

Weak Intramolecular Exchange Interaction between Two Carbenic Units in a Novel Organic High-Spin Ion. ESR Studies on a Monoanion of Biphenyl-3,3'-diylbis(phenylmethylene)

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Received July 25, 1995[⊗]

Abstract: A monoanion of biphenyl-3,3'-diylbis(phenylmethylene) (BP-3,3'-BPM) with a low-lying quintet and a triplet state near the singlet ground state was generated by γ -radiolysis followed by a subsequent visible light photolysis in a frozen solution of 2-methyltetrahydrofuran. BP-3,3'-BPM was chosen as a prototypical example whose electronic spin structure is characterized by the possession of an intramolecular weak exchange interaction between two carbenic units. A spin-quartet state was detected for the monoanion of BP-3,3'-BPM at 77 K by ESR spectroscopy. The ground state was determined to be a spin doublet from the measurement of the temperature dependence of the ESR signal intensity of the quartet state. The energy gap between the doublet ground and the quartet excited states was estimated to be about 35 cm⁻¹. The effective exchange interaction between the two carbenic units of the monoanion was compared with that of the neutral BP-3,3'-BPM to conclude that the π -spin polarization dominates in the spin alignment of the monoanion.

Introduction

Organic/molecular-based magnetism is being studied intensively in its own right of scientific interest and in quest of discovering new functionality materials.¹ Among the diverse topics of organic/molecular-based magnetism, aromatic high-spin polycarbenes are one of the most important model systems for purely organic magnetic materials with the potentiality of high transition temperatures; the potentiality is due to the topologically controlled robust π -spin polarization which underlies the through-bond approach for organic magnetism.^{2–12} The through-bond approach basically exploits strong intramolecular exchange interaction via chemical bonding in π -conju-

gated systems, contrasting with weak intermolecular exchange interaction among organic radical crystals.^{13–15}

More recently, studies have been extended to the system of charged organic high-spin polycarbenes with the intention of

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1995.

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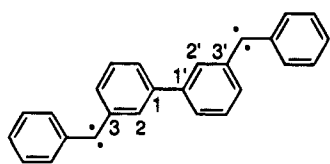
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Chart 1



disclosing the possible interplay between the electric charge and spin polarization.^{16,17} Such a study may have general significance in the physics and chemistry of organic magnetism, electric conductivity, and the related interdisciplinary research field. Our previous studies have uncovered the occurrence of the highest possible spin multiplicity of $S = 3/2$ in the ground state of *m*-phenylenebis(phenylmethylene)^{±•} (*m*-PBPM^{±•}).^{16b,c} The finding indicates that the underlying mechanism for spin alignment is the topologically controlled π -electron spin polarization rather than the spin delocalization which favors the low-spin multiplicity. Theoretical work also indicates that ionization of neutral high-spin organic systems cannot drive the ground state of the ionized system to a low-spin state.^{18,19}

Our previous studies on a particular series of neutral high-spin polycarbenes have disclosed that the spin correlation has preference of giving excited high-spin states lying close to the singlet ground state.^{3,20,21} Such high-spin polycarbenes are characterized either by the possession of an intramolecular linkage connecting the carbenic units via the weak exchange interaction or by the lack of the additivity of topologically controlled dynamic spin polarization. Biphenyl-3,3'-diylbis(phenylmethylene) (BP-3,3'-BPM) shown in Chart 1 is a prototype system representing the former category.^{3,20}

Neutral BP-3,3'-BPM has four nonbonding MO's, i.e., two degenerate out-of-plane and two degenerate in-plane orbitals localized on the two divalent carbon sites. The former and the latter are conveniently called π - and n -orbitals, respectively. The four orbitals are nearly degenerate in energy. It is found that the first three electronic states are spin-singlet, -triplet, and -quintet in the order of increasing energy. All of them lie within a narrow range of 60 cm^{-1} .^{3,22} The electronic structure of the three levels is interpreted as determined by the weak intramolecular exchange interaction through the 3,3'-connectivity of the biphenyl ring.^{3,22} It is remarkable that the magnitude of the effective exchange interaction is much smaller (by a factor of $\approx 10^{-2}$) than that of the interaction in systems such as *m*-PBPM. It should be also noted that BP-3,3'-BPM provides a case for the only apparent breakdown of Hund's rule in terms of the molecular orbital theory.³

The present work on the monoanion of BP-3,3'-BPM was motivated by these unique characters of BP-3,3'-BPM. In particular, it seems interesting to see any possible effect of the spin delocalization caused by the excess electron upon the spin polarization in view of the subtlety of the electronic structure

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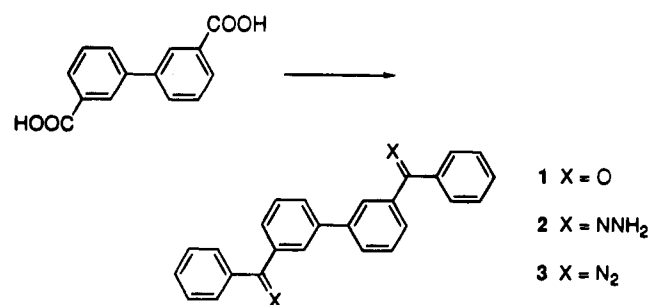
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(22) The two conformers of BP-3,3'-BPM have been reported in ref 3. An irreversible transition from one to the other took place in magnetically diluted benzophenone host lattices with increasing temperature. The energy of 60 cm^{-1} is for the conformer appearing in the low-temperature phase. The other conformer in the high-temperature phase appeared at 140 K.

