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Magnetic Properties of 1,3,5-Tris[bis(*p*-methoxyphenyl)amino]benzene Cation Radicals

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In order to pursue the possibility of charge-transfer organic ferromagnets, magnetic properties of the monocationic ClO_4- and BF_4-salts of a triaminobenzene derivative, 1,3,5-tris[bis(*p*-methoxyphenyl)amino]benzene (TBMAB), were characterized by means of ESR and a Faraday-type magnetic balance. MNDO-PM3 calculations predicted 1,3,5-tris(diphenylamino)benzene (TDAB) dication and trication to be ground-state triplet and quartet, respectively. Thus these triaminobenzenes fulfill the necessary precondition for the appearance of intermolecular ferromagnetic coupling based on so-called McConnell's second model. Negative Weiss constants (−1 to 0 K) and low spin concentrations (7—8 %) were observed for TBMAB–ClO_4 and TBMAB–BF_4, although, according to this rule, intermolecular ferromagnetic coupling is expected to occur for these systems.

There has been increasing interest in the design and synthesis of organic or molecular ferromagnets.1) The first traditional strategy to obtain organic ferromagnets is based on the spin-preference theorem of through-bond interactions between localized spins in extended molecular systems.2—6) High-spin organic molecules such as polycarbenes7,8) and polyradicals9,10) have been well established along this strategy. The first organic ferromagnet was found by Kinoshita and co-workers11) from the other strategy using through-space magnetic coupling in molecular crystals containing a stable nitroxide radical. Several organic ferromagnets have been prepared so far along this strategy.12,13) The third strategy is based on charge-transfer complexes with cation or anion radicals. TDAE-C_{60}14,15) belongs to this class. In this strategy there is an intriguing proposal known as McConnell's second model,16) which suggests intermolecular ferromagnetic interactions in charge-transfer complexes. However, ferromagnetic interaction based on McConnell's second model has not yet been observed, although this model has been modified in various ways by several groups.17—22) Interesting attempts are now in progress using unique charge-transfer complexes.23,24)

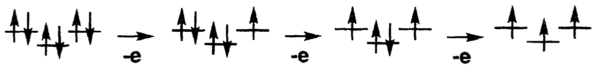
In previous papers,25) we have investigated cationic triradical of 1,3,5-tris(diphenylamino)benzene (TDAB) both experimentally and theoretically. In these studies we have shown that the 1,3,5-benzenetriyl coupling unit is effective for the realization of quartet states in aminium radicals as well as methyl radicals. Also ferromagnetic interaction between aminium radicals through a *m*-phenylene coupling unit was reported by Nakamura and Iwamura.26) Since TDAB has a threefold axis and nearly threefold topologically degenerate HOMOs (highest occupied molecular orbitals), the dication is also expected to have a triplet ground state, as indicated in Scheme 1.

Let us now consider a ferromagnetic configuration interaction according to Torrance's model,19) one of modified McConnell's models shown below:

$$D^{+}(\uparrow) + D^{+}(\uparrow) \leftrightarrow D^{2+}(\uparrow\uparrow) + D^{0}, \qquad (1)$$

where D is a donor molecule whose dication is ground-state triplet. This equation means that if D^{2+}, which is formed by further forward charge transfer, is ground-state triplet, a ferromagnetic (or triplet) state could be stabilized between D^+s. According to this model, ferromagnetic interaction can work between the TDAB monocations, if the triplet state of TDAB dication lies below the corresponding singlet state. We are therefore much interested in the bulk magnetic properties of cation radicals of TDAB.

However, we could not prepare analytically satisfactory charge-transfer complexes of TDAB, because of its limited stability under acidic conditions at ambient temperature. In order to obtain more stable cationic species, we have designed and synthesized a triaminobenzene derivative, 1,3,5-tris[bis(*p*-methoxyphenyl)amino]benzene (TBMAB) which has six methoxy groups as substituents on the basic skeleton of TDAB.27) Solution-stable mono-, di-, and tricationic states of this compound were detected with ESR at low temperatures by Stickley and Blackstock.28) On the other hand, we concentrate our attention on the solid-state magnetic properties of the monocationic species of TBMAB, on the basis of the reason mentioned above. TBMAB is easily oxidized to form monocation salts with various anions such as ClO_4,



Scheme 1.

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BF_4, and PF_6. In this paper we show the magnetic properties of TBMAB–ClO_4 and TBMAB–BF_4 by means of MO calculations, ESR, and a Faraday-type magnetic balance.

