solution in propylene carbonate leads to films where exchange of the transition metal by lithium cation has occurred (Figure 9). The similar Li^+ and Ag^+ complexing ability of the catenand cat-30 and of the preorganized bis(2,9-diphenyl-1,10-phenanthroline) coordination sites covalently incorporated in the polypyrrole films is striking. This effect may be attributed to the particular rigidity of the complexing core, resulting from cross-linking of the coordinating moieties in an analogous manner as in the catenates.

IV. Conclusion

In conclusion, a new type of functionalized polypyrrole has been made and studied. It is synthesized by entwining two chelates around a transition metal, with each chelate being end functionalized by a pyrrole. This strategy provides a means of intertwining the molecular fragments, which are converted to a highly entangled polymer after electropolymerization of the N-bonded pyrrole units. The coordinating moieties used in the present work are 2,9-diphenyl-1,10-phenanthroline derivatives. The pyrrole nuclei are connected to the chelate via polymethylene chains of various lengths (3, 6, or 11 methylene fragments). It is shown that copper(I) is an ideal templating metal center, leading to an electroactive complex acting as an electron relay during electropolymerization. The same procedure can be applied with other metallic species (cobalt(II), zinc(II), or silver(I)), although no electron relay process takes place in these cases during electropolymerization and film growth. By electrochemical methods, it is shown that each metal complex subunit incorporated in the film is very similar in nature to the corresponding homogeneous species, the catenate.

The conductivity properties of the materials are reminiscent of those of the previously prepared and studied N-substituted polypyrroles, with no particular contribution of the transition metal complex.

Demetalation of the various systems was carried out using either CN^- (for copper(I)) or SCN^- (for cobalt(II) and zinc(II)). Interestingly, the material retains partial memory of its complex precursor. This property leads in some cases to relatively easy re-incorporation of a metal into the coordinating cavity. The highly entangled nature of the polymeric material helps to maintain the relatively rigid complexing cavities of the film.

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Registry No. 1, 100890-92-4; **2**, 104104-93-0; **3**, 104104-94-1; **4**, 88498-43-5; **5**, 141484-30-2; **6**, 115748-16-8; **6** (homopolymer), 141484-32-4; **7**, 141484-31-3; $[Cu(\mathbf{6})_2]^+$, 116141-15-2; $[Cu(\mathbf{6})_2]^+$ (homopolymer), 141484-38-0; $[Zn(\mathbf{6})_2]^{2+}$, 141484-33-5; $[Zn(\mathbf{6})_2]^{2+}$ (homopolymer), 141484-39-1; $[Ag(\mathbf{6})_2]^+$, 141484-34-6; $[Ag(\mathbf{6})_2]^+$ (homopolymer), 141484-40-4; $[Co(\mathbf{5})_2]^{2+}$, 141484-35-7; $[Co(\mathbf{5})_2]^{2+}$ (homopolymer), 141484-41-5; $[Co(\mathbf{6})_2]^{2+}$, 141484-36-8; $[Co(\mathbf{6})_2]^{2+}$ (homopolymer), 141484-42-6; $[Co(\mathbf{7})_2]^{2+}$, 141484-37-9; $[Co(\mathbf{7})_2]^{2+}$ (homopolymer), 141484-43-7.

ESR of the Cationic Triradical of 1,3,5-Tris(diphenylamino)benzene

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Abstract: The ESR spectrum of the cationic triradical of 1,3,5-tris(diphenylamino)benzene (TDAB) is discussed. The tricationic state of TDAB was observed by means of cyclic voltammetry. The orange cationic triradical was prepared by oxidation of TDAB with trifluoroacetic anhydride in the presence of tetra-*n*-butylammonium tetrafluoroborate in CH_2Cl_2. The ESR spectrum of the randomly oriented radicals in the CH_2Cl_2 glass agrees well with the theoretical prediction of a quartet ($S = {}^3/_2$) spin state with a zero-field splitting parameter D' of 13.1 G (0.0012 cm^{-1}). This is the first observation of a high-spin state of a cationic radical.

