

# Novel High-Spin Molecules: $\pi$ -Conjugated Polyradical Polyanions. Ferromagnetic Spin Coupling and Electron Localization<sup>1</sup>

Suchada Rajca and Andrzej Rajca\*

Contribution from the Department of Chemistry, University of Nebraska,  
Lincoln, Nebraska 68588-0304

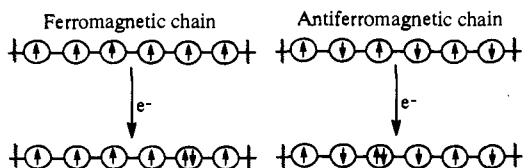
Received May 10, 1995<sup>®</sup>

**Abstract:** The three- and four-site spin coupled chains, based on polyarylmethyl high-spin tri- and tetradicals, with additional electrons, i.e., diradical anions, radical dianions, and diradical dianions, are prepared and studied. These  $\pi$ -conjugated polyradical polyanions have their charge and spin localized at the separate triarylmethyl sites. In diradical anions, modification of the aryl substituents at the center triarylmethyl sites allows for control of charge/spin localization at the center or terminal sites. It is shown that when the charge (electron pair) is localized at the terminal site, ferromagnetic coupling between the remaining "unpaired" electrons is found; i.e., ferromagnetic coupling of the spin chain is unaffected by the additional electron. However, when the charge (electron pair) is localized at the center site, antiferromagnetic coupling between the remaining "unpaired" electrons is observed. Therefore, a control of spin coupling via control of electron localization is attained. Also, a new stable triradical, with quartet ( $S = 3/2$ ) ground state, is prepared. Electrochemistry, UV-vis and ESR spectroscopy, and magnetic data of these novel species are reported.

## Introduction

Ferromagnetic and antiferromagnetic spin coupled chains are two important models of electronic structure relevant to both materials and biological systems.<sup>2</sup> High-spin organic molecules are examples of well-defined ferromagnetically coupled chains with a simple electronic structure.<sup>3</sup>

An interesting problem of the relationship between spin coupling and electron transfer arises when an extra electron is added to the spin coupled chain.<sup>3a</sup>

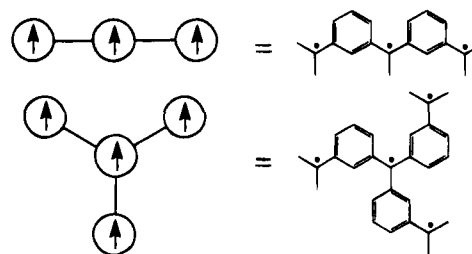


(1) Is the electron transfer affected by ferro- vs antiferromagnetic coupling in the original chain (e.g., localization vs delocalization of negative charge)? (2) Does the added electron influence the spin coupling between the remaining "unpaired" electrons in the chain? An analogous problem is encountered when one or more electrons are removed from the chain, i.e., concerning "holes". Insight into these problems may provide the foundation for the progress toward the rational design of structures for electron transfer (and ultimately electrical conductivity) by controlling spin coupling.<sup>3a</sup>

The first question in the preceding paragraph can be addressed using the two-site spin coupled chains (e.g., radical anions

derived from diradicals or, more complex, anions of dicarbenes), which are relevant to the problem of mixed valence in organic compounds.<sup>4-6</sup> In particular, electron localization (delocalization) in polyarylmethyl radical anions has been found to be related to ferromagnetic (antiferromagnetic) spin coupling in the corresponding diradicals.<sup>5</sup>

The second question is considered in the present work. It can be addressed using ferromagnetically coupled multi-site chains; such chains may be modeled by  $\pi$ -conjugated high-spin polyarylmethyl polyradicals.<sup>3a</sup> "Linear" triradicals and "branched" tetradicals are examples of three- and four-site chains, respectively, which formally consist of spin sites (triarylmethyl moieties) linked with ferromagnetic coupling units (1,3-phenylenes).<sup>7</sup>



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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, August 15, 1995.

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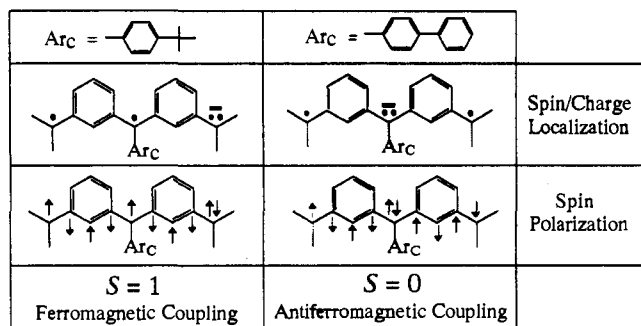


Figure 1. Control of electron localization and spin coupling in diradical anions.