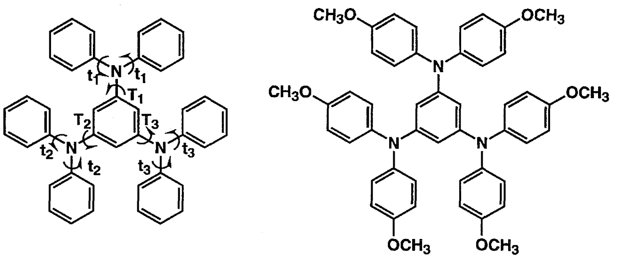
Molecular Orbital Analysis

Before discussing the experimental results, it is wise to predict the magnetic properties of the cation states of TDAB by MO calculations. Since TDAB has nearly threefold degenerate HOMOs, the cationic states are magnetically interesting, as discussed above. On the basis of semiempirical MO calculations, let us first consider the magnetic properties of mono-, di-, and tricationic states of TDAB. As shown in Fig. 1, the dihedral parameters (T_i and t_i; i=1,2,3) of TDAB determine the geometry of this propeller-like molecule. There are three types of molecular shapes in TDAB, i.e., D_3, conrotatory C_2, and disrotatory C_2 geometries, depending on these dihedral parameters. All the C–C and C–N bond lengths and bond angles were frozen at 1.4 Å and 120°, respectively, in these calculations, because of the size of this molecule.

The dihedral parameters and relative energies of the neutral, mono-, di-, and tricationic states calculated from the MNDO-PM3 method[29)] are listed in Table 1. It is well known that the PM3 method gives quite reasonable dihedral angles of π-conjugated molecules.[30)] To obtain the total energies, the restricted Hartree–Fock (RHF) method was used, since significant spin contamination occurred in the unrestricted Hartree–Fock (UHF) calculations of this molecule.

In the neutral state, the disrotatory C_2 geometry is 0.2 kcal mol^{-1} more stable than the D_3 geometry, which is consistent with the X-ray structure analysis.[25a)] However, it is difficult to discuss this small energy difference quantitatively in the present MO theory as well as in the high-performance ab initio theory. Although it is clear from X-ray structural analysis that TDAB loses a threefold axis of symmetry in the crystal structure of neutral state, there appear nearly threefold HOMOs in TDAB, due to topological symmetry.

It is interesting to note that in the monocationic state, the conrotatory C_2 and disrotatory C_2 geometries have the same energy. The difference between these geometries is just the direction of the dihedral angles of the symmetry-top substituent.



TDAB **TBMAB**

Fig. 1. Molecular structures of 1,3,5-tris(diphenylamino)benzene (TDAB) and 1,3,5-tris[bis(p-methoxyphenyl)amino]benzene (TBMAB). The dihedral parameters of TDAB determine the shapes of this propeller-like molecule.

Table 1. Geometrical Parameters (unit in degree) and Relative Energies (unit in kcal mol^{-1}) of the Neutral, Mono-, Di-, and Trication States of TDAB, Using the PM3 Method

	T_1	t_1	$T_2(=T_3)$	$t_2(=t_3)$	Relative energy
TDAB (S=0)					
D_3	34.5	40.0	T_1	t_1	+0.2
C_2 (disrotatory)	−33.9	−37.7	35.4	38.3	0.0
TDAB$^+$ (S=1/2)					
C_2 (conrotatory)	32.4	36.7	21.1	51.7	+0.0
C_2 (disrotatory)	−32.0	−36.2	22.0	50.6	0.0
TDAB^{2+} (S=1)					
D_3	30.9	39.8	T_1	t_1	+3.5
C_2 (conrotatory)	16.4	55.8	37.6	35.1	0.0
C_2 (disrotatory)	−38.7	−34.1	26.0	43.9	+5.5
TDAB^{2+} (S=0)					
C_2 (conrotatory)	24.1	42.2	26.9	42.8	+23.0
C_2 (disrotatory)	−27.5	−39.5	28.2	42.1	+23.1
TDAB^{3+} (S=3/2)					
D_3	38.9	34.9	T_1	t_1	0.0
C_2 (disrotatory)	−39.4	−34.8	53.4	33.0	+1.1
TDAB^{3+} (S=1/2)					
C_2 (conrotatory)	39.5	34.8	53.3	33.2	+40.5
C_2 (disrotatory)	−62.8	−32.3	40.6	34.0	+37.8

