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

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Version of record first published: 24 Sep 2006.

To cite this article: Daisuke Shiomi , Hiroko Aruga Katori , Tsuneaki Goto , Hiroshi Sawa , Reizo Kato , Masafumi Tamura & Minoru Kinoshita (1993): Magnetic Energy Gap in the Crystal of an Organic Biradical, m-BNN: m-Phenylene Bis(α-Nitronyl Nitroxide), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 232:1, 109-116

To link to this article: http://dx.doi.org/10.1080/10587259308035705

Mol. Cryst. Liq. Cryst. 1993, Vol. 232, pp. 109–116
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Printed in the United States of America

MAGNETIC ENERGY GAP IN THE CRYSTAL OF AN ORGANIC BIRADICAL, *m*-BNN: *m*-PHENYLENE BIS(α-NITRONYL NITROXIDE)

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Abstract A novel phase transition is observed in the crystal of a triplet (S=1) biradical, *m*-BNN. The crystal is composed of equivalent dimers of the biradicals at room temperature. From susceptibility, high-field magnetization and X-ray diffraction at low temperatures, it is shown that below about 10 K imperfect cancellation of magnetic moment occurs between antiferromagnetically coupled S=1 spins only in half the number of dimers in the crystal.

INTRODUCTION

Organic radicals containing only light elements (H,C,N,O), owing to weak spin-orbit coupling, give rise to highly isotropic (Heisenberg type) spin systems. In these systems, the spin quantum number, S, may play a crucial role in magnetic properties. Here we report the magnetic properties of a stable organic biradical with a triplet (S=1) ground state, *m*-phenylene bis(α-nitronyl nitroxide) (abbreviated as *m*-BNN; see Fig. 1). On the basis of magnetic susceptibility and high-field magnetization results, we discuss the magnetic energy spectrum of the *m*-BNN crystal at low temperatures. By taking account of the symmetry breaking revealed by low temperature X-ray diffraction, the magnetic structure of the *m*-BNN crystal at low temperatures is presented.

CRYSTAL STRUCTURE AT ROOM TEMPERATURE

The crystal structure, analyzed at room temperature, is shown in Fig. 1. (crystallographic data: monoclinic, $P2_1/n$; a=11.657, b=25.453, c=7.311 Å, β=104.96°, Z=4) As depicted in Fig. 1, the *m*-BNN molecules are dimerized. The two molecules in the dimer are related by inversion symmetry. All the dimers are crystallographycally equivalent because of the two-fold screw axis or the glide plane.

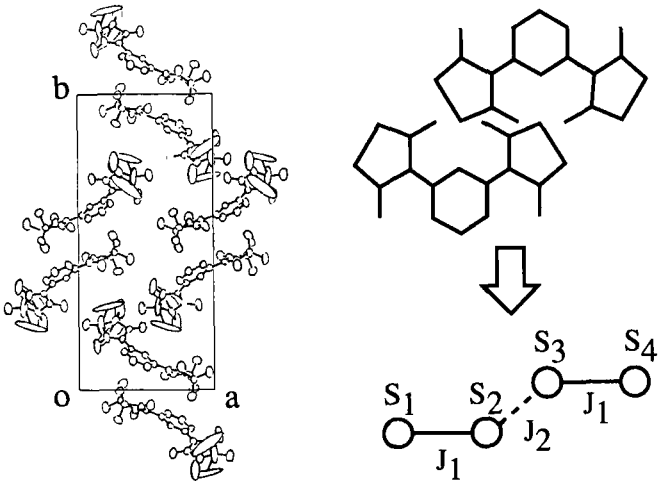

FIGURE 1 Left: Crystal structure of *m*-BNN viewed along the *c*-axis. Right: Four-spin model.

ELECTRON PARAMAGNETIC RESONANCE

EPR signal intensity of Δm=2 transitions measured in a dilute glassy solution exhibits Curie-like temperature dependence. This result indicates that the molecular ground state of *m*-BNN is triplet; namely the intramolecular coupling between the two unpaired electrons is ferromagnetic.

