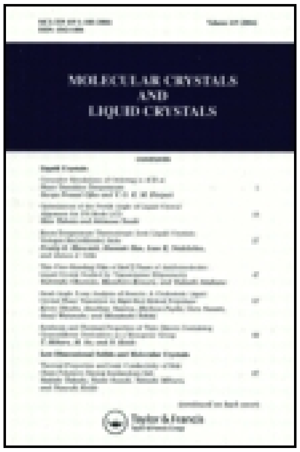


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gmcl19

Pressure Effects on Intermolecular Interactions in Genuine Organic Radical Crystals

Kazuyoshi Takeda [a], Masaki Mito [a], Masakazu Ito [a], Tatsuya Kawae [a], Masako Hitaka [a], Mttsuhide Matsubara [b] & Kazuo Mukai [b]

[a] Department of Applied Science, Faculty of Engineering, Kyushu University, Fukuoka, 812-81, Japan

[b] Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, 790, Japan

Version of record first published: 04 Oct 2006

To cite this article: Kazuyoshi Takeda, Masaki Mito, Masakazu Ito, Tatsuya Kawae, Masako Hitaka, Mttsuhide Matsubara & Kazuo Mukai (1997): Pressure Effects on Intermolecular Interactions in Genuine Organic Radical Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 177-184

To link to this article: http://dx.doi.org/10.1080/10587259708044564

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 177–184
Reprints available directly from the publisher
Photocopying permitted by license only

PRESSURE EFFECTS ON INTERMOLECULAR INTERACTIONS IN GENUINE ORGANIC RADICAL CRYSTALS

KAZUYOSHI TAKEDA, MASAKI MITO, MASAKAZU ITO,
TATSUYA KAWAE, MASAKO HITAKA, MITSUHIDE MATSUBARA[A],
AND KAZUO MUKAI[A]
Department of Applied Science, Faculty of Engineering, Kyushu University,
Fukuoka 812-81,Japan; [A]Department of Chemistry, Faculty of Science,
Ehime University, Matsuyama 790, Japan

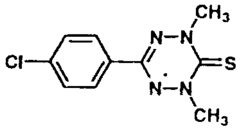
Abstract Pressure induced enhancement of magnetic ordering temperature has been found in a quasi-one-dimensional ferromagnetic organic radical crystal, 3-(4-chlorophenyl)-1,5-dimethyl-6-thioxoverdazyl by the measurements of magnetic susceptibility and heat capacity under hydrostatic pressures up to 13 kbar (1.3 GPa). This pressure dependence is the opposite direction to the results in the ferromagnetic β-phase *p*-NPNN observed recently, and in the same way as in ordinary antiferromagnets. The effects of pressurization suggest to bring about frustration in kinetic exchange interactions via various charge transfer paths between molecular orbitals.

INTRODUCTION

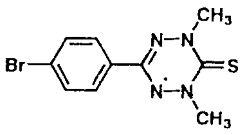
In the course of studying pressure effects of magnetic transition temperature of genuine organic radical crystals, we have found that the Curie temperature of the ferromagnetic β-phase *p*-NPNN (nitrophenyl nitronyl nitroxide) crystal exceptionally decreases with increasing pressure,[1] whereas almost all of the antiferromagnets indicate the enhancement of the Néel temperature with pressure.[2–4] Recently, we have reported another organic ferromagnetic radical crystals, 3-(4-chlorophenyl)-1,5-dimethyl-6-thioxoverdazyl (*p*-CDTV), which shows characteristics of prototype one-dimensional quantum ferromagnet above its magnetic transition temperature of

T_m=0.67±0.02 K.[5,6] Ferromagnetism in the ordered state of this crystal is inferred from rather gradual temperature dependence of magnetic susceptibility below T_m, as in ordered state of ordinary ferromagnets. However, some detailed experiments at low temperatures will be necessary before concluding its ferromagnetism.

