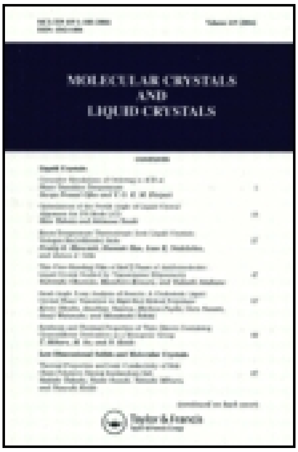

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Antiferromagnetic Long-Range Ordering of Organic Free Radicals Under High Pressure

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ANTIFERROMAGNETIC LONG-RANGE ORDERING OF ORGANIC FREE RADICALS UNDER HIGH PRESSURE

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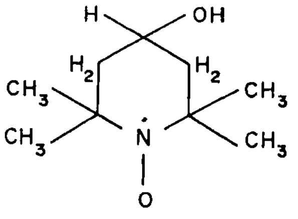
Abstract Heat capacity measurements of some organic free radicals were carried out under high pressure in the liquid helium temperature region. The magnetic phase-transition temperatures increased linearly with the applied hydrostatic pressure, and normalized slopes were much larger than those of the usual inorganic magnetic materials.

INTRODUCTION

One-dimensional magnetic compounds with a quantum system S=1/2 are fascinating from experimental as well as theoretical point of view. It is, however, rather difficult to prepare ideal quantum systems without anisotropies which may cause some extrinsic energy gaps and make intrinsic quantum effect obscure. Therefore, attention has been paied to unpaired electron systems of organic free radicals. These magnetic compounds usually possess almost isotropic g-values and some undergo purely magnetic phase transitions at low temperatures.

In this paper we would like to report on the results of heat capacity measurements of some organic free radicals under hydrostatic pressure in a liquid-helium-temperature region, and discuss the pressure variations of the magnetic phase-transition temperature in terms of low-dimensionality in magnetic interaction schemes of the organic free radicals. Since the magnetic origin of the organic free radicals is the unpaired electron occupying $2p_z$ π-orbital whose electron distribution is uniaxial, it is likely to form low-dimensional magnetic interations,[1] that is, linear magnetic chains or magnetic planes. It is well established that the three-dimensional magnetic ordering is governed by those main interactions within the chain or plane and in addition weak inter-chain or inter-plane interactions.[2] These exchange interactions between the unpaired electrons are very isotropic, that is, expressed by a Heisenberg-type Hamiltonian, $-2J_{ij}S_iS_j$, reflecting a small g-anisotropy of the free radicals.[1] The applied pressure would have an influence upon those exchange-interaction parameters J_{ij} and, therefore, upon the enhancement of magnetic transition temperatures. The organic free radicals discussed here are 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (**1**), triphenyl verdazyl (**2**), 1,3-bisdiphenylene-2-p-chlorophenyl allyl (**3**). These



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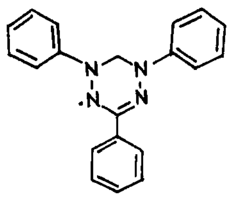

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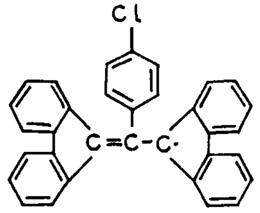

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radicals are antiferromagnets having the Néel temperatures 0.49,[3] 1.7,[4] and 3.25 K,[5] respectively.

EXPERIMENTAL

The samples of **1**, **2**, and **3** were prepared by the same methods employed in the previous work, and purified a few times through recrystallization.[6-8] The results of elementary analyses for carbon, hydrogen, and nitrogen were in good accord with the values calculated for the respective radicals. Adiabatic calorimetry of the usual type was employed, by which heat capacities were measured in the temperature range between 0.5 and 15 K for **1** and 0.8 and 10 K for **2** and **3**. The procedure of measuring heat capacities under hydrostatic pressures was almost the same as carried out before.[9] In the case of **1**, for example, a powdered sample of 0.389 g and a pressure transmitting oil, Apieson-J oil, of 0.325 g were put into a pressure-clamp cell together with a small tip of Sn metal, which was used for calibrating the value of pressure from its pressure dependence of the superconducting transition temperature.[10] We paied much attention to the pressure dependence of the heat capacity of the transmitting oil which had to be subtracted from the total heat capacity. In view of the heat capacities of the sample, the transmitting oil, and the clamp cell, at less than 5 K, the sample made relatively larger contribution to the total heat capacity. Therefore, the experimental accuracy below 5 K was estimated to be relatively good.