Introduction

Previously observed cases of ferromagnetism usually involve the spins of either d or f electrons, which presumably play an essential role in magnetic interactions. In recent years, several groups have launched efforts toward the preparation of organic ferromagnets based on molecular crystals and polymers.[1-9] In particular, ferromagnetic intramolecular interaction has been clearly observed in carbenes[3,10] and nitrenes.[6,11] However, the goal of obtaining bulk ferromagnetism in organic solids has been elusive.[12,13] Recently, however, an organic ferromagnet, the β-phase crystal of *p*-nitrophenyl nitronyl nitroxide, with a Curie temperature of 0.60 K was reported by Kinoshita et al.[9]

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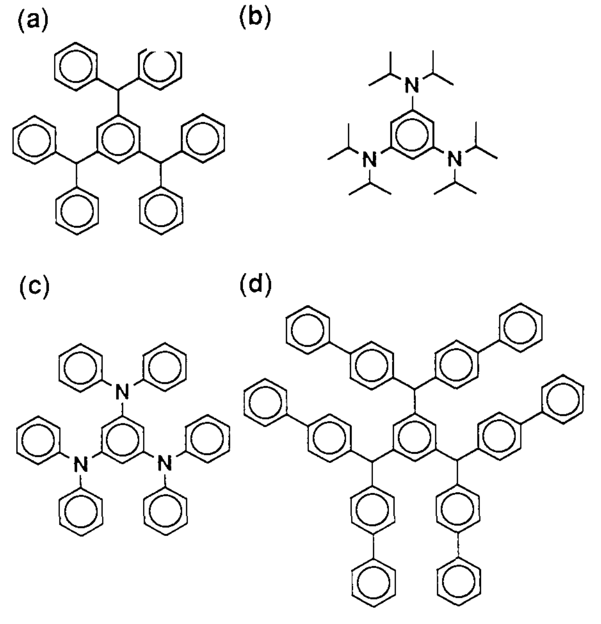


Figure 1. Molecular structures of (a) 1,3,5-tris(diphenylmethyl)benzene (TDMB), (b) 1,3,5-tris(diisopropylamino)benzene (TDIAB), (c) 1,3,5-tris(diphenylamino)benzene (TDAB), and (d) 1,3,5-tris[bis(biphenyl)-methyl]benzene (TDBMB).

Ovchinnikov[14] has suggested on the basis of valence bond theory that the triradical of 1,3,5-tris(diphenylmethyl)benzene (TDMB), which is assumed to be a planar molecule, has $S = {}^3/_2$ in the ground state (Figure 1). The ground state of such alternant hydrocarbons, where the conjugated atoms are alternately labeled n and n^* such that no two atoms of the same label are directly linked, has a total spin quantum number $S = (n^* - n)/2$.[14] This conclusion can be extended to alternant systems containing heteroatoms, resulting in quasi-alternant character, as described by Tyutyulkov et al.[15] In the time since the last theoretical study of conjugated polymers with polaronic ferromagnetism was reported,[16] evidence for ferromagnetic coupling in such polymers[17,18] has increased and provides the basis for consideration of a novel type of organic magnetism. The preparation and characterization of a nitrogen-based cationic triradical similar to the TDMB triradical would be interesting from the viewpoint of chemical stability. The magnetic properties of the cationic radicals of 1,3,5-tris(diisopropylamino)benzene (TDIAB) have been examined by Chiang et al.[7] Further stabilization of radicals of this type of molecule appears to require conjugation between the π-electrons of the benzene rings and the unpaired electrons of the nitrogen atoms. Recently, Ishikawa et al.[19] reported a synthesis of and the thermal properties of 1,3,5-tris(diphenylamino)benzene (TDAB). However, the details of these characterizations of TDAB have not been reported.

