

Bistable Polymorphs Showing Diamagnetic and Paramagnetic States of an Organic Crystalline Biradical Biphenyl-3,5-diyl Bis(*tert*-butylnitroxide)

Hirokazu Nishimaki,[†] Shinichiro Mashiyama,[†]
Masanori Yasui,[†] Takashi Nogami,[†] and
Takayuki Ishida^{*,†,‡}

Department of Applied Physics and Chemistry and Course of
Coherent Optical Science, The University of
Electro-Communications, Chofu, Tokyo 182-8585, Japan

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There have been numerous reports on ferromagnetic interactions in genuine organic radical crystals in pursuit of magnetism-based functional materials.^{1–3} For further development of switching, sensing, memory, display, and other devices, bistable materials without any change in chemical composition are of increasing interest, and various spin-crossover systems are intensively studied in coordination compounds.⁴ On the other hand, there are few examples of organic materials showing such a drastic magnetic change.⁵ The change appearing at ambient temperatures seems preferable for application to devices.

The *meta*-phenylene bridge is supposed to be a robust ferromagnetic exchange coupler, as supported by the extensive works on high-spin polycarbenes, -nitrenes, and -radicals⁶ (including di- and trinitroxide radicals).⁷ Though the title biradical (BPBN, see Figure 1) was designed as a ground triplet molecule, the magnetic susceptibility measurements revealed the practically diamagnetic properties of the BPBN solid contrary to our expectation.⁸ The very large intermolecular antiferromagnetic interactions buried a possible intramolecular ferromagnetic coupling. We will report here thermally induced paramagnetic properties of BPBN before it melts, accompanied by the switch of spin multiplicity from $S = 0$ to 1.

Diradical BPBN was prepared according to the method reported.⁸ Pale red plates of BPBN (mp 86–87 °C) were

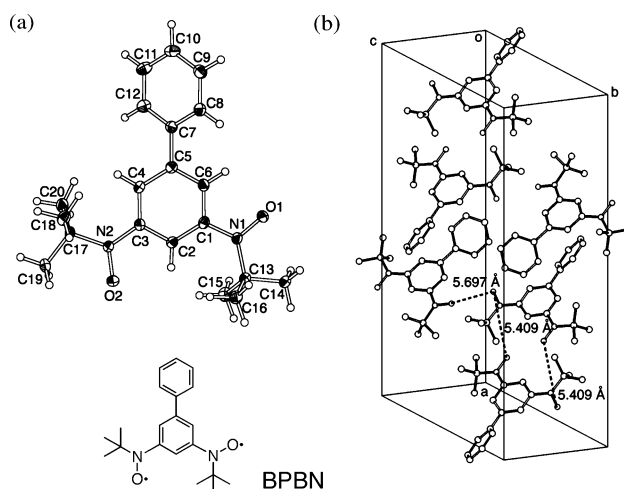


Figure 1. (a) Ortep drawing of the BPBN molecule in the β -phase with thermal ellipsoids at the 50% probability level for non-hydrogen atoms. (b) Molecular arrangement in the crystal of β -BPBN.

obtained by crystallization from CH_2Cl_2 –hexane in a refrigerator and assigned as the known $P\bar{1}$ phase (α -phase) by the cell parameters⁸ from X-ray diffraction (XRD) study.

The β -phase of BPBN has newly been prepared and characterized as follows. Recrystallization of BPBN from hot hexane gave dark red blocks (β -BPBN; mp 134–136 °C (decomp)).⁹ We found a remarkable hyperchromic effect compared with α -BPBN, suggesting a decrease of intermolecular interaction. Figure 1 shows the X-ray crystal structure of β -BPBN solved in a $C2/c$ space group.¹⁰ The N–O radical groups are separated from each other (5.409(1) Å at the shortest), and the geometry of the C–N(O)–C is quite usual¹¹ and highly planar (Figure 1b). The biphenyl group is twisted as indicated by the C(4)–C(5)–C(7)–C(12) torsion angle of 40.2(1)°.

The intermolecular N–O...N–O distances in the β -phase are very long, while in the α -phase the distances are 23–24% shorter than the sum of the van der Waals radii.⁸ The geometry of the N–O group is normal in the β -phase, whereas the N–O nitrogen atoms of α -BPBN are consider-

* To whom correspondence should be addressed. E-mail: ishi@pc.uec.ac.jp.