The principal values of the *g*-tensor determined at room temperature are g_1=2.0083, g_2=2.0076 and g_3=2.0039. The deviation of the *g*-factor from the free electron value (g=2.0023) is very small. The anisotropy parameters[1] determined by solution EPR measurements, which originate from the dipolar coupling between the two spins in a molecule, are also negligible compared with the thermal energy ($|D|$=89 G, $|E|$~6 G). These results indicate the highly isotropic nature of the spins in *m*-BNN.

MAGNETIC SUSCEPTIBILITY

The product of paramagnetic susceptibility, corrected for diamagnetic contribution by Pascal's method, and temperature, $\chi_p T$, is plotted against T in Fig. 2. The $\chi_p T$ value at room temperature is about 0.75 emu K mol^{-1}, corresponding to two independent S=1/2 spins in a molecule. The decrease in $\chi_p T$ at low temperatures suggests the

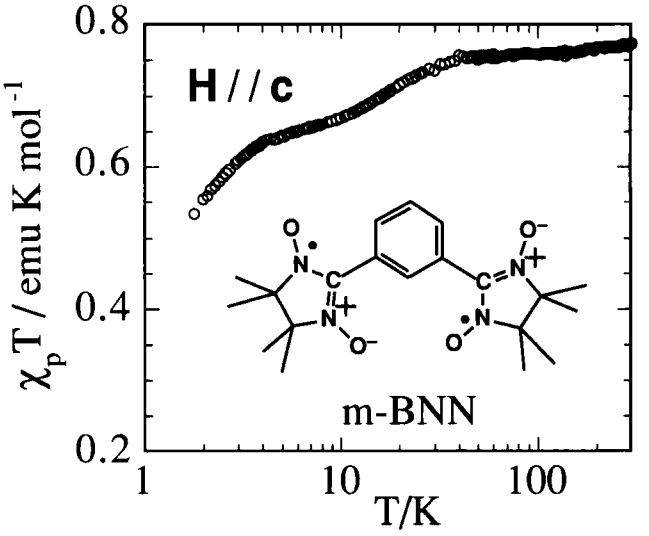

FIGURE 2 Temperature dependence of $\chi_p T$ for *m*-BNN.

existence of antiferromagnetic intermolecular interaction in the crystal.

The $\chi_p T$ vs. T curve exhibits stationary behavior around 10K. In order to explain such anomaly, we have to consider the competition between different types of magnetic interactions, intra- and intermolecular ones, or ferro- and antiferromagnetic ones. The direct overlap between the orbitals of unpaired electron on the NO groups gives rise to antiferromagnetic intermolecular interaction. In fact, within the *m*-BNN dimer, a relatively short intermolecular distance is found between the NO groups as drawn in Fig. 1. Thus, we first take the following four-spin Hamiltonian as a starting model,

$$H = -2J_1(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_3\cdot\mathbf{S}_4)-2J_2(\mathbf{S}_2\cdot\mathbf{S}_3), \tag{1}$$

where the antiferromagnetic interaction J_2 connects the two biradical molecules having positive J_1.

The magnetic susceptibility χ_p, or the product $\chi_p T$, is generally expressed as,

$$\chi_p T = A\,\frac{\Sigma_i[S_i(S_i+1)(2S_i+1)\exp(-\varepsilon_i/k_BT)]}{\Sigma_i[(2S_i+1)\exp(-\varepsilon_i/k_BT)]} \tag{2}$$

$$A = 2Ng^2\mu_B^2/3nk_B,$$

where n refers to the number of spins in the system (*i.e.*, four in this case). S_i and ε_i are the spin quantum number and the energy eigenvalue of the i-th spin state, respectively. By using eqs.(1) and (2), we can simulate the temperature dependence of $\chi_p T$. The stationary behavior similar to the one observed is obtained. However, the calculations give sizable difference in the $\chi_p T$ value around the stationary region ($\chi_p T$(st)) between the calculated and the observed one.

