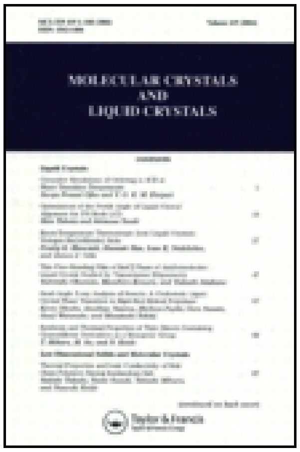

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Novel Organic Ions of High-Spin States VI.: ESR Study on a Monocation of a Prototyoical High-Spin Molecular with a Weak Intramolecular Exchange Interaction, Biphenyl-3,3′-Diylbis (Phenylmethylene)

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NOVEL ORGANIC IONS OF HIGH-SPIN STATES VI.: ESR STUDY ON A MONOCATION OF A PROTOTYPICAL HIGH-SPIN MOLECULE WITH A WEAK INTRAMOLECULAR EXCHANGE INTERACTION, BIPHENYL-3,3'-DIYLBIS(PHENYLMETHYLENE)$^{+\bullet}$

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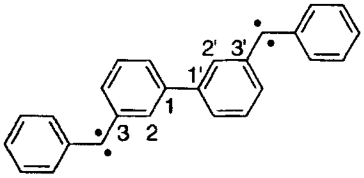
Abstract A monocation of biphenyl-3,3'-diylbis(phenylmethylene) (BP-3,3'-BPM) was produced by γ-irradiation of biphenyl-3,3'-diylbis(phenyldiazomethane) (BP-3,3'-BPD) followed by denitrogenation by a visible light photolysis. ESR spectra at 77 K indicated the formation of a spin-quartet cation. However, the ground state of the cation was determined to be spin-doublet from the temperature dependence of the intensity of the quartet ESR signal. The doublet-quartet energy gap of the cation was estimated to be about 24 cm^{-1}. The electronic state and the molecular structure of the cation were discussed by referring to a semiempirical calculation and by comparing with those of the anion.

INTRODUCTION

Biphenyl-3,3'-diylbis(phenylmethylene) (BP-3,3'-BPM) is known as the first example of the only apparent breakdown of Hund's rule in terms of the molecular orbital theory.[1-3] Although the neutral BP-3,3'-BPM has four singly-occupied electrons in the nearly degenerate π- and n-orbitals at the two divalent carbon atoms, the spin multiplicity of the ground state is singlet. This fact is explained by taking the electron correlation into account in various terms such as a dynamic spin polarization mechanism,[4] a disjoint-nondisjoint theory,[5] and the Heisenberg valence-bond Hamiltonian approach.[6,7] As for charged polycarbenes, however, we should take account of the spin delocalization mechanism. So far, we have made comparative studies on the monoanion[8,9] and monocation[10] of *m*-phenylenebis(phenylmethylene)



Biphenyl-3,3'-diylbis(phenylmethylene) (BP-3,3'-BPM)

and the monoanion of BP-3,3'-BPM[11] with the corresponding neutral polycarbenes. In all these cases ionization does not reverse the order of the energies of the low- and high-spin states which suggests that the spin polarization mechanism predominates over the spin delocalization mechanism in the ionized systems also.

In the present work we have generated the monocation of BP-3,3'-BPM to see whether the above stated general tendency holds or not in this cation.

EXPERIMENTAL

The precursor of the cation studied in the present work is biphenyl-3,3'-diylbis(phenyldiazomethane) (BP-3,3'-BPD) which was synthesized according to the method described before.[11] As for the formation of the cation the same technique as that employed for the study of *m*-PBPM$^{+\bullet}$ was used,[10] that is, γ-irradiation of the diazo precursor in a glass *s*-buthyl chloride (BuCl)[12-14] followed by a visible light photolysis both at 77 K. Commercial BuCl was refluxed with CaH_2 for dehydration and distilled just before the use.

RESULTS AND DISCUSSION

ESR Spectra of BP-3,3'-BPM$^{+\bullet}$

When the γ-irradiated sample was photolyzed with $\lambda > 530$ nm, several new ESR signals appeared in the wide range of 0 – 600 mT (see Figure 1). The appearance of the new ESR signals indicated the formation of new high-spin species. The ESR signals denoted by T was assigned as due to a by-produced spin-triplet monocarbene. The ESR spectrum in Figure 1 is similar to that of the anion of BP-3,3'-BPM. The similarity will be accounted for by the pairing theorem of conjugated π-electron systems.

