

# Novel Organic Ions of High-Spin States. 5. Generation of a High-Spin Ground-State Anion from an Intramolecularly Spin-Frustrated System

Toshihiro Nakamura,<sup>†</sup> Takamasa Momose,<sup>†</sup> Tadamasa Shida,<sup>\*,‡</sup> Kazunobu Sato,<sup>‡</sup> Shigeaki Nakazawa,<sup>‡</sup> Takamasa Kinoshita,<sup>‡</sup> Takeji Takui,<sup>\*,‡</sup> Koichi Itoh,<sup>\*,§</sup> Tsunehisa Okuno,<sup>#</sup> Akira Izuoka,<sup>#</sup> and Tadashi Sugawara<sup>\*,#</sup>

Contribution from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606-01, Japan, the Department of Chemistry and Department of Material Science, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan, and the Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

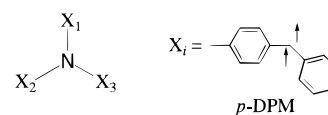
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**Abstract:** 4,4',4''-Tris(diphenylmethylene)amine (N(*p*-DPM)<sub>3</sub>) may be regarded as a prototype of intramolecularly spin-frustrated organic systems. In the present work the monoanion of N(*p*-DPM)<sub>3</sub> was obtained by thermal electron attachment and studied by ESR spectroscopy to find that the ground state is a spin quartet with the fine-structure parameters of  $|D| = 0.123 \text{ cm}^{-1}$  and  $|E| = 0.005 \text{ cm}^{-1}$  and an isotropic *g* factor of 2.003. These results are explained consistently if the excess electron occupies an in-plane *n* non-bonding MO predominantly localized at the divalent carbon sites and if the molecular structure of N(*p*-DPM)<sub>3</sub><sup>•−</sup> is of non-C<sub>3</sub> symmetry which indicates the quantum nature of the spin alignment in the spin-frustrated finite system. The temperature dependence of the ESR signal indicates that the lowest excited doublet state of the anion is located at least 300 cm<sup>−1</sup> above the quartet ground state.

## Introduction

High-spin organic molecules are important not only in the quest for molecular based magnetism and new magnetic material<sup>1</sup> but also in exploring new concepts in chemistry and physics. One of the highlights is the introduction of the concept of topological symmetry in  $\pi$ -conjugated organic systems which gives rise to an unlimited number of the degeneracy in molecular orbitals. The topological degeneracy contrasts the ordinary orbital degeneracy which never allows the spin multiplicity greater than three in the electronic ground state of organic molecules consisting of 2s and 2p atomic orbitals.<sup>2</sup> The first  $\pi$ -topological degeneracy giving rise to high-spin molecules of  $S = 2$  was shown some 30 years ago.<sup>3</sup> During the last decade, spin manipulation chemistries have developed to bring about diverse topics in chemistry and physics.<sup>1</sup> Among these, charge

delocalization and spin polarization in organic high-spin systems have attracted increasing interest.<sup>4–8</sup> In particular, attention has been paid to a deeper understanding of chemical bonds and possible controlling of the interplay between spin and charge fluctuation on the microscopic and semimicroscopic scale.<sup>9</sup> In this paper, we report a prototypical system of organic anion which is related to an intramolecular (through-bond) spin-frustrated system.



The system studied is the monoanion of 4,4',4''-tris(diphenylmethylene)amine, (N(*p*-DPM)<sub>3</sub>). The salient feature of the amine is that the lone-pair electrons on the nitrogen atom may play a role of coupling two of the three diphenylmethylene (DPM) units antiferromagnetically by superexchange interaction.

<sup>†</sup> Kyoto University.

<sup>‡</sup> Department of Chemistry, Faculty of Science, Osaka City University.

<sup>§</sup> Department of Material Science, Faculty of Science, Osaka City University.

<sup>#</sup> The University of Tokyo.