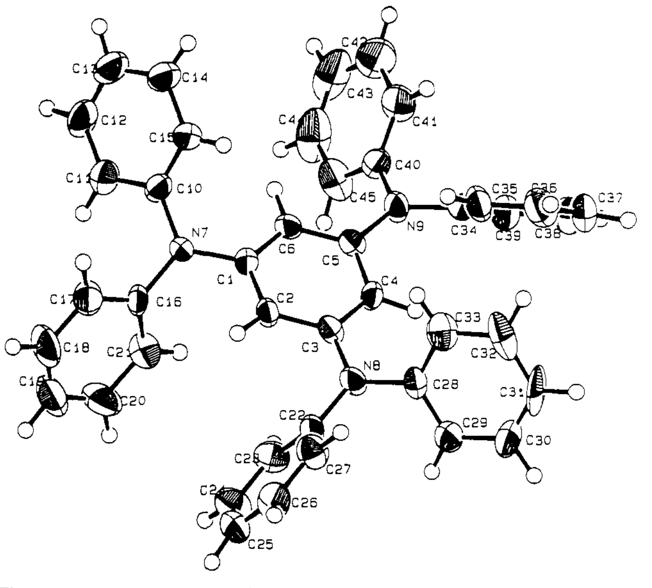
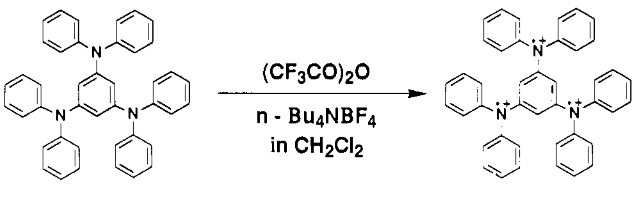


Figure 2. ORTEP drawing of the molecular structure of TDAB.

Scheme I



Here, we report the characterizations of TDAB based on IR, UV–vis, ^{1}H-NMR, cyclic voltammetry, and ESR measurements as well as the molecular and crystal structures. The present work focuses mainly on the unique magnetic properties of TDAB. The cationic triradical of TDAB turns out to be stable under either vacuum or nitrogen atmosphere at room temperature and appears to have a quartet ground state on the basis of temperature-dependent ESR intensity measurements.

Experimental Section

TDAB was synthesized from 1,3,5-tribromobenzene and diphenylamine using a modification of a procedure given previously.[19] Under a flow of high-purity nitrogen, 3.14 g (0.01 mol) of 1,3,5-tribromobenzene, 5.08 g (0.03 mol) of diphenylamine, 0.2 g (0.001 mol) of CuI, 2.0 g (0.015 mol) of K_2CO_3, and 5.0 mL of diphenyl ether were placed into a flask. After reflux at 259 °C for 24 h, the reaction mixture was washed with methanol to remove unreacted reagents. An impure powder was obtained via precipitation from a toluene and methanol solution of the crude product and was further purified by recrystallization from toluene three times to give 0.60 g (10.3%) of white crystals. The product is an air stable, colorless, crystalline solid, which is soluble in benzene, toluene, tetrahydrofuran, CH_2Cl_2, and $CHCl_3$ but not in hexane, methanol, acetonitrile, benzonitrile, acetone, acetic acid, dimethylformamide, or dimethyl sulfoxide.

Anal. Calcd for $C_{42}H_{33}N_3$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.30; H, 5.70; N, 7.14. Mp: 257.0–257.5 °C. IR spectrum (cm^{-1}): 3050 w, 1585 s, 1572 s, 1498 s, 1490 s, 1470 s, 1462 m, 1443 w, 1330 m, 1320 m, 1293 s, 1279 m, 1252 s, 1248 s, 1179 w, 1154 w, 1080 w, 1045 w, 1030 w, 905 w, 850 w, 832 w, 760 s, 742 w, 700 s, 642 m, 630 m, 620 w, 510 m. UV–vis [λ_{max} (ϵ), CH_2Cl_2]: 304 nm (8.0×10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR ($CDCl_3$ ppm relative to TMS): 6.41 (3 H, s), 7.08 (30 H, m).

A single crystal was obtained as a colorless needle crystallized from CH_2Cl_2 solution and measured $0.5 \times 0.1 \times 0.05$ mm^3. A total of 2689 reflections were collected at 23 ± 1 °C using the ω–2θ scan technique on a Rigaku AFC 5R diffractometer ($2\theta_{max} = 120.2°$) with use of graphite-monochromated Cu Kα radiation. The crystal structure was analyzed by direct methods, and non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1583 observed reflections ($I > 1.50\sigma(I)$) and 406 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.058$ and $R_w = 0.060$.

