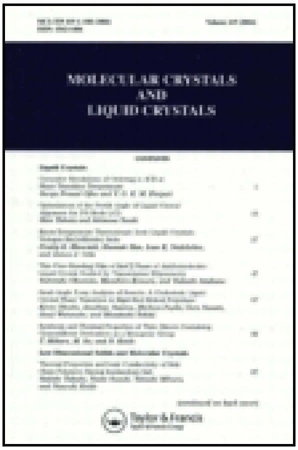

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this article: Mitsutaka Okumura, Takashi Kawakami, Akifumi Oda, Kizashi Yamaguchi, Masaki Mito & Kazuyoshi Takeda (1999): Theoretical Studies of the Pressure Effects for β-Phase of p-NPNN, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 623-632

To link to this article: http://dx.doi.org/10.1080/10587259908028903

*Mol. Cryst. and Liq. Cryst.*, 1999, Vol. 335, pp. 623-632
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# Theoretical Studies of the Pressure Effects for β-Phase of *p*-NPNN

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Molecular orbital calculations were carried out for model clusters of paranitrophenyl nitronyl nitroxide (*p*-NPNN) whose geometrical structures were based on its crystal structure of the β-phase. The effective exchange integrals between *p*-NPNN were calculated for qualitative understanding of the recently discovered pressure-induced transition from ferro- to antiferromagnetic state. Taking the high pressure condition into consideration, *p*-NPNN in the clusters was gradually shifted along several lines or was rotated around appropriate axes. From these model calculations, it was found that the ferromagnetic exchange interaction changed to antiferromagnetic one by the structure deformations. Qualitative models of the pressure effects on the magnetic orders in the β-phase were presented on the basis of these calculated results.

*Keywords:* *p*-NPNN; pressure effect; MO calculation; phase transition

## INTRODUCTION

Active control of electronic, magnetic and optical properties by external conditions such as the high pressure is challenges in molecule-based materials.[1] Theoretical computations have indeed revealed such possibilities. For example, previous molecular orbital (MO) calculations[2,3] showed that the sign and magnitude of effective exchange integrals ($J_{ab}$) in the Heisenberg model ($H = -\Sigma\ 2J_{ab} S_a \cdot S_b$) were highly variable by rotation of nitroxide group in the cluster of para-nitropheyl nitronylnitroxide (*p*-NPNN) or with change of the intermolecular distance (R) between m-N-methylpridinium nitronyl nitroxide (*m*-MPYNN$^+$). These results suggest that the molecular magnetism of *p*-NPNN and *m*-MPYNN$^+$ is sensitive to the structural changes. In fact, the sharp decrease of the magnitude of $J_{ab}$ by the elongation of the intermolecular distance was observed for *m*-MPYNN$^+$ crystal.[4] Recent theoretical studies have also elucidated important roles of conformations of methyl group and hydrogen bonds to determine the sign and magnitude of effective exchange integrals ($J_{ab}$) in TEMPO[5] and HQNN[6] crystals.

Very recently,[7,8] the pressure effect on the intermolecular effective exchange interactions in the β-phase of *p*-NPNN was investigated by the simultaneous measurements of magnetic susceptibility and heat capacity under the high pressure. From these experiments, it was found that the effective exchange integrals were dramatically changed from positive (ferromagnetic) to negative (antiferromagnetic) depending on the pressure conditions. Here, this pressure effect has not been theoretically explored yet. In this paper we wish to perform the MO calculations of the clusters of *p*-NPNN for theoretical understanding of the pressure-induced ferro-to-antiferromagnetic transition.[7,8] Theoretical backgrounds are given in refs. 9-12.

