ESR Studies of Stable Free Radical Pairs in the Diamagnetic Matrix Crystal

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The radical pair system of a stable free radical, di-*p*-anisyl-nitric-oxide (DANO), has been observed in the magnetically-diluted crystal of 4,4-dimethoxy-benzophenone. The existence of the radical pair has been ascertained by the characteristic ESR absorptions, which give rise to the zero-field splitting and half-field resonance, of the powdered sample as well as by a comparison of the magnitude of the hyperfine coupling constant of the isolated radical with that of the pair system. The precise ESR measurements were performed using a single crystal containing 7.5% DANO radicals oriented well in the diamagnetic matrix. The fine structure parameters, $|D|$ and $|E|$, have been determined to be 186 Gauss and 2 Gauss respectively, from which the distance between the two radical molecules in the pair system is estimated to be 5.4 Å. In order to deduce the structures of the radical pair, the *g*-value and the hyperfine coupling constant of the isolated radical have also been determined.

Paramagnetic entities diluted in the crystals have been fruitfully investigated by electron spin resonance (ESR) techniques in order to gather information on the structures and magnetic properties of solids. Many of these works are concerned with the color center or with the radiation damage in diamagnetic matrix crystals, and some authors have studied the stable radicals in the matrix.[1-3] One of the present authors (Y.D.) has reported on the ESR measurement of the organic stable radical, diphenyl-nitric-oxide (DPNO), in a diamagnetic matrix crystal of benzophenone.[1] Analyzing the dependence of the line shape on the radical concentration, he elucidated the property of an exchange interaction between neighboring radicals and discussed the effects of exchange narrowing in the concentrated radical solid. He has also found that, in the very diluted radical crystal, the exchange interaction is so weak that the ESR line-width broadening is attributable dominantly to the dipolar interaction between two radicals. Griffith *et al.* established experimentally an exact and approximate method for determining the $\tilde{g}$- and hyperfine-tensors of the nitroxide free radical, di-*tert*-butyl-nitric-oxide.[2]

On the other hand, the triplet states of radical pairs in the irradiated organic crystals and polymers have been found by many authors.[4,5] By determining the $\tilde{g}$-tensors and the fine and hyperfine splitting tensors of the radical pair in the X-ray-irradiated single crystal of dimethyl-glyoxime at the temperature of liq. N_2, Kurita has elucidated the position of the radiation damage in the molecule and clarified the tructures of the radical pairs formed between the two neighboring molecules.[4]

The ESR of the triplet state has been utilized for the analysis of the magnetic properties of solids after the work of Bleany and Bowers.[6] One such study has been of the triplet state in the crystal of anion radical salt of 7,7,8,8-tetra-cyanoquinodimethane (TCNQ) reported by Chesnut *et al.*, who have observed the mobile triplet exciton.[7] From the analysis of the temperature dependence of the signal intensity, they have also determined the magnitude of a singlet-triplet energy separation, which is in fairly good agreement with the results of some other magnetic measurements.

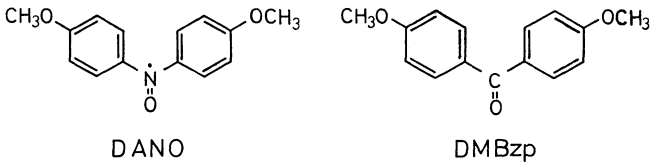


Fig. 1. Molecular structures of the radical and diamagnetic matrix.

In the present work we observed the "radical pair" of a stable free radical DANO diluted in a diamagnetic matrix crystal in order to discuss the structures and properties of DANO radical pairs. The diamagnetic matrix carefully chosen was 4,4-dimethoxy-benzophenone (DMBzp), in which the radical molecules are considered to be uniformly oriented. From the angular dependence of the ESR spectra of the radical pairs and the isolated radicals, the magnitude of the dipolar interaction is estimated and the structure of the radical pair in the diamagnetic matrix is clarified. We will discuss only the sample with a 7.5% radical concentration, the concentration dependence of the ESR spectrum will also be discussed in the last part of this paper.