Cyclic voltammograms were recorded by using a three-electrode cell with a Pt wire as the counter electrode and SCE linked to an agar salt

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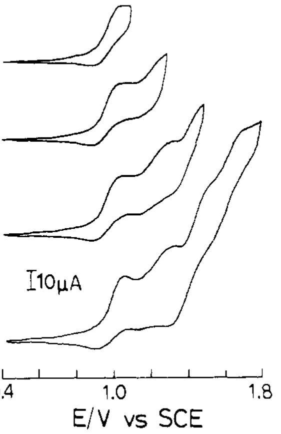

Figure 3. Cyclic voltammograms of TDAB in CH_2Cl_2. Supporting electrolyte was *n*-Bu_4NBF_4 and voltage sweep rate was 0.2 $V{\cdot}s^{-1}$.

(KCl) bridge as the reference electrode in a solution of 1 $mmol{\cdot}L^{-1}$ TDAB and 0.1 $mol{\cdot}L^{-1}$ tetra-*n*-butylammonium tetrafluoroborate (*n*-Bu_4NBF_4) in CH_2Cl_2 under nitrogen atmosphere at room temperature. A Teflon-coated Pt wire having a diameter of 1 mm, the end of which was open, was used as the working electrode.

The triradical of TDAB was easily prepared in an ESR sample tube under nitrogen atmosphere by oxidation of TDAB with trifluoroacetic anhydride in the presence of *n*-Bu_4NBF_4 in CH_2Cl_2 as shown in Scheme I. The cationic triradical is orange and is stable under vacuum or purified nitrogen at room temperature. However, we have not yet succeeded in isolating the triradical. JEOL FEX1G and Varian E-112 ESR spectrometers operating at a microwave frequency of 9.3 GHz and a field modulation of 100 kHz between 15 K and room temperature were employed for the present ESR measurements. The determination of *g* value and field calibration were performed using an Mn^{2+}/MgO solid solution as a standard.[20]

Results and Discussion

Crystal Structure of TDAB. The crystal data for TDAB revealed orthorhombic symmetry with a space group assigned as $Pna2_1$ with the following lattice parameters: a = 10.051 (3), b = 13.352 (6), c = 23.390 (4) Å; V = 3139 $Å^3$; Z = 4; D_c = 1.227 $g{\cdot}cm^{-3}$. As shown in Figure 2, the molecular structure of TDAB is not planar. The central benzene ring is slightly deformed owing to the three large substituents. The mean deviation from the least-squares plane of the central benzene is 0.0163 Å. The selected bond lengths and bond angles are as follows: C1–C2 = 1.40 (1), C1–C6 = 1.38 (1), C2–C3 = 1.395 (9), C3–C4 = 1.380 (9), C4–C5 = 1.380 (9), C5–C6 = 1.400 (9), C1–N7 = 1.422 (8), C3–N8 = 1.404 (9), C5–N9 = 1.422 (9) Å; C6–C1–C2 = 120.8 (6), C1–C2–C3 = 119.6 (6)°. Dihedral angles between the planes of the central benzene and the substituents' benzene rings are 56.53–67.65°. The substituents' benzene rings themselves are nearly all planar. Dihedral angles between least-squares planes of the benzene rings of the substituents are 72.52–82.17°.

As mentioned above, the molecular structure of TDAB is not planar. We are therefore concerned with the actual spin multiplicity of the triradical of TDAB, since the theoretical prediction[14] is based on the simple assumption that the structure is planar.

ESR of the Cationic Triradical of TDAB. Purified TDAB was examined by cyclic voltammetry under nitrogen atmosphere at room temperature. Four oxidation waves were observed at +1.00, +1.24, +1.45, and +1.58 V vs SCE as shown in Figure 3. This result demonstrates that TDAB can be oxidized to a monocation, a dication, a trication, and a tetracation in solution. However, these cations show limited stability on the voltammetric time scale in CH_2Cl_2 solution. Since the reduction current was less than the oxidation current, the reaction is quasi-reversible and the cations generated are sensitive to low concentrations of water or oxygen in solution. After about ten cycles between +0.4 and +1.8 V vs SCE, the solution became yellow and the working electrode was coated with an organic thin film.