[†] Department of Applied Physics and Chemistry.

[‡] Course of Coherent Optical Science.

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- (9) Using a “seed” obtained after the thermal experiments of BPBN facilitated the preferential recrystallization of the β -phase.
- (10) Diffraction data of a single crystal of β -BPBN were collected on a Rigaku R-axis RAPID diffractometer with graphite monochromated Mo K α radiation at 100 K. Selected data for the β -BPBN are $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$; fw 326.4; monoclinic $C2/c$; $a = 29.2720(19)$, $b = 11.7396(7)$, and $c = 11.2259(7)$ Å; $\beta = 110.548(3)^\circ$; $V = 3612.3(4)$ Å³; $Z = 8$; $d_{\text{calcd}} = 1.200$ g cm⁻³; $\mu(\text{Mo K}\alpha) = 0.078$ mm⁻¹; and $R_{\text{int}} = 0.0511$, $R(F) (I > 2\sigma(I)) = 0.0358$, and $R_w(F^2)$ (all data) = 0.1001 for 4141 unique reflections. We found an anomaly of the residual electron density in the differential Fourier map and assumed the presence of a small portion of an isomeric and diamagnetic 3-*tert*-butylamino-5-phenyl-1,4-quinone-1-*tert*-butyliminooxide as a lattice defect. We applied a disorder model at the relating O and H atoms, and their occupancy parameter was included in the refinement. The purity of β -BPBN was determined to be 94.4%, being consistent with the magnetic measurements within an experimental error. The minor impurity might be formed via a thermal disproportionation process giving quinone imine *N*-oxides and *N*-*tert*-butylanilines.¹³
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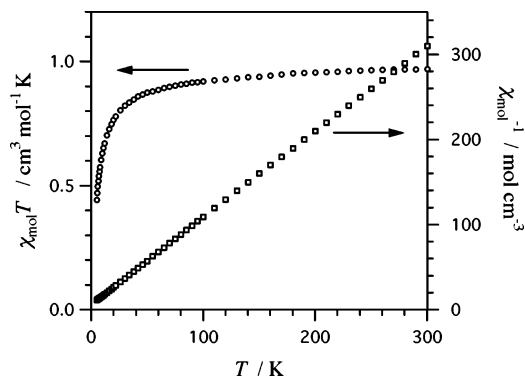


Figure 2. Temperature dependence of $\chi_{\text{mol}}T$ (circles) and χ_{mol}^{-1} (squares) for freshly crystallized β -BPBN measured at 5000 Oe.

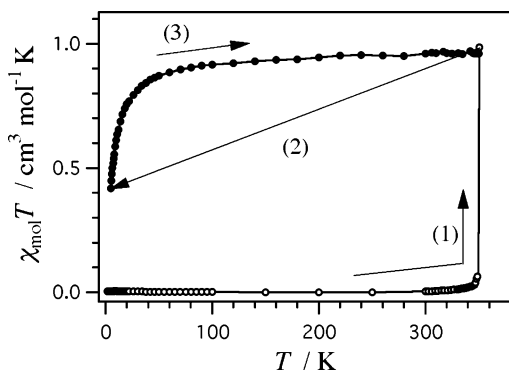


Figure 3. Temperature dependence of $\chi_{\text{mol}}T$ for α -BPBN measured at 5000 Oe. The solid lines are drawn as a guide to the eye. Arrows denote the direction of temperature scans: (1) heating, (2) rapid cooling, and (3) heating.

ably pyramidalized and the N–O bonds are elongated. We can expect from these geometrical features that β -BPBN would show magnetic properties dominantly from a single molecule origin, that is, intramolecular ferromagnetic coupling, whereas α -BPBN showed strong intermolecular anti-ferromagnetic coupling.

