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Novel Organic Ions of High-Spin States IV.: ESR Studies on a Monoanion of a Prototype System Having Two Carbenic Units Coupled by a Weak Intramolecular Exchange Interaction, Biphenyl-3,3′-Bis(Phenylmethylene)

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NOVEL ORGANIC IONS OF HIGH-SPIN STATES IV.: ESR STUDIES ON A MONOANION OF A PROTOTYPE SYSTEM HAVING TWO CARBENIC UNITS COUPLED BY A WEAK INTRAMOLECULAR EXCHANGE INTERACTION, BIPHENYL-3,3'-BIS(PHENYLMETHYLENE)-•

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Abstract The monoanion of biphenyl-3,3'-bis(phenylmethylene) (BP-3,3'-BPM) was produced and its electronic states were studied by ESR spectroscopy to conclude that the ground state is spin-doublet and that the first excited state is quartet lying above the ground state by 35cm^{-1}. The effective exchange interaction between the two carbenic units was analyzed in comparison with the interaction in the neutral parent BP-3,3'-BPM. The spin polarization of the π-electrons dictates the spin alignment in the anion as in the case of the previously studied neutral BP-3,3'-BPM.

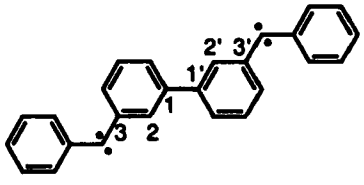
INTRODUCTION

Organic/molecular based magnetism and the quest for the related intriguing functionality materials are one of the hot issues in materials science.[1,2] The π spin polarization in aromatic high-spin polycarbenes is topologically controlled and the systems are viable for getting organic magnetic materials of high transition temperatures.[3-10] Likewise, the robust spin polarization in several high-spin polyradical systems allows the through-bond approach to design molecular magnetism.[11-14] The strong intramolecular exchange interaction in the above systems contrasts with the weak intermolecular exchange interaction in organic radical crystals.[15-18]

In addition to neutral organic high-spin polycarbenes extensively studied so far, we have recently extended our study to charged high-spin organic systems.[19-22] They are regarded as a pertinent model system to understand the effect of the charge on the spin polarization, which is an important topic in interdisciplinary fields dealing with molecular

magnetism and electric conductivity. Our previous papers[20,21] uncover the occurrence of the highest possible spin multiplicity ($S = 3/2$) in the ground state of charged quintet dicarbenes, *m*-phenylenebis(phenylmethylene)$^{\pm\bullet}$ (*m*-PBPM$^{\pm\bullet}$), indicating that the underlying mechanism for spin alignment is the topologically controlled π-spin polarization in the systems. The spin polarization overwhelms the spin delocalization which favors low spin ground states. Theoretical predictions also indicate that ionization in the robust high-spin organic system cannot drive the ground state into low spin ground states.[23,24]

Biphenyl-3,3'-bis(phenylmethylene) (BP-3,3'-BPM) (see Scheme I) has a low-lying excited triplet and a quintet state nearby the singlet ground state. These states are interpretable in terms of the possession of a weak intramolecular exchange linking mode.[6,25,26]



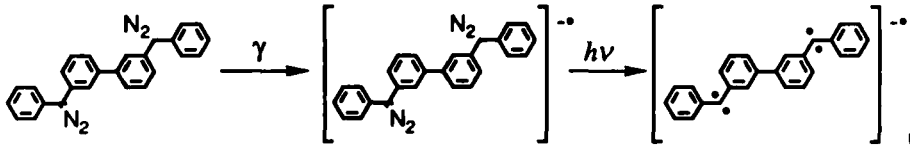
(I)

The magnitude of the effective exchange interaction between the two carbenic units in BP-3,3'-BPM is much smaller (by a factor of $\approx 10^{-2}$) than the interaction in meta-linked phenylene polycarbenic systems such as *m*-PBPM.

The present work was motivated by these unique characters of BP-3,3'-BPM. The system chosen is suited for understanding the influence of the spin delocalization caused by the ionization upon the spin polarization.