Scheme 1. Preparation of the Diazo Precursor BP-3,3'-BPD



of neutral BP-3,3'-BPM dictated by the weak intramolecular exchange interaction between the two carbenic units. In view of the lack of any guiding principle to predict such an effect, attempts to accumulate experimental data are desired to get a general correlation between the excess charge and the spin alignment in organic high-spin systems. The electronic spin states derived from the effective exchange interaction in the monoanion are compared with those derived from the neutral BP-3,3'-BPM. The comparison of the exchange interaction is a highlighted part of the discussion section.

Experimental Section

The precursor of the anion studied in the present work is biphenyl-3,3'-diylbis(phenyldiazomethane) (BP-3,3'-BPD), which is synthesized according to the following procedure different from the method described before (see Scheme 1).^{3b}

1. Materials. Melting points were determined on a micro hot-stage and are uncorrected. IR spectra were taken on a JASCO A-102 IR spectrophotometer. ¹H (100 MHz) and ¹³C NMR (25 MHz) spectra were recorded on a JEOL FX-100 instrument.

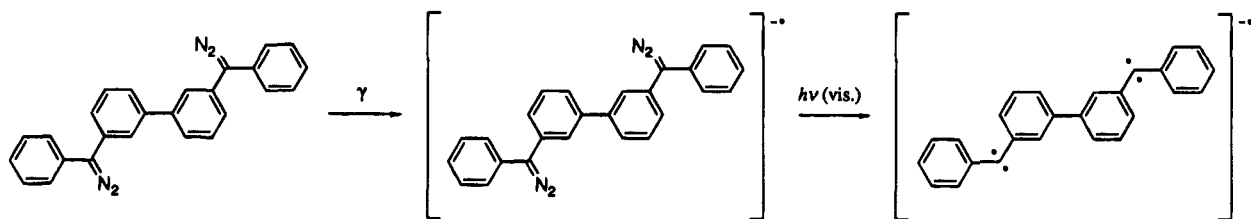
3,3'-Dibenzoylbiphenyl (1). A mixture of 4.4 g (18.3 mmol) of biphenyl-3,3'-dicarboxylic acid²³ and 20 mL of thionyl chloride was heated to a gentle reflux for 2 h under exclusion of moisture. The excess thionyl chloride was distilled off. The bis(acid chloride) was obtained as a light-brown residue and used without purification for the following reaction. A solution of the bis(acid chloride) in 100 mL of dry benzene was added dropwise at room temperature to suspension of 5.31 g of anhydrous aluminum chloride in 100 mL of dry benzene. The mixture was boiled with stirring for 3 h. The mixture was poured onto ice-water containing hydrochloric acid, and the organic layer was separated. The water layer was extracted with dichloromethane. The two organic solutions were washed separately with water and aqueous sodium hydroxide and dried over sodium sulfate. The crystals obtained after evaporation of the solvents were combined and recrystallized from ethanol to give 4.94 g (78%) of colorless prisms: mp 131–132 °C; IR (Nujol) 1650 cm^{-1} ; ¹³C NMR (CDCl₃) δ 128.4, 128.6, 128.9, 129.4, 130.1, 131.1, 132.6, 137.4, 138.4, 140.4, 196.4; MS (70 eV) *m/e* 362 (90%, M⁺), 285(95, M – C₆H₅), 105(100, C₆H₅CO). Anal. Calcd for C₂₆H₁₈O₂: C, 86.17; H, 5.01. Found: C, 86.12; H, 5.01.

3,3'-Dibenzoylbiphenyl Dihydrazone (2). A mixture of 4.0 g (11 mmol) of the diketone **1** and 35 mL of hydrazine hydrate in 150 mL of ethanol was heated under reflux for 48 h. The solution was then concentrated, and water was added and extracted with dichloromethane. The residue was chromatographed on silica gel using benzene–ethyl acetate (5:1), giving 3.3 g (77%) of powdered hydrazone **2**: mp 66–69 °C; IR (Nujol) 3400, 3270, 3200 cm^{-1} ; ¹H NMR (CDCl₃) δ 5.43 (br s, 4H, exchangeable with D₂O), 7.20–7.82 (m, 18H, aromatic).