We measured magnetic properties of β -BPBN (Figure 2) and clarified that the magnetic susceptibility obeyed the Curie–Weiss law [$\chi_{\text{mol}} = C/(T - \theta)$] with the Curie constant, C , of 1.00(7) $\text{cm}^3 \text{K mol}^{-1}$ and the Weiss constant, θ , of $-6.0(8)$ K. The C value coincides with the theoretical paramagnetic $S = 1$ value, and furthermore, the $\chi_{\text{mol}}T$ value remained constant around 300 K, indicating that β -BPBN shows strong intramolecular ferromagnetic coupling like other known *m*-phenylene-bridged bisnitroxides.⁷ On the other hand, in the α -phase, the intermolecular antiferromagnetic coupling is very strong on both contacting sides, leading to $C \leq 0.004 \text{ cm}^3 \text{K mol}^{-1}$ at 300 K.⁸

We found thermally induced magnetization of α -BPBN (Figure 3, open circles). In the initial temperature scan from 2 K, the $\chi_{\text{mol}}T$ value was practically null up around 300 K and exhibited a sharp upsurge at 350 K. The final $\chi_{\text{mol}}T$ value was $0.99 \text{ cm}^3 \text{K mol}^{-1}$ at 351 K, which is very close to the theoretical triplet value of $1.0 \text{ cm}^3 \text{K mol}^{-1}$. Note that this transition took place below the melting point of α -BPBN.¹² After the specimen was cooled again at a rate of about -35°

(12) The mp of the α -phase was observed only when heated rapidly; two endothermal peaks ascribable to the phase transition and mp were found at a heating rate of $20^\circ \text{ min}^{-1}$ in DSC measurements.

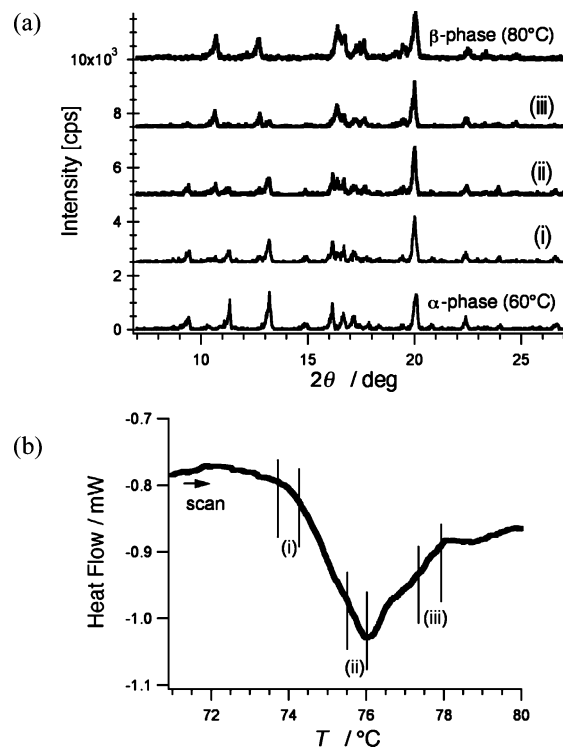


Figure 4. Simultaneous DSC-XRD results of α -BPBN (a) recorded with a temperature scan rate of $0.5^\circ \text{ min}^{-1}$ monitored by DSC (b). XRD profiles i, ii, and iii were measured in temperature regions indicated by i, ii, and iii in DSC, respectively. The XRD of the β -phase (top, a) was independently measured at 80°C using freshly crystallized β -BPBN.

min^{-1} , the $\chi_{\text{mol}}T$ curve of the second run did not trace that of the initial one (Figure 3, filled circles). The specimen behaved as a paramagnetic species with $S = 1$; the $\chi_{\text{mol}}T$ value increased on heating and reached again to $0.96 \text{ cm}^3 \text{K mol}^{-1}$ at 350 K. The $\chi_{\text{mol}}T$ – T profile after the thermal treatment was quite similar to that of β -BPBN measured independently (Figure 2).

We attempted to recover the low-spin state by experiments in a slow-cooling process (with a rate of $0.25^\circ \text{ min}^{-1}$), but the $\chi_{\text{mol}}T$ versus T plot was practically the same as that of the rapid-cooling experiments. The switch from diamagnetic to paramagnetic phases was proved to be irreversible. Slight thermal decomposition was observed during prolonged thermal treatment; 5.0% of the radical entity was lost after being allowed to stand at 355 K for 30 min. A possible decomposition product is a diamagnetic quinoneimine as characterized as a defect in the X-ray crystal structure analysis,¹⁰ which is supported with the extensive studies on related compounds by Forrester and Hepburn.¹³

We turned our attention to characterization of the high-spin state. The powder XRD and differential scanning calorimetry (DSC) data were acquired simultaneously on heating (Figure 4).¹⁴ We found only one endothermal peak in DSC at 76°C (Figure 4b).¹² The powder patterns measured

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(14) Simultaneous XRD-DSC measurements of BPBN were performed on a RIGAKU XRD-DSC II, using a monochromated Cu K α irradiation ($\lambda = 1.54184 \text{ \AA}$). The temperature scan rate was $0.5^\circ \text{ min}^{-1}$ from 70 to 80°C .

below 74 °C were attributed to α -BPBN. The pattern at 76 °C became different from that of α -BPBN, and finally a new solid phase appeared at 78 °C. The XRD of β -BPBN was independently measured (Figure 4a (top)), which seems identical with that of the high-temperature phase.