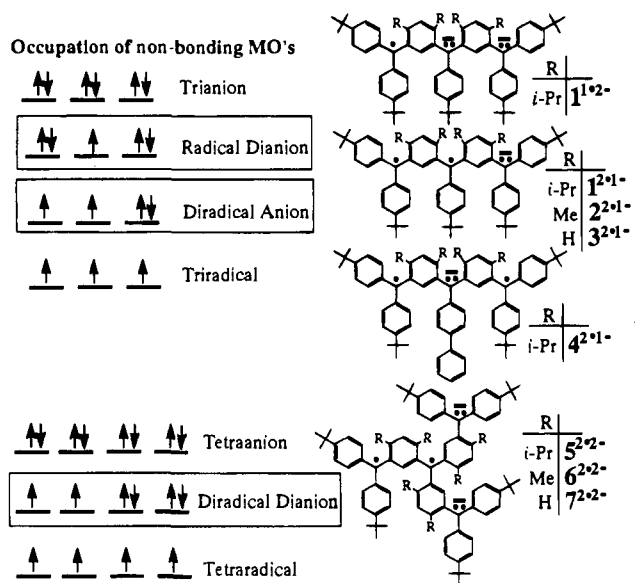


Figure 2. Polyradical polyanions and their occupations of nonbonding MO's. Occupations of the MO's, indicated with boxes, and all structures correspond to polyradical polyanions studied in this work.

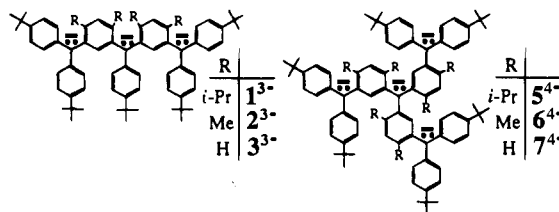
In analogy with previously studied homologous diradicals,<sup>5</sup> addition of an electron to a triradical (such as to form a diradical anion) should localize spin and charge density at different sites. Because two types of sites, "terminal" and "central", are present in a "linear" triradical, two limiting structures depicting spin/charge localization are possible. A straightforward control of the electron localization could be implemented by modification of the substituents (Arc) at the center site; i.e., the enhanced stabilization (destabilization) of negative charge by Arc should prefer the limiting structure with negative charge localized at the center (terminal) site (Figure 1). "Linear" diradical anions are simple models for studying the relationship between electron localization and spin coupling in ferromagnetic chains; a valence bond model would predict a ferromagnetic and antiferromagnetic spin coupling, when the negative charge (electron pair as a superexchange center) is localized at the "terminal" and "center" site, respectively (Figure 1).<sup>8</sup>

Now we report the study of the three- and four-site spin coupled chains with additional electrons: diradical anions, radical dianions, and diradical dianions. These systems are related to polyarylmethyl polyanions and high-spin polyradicals by different occupancy of their non-bonding MO's (Figure 2). An approach to control of electron localization and, consequently, spin coupling, as illustrated in Figure 1, is described.

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## Results and Discussion

1. **Trianions 1<sup>3-</sup>, 2<sup>3-</sup>, 3<sup>3-</sup> and Tetraanions 5<sup>4-</sup>, 6<sup>4-</sup>, 7<sup>4-</sup>.** Polyanions are generated in tetrahydrofuran (THF) from the corresponding polyethers, as described previously.<sup>5,7</sup>



UV-vis spectra for the trianions and tetraanions in THF/MeLi consist of broad peaks (in some cases with shoulders) centered in the  $\lambda = 450\text{--}500$  nm range, reminiscent of the previously reported spectra for the related dianions and tetraanion 7<sup>4-</sup>.<sup>5</sup> Thus, steric hindrance and extension of  $\pi$ -conjugation in the polyanions exerts only a minor perturbation on their UV-vis spectra (Table 1).