Biphenyl-3,3'-diylbis(phenyldiazomethane) (3). To a stirred suspension of active manganese dioxide (3.2 g, freshly prepared by Attenburrow's method²⁴) in 20 mL of dry dichloromethane were added a few drops of saturated ethanolic potassium hydroxide under nitrogen in the dark. The reaction was monitored by measuring the growth of

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Scheme 2. Formation Process of the Monoanion of BP-3,3'-BPM

the IR absorption at 2050 cm^{-1} due to the diazo group of the aliquots. The absorbance reached a maximum after 1 h, when the mixture was filtered. The wine-red solution was concentrated to a few milliliters under reduced pressure. Purple crystals of **3** (880 mg, 74%) were precipitated by addition of pentane: mp $82\text{--}83\text{ }^{\circ}\text{C}$ (dec); IR (Nujol) 2050 cm^{-1} . Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{N}_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.37; H, 4.32; N, 14.25.

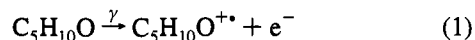
2. Preparation of the Sample. As for the formation of the target monoanion of BP-3,3'-BPM, the same technique as that employed for the study of the anion of *m*-PBPM was used, that is, γ -irradiation of the diazo precursor in glassy 2-methyltetrahydrofuran (MTHF) followed by visible light photolysis, both at 77 K (see Scheme 2). The experimental procedure employed here is essentially the same as that in the previous work^{16a,b} and will be recapitulated only briefly.

The diazo precursor **3** (BP-3,3'-BPD) was dissolved in MTHF. Commercial MTHF was purified with Na-K alloy and lithium aluminum hydride as in the previous work.^{16a} A solution of BP-3,3'-BPD concentrated to ca. 10 mM was sealed in ESR cells after degassing. The sample was then γ -irradiated at 77 K by a dose of ca. 10^{19} eV/g. This procedure led to the formation of the spin-doublet radical anion of BP-3,3'-BPD. The radical anion exhibiting an absorption in the visible to near-infrared region was successively photolyzed at 77 K with light of wavelength $\lambda > 620\text{ nm}$ from a xenon lamp with a cut-off glass filter (Toshiba R-62). The photolysis brought about the elimination of nitrogen molecules from the diazo groups in the radical anion of BP-3,3'-BPD to generate the desired anion, BP-3,3'-BPM^{-•}.

The ESR measurement was carried out with a JEOL JES-RE2X spectrometer equipped with an Oxford 910 variable-temperature controller. A Hitachi U-3300 spectrophotometer was used for the optical measurement.

Results and Discussion

1. Formation of BP-3,3'-BPM^{-•}. The major processes in the γ -irradiated MTHF ($\text{C}_5\text{H}_{10}\text{O}$) glass can be summarized as follows:²⁵



Reaction 2 represents the electron attachment to the solute denoted by S. In the present work S corresponds to the diazo precursor BP-3,3'-BPD. Since the concentration of the solute is only ca. 10 mM, the direct action of the γ -photons from a ^{60}Co source to the solute is ignorable and the solute is reduced to its anion by the thermal electron attachment of reaction 2. The electronic absorption spectrum at this stage is shown in curve 2 of Figure 1. The absorption band at about $(17\text{--}25) \times 10^3\text{ cm}^{-1}$ in curve 1 is due to the diazo group of the intact solute. The ESR spectrum corresponding to curve 2 of Figure 1 was

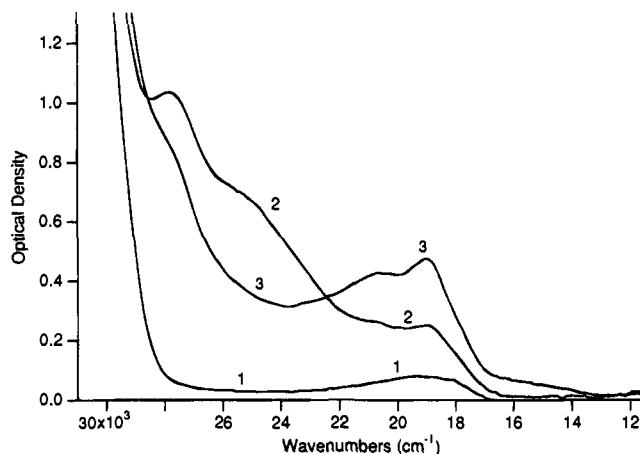


Figure 1. Optical absorption spectra of the diazo precursor of BP-3,3'-BPM in the MTHF solution at 77 K: 1, before γ -irradiation; 2, after γ -irradiation; 3, same as 2 after photolysis with $\lambda > 620\text{ nm}$.