In this paper, we will focus on the pressure effects on *p*-CDTV crystal to examine whether the pressure induced reduction of the Curie temperature is a inherent tendency of organic ferromagnets. We will see that the transition temperature of *p*-CDTV increases with pressure, and compare the results with pressure effects for various compounds. The pressurization is suggested to bring about frustration in kinetic exchange interactions among the pressure-influenced molecular orbitals, as well as potential exchange interactions.



p-CDTV



p-BDTV

EXPERIMENTALS

The measurements of magnetic susceptibility and heat capacity under hydrostatic pressures were performed as previously reported.[1,7] The powdered sample of *p*-CDTV (0.151 gr) was clamped in a CuBe pressure bomb (12$\phi\times$ 90 mm) with the pressure transmission oil (Apiezon J) and a small tip of metallic Sn for the pressure calibration at low temperatures.

The sample of *p*-CDTV was prepared according to a procedure similar to that used by Neugebauer et al..[8] At the present stage of syntheses, only fine powdered sample is available; large single crystals enough to be used for determination of crystal structure have not been obtained.

RESULTS AND DISCUSSION

The magnetic properties of *p*-CDTV and the bromide compound *p*-BDTV crystals were studied in detail, especially in their paramagnetic state. Both of them show the characteristics of prototype one-dimensional (1-d) quantum Heisenberg system.[5,6] Figure 1 shows the inverse magnetic susceptibility of *p*-CDTV crystal below 20 K, which can be explained by the theories for 1-d Heisenberg ferromagnet with $S=1/2$ and the intrachain exchange constant $|J_1/k_B|=5.5$ K.[5,6,9] By the weak interchain interaction $|z'J'/J| \simeq 4 \times 10^{-2}$, three-dimensional ordering is induced at $T_m=0.67\pm0.02$ K.