The observed high-spin ESR signals were simulated in terms of the following spin Hamiltonian.[15]

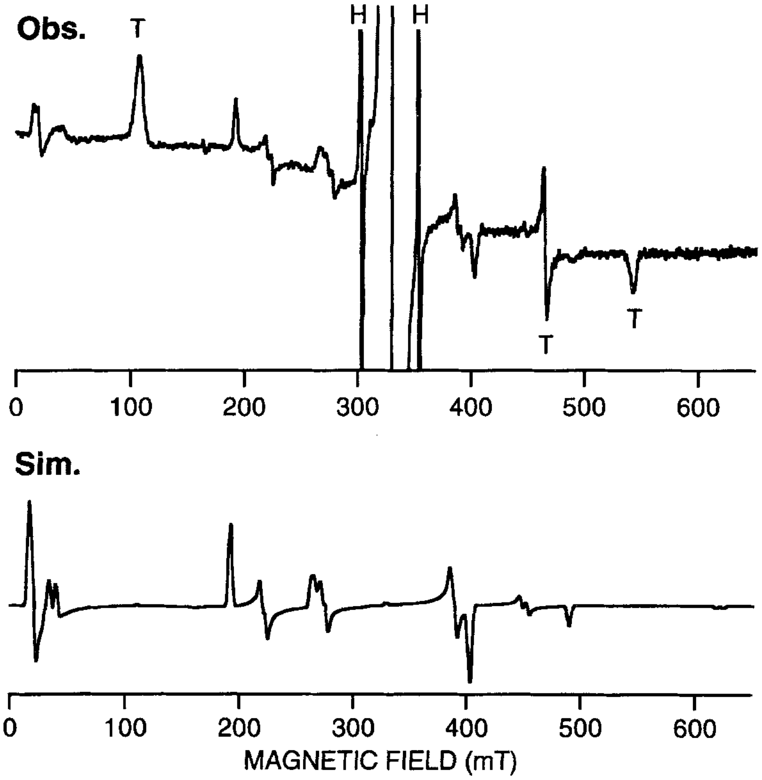


FIGURE 1 Observed and simulated X-band ESR spectra for the quartet state of BP-3,3'-BPM$^{+\bullet}$. Microwave frequency employed was 9.227 GHz. The simulated spectrum is a superposition of two spin-quartet conformers with slightly different fine-structure parameters (see text).

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

As a result, the observed ESR spectrum is concluded to be a superposing of two spin-quartet elements as in the case of the anion.[11] The parameters used for the simulation are $S = 3/2$, $g = 2.003$ (isotropic), $|D| = 0.138$ cm^{-1}, $|E| = 0.0057$ cm^{-1}, and $\Delta B = 3.0$ mT (Conformer 1) and $S = 3/2$, $g = 2.003$ (isotropic), $|D| = 0.135$ cm^{-1}, $|E| = 0.0065$ cm^{-1}, and $\Delta B = 3.0$ mT (Conformer 2). ΔB is a Gaussian linewidth of a single transition.

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

In Figure 2 is shown the temperature dependence of the intensity of the ESR signal due to spin-quartet BP-3,3'-BPM$^{+\bullet}$. The convex curve of the intensity vs. $1/T$ plot

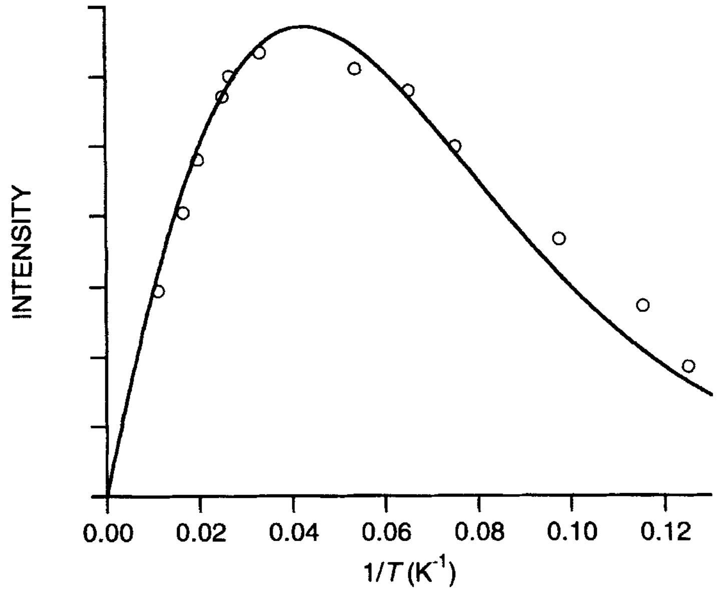


FIGURE 2 Temperature dependence of the intensity of the ESR signal of the low-field Y-axis canonical peak of the quartet cation. The intensity was calculated by double integration of the first derivative peak. The signal intensity of the by-produced spin-triplet monocarbene was used as an internal standard of the temperature as in the case of the anion. The circles are experimental and the solid curve are calculated by Equation (3) in the case of ΔE = 24 cm^{-1}.

manifests that the quartet state is not the ground state but the thermally populated excited state, that is, the ground state of the cation is spin-doublet. The analysis of the experimental data in Figure 2 was made under the assumption of the doublet-quartet two spin states model as in the case of the monoanion. The following equation is derived under the high temperature approximation, $kT >> h\nu \approx 0.3$ cm^{-1}.