Voltammetric studies of polyanions in THF, using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, are carried out at low temperature ( $\sim 200$  K). Scanning rates in all voltammetric measurements correspond to the 0.002–0.5 V/s range in cyclic voltammetry (CV). All redox processes in the  $-1.0$  to  $-2.2$  V potential range (vs SCE) correspond to the oxidation of polyanions to polyradicals and reduction of polyradicals to polyanions. Typically, three waves are resolved in this potential range with the relative peak currents ( $i_p$ ) 1:1:1 and 1:2:1 (or 1:1:2) for trianions and tetraanions, respectively; the relative  $i_p$ 's are compatible with transfer of three electrons from trianion and four electrons from tetraanion to form triradical and tetradical, respectively (Figure 3). From the most negative to less negative potentials, these waves should correspond to sequential one-electron oxidations of trianion to radical dianion, diradical anion, and triradical or oxidations of tetraanion to radical trianion, diradical dianion, triradical anion, and tetradical.<sup>9</sup> For each polyanion, the peak-to-peak width ( $\Delta E$ ) for the most negative wave (corresponding to  $E_{p,1}$  in Table 1) is greater than  $\Delta E$ 's for the following, less negative, waves ( $E_{p,2}$  and etc.), especially for tetraanions, where  $\Delta E$ 's are  $\geq 0.2$  V.<sup>10,11</sup> Furthermore, because  $E_{p,1}$  is more negative than  $E_{p,2}$  by  $\sim 0.3$  V, disproportionation equilibrium should not interfere with generation of radical dianions and radical trianions under similar conditions.<sup>12</sup>

2. **Polyradical Polyanions 1<sup>2·1-</sup>, 2<sup>2·1-</sup>, 3<sup>2·1-</sup> and Diradical Dianions 5<sup>2·2-</sup>, 6<sup>2·2-</sup>, 7<sup>2·2-</sup> and Attempted Preparation of Triradical Anions.** Polyradical polyanions can be prepared by (1) partial oxidation of polyanion with iodine, (2) mixing stoichiometric amounts of polyanion and polyradical in THF, (3) partial reduction of polyradical with lithium, and (4) partial reduction of polyether with lithium. The first method is applied

(9) Additional small CV waves (and SQW/DPV peaks) are also detectable but their origin is unclear (Figure 3). Similar observations were made in the previous voltammetric study of triradical 1<sup>3·</sup> (ref 7).

(10) Foley, J. K.; Korzeniewski, C.; Daschbach, J. L.; Pons, S. *Electroanal. Chem.* **1986**, *14*, 309. One of the possible causes of large peak-to-peak widths ( $\Delta E$ ), i.e., lack of reversibility, for the most negative waves in tetraanions may arise from a significant difference in geometry (structure) between tetraanion and radical trianion; for a review on conformational change and isomerization associated with electrode reactions, see: Evans, D. H.; O'Connell, K. M. *Electroanal. Chem.* **1986**, *14*, 113.

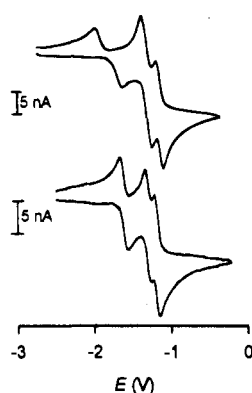
(11) Cyclic voltammograms for 7<sup>4-</sup> are similar (except for the expected changes of  $i_p$ 's) in the  $T = 200\text{--}220$  K range, including CV's with narrow potential ranges (containing either the most negative  $E_p$  wave or the remaining waves).

(12) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980. Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1429.

**Table 1.** UV-Vis Spectroscopic, Cyclic Voltammetric (CV), Differential Pulse Voltammetric (DPV), and Square Wave Voltammetric (SQWV) Data for Trianions and Tetraanions<sup>c</sup>