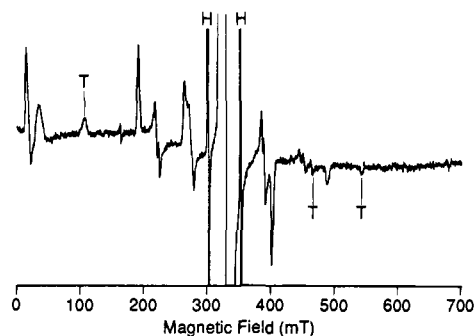


Figure 2. X-band ESR spectra for a γ -irradiated and subsequently photolyzed diazo precursor of BP-3,3'-BPM in the MTHF solution at 77 K. Prior to photolysis, the spectrum showed only the signal at 320–340 mT and the doublet due to the hydrogen atom produced in the quartz cell by γ -irradiation. Upon photolysis, several new peaks appeared in the ESR spectrum over the wide range of 0–600 mT. The new peaks are assigned to the spin-quartet state of BP-3,3'-BPM^{-•}. The symbol T indicates the signals due to the byproduct neutral triplet monocarbene.

observed in the range of 320–340 mT, which was assigned to the radical anion of BP-3,3'-BPD and the radicals generated from the solvent MTHF.

When the γ -irradiated sample was photolyzed with light of $\lambda > 620\text{ nm}$, several new ESR signals appeared in the wide range of 0–600 mT (see Figure 2). The appearance of the new ESR signals indicates the formation of new high-spin species. Parallel measurements of optical spectra also showed a remarkable change from curve 2 to curve 3 in Figure 1. This optical change is regarded as due to the formation of BP-3,3'-BPM^{-•}, which corresponds to the ESR spectral change in Figure 2.

2. Analysis of the ESR Spectra. In order to determine the spin multiplicity of the observed high-spin state, the observed ESR spectra were analyzed by comparing with the simulated spectra constructed on the basis of the following spin Hamiltonian, where each term has the usual meaning:^{16,26}

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$$\mathcal{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \quad (4)$$

The energy matrix corresponding to a particular orientation of the magnetic field was directly diagonalized to obtain the resonance field and the transition probability. Generally, the fine structure spectrum for each orientation must be summed over the whole spherical angle of the 4π in order to get the powder-pattern spectrum. Since the \mathbf{g} tensor, whose anisotropy is usually negligibly small for hydrocarbons, was assumed to be isotropic, the integration range could be reduced to one-eighth of the whole sphere.²⁶ A total of 64 800 orientations was sampled, and a Gaussian line width of 3.0 mT was assumed in common to all ESR transitions. The observed ESR spectrum was reproduced by superposing two simulated spin-quartet spectra with slightly different fine structure parameters. The best-fit parameters for these two calculated spectra are found to be $S = 3/2$, $g = 2.003$ (isotropic), $|D| = 0.137 \text{ cm}^{-1}$, and $|E| = 0.0055 \text{ cm}^{-1}$ (conformer 1) and $S = 3/2$, $g = 2.003$ (isotropic), $|D| = 0.134 \text{ cm}^{-1}$, and $|E| = 0.0063 \text{ cm}^{-1}$ (conformer 2). In Figure 3 are shown the observed and simulated ESR spectra constructed with the above parameters. The principal axis transitions are labeled X, Y, and Z under the assumption of $E > 0$, while the off-axis extra lines²⁷ and the forbidden lines corresponding to the transitions of $\Delta m_s = \pm 2$ and ± 3 are marked by A and F, respectively. The agreement between the observed and the simulated spectrum is satisfactory. The possibility of quantum spin mixing between different spin states can be ruled out because of the satisfactory agreement which suggests that the energy gap between the spin states of the anion is greater than $\approx 1 \text{ cm}^{-1}$.²⁸

3. Spin Multiplicity of the Ground State of BP-3,3'-BPM⁻. In order to identify the spin multiplicity of the ground state of BP-3,3'-BPM⁻, the temperature dependence of the intensity of the signal due to the quartet state of BP-3,3'-BPM⁻ was measured by monitoring the low-field Y-axis canonical peak at about 200 mT. The intensity was calculated by double integration of the first-derivative peak. The temperature of the sample was determined by referring to the signal assigned to the byproduct ground-state triplet monocarbene as an internal standard of the temperature.^{16b,c} The observed intensity is represented by circles in Figure 4. The convex shape of the plots against the inverse of the temperature indicates that the observed quartet spectrum is not due to the ground state but to a thermally populated excited state, that is to say, the ground state is in a low-spin doublet. Unfortunately, the ESR signal of the spin-doublet ground state is completely masked by the spectrum of radicals originating from radiolyzed MTHF. Since the electronic spin structure of the neutral BP-3,3'-BPM is established as having a low-lying quintet and a triplet state near the singlet ground state, the electron attachment to BP-3,3'-BPM gives only a single doublet and a single quartet state. (See Scheme 3. The three states of BP-3,3'-BPM are correlated with the pair of the doublet and quartet states of the anion. This is true irrespective of the type of the nonbonding orbitals of π - or n -character of BP-3,3'-BPM in which the excess electron is to be accommodated.)