EXPERIMENTAL

The precursor of the anion of BP-3,3'-BPM studied in the present work is biphenyl-3,3'-bis(phenyldiazomethane). The anion was formed by the same technique as that employed for the anion of *m*-PBPM, that is, γ-irradiation of the diazo precursor in a glassy 2-methyltetrahydrofuran (MTHF) at 77K[28-30] and the subsequent photolysis by visible light at the same temperature.[19-21] The consecutive reactions are schematically shown in Scheme II.



(II)

RESULTS AND DISCUSSION

ESR Spectra of the Spin-Quartet State of BP-3,3'-BPM$^{-\bullet}$

When the γ-irradiated sample was photolyzed with the light of λ>620nm, several new ESR signals appeared in the wide range of 0~600mT (see Figure 1a). The appearance of the new ESR signals indicates the formation of new high-spin species. 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.[19-21,31]

$$\mathcal{H} = g\beta \mathbf{S}\cdot\mathbf{H} + D\left[S_Z^2 - S(S+1)/3\right] + E\left(S_X^2 - S_Y^2\right) \quad (1)$$

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), $|D| = 0.137$ cm^{-1}, and $|E| = 0.0055$ cm^{-1} (Conformer 1) and $S = 3/2$, $g = 2.003$ (isotropic), $|D| = 0.134$ cm^{-1}, and $|E| = 0.0063$ cm^{-1} (Conformer 2). In Figure 1b is shown the simulated ESR spectrum constructed with the above parameters. The agreement between the observed and the simulated spectra is satisfactory. The possibility of quantum spin mixing between different spin states can be ruled out because of the satisfactory agreement.

Spin Multiplicity of the Ground State of BP-3,3'-BPM$^{-\bullet}$

In order to identify the spin multiplicity of the ground state of BP-3,3'-BPM$^{-\bullet}$ the temperature dependence of the intensity of the signal due to the quartet state of BP-3,3'-BPM$^{-\bullet}$ was measured by monitoring the low-field Y-axis canonical peak at about 200mT. The observed intensity is represented by circles in Figure 2. The convex shape of the plots against the inverse of temperature indicates that the observed quartet spectrum is not due to the ground state but to a thermally populated excited state, viz., the ground state is in a low-spin doublet state. Unfortunately, the ESR signal of the spin doublet ground state is completely masked by the spectrum of radicals originating from radiolyzed MTHF. The result indicates that ionization of BP-3,3'-BPM does not reverse the order of low (singlet) and high-spin (triplet and quintet) states of neutral BP-3,3'-

