25% to 15% or 40% gave coalescence temperatures of −90 and −85 °C, respectively, indicating that the process is intramolecular, and the populations for the different concentrations also did not change appreciably. *E–Z* isomerism of the dimer could account for the doubling of peaks, but we have been unable to observe decoalescence for ethyl dithioacetate,[25] and a large population of the *E* isomer was not expected for the dimer. Also, the sensitivity of the two populations to solvent changes is unlike the behavior of **1** or phenyl dithioacetate,[25] which were found to have populations that changed only by small amounts in the several solvents tried. Rotation about the other three carbon–sulfur bonds can occur, but the experimental barriers seem high for these processes.

From integration of spectrum c of Figure 4, the percentages of monomer, dimer, and cyclic trimer were determined to be 35%, 52%, and 13%.

The barriers for monomeric dithioacetic acid (8.8_5 and 8.9_7 kcal/mol) are larger than for thioacetic acid (7.0 and 7.3 kcal/mol),[26] as expected, and the free energy difference for **1** is smaller (0.05_5 kcal/mol for **1** in 1:3:1 CHF_3, $CHClF_2$, $CHCl_2F$ vs 0.3 kcal/mol for thioacetic acid[26] in $CHClF_2$).[27] The finding of a large amount of the *E* isomer is consistent with the lack of aromaticity[18] of the *Z* conformation, as the acidic hydrogen cannot complete an aromatic sextet. Some of the earlier studies of dithio acids should be re-interpreted, in view of the large amounts of dimer and trimer found under some conditions. We are continuing our NMR studies of dithio acids.

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[27] In contrast, the gas-phase *E–Z* energy difference reported for dithioformic acid (1.0 kcal/mol)[3,4] is larger than that for thioformic acid (0.66 kcal/mol).[28]

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Novel Organic Ions of High-Spin States: ESR Detection of a Monoanion of *m*-Phenylenebis(phenylmethylene)

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Abstract: 1,3-Bis(α-diazobenzyl)benzene (1,3-BDB), known as the precursor of the spin-quintet *m*-phenylenebis(phenylmethylene) (*m*-PBPM), has been subject to a sequential treatment of γ-radiolysis followed by photolysis in 2-methyltetrahydrofuran at 77 K. ESR and optical measurements indicate the formation of a monoanion of *m*-PBPM. The spin multiplicity in the ground state is doublet but is quartet in the first excited state, the energy gap between the two states being only 4.5 ± 0.5 cm^{-1} as estimated from the temperature dependence of the ESR signal over 3.1–77 K. The present work seems to be the first report of the electronically charged hydrocarbon with high-spin states.

As a model for organic ferromagnets, one of our groups in Osaka has been studying, during the past two decades, aromatic polycarbenes with spin multiplicities up to 11.[1-5] It has now been firmly established that spin alignment in these neutral high-spin molecules is dictated by the topology of the π-electron network.[1d,h,2f-h]

With the intention of developing new aspects of such high-spin molecules, we have attempted to prepare charged high-spin aromatics that may be potentially interesting not only from an experimental but also from a theoretical viewpoint. A brief predictive discussion of charging the neutral high-spin molecules has been made by Yamaguchi.[6] As a prototype of charged polycarbenes a monoanion of *m*-phenylenebis(phenylmethylene) (*m*-PBPM) has been generated for the first time, and the ground and the first excited states have been characterized by ESR.

The method of generation will be described in the subsequent section, but the general feature of the method is briefed here: the group in Kyoto has demonstrated that γ-ray irradiation of dilute frozen solutions of a solute in 2-methyltetrahydrofuran (MTHF) leads to a selective formation of the radical anion of the solute via attachment of electrons that are generated by ionization of the matrix MTHF molecule.[7] This has been verified for several hundred cases by recording the electronic absorption spectrum characteristic of the radical anion of the solute molecules.[8] Thus, it is expected that the irradiation of 1,3-BDB dissolved as the solute in MTHF yields the radical anion of 1,3-BDB. By analogy with