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The interaction can be described by a phenomenological Heisenberg–Dirac spin Hamiltonian,  $\mathcal{H} = -\sum_{i,j} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$  ( $i \neq j$ ,  $i, j = 1, 2, 3$ ), where  $\mathbf{S}_i$  and  $\mathbf{S}_j$  stand for the electron spins on the units  $X_i$  and  $X_j$ , respectively. Due to the *para* connectivity of the  $\pi$ -network in this system, the coupling is antiferromagnetic, i.e.,  $J_{ij} < 0$ . Thus, spins  $\mathbf{S}_2$  and  $\mathbf{S}_3$  can be antiparallel against  $\mathbf{S}_1$  via superexchange interaction, but this situation can equally force  $\mathbf{S}_2$  and  $\mathbf{S}_3$  to align to be parallel. Therefore, the antiparallel alignment between  $\mathbf{S}_2$  and  $\mathbf{S}_3$  via superexchange interaction cannot be fulfilled to result in spin instability (spin frustration). The instability arises from the quantum nature of the spin alignment in systems with  $C_3$  symmetry. In the context of charge delocalization and spin polarization in the monoanion of  $N(p\text{-DPM})_3$ , intriguing issues are, first, which MO is occupied, the out-of-plane  $\pi$  non-bonding orbital or the in-plane  $n$  non-bonding orbital localized at the divalent carbon site, and second, what electronic spin state is stabilized in the ground state of  $N(p\text{-DPM})_3^{\bullet-}$ .

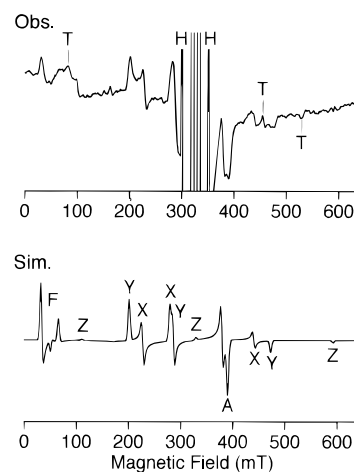
## Experimental Section

The monoanion of  $N(p\text{-DPM})_3$  was generated by essentially the same method as in our previous study on the monoanion of *m*-phenylenebis(phenylmethylene),<sup>4a,b</sup> i.e., visible light photolysis of the radical anion of the diazo precursor of  $N(p\text{-DPM})_3$ . The diazo precursor was synthesized from 4,4',4''-trisbenzoyltriphenylamine<sup>10</sup> by a sequence of the following reactions: a reaction with hydrazine hydrate in ethanol and a reaction in the dark with HgO in benzene containing a small amount of concentrated KOH in ethanol. The diazo precursor was purified by chromatography on alumina eluted with dichloromethane at room temperature in the dark. The diazo precursor was dissolved in 2-methyltetrahydrofuran (MTHF) which was purified with Na-K alloy and lithium aluminium hydride as in the previous work.<sup>4a,b,d</sup> The solution of a concentration of approximately 10 mM was sealed in ESR or optical cells after degassing. It was then  $\gamma$ -irradiated at 77 K to a dose of ca.  $10^{19}$  eV/g to yield the spin-doublet radical anion ( $S = 1/2$ ) of the diazo precursor. It is established that this procedure gives almost exclusively the radical anion of the precursor because  $\gamma$ -irradiation causes almost solely the ionization of MTHF in the dilute solution of the precursor and the ejected electron reaches the precursor molecule to be attached thermally.<sup>11</sup> The radical anion was successfully photolyzed with light of wavelength  $\lambda > 620$  nm at 77 K. The photolysis brought about the elimination of nitrogen molecules of the doublet radical anion of the diazo precursor to generate the high-spin monoanion of the neutral parent molecule  $N(p\text{-DPM})_3$ . The ESR measurement was carried out with a JEOL JES-RE2X spectrometer equipped with an Oxford 910 variable-temperature controller. For the optical measurement a Hitachi U-3300 spectrophotometer was used.

