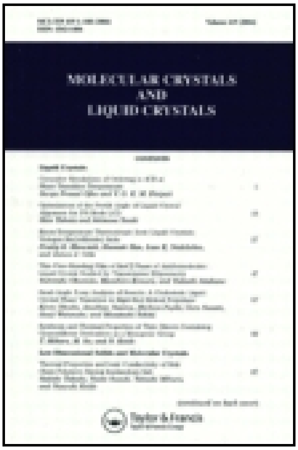

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# Pressure Effect of Organic Ferromagnetic Radical Crystal p-Cl-$C_6H_4CH=N$-TEMPO

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# Pressure Effect of Organic Ferromagnetic Radical Crystal *p*-Cl-$C_6H_4CH=N$-TEMPO

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4-(*p*-chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-yloxyl) (*p*-Cl-$C_6H_4CH=N$-TEMPO) radical crystal is the organic bulk-ferromagnet with $T_c(P_0) = 0.28$ K ($P_0$; ambient pressure). In realizing the ferromagnetic intermolecular interaction, the spin polarization on the hydrogen of the methyl moiety is considered to play an important role. We expected that the pressurization would change the environment around the methyl moiety, and influence the bulk-ferromagnetic transition. So we measured the ac magnetic susceptibility under the pressure up to 10.9 kbar. With increasing pressure, the periodical down-and-up of $T_c(P)$ and the pressure-induced ferro- to antiferromagnetic transition were observed. These experimental results may suggest that the pressurization destroys the bulk-ferromagnetism of *p*-Cl-$C_6H_4CH=N$-TEMPO as in β-phase *p*-NPNN, making the methyl moiety rotate.

*Keywords:* pressure effect; organic bulk-ferromagnet

## INTRODUCTION

Since the discovery of β-phase *p*-nitrophenyl nitronyl nitroxide (abbreviated as β-phase *p*-NPNN; $T_c(P_0) = 0.61$ K ($P_0$; ambient pressure))[1], some organic bulk-ferromagnets have been reported[2-5]. But the transition temperature ($T_c(P_0)$), below which the bulk-ferromagnetism can be realized, has not exceeded 1.5 K, and the mechanism has not been clarified in detail yet. We have ever studied the pressure effect of some organic radical crystals, by controlling the overlap of molecular orbitals continuously[6-12]. In the study of $\beta$-phase *p*-NPNN, the pressure-induced ferromagnetic (F) to antiferromagnetic (AF) transition was observed as the first experimental fact in organic magnets[9,10]. This result of $\beta$-phase *p*-NPNN suggests that the organic bulk-ferromagnetism is barely realized on the delicate balance between F exchange paths and AF ones[9,10]. The transition from F to AF is considered to be caused by the rotation of the nitrophenyl group by the pressurization[13].

4-(*p*-chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-yloxyl (abbreviated as *p*-Cl-$C_6H_4CH{=}N$-TEMPO) is the organic bulk-ferromagnet with $T_c(P_0) = 0.28$ K[4]. The state below $T_c$ is confirmed to be of the bulk-ferromagnet from the result of the magnetization curve[4]. In this series of TEMPO compounds, the spin polarization on the hydrogen of the methyl moiety (abbreviated as $\beta$-hydrogen) is considered to play an important role[14,15]. Figure 1 shows the molecular structure of *p*-Cl-$C_6H_4CH{=}N$-TEMPO and the spin polarization mechanism through the intervening methyl moieties. The molecular orbital calculation reveals that a slight negative spin density is induced on the $\beta$-hydrogen, and in the case of *p*-Cl-$C_6H_4CH{=}N$-TEMPO, the spin density on the $\beta$-hydrogen is calculated to be -0.1 $\sim$ -0.2 %[14]. The $\pi^*$ orbital on the N-O moiety and the nearest 1s orbital on the $\beta$-hydrogen in the neighboring molecule are not geometrically orthogonal, and the negative spin on the $\beta$-hydrogen can induce the positive spin on the adjacent N-O site through the orbital overlap. Thus the ferromanetic coupling between the N-O sites, which are about 6 $\mathring{A}$ apart each other, can be explained as drawn in Fig. 1(b). But at present, the spin polarization on the $\beta$-hydrogen has not been considered in the case of $\beta$-phase *p*-NPNN. We attempted the pressure effect of *p*-Cl-$C_6H_4CH{=}N$-TEMPO to get new experimental proof of the