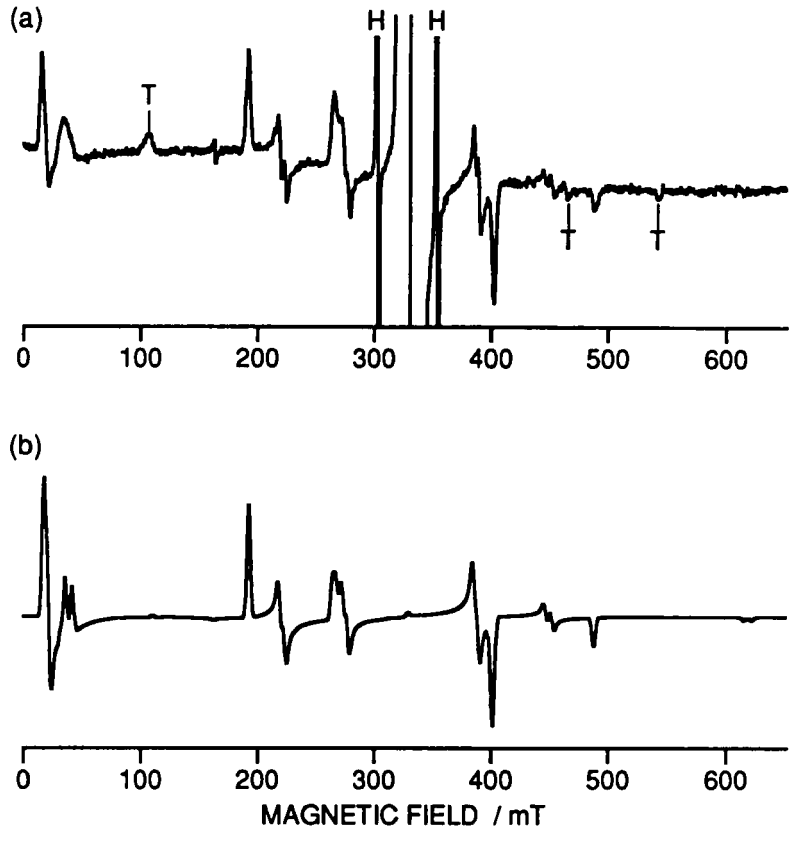


FIGURE 1 (a) X-band ESR spectrum for a γ-irradiated and subsequently photolyzed diazo precursor of BP-3,3'-BPM in the MTHF solution at 77 K. Microwave frequency employed was 9.227GHz. The symbol T indicates the signals due to the by-product neutral triplet monocarbene. (b) Simulated X-band ESR spectrum for the quartet state of BP-3,3'-BPM$^{-\bullet}$, which was constructed by superposing two simulated spin-quartet spectra with slightly different fine structure parameters (see text.).

BPM. The result also suggests that the spin polarization is the dominant mechanism to determine the spin alignment in the ionized species as in the neutral BP-3,3'-BPM. The analysis of the data in Figure 2 was made by the doublet-quartet two spin states model (see below). As a result, the doublet-quartet energy gap $\Delta E = E$(Quartet) - E(Doublet) was estimated as 35cm^{-1} by using the following equation derived under the assumption of the Boltzmann distribution and the high temperature approximation, $kT >> h\nu \approx$ 0.3cm^{-1}. The solid curve in Figure 2 was theoretical with ΔE = 35cm^{-1}.

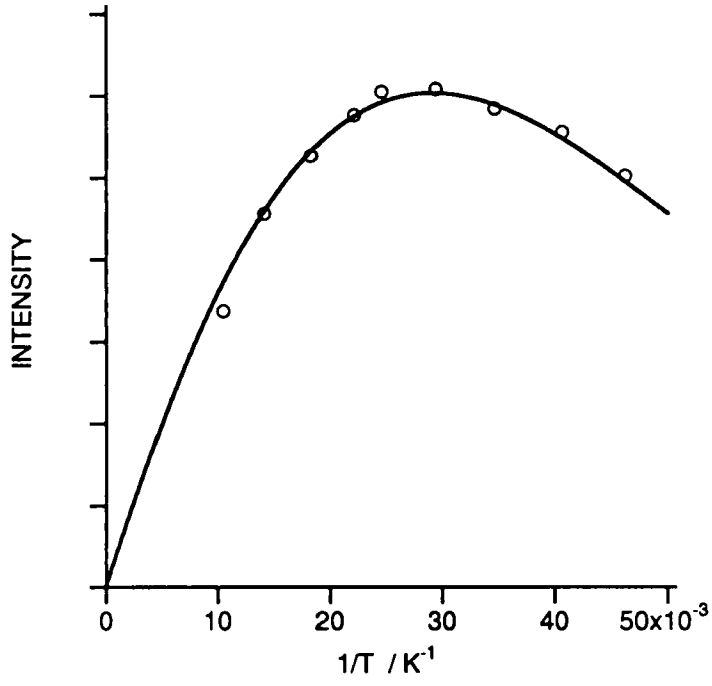


FIGURE 2 Temperature dependence of the intensity of the ESR signal of the low-field Y-axis canonical peak of the quartet anion. The circles are experimental and the solid curve is calculated by Equation (2) in the case of $\Delta E = 35\text{cm}^{-1}$.

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

We note that the Y peak at ≈200mT 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 within our experimental accuracy.