The result that the ground state of the anion is a spin-doublet indicates that the electron attachment to BP-3,3'-BPM does not reverse the order of low-spin (singlet) and high-spin (triplet and quintet) states of neutral BP-3,3'-BPM. The result also suggests that the spin polarization is the dominant mechanism to

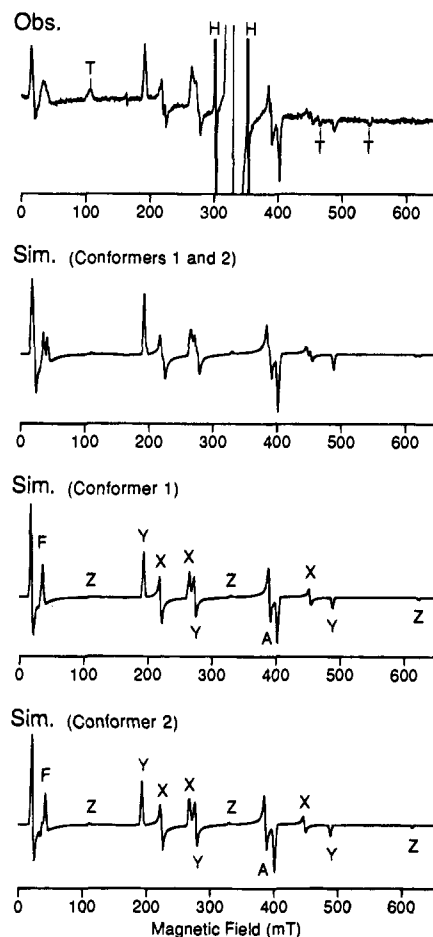


Figure 3. Observed and simulated X-band ESR spectra for the quartet state of BP-3,3'-BPM⁻. The microwave frequency employed was 9.227 GHz. Symbols A and F in the simulated spectra denote the off-axis extra line and the forbidden transition with $\Delta m_s = \pm 2$ and ± 3 . The fine structure parameters of the two spin-quartet conformers were determined to be $|D| = 0.137 \text{ cm}^{-1}$ and $|E| = 0.0055 \text{ cm}^{-1}$ for conformer 1 and $|D| = 0.134 \text{ cm}^{-1}$ and $|E| = 0.0063 \text{ cm}^{-1}$ for conformer 2.

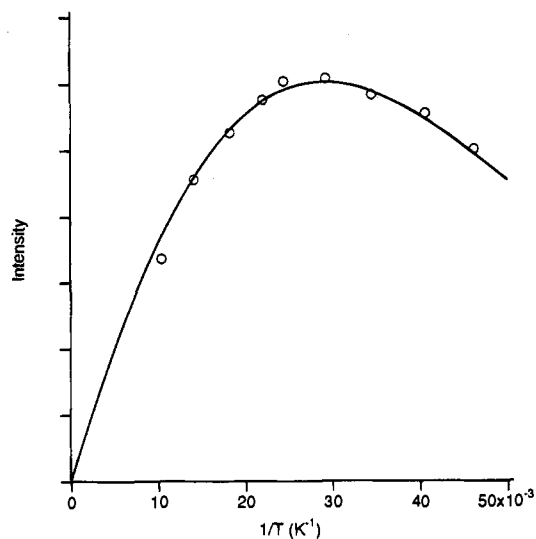


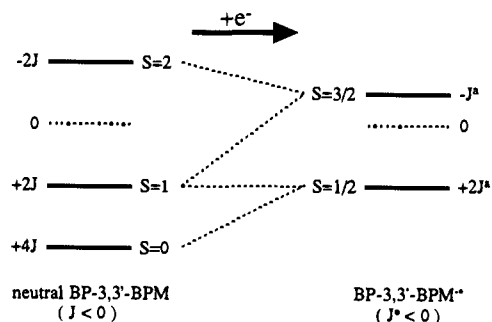
Figure 4. Temperature dependence of the intensity of the ESR signal of the low-field Y-axis canonical peak of the quartet anion. The circles are experimental, and the solid curve is calculated by eq 5 in the case of $\Delta E = 35 \text{ cm}^{-1}$.

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determine the spin alignment in the anion as in the neutral BP-3,3'-BPM. Now the question is whether or not a significant

Scheme 3. Correlation of the Spin States between the Neutral BP-3,3'-BPM and BP-3,3'-BPM^{-•} ^a

^a The symbols J and J^{\bullet} represent the effective exchange interaction parameters of the neutral species and the monoanion, respectively. Both are negative, which indicates that the interaction between the two diphenylmethylene units is antiferromagnetic in the ground state of both systems.

change in the magnitude of the effective exchange interaction occurs in the monoanion. Thus, we have attempted to determine the energy gap between the spin-quartet excited and the doublet ground state. Besides the ESR spectrum due to the doublet ground state, only the spectrum due to the quartet state was observed at temperatures below 77 K. The analysis of the data in Figure 4 was made under the assumption of the doublet-quartet two-spin-state model which is justifiable by the above theoretical argument of the correlation of spin states between BP-3,3'-BPM and its anion. As a result, the doublet-quartet energy gap ΔE was estimated as 35 cm^{-1} by using the following equation derived under the assumption of the Boltzmann distribution and the high-temperature approximation, $kT \gg h\nu \approx 0.3 \text{ cm}^{-1}$. The solid curve in Figure 4 was theoretical with $\Delta E = 35 \text{ cm}^{-1}$.

$$I(T) \propto \frac{1}{T} \frac{1}{4 + 2 \exp(\Delta E/kT)} \quad (5)$$

We note that the Y peak at $\approx 200 \text{ mT}$ which was monitored in the intensity measurement as a function of temperature is contributed almost equally by the two conformers, and thus ΔE is considered to be the same between the two within our experimental accuracy. The closeness of the fine structure parameters of the two conformers suggests that they originate from the same electronic spin states with only a slight difference in the molecular structure.