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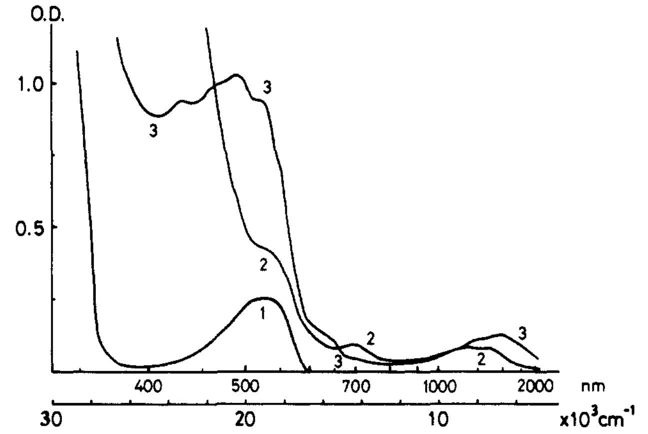


Figure 1. Electronic absorption spectra of 1,3-BDB/MTHF solutions at 77 K: 1, before γ-irradiation; 2, after γ-irradiation; 3, same as 2, but followed by photobleaching with $\lambda > 620$ nm. Optical path length 1.5 mm.

the exceptionally facile photoinduced denitrogenation of the parent 1,3-BDB,[1a] it was anticipated that the radical anion also suffers an easy denitrogenation, leaving *m*-PBPM$^{\bullet-}$, the target species in the present study. It was indeed found that the anticipated radical anion was formed by the above procedure and that the ESR spectrum in the MTHF matrix at 77 K could be attributed to a spin quartet negatively charged *m*-PBPM. This seems the first example of charged high-spin hydrocarbons and could be a testing ground for the investigation of the interrelation between an excess electron and spin-aligned molecules.

Experimental Procedures and Results

1. Sample Preparation and Formation of the Radical Anion of the Parent Diazo Compound. Commercial MTHF was purified by distillation, followed by contacting with Na-K alloy in a vacuum line. If the stored MTHF was treated with $LiAlH_4$[9] immediately prior to use, a slight difference in the experimental results was noticed. However, since the omission of the $LiAlH_4$ treatment did not alter the essential feature of the experimental result of the present work, most experiments were carried out without the treatment.

1,3-Bis(α-diazobenzyl)benzene was synthesized according to the usual method.[10] It was fairly soluble in MTHF. The solution introduced into Suprasil cells for ESR and optical measurements was degassed and sealed off. The solution yielded a transparent purple glassy solid at 77 K, the color being due to the $n\pi^*$-transition of the diazo group[4] (see curve 1 of Figure 1). Since the molar extinction coefficient at $\lambda_{max} = 530$ nm is determined as 254, the concentration of the solute could be estimated quantitatively. The samples were then γ-irradiated at 77 K to a dose of $\approx 3 \times 10^{19}$ eV/g. 1,3-BDB at ≈ 10 mM concentration was sufficient to scavenge almost all the electrons generated by ionization of MTHF molecules. This was confirmed by observing the optical absorption spectrum before and after γ-irradiation:[7,8] the band at 530 nm diminished upon irradiation, and an intense absorption set in at about 500 nm, increasing sharply toward shorter wavelengths (Figure 1). The absorption was accompanied with feeble absorptions appearing throughout the visible and near-IR regions. If the electron had not been scavenged by 1,3-BDB, one must observe the well-known absorption band due to the matrix-trapped electron in the same spectral region.[8] Thus, the absorption appearing after irradiation is regarded as due to the radical anion of 1,3-BDB consistent with a number of systems so far studied.[7,8] To reinforce this inference, the following subsidiary experiment was also carried out: a sufficient amount of alkyl halides such as CF_2BrCF_2Br was dissolved (≈ 100 mM) along with 1,3-BDB, and exactly the same procedure as that without the halide was repeated. Since the halide denoted by RX scavenges electrons efficiently by the dissociative electron attachment, $RX + e^- \rightarrow R^\bullet + X^-$, it was expected that the optical change observed for the 1,3-BDB/MTHF solution would be suppressed drastically by the competition for the electron, which was indeed found to be the case. Furthermore, the X-band ESR spectrum after γ-irradiation showed a featureless signal in a narrow range of magnetic field around $g = 2.00$. The signal was attributable to the radical anion of 1,3-BDB superimposed on the concomitantly produced MTHF radicals (see the inset of Figure 2).