Effective Exchange Interaction between the Two Carbenic Units in the Anion

As for the monoanion of BP-3,3'-BPM there are two approaches for the interpretation of 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 Figure 3). This approach allows us to correlate the spin states of BP-3,3'-BPM with those of its monoanion. The second approach is to invoke the

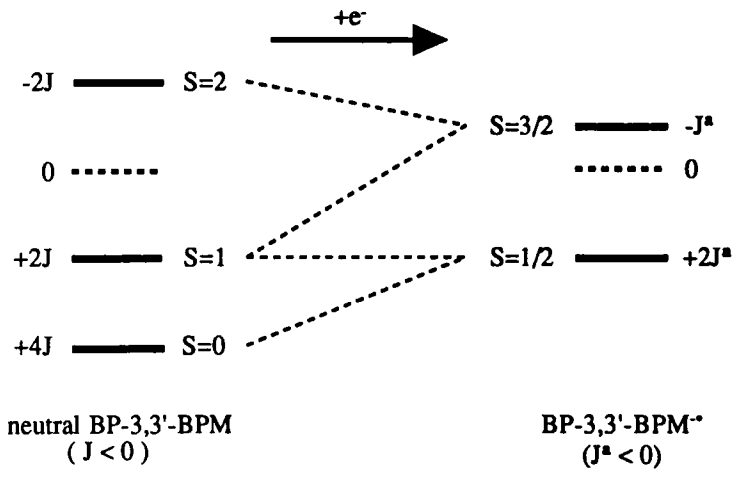


FIGURE 3 Correlation of the spin states between the neutral BP-3,3'-BPM and BP-3,3'-BPM$^{-\bullet}$. J and J^a are effective exchange interaction parameters of the neutral species and the monoanion, respectively. Both the parameters, J and J^a , are negative, which indicates that the interaction between the two carbenic units is antiferromagnetic in the ground state of both the systems.

intramolecular triplet-doublet exchange model which is a straightforward modification of the model employed for the interpretation of the neutral BP-3,3'-BPM: The second approach gives only a pair of doublet and quartet states assuming that either an n-anion or a π-anion[20] is generated upon the soft electron attachment under study. Both approaches give the same result as schematically shown in Figure 3.

We adopt the latter approach which provides the intramolecular effective exchange interaction by Equation (3) below.

$$\mathcal{H} = -2JS_A \bullet S_B \tag{3}$$

S_A and S_B represent the spin quantum numbers of the exchange-interacting parts A and B in the anion. The eigenenergy is given by Equation (4) where the total electron spin quantum number S runs from S_A+S_B to $|S_A-S_B|$.

$$E(S) = -J\left[S(S+1) - S_A(S_A+1) - S_B(S_B+1)\right] \tag{4}$$

When already applied to neutral BP-3,3'-BPM, J is determined to be $-10cm^{-1}$ by comparison with the experimental values of $20cm^{-1}$ and $60cm^{-1}$ for the triplet and quintet states relative to the ground state.[6] The negative sign of J means that the interaction between the two carbenic units is antiferromagnetic. Analogously, for the

monoanion of BP-3,3'-BPM we have $J^a = -11.7 cm^{-1}$, which may be regarded the relation $|J^a| \gtrsim |J|$ as significant. The result, nevertheless, indicates that the addition of electron to neutral BP-3,3'-BPM does not cause drastic changes in the exchange interaction.