Experimental

The DANO radical was synthesized by the method of Meyer *et al.*[8] After the recrystallization from ether, the

1) Y. Deguchi, This Bulletin, **34**, 910 (1961).
2) O. H. Griffith, D. W. Cornell, and H. M. McConnel, *J. Chem. Phys.*, **43**, 2909 (1965); L. J. Libertini, and O. H. Griffith, *ibid.*, **53**, 1359 (1970).
3) R. W. Holmberg, R. Livingston, and W. T. Smith, Jr., *ibid.*, **33**, 541 (1960).
4) Y. Kurita, *ibid.*, **41**, 3926 (1964); Y. Kurita, *Nippon Kagaku Zasshi*, **85**, 833 (1964).
5) M. Iwasaki and T. Ichikawa, *J. Chem. Phys.*, **46**, 2851 (1967).
6) B. Bleany and K. D. Bowers, *Proc. Roy. Soc., Ser A*, **214**, 451 (1952).
7) D. B. Chesnut and P. Arthur, Jr., *J. Chem. Phys.*, **36**, 2969 (1962); D. B. Chesnut and W. D. Phillips, *ibid.*, **35**, 1002 (1961); D. B. Chesnut, *ibid.*, **41**, 472 (1964); J. C. Bailey and D. B. Chesnut, *ibid.*, **51**, 5118 (1969).
8) K. H. Meyer and G. Brilloth, *Ber.*, **52**, 148 (1919); K. H. Meyer and W. Reppe, *ibid.*, **54**, 330 (1921).

radical and DMBzp were dissolved together in an acetone–ethanol mixed solvent. The sample crystals were obtained by recrystallization from a slow evaporation of the solvent. The radical concentration was determined by a precise ultimate analysis of the amount of nitrogen in the sample. The appearance of the mixed crystal was greatly dependent on the radical concentration. In the concentrated region, the single crystal could not be grown well; it formed only a thin, plate-like feather.[9] In the low-concentration region (especially less than 10% concentration) well crystallized samples like needles or oblique prisms were obtained. The simplicity of the ESR spectra obtained from these crystals indicate that the radical molecules are almost uniformly mixed with the matrix molecules.

The DMBzp single crystal containing 7.5% DANO radicals was grown in the form of a mono- or triclinic prism. As the crystallographic study has not yet been done, a rectangular coordinate system, a, b, and c, was defined for convenience from its shape. The c axis was selected parallel to the long edge, and the a axis, normal to the well-developed face. One of the single crystals is shown in Fig. 2, with a, b, and c axis.

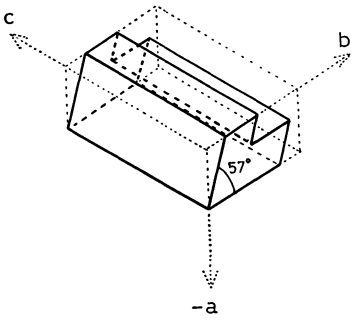


Fig. 2. A sketch of a single crystal of DMBzp containing 7.5% DANO radical. a, b, and c indicate a rectangular coordinate system adopted in the present paper.

The ESR measurements were carried out using a X-band spectrometer ME3X of JEOLCO at room temperature. The angular dependence of the ESR spectra was obtained by rotating the crystal around the a, b, or c axis, which is set perpendicular to the magnetic-field direction. The magnetic field was calibrated by the hyperfine splittings of Mn^{2+} doped in MgO and of the peroxylamine-disulfonate ion,[10] as well as by the signal of DPPH (g=2.0036).