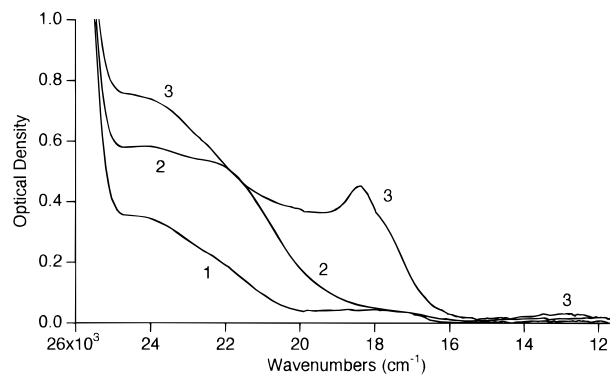
## Results and Discussion

**1. ESR and UV–vis Spectra.** When the  $\gamma$ -irradiated frozen solution was photolyzed with  $\lambda > 620$  nm, several new ESR transitions appeared in the wide range of 0–600 mT (see Figure 1). The appearance of the wide-spread ESR signals indicates the formation of high-spin anionic species. The optical spectra also showed a remarkable change upon visible light photolysis as shown in the change from curves 2 to 3 in Figure 2. As in the previous study,<sup>4a,b,d</sup> the optical spectrum in curve 3 of Figure 2 and the ESR spectrum outside the range of 320–340 mT in Figure 1 are attributable to the formation of the high-spin anion,  $N(p\text{-DPM})_3^{\bullet-}$ .

The observed ESR spectrum with large anisotropy was analyzed by the established spectral simulation procedure<sup>4</sup> for



**Figure 1.** Observed and simulated X-band ESR spectra for the quartet state of  $N(p\text{-DPM})_3^{\bullet-}$ . The microwave frequency employed was 9.215 GHz. Symbols A and F in the simulated spectra denote the off-principal-axis extra line and the forbidden transition with  $\Delta m_s = \pm 2$  and  $\pm 3$ . The parameters used for the simulation are  $S = 3/2$ ,  $g = 2.003$  (isotropic),  $|D| = 0.123 \text{ cm}^{-1}$ , and  $|E| = 0.005 \text{ cm}^{-1}$ .



**Figure 2.** UV–vis spectra of the diazo precursor of  $N(p\text{-DPM})_3$  in the MTHF solution at 77 K: (1) before  $\gamma$ -irradiation; (2) after  $\gamma$ -irradiation; (3) same as 2 after photolysis with light of wavelength  $\lambda > 620$  nm.

randomly orientated paramagnetic species in the static magnetic field. The relevant spin Hamiltonian is given in eq 1,

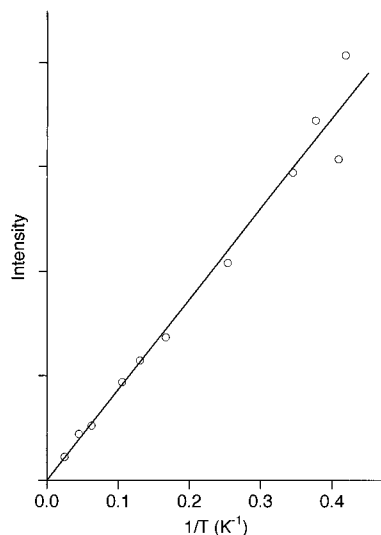
$$\mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \quad (1)$$