## MO-THEORETICAL CALCULATIONS

The mutual orientations of *p*-NPNN in the β-phase crystal[13] are rather complex as shown in Fig. 1(a). The three different types of the nearest neighbor *p*-NPNN pairs exist in the β-phase,[14,15] and they are referred to as (12), (13) and (14) pairs, respectively. The corresponding $J_{ab}$ values are also defined by $J_{12}$, $J_{13}$ and $J_{14}$ as shown in Fig. 1(a). As elucidated by previous MO calculations,[14,15] the sign and magnitude of $J_{ab}$ for these clusters are determined by the detailed balance of several terms which exhibit different functional behaviors on changes of local conformations of substituents and stacking modes. The $J_{12}$ and $J_{13}$ values were first calculated assuming the crystal structure determined at the normal pressure[13] by the density functional method (UB3LYP/4-31G).[16,17] These are shown in Table I. The calculated $J_{ab}$ values were positive in accord with the observed ferromagnetism,[18] but they were by several times larger than the experimental value. Previous $J_{ab}$

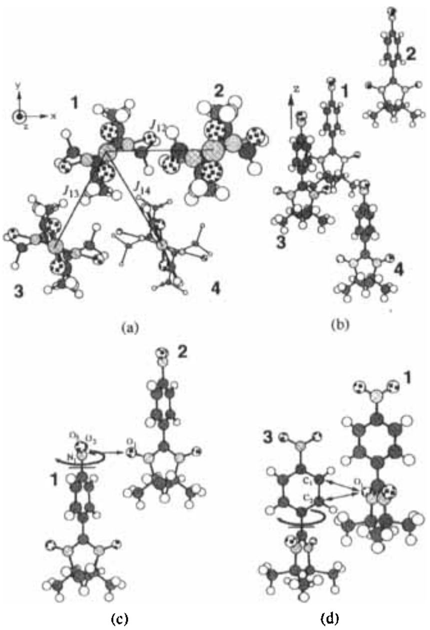

FIGURE 1 (a) The crystal structure of the β-phase of *p*-NPNN with the Fdd2 space symmetry where 1-4 denote the nearest neighbor *p*-NPNN molecules. $J_{pq}$ (p,q =1-4) denote the effective exchange integrals between them. (b) Sliding modes of p-NPNN along the lattice axes which induce variations of the $J_{12}$ and $J_{13}$ interactions. (c) Rotational deformation of nitroxide group of *p*-NPNN which is responsible for variation of $J_{12}$. (d) Rotatioanl deformation of nitrophenyl group of *p*-NPNN which is responsible for variation of $J_{13}$.

values[14,15] (see Table I) obtained by UHF INDO are rather reasonable as compared with the experiments:[18] note that the ferromagnetic transition temperature was calculated to be 0.64 K in accord with the experiment (0.60 K)[16] by the Langevin-Weiss model using the calculated $J_{ab}$ values.[14,15] As a continuation of previous work, we here perform the UHF INDO calculations for various structures of the clusters of *p*-NPNN as shown below. The

TABLE I Effective exchange integral $J_{ab}$ (cm$^{-1}$) of the shifted stacking models of β-phase *p*-NPNN by UHF INDO method.

| | $J_{12}$ | | $J_{13}$ | | $J_{14}$ | |
|---|---|---|---|---|---|---|
| ΔR /A | x-axis | z-axis | xy-plane | z-axis | xy-plane | z-axis |
| -1.0 | 27.739 | 0.205 | -0.276 | 0.271 | -0.288 | 0.000 |
| -0.8 | 10.430 | 0.205 | 0.311 | 0.316 | -0.190 | -0.001 |
| -0.6 | 3.773 | 0.202 | 0.407 | 0.325 | -0.111 | -0.004 |
| -0.4 | 1.338 | 0.196 | 0.295 | 0.286 | -0.059 | -0.008 |
| -0.2 | 0.472 | 0.185 | 0.170 | 0.202 | -0.030 | -0.012 |
| 0.0 | 0.167 | 0.167 | 0.086 | 0.086 | -0.014 | -0.014 |
| | (0.439)$^{a)}$ | | (0.595)$^{a)}$ | | | |
| +0.2 | 0.060 | 0.142 | 0.040 | -0.042 | -0.063 | -0.015 |
| +1.0 | 0.001 | 0.028 | 0.001 | -0.254 | -0.002 | -0.007 |

a)UB3LYP/4-31G

expensive UB3LYP/4-31G and 6-31G* calculations will be given elsewhere.