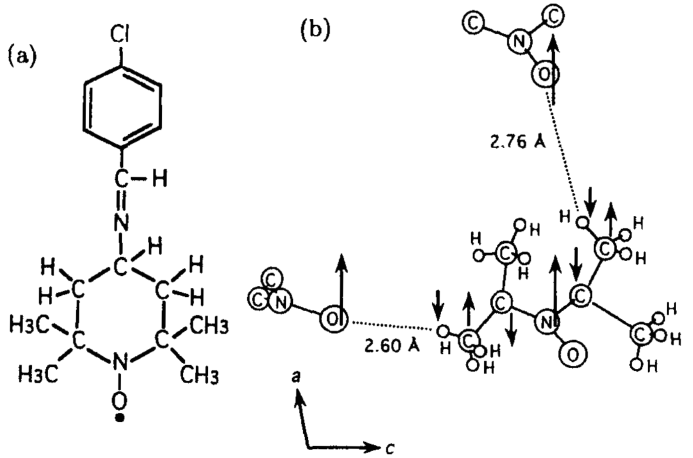

FIGURE 1: (a) Molecular structure of $p$-Cl-$C_6H_4$CH=N-TEMPO and (b) the spin polarization mechanism through the intervening methyl moieties[4,14].

above $\beta$-hydrogen mechanism. We measured the ac magnetic susceptibility of $p$-Cl-$C_6H_4$CH=N-TEMPO radical crystal under the pressure up to 10.9 kbar, expecting that the pressurization would change the environment around the $\beta$-hydrogen, and the bulk-ferromagnetism might be destroyed.

## EXPERIMENTAL

The preparation of $p$-Cl-$C_6H_4$CH=N-TEMPO has been already described elsewhere [4]. The crystal structure of $p$-Cl-$C_6H_4$CH=N-TEMPO belongs to monoclinic with the space group $P2_1/c$, and the lattice parameters $a = 5.909(3)$ Å, $b = 24.475(5)$ Å, $c = 11.421(4)$ Å and $\beta = 103.84(3)°$[4].

The ac magnetic susceptibility ($\chi$) of polycrystalline $p$-Cl-$C_6H_4$CH=N-TEMPO was measured by the ac-bridge ($H_{ac} = 0.1$ Oe peak-to-peak and

$f$ = 15.9 Hz) in the hydrostatic pressure up to 10.9 kbar. The hydrostatic pressure was attained with the Cu-Be pressure clamp cell, in which the polycrystalline sample of $p$-Cl-$C_6H_4CH{=}N$-TEMPO (75.9 mg) mixed with the pressure transmission oil (Apiezon-K grease; 36.1 mg) and some tips of Al (3.9 mg) was enclosed in the teflon sample cell. The absolute value of real pressure at low temperatures was estimated by the pressure dependence of superconducting transition temperature $T_s(P)$ of Al with $T_s(P_0)$ = 1.17 K[16]. The susceptibility of the blank cell (i.e. the clamp cell, Al etc.) is so small as to be ignored for that of $p$-Cl-$C_6H_4CH{=}N$-TEMPO.

## EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the pressure dependences of $\chi'$. Here we define $T_c(P)$ as the temperature with the maximum of $\chi'$, since the remnant magnetization of $p$-Cl-$C_6H_4CH{=}N$-TEMPO exists below the temperature with the maximum of $\chi$ in the experiment of $\mu$SR at ambient pressure[17]. The behavior similar to $\chi'$ is also seen in the pressure dependence of $\chi''$, whose magnitude is about 30 % of $\chi'$. At first, we notice that the intensity of $\chi'$ reduces gradually as increasing pressure. This fact makes us image that the F intermolecular interaction, which triggers the bulk-ferromagnetism, becomes weaker by the pressurization, and alternatively some inherent AF interaction may be comming into effect. In the case of $p$-Cl-$C_6H_4CH{=}N$-TEMPO, the main interaction is of two-dimensional interaction[18]. Secondary, $T_c(P)$ shows a strange change (i.e. down-up-down-up-down-up) as increasing the pressure. This pressure dependence of $T_c(P)$ is shown in Fig. 3. We can see a periodicity with the period of about 4 kbar. This periodical change of $T_c(P)$ may be brought about by the periodical change of exchange interactions, which trigger the three-dimensional magnetic ordering. At this stage without the crystal data under the pressure, we cannot discuss the exchange interaction paths in