Results

ESR Spectrum of Powdered Sample. The ESR spectrum in the g=2 region (near 3300 Gauss) is shown in Fig. 3a). In addition to a sharp absorption due to isolated radicals in the matrix, there exist a pair of broad peaks separated by about 185 Gauss and some other feeble and broad absorptions in both the higher and lower external fields. The side peaks are regarded as the triplet absorptions due to radical pairs, and so the zero-field splitting parameters, $|D|$ and $|E|$, are evaluated as 185 and 0 Gauss respectively by the method of Wasserman *et al.*[11]

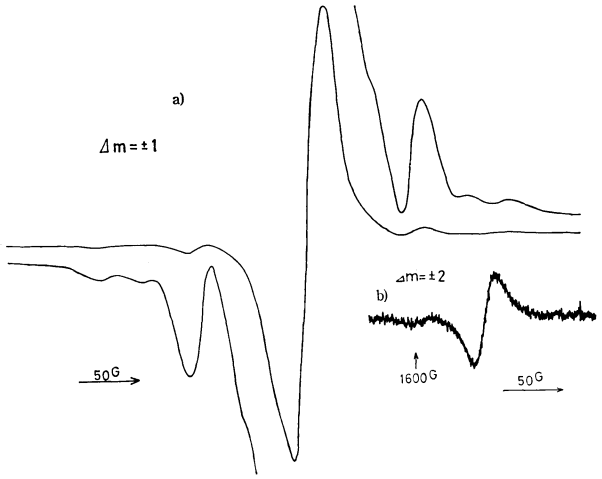


Fig. 3. a) ESR spectrum of the powdered sample of diluted DANO radical, b) $\Delta m_s = \pm 2$ transition spectrum of powdered sample.

The absorption near g=4 (1650 Gauss) shown in Fig. 3b) is the characteristic triplet absorption due to the $\Delta m_s = \pm 2$ transition. This forbidden transition was observed under the conditions of about a 100-times higher ESR spectrometer gain than that for the allowed triplet absorption, $\Delta m_s = \pm 1$ in Fig. 3a).

ESR Spectra from Single Crystal. Some of the typical ESR spectra of the single crystal are shown in Fig. 4. In (a) a pair of absorptions can be seen, one on each side of the central peak. Some other pairs of absorptions which are hidden in (a) appear in (b). When the hyperfine (hf) splitting of the central peak becomes large in some field directions, the absorptions at both sides split further into several peaks, as

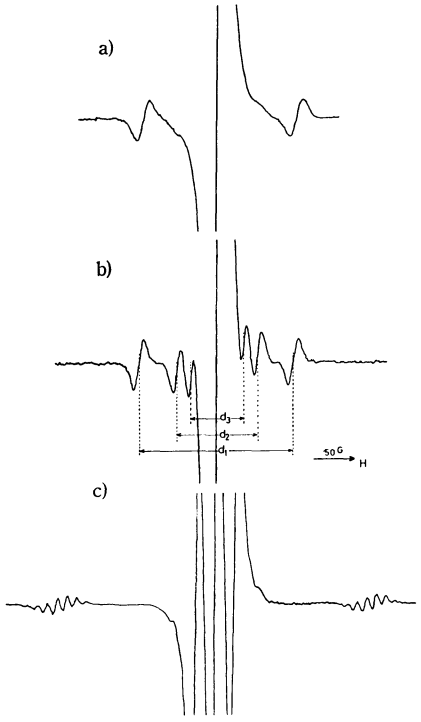


Fig. 4. Some of the ESR spectra of a single crystal of diluted DANO radical. The spectra are explained in the text. a) a//H, b) b//H, c) c//H.

9) A. W. Hanson, *Acta. Crystallogr.*, **6**, 32 (1953).
10) G. E. Pake, J. Townsent, and S. I. Weissman, *Phys. Rev*, **85**, 682 (1952).
11) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

is sohwn in (c). These can be attributed to the hf structure of two nitrogen nuclei in triplet-state radical pairs. This explanation is also supported by the fact that the splitting width of the side peaks is about half as wide as that of the central peak. The observed splittings due to the zero-field interaction are denoted by d_1, d_2, and d_3 in Fig. 4b).