The appearance of the stationary behavior can be related with the change in the statistical distribution over the spin states across some kind of magnetic energy gap. According to eq.(2), a large energy separation, $\Delta\varepsilon$, between the excited spin states with different spin multiplicity should cause significant change in $\chi_p T$ as thermal energy $k_B T$ passes through $\Delta\varepsilon$. The situation is illustrated in Fig. 3 for the case of the four-spin model. The value of $\chi_p T$(st) is basically governed by the states below the gap $\Delta\varepsilon$, that is,

$$\chi_p T(\mathrm{st}) \sim A\{\Sigma_i [S_i(S_i+1)(2S_i+1)]\}/[\Sigma_i (2S_i+1)], \qquad (3)$$

where i runs over the spin states below the gap.

It can be shown that for any possible combination of the spin states of a four-spin model eq.(3) does not yield $\chi_p T$(st) value suitable for explain the observed anomaly. The possibility that the anomaly is attributed to the coexistence of the only two types of magnetic interactions is thus ruled out. A larger system should be considered.

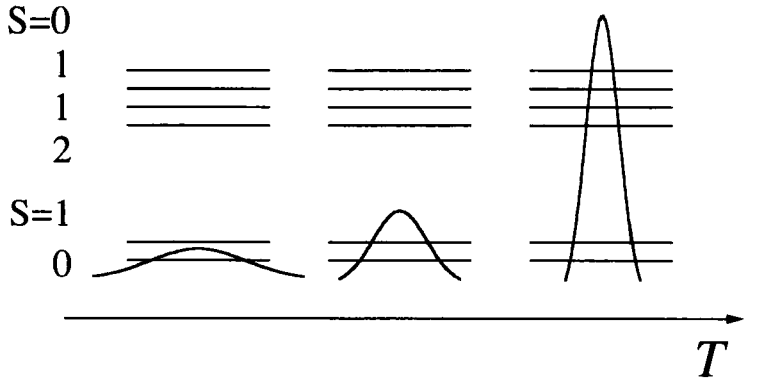

FIGURE 3 Distribution over the spin states for the four-spin model.

ENERGY SPECTRUM OF EIGHT-SPIN SYSTEM

As a phenomenological model, we take a combination of two dimers (an eight-spin system) in the following in order to describe the energy spectrum structure of *m*-BNN. In this framework, the observed $\chi_p T$ behavior can be reproduced by adjusting the energy levels. An example of such results is shown in Fig. 4, in which the states are separated into two groups by a large energy gap of about 50 K. The presence of one nonet (S=4) above the gap and one septet (S=3) below is the essential feature crucial to give the $\chi_p T$(st) value close to the observed one.

The ground state is singlet (S=0), which is separated from other states by a small energy gap (about 3 K). This smaller gap is required to reproduce the temperature dependence of $\chi_p T$ below the stationary region. The singlet ground state is consistent with the antiferromagnetic interaction between the triplet molecules in the both dimers.

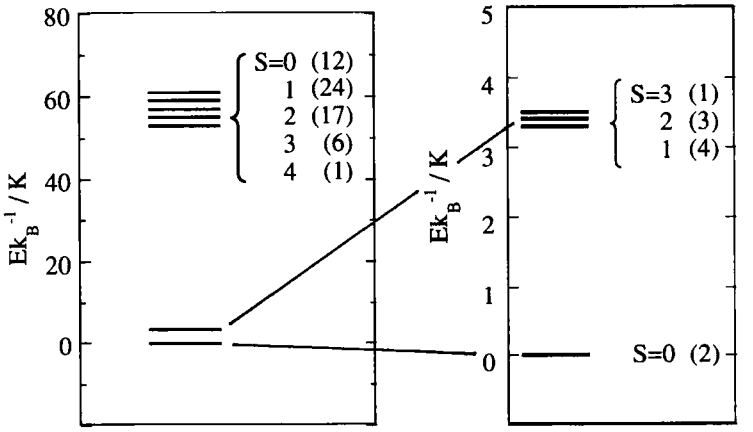

FIGURE 4 Energy spectrum of the eight-spin model. The number of the states with the same spin multiplicity is presented in the parenthesis.