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

The doublet-quartet energy gap ΔE, i.e., $\Delta E = E$ (quartet) $-$ E (doublet), was estimated by Equation (2). As a result, the best fit parameter was found to be ΔE = +24 cm^{-1}, which was used to draw the solid curve in Figure 2. This value of the cation is smaller than that of the anion as discussed in a later section.

The exchange interaction between the two carbenic units of the cation can be described by the Heisenberg Hamiltonian.

$$\mathcal{H} = -2J\mathbf{S}_A \cdot \mathbf{S}_B \tag{3}$$

In Equation (3), A and B stand for the two DPM spin units of BP-3,3'-BPM$^{+\bullet}$. With the energy gap of 24 cm^{-1} a value of $J = -8$ cm^{-1} is obtained for the cation. This value of the cation is close to the values of the neutral species of BP-3,3'-BPM, i.e., $J = -10$ cm^{-1}. The relation $|J| \gtrsim |J^{c}|$ manifests that the electron removal does not disturb violently the spin polarization of the neutral BP-3,3'-BPM.

Comparison of the Electron Configuration of the Cation with that of the Anion of BP-3,3'-BPM

The neutral BP-3,3'-BPM has four unpaired electrons in four nearly degenerate orbitals, two of which are π nonbonding orbitals and the other two are in-plane n-orbitals localized at the divalent carbon atoms. The removal of one electron from the π-orbital or from the n-orbital yields a π-cation or an n-cation, respectively (see Figure 3a). One of the four singly occupied molecular orbitals (SOMO's) becomes a vacant orbital leading to a doublet or quartet state as far as these four SOMO's are concerned. By comparing the electron configuration of the π-cation and that of the n-cation, we can estimate that the energy difference between the π- and the n-cation corresponds to that between the n- and the π-orbital in either the doublet or quartet state.

$$E_{\pi\text{-cation}} - E_{\text{n-cation}} = \varepsilon_n - \varepsilon_\pi \tag{4}$$

In general, the n-orbital has lower energy than the π-orbital owing to the hybridization of the 2s orbital. Therefore the π-cation is more probable than the n-cation.

In the case of the anion, the excess electron can occupy either the π- or the n-orbital. The addition of one electron to the π-orbital or to the n-orbital generates a π-anion or an n-anion, respectively (see Figure 3b). In either doublet or quartet state, the energy difference between the π- and the n-anion is given by Equation (5).

$$E_{\pi\text{-anion}} - E_{\text{n-anion}} = (\varepsilon_n - \varepsilon_\pi) + (\langle \pi\pi | \pi\pi \rangle - \langle nn | nn \rangle) \tag{5}$$

Whether the excess electron of the anion is in the π-orbital or in the n-orbital is dependent on the balance of the orbital energy of the π- or the n-orbital and the electron repulsion between the π- or the n-electrons. As a result, the preference of the π-cation over the n-cation is concluded to be larger than that of the π-anion over the n-anion. The discrepancy of the preference between the cation and the anion is due to the difference of the number of electrons between the cation and the anion. This difference