Moreover, in the dicationic state the ground state is especially important in McConnell's second model, as discussed above. The three triplet states at the different D_3, conrotatory C_2, and disrotatory C_2 geometries lie about 20 kcal mol^{-1} below the corresponding singlet states. In these triplet states, the conrotatory C_2 geometry is the most stable, although the energy difference between the conrotatory C_2 and D_3 is only 3.5 kcal mol^{-1}. This result is consistent well with the detectable zero-field splitting parameter E for TBMAB^{2+},[28)] which is expected to be zero for the structure with D_3 symmetry. If McConnell's second model is correct, we can expect that ferromagnetic intermolecular interaction works between the monocation radicals of TDAB, as shown in Eq. 1. Thus, we are interested in the magnetic properties in the bulk of the monocationic species of TDAB such as TDAB–ClO_4, TDAB–BF_4, and related compounds.

In the tricationic state, the quartet states are much more stable than the corresponding doublet states. In this state, D_3 is the most stable geometry, as expected. As a result, the tricationic state of TDAB in the rigid glass shows an ESR spectrum typical of a quartet molecule.[25a,25b)]

Experimental

Synthesis of TBMAB was carried out using the modified Ullmann reaction.[31)] Three grams of 1,3,5-tris[(p-methoxyphenyl)amino]benzene, which was prepared from phloroglucinol and p-anisidine according to Ref. 32, and 9.5 g of 4-iodoanisole were reacted at 130 °C for 20 h in the presence of 0.8 g of CuI and 5.0 g of KOH under a nitrogen flow. The reaction mixture was extracted by CH_2Cl_2 and reprecipitated from hexane. The crude product was purified by column-gel chromatography and recrystallized from toluene–methanol (1 : 1), giving 0.91 g (19%) of white powder. Found: C, 75.87; H, 5.97; N, 5.53%. Calcd for $C_{48}H_{45}N_3O_6$: C, 76.13; H, 5.95; N, 5.50%. Mp 185—188 °C. IR spectrum: 3020 w, 2975 w, 2925 m, 2810 m, 2025 w, 1865 w, 1580 s, 1565 s, 1510 s, 1498 s, 1455 s, 1432 s, 1409 w, 1272 m, 1230 s, 1175 m, 1145 m, 1138 m, 1100 m, 1128 s, 818 s, 800 m, 772 m, 733 m, 705 m, 694 m, 638 w, 620 w, 604 w, 581 m, 560 w, 550 w, 518 m. ^{1}H NMR ($CDCl_3$) $\delta=3.75$ (s, 18H), 5.82 (s, 3H), 6.85 (m, 24H).

Cyclic voltammogram was recorded using Pt wires as the counter and working electrodes and SCE as the reference electrode in a solution of 1 mmol L^{-1} TBMAB and 0.1 mol L^{-1} tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4) in CH_2Cl_2 at room temperature.

The monocationic salts of TBMAB was prepared by chemical oxidation in a glove box under a nitrogen flow. TBMAB was readily oxidized in CH_2Cl_2–ether by addition of the equivalent $AgClO_4$ or $AgBF_4$ in the presence of I_2, to afford dark-brown polycrystals of TBMAB–ClO_4 and TBMAB–BF_4. These oxidizing reagents are often employed for the preparation of aminium radical salts.[33] $NOPF_6$ also oxidized TBMAB to afford a black polycrystal; however, the PF_6 salt was not pursued further in this study. The polycrystals were purified by reprecipitation from ether and CH_2Cl_2. From elemental analysis described below, these salts were found to contain TBMAB and the counter anions in the ratio 1 : 1. Found: C, 67.29; H, 4.98; N, 4.89; Cl, 3.30%. Calcd for $C_{48}H_{45}N_3O_6$–ClO_4: C, 67.09; H, 5.28; N, 4.89; Cl, 4.13%. Found: C, 67.29; H, 5.01; N, 4.95%. Calcd for $C_{48}H_{45}N_3O_6$–BF_4: C, 68.09; H, 5.36; N, 4.96%. The color of the solution of these salts is orange, although the neutral form of TBMAB is colorless. UV-vis spectra were recorded on Shimadzu MPS-2000.

ESR spectra were recorded on a Brucker ESP 300E spectrometer equipped with an Oxford liquid-helium-flow cryostat at the X band with a field modulation of 100 kHz in the temperature range 2—300 K. During a single ESR measurement, the temperature was maintained within ±0.5 K of its set value. Peak-to-peak line width (ΔH_{pp}) and g values were determined using a Mn^{2+}–MgO standard. ESR intensities were calculated from double integration of ESR spectra of differential form.