|             | $\lambda_{\max}$ (nm) | CV (V $\pm$ 40 mV)  |                     |                     |                     | DPV or SQWV (V $\pm$ 30 mV) |       |       |       |
|-------------|-----------------------|---------------------|---------------------|---------------------|---------------------|-----------------------------|-------|-------|-------|
|             |                       | $E_{p,1}(\Delta E)$ | $E_{p,2}(\Delta E)$ | $E_{p,3}(\Delta E)$ | $E_{p,4}(\Delta E)$ | $E_1$                       | $E_2$ | $E_3$ | $E_4$ |
| trianions   |                       |                     |                     |                     |                     |                             |       |       |       |
| $1^{3-}$    | 458 <sup>a,b</sup>    | -1.68 (0.13)        | -1.36 (0.08)        | -1.28 (0.08)        |                     | -1.72                       | -1.42 | -1.35 |       |
| $2^{3-}$    | 457 <sup>a</sup>      | -1.61 (0.16)        | -1.32 (0.08)        | -1.25 (0.07)        |                     | -1.74                       | -1.39 | -1.34 |       |
| $3^{3-}$    | 496 <sup>c</sup>      | -1.58 (0.10)        | -1.28 (0.07)        | -1.16 (0.07)        |                     | -1.64                       | -1.33 | -1.21 |       |
| $4^{3-}$    | 490, 593 <sup>d</sup> | -1.42 (0.12)        | -1.42 (0.12)        | -1.18 (0.08)        |                     | -1.46                       | -1.46 | -1.22 |       |
| tetraanions |                       |                     |                     |                     |                     |                             |       |       |       |
| $5^{4-}$    | 472                   | -2.03 (0.35)        | -1.41 (0.18)        | -1.34 (0.12)        | -1.34 (0.12)        | -2.28                       | -1.48 | -1.38 | -1.38 |
| $6^{4-}$    | 468                   | -1.72 (0.20)        | -1.32 (0.11)        | -1.21 (0.11)        | -1.21 (0.11)        | -1.86                       | -1.46 | -1.33 | -1.33 |
| $7^{4-}$    | 485                   | -1.63 (0.33)        | -1.26 (0.14)        | -1.26 (0.14)        | -1.12 (0.08)        | -1.71                       | -1.33 | -1.33 | -1.18 |

<sup>a</sup> Center of the band is at  $\lambda \approx 470$  nm. <sup>b</sup>  $\lambda_{\max} = 465$  nm in THF. <sup>c</sup> sh,  $\lambda \approx 409$  nm. <sup>d</sup> In THF. <sup>e</sup> UV-vis spectra and electrochemical data are obtained in THF/MeLi at ambient temperature and THF/TBAP at 200 K, respectively, unless indicated otherwise. For electrochemical data, potentials are given vs Ag wire quasireference electrode with ferrocene (0.510 V vs SCE) as a reference and CV scan rates are 0.050 V/s.

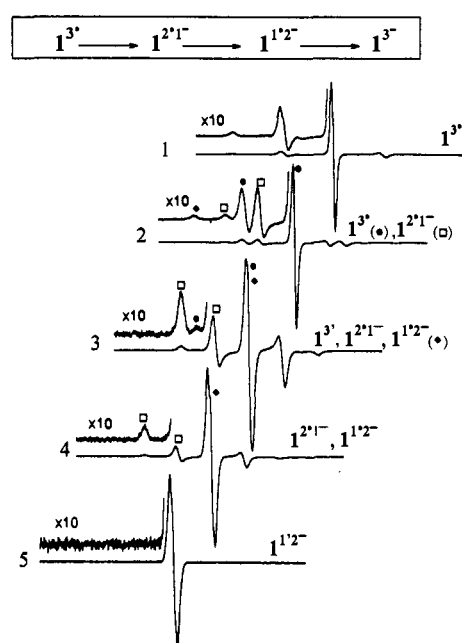


**Figure 3.** Cyclic voltammetry for trianion  $3^{3-}$  (bottom) and tetraanion  $7^{4-}$  (top) in THF/TBAP at 200 K. Scan rates are 50 mV/s. Potentials are given vs SCE using ferrocene (0.510 V) as the reference.

to the majority of polyradical polyanions. The second and third methods are only used where stable polyradicals are available; the second method is particularly suited for preparation of solid polyradical polyanions. The fourth method is applied to radical dianion  $1^{1,2-}$ .