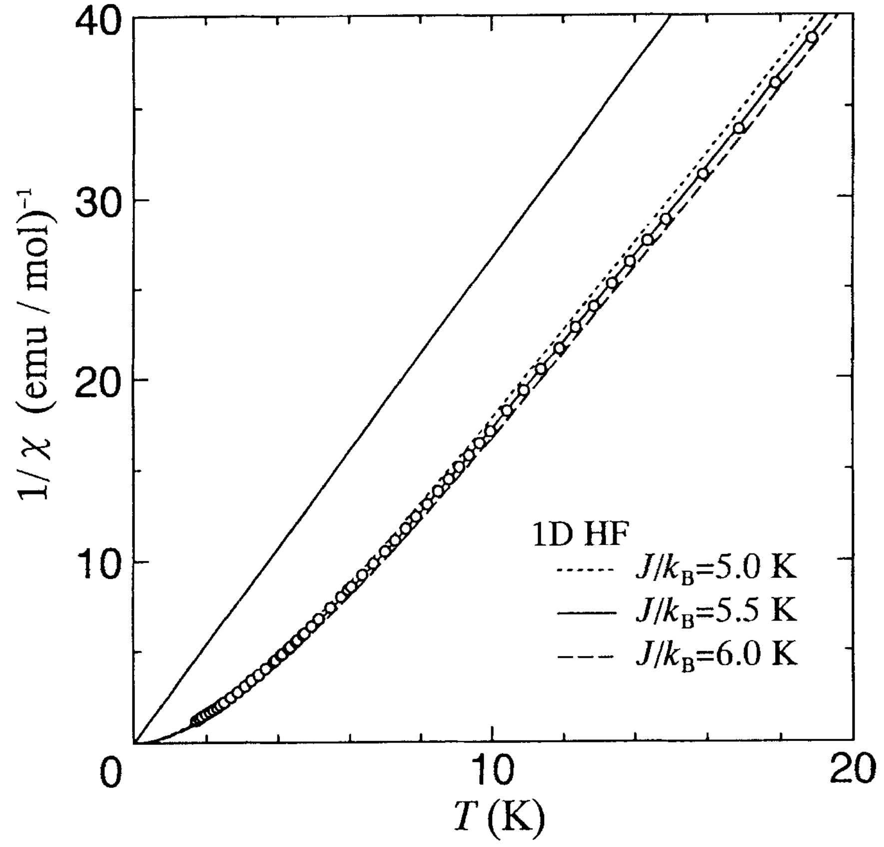


FIGURE 1 Inverse magnetic susceptibility of *p*-CDTV crystal below 20 K.[5,6,9] The observed value (open circles) obey the theories for 1-d isotropic Heisenberg ferromagnet. The straight line corresponds to χ of the paramagnet with g=2.00 and $S=1/2$.

Figure 2 shows the results of pressure dependence of magnetic susceptibility χ of *p*-CDTV crystal up to the pressure $P \approx 6$ kbar. (We use the unit of pressure kbar(=101MPa) in this paper). At $P=0$ kbar, χ shows a sharp peak at T_m, and a second small hump just below T_m. The origin of this hump is not clear at present. At lower temperatures, χ exhibits a plateau as observed in ferromagnets in their ordered phases.

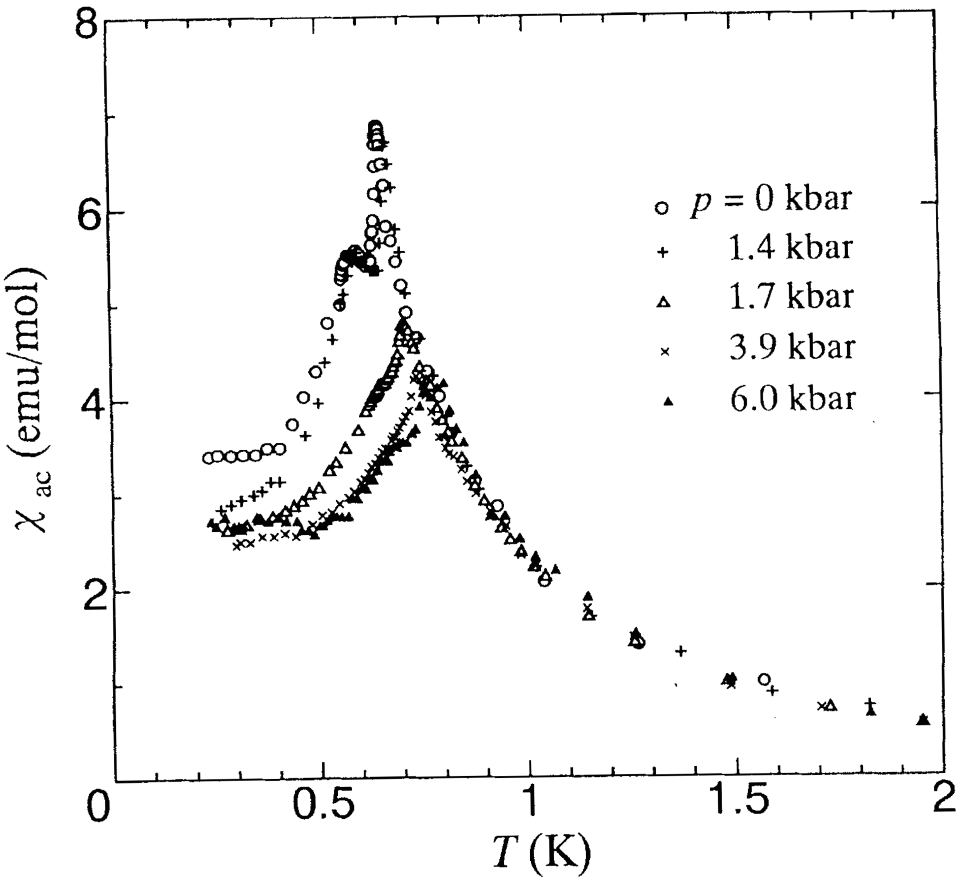


FIGURE 2 Pressure dependence of magnetic susceptibility of p-CDTV crystal around the transition temperature.