Magnetic susceptibilities (χ) were measured using an Oxford Instrument's Faraday-type magnetic balance in the temperature range 2—260 K at the constant magnetic field of 5 kG. A quartz cell was stuffed with 30 mg of the materials, and then 80 mg of liquid

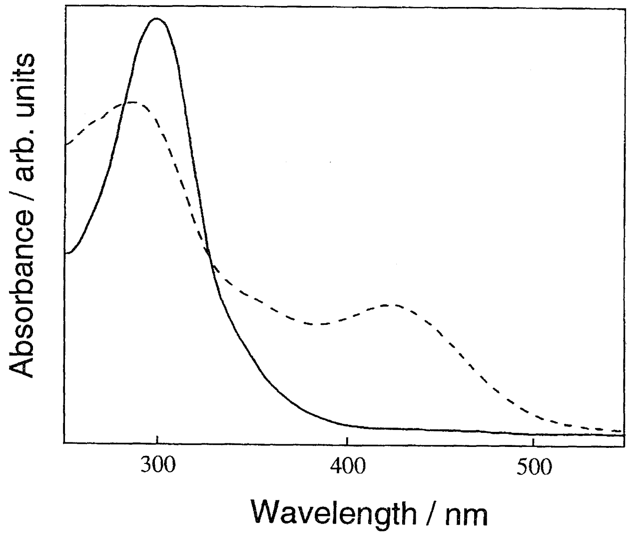


Fig. 2. UV-vis spectra of TBMAB (solid line) and TBMAB–BF_4 (broken line).

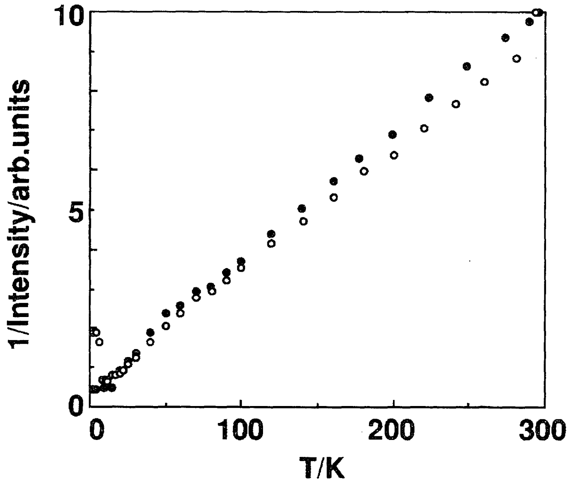


Fig. 3. Temperature dependence of the inverse ESR intensities for TBMAB–ClO_4 (closed circle) and TBMAB–BF_4 (open circle).

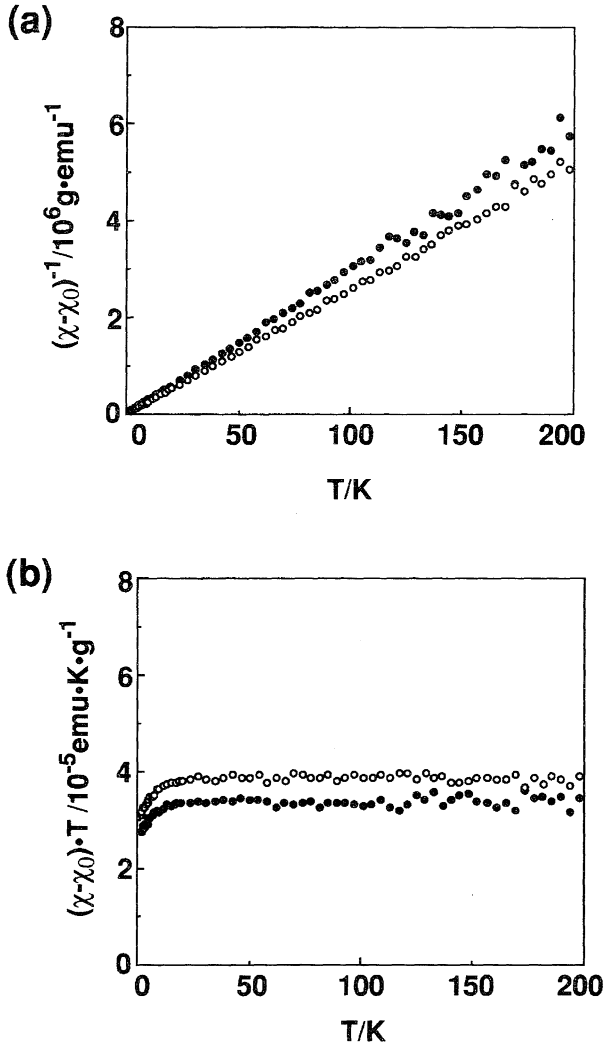


Fig. 4. (a) $1/(\chi-\chi_0)$ and (b) $(\chi-\chi_0)T$ plots of TBMAB–ClO_4 (closed circle) and TBMAB–BF_4 (open circle) as a function of temperature.