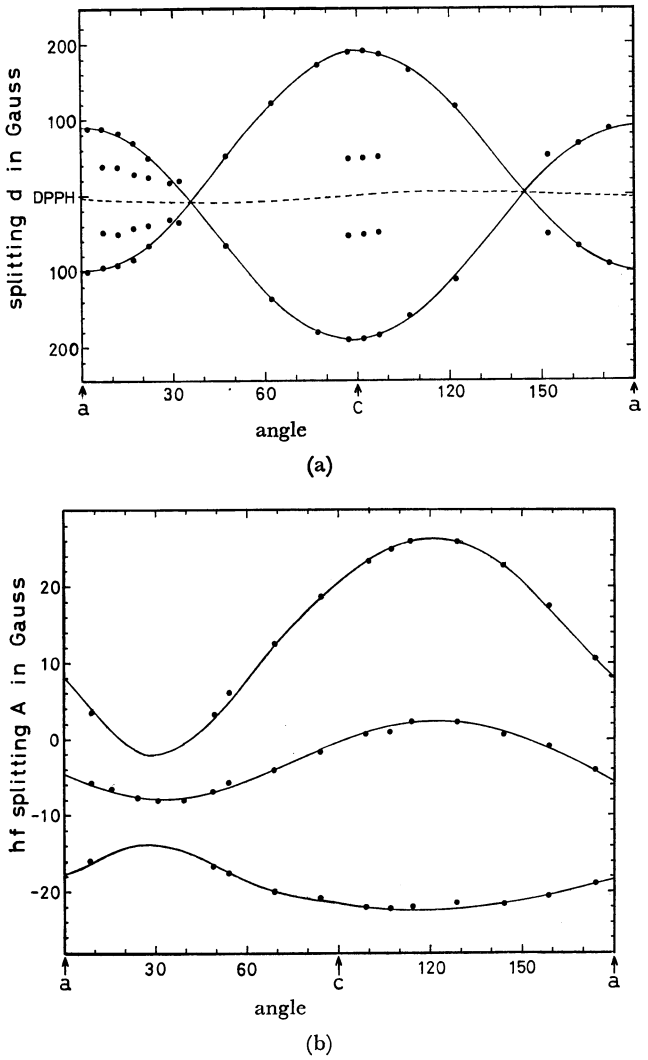


Fig. 5. Angular variation of the spectral line position in the ca plane. The position are measured from the absorption of DPPH.
a) Doublet splittings due to radical pair.
b) Nitrogen hf splittings of isolated radical.

The angular dependences of d_1 and d_2, as measured with the external magnetic field, H, in the ac plane, are shown in Fig. 5a). The nitrogen hf splitting and the g-value (denoted as g_{isol}) of the isolated radicals in the matrix, measured on the same plane, are also shown in Fig. 5b). The well-separated structures of the central peak and the simple angular variation in the hf structure parameter and g_{isol} indicate that the $\tilde{\boldsymbol{g}}$- or $\tilde{\boldsymbol{A}}_N$-tensor has the same principal axes and principal values for all radicals in the matrix.

The d_1 of the triplet-state absorption as well as the g_{isol} and hf parameters of the isolated radicals are also discussed.

Discussion

Two-spin System. In order to analyze the zero-field splittings observed, we can introduce the spin Hamiltonian of the triplet state of the radical pair, assuming that the principal axes of the $\tilde{\boldsymbol{g}}$-tensors of the two radicals are common;

$$\boldsymbol{H} = \beta \boldsymbol{H}\cdot\tilde{\boldsymbol{g}}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\tilde{\boldsymbol{D}}\cdot\boldsymbol{S} \quad (1)$$

where $\boldsymbol{S}=\boldsymbol{S}^1+\boldsymbol{S}^{11}$ and where the subscripts 1 and 11 indicate the radicals which form the radical-pair system. The energy levels and the separation, d, of the dipole-dipole doublet splitting at an arbitrary crystal orientation relative to the magnetic field are analyzed by Kurita[4] in the case of the axially-symmetric $\tilde{\boldsymbol{D}}$-tensor; this method is well suited for triplet species of the radical pair in the irradiated single crystal. For the nonaxial $\tilde{\boldsymbol{D}}$-tensor, if the principal axis can be set parallel or perpendicular to the external field, $\boldsymbol{H}$, the method of analysis without approximation has been reported by many authors.[12,13] In this paper the approximate method using the perturbation theory given by Itoh[14] will be used, for it needs no supposition about its crystal structure and principal-axis direction. In this method, the following assumptions are made: 1) the g-anisotropy is small, and 2) $g\beta\boldsymbol{H} \gg |D|, |E|$. Both of these assumptions are considered to be valid in the present case of the organic radical.