4. Effective Exchange Interaction between the Two Carbenic Units of BP-3,3'-BPM^{-•}. Neutral BP-3,3'-BPM is the first prototypical molecule having two spin-triplet carbenic units which are coupled by a weak intramolecular exchange interaction to give the singlet ground state, the triplet first excited state, and the quintet second excited state. The electronic structure has been interpreted in terms of an intramolecular triplet-triplet exchange model.^{3,20} The Heisenberg-Dirac valence-bond Hamiltonian describing the interaction between two carbene sites i and j is employed in combination with the full basis set of $|S_1^z S_2^z \dots S_N^z\rangle$, where all the N π -electrons are taken into account.²⁹

As for the monoanion of BP-3,3'-BPM there are two approaches to interpret the electronic structure. The first is to construct the spin states of the anion by coupling the nearly degenerate spin states of $S = 0, 1$, and 2 of the neutral BP-3,3'-BPM with the single excess electron (see Scheme 3). This approach allows us to correlate the spin states of BP-3,3'-BPM

with its monoanion. The second approach is to invoke the intramolecular triplet-doublet exchange model which is a straightforward modification of the model employed for the interpretation of the neutral BP-3,3'-BPM. Both approaches give the same result as schematically shown in Scheme 3. We adopt the latter approach which provides the intramolecular effective exchange interaction between two spin units, S_A and S_B , by eq 6:

$$\mathcal{H} = -2JS_A \cdot S_B \quad (6)$$

The eigenenergy is given by eq 7, where the total electron spin quantum number S runs from $S_A + S_B$ to $|S_A - S_B|$:

$$E(S) = -J[S(S+1) - S_A(S_A+1) - S_B(S_B+1)] \quad (7)$$

According to eq 7, the low-lying quintet and triplet states are located by $-6J$ and $-2J$ above the singlet ground state, respectively, for the neutral BP-3,3'-BPM. These energy gaps have been compared with the experimental values, 60 and 20 cm^{-1} , respectively to give $J = -10 \text{ cm}^{-1}$ for the neutral BP-3,3'-BPM.³ The minus sign of J means that the spin coupling between the two carbenic units is antiferromagnetic.

According to the doublet-triplet heterospin interaction model the low-lying quartet state of the monoanion is located by $-3J^{\bullet}$ above the doublet ground state. The experimentally determined energy gap $\Delta E = 35 \text{ cm}^{-1}$ can be compared with $-3J^{\bullet}$ for the monoanion of BP-3,3'-BPM to give $J^{\bullet} = -11.7 \text{ cm}^{-1}$ for BP-3,3'-BPM^{-•}. Although a quantitative argument on J^{\bullet} as compared with J is hard, we regard that the relation $|J^{\bullet}| \geq |J|$ as significant. At the same time, the relative proximity of the two values seems to indicate that the electron attachment does not cause drastic influence upon the spin polarization.

5. Molecular Conformation of the Spin-Quartet BP-3,3'-BPM^{-•}. The fine-structure tensor of aromatic high-spin polycarbenes can be described approximately as a superposition of the one-center spin-spin interaction of $n-\pi$ type at each divalent carbon site.⁴ Thus, the fine-structure tensor depends sensitively on the relative orientation of the one-center interaction local tensors and the spin densities at the divalent carbon sites. The electronic spin and molecular structures of charged high-spin polycarbenes have been argued semiquantitatively on the basis of this property of the fine-structure tensor.^{16b,c} A semiquantitative expression for the fine-structure tensor for BP-3,3'-BPM^{-•} is given by eq 8 under the assumption that the one-center spin-spin interaction at the diphenylmethylene (DPM) unit dominates:⁴

$$D_{ij} = [S(2S-1)]^{-1} \sum_k (\rho_k / \rho_{\text{DPM}}) (\mathbf{U}_k \cdot \mathbf{D}_{\text{DPM}} \cdot \mathbf{U}_k^{-1})_{ij} \quad (8)$$