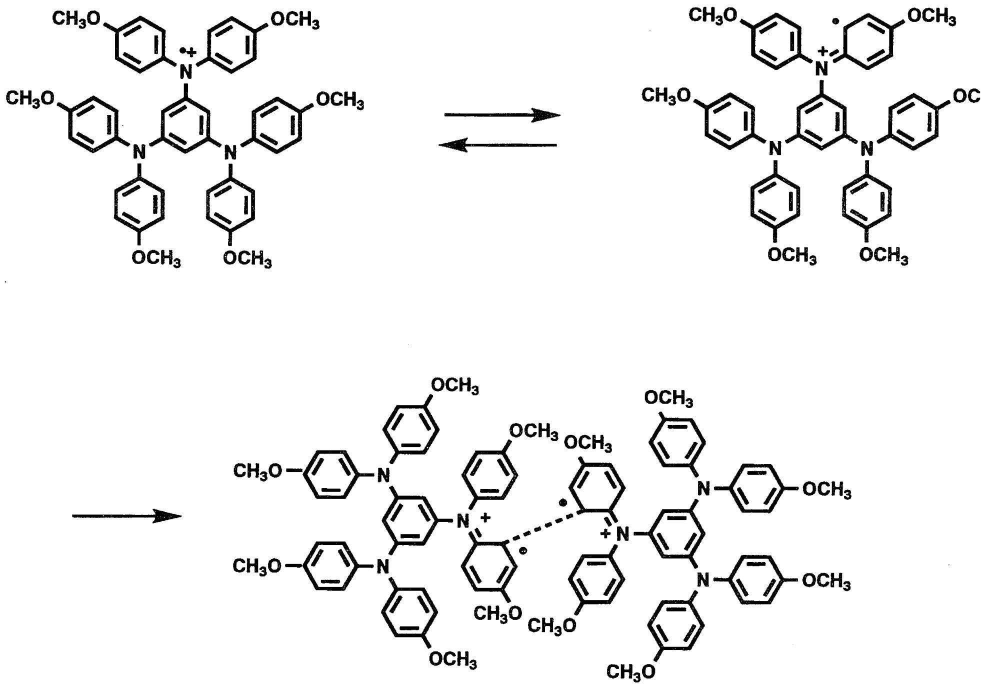


Fig. 5. Possible formation of *o*-benzidine-linked dimer.

paraffin was added to fix the powder. The outputs were corrected for the diamagnetism of the blank cell and temperature-independent terms (χ_0) of the materials themselves as usual.

Results and Discussion

Cyclic voltammogram of TBMAB in CH_2Cl_2 at room temperature showed the peaks of quasi-reversible oxidation waves at +0.73 V, +0.98 V, and irreversible one at +1.37 V vs. SCE. The first peak corresponds to the monocationic state of TBMAB, which is consistent well with the Stickley and Blackstock's data.[28] The first oxidation potentials are 0.23 V lower than that of TDAB (+1.00 V vs. SCE). Thus, the first ionization potential was effectively reduced compared with TDAB, by introducing methoxy groups as substituents. The second and third oxidation waves observed at room temperature probably does not correspond to the di- and tricationic states of TBMAB, as is discussed below. Clear chemically reversible redox waves at −78 °C corresponding to the mono-, di-, and tricationic states of TBMAB were reported in Ref. 28. The peak height of the reduction wave corresponding to the monocationic state of TBMAB was slightly smaller than that of the oxidation wave, indicating that the monocationic state of TBMAB has limited lifetime at ambient temperature in solution.

In order to confirm cationic species in TBMAB–ClO_4 and TBMAB–BF_4, UV-vis spectra of these were recorded using CH_2Cl_2 solvent. The UV-vis spectra of TBMAB and TBMAB–BF_4 are shown in Fig. 2. Although TBMAB itself is colorless, the solution of TBMAB–BF_4 is orange, due to a charge-transfer reaction. The charge-transfer band was observed in 423 nm. The spectrum obtained for TBMAB–ClO_4 was virtually identical to that of TBMAB–BF_4.