RESULTS AND DISCUSSION

First we summarize magnetic behaviors of **1**, **2**, and **3** at ambient pressure (p_0). Basically all of the magnetic susceptibilities can be analyzed in terms of a one-dimensional Heisenberg Hamiltonian with the exchange parameter J,

$$\mathscr{H} = -2J \sum_{\langle ij \rangle} S_i S_j \qquad (1)$$

In the case of **2**, however, one-dimensionality is a little modified, that is, railroad-trestle-type interaction network was pointed out.[4] Virtually almost the same exchange parameters for **1**, **2**, and **3** were obtained from the magnetic heat capacity measurements. It is well understood that an inter-chain exchange interaction J' can trigger the magnetic phase transiton at Nêel temperature T_N. It is possible to speculate the value J' if one assumes a certain model. We used Oguchi's relationship between J, J', and T_N deduced from the Green function method.[11] These magnetic data are summarized in Table I.

Figure 1 shows magnetic heat capacities of **1** at some representative pressures which were extracted precisely from the observed data taking the lattice contribution into account. The result in the temperature region below 0.5 K is referred to the literature.[15]

TABLE I Magnetic data of **1**, **2**, and **3**.

radical	J/k/K	T_N/K	J/kT_N	|J'/J|	|J'/k|	comment and reference
1	-5.0	0.49	-10.2	0.004	0.02	one-dimensional 1, 3, 4, 10, 12, 13
2	-6.0	1.70	-3.5	0.025	0.15	railroad trestle 4, 14
3	-4.4	3.25	-1.4	0.2	0.88	one-dimensional 1, 5, 13

The characteristic broad maximum of the magnetic heat capacity shifts to the higher temperature with increasing pressure, keeping the same shape of a heat capacity curve as in the case of $p=p_0$. This shift is mainly associated with the increase of the intra-chain interaction J(p) with increasing p. The three-dimensional ordering at T_N which accompanies a sharp peak in the magnetic heat capacity shifts also to the higher temperature side with the sharpness of the peak becoming obscure. Next we estimate the pressure dependence of the inter-chain interaction J'(p) using J(p) and $T_N(p)$ obtained above. We utilized two evaluation methods, the mean molecular field theory and Oguchi's Green function method, in which the following relations are deduced.

$$k_B T_N(p) \simeq S^2 \sqrt{2z|J(p)\cdot J'(p)|} \tag{2}$$

$$k_B T_N(p)/J(p) = 4S(S+1)/3I(\eta) \tag{3}$$

where z is the number of inter-chain interaction paths and I(η) is the following integral with $\eta = |J'(p)/J(p)|$.

$$I(\eta) = \frac{1}{\pi^3} \int\int_0^\pi \int \frac{dq_x\, dq_y\, dq_z}{\eta(1-\cos q_x)+\eta(1-\cos q_y)+(1-\cos q_z)} \tag{4}$$

Both theories predict nearly coincident results on the inter-chain interaction when it is compared as a pressure dependence of a normalized form like $J'(p)/J'(p_0)$. The relative changes of $J(p)/J(p_0)$,

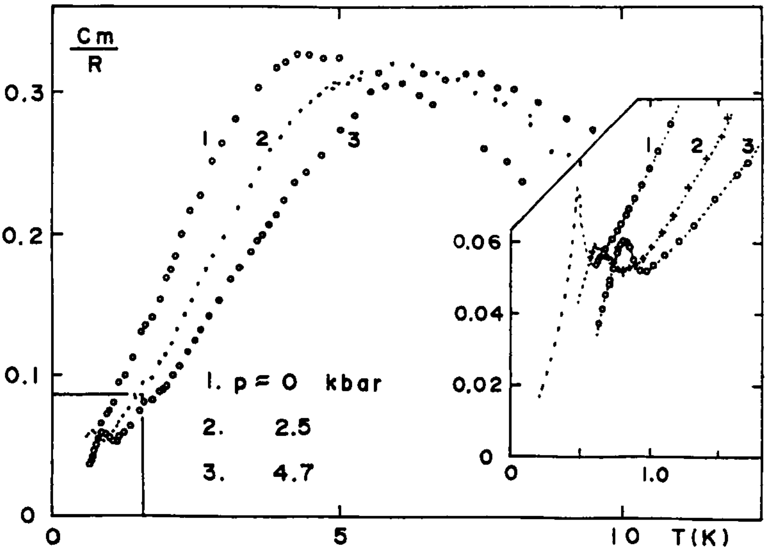


FIGURE 1 Magnetic heat capacity of **1** at some hydrostatic pressures.

$T_N(p)/T_N(p_0)$, and $J'(p)/J'(p_0)$ are depicted in Figure 2, and expressed linearly as a function of p as follows.