The method may be summarized as follows: the second term of Eq. (1) is treated as a perturbing Hamiltonian, and then the $\tilde{\boldsymbol{D}}$-tensor is represented as D_{ij} (i, j=a, b, c) on the basis of the rectangular coordinate axes, a, b, and c, which are fixed in the crystal. When the crystal is rotated around the c axis and when the external field, $\boldsymbol{H}$, makes an angle, θ, with the a axis, the resonance-field separation of the two absroptions is given, after second-order perturbation calculations, by:

$$d = 3(g_e/g_{zz})(D_{aa}\cos^2\theta + 2D_{ab}\sin\theta\cdot\cos\theta + D_{bb}\sin^2\theta) \quad (2)$$

where g_e is the g-factor of the free electron, g_{zz} is the zz-component of the $\tilde{\boldsymbol{g}}$-tensor, and z refers to the external-field direction. The tensor components with respect to the experimental coordinate system were determined by the least-squares method. Then, the $\tilde{\boldsymbol{D}}$-tensor was diagonalized to obtain the principal values.

We will not discuss the hfs of the radical-pair system in detail, but when $\boldsymbol{A}^1=\boldsymbol{A}^{11}$ the hfs Hamiltonian can be expressed[4] as:

$$\boldsymbol{H}_{hfs} = (1/2)\boldsymbol{I}\cdot\tilde{\boldsymbol{A}}\cdot\boldsymbol{S} \quad (3)$$

This equation suggests that a hf coupling of the pair system will be observed with a half of that of the isolated radicals, as may be seen in Fig. 4c).

One-spin System. An organic radical oriented in

12) R. W. Brandon, G. L. Closs, and C. A. Hutchison, *ibid.*, **37**, 1878 (1962); C. A. Hutchison and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958), **34**, 908 (1961).
13) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).
14) K. Itoh, "Jikken Kagaku Koza," ed. by the Chemical Society of Japan, Maruzen, Tokyo (1967), Vol. 13, p. 153.

the diamagnetic crystal can be described by the following Hamiltonian:

$$\boldsymbol{H} = \beta \boldsymbol{S}\cdot\tilde{\boldsymbol{g}}\cdot\boldsymbol{H} + \boldsymbol{I}\cdot\tilde{\boldsymbol{A}}\cdot\boldsymbol{S} \quad (4)$$

The results of the calculation when $I=1$, and especially in nitroxide radicals, have been reported by Griffith *et al.*[2] In the present paper, as the crystal structure is not known, the method described in the textbook of Carrington and McLachlan[15] is used. The principal values of $\tilde{g}$- and hf-tensors and their directions can be obtained by the next equations:

$$(g_{obs})^2 = g_{aa}^2\cos^2\theta + 2g_{ab}^2\sin\theta\cdot\cos\theta + g_{bb}^2\sin^2\theta \quad (5a)$$

$$(A_{obs})^2 = A_{aa}^2\cos^2\theta + 2A_{ab}^2\sin\theta\cdot\cos\theta + A_{bb}^2\sin^2\theta \quad (5b)$$

where θ and the a, b, and c indices are defined as in the discussion of the two-spin system and where g^2_{ij} and A^2_{ij} are defined as the ij components of the $\boldsymbol{g}^2=({}^t\tilde{\boldsymbol{g}}\cdot\tilde{\boldsymbol{g}})$ and $\boldsymbol{A}^2=({}^t\tilde{\boldsymbol{A}}\cdot\tilde{\boldsymbol{A}})$ tensors respectively. The treatment of Eq. (5) is the same as that of Eq. (2).