## UNIFORM COMPRESSION MODEL

Since the X-ray structure of the β-phase under the high-pressure at low temperature is not known, we here consider plausible models for structure changes which would be essential for qualitative understanding of the pressure effect. Takeda and co-laborators reported relations between induced pressures (kPa) and cell parameters (a, b, c). All the cartesian coordinates (i.e., both of the molecular geometries and intermolecular distances) were first shortened assuming the uniform compression of lattice constants under the high pressure. Figure 2 illustrates variations of the calculated $J_{ab}$ values with the pressure. The calculated results were not consistent with the experimental tendency, because the sign and magnitude of the $J_{ab}$ values varied independently under condition of the compression. Therefore, it was difficult to explain the pressure-induced ferro-to-antiferromagnetic transition by the

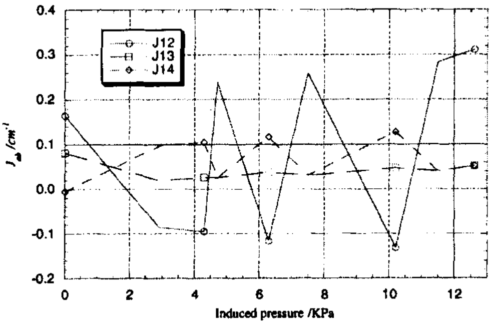

FIGURE 2 The schematic illustrations of variations of the effective exchange integrals ($J_{ab}$) between *p*-NPNN by the uniform compression model, which is one of the possibilites for the pressure effect.

simplest model.

Next, we examined a lattice compression model that lattice constants were varied so as to account for the decrease of intermolecular distances for the model clusters in Fig. 1(a), but the molecular geometry itself was not changed. The calculation results are shown in Fig. 3. While the absolute values of three types of $J_{ab}$ values are increasing with increase of induced pressure, the signs of $J_{ab}$ values are not changed in contradiction to the experiments[7,8]. Thus the situation is quite different from the usual cases in inorganic magnetic solids. This in turn suggests that the changes[3] of stacking modes and/or the rotations[2] of substituents must be considered for explanation of the pressure-induced change of the magnetism.[7,8]

## SLIDING DEFORMATIONS

Several sliding models of *p*-NPNN along the several lines were examined to elucidate variations of three $J_{ab}$ values shown in Figs. 1 (a) and (b). Table I summarizes the calculated results. The magnitude of the $J_{12}$ value was variable with the sliding along the x- or z-axis, but its sign was not changed by this type of deformations. The ferromagnetic spin alignment within the ac

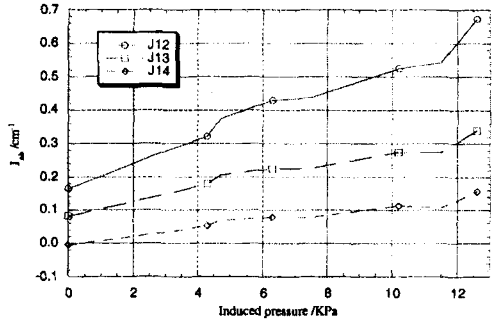

FIGURE 3 The schematic illustrations of variations of the effective exchange integrals ($J_{ab}$) between *p*-NPNN by the lattice compression model, which is one of the possibilites for the pressure effect.

plane remains intanct after the sliding deformation of *p*-NPNN along the x- or z-axis.

The $J_{13}$ value is responsible for the effective exchange interaction between the ac-planes.[14,15] As a model for the pressure effects for the interplane interaction, *p*-NPNN (**3**) in Fig. 1 was shifted to the central *p*-NPNN (**1**) on the xy-plane (i.e., the interplane distance between the ac planes was retained to be constant). The intermolecular distance (R) was expressed by the interatomic distance between the central carbon atoms of the nitronyl nitroxide groups, and the negative ΔR means the decrease of the intermolecular distance (see Table I). From Table I, the sign of $J_{13}$ remained unchanged since this deformation did not affect the contacting points interactions. On the other hand, the sliding of *p*-NPNN along the z-axis altered the sign of $J_{13}$. Since the key contacting sites are the O-C1 and O-C2 atomic pairs in the β-phase,[14,15] the sign of $J_{13}$ is determined by the subtle balance of these two terms: the ferromagnetic O-C2 interaction overweighs the antiferromagnetic O-C1 interaction in the normal condition.[14,15] The latter became predominant if R was elongated, namely in the case of ΔR=0.2 - 1.0 Å as shown in Table I.