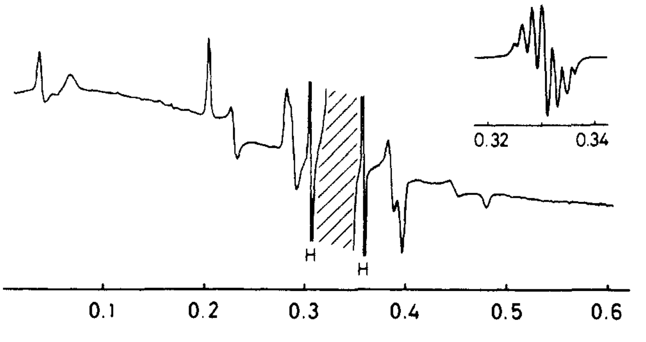
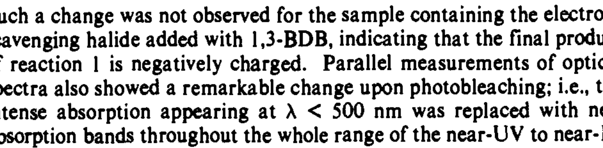


Figure 2. X-band ESR spectrum for a γ-irradiated and subsequently photobleached 1,3-BDB/MTHF solution at 77 K. Prior to photobleaching with $\lambda > 620$ nm, the spectrum showed only the signal at 0.3–0.35 T (marked by the hatch) and the doublet due to the hydrogen atom produced in the quartz cell by irradiation. A reduced-scale spectrum at this stage is shown in the inset. Upon photobleaching several peaks appeared in the ESR spectrum over a wide range of 0.05–0.6 T in addition to the above-mentioned hatched spectrum. The new peaks are assinged to the spin quartet *m*-PBPM$^{\bullet-}$.

With the dose given and with the known G value of the total scavengeable electron,[8] the concentration of the radical anion of 1,3-BDB was estimated as to be ≈ 1.5 mM; that is, conversion from the neutral 1,3-BDB to the radical anion was roughly 15% under the present experimental condition.

The ESR measurement was carried out with an X-band spectrometer, JEOL PES-PE-2X, at Kyoto University with a temperature control system, an Air Products LTR-3 liquid helium transfer Heli-Tran refrigerator. The ESR measurement was also made with an X-band spectrometer, Bruker ESR 300, at Osaka City University, equipped with an Oxford 910 variable-temperature controller. The calibration of temperature was performed by a germanium resistance thermometer. A Cary 14RI spectrophotometer was used for the optical measurement.

2. Formation of *m*-PBPM$^{\bullet-}$. The γ-irradiated 1,3-BDB/MTHF solution in the preceding subsection was succeedingly photolyzed with $\lambda > 620$ nm at 77 K with the use of a xenon lamp and a cut-off glass filter. Upon photobleaching the solution, several new peaks appeared in the ESR spectrum over a wide range of 0.05–0.6 T, indicating the generation of a new high-spin molecule (Figure 2). The change is most plausibly associated with the following reaction.



(1)

Such a change was not observed for the sample containing the electron-scavenging halide added with 1,3-BDB, indicating that the final product of reaction 1 is negatively charged. Parallel measurements of optical spectra also showed a remarkable change upon photobleaching; i.e., the intense absorption appearing at $\lambda < 500$ nm was replaced with new absorption bands throughout the whole range of the near-UV to near-IR region, the major band being $\lambda_{max} = 500$ nm (Figure 1). This optical change can be associated with the formation of *m*-PBPM$^{\bullet-}$ upon photobleaching.

3. ESR Simulation of *m*-PBPM$^{\bullet-}$. At the top of Figure 3 the observed ESR spectrum shown in Figure 2 is reproduced for the convenience of comparison with the simulated spectrum. The simulation was carried out for randomly oriented high-spin molecules, whose ESR absorption line shape arises from the fine-structure spin Hamiltonian with the assumption of spin multiplicity $2S + 1 = 4$.