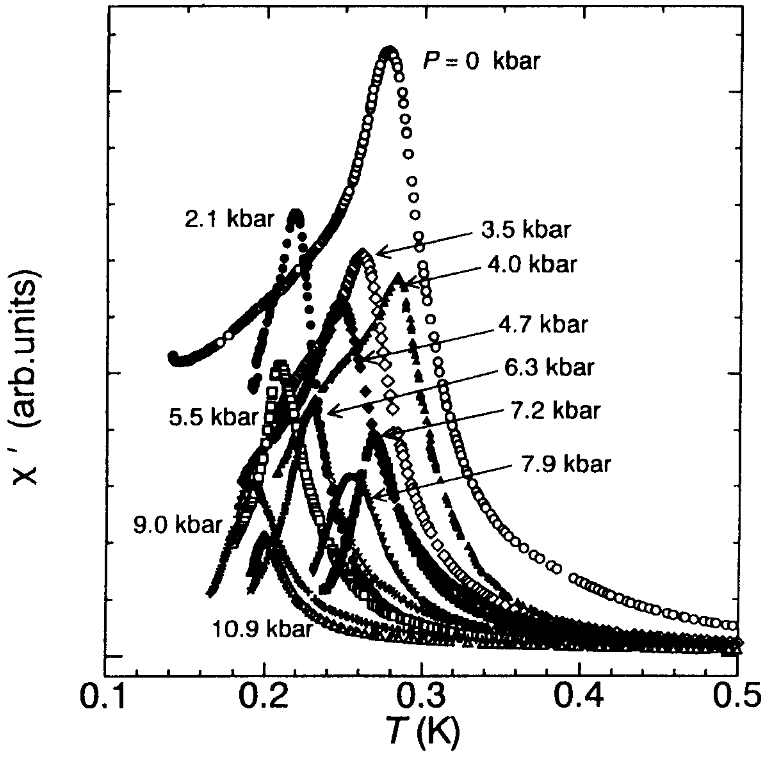

FIGURE 2: Pressure dependence of $\chi'$ of $p$-Cl-$C_6H_4CH$=N-TEMPO in the pressure region up to 10.9 kbar.

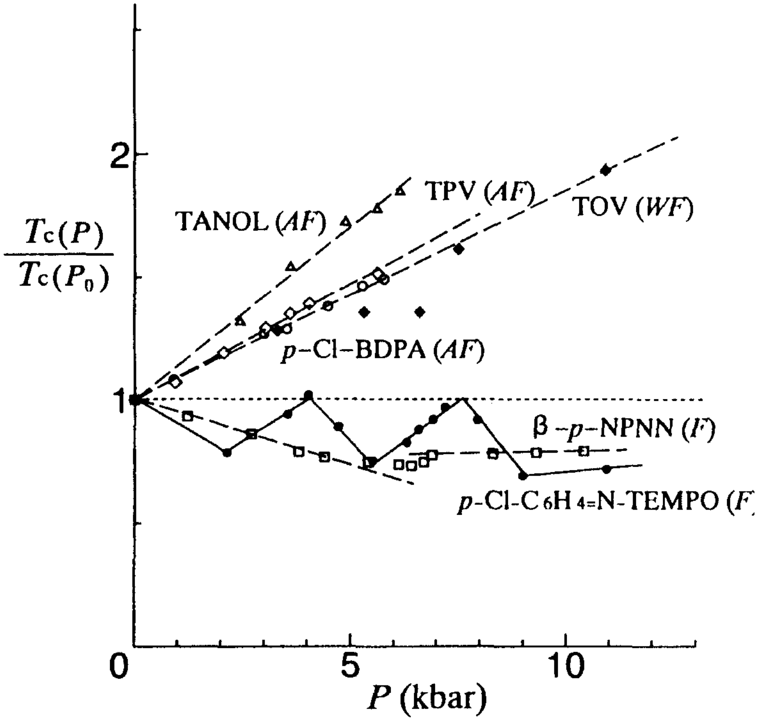

FIGURE 3: Pressure dependence of $T_c(P)$ of *p*-Cl-$C_6H_4$CH=N-TEMPO (•). Here each $T_c(P)$ is normalized with $T_c(P_0)$. The results of TANOL (△), TPV (◇), *p*-Cl-BDPA (○), TOV (◆) and *β*-*p*-NPNN (□) were referred to refs.6,7, ref.7, ref.7, ref.12 and refs.9,10, respectively. AF, WF and F stand for the antiferromagnet, the weak-ferromagnet and the ferromagnet, respectively.

detail, but we assume that the above periodical change of exchange interaction originates from the pressure-induced rotation of the methyl moiety. The rotation of the methyl moiety, of course, changes the position of $\beta$-hydrogen, and hence changes the balance between F exchange paths and AF ones. The conformation of piperidine-ring (-$C_5N$-) is found to be the most stable chair form by an X-ray crystallography[4]. Thus, its conformation would not change appreciably by the pressurization. On the other hand, the methyl groups attached to the piperidine-ring can rotate with relative ease. Hence we consider that the periodical change of $T_c(P)$ will be brought about by the rotation of the methyl moiety. Finally we notice that there is a slight difference between the shape of $\chi'$ at $P < 5.5$ kbar and that at $P \geq 5.5$ kbar: For $P < 5.5$ kbar, we can see a trace or a shoulder of the low-temperature tail of $\chi'(P_0)$. At $P \geq 5.5$ kbar, however, $\chi'(P)$ comes to show a sharp and monotonous peak around $T_c(P)$. Concerning this point, we will comment later at the discussion in the magnetization.