$J(p)/J(p_0)=1+0.076p$ (5)

$T_N(p)/T_N(p_0)=1+0.15p$ (6)

$J'(p)/J'(p_0)=1+0.22p$ (line a in Figure 2) (7)

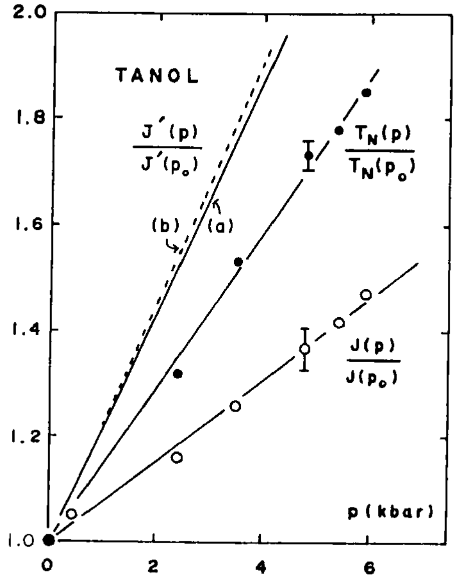


FIGURE 2 Pressure dependence of the transition temperature T_N, intra-chain interaction J, and inter-chain interaction J' of **1**.
(a) and (b) are derived from the mean field theory and the Green function method, respectively.

In the cases of **2** and **3**, only the pressure dependence of the Néel temperature can be discussed because of the experimental accuracy. For instance, original heat capacity data of **2** are shown in Figure 3, from which reliable intra-chain interaction J is difficult to obtain, and much more inter-chain interaction J'. The peak anomaly associated the magnetic phase transition at $T_N(p)$ in Figure 3 becomes obscure with the compression of the sample as in the case of **1**, probably either due to the possible inhomogeneity of the magnetic interactions under hydrostatic pressures or intrisic reason that the electron spins are more delocalized over the molecule in these organic free radicals **2** and **3**. However, the value of $T_N(p)$ is rather reliable under 5 K. Thus, the pressure dependences of T_N were determined from Figures 4-a, b as

$T_N(p)/T_N(p_0)=1+0.093p$ for **2** (8)

$T_N(p)/T_N(p_0)=1+0.10p$ for **3** (9)

Considering the $T_N(p_0)=3.2$ K for **3**, the Néel temperature is enhanced up as high as 5.03 K at 5.4 kbar.[16] This value belongs to the highest

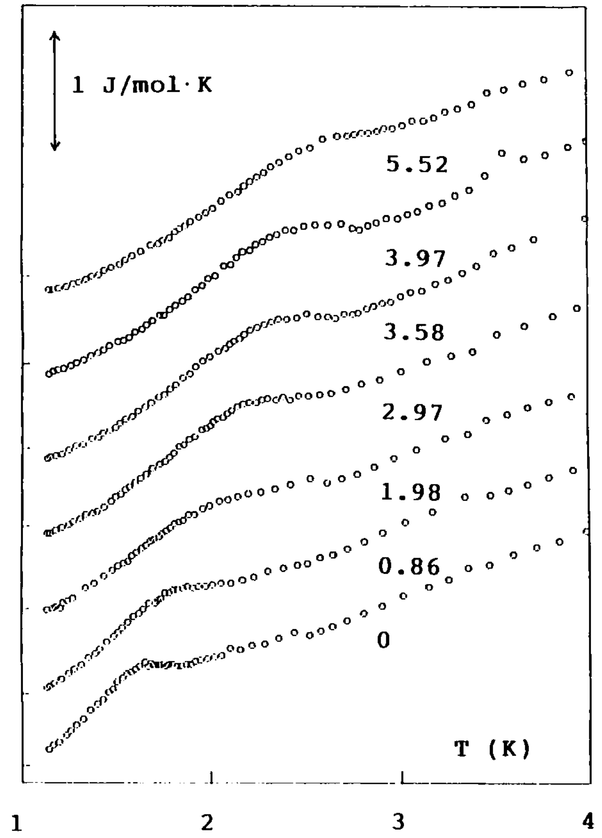
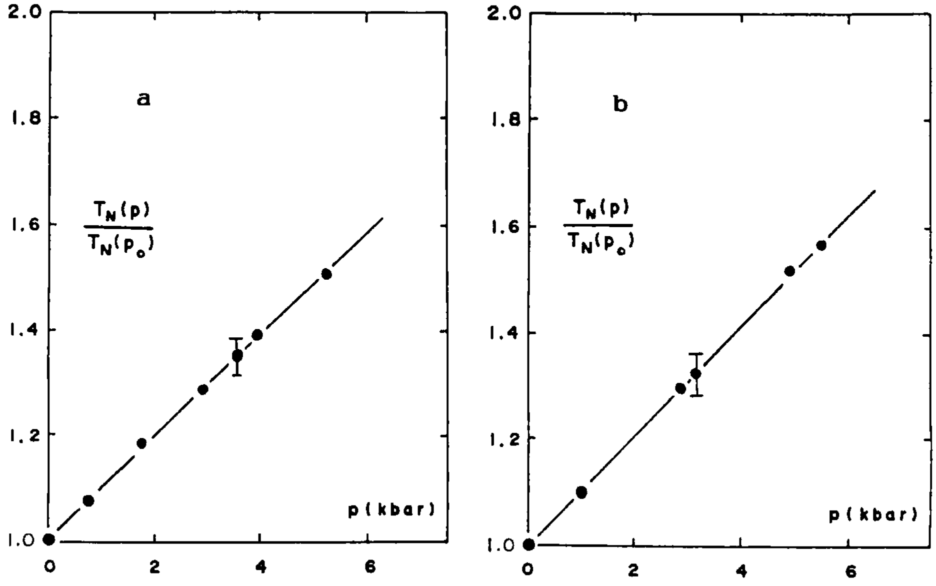