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

Here, D_{ij} stands for the ij element of the fine structure tensor of the anion and D_{DPM} denotes the fine-structure tensor of the DPM unit represented in terms of the local principal axis system of the carbene site k . In the present work the following observed values were used: $D_{\text{DPM},XX} = -0.15420 \text{ cm}^{-1}$, $D_{\text{DPM},YY} = -0.11584 \text{ cm}^{-1}$, $D_{\text{DPM},ZZ} = 0.27003 \text{ cm}^{-1}$, respectively.³⁰ The subscript k runs over all the divalent carbon atoms whose in-plane n -orbital is assumed not to be filled by the excess electron. The symbols ρ_k and ρ_{DPM} represent the spin density of the π -electron at the k th divalent carbon atoms of the anion and DPM, respectively. The values of ρ_k and ρ_{DPM} were evaluated by the Hückel MO method. The unitary matrix \mathbf{U}_k transforms

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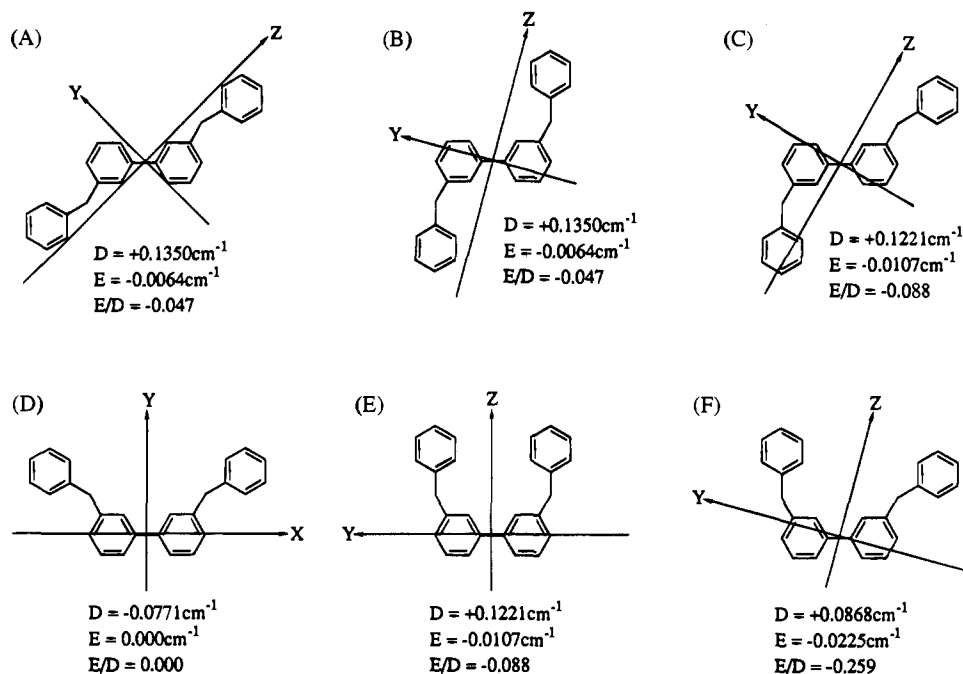
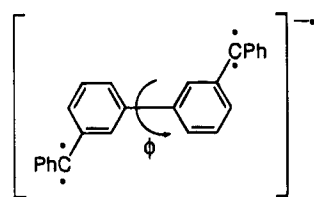


Figure 5. Possible molecular conformations of the spin-quartet BP-3,3'-BPM^{-•}. The fine-structure parameters and principal axes were calculated by eq 8.

Scheme 4



the principal axes of the one-center interaction tensor at the k th divalent carbon atom to appropriate molecule fixed axes.

The neutral BP-3,3'-BPM in the low-lying quintet state has four singly-occupied orbitals, that is, the two topologically degenerate π -orbitals and the two degenerate in-plane n -orbitals at the divalent carbon atoms. In order to obtain information on the molecular conformation of the monoanion of BP-3,3'-BPM, we assume that an excess electron occupies the π nonbonding MO's.^{16b,c,31} We will discuss the case for the n -monoanion later.

If the excess electron of the anion is in the π -orbital, the two one-center $n-\pi$ interactions must be summed. The relative orientation of these two one-center interaction tensors is critical in determining the fine-structure tensor of the whole molecule.

If the biphenyl group of BP-3,3'-BPM^{-•} is planar, there are six different conformations as shown in Figure 5. We calculated D_{ij} , viz. the \mathbf{D} tensor for these six possible conformations referring to eq 8 and assuming the π -anion. Diagonalization of the \mathbf{D} tensor gives the D , $|E|$, and $|E/D|$ values and the directions of the principal axes of the \mathbf{D} tensor. The fine-structure parameters were calculated under the following two assumptions: (1) The π -spin density of the anion of BP-3,3'-BPM at each divalent carbon atom is a one-half of the density of the neutral species. (2) The bond angles at the divalent carbon atoms are assumed to be 150° . The calculated values of the principal values of the tensor for all the six possible conformations are shown in Figure 5 together with the principal axes, X , Y , and Z . From the comparison with the observed