Let us next look at the ESR measurements of TBMAB monocations. Both TBMAB–ClO_4 and TBMAB–BF_4 polycrystals exhibited Lorentzian-type ESR spectra at the 3300 G ($\Delta m=1$) region with ΔH_{pp} of 6.3 and 6.0 G, respectively, at room temperature. ΔH_{pp} increased with decreasing temperature and became 8.6 and 8.2 G, respectively, at very low temperature. For both salts the g value at $\Delta m=1$ was 2.0029, being independent of temperature. This value is slightly smaller than that of other aminium salts such as Wurster's blue (2.00325)[34,35] and tris(*p*-methoxyphenyl)aminium cation radical (2.0032).[36] The unpaired electron of TBMAB is therefore found to be located on the phenyl rings (probably on the central one) as well as on the three nitrogen atoms. The half-field signal in the 1550 G region was not detected even at very low temperature. Thus, spin species with $S>1$ are not present in these charge-transfer complexes. The ESR intensities depicted in Fig. 3 obeyed the Curie law within an experimental error.

Here we look at the static magnetic susceptibility measurements. Figures 4a and 4b show the temperature dependence of the paramagnetic susceptibilities $\chi-\chi_0$ and $(\chi-\chi_0)T$ values, where temperature-independent χ_0 were 1.3×10^{-7} and 9.1×10^{-8} emu g^{-1} for TBMAB–ClO_4 and TBMAB–BF_4, respectively. Such positive χ_0 has been observed in TDAE-C_{60} charge-transfer complex, but not in TDAE-C_{70}.[15] This is not due to metallic impurities such as iron and copper because ESR did not detect any metallic signals in TBMAB–ClO_4 and TBMAB–BF_4 as well as in TDAE-C_{60} and TDAE-C_{70}. The $\chi-\chi_0$ values obeyed the Curie–Weiss law for both salts with Weiss constants of −1 to 0 K. These small Weiss constants indicate that the molecular field felt by each unpaired electron is very weak. The $(\chi-\chi_0)T$ values are almost constant, indicating the invariant average magnetic moments. Slight decrease of $(\chi-\chi_0)T$ values at very low temperature is probably due to the small antiferromagnetic interactions between these cation radicals.

The reason why the antiferromagnetic interactions are dominant in the present materials is not clear at present. We could not perform the X-ray analysis because these materials are powder. The spin concentrations determined from the Curie–Weiss law were only 7 and 8% for TBMAB–ClO$_4$ and TBMAB–BF$_4$, respectively. These low spin concentrations suggest that most of the unpaired electrons are coupled antiferromagnetically leading to the formation of dimers in the solid. Since these salts were prepared under oxygen-free condition, these small spin concentrations are probably due to the dimerization of the TBMAB cation radicals.

The quasi-reversible first oxidation wave shows a high reactivity of the monocationic state of TBMAB. As is known in chemistry of aminobenzenes, aromatic aminium radicals undergo further reactions to form benzidine-linked dimers.[37,38] The second and third oxidation waves observed at room temperature probably originates from benzidine-like compounds. We tentatively identified these two materials as dicationic salts of *o*-benzidine-linked dimers of TBMAB containing monocationic salts. Figure 5 shows the formation of the dimer of TBMAB. As a result, monocationic unpaired electrons which failed to be dimerized were observable by magnetic measurements. Interactions among these residual spins would be very weak, because they are separated by nonmagnetic dimers. Thus weak magnetic interaction and resultant small Weiss constants are rationalized.

Conclusions

In summary, we have designed a possible charge-transfer organic ferromagnet based on a triaminobenzene derivative, TBMAB, and characterized the magnetic properties of its monocationic ClO$_4$- and BF$_4$-salts by means of ESR and a static magnetic balance. Semiempirical MNDO-PM3 calculations predicted that the dicationic and tricationic states of TDAB are ground-state triplet and quartet, respectively. Therefore on the basis of McConnell's second model, ferromagnetic intermolecular interaction should work between the monocation radicals of TBMAB. However, ferromagnetic intermolecular interactions have not been observed in these materials even at low temperatures. Although the reason why the theoretical prediction is probably not effective in these materials is not clear at present, dimerization of the monocation radicals is suggested from the present magnetic study. We will continue to pursue the possibility of charge-transfer organic ferromagnets based on McConnell's second model, by using chemically stable cation radicals of TDAB families with proper degree of steric hindrance which could reduce the possibility of the dimerization between donor molecules.

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