where each term has the usual meaning. A total of 64800 orientations was sampled and a Gaussian line shape with 4.0 mT of line width was assumed for each ESR transition. The resonance field and transition probability for all possible ESR transitions were calculated by diagonalizing the spin Hamiltonian matrix constructed for a given magnetic field. The best fit spin Hamiltonian parameters were found to be  $S = 3/2$ ,  $g = 2.003$  (isotropic),  $|D| = 0.123 \text{ cm}^{-1}$ , and  $|E| = 0.005 \text{ cm}^{-1}$ . Figure 1 compares the observed fine-structure ESR spectrum with the simulated one. The transitions corresponding to the principal axes of the fine-structure tensor are labeled by X and Y under the assumption of  $E > 0$ . The off principal-axis extra lines and absorption peaks for forbidden transitions of  $\Delta m_s = \pm 2$  and  $\pm 3$  are denoted by A and F, respectively. All the transitions are in good agreement with the observed spectrum in the upper panel of Figure 1, where T denotes the signals arising from the neutral ground-state triplet of a diphenylmethylene derivative as a reaction byproduct.

Particular attention should be paid to the observed non-vanishing  $E$  and relatively large  $D$  values. The  $E \neq 0$  value

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**Figure 3.** Temperature dependence of the intensity of the ESR signal of the quartet state of  $N(p\text{-DPM})_3^{*-}$ .

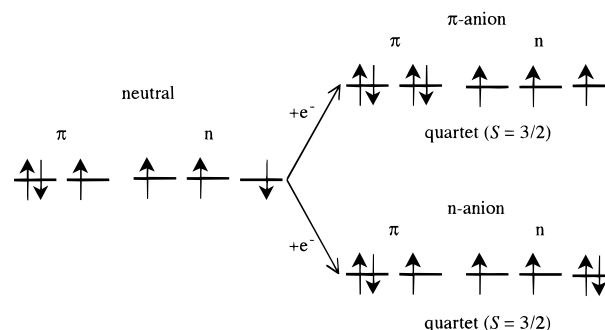
shows the deviation from  $C_3$  symmetry of  $N(p\text{-DPM})_3^{*-}$  in the MTHF glass. As discussed later, the magnitude of the  $D$  value is attributable to the dominant contribution from one-center  $n-\pi$  spin-spin interaction at the divalent carbon sites.

**2. Ground-State Spin Multiplicity of  $N(p\text{-DPM})_3^{*-}$ .** In order to determine the ground-state spin multiplicity of  $N(p\text{-DPM})_3^{*-}$ , the temperature dependence of the intensity of the spin-quartet signal was measured by monitoring the low-field Y axis canonical peak at about 200 mT. The intensity was calculated by double integration of the observed first derivative peak. The intensity of the signal denoted by  $T$  was used as an internal standard of the temperature. Figure 3 shows the observed temperature dependence of the quartet state. An approximately linear plot was obtained, which indicates that the ground state is the spin-quartet.

**3. Electron Configuration of the Quartet Anion.** According to a simple  $\pi$ -electron MO calculation assuming a molecular structure of  $C_3$  symmetry, the highest occupied molecular orbitals (HOMO's) of the neutral  $N(p\text{-DPM})_3$  are doubly-degenerate non-bonding orbitals which accommodate three  $\pi$ -electrons.<sup>12,13</sup> On the other hand, the three in-plane  $n$ -orbitals localized at the divalent carbon atoms are approximately degenerate in energy with  $\pi$  non-bonding orbitals. The three  $n$ -orbitals are occupied by two  $\alpha$ -spin electrons and one  $\beta$ -spin electron: This allotment of the electron spin by the VB approach reflects the spin frustration caused by the antiferromagnetic superexchange interaction via the lone-pair electrons on the nitrogen atom and the ferromagnetic one-center  $n-\pi$  coupling on each divalent carbon atom, leading to the triplet ground state for the neutral  $N(p\text{-DPM})_3$ .