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

All the resonance fields and transition probabilities were obtained by an exact diagonalization of the spin Hamiltonian. We assumed the Gaussian function for the line-shape function of a single transition and a constant

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[9] 2-Methyltetrahydrofuran (Aldrich Chemical Co.) was refluxed over sodium for 30 h and then fractionated. The prepurified 2-methyltetrahydrofuran was again refluxed over lithium aluminum hydride until there was no further reaction with an additional small amount of lithium aluminum hydride. The period of reflux was extended up to 30 h. Then the solvent was fractionated with a Widmer distillation column. All the processes were performed under an atmosphere of dry nitrogen. The purified solvent was outgassed under vacuum prior to use, and a proper amount of it was vacuum-distilled into optical or ESR cells.

[10] Murahashi, S.-I.; Yoshimura, Y.; Yamamoto, Y.; Moritani, I. *Tetrahedron* **1972**, *4*, 1485–1496. 1,3-Dibenzoylbenzene hydrazone was oxidized with activated MnO_2 instead of HgO.

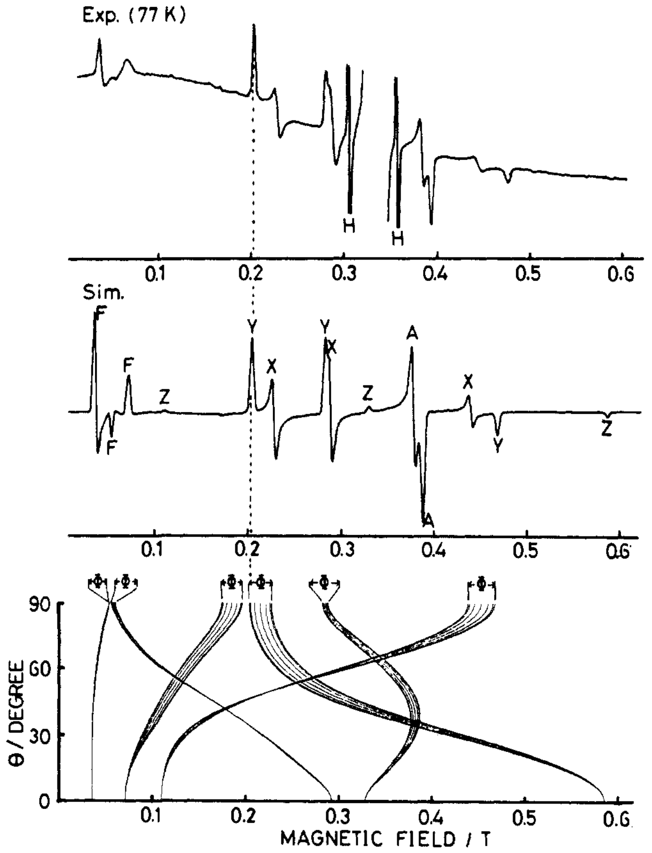

Figure 3. Observed and simulated X-band ESR spectra for the quartet state of *m*-PBPM$^{\bullet-}$. The angular dependence of resonance fields for random orientation is shown at the bottom. Symbols A and F denote the extra line[5] and the "forbidden" bands corresponding to the transitions with $\Delta M_s = \pm 2$ and ± 3. The parameters used for the simulation are $\nu = 9.218$ GHz, $g = 2.003$ (isotropic), $|D| = 0.1200$ cm^{-1}, and $|E| = 0.0045$ cm^{-1}.

line width (3.6 mT) for all the transitions with the static magnetic field perpendicular to the oscillating microwave field. The number of orientations in the simulation for a single spectrum was 29 859 840. The simulations were carried out with a HITAC M660K at Osaka City University Computer Center and a FACOM M-780/30 at the Data Processing Center of Kyoto University.

The best fit spin Hamiltonian parameters were found to be $g = 2.003$ (isotropic), $|D| = 0.1200$ cm^{-1}, and $|E| = 0.0045$ cm^{-1}. The microwave frequency was equal to 9.218 GHz, with which the experiment was performed. Figure 3 shows the angular dependence for random orientation (bottom) as well as the simulated spectrum (middle) obtained by the above best fit parameters. Except for the masked area of 0.3–0.4 T, the agreement is excellent between the observed and simulated spectra. It should be noted that an off-axis extra line denoted by A in Figure 3 appears as expected for the case of half-integral spins and that the off-axis extra line is a key absorption peak in the spin multiplicity assignment.[5] The appearance of the off-axis extra line assures that the observed fine-structure spectrum arises from a quartet spin state. The observation of the extra line in this work is the first example of extra lines from organic high-spin systems with half-integral spins. As for the absolute signs of D and E, see below.