HIGH-FIELD MAGNETIZATION PROCESS

The high-field magnetization measured for polycrystalline samples at 1.8 K is depicted in Fig. 5. Above 30 T, the magnetization takes a

constant value of 1.1×10^3 erg Oe^{-1} mol^{-1}, corresponding to parallel alignment of all the spins. There is an anomaly around 20 T; the magnetization exhibits seeming saturation to about 8×10^3 erg Oe^{-1} mol^{-1}, about 3/4 of the complete saturation value at the higher fields.

The observed peculiar behavior above 20 T evidences the existence of the septet and nonet states. The situation is schematically illustrated in Fig. 5. The Zeeman-split M_S=-3 state arising from the lowest septet is responsible for the seeming 3/4 saturation around 20 T, whereas the complete saturation corresponds to M_S=-4 state coming from the nonet. At about 25 T, these two Zeeman sublevels cross. This enables us to estimate the zero-field energy separation between the septet and nonet; it is about 30 K.

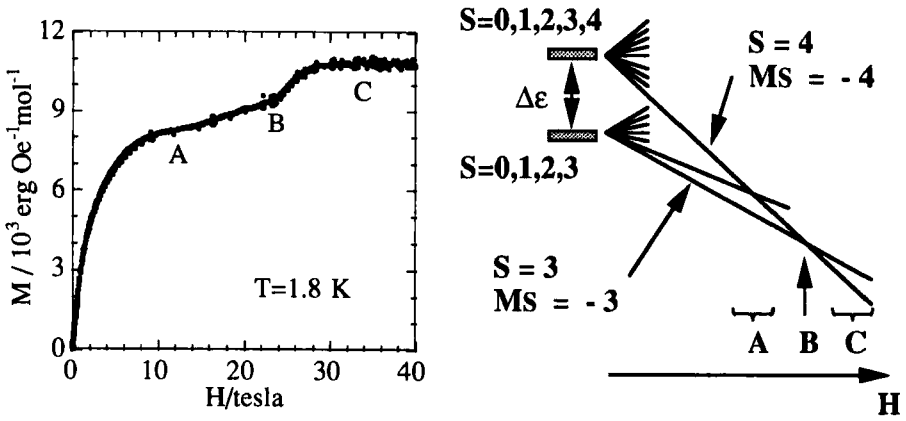

FIGURE 5 Left: High-field magnetization of m-BNN. Right: Level-crossing betwen Zeeman sublevels.

MAGNETIC STRUCTURE AT LOW TMPERATURES

As shown in the above sections, one septet state in the lower group in the energy spectrum plays an essential role in both the susceptibility anomaly and the two-fold saturation in the high-field magnetization process. However, a pair of equivalent dimers cannot give the relevant septet state below the gap. In order to reproduce both the observed susceptibility and magnetization, it is necessary to break down the symmetry of the room temperature structure.

We performed powder X-ray diffraction measurements. At low temperatures there appeared extra-peaks due to a lowered symmetry of the structure. Although the detailed analysis of the temperature dependence of the lattice distortion is not settled, it is evident that the dimers are no longer equivalent at low temperatures.

