Weak ferromagnetism and antiferromagnetic ordering of 2*p* electrons in the organic radical compound 2,4,6-triphenylverdazyl

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High-quality sizable single crystals of the radical compound 2,4,6-triphenylverdazyl (TPV) have been prepared and their magnetic properties investigated by neutron-diffraction and magnetization measurements. Neutron-diffraction peaks corresponding to long-range antiferromagnetic ordering have been observed below the Néel temperature of 1.78 K. The determined spin structure has intrachain antiferromagnetic coupling extending toward the *c* axis with the spins aligned to the *b* axis. Magnetization measurements also reveal that weak ferromagnetism appears below T_N with the ferromagnetic components in directions parallel and perpendicular to the spin direction. The magnetization curve shows no hysteresis, which is consistent with small anisotropy of 2*p* electrons in organic magnets.

Magnetic moments in organic radical compounds originate from an unpaired 2*p* electron in molecular orbitals. Hence the magnetic properties of such compounds are expected to exhibit a unique nature compared with that of the usual magnetic materials. Until now a number of magnetic organic compounds have been investigated by means of various experimental methods such as magnetization, specific heat, ESR, NMR, etc., and it is found that some materials show antiferromagnetic behavior.[1-5] Very recently, several organic crystals have been found to exhibit ferromagnetism.[6,7] However, magnetically ordered states in these organic magnetic materials are not well understood.

Neutron diffraction is one of the most powerful experimental techniques for the investigation of magnetically ordered states. However, because of the difficulties due to low spin density and very high neutron background arising from hydrogen atoms, the application of this technique to organic compounds has not been extensive and has been confined to investigations of the field-induced magnetic form factor in the paramagnetic state[8,9] except for powder-diffraction work on tanol suberate.[10] Furthermore, all of the works have been confined to the study of magnetic systems with unpaired electrons on the N-O bond where the spin density localizes.[8-10]

In the present work, we studied the antiferromagnetic ordering of a radical compound 2,4,6-triphenylverdazyl (TPV) by neutron-diffraction and magnetization measurements using single-crystal samples. TPV is a radical of the formula ($C_{20}N_4H_{17}$) with a planar molecule shown in Fig. 1(a), where a verdazyl ring at the center is surrounded by three phenyl groups. The crystal structure is orthorhombic, with the space group $P2_12_12_1$ and four molecules are accommodated in a unit cell. The lattice parameters are $a=18.467$ Å, $b=9.854$ Å, and $c=8.965$ Å.[11] The crystal structure projected on the *a*-*c* plane is shown in Fig. 1(b). A distinctive feature of the crystal structure is the zigzag packing of the molecules toward the *c* direction.

Until now, the magnetic properties of TPV have been investigated by magnetization, ESR, and specific-heat measurements, and TPV is found to be an antiferromagnet with a Néel temperature of 1.7 K.[3,4] A low-dimensional magnetic nature is also suggested from the magnetic-susceptibility and specific-heat measurements.[3,4] Azuma *et al.*[3] pointed out that the spin density distributes over four nitrogen atoms in the verdazyl ring, which means delocalization of the unpaired electron over the TPV molecule. Such a delocalization of unpaired electrons in the most characteristic point of the magnetism of TPV, in contrast to the localized electron on N-O bonds. To reveal how this delocalization is reflected in the magnetic properties is most important, and the present spin-structure study is a step toward understanding such magnetic properties of this radical.

Polycrystalline samples of TPV were prepared in a similar manner to that of Kuhn and Trischmann[12] and large single-crystal samples were grown by using recrystallization from acetone solution. The crystals thus obtained have a hexagonal plate with its plane normal to the *a* axis and its long edge along the *c* axis. The largest crystal we succeeded in growing has a weight of 18 mg and a mosaic width of 20 min.

The magnetization of the TPV crystals was measured

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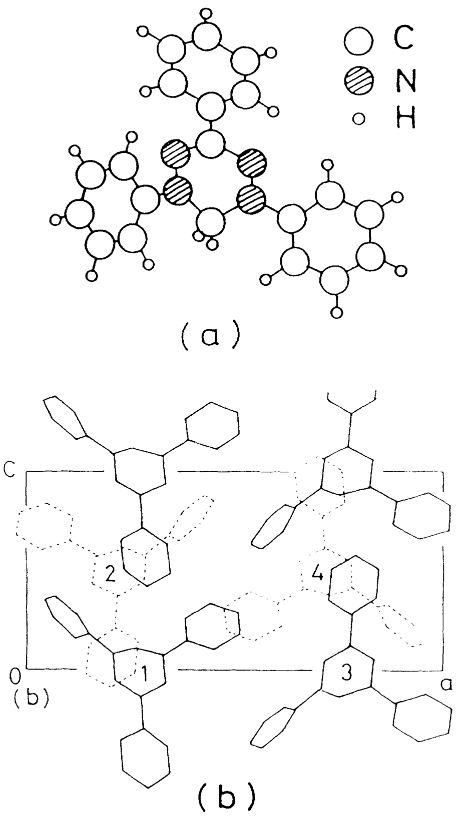