FIGURE 3 Heat capacity of 2 at some hydrostatic pressures indicated (kbar).



FIGURES 4-a, b Pressure dependences of the transition temperatures T_N of 2 (a) and 3 (b).

category for the magnetic long-range ordering temperatures in the organic free radical crystals.[17]

The pressure dependences of $T_N(p)$, $J(p)$, and $J'(p)$ of **1** disclose that the application of the hydrostatic pressure gives relatively stronger effect on the inter-chain interaction rather than the intra-chain interaction. One of the reasons may be the weak molecular interaction or chemical bond along the inter-chain directions compared to those within the intra-chain. Because of this anisotropic pressure effect upon the interactions, the law of correspondence for the p-T phase diagram as examined in $CuCl_2 2H_2O$ can not be expected in **1** and probably in organic free radicals in general.

As a measure of the pressure dependence, we compare for **1**, **2**, and **3** the quantity γ defined as $(1/T_N(p_0))\cdot dT_N(p)/dp$; 0.15, 0.093, and 0.10, respectively. The biggest value for **1** may be related to the fact that **1** is a very good low-dimensional compound as shown in Table I, that is, J' is very small. This also means much greater enhancement of the inter-chain interaction J' by pressure and hence of the transition temperature. This is another characteristic property of the organic free radicals. In fact, as one can see from Table II which shows comparison of γ between our results and those of inorganic magnetic materials,[18] the pressure dependence of T_N of a free radical group is remarkable. This may be attributable to the softness of molecular crystals including organic free radicals and moreover to the great enhancement of the weak inter-chain interaction J'.

One more interesting property of the organic free radicals as compared to inorganic compounds listed in Table II is an interaction mechanism different from the usual superexchange scheme.[10] The 10-th power law is possibly applied for inorganic magnetic systems.[19] If we write $J(p) \propto J(r) \propto r^{-n}$, n can be estimated from $n \sim -d(\ln J)/d(\ln r) = (1/J)dJ/dp\cdot(1/\alpha_T)$ where $\alpha_T = -d(\ln r)/dp$. For superexchange interaction $n \sim 10$ is phenomenologically conjectured. Since there is no knowledge about α_T of **1**, **2**, or **3**, we can tentatively assume the same order of α_T values of molecular crystals, for example, 0.002 $kbar^{-1}$ at 300 K for diphenylamine. Then much rapid dependence on r rather than 10-th power is predicted. This characteristic distance dependence for the organic free radicals could contribute to the large dependence of J(p) and hence T_N.

TABLE II Coefficients of the pressure dependence of T_N.

compound	γ /kbar^{-1}	compound	γ /kbar^{-1}	radical	γ /kbar^{-1}
$(NH_4)_2CuBr_4 2H_2O$	0.019	$CuCl_2 2H_2O$	0.048	1	0.15
$K_2CuCl_4 2H_2O$	-0.016	DMMC	0.026	2	0.093
$MnBr_2 4H_2O$	0.014	TMMC($p < 3.0$ kbar)	0.019	3	0.10
$Mn(HCOO)_2 2H_2O$	0.022	TMMC($p \geq 3.2$ kbar)	0.058		
$CoCl_2 6H_2O$	0.038				

Finally it is useful to comment that, according to the pressure dependences of T_N in Figures 2 and 4, no anomalous changes such as discontinuity or deflection in the pressure-dependent slopes were observed, indicating that there seems no new magnetic phase within the pressure applied in this experiment.

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