-angle 90° (c).



Structure **1**

Table 1. Principal values of the nitrogen hyperfine tensor (A) and the spectroscopic splitting factor (g)

$A_x=21.2$ G	
	$g_\perp=2.0025$
$A_y=24.8$ G	
	$g_{//}=1.9985$
$A_z=21.8$ G	

The x, y and z axes are given in Structure **1**.

the radicals. The principal values 24.8 and 21.2 G were obtained when the Y axis of the oriented solid was rotated around the Z axis by 0° and 90°, respectively (Fig. 5). Another principal value, 21.8 G, was also obtained when the magnetic field was applied in a direction parallel to the Z axis (Fig. 3a). Structure **1** shows the directions of the g-tensor and the nitrogen hyperfine tensor, and also the radical structure. The experimental g-values and hyperfine splitting constants of nitrogen are given in Table 1.

For the sake of comparison, isocyanic acid in a Spectrosil tube was solidified by cooling with liquid nitrogen without aluminum rod and subsequently γ-irradiated (1×10^6 rad) at −196 °C; this procedure of preparation of specimen for ESR measurement is hereafter referred to as the usual method. The specimen made in this manner exhibits a spectrum as shown in Fig. 8. Almost no changes in the pattern occurred when the Spectrosil tube was rotated about its longitudinal tube axis. The spectrum consisted of six strong lines and additional weak three lines. The six strong lines were centered at $g=2.0025$ and separated by 22 G with equal intensity, though the lines in the higher field also became broader. The absorption lines of hydrogen atom separated by 508 G and two weak lines separated by about 170 G were also recorded.

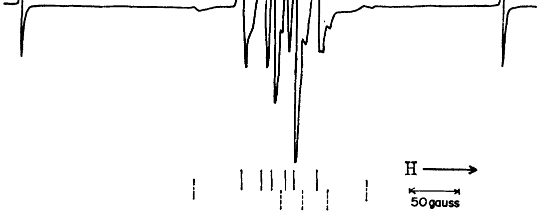


Fig. 8. ESR spectrum of isocyanic acid prepared by the usual method and three kinds of line-spectra shown at the bottom of this figure.

In order to examine the orientation of the isocyanic acid molecule in the solid prepared by the usual method, the spectra were also measured with the dc magnetic field perpendicular to the longitudinal axis of the Spectrosil tube in the following manner similar to the oriented solid method; the Spectrosil tube containing the γ-irradiated isocyanic acid solid was broken in liquid nitrogen and the resulting wedge-form piece of isocyanic acid solid was inserted in a crack of Teflon tube so as to hold the longitudinal axis of the piece horizontally. The spectra obtained at orientation-angles 0° and 90° are shown in Fig. 9. The dependence of the ESR pattern on the angle was similar to that in the case of the oriented solid method, while the absorption lines in the former case were less anisotropic and broader.

A wider wedge-angle (*ca.* 150°) of the wedge-formed specimen gave a broader absorption lines where the separation of the absorption lines of Radical II from that of Radical I at 90° was not observable (Fig. 10). This suggests that the isocyanic acid molecule in the oriented solid is oriented radially.

The subsequent light irradiation (wavelengths>

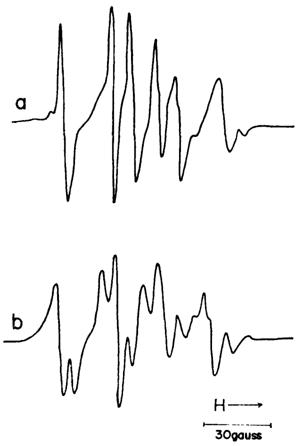


Fig. 9. ESR spectra of isocyanic acid prepared by the usual method with γ-irradiation 1×10^6 rad at −196 °C measured by keeping the longitudinal axis horizontal; orientation-angle 0° (a) and 90° (b).

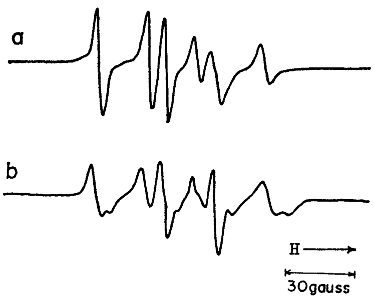


Fig. 10. ESR spectra of a piece of oriented solid of isocyanic acid with a wider wedge-angle (*ca.* 150°); orientation-angle 0° (a) and 90° (b).