FIG. 1. (a) Molecular structure of TPV. (b) Crystal structure of TPV projected on the *a*-*c* plane. The dotted figures show the molecules in a lower section.

by a superconducting quantum interference device (SQUID) magnetometer. As shown in Fig. 2, the magnetic susceptibility for the *a* axis follows a Curie-Weiss law above 20 K with a Weiss temperature of -8 K, but below that it deviates from Curie-Weiss behavior, having a broad maximum around 5 K. The temperature dependence of the magnetic susceptibility for other directions exhibits similar behavior to that shown in Fig. 2, indicating the possibility of a Heisenberg-type low-dimensional system as suggested by Azuma *et al.*[3] The effective magnetic moment determined from the Curie constant is $1.64\mu_B$, which is a little smaller than that expected from spin $\frac{1}{2}$. The magnetic susceptibility shows an abrupt increase just below the Néel temperature. We find that this sharp increase of the susceptibility corresponds to the onset of weak ferromagnetism associated with three-dimensional antiferromagnetic ordering. Azuma *et al.*[3] derived the Néel temperature as a point corresponding to the susceptibility minimum around 1.7 K, but the reason for the minimum has not been explained. Our results indicate that the onset of ferromagnetism makes the minimum in the susceptibility at T_N. Because the increase of the magnetization at T_N is very sharp in lower fields, the Néel temperature of TPV was precisely determined to be as 1.78 K from this transition.

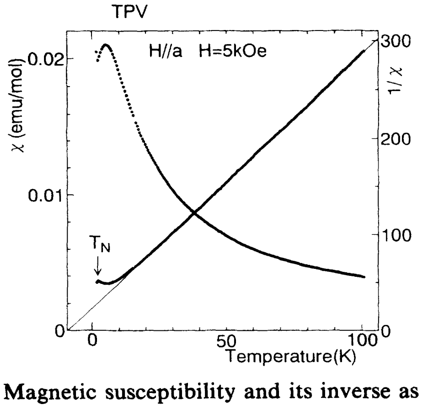

FIG. 2. Magnetic susceptibility and its inverse as a function of temperature measured under an applied field of 5 kOe along the *a* axis.

Figure 3 shows the magnetization curves for the field direction parallel to the *a*, *b*, and *c* axis, respectively. At 1.70 K the extrapolation of the linear part of the magnetization to zero field shows a finite magnetization. These results clearly indicate the weak ferromagnetism of TPV. The magnitude of the ferromagnetic component is 3 emu/mol at 1.70 K, corresponding to the order of $10^{-3}\mu_B$/mol, which is a reasonable value for the usual weak ferromagnet. The magnetization curve shows no hysteresis, probably due to the very small magnetic anisotropy observed in organic ferromagnets.[7] The magnetic susceptibility in the antiferromagnetic state has a maximum value for the *a* axis and a slightly lower value for the *c* axis, and a minimum value for the *b* axis. These results suggest that in the antiferromagnetic state the spin direction may be parallel or nearly parallel to the *b* axis.

Neutron-diffraction experiments were carried out with the Tohoku University triple-axis spectrometer TOPAN installed at the JRR-3M reactor at JAERI Tokai. Neutrons of a wavelength of 2.44 Å monochromated by (002) plane of a pyrolitic graphite (PG) were used as the incident beams and the contamination of half-wavelength neutrons was removed by a PG filter. In order to reduce the background from the inelastic scattering by hydrogen atoms, an elastic scan was made with a PG analyzer. A ^{4}He cryostat was used to decrease the sample temperature and the lowest temperature of 1.37 K was obtained, which corresponds to 0.80 times the Néel temperature.

A search for magnetic Bragg scattering was carried out for reflections in the a^*-b^* and the a^*-c^* reciprocal planes. It is found that the (101) peak has magnetic scattering, but other peaks such as (100), (010), (001), etc.

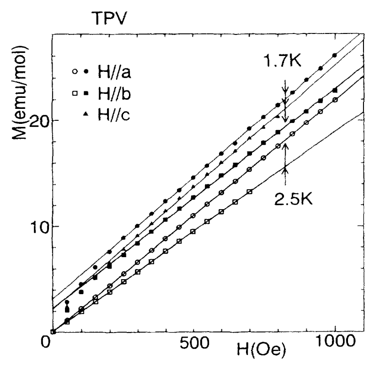

FIG. 3. Magnetization as a function of magnetic fields measured at 1.70 and 2.50 K.

have no detectable magnetic intensity within the experimental resolution. Figure 4(a) shows the temperature dependence of the peak intensity of the (101) reflection. As the temperature is decreased the peak intensity increases below the Néel temperature of 1.78 K, indicating a magnetic origin. Figure 4(b) shows the difference in intensities of the (101) peak measured at 1.38 and 2.00 K. Although the intensities are not large, the magnetic part of the reflection makes a clear peak with a width comparable with the instrumental resolution shown in the figure as a solid line.