Under hydrostatic pressures, the peak of χ shifts to the higher tempertaure. When we define $T_m(P)$ as the temperature which gives the peak of χ, $T_m(P)$ may be approximated

$$T_m(P) = T_m(P_o)(1 + \alpha P), \tag{1}$$

with a positive value of α=0.026 kbar^{-1}. This positive pressure dependence of $T_m(P)$ is in the same way as in the almost all of the antiferromagnets with nearly the same order of magnitude as given in Figure 3 and Table 1.[1-3,10-16]

Mainly two effects are considered on governing $T_m(P)$ under hydrostatic pressures, one is by dipole-dipole coupling and the other by exchange interactions. The lattice constants of organic radical crystals is estimated to shrink by about 1% in the present pressure range, at most. The dipole-dipole coupling, which is of the order of 10^{-2} K, can not explain fairly large change of observed $T_m(P)$, though it may determine the spin axis in the ordered state.

At the present stage of experiments without detailed crystal structure, it is rather difficult to discuss pressure effects on exchange interactions in this crystal. Here we give a speculation based on the previous study of pressure effects on β-phase p-NPNN .[1]

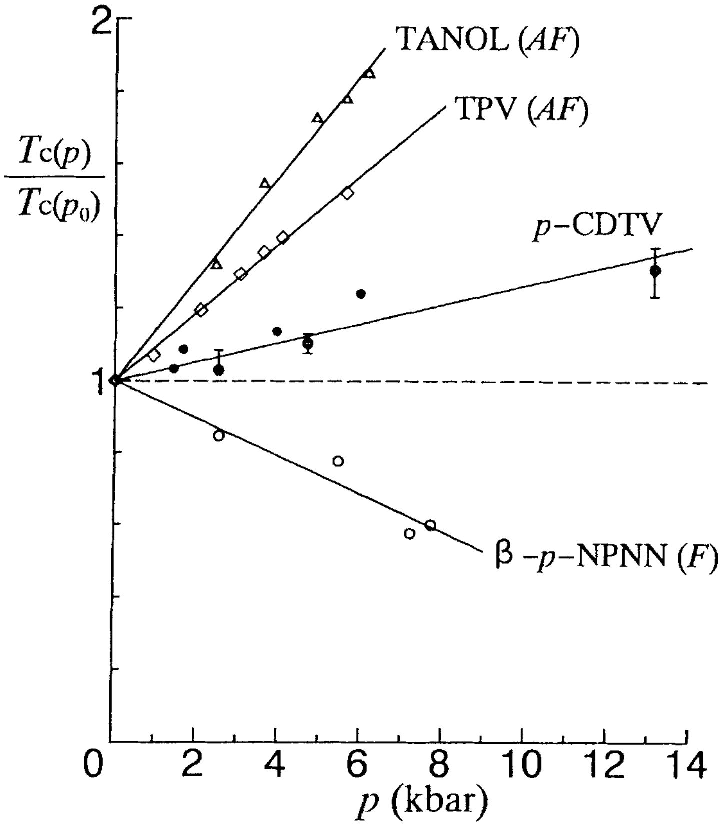


FIGURE 3 Pressure dependence of magnetic phase transition temperature for organic radical crystals, normalized for the value at ambient pressure(P_0). Circles with error bar are determined by heat capacity measurements.