Now let us examine an eight-spin system comprised of two different dimers (units a and b in Fig. 6). Here, for simplicity, weak interactions between the dimers are neglected. The spin Hamiltonian for this model is expressed as,

$$H = \Sigma_i [-2J_{1i}(\mathbf{S}_{1i}\cdot\mathbf{S}_{2i}+\mathbf{S}_{3i}\cdot\mathbf{S}_{4i})-2J_{2i}(\mathbf{S}_{2i}\cdot\mathbf{S}_{3i})], \quad (i=a, b) \quad (4)$$

where J_{1i} and J_{2i} represent the intra- and intermolecular exchange interaction in the dimer i, respectively. We found that the set of the exchange parameters, $J_{1a}/k_B \sim J_{1b}/k_B \sim 30$ K, $J_{2b}/k_B \sim -30$ K, together with J_{2a} less than about 1/10 of the others, yields a suitable result for both the $\chi_p T$(st) value below 10 K and the level-crossing around 25 T. As for the symmetry breaking, it is interesting to note that in this picture the two antiferromagnetic J differ considerably from each other. The energy spectrum calculated from these exchange parameters has a distinct energy gap. Below this gap there is, indeed, only one septet state, which is the origin of the anomaly observed in the susceptibility and the magnetization. In this way we can relate the magnetic features of this compound to the breakdown of the structural symmetry.

The characteristics of the magnetic structure in the low

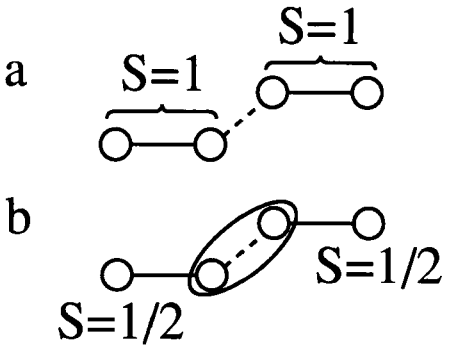

FIGURE 6 Nonequivalent pair of the *m*-BNN dimers at low temperatures.

temperature phase of *m*-BNN is described by the following two concepts: The breakdown of the translational symmetry of the dimers and the incomplete cancellation of the magnetic moment in the half numbers of the dimers. As a result of the broken symmetry, the half numbers of the dimers possess stronger antiferromagnetic interactions, J_{2b}, while only the weaker ones, J_{2a}, remain in the other dimers. This removes the validity of the four-spin picture based on the room temperature structure.

Below about $T=|J_{2b}|/k_B$, the biradicals within the dimers b are coupled antiferromagnetically by J_{2b}. Consequently, a singlet pair is formed between the biradical. However, the magnetic moments are not completely cancelled; the two remaining $S=1/2$ spins are still magnetically active even at $T\sim J_{2b}/k_B$. In spite of the strong coupling within the dimer, the two spins behave as if they were decoupled. This is ascribable to the closely situated lowest singlet and triplet states. In connection with the Haldane gap systems, a similar feature (four-fold quasi-degeneracy) is reported[2] for finite antiferromagnetic chains of $S=1$ spins.

The septet state relevant to the magnetism of *m*-BNN is formed by combining the two active $S=1/2$ spins in the dimer b with the two approximately free $S=1$ spins in the dimer a. The level-crossing at about 25 T corresponds to the breaking of singlet pair in the dimer b. In this way the magnetic structure of the low-temperature phase of *m*-BNN is characterized.

ACKNOWLEDGMENT

We would like to thank professor Yutaka Ueda and Dr. Akihiko Hayashi of ISSP for powder X-ray diffraction measurements. This work was partly supported by the Grant-in-aid for Scientific Research, No. 02403001, and that on Priority Area "Molecular Magnetism"(Area No. 228/04242103) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. The obtained *D* and *E* parameters are essentially the same as those reported by Ullman *et al*; E. F. Ullman, J. H. Osiecki, D. G. B. Boocock and R. Darcy, J. Am. Chem. Soc., 94, 7049(1972).
2. M. Hagiwara, K. Katsumata, I. Affleck, B. I. Halperin and J. P. Renard, Phys. Rev. Lett., 65, 3181(1990).