The reaction of triradical  $1^{3\bullet}$  with an excess of Li in 2-methyltetrahydrofuran (2-MeTHF) is monitored by ESR spectroscopy of the frozen reaction mixture ( $T = 77-100$  K). The characteristic dipolar patterns (or their absence) for states with different spin values ( $S$ ) are detected in the following order: quartet ( $S = 3/2$ )  $\rightarrow$  triplet ( $S = 1$ )  $\rightarrow$  doublet ( $S = 1/2$ )  $\rightarrow$  singlet ( $S = 0$ ) (Figure 4). Analogously, ESR spectroscopy of the liquid reaction mixture (THF or 2-MeTHF, ambient  $T$ ) reveals decreasing intensity of the broad center peak with collapsed dipolar pattern for the  $S > 1/2$  states and a partially resolved hyperfine pattern for the doublet state ( $S = 1/2$ ). In the corresponding UV-vis spectra (THF, ambient  $T$ ), absorbance of the  $\lambda_{\max} \approx 350$  nm band of the triarylmethyl radical is decreasing and the  $\lambda_{\max} \approx 465$  nm band of the triarylmethyl anion is increasing; an isosbestic point at  $\lambda \approx 374$  nm is observed (Figure 5). Diradical anion  $1^{2,1-}$  and radical dianion  $1^{1,2-}$  are the proposed triplet ( $S = 1$ ) and doublet ( $S = 1/2$ ) intermediates, respectively (Figure 4).

**A. Electron Localization in Radical Dianion  $1^{1,2-}$ .** The final ESR-active ( $S = 1/2$ ) product of the reaction of triradical  $1^{3\bullet}$  in THF with an excess of Li is assigned to radical dianion  $1^{1,2-}$ . A similar ESR spectrum at ambient temperature is obtained for the final ESR-active product of the reaction of triether  $1-(\text{OMe})_3$  in THF with an excess of Li (Scheme 1, method 4). The best-resolved ESR spectrum is observed when  $1^{1,2-}$  is prepared by combining 1 equiv of triradical  $1^{3\bullet}$  with 2 equiv of trianion  $1^{3-}$  in THF (method 2). Notably, when monoether  $1-(\text{H})_2(\text{OMe})$  is reacted with Li in THF, the ESR

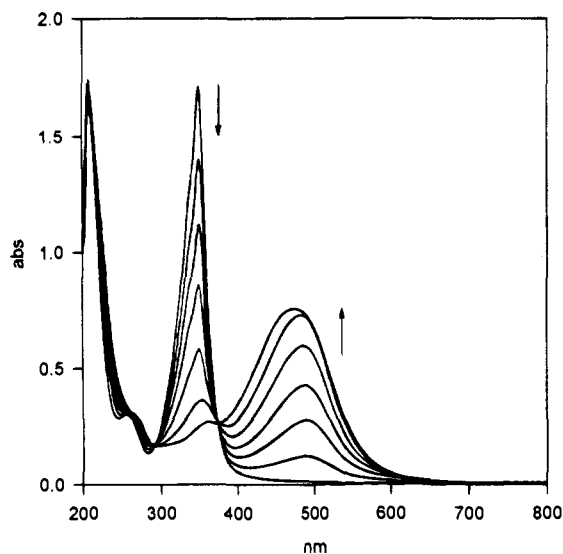


**Figure 4.** ESR spectra following the reaction of triradical  $1^{3\bullet}$  with Li in 2-MeTHF. The reaction is carried out at  $T < 273$  K and the spectra are recorded at  $T \approx 80$  K. The center field and width are 3390 and 400 G, respectively. The relative gain settings for spectra 1-5 are 1, 2, 16, 13, 32; all other instrumental parameters are identical. Extended reaction time leads to complete disappearance of the ESR signal due to formation of diamagnetic  $1^{3-}$ .

spectrum of the intermediate radical, which should be  $1-(\text{H})_2^{1\bullet}$ , has the hyperfine coupling pattern indistinguishable, within the spectral resolution, from that for radical dianion  $1^{1,2-}$  (Scheme 1, Figure 6). Analogously, similar ESR spectra for the previously studied radical anion  $8^{1,1-}$  (ref 5) and the intermediate radical obtained from the reaction of monoether  $8-\text{H-OMe}$  with Li in THF are obtained (Scheme 1). These results imply that the spin density in radical dianion  $1^{1,2-}$  is localized at the central triarylmethyl moiety.<sup>13</sup>