Table 1. Experimental parameters for DANO radical in DMBzp

	Principal value	Angle with a	b	c	Parameters
	Radical pair				
D_x	± 63.7 ±0.5	0	90	90	$\|D\|=186\pm1$ G
D_y	± 59.7 ±0.5	90	0	90	$\|E\|=2\pm1$ G
D_z	∓124.4 ±1.0	90	90	0	$r=5.4\pm0.11$ Å
	Isolated radical				
g_1	2.0089±0.0002	31	92	59	
g_2	2.0059±0.0002	86	4	90	
g_3	2.0022±0.0002	121	89	31	
A_1	9.4±0.1	33	97	58	
A_2	4.4±0.1	84	7	87	
A_3	24.6±0.2	122	90	32	

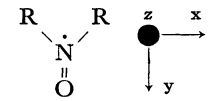
Structure of the Two-spin System in the Matrix. The $\tilde{\boldsymbol{D}}$-tensor is analyzed for the side peak, d_1, which is clearly observed in all the external-field directions. The principal values and principal axes of the $\tilde{\boldsymbol{D}}$-, $\tilde{\boldsymbol{g}}$-, and hf-tensors are shown in Table 1. The D value is consistent with the data estimated from the powdered sample in Fig. 3a). By applying the measured D and E values to the equation of the resonance field of the $\Delta m_s=\pm2$ transition, $g\beta H_{dq}=\sqrt{(1/4)(h\nu)-(1/3)(D^2+3E^2)}$, one can obtain $H_{dq}=1620$ Gauss, which also agrees well with our measurement of the powdered sample (Fig. 3b).

The radical pairs in the organic crystal produced by irradiation have been reported to be $E=0$ or $E/D\neq0$: this is considered to be due to the localization of the unpaired electron in the molecule.[16] This holds also in the present case for the DANO stable radical pair. Comparing with a transition-metal complex or a TCNQ salt, in which the E/D value is not small (~0.1), the unpaired electron of the DANO radical, which has a spin density of more than 70% on the N=O bond, may be considered as a point dipole. By applying the equation: $|D|=3g^2\beta^2/2r^3$, where r is the distance between the two radicals, one can obtain $r=5.4$ Å. From the principal axes of $\tilde{\boldsymbol{D}}$, one can also determine the direction of the radical-pair axis to be parallel to the c axis.

Since one-site spectra are obtained for the isolated radical in any crystalline orientation, all the DANO radicals are considered to be oriented with the N=O bond aligned along the unique direction in the matrix even if there is more than one site in a unit cell. Consequently, one can assume that the $\tilde{\boldsymbol{g}}$-tensor orientation of radicals forming a radical pair is the same as that of the isolated radicals.

Kikuchi has calculated the g-values of several nitric-oxide radicals using the CNDO/2 molecular orbital calculation method.[17] The calculated principal g-values in the case of H_2NO and a conjugated radical, diphenyl-nitric-oxide (DPNO), are cited in Table 2, along with the principal axes from his paper. The principal values are in fairly good agreement with those of our results shown in Table 1.

Table 2. Calculated g-values for some nitric-oxide radicals[17]

	$H_2N\dot{O}$	DPNO	Axis
g_x	2.0062	2.0046	
g_y	2.0091	2.0086	
g_z	2.0023	2.0023	
g_{av}	2.0059	2.0051	

Assuming the same principal axis system, one can estimate the orientation of the paired DANO molecules in the matrix crystal. Figure 6 shows a model of the two-spin system obtained from the relative orientation of the $\tilde{\boldsymbol{D}}$- and $\tilde{\boldsymbol{g}}$-tensors. Although the crystal structure of the matrix crystal is not known, the distance of the two radical molecules, r, and their alignment in the matrix determined experimentally may be compared with the crystal structure of DANO[9] cited in Fig. 7. The crystal structure of the DANO radical in Fig. 7 is orthorhombic, with four sites per unit cell; all the N=O bonds of molecules, however,