2800 Å) on the specimen caused no change in those spectra obtained in the dark at −196 °C. Raising the temperature of the specimen to about −110 °C gave no change either in intensity or in shape of the spectra. The intensity, however, decreased remarkably at −90 °C with the disappearance of Q-dip on mode check.

ESR Spectrum of Deuterated Isocyanic Acid. Figure 11 shows an ESR spectrum of deuterated isocyanic acid γ-irradiated in a Spectrosil tube at −196 °C according to the usual method. The spectrum consists of nine strong lines with equal intensity due to the hyperfine splitting with ^{14}N nucleus and ^{2}H nucleus. The small line spacing is 4.6 G, corresponding to 1/6.43 of the splitting constant of ^{1}H and ascribed to the deuteron splitting. The large spacing is 22.1 G, corresponding to the coupling of N nucleus. Two weak lines on both ends of he spectrum are due to the coupling of ^{1}H nucleus of undeuterated isocyanic acid. Deuterated isocyanic acid behaves in the same manner as isocyanic acid both on cooling and on γ-irradiation according to the usual method.

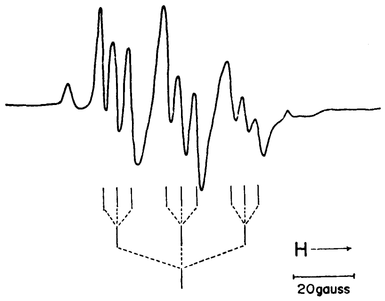
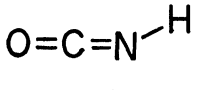


Fig. 11. ESR spectrum of deuterated isocyanic acid irradiated with γ-rays of 1×10^{6} rad at −196 °C.

Discussion

Analysis of ESR Spectrum. The structure of isocyanic acid determined by Jones *et al.*[5] using the microwave absorption spectroscopy, is represented by the following structure. The equivalent doublet pattern (Fig. 3) should arise from one β-proton coupling, since the proton splitting almost remains constant throughout the orientation-angle change. The result of deuterated isocyanic acid confirms this conclusion.



$$O{=}C{=}N{-}H$$

Formula 1.

From the experimental values of nitrogen hyperfine tensor, an unpaired electron spin density on nitrogen atom ($=\rho_N$) can be calculated. Isotropic Fermi contact component (A_f) and anisotropic component (A_d) arising from dipole-dipole interaction can be written, respectively, as

$$A_f = \pm 1/3(A_{/\!/} + 2A_{\perp}) \qquad (1)$$

$$A_d = \pm 1/3(A_{/\!/} - A_{\perp}) \qquad (2)$$

where $A_{/\!/}$ and $A_{\perp}$ represent the principal values of the axially symmetric hyperfine tensor. For this case, $A_{\perp}$ is the average value of A_x and A_z, since the value of A_x is nearly equal to that of A_z. In formulas (1) and (2), we can obtain A_f and A_d, using the observed values, $A_{/\!/}=24.8$ and $A_{\perp}=21.5$ G

$$A_f = 22.6 \text{ (G) and } A_d = 1.1 \text{ (G)}$$

Although it could not be determined in this experiment, A_f and A_d may have the same sign. The dipole-dipole term for the 2p electron and Fermi term on a nitrogen atom can be estimated, respectively, by use of the data by Barns and Smith:[6] $A_{2p}=17.1$ G and $A_{2s}=550$ G. Consequently, the spin density of the 2p$_z$ orbital and of the 2s orbital can be set, respectively, as

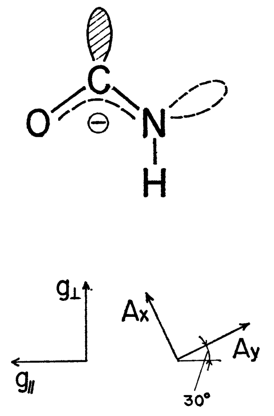
$$\rho_{2p} = A_d/A_{2p} = 0.064$$

$$\rho_{2s} = A_f/A_{2s} = 0.041$$

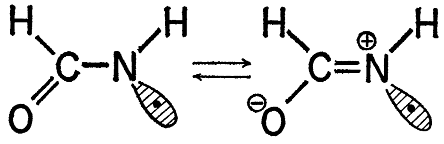
Thus, the spin density on nitrogen atom ($\rho_N=\rho_{2p}+\rho_{2s}$) is estimated to be 0.11. The value is similar to that on oxygen atom of CO_2^- anion radical ($\rho_O=0.11$).[7] The results indicate that the unpaired electron occupies an orbital of carbon atom and the unpaired electron spin density is produced upon the sp^2 hybrid orbital of nitrogen atom by the spin delocalization. The radical represented by Structure **1** whose structure is similar to that of CO_2^- anion radical[7] might give a large negative shift of g-value through the effect of spin-orbital coupling of the unpaired electron in the sp^2 hybrid orbital of carbon atom with the in-plane 2p orbitals of oxygen atom and nitrogen atom.