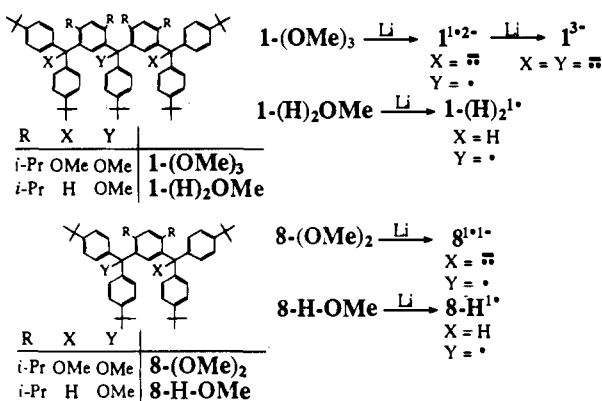
**B. Electron Localization in Diradical Anions  $1^{2,1-}$ ,  $2^{2,1-}$ ,  $3^{2,1-}$  and Diradical Dianions  $5^{2,2-}$ ,  $6^{2,2-}$ ,  $7^{2,2-}$ .** The initial ESR-active ( $S = 1$ ) product of the reaction of triradical  $1^{3\bullet}$  ( $S = 3/2$ ) in 2-MeTHF with an excess of Li is assigned to diradical anion  $1^{2,1-}$ . An identical ESR spectrum in THF/2-MeTHF glass at  $T = 77-100$  K is obtained for the product of oxidation of trianion  $1^{3-}$  with 1 equiv of  $\text{I}_2$  at low temperature (method 1). Notably, zero field splitting (zfs) parameters,  $|D/hc|$ , are similar

(13) A set of hyperfine coupling constants to provide an adequate fit to the experimental ESR spectra for  $1^{1,2-}$  is not found, unlike for the previously studied less hindered derivative of  $8^{1,1-}$  (ref 5).



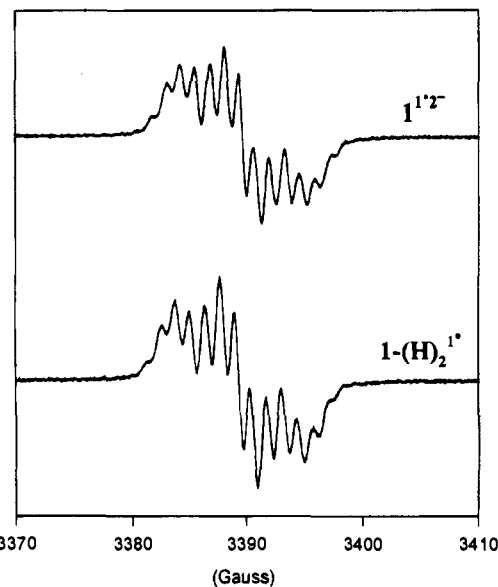
**Figure 5.** UV-vis spectra following the reaction of triradical  $1^{3\bullet}$  with Li in THF:  $1^{3\bullet} \rightarrow 1^{2\bullet 1-} \rightarrow 1^{1\bullet 2-} \rightarrow 1^{3-}$ . The first and the last spectra correspond to triradical  $1^{3\bullet}$  ( $\lambda_{\max} \approx 350$  nm) and trianion  $1^{3-}$  ( $\lambda_{\max} \approx 465$  nm), respectively. The isosbestic point is at  $\lambda \approx 374$  nm. The spectra are acquired with low resolution (bandwidth 4 nm) to allow for fast scanning without band distortion.

**Scheme 1**

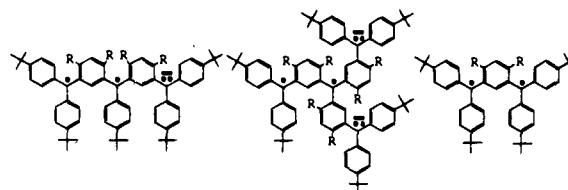


for the diradical anion  $1^{2\bullet 1-}$  and the corresponding diradical  $8^{2\bullet}$  (Figure 7); furthermore, protonation of diradical anion  $1^{2\bullet 1-}$  with MeOH gives an ESR spectrum with unchanged zfs parameter,  $|D/hc| = 0.0096 \text{ cm}^{-1}$ . Because  $|D/hc|$  measures spatial spin density distribution in triplet states,<sup>14a</sup> these results suggest spin density localization at the two adjacent triarylmethyl moieties in diradical anion  $1^{2\bullet 1-}$ .<sup>14</sup>