The Hamiltonian for the magnetic interaction between neighboring two molecules, where radical spin $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ are localized, is given in the Heisenberg model as

$$H_{ij} = -2\boldsymbol{J}_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_i. \tag{2}$$

The exchange interaction J_{ij} is expressed as

$$J_{ij} = J_{ij}^{P} + J_{ij}^{K}, \tag{3}$$

where J_{ij}^{P} and J_{ij}^{K} are the potential and kinetic exchange interactions, respectively. Both of them depends on the overlap of the molecular orbital. J_{ij}^{P} is usually positive when the relevant orbitals are orthogonal. J_{ij}^{K} comes from the second or third order perturbation of the charge transfer under the Pauli's principle, and is written

$$J_{ij}^{K} = \Delta E(S) - \Delta E(T), \tag{4}$$

as the energy difference between the spin singlet state(S) and triplet(T) states. In the case where the transfer is possible in the single band of SOMO's only, we have $J_{ij}^{K} = -t_{SS}^2/V$, where t_{SS} and V are the transfer integral between SOMO's and on-site Coulomb repulsion in SOMO's, respectively.

TABLE 1 Pressure dependence of magnetic transition temperature of paramagnetic and insulating compounds.

compound	(F/AF)	T_m/K	α/kbar	ref.
$(NH_4)_2CuBr_4 \cdot 2H_2O$	(F)	1.74	0.019	16
$K_2CuCl_4 \cdot 2H_2O$	(F)	0.88	−0.016	16
$MnBr_2 \cdot 4H_2O$	(AF)	2.12	0.014	10
$FeCl_2$ (I)	(AF)	22.91	0.011	11
$FeCl_2$ (II)	(AF)	24.81	0.028	11
$Mn(HCOO)_2 \cdot 2H_2O$	(AF)	3.68	0.022	12
$CoCl_2 \cdot 6H_2O$	(AF)	2.29	0.038	13
$CuCl_2 \cdot 2H_2O$	(AF)	4.36	0.049	14
DMMC	(AF)	3.60	0.026	15
TMMC(P<3.2kbar)	(AF)	0.84	0.019	15
TMMC(P>3.2kbar)	(AF)	0.84	0.058	15
p-Cl-BDPA	(AF)	3.25	0.083	3
TANOL	(AF)	0.49	0.151	2
$\beta-p$NPNN	(F)	0.61	−0.050	1,3
p-CDTV	(–)	0.67	0.026	present

This always gives negative or antiferromagnetic coupling. However, when the different charge transfer such as t_{SF} exceeds t_{SS}, where t_{SF} stands for the transfer integral between SOMO and fully occupied molecular orbital such as NHOMO, the positive sign of the net exchange interaction in Eqs.(3) and (4) is possible, as in ferromagnetic interactions in galvanoxyl[17] or the β-phase p-NPNN.[18]

In the present p-CDTV crystal, the strong intrachain ferromagnetic coupling $J/k_{\mathrm{B}}= 5.5$ K may mostly originate in larger t_{SF} than t_{SS} along 1-d magnetic chain. The weak interchain interaction J' is related with J and the transition temperature $T_{\mathrm{m}}(P)$ as,

$$\begin{aligned} T_{\mathrm{m}}(P)/T_{\mathrm{m}}(P_{\mathrm{o}}) &= |J(P)J'(P)/J(P_{\mathrm{o}})J'(P_{\mathrm{o}})|^{1/2} \\ &= (1+\alpha P), \end{aligned} \tag{5}$$

With the knowledge of $J(P)$, we may evaluate $J'\ (P)$ as done in the case of TANOL.[2]

Looking at the pressure dependence of the magnetic ordering temperature of various compounds in Table 1, with the value

$$\alpha \equiv (dT_m(P)/dP)/T_m(P_{\mathrm{o}}), \tag{6}$$

we notice that the negative pressure effects of the ferromagnetic β-phase p-NPNN is quite a rare case. The unpaired electron is mainly localized on -NO in this ferromagnet and the direct charge transfer to the adjacent -NO is rather difficult by the intervening -NO_2. In other words, the SOMO-SOMO charge transfer is difficult. In p-CDTV crystal, the spin density is dominant and delocalized on the centered four nitrogens, and the direct charge transfer to the adjacent molecule may be easier, though the molecular configuration is not determined in this crystal. Recently, we have found that the transition temperature of p-CDTV decreases with external fields up to 1 kOe. This reminds us the field-induced reduction of the transition temperature of the γ-phase p-NPNN with intrachain ferromagnetic and interchain antiferromagnetic interactions.[19] It is presumed that the pressurization in p-CDTV crystal enhances the charge transfer t_{SS} between the magnetic chains, as well as the intrachain t_{SF} transfer, making both of absolute value of $J(P)$ and $J'\ (P)$ larger.