The direction of the largest principal value of nitrogen hyperfine tensor of Structure **1** should be expected to correspond reasonably to the direction of the lobe of the nitrogen sp^2 hybrid orbital occupied by the lone pair electrons, since the unpaired electron spin density is caused upon the sp^2 hybrid orbital by the spin polarization of the lone pair electrons. This is supported by the results for CO_2^- anion radical,[7] $\cdot NO_2$ radical[8] and the radical of γ-irradiated dimethyl glyoxime.[9] The largest principal value (A_y) and the maximum g-value of Radical I were obtained when the Y axis of the oriented solid was rotated around the Z axis by 90° from the position where the Y axis became parallel to the dc magnetic field (Figs. 5 and 6). The direction of A_y of Structure **1** might not coincide with that of $g_{\perp}$ axis, since the $g_{\perp}$ axis is not a symmetrical axis of Structure **1**. However, the shift between the two directions can not be distinguished from the experimental results. Therefore, the A_y axis is almost parallel to the $g_{\perp}$ axis.

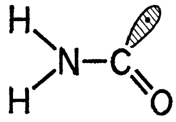
In Structure **1**, the N–H bond of the radical is in the *cis*-position with respect to the carbon sp^2 hybrid orbital occupied by the unpaired electron. On the other hand, the N–H bond of Structure **1′** is in the *trans*-position. If the N–H bond is in the *trans*-position, the direction of the lobe of the nitrogen sp^2 hybrid orbital occupied by the lone pair electrons might cut the $g_{/\!/}$ axis at an angle 30° (Structure **1′**). This is in line with the result where the A_y axis cuts the $g_{/\!/}$ axis at an angle 90°. The N–H bond of the radical is, therefore, in the *cis*-position with respect to the carbon sp^2 hybrid orbital.



Structure **1**



Structure **2**



Structure **3**

Two possible structures for the radical are given in the following.

They represent the σ-type neutral radicals produced by the addition reactions of a hydrogen atom to isocyanic acid. In each structure, an unpaired electron occupies in sp^2 orbital of nitrogen atom or carbon atom. The large negative shift of *g*-value can not be explained by Structure **2** which has a similar structure to that of the vinyl radical. Structure **2**, thus, seems to be less acceptable. The resonance pattern arising from Structure **3** might consist of a triplet of triplets, since the unpaired electron couples with two hydrogen nuclei and nitrogen nucleus. The observed pattern, however, consists of a doublet of triplets. Consequently, Structure **3** is discarded and Structure **1** is the most preferable for the assignment of the radical.

The weak absorption separated by 170 G (Fig. 8) may be ascribed to a moiety of decomposed molecule.

Orientation of Isocyanic Acid. From the spectrum 3d, the population of Radical I in the isocyanic acid solid should be equal to that of Radical II. Thus it seems that the N=C=O axis of the isocyanic acid molecule is perpendicular to that of the adjacent acid molecule through a hydrogen bond (Fig. 12). When isocyanic acid molecule (A) traps an electron produced by γ-irradiation, the unpaired electron of the resulting radical (A) occupies the sp^2 hybrid orbital in the *cis*-position to the proton of the molecule (A). This is why the proton is in the *cis*-position of the unpaired electron.

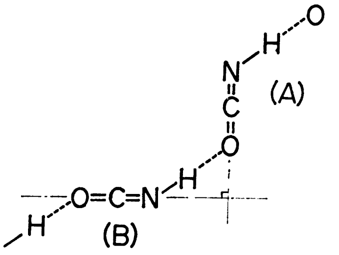


Fig. 12. Alignment of isocyanic acid molecule in the oriented solid.

Radicals which locate on both outer sides of Radicals I and II (Fig. 7), making a wider wedge-angle, should have slightly different orientations of the *g*-tensors, since they are oriented radically around the aluminum rod. Thus, a wider wedge-angle of the wedge-formed specimen makes the absorption lines broader resulting in a coalescence of the absorption lines of Radical II with those of Radical I (Fig. 10).

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