Other diradical anions ( $2^{2\bullet 1-}$ ,  $3^{2\bullet 1-}$ ) and diradical dianions ( $5^{2\bullet 2-}$ ,  $6^{2\bullet 2-}$ ,  $7^{2\bullet 2-}$ ) are prepared by method 1. The  $\Delta m_s = 1$  regions of ESR spectra for  $2^{2\bullet 1-}$ ,  $3^{2\bullet 1-}$ ,  $5^{2\bullet 2-}$ ,  $6^{2\bullet 2-}$ , and  $7^{2\bullet 2-}$  in THF/2-MeTHF glass typically reveal four-line dipolar patterns readily assigned to approximately axial ( $E \approx 0$ )  $S = 1$  states; the additional center lines are associated with half-integral spin impurities,  $S = 1/2$  monoradical polyanions or  $S = 3/2$  triradicals (or triradical anions), i.e., "underoxidized" or "overoxidized" polyanions (Figure 8). However, for samples of diradical anions  $2^{2\bullet 1-}$  and  $3^{2\bullet 1-}$ , and diradical dianion  $7^{2\bullet 2-}$ , more than four side lines are detected and the center lines are intense (but within a



**Figure 6.** ESR spectra of radical dianion  $1^{1\bullet 2-}$  in 2-MeTHF and radical  $1-(\text{H})_2 1^{\bullet}$  in THF. Radical dianion  $1^{1\bullet 2-}$  is obtained by method 2. Radical  $1-(\text{H})_2 1^{\bullet}$  is detected as an intermediate in the reaction of ether  $1-(\text{H})_2\text{OMe}$  with Li (Scheme 1).



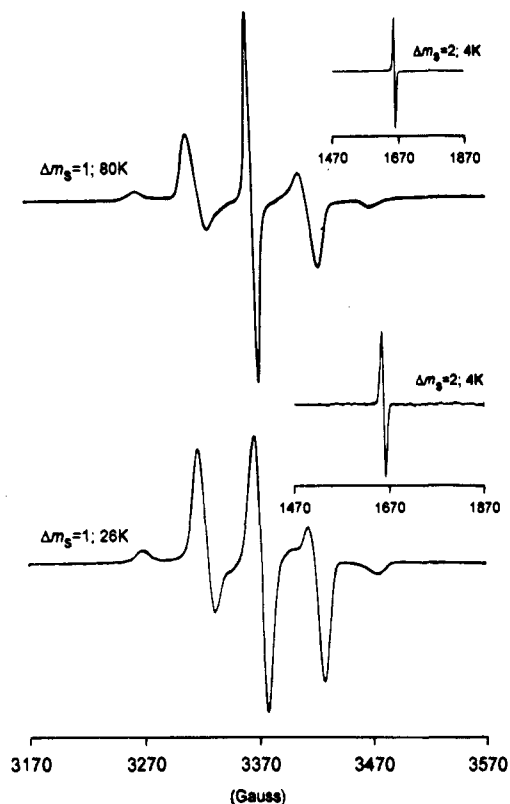
| R    | diradical anion   | $ D/hc $ (10 <sup>-3</sup> cm <sup>-1</sup> ) | diradical dianion | $ D/hc $ (10 <sup>-3</sup> cm <sup>-1</sup> ) | diradical       | $ D/hc $ (10 <sup>-3</sup> cm <sup>-1</sup> ) |
|------|-------------------|---|-------------------|---|-----------------|---|
| i-Pr | $1^{2\bullet 1-}$ | 9.6   | $5^{2\bullet 2-}$ | 9.4   | $8^{2\bullet}$  | 9.9   |
| Me   | $2^{2\bullet 1-}$ | 8.6   | $6^{2\bullet 2-}$ | 9.5   | $9^{2\bullet}$  | 8.7   |
| H    | $3^{2\bullet 1-}$ | 6.9, 5.0                                      | $7^{2\bullet 2-}$ | 7.1, 5.2                                      | $10^{2\bullet}$ | 6.6   |

**Figure 7.** Zero field splitting (zfs) parameters for diradical anions  $1^{2\bullet 1-}$ ,  $2^{2\bullet 1-}$ ,  $3^{2\bullet 1-}$ , diradical dianions  $5^{2\bullet 2-}$ ,  $6^{2\bullet 2-}$ ,  $7^{2\bullet 2-}$ , and the corresponding diradicals.

factor of 10 compared to the side lines). These more complicated spectra are ascribed to either a mixture of two  $S = 1$  isomers (for  $3^{2\bullet 1-}$  and for  $7^{2\bullet 2-}$ ) or an admixture of  $S = 3/2$  triradical (for  $2^{2\bullet 1-}$ ). (Two  $S = 3/2$  isomers have been assigned to the triradical derived from the diradical anion  $3^{2\bullet 1-}$ ).<sup>7</sup> Because the zfs parameters ( $|D/hc|$ ) for all studied diradical anions and diradical dianions are comparable to those for the corresponding diradicals (Figure 7), the "unpaired" electrons are localized at the adjacent triarylmethyl moieties, as already concluded for  $1^{2\bullet 1-}$ .