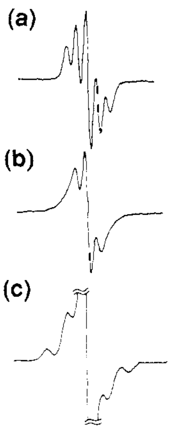

Figure 4. Solution ESR spectra of the cationic triradical of TDAB at (a) 243, (b) 213, and (c) 183 K recorded under the same conditions. The counteranion is BF_4^-.

The ESR spectrum of the cationic triradical of TDAB was also recorded. The triradical is easily obtained by oxidation with trifluoroacetic anhydride in an ESR sample tube. We first used a combination of lead tetraacetate and trifluoroacetic anhydride as the oxidation agent.[21] Although the role of trifluoroacetic anhydride is currently not clear, the charge-transfer reaction between TDAB and *n*-Bu_4NBF_4 is considered to be activated by this agent. Interestingly, it has been reported that cationic radicals of hexamethoxytriphenylene (HMT) are stable in a solution of trifluoroacetic acid–CH_2Cl_2.[22] TDAB is thus oxidized to the trication in the trifluoroacetic anhydride–CH_2Cl_2 solution containing *n*-Bu_4NBF_4, and the ESR spectrum is described below.

As shown in Figure 4, hyperfine splitting, which is probably due to the nitrogen nuclei, was observed in the solution ESR spectrum. The solution spectrum was strongly dependent on temperature. The hyperfine splitting disappeared and the spectrum typical of quartet ($S = {}^3/_2$) states appeared as the solution was frozen around 183 K. The ESR spectrum of the randomly oriented radicals in the frozen glass (Figure 4c) results from the magnetic dipole interactions among unpaired electrons, not from the anisotropy of the *g* value. Since the orbital angular momentum is generally quenched in organic radicals,[23] the *g* value is therefore isotropic. This radical species is stable at room temperature in the evacuated sample tube in the presence of trifluoroacetic anhydride and counteranions, i.e. BF_4^- among others. No intensity change in the ESR spectrum was observed even over a 1-month period. An identical spectrum was obtained for a sample of TDAB which was electrochemically oxidized in an ESR sample tube. The intensity was observed to increase with an increase in electrochemical oxidation time. These results are consistent with the cyclic voltammetry described above. The stability of this radical is due to the large conjugation between π-electrons of the benzene rings and unpaired electrons located on the nitrogens. These unpaired electrons must be largely delocalized to the benzene rings, reflecting the zero-field-splitting parameters.

Let us consider the theoretical predictions for quartet molecules of this type.[24] This spin Hamiltonian can be written as

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

where β is the Bohr magneton, H is the applied magnetic field, g is the g tensor, and D and E are the zero-field-splitting parameters. E is zero for a linear radical or for one with a trigonal

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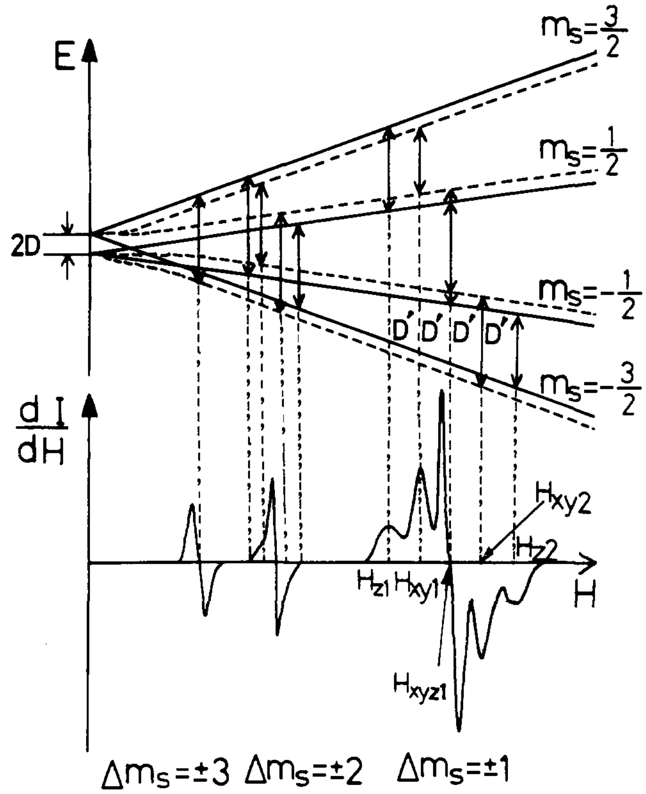