Therefore, we can conclude that BPBN underwent a solid-to-solid-phase transition, that is, from the α - to the β -phase, at 350 K (Figure 4) accompanied by the abrupt $\chi_{\text{mol}}T$ jump (Figure 3). The $\chi_{\text{mol}}T$ versus T plot of β -BPBN also clarifies that the triplet population is nearly 100% even at 350 K, indicating that the singlet–triplet energy gap (ΔE_{ST}) is larger than 350 K. Though we could not observe intramolecular interaction in α -BPBN, we have now confirmed the presence of considerably large intramolecular ferromagnetic interaction in BPBN. Fortunately, α -BPBN also has $|\Delta E_{\text{ST}}|$ much larger than 350 K ($\Delta E_{\text{ST}}/k_{\text{B}} = -1700$ K as an average of two independent radical–radical contacts).⁸ Thus, the phase transition takes place with a theoretical maximum jump of the $\chi_{\text{mol}}T$ value by 1 $\text{cm}^3 \text{K mol}^{-1}$.

One may wonder what happens when the low-spin phase α -BPBN is illuminated by light. We investigated photo-switching of the magnetism of BPBN just below the phase transition temperature (T_{c}). The fine polycrystalline α -BPBN was nominally kept at 340 K, lower than T_{c} by 10 K, and the magnetic susceptibility was monitored during and after laser light illumination (532 nm) for 3 min (Figure 5).¹⁵ The first illumination gave rise to an increase of 45% of the triplet $\chi_{\text{mol}}T$ value, as indicated by a jump at 80 min. Another two shots of illumination gave a very slight increase of the $\chi_{\text{mol}}T$ value. After the sample chamber was warmed to 350 K and thermally equilibrated, the phase transition was completed.

The specimen could very locally be heated to a temperature above T_{c} during the illumination, because there is an intrinsic

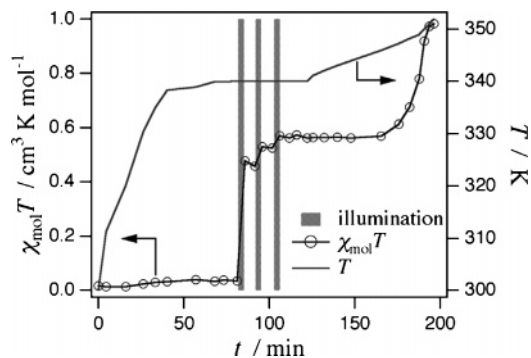


Figure 5. $\chi_{\text{mol}}T$ value plotted for α -BPBN as a function of time (t) during photo-illumination on and off. The temperature (T) was recorded for the sample chamber. The solid lines are drawn as a guide to the eye. Illumination periods are indicated with hatched areas.

thermal gradient within the sample chamber. The light caused solely a thermal effect, because no illumination-induced magnetic behavior was observed at temperatures much below T_{c} .

In summary, we have clarified the thermally induced magnetic moments of the crystalline BPBN. The drastic and irreversible change of magnetic properties occurs between the two phases, both of which are quite stable at room temperature, suggesting a potential utility of BPBN as a genuine organic write-once information-storage material.

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Supporting Information Available: CIF file of β -BPBN including experimental details in the crystallographic analysis and tables of selected geometrical parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) A laser beam was introduced into a Quantum Design MPMS-7 SQUID probe through a quartz optical fiber. The light source was a CrystalLaser GCL-150-M (532 nm; diode-pumped green laser). The quartz fiber was purchased from Fujikura (large-core fiber S.800/1000; core diameter 800 μm). The polycrystalline specimen of α -BPBN was stuck on a small piece of a polyimide Kapton tape (duPont). The precise mass of BPBN was estimated from the magnetic susceptibility.