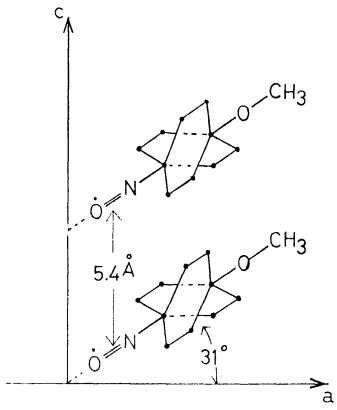


Fig. 6. A model of two spin system in a diamagnetic matrix crystal.

15) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York (1967).

16) H. Ohigashi and Y. Kurita, This Bulletin, **40**, 704 (1967).

17) O. Kikuchi, *ibid.*, **42**, 47, 1187, 1472 (1969).

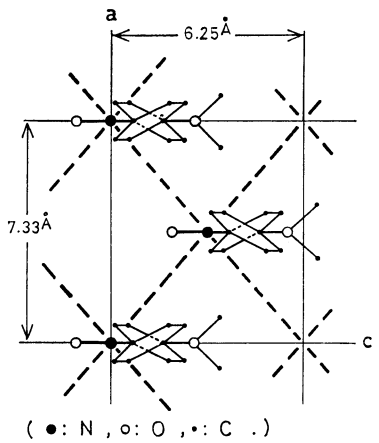


Fig. 7. Crystal structure of DANO reported by Hanson,[9] as viewed on a (010) projection
------: the nearest neighbor direction (4.81 Å)

are aligned along the c axis direction of the crystal. The distance of the nearest neighbor molecule of DANO is 4.81 Å, which is of the same order of experimental value, 5.4 Å, for DANO in DMBzp. Unlike the DANO crystal with the two distinct directions of the nearest-neighbor molecules, there is only one nearest-neighbor direction in DMBzp. This may mean a lower symmetry of the DMBzp crystal than that of the DANO crystal.

Our model for the radical pairs diluted in DMBzp is appropriate considering the alignment and the packing structure of the molecules in the matrix crystal.

Effect of the Radical Concentration. The radical concentration has great effects on both the line shape and the triplet absorption intensity. In the crystal with more than 30% DANO, the triplet absorption was not clearly observed because of the exchange narrowing effect. In a very diluted system, on the other hand, it was observed with a very weak intensity. For the 7.5% sample, the main subject of the present paper, the integrated absorption intensity ratio of the side peaks to the main peak was estimated to be 1900/11000~0.17. Assuming a one-dimensional lattice containing the radical molecule with the fractional concentration, c, the probabilities of making the radical pair and the isolated radical are approximately $2c^2$ and $c-2c^2$ respectively in the small c region. By this simple model with $c=0.075$, one can enumerate the ratio, $2c^2/(c-2c^2)$, as 0.18, which is consistent with the experimental intensity ratio.

The other peaks in Fig. 4b), whose intensities are nearly equal to each other, are considered to be due to the next-nearest neighbor molecules in the matrix. The other weak absorptions in Fig. 3a) suggest the possibility of another radical pair or a three-spin system. No more detailed discussions of these ESR absorptions can be done at present because the crystal structure of a matrix crystal is not known.

Conclusion

The existence of the stable radical triplet state is confirmed from: (1) the ESR line shape of the powdered sample; (2) the D and E values of the triplet state obtained from measurements of powdered and single-crystal samples, (3) a comparison of the hf coupling in the pair system with that in the isolated radical; (4) the forbidden transition of $\Delta m_s=\pm 2$, and (5) the ESR intensity compared with the estimation of the chance of making the two-spin system in the small radical-concentration region. The magnetic properties of this triplet radical pair and isolated radicals have been discussed. The structure of the radical pair in the diamagnetic matrix has been proposed on the basis of an analysis of the ESR spectra.

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