In the case of $\beta$-phase $p$-NPNN, the pressure-induced F to AF transition occurs under the pressure about 6.5 kbar. This phenomenon was confirmed mainly by the measurement of the magnetization ($M$). In order to confirm whether the bulk-ferromagnetism of $p$-Cl-$C_6H_4CH$=N-TEMPO is maintained or not under the pressure, we measured $M$ under some pressures in the temperature region below $T_c(P)$. $M$ is obtained by integrating $\chi'$ under the magnetic field ($H$) against $H$. Figure 4 shows the $M$-$H$ curve in the weak $H$ region below 50 Oe. At the ambient pressure, $M$ rapidly grows up to 75 % of the saturation moment in the applied $H$ up to $H = 50$ Oe. $M$ saturates at $H \simeq 150$ Oe, and this result is consistent with the previous work by Nogami *et al.*[4]. As increasing the pressure, the growth of $M$ gradually become restricted. At $P \geq 6.9$ kbar, the phenomenon of the spin flop, which is the characteristic of the bulk-antiferromagnetic ordering, can be clearly seen. This behavior of $M$ peculiar to the spin flop corresponds to the shape of $\chi'$ as seen at $P \geq 5.5$ kbar, which rapidly approaches to zero just below $T_c(P)$. Judging from

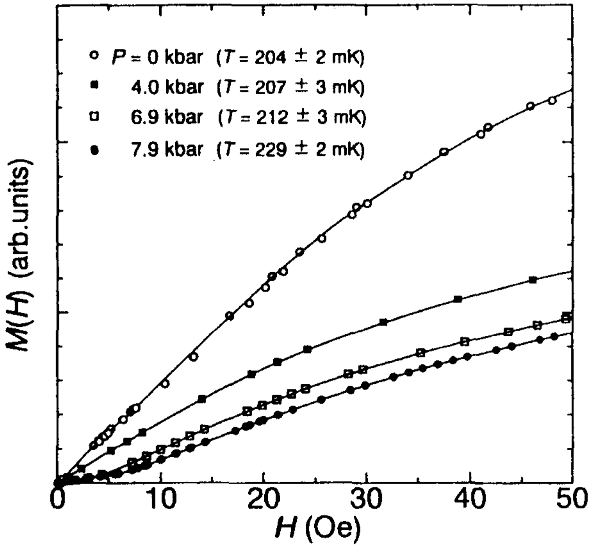

FIGURE 4: Magnetization of $p$-Cl-$C_6H_4CH$=N-TEMPO under the pressure. Each solid curve is a guide for the eye.

the behavior of $\chi'(P)$, we can suppose that there is a transition from F to AF around $P = 5.5$ kbar.

## CONCLUSION

We measured the ac magnetic susceptibility of $p$-Cl-$C_6H_4CH$=N-TEMPO under the pressure, and found the pressure-induced ferro- to antiferromagnetic transition accompanying the periodical down-and-up of $T_c(P)$. The observation of pressure-induced ferro- to antiferromagnetic transition is the second example next to the case of $\beta$-phase $p$-NPNN, and the periodical down-and-up of $T_c(P)$ by the pressurization may be the first observation in the organic radical crystals. These results teach us the following physics: The organic bulk-ferromagnetism can be realized on the delicate balance between the ferromagnetic exchange paths and the antiferromagnetic ones. We consider that the periodical down-and-up of $T_c(P)$ will suggest the rotation of the methyl moiety, bearing in mind that the conformation of the piperidine-ring itself would not change appreciably by the pressurization. The radical rotation on the exchange interactions is theoretically suggested in the pressure effect of $\beta$-phase $p$-NPNN by Okumura *et al.*[13]. In such a TEMPO compound as $C_6H_5$-CH=N-TEMPO, Kawakami *et al.* have suggested that the rotation of the methyl moiety causes the periodical change of the intermolecular interaction[15]. The present result of $p$-Cl-$C_6H_4$CH=N-TEMPO is more decisive experimental evidence for detecting the rotation of a part of oraganic molecule by the pressurization. Finally in connection with the $\beta$-hydrogen mechanism for the intermolecular interaction, the periodical change of $T_c(P)$ strongly supports that the spin polarization on the hydrogen of the methyl moiety of $p$-Cl-$C_6H_4$CH=N-TEMPO plays an important role to realize the ferromagnetic intermolecular interaction. Now we are performing the crystal structure analysis under the pressure, in order to confirm the rotation of a part of $p$-Cl-$C_6H_4$CH=N-TEMPO. Furthermore we are interested in the NMR measurement under the pressure, to detect the motion of the methyl moiety under the pressure directly.

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