4. Temperature Dependence of the ESR Signal. In order to see whether or not the quartet state is the ground state, the temperature dependence of the ESR spectrum in Figure 3 was attempted. Since the line shape was unchanged, we employed the derivative height of the low-field Y-axis canonical peak marked by the broken line in Figure 3.

The circles in Figure 4 represent the above peak height in an arbitrary unit. The convex shape of the plots against the inverse of temperature indicates that the observed quartet spectrum is due not to the ground state but to the thermally populated first excited state. The doublet signal due to the ground state must have been merged into the interfering MTHF radicals at about 0.33 T (see the inset of Figure 2). Assuming the Boltzmann distribution, we could estimate the energy gap between the ground and the first excited states by the standard procedure.[2d] Since the observed spectrum in Figure 3 is compatible with both cases of $D > 0$ and $D < 0$, the absolute signs cannot be decided. In the former case we are measuring the transition between the two sublevels shown in the inset of the upper panel of Figure 4, and in the latter case, the lower panel. In both cases we have assumed several parameters for the energy gap between the two states and drawn curves as shown in Figure 4. It is seen that for the case of $D > 0$ the best fit is obtained by taking the energy gap as 4.7 cm^{-1} whereas for the case of $D < 0$ the gap is determined as 4.3 cm^{-1}. In any case we may safely conclude that the gap is about 4.5 ± 0.5 cm^{-1}. Such a small energy gap between the quartet state and the doublet ground state seems quite remarkable.

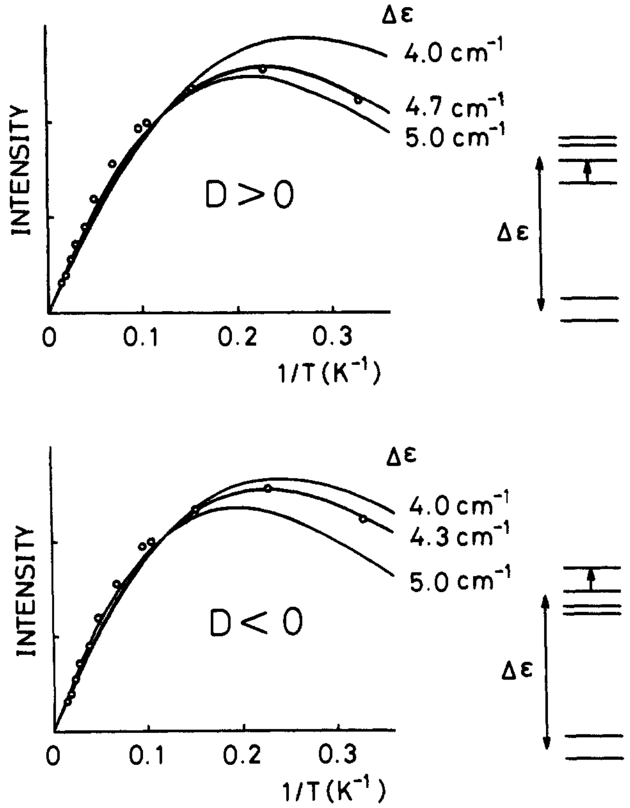

Figure 4. Temperature dependence of the ESR signal at the derivative height of the low-field Y-axis canonical peak in Figure 3. The circles are experimental, and the curves are drawn assuming the Boltzmann distribution in the first two states.

Discussion

The most remarkable features of the charged carbene are the spin doublet ground state and the low-lying quartet excited state with the very small energy gap between these states. This electronic structure shows a diametrical contrast with that of the parent neutral high-spin molecule that has the high-spin ground state and the lower spin excited states lying much higher than 300 cm^{-1} above the ground state.[1a] The present results indicate that the exchange parameters between the carbon sites in the charged high-spin molecule are to a large extent different from those in the neutral molecule. This seems to give experimental support to the prediction by Yamaguchi.[6] To elucidate these findings, it is necessary to explore the electronic structure of *m*-PBPM$^{\bullet-}$. In particular, we should clarify how the excess electron is distributed in the *m*-PBPM framework and how the electron dictates the spin alignment in the charged species. Experimental studies on related systems and theoretical analysis of the result are now in progress.

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