REFERENCES

1. K.Takeda, K.Konishi, M.Tamura and M.Kinishita, Phys.Rev. **B53**,3374(1996)., K.Konishi, K.Takeda, M.Tamura, and M.Kinoshita; Mol.Cryst.Liq.Cryst., **279** 115(1996)., K.Takeda, K.Konishi, M.Hitaka, T.kawae, T.Tamura and M.Kinishita, J.Magn.Magn.Mater., **140-144**, 1451(1995).

2. K.Takeda, N.Uryu, M.Inoue and J.Yamauchi: J.Phys.Soc.Jpn., **56**,736(1987).
3. J.Yamauchi, K.Takeda and M.Inoue, Chem.Lett.,1551(1990).
4. J.Yamauchi, K.Takeda and K.Konishi, Mol.Cryst.Liq.Cryst. **233**,97(1993).
5. K.Takeda, K.Konishi, K.Nedachi and K.Mukai, Phys.Rev.Lett.**74**,1673(1995).
6. K. Mukai, K.Konishi, K.Nedachi, and K.Takeda, J.Chem.Phys.,**100**, in press (1996).
7. Takeda, M.Wada, M.Inoue and T.Haseda, Jpn.J.Appl.Phys. **26**,947.(1987).
8. F.A.Neugebauer, and R.Siegel, Angrew.Chem.Int.Ed.Engl.,**22**,320(1983) F.A.Neugebauer, H.Fisher and R.Shiegel, Chem.Ber.,**121**,815(1988).
9. K.Mukai, K.Konishi, K.Nedachi, and K.Takeda, Mol.Cryst.Liq.Cryst.,**279**,195 (1996).
10. W.A.Ortiz, F.P.Missel, Phys.Rev., **B24**,4013(1981).
11. C.Vettier, E.B.Yellon, Phys.Rev., **B11**,4700(1975); A.Liowski and Z.Oryszkiewicz, Phys.Stat.Sol.,**(b)131**,K117(1985).
12. K.Takeda, K.Koyama and K.Yamagata, J.Phys.Soc.Jpn., **55**, 3725(1986).
13. M.Wada, K.Takeda, A.Ohtani, A.Onodera and T.Haseda, J.Phys.Soc.Jpn. **52**, 3188(1983).
14. K.Takeda, T.Idogaki, K.Tsuru, N.Uryu, and M.Inoue, Jpn.J.Appl.Phys., **26-3**, Suppl. 863(1987).
15. K.Takeda and T.Suzuki, Jpn.J.Appl.Phys., **26-3**, Suppl.859(1987).
16. A.A.Galkin, V.P.Dyakonov, G.A.Tsintsadze, and I.M.Fita, Sov.Phys.Solid State, **18**,928(1976).
17. K.Awaga, T.Sugano and M.Kinoshita: Chem.Phys.Lett., **141**,540((1987).
18. M.Kinoshita, P.Turek, M.Tamura, K.Nozawa, D.Shiomi, Y.Nakazawa, M.Ishikawa, M.Takahashi, K.Awaga, T.Inabe and Y.Maruyama, Chem.Lett., 1225(1991).
19. M.Takahashi, P.Turek, Y.Nakazawa, T.Tamura, K.Kozawa, D.Shimoi, M.Ishikawa and M.Kinoshita, Phys.Rev.Lett.**67**,746(1991).