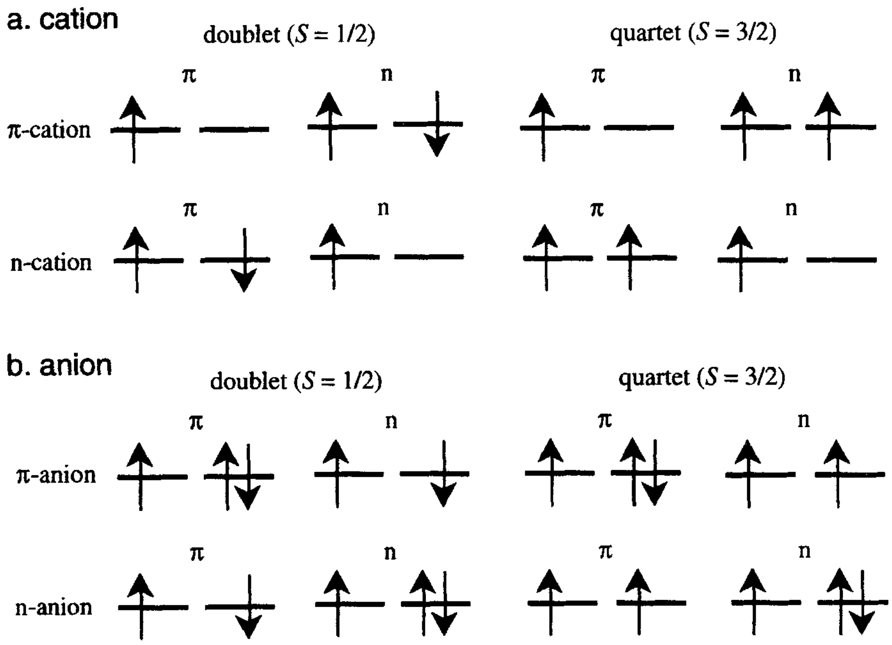


FIGURE 3 (a) Electron configurations of the π-cation and n-cation of BP-3,3'-BPM. (b) Electron configurations of the π-anion and n-anion of BP-3,3'-BPM.

of the number of electrons causes the effect of the electron correlation, which reflects the experimental result that the doublet-quartet energy gap $|\Delta E|$ is smaller in the cation than in the anion.

Probable Conformations of the Spin-Quartet BP-3,3'-BPM$^{\pm\bullet}$

As stated above, the hole of the cation can occupy either the π- or the n-orbital.[10,16] If the hole of the cation is in the π-orbital, the relative orientation of the two one-center n-π interaction tensors makes a crucial contribution to the fine structure tensor of the cation. If the biphenyl group of BP-3,3'-BPM$^{+\bullet}$ is planar, there could be six different conformations. We have calculated the values of $|D|$, $|E|$, and $|E/D|$ for these six possible conformations by the well-established semiempirical calculations for high-spin polycarbenes[17] and compared them with the observed values. As a result, two out of the six seem to be favored which are shown in Figure 4.

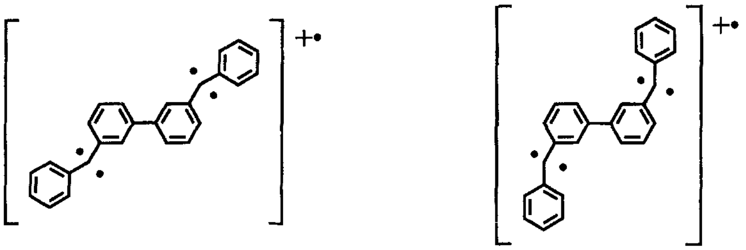


FIGURE 4 Two most probable molecular conformations of the spin-quartet BP-3,3'-BPM$^{+\bullet}$.

Calculations were also made by rotating the central C–C bond in the biphenyl skeleton.[13,17] The planarity of the π-electron system is crucial for the magnetic coupling between the spin units. Steric hindrance leads to the lack of the overlap of the π-orbitals. Therefore, the interpretation of the spin alignment in terms of the up-and-down spin network of the π-electron spin can not be applied to the sterically-hindered species.[18] As a result, however, the calculated values of the fine structure parameters did not become closer to the observed ones by twisting the phenyl rings in the biphenyl skeleton. Consequently, the biphenyl group of the spin-quartet cation of BP-3,3'-BPM is probably planar as shown in Figure 4.

If it was in the in-plane n-orbital, one of the two one-center n-π interactions must vanish and the fine structure tensor of the spin-quartet cation would become essentially the same as that of the neutral spin-triplet diphenylmethylene except from the difference of the spin multiplicity. Although the possibility of the n-cation cannot be ruled out by the argument above, the possibility of the π-cation 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-cation is the case for *m*-PBPM.[10]

CONCLUSION

A monocation of BP-3,3'-BPM was formed in a frozen solution of BuCl via γ-radiolysis following photolysis at 77 K. The spin-quartet state was detected by ESR spectroscopy at 77 K. From the temperature dependence of the ESR signal intensity, however, the ground state of BP-3,3'-BPM$^{+\bullet}$ was determined to be spin-doublet and the quartet state was concluded to be about 24 cm^{-1} above the ground state. The electron removal did not reverse the order of low and high-spin states which indicates that the spin polarization mechanism is predominant in the cation studied. The hole of the cation was regarded most probably as in the π-orbital. The two most probable conformations of the spin-quartet BP-3,3'-BPM$^{+\bullet}$ were found with the help of the semiempirical calculations.

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