There are two possibilities for the excess electron of the monoanion, that is, it may occupy either the non-bonding  $\pi$ -orbital or the  $n$ -orbital (see Scheme 1). In the case of the occupation of  $\pi$ -orbital the doubly-degenerate orbitals are filled by a total of four electrons to annihilate the spin density in the  $\pi$ -electron system. Therefore, the one-center  $n-\pi$  spin-spin

**Scheme 1.** Electron Configurations of the Quartet  $\pi$ -Anion and  $n$ -Anion



interaction should vanish to zeroth order. Since the observed  $|D|$  of  $0.123 \text{ cm}^{-1}$  is significantly large and the contribution of  $n-\pi$  configurational mixing to the  $D$  value is negligibly small, it is obvious that the fine structure is determined mainly by the  $n-\pi$  interaction in  $N(p\text{-DPM})_3^{*-}$ . Therefore, it is safely concluded that the excess electron is accommodated in the  $n$ -orbital, and not in the  $\pi$ .

**4. Molecular Conformation of the Quartet Anion.** The fine-structure parameters of the quartet  $N(p\text{-DPM})_3^{*-}$  can be calculated semiempirically and compared with the observed ones. The fine-structure tensors of aromatic polycarbenes can be approximated by a superposition of the one-center spin-spin interaction tensors of the  $n-\pi$  type at each divalent carbon atom. Assuming that the one-center interaction can be represented by the fine-structure tensor of diphenylmethylene (DPM), a semiempirical expression for the fine-structure tensor is given as follows,<sup>2de,14</sup>

$$D_{ij} = [S(2S - 1)]^{-1} \sum_k (\rho_k / \rho_{\text{DPM}}) (\mathbf{U}_k \cdot \mathbf{D}_{\text{DPM}} \cdot \mathbf{U}_k^{-1})_{ij} \quad (2)$$

$$i, j = X, Y, Z$$

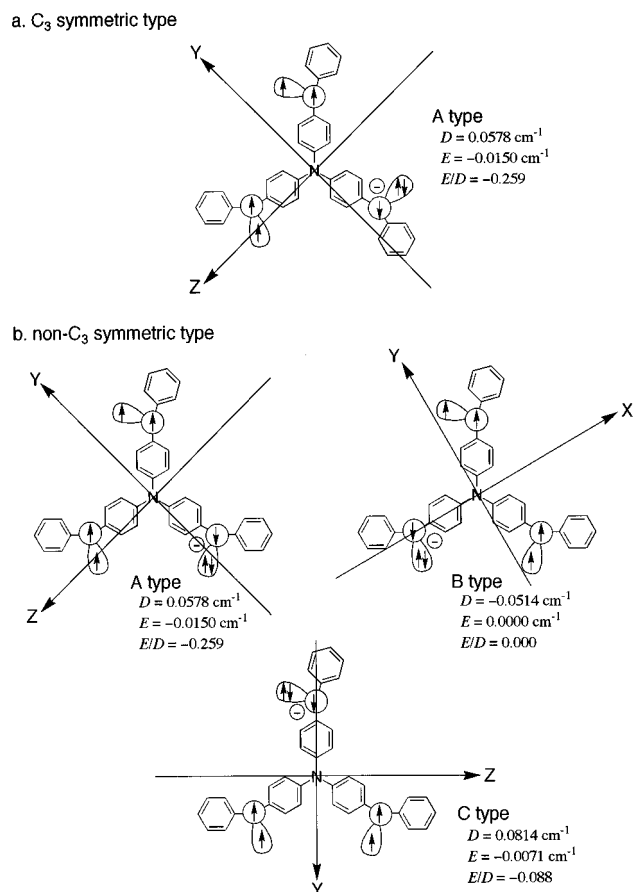
where  $D_{ij}$  stands for the  $ij$  element of the fine-structure tensor of the anion and  $\mathbf{D}_{\text{DPM}}$  denotes the fine-structure tensor of DPM represented in the principal-axis system. The symbols  $\rho_k$  and  $\rho_{\text{DPM}}$  represent respectively the spin density of the  $\pi$ -electron at the  $k$ th divalent carbon atom and the spin density at the divalent carbon atom of DPM. These spin densities at the divalent carbons were estimated by the Hückel MO calculation. The unitary matrix  $\mathbf{U}_k$  transforms the principal axes of the one-center interaction tensor at the  $k$ th divalent carbon atom to the principal axes of the fine-structure tensor of the anion. Since the excess electron is considered to be in the  $n$ -orbital, the fine-structure tensor of the quartet anion is evaluated by the superposition of the two one-center interaction tensors at the divalent carbon atoms whose  $n$ -spin remains unannihilated. In the present calculation the bond angle at the divalent carbon is assumed to be  $150^\circ$ .