The sign and magnitude of $J_{14}$ were almost constant by the sliding deformations along the 1-4 line on the xy-plane and z-axis as shown in Table I. The $J_{14}$ term is not essential for variations of the magnetism because its magnitude is quite small.[14,15]

## ROTATIONAL DEFORMATIONS

The rotations of substituents provide another possibilities for modeling conformational changes under the high pressure conditions.[5,6] We here examined variations of the interplane angle between nitronyl nitroxide and nitroxide groups. The side view of the rotational process was illustrated in Fig. 1(c). The deformations were restricted to retain the crystal symmetry by assuming the concerted rotations of both components in Fig. 1. Figure 4 shows variations of $J_{12}$ with the rotational angle (θ). The $J_{12}$ value certainly became negative by the rotation of nitroxide group at the ranges of the rotational angle from -10° to -20° and from 30° to 75° ; note that the region $\theta <$ -20 is out of consideration because of strong steric repilsion. Thus the *ferromagnetic interaction within the ac plane can be destroyed if the rotation of* nitroxide group is variations of $J_{12}$ with the rotational angle.

The rotation of nitrophenyl group was also examined as illustrated by the side and upper views in Fig. 1(d). Figure 5 shows variations of $J_{13}$ with the rotational angle. The calculated $J_{13}$ values, which exhibited antiferromagnetic behavior at the ranges of the rotational angle from 5° to 40° and from -50° to -90°. Therefore, the ferro- to antiferromagnetic transition for the interplane interaction was caused by the rotation which would be reasonable from the view point of the lattice compression by the high pressure. The experimental examinations are desirable in future.

## CONCLUDING REMARK

In summary, we found three characteristic modes to understand the observed pressure-induced ferromagnetic to antiferromagnetic transition in the β-phase; (1) the sliding of *p*-NPNN along the z-axis to alter the sign of the interplane exchange integral ($J_{13}$), (2) the rotation of nitrophenyl group to provide the

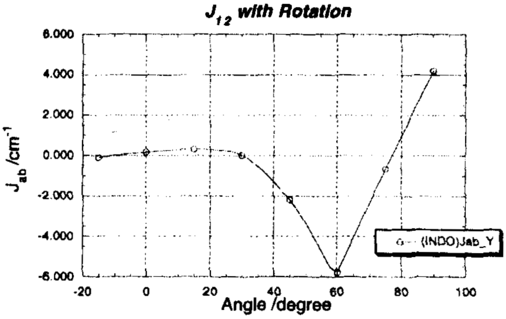

FIGURE 4 Variations of the $J_{12}$ values with the rotational process of nitroxide group of *p*-NPNN molecules; two nitroxide groups were rotated concertedly in Fig. 1(c) to retain the Fdd2 space symmetry.

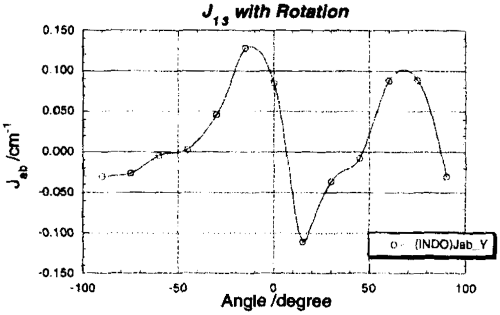

FIGURE 5 Variations of the $J_{13}$ values with the rotational process of nitrophenyl group of *p*-NPNN molecules; two nitrophenyl groups were rotated concertedly in Fig. 1(d) to retain the Fdd2 space symmetry.

negative $J_{13}$ and (3) the rotation of nitro group to inverse the sign of the intraplane exchange integral ($J_{12}$). However, the first makes the lattice constant larger, so it is hardly acceptable unless other conformational changes are coupled together. The second induces the antiferromagnetic interaction between the ac-planes as in the case of γ-phase crystal of *p*-NPNN[19], while the third destroys the two-dimensional (2D) ferromagnetic interaction in the ac-plane. Since the heat capacity data exhibit the 2D character under the high pressure,[7,8] the second mode is conceivable as the simplest model for possible theoretical explanation of the pressure effect in the β-phase of *p*-NPNN. Although the real conformational changes in the β-phase under the high pressure are probably more complex, the present model calculations clearly demonstrated that the signs of effective exchange integrals are variable by conformational changes of component radicals in organic ferromagnets.