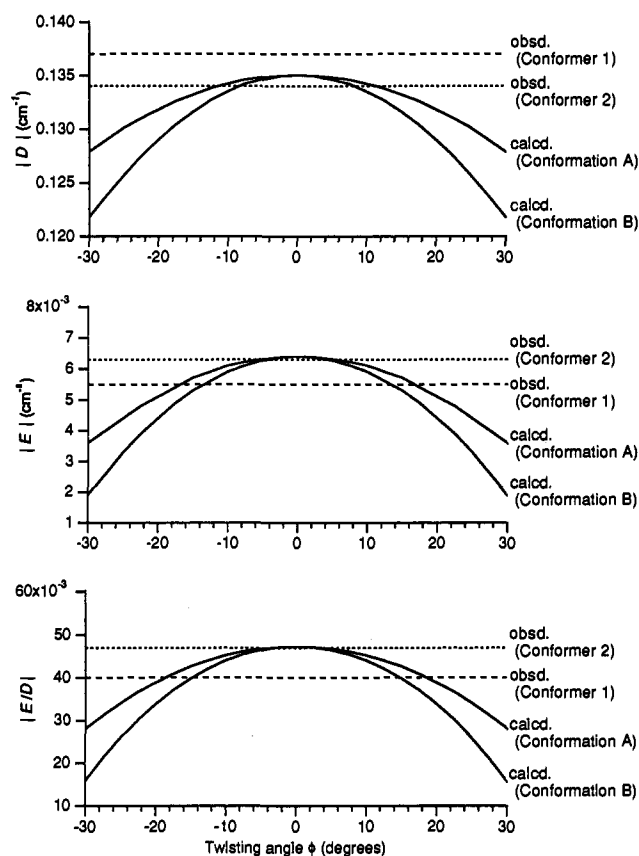


Figure 6. Dependence of the fine-structure parameters, $|D|$, $|E|$, and $|E/D|$ on the twisting angle ϕ of the biphenyl group of the spin-quartet BP-3,3'-BPM^{-•}. The two solid curves were calculated for conformations A and B, while the broken lines represent the values observed for conformers 1 and 2.

values, the most probable conformations were found to be conformations A and B with the common values of $D = +0.1350 \text{ cm}^{-1}$, $|E| = 0.0064 \text{ cm}^{-1}$, and $|E/D| = 0.047$. It should be noted that the above assumption does not require the planarity of the local DPM unit.

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In order to see the effect of the restriction of the planarity (collinearity of the two local tensors), calculations were also made by twisting the phenyl rings in the biphenyl skeleton (see Scheme 4).⁴ The results for the two possible conformations A and B are shown in Figure 6. The calculated values of the fine-structure parameters for both cases depart from the observed ones when the twisting angle ϕ becomes larger than 20° . Therefore, the spin-quartet anion of BP-3,3'-BPM probably gives preference to conformation A or B with $|\phi| \leq 20^\circ$. The slightly twisting of the biphenyl group is conjectured to bring about the small discrepancy of the fine-structure parameters of the two conformers observed.

If the excess electron of the anion is in the in-plane degenerate n-orbital, one of the two one-center n- π interactions will be zero without configurational mixing. Considering the projection factor, the D and E values for the n-monoanion of BP-3,3'-BPM are calculated to be one-third of those of nonsubstituted DPM. The calculated D and E values also reproduce the observed ones. Although the possibility of the n-anion cannot be ruled out by the argument above, the possibility of the π -anion case seems favored in view of the fact that both of the electron spin structures of the high-spin quintet states of BP-3,3'-BPM and *m*-PBPM are governed by the π -topological electron network and that the π -anion is the case for *m*-PBPM.^{16b}

Conclusion

The system of BP-3,3'-BPM studied in the present work contrasts with the system of *m*-PBPM studied previously because in the former two carbenic units are coupled by a weak intramolecular exchange interaction giving two low-lying excited

states of high-spin multiplicities near the singlet ground state whereas in the latter the strong spin polarization dominates to yield the highest spin multiplicity of five for neutral *m*-PBPM. Comparison of the effect of ionization upon the spin alignment in the two systems is considered to be interesting because the spin polarization mechanism found to be predominant in both neutral and ionized *m*-PBPM may fail in the more subtle system of BP-3,3'-BPM. As a matter of fact, it is found that the spin polarization mechanism operates effectively in both neutral and ionized BP-3,3'-BPM just as in *m*-PBPM system. Furthermore, the effective exchange interaction between the two carbenic units of ionized BP-3,3'-BPM turned out to be only slightly larger than that of neutral BP-3,3'-BPM, implying that the excess electron in the monoanion of BP-3,3'-BPM does not cause a drastic effect on the spin polarization. In order to settle the guiding principle to predict the effect of the charge on the spin alignment in organic high-spin systems, we maintain that it is necessary to accumulate the experimental facts, such as in the present as well as in our previous work.

Acknowledgment. The study was supported by Grants-in-Aid for Scientific Research on Priority Areas "Molecular Magnetism" (Area No. 228/04 242 103 and 105) from the Ministry of Education, Science, and Culture in Japan. This work was partly supported by the NEDO project on "Organic Magnetism". T.N. acknowledges support from the Fellowships of the Japan Society of the Promotion of Science for Japanese Junior Scientists.

JA952498O