There are two possible conformations for  $N(p\text{-DPM})_3^{*-}$ : one is a  $C_3$  symmetric type and the other is a non- $C_3$  symmetric type. In the case of the  $C_3$  symmetric type the relative orientation of the two  $n-\pi$  interactions at the divalent carbons has only one type as shown in A of Figure 4, while in the non- $C_3$  symmetric type three types, i.e., A, B, and C, are possible. Figure 4 shows also the calculated values of  $D$ ,  $E$ , and  $E/D$  and the directions of the principal axes of the  $\mathbf{D}$  tensor. The  $E$  value of B-type is accidentally zero due to the perpendicularity of the two principal axes of the two one-center tensors in the

(12) The lowest unoccupied molecular orbital (LUMO) of  $a_1$ -symmetry is located nearby above the doubly-degenerate HOMO's of  $e$ -symmetry. However, an excited electron configuration where one electron occupies LUMO turned out to be higher according to a VB description in terms of MO calculation.<sup>13</sup> In the present work, as a zeroth order approximation, we neglect the contribution from such an excited electron configuration.

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**Figure 4.** Possible relative orientations of the two one-center  $n-\pi$  interaction tensors of  $N(p\text{-DPM})_3^{\bullet-}$ . Note that in B the Z axis is perpendicular to the sheet of paper. Also, at the bond angle of  $150^\circ$  the choice of X and Y in B is arbitrary. The C-type of the non- $C_3$  symmetric structure is concluded to be the most probable.

molecular plane. The calculated  $D$  value is smaller than the observed one since an excited electron configuration where one

electron occupies the lowest unoccupied molecular orbital (LUMO) is neglected in the estimation of the spin densities.<sup>12</sup> The  $E/D$  ratio is considered to be more reliable due to the cancellation of the effect of the neglect of excited configurations. The calculated values of C-type are the closest to the observed ones. Therefore, the most probable orientation of the two  $n-\pi$  interactions is concluded to be as in C, which leads, in turn, to the conclusion that the molecular conformation of  $N(p\text{-DPM})_3^{\bullet-}$  is non- $C_3$  symmetric. As a result, the VB description of the electron configuration of  $N(p\text{-DPM})_3^{\bullet-}$  in its ground state may be depicted as shown in C of Figure 4. One may rephrase that the  $\pi$ -spin polarization controls the spin alignment of  $N(p\text{-DPM})_3^{\bullet-}$ .

## Conclusion

A monoanion of an intramolecularly spin-frustrated molecule,  $N(p\text{-DPM})_3$ , is produced in a frozen solution of MTHF at 77 K by  $\gamma$ -radiolysis and visible light photolysis. The ground state of  $N(p\text{-DPM})_3^{\bullet-}$  is determined to be the spin-quartet from the temperature dependence of the ESR signal intensity. The fine-structure parameters of the quartet anion are determined to be  $|D| = 0.123 \text{ cm}^{-1}$  and  $|E| = 0.005 \text{ cm}^{-1}$  from the ESR spectral simulation. These fine-structure parameters suggest that the excess electron of the quartet anion occupies the in-plane  $n$ -orbital at the divalent carbon atoms and that the molecular conformation of the quartet anion is non- $C_3$  symmetric. The formation of the non- $C_3$  symmetric structure releases the spin frustration of the monoanion of  $N(p\text{-DPM})_3$ .

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