Figure 5. Zeeman levels and transitions for $\Delta m_s = \pm1$, ±2, and ±3 of a quartet molecule with axial symmetry as a function of the applied field. The solid and dotted lines correspond to a field parallel and perpendicular, respectively, to the rotational axis z.

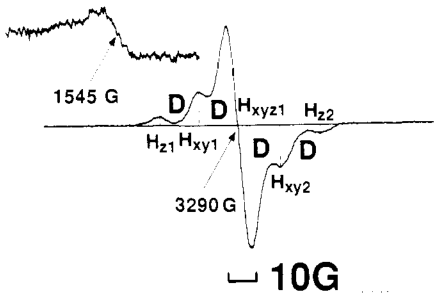

Figure 6. ESR spectrum of the triradical of TDAB in CH_2Cl_2 glass at 123 K. H_{z1}, H_{xy1}, H_{xyz1}, H_{xy2}, and H_{z2} are the axial resonance fields. D' is a zero-field-splitting parameter. The half-field resonance corresponding to the forbidden $\Delta m_s = \pm2$ transition is observed below 50 K.

axis of symmetry. For the magnetic field parallel to the molecular axis z ($H_\parallel$), the eigenvalues are

$$W_{\pm3/2} = D \pm \tfrac{3}{2} g_\parallel \beta H_\parallel \qquad W_{\pm1/2} = -D \pm \tfrac{1}{2} g_\parallel \beta H_\parallel \tag{2}$$

where $g_\parallel = g_z$. For the magnetic field perpendicular to z ($H_\perp$)

$$\begin{aligned} W_{\pm3/2} &= \pm\tfrac{1}{2} g_\perp \beta H_\perp + [(D \pm \tfrac{1}{2} g_\perp \beta H_\perp)^2 + \tfrac{3}{4}(g_\perp \beta H_\perp)^2]^{1/2} \\ W_{\pm1/2} &= \pm\tfrac{1}{2} g_\perp \beta H_\perp - [(D \pm \tfrac{1}{2} g_\perp \beta H_\perp)^2 + \tfrac{3}{4}(g_\perp \beta H_\perp)^2]^{1/2} \end{aligned} \tag{3}$$

where $g_\perp = g_x = g_y$. $g_\parallel$ should be equal to $g_\perp$, since the orbital angular momentum of organic molecules is generally frozen. Thus, the g value is isotropic as mentioned above. The tensor components $g_\parallel$ and $g_\perp$ are close to the value seen for a free electron, g_e = 2.0023.[24] The theoretical prediction of the Zeeman levels and the transitions of $\Delta m_s = \pm1$, ±2, and ±3 for an axial-symmetric quartet molecule is schematically represented in Figure 5, where the solid line corresponds to the field parallel to the rotational axis z and the dotted line to the field perpendicular to z. When D is small ($D \ll g_e\beta H$), the two lines are parallel. H_{z1}, H_{xy1}, H_{xyz1}, H_{xy2}, and H_{z2} are the axial resonance fields.