Here we describe the details of the magnetic structure. Magnetic reflections with nonintegral indices have not been observed. Hence the magnetic unit cell must coincide with the chemical one. Since the unit cell includes four molecules, three types of collinear spin-structure models A, B, and C are possible: model A has the spin arrangement $+,-,-,+$, corresponding to the sequence of molecules 1,2,3,4 shown in Fig. 1(b), model B has $+,+,-,-$, and model C has $+,-,+,-$.

The magnetic structure factors for these spin structures were calculated assuming that in the TPV molecule only four nitrogen atoms in a verdazyl ring carry magnetic moments with the same magnitude, with their spins keeping each parallel, because the spin density distributes equivalently on the four nitrogen atoms.[3] The observed and calculated magnetic structure factors for lower-index lines are summarized in Table I, in which F^2_{obs} indicates the Lorenz-factor-corrected intensity which is deduced by subtracting the integrated intensity measured above T_N from that at 1.38 K for the indicated reflections. The calculated structure factors show contrasting intensity distributions depending on the model. Model A has (101) as a main peak and very weak intensity on other peaks, whereas model B has (100) as the main peak and has very weak intensity on other peaks listed in the table. Model C has a similar tendency to model B except that (100) is replaced by (001). If the (100) peak had the magnetic intensity predicted by model B, the observation of its magnetic intensity would be much easier than that of (101) because there is no nuclear intensity on this peak. However, as mentioned above, no detectable intensity has been observed on the forbidden lines of (100) and (001). Thus models B and C can be rejected. On the other hand, model A explains quite well the experimental data as shown in the table. Therefore we can conclude that model A is the most plausible spin structure of TPV.

TABLE I. Calculated (for models A, B, and C) and observed magnetic structure factors for several lower-index lines in arbitrary units. The observed one is the difference of integrated intensities $I(T=1.38)-I(T>T_N)$. Two sets of data are shown for the (110) reflection.

Index	F^2_{obs}	F^2_{cal} (A)	F^2_{cal} (B)	F^2_{cal} (C)
100	0.15±0.14	0.02	0.96	0.00
010	0.06±0.32	0.00	0.00	0.00
001	0.01±0.15	0.01	0.00	0.82
101	0.68±0.24	0.68	0.02	0.01
110	0.95±0.73	0.14	0.00	0.00
	−2.60±0.73			

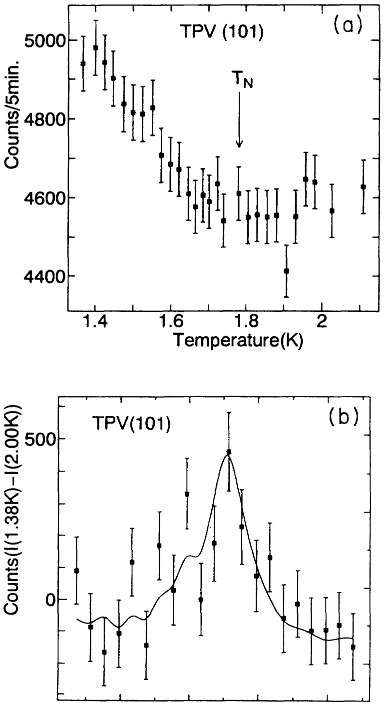

FIG. 4. (a) Temperature dependence of the peak intensities of the (101) reflection. (b) Magnetic part of the (101) reflection deduced from the difference in intensities measured at 1.38 and 2.00 K. The (101) peak at 2.00 K with a reduced scale is inserted as a solid line to show the resolution function.

In this model, the (110) peak should have appreciable magnetic scattering as shown in the table; however, the experimental value exhibits a large fluctuation of the intensity. This is because the (110) reflection has very large nuclear intensity, more than several hundreds times greater than that of the (101) reflection, and the expected magnetic intensity is only 20% of that of the (101) reflection.

In this calculation, the spin direction is assumed to be along the b axis, which is found to explain the neutron data quite well. This result is also supported by the magnetic-susceptibility data. Therefore we can conclude that the magnetic moments align almost perpendicular to the plane of the verdazyl group, namely, normal to the molecular plane. The value of the magnetic moment per TPV molecule determined from comparing nuclear and magnetic intensities is $(0.6\pm0.2)\mu_B$ at 1.38 K, which can be extrapolated to be $(0.8\pm0.3)\mu_B$ at 0 K. This value is smaller than that determined from the magnetic susceptibility; however, this includes large experimental errors due to poor counting statistics and in addition uncertain factors arising from the crystal parameters which might vary at low temperatures, while the crystal parameters at room temperature were used in this analysis. Therefore, for further experiments, crystal parameters determined at low temperature must be used and the counting statistics must be improved. The smaller value of the magnetic moment is very interesting in connection with a spin reduction in the spin $\frac{1}{2}$ Heisenberg chain,[13] but as mentioned above the accuracy is not enough to discuss this problem.