Since rotations of substituents such as methyl group are feasible by the high pressure, the present calculations suggest that the pressure-induced ferro to antiferro-magnetic (vice versa) transitions would be equally anticipated for many other organic ferromagnets composed of alkylnitroxides and other organic radicals.[20,21] In fact, Takeda and co-laboratores reported the presure induced antiferro to ferro-magnetic transitions in TEMPO derivatives.[22] Probably such softness is a characteristic of organic ferromagnets in general.

## Acknowledgments

The authors thank Professor Kinoshita for helpfull discussions and Grant-in-Aid for Scientific Research on Priority area (No. 10149101) from the Ministory of Education, Science and Culture, Japan.

## *References*

[1] D. Gatteschi and K. Yamaguchi, *"From Molecular Assemblies to the Devices"* (E. Coronado Eds., Kluwer Pub.,1996) p561.

[2] K. Yamaguchi, M. Okumura, J. Maki, T. Noro, H. Namimoto, M. Nakano, T. Fueno and K. Nakasuji, Chem. Phys. Lett., **190,** 353 (1992).

[3] M. Okumura, K. Yamaguchi and K. Awaga, Chem. Phys. Lett., **228,** 575 (1994).

[4] K. Awaga, T. Okuno, A. Yamaguchi, M. Hasegawa, T. Inabe, Y. Maruyama and N. Wada, Phys. Rev., **B49,** 3975 (1994).

[5] T. Kawakami, A. Oda, S. Takeda, W. Mori, T. Ishida, M. Yasui, F. Iwasaki, T. Nogami and K. Yamaguchi, Mol. Cryst. Liq. Cryst., **306,** 141 (1997).

[6] A. Oda, T. Kawakami, S. Takeda, W. Mori, K. Yamaguchi, M. M. Matsushita, A. Izuoka and T. Sugawara, Mol. Cryst. Liq. Cryst., **306,** 151 (1997).

[7] K. Takeda, K. Konishi, M. Tamura and M. Kinoshita, Phys. Rev., **B53,**3374 (1996).

[8] M. Mito, T. Kawae, M. Takumi, K. Nagata, M. Tamura, M. Kinoshita, and K. Takeda, Phys. Rev., **B56,** R14255 (1997).

[9] H. M. McConnell, J. Chem. Phys., **39,**1930 (1963).

[10] K. Yamaguchi, T. Fueno, K. Nakasuji and I. Murata, Chem. Lett., 629 (1986).

[11] K. Yamaguchi and T. Fueno, Chem. Phys. Lett., **159,** 465 (1989).

[12] K. Yamaguchi, M. Okumura and M. Nakano, Chem. Phys. Lett., **191,**237 (1992).

[13] K. Awaga, T. Inabe, U. Nagashima and Y. Mayuyama, J. C. S. Chem. Commun. 1617 (1989).

[14] M. Okumura, W. Mori and K. Yamaguchi, Mol. Cryst. Liq. Cryst., **232,**35 (1993).

[15] M. Okumura, K. Yamaguchi, M. Nakano and W. Mori, Chem. Phys. Lett., **207,** 1 (1993).

[16] A. D. Becke, Phys. Rev., **A38,** 3098 (1988).

[17] C. Lee, W. Yang and R. G. Parr, Phys. Rev., **B37,** 785 (1988).

[18] Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita and M. Ishikawa, Phys. Rev., **B46,** 8906 (1992).

[19] M. Okumura, W. Mori and K. Yamaguchi, Chem. Phys. Lett., **219,** 36 (1994).

[20] T. Kawakami, S. Takeda, W. Mori and K. Yamaguchi, Chem Phys Letters, **261,** 129 (1996).

[21] T. Nogami, T. Ishida, M. Yasui, F. Iwasaki, N. Takeda, M. Ishikawa, T. Kawakami and K. Yamaguchi, Bull. Chem. Soc. Jpn., **69,** 1841 (1996).

[22] M. Mito, T. Takeda, K. Takeda, T. Ishida and T. Nogami, Mol. Cryst. Liq. Cryst., in press.