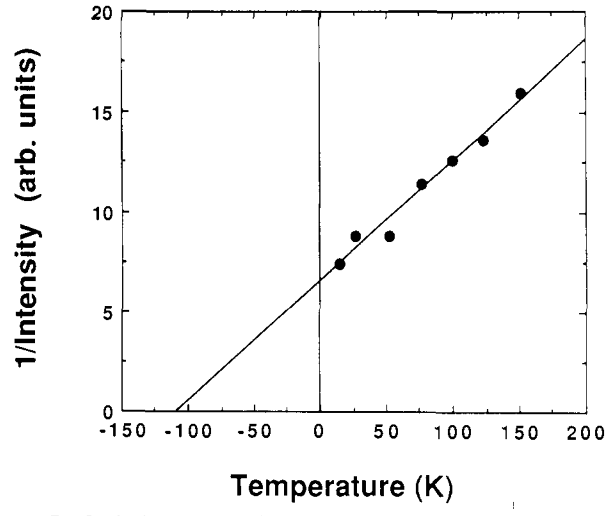

Figure 7. Curie–Weiss plot of the intensity based on the double integration of the observed ESR signals between 15 and 150 K. The Weiss constant Θ is estimated to be −110 K.

In Figure 6, the ESR spectrum of the CH_2Cl_2 solution of the triradical of TDAB frozen into rigid glass at 123 K is shown. The spectrum consists of several $\Delta m_s = \pm1$ signals and is quite similar to that of the triradical of 1,3,5-tris[bis(biphenyl-4-yl)methyl]benzene (TDBMB) observed by Brickmann and Kothe.[25] The ESR g value of the TDAB triradical was determined to be 2.002, thus isotropic and close to g_e. We have confirmed that the monoradical is not present in the sample oxidized by trifluoroacetic anhydride, since the same spectrum was obtained under more strongly oxidizing conditions, where lead tetraacetate was used as the oxidizing agent.

The zero-field-splitting parameter D' ($=D/g\beta$) was determined to be 13.1 G (1 G = 10^{-4} T) (0.0012 cm^{-1}) from the difference of H_{z1} and H_{z2}. This value is about one-third of the value of D' for TDBMB.[25] This reflects the difference in the spin density distribution between the carbon- and the nitrogen-centered radical species. Assuming the point-dipole approximation in the expression of D,[26] the extent of the spin delocalization for the cationic radical is probably slightly larger than that for the neutral one, likely due to the presence of heteroatoms. Such diminished interactions of unpaired electrons in a heteroatomic system have been reported by Breslow et al.[27] As shown also in Figure 6, the half-field resonance corresponding to the $\Delta m_s = \pm2$ transition was detected below 50 K. This clearly indicates that the observed species is in a multiplet state. However, the $\Delta m_s = \pm3$ transition associated with a three-electron flip has not been observed. The intensities of the three transitions $\Delta m_s = \pm1$, ±2, and ±3 are expected in a ratio of $1{:}(D'/H)^2{:}(D'/H)^4$.[28] In the cationic triradical of TDAB with D' = 13.1 G, the intensity of the $\Delta m_s = \pm3$ transition may be only 10^{-8} relative to that of the $\Delta m_s = \pm1$ transition. Thus, there are obviously difficulties in detecting the $\Delta m_s = \pm3$ transition.

The temperature dependence of the ESR signal intensity indicates whether the observed quartet is the ground state or an excited one. The intensity of the $\Delta m_s = \pm1$ transition, which was determined from double integration of the signals, was observed to increase with a decrease in temperature as shown in Figure 7, where the signal intensity obeys the Curie–Weiss law between 15 and 150 K. Therefore, either the observed quartet is the ground state or the doublet and quartet are nearly degenerate ground states. In light of theoretical predictions,[14] we consider the quartet to be much more likely. However, since the molecular structure of TDAB is not planar as described in Figure 2, the energy dif-

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ference between the quartet and doublet may be small.

Let us now turn to the magnetic coupling between the randomly oriented quartet molecules in the frozen glass. Intermolecular magnetic coupling observed in the CH_2Cl_2 glass is found to be antiferromagnetic with negative Weiss constant $\Theta = -110$ K, obtained from the intercept of the temperature axis in Figure 7. Since the Weiss constant is very large and negative, the antiferromagnetic coupling between neighboring molecules is strong. Such strong coupling is unusual for organic molecules; therefore, TDAB is very interesting as an organic ferro- or rather antiferromagnetic material. This strong intermolecular coupling may, however, be attributable to the superexchange interaction[29] involving BF_4^- anions. We must also note that the intermolecular magnetic coupling is normally dependent on the molecular packing and crystalline forms, as has been seen in the case of *p*-nitrophenyl nitronyl nitroxides.[9] Moreover, in these materials, the intermolecular magnetic coupling is known to be ferromagnetic, while it is antiferromagnetic in the crystals of phenyl and *m*-nitrophenyl nitronyl nitroxides.[8] The difference in the magnetic coupling among these members has been explained on the basis of π-electron delocalization and spin polarization, which are considerably dependent on the type of substituent and the crystalline form. It is therefore important to examine the magnetic properties of the crystals of TDAB families mixed with various anions in order to achieve quantitative spin control.