Molecular Conformation of the Spin-Quartet Monoanion of BP-3,3'-BPM

A semiquantitative expression for the fine structure tensor for BP-3,3'-$BPM^{-\bullet}$ is given by Equation (5) under the assumption that the one-center spin-spin interaction at the diphenylmethylene (DPM) unit dominates.[6,7]

$$D_{ij} = [S(2S-1)]^{-1} \sum_k (\rho_k/\rho_{DPM}) (\mathbf{U}_k \cdot \mathbf{D}_{DPM} \cdot \mathbf{U}_k^{-1})_{ij}, \quad i, j = X, Y, Z \tag{5}$$

Here D_{ij} stands for the ij element of the fine structure tensor of the anion and $\mathbf{D}_{DPM}$ denotes the fine structure tensor of the DPM unit represented in terms of the local principal axis system of the divalent carbon site k. In the present work the following observed values were used: $D_{DPM,XX} = -0.15420\ cm^{-1}$, $D_{DPM,YY} = -0.11584\ cm^{-1}$, $D_{DPM,ZZ} = 0.27003\ cm^{-1}$, respectively.[32] 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 kth 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 the principal axes of the one-center interaction tensor at the kth divalent carbon atom to the principal axes of the fine structure tensor of the whole molecule.

Neutral BP-3,3'-BPM has four non-bonding 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. Thus, the electronic structure of BP-3,3'-$BPM^{-\bullet}$ depends on whether an excess electron of the anion occupies one of the non-bonding π-orbitals or n-orbitals. If the excess electron is in the out-of-plane degenerate π-orbital, the two one-center n-π interactions must be summed up. If the biphenyl group of BP-3,3'-$BPM^{-\bullet}$ is planar, there are six different conformations. 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 half of the density of the neutral species. (2) The bond angle at the divalent carbon atom is 150°. From the comparison with the observed values, the most probable conformations were found to be conformations A and B with the common values of $D = +0.1350\ cm^{-1}$, $|E| = 0.0064$

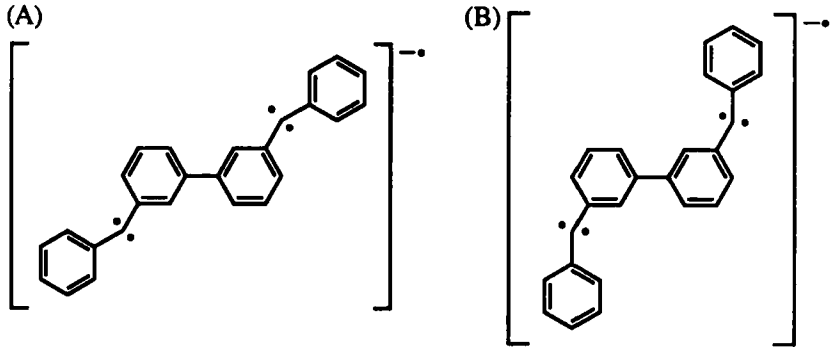
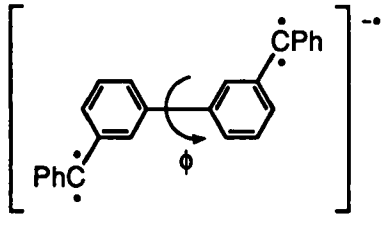


FIGURE 4 Two most probable molecular conformations of the spin-quartet BP-3,3'-BPM$^{-\bullet}$.

cm^{-1}, and $|E/D| = 0.047$ (see Figure 4). It should be noted that the above assumption does not require the planarity of the local DPM unit.

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 angle ϕ in Scheme III.[7] The calculated values of the fine structure parameters for both cases depart from the observed ones when the twisting angle becomes larger than 20°.



(III)

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 unless configurational mixing is considered. Considering the projection factor, the D and E values for the n-monoanion of BP-3,3'-BPM are calculated to be 1/3 of those of non-substituted 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 the electron spin structure of the high-spin quintet state 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.[20]

CONCLUSION

The ground state of BP-3,3'-BPM$^{-\bullet}$ was determined to be spin-doublet from the temperature dependence of the ESR signal intensity. The energy gap between the doublet ground state and the quartet excited state was estimated to be about 35cm^{-1}. The ionization did not reverse the order of low and high-spin states. Furthermore, it turned out that the effective exchange interaction between the two carbenic units of BP-3,3'-BPM$^{-\bullet}$ is 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 drastic effect on the spin polarization. The present work illustrates that π spin polarization is conceptually important in designing novel multifunctionality organic materials in which both charge and spin feature.

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