The spin structure determined in the present experiments is shown in Fig. 5. The antiferromagnetic chain extends toward the *c* direction, keeping antiphase coupling between the neighboring chains in the *a*-*c* plane and in-phase coupling between the neighboring chains in the *b*-*c* plane. The separation between magnetic moments located at the center of the verdazyl ring in the chain is 5.5 Å and that between the chain in the *a* and *b* directions is about 9 Å. Therefore, the exchange interaction between the chains is considered to be very weak and the antiferromagnetic interaction in the chain is dominant, leading to a low-dimensional nature as anticipated from the susceptibility and specific-heat data. A predicted spin-structure model based on McConnell's spin-density Hamiltonian[14] is consistent with the present spin structure.

In this experiment a weak ferromagnetism has been observed in TPV crystals. As this crystal has no center of inversion symmetry, it is reasonable to consider that the weak ferromagnetism arises from a Dzyaloshinksi-Moriya interaction. Since three twofold screw axes are present in this crystal, the ferromagnetic components will appear along all the crystallographic axes. But the ferromagnetic components along the spin direction (*b* axis) should be zero by this mechanism; however, in the present experiment the component along the *b* axis has a value comparable with that of the *c* axis. This point is difficult to interpret by the Dzyaloshinski-Moriya mechanism. This may be explained by very weak anisotropy of the 2*p* electrons, but we need further study to understand this problem.

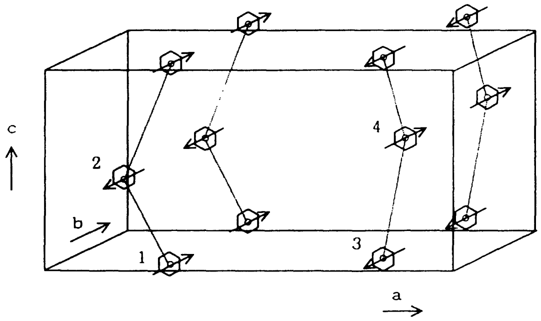

FIG. 5. Spin structure determined by the present experiment. The hexagon shows the verdazyl ring and the arrow shows the spin direction. The dotted line indicates the zigzag chain of spins toward the *c* axis.

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[1] J. Yamauchi, Bull. Chem. Soc. Jpn. **44**, 2301 (1971).

[2] W. Duffy, Jr., J. F. Dubach, P. A. Pianetta, J. F. Deck, D. L. Strandburg, and A. R. Miedema, J. Chem. Phys. **56**, 2555 (1972).

[3] N. Azuma, J. Yamauchi, K. Mukai, H. Ohya-Nishiguchi, and Y. Deguchi, Bull. Chem. Soc. Jpn. **46**, 2728 (1973).

[4] K. Takeda, H. Deguchi, T. Hoshiko, K. Konishi, K. Takahashi, and J. Yamauchi, J. Phys. Soc. Jpn. **58**, 3361 (1989).

[5] K. Uchino, J. Yamauchi, H. Ohyama-Nishiguchi, and Y. Deguchi, Bull. Chem. Soc. Jpn. **47**, 285 (1974).

[6] M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Agawa, T. Inabe, and Y. Maruyama, Chem. Lett. **1991**, 1225 (1991).

[7] R. Chiarelli, M. A. Novak, A. Rassat, and J. L. Tholence, Nature **363**, 147 (1993).

[8] P. J. Brown, A. Capiomont, B. Gillon, and J. Schweizer, J. Magn. Magn. Mater. **14**, 289 (1979).

[9] J. X. Boucherle, B. Gillon, J. Maruni, and J. Schweizer, J. Phys. C **7**, 227 (1982).

[10] A. Benoit, J. Flouquet, B. Gillon, and J. Schweizer, J. Magn. Magn. Mater. **31-34**, 1155 (1983).

[11] D. E. Williams, Acta Crystallogr. Sect. B **29**, 96 (1973).

[12] R. Kuhn and H. Trischmann, Monatsh. Chem. **95**, 457 (1964).

[13] L. S. J. M. Henkens, M. W. van Tol, K. M. Diederix, T. O. Klaassen, and N. J. Poulis, Phys. Rev. Lett. **36**, 1252 (1976).

[14] N. Azuma, Bull. Chem. Soc. Jpn. **55**, 1357 (1982).