Conclusion

We have analyzed the molecular and the crystal structures of TDAB and have observed the quartet state of TDAB. The observed ESR spectrum of the cationic radicals, which are rigidly held but randomly oriented with respect to the magnetic field in CH_2Cl_2 glass, agreed well with the theoretical prediction for a quartet spin state. The temperature dependence of the intensity for the $\Delta m_s = \pm 1$ transition confirmed that the quartet is the ground state. Although organic molecules with multiplet ground states, such as carbenes and nitrenes, have been prepared, these types of species are only observable under irradiation at low temperatures. In contrast to these species, the cationic triradical of TDAB is stable under vacuum or nitrogen atmosphere even at room temperature. This material is therefore of interest as an example of a novel type of organic magnetism. The stability of this radical is probably attributable to the presence of heteroatoms in the π-conjugation as seen in the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. A particularly unique feature of TDAB is that the observed intramolecular ferromagnetic interaction operates among the cationic radicals. This is the first observation of a high-spin state ($S = {}^3/_2$) for such a cationic radical. The present ferromagnetic interaction might provide important information about the still unknown chemical nature of the organic ferromagnetic material poly(1,3,5-triaminobenzene).[1] In this case, however, the intermolecular magnetic coupling of TDAB in the CH_2Cl_2 glass has turned out to be strongly antiferromagnetic. Therefore, examination of the role of counteranions may be necessary for an understanding of the stability of this cationic triradical and the observed intermolecular magnetic coupling.

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Supplementary Material Available: Tables of positional parameters, thermal parameters, distances, angles, and least-squares planes and a stereoview of the unit cell of TDAB (14 pages). Ordering information is given on any current masthead page.

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Cyclopropanones from the Oxidation of Hindered [4]- and [5]-Cumulenes with Epoxidation Reagents

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Abstract: The oxidation of *tert*-butyl-substituted [5]-cumulene **4** with epoxidizing agents was shown to give sequentially formed conjugated cyclopropanones **15** and **11**. The more stable cyclopropanone **11** was isolated and shown to add carboxylic acids to give allenyl ketones of type **5** and to thermally and photochemically lose carbon monoxide to give the [4]-cumulene **6**. The oxidation of **4** with peracids leads directly to allenyl ketones **5** as isolated products. Hydrolysis of **5a** produced the novel furofuran **9**. The oxidation of the hindered [4]-cumulene **6** gave conjugated cyclopropanone **19**, which underwent chemical transformations similar to those of **11**. These oxidations are rationalized in terms of hypothetical cumulene oxide intermediates that rapidly isomerize to the observed cyclopropanones.

As an extrapolation of our long-standing interest in the epoxidation chemistry of allenes,[1] we recently reported on the reaction of butatriene **1** with peracids to give methylenecyclopropanone **2**.[2,3] This was shown to proceed via an unstable intermediate, whose low-temperature ^{1}H and ^{13}C NMR spectra suggested the triene oxide structure **3**. We now confirm this assignment by an FT-IR experiment which clearly shows a transient allene band at 1998 cm^{-1} that rapidly accumulates and then disappears during the course of the conversion of **1** to **2** by *m*-chloroperbenzoic acid (mCPBA); see Scheme I.

The observation of cumulene oxide **3** prompted an extension of our studies to the oxidation of hexapentaene **4**, the most readily available higher homologue of **1**.[4] Reaction of **4** with 3 equiv of mCPBA in $CHCl_3$ generated a modest yield (26%) of a

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