At 4 K, the  $\Delta m_s = 2$  regions for diradical anions and diradical dianions typically consist of an intense single line at the half-field, as expected for  $S = 1$  states with moderate values of zfs parameters (Figure 8); an exception is the spectrum of  $2^{2\bullet 1-}$ , which possesses weak side lines arising from the triradical  $2^{3\bullet}$ ,<sup>7</sup> as discussed earlier. The plots of the product ( $IT$ ) of the intensity ( $I$ ) for the half-field  $\Delta m_s = 2$  signal and the temperature ( $T$ ) versus  $T$  are constant in the 10–80 K range; similarly, the Curie plots ( $I$  vs  $1/T$ ) are linear in this temperature range. Therefore, diradical anions  $1^{2\bullet 1-}$ ,  $2^{2\bullet 1-}$ ,  $3^{2\bullet 1-}$  and diradical dianions  $5^{2\bullet 2-}$ ,  $6^{2\bullet 2-}$ ,  $7^{2\bullet 2-}$  possess either  $S = 1$  ground states or nearly degenerate  $S = 1$  and 0 states. Because the corresponding diradicals  $8^{2\bullet}$ ,  $9^{2\bullet}$ ,  $10^{2\bullet}$  possess  $S = 1$  ground states,<sup>3a,15</sup> nearly complete electron localization in the studied

(14) (a) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman and Hall: New York, 1986; Chapter 10. (b) For a triplet state,  $D$  may approximately be related to  $1/r^3$ , where  $r$  is the distance between the "unpaired" electrons. Assuming that extended and partially extended conformations dominate for the diradical anions, the limiting structure with the spin density localized at the non-adjacent (terminal) sites should have  $|D/hc|$  several times smaller compared to that for the limiting structure with the spin density localized at the adjacent sites (Figure 1).



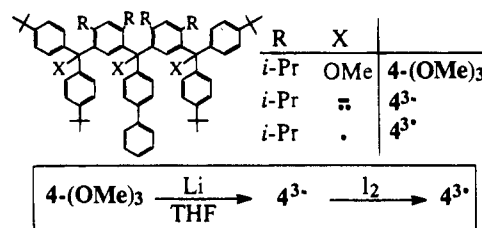
**Figure 8.** ESR spectra of diradical dianions  $5^{2,2-}$  and  $6^{2,2-}$  in 2-MeTHF/THF glass. Top spectrum with insert:  $\Delta m_s = 1$  and 2 regions for  $5^{2,2-}$  at 80 and 4 K. Bottom spectrum with insert:  $\Delta m_s = 1$  and 2 regions for  $6^{2,2-}$  at 26 and 4 K. The center peaks in the  $\Delta m_s = 1$  regions correspond to half-integral spin impurities.

diradical anions and diradical dianions would suggest that the  $S = 1$  ground states are more likely than the near degeneracies. Thus, the ferromagnetic coupling should be preserved between the remaining "unpaired" electrons at the adjacent spin sites in these diradical anions and diradical dianions.

**C. Attempted Preparation of Triradical Anions.** Application of method 1 to preparation of triradical anions produces ESR spectra that are qualitatively different from those for diradical species. The  $\Delta m_s = 1$  regions are dominated by the center line. ESR spectra for the triradical anion corresponding to diradical dianion  $6^{2,2-}$  are obtained in the liquid helium range; the  $\Delta m_s = 2$  region possesses a relatively weak center line and strong side lines, compared to the corresponding tetradical.<sup>7</sup> Although these features are supportive of the  $S = 3/2$  state, as expected for triradical anions, the complexity of the  $\Delta m_s = 1$  regions does not permit adequate simulation of the ESR spectra. In particular, admixtures of diradical dianions and tetradicals cannot be excluded; their presence would be compatible with the electrochemical data for tetraanions.

**3. Control of Electron Localization: Diradical Anion  $4^{2,1-}$  and the Corresponding Triradical and Trianion.** In the preceding section, it is shown that diradical anion  $1^{2,1-}$  (and the related diradical anions and diradical dianions) has its spin density localized at the adjacent sites; its ESR spectra are compatible with ferromagnetic coupling between the two "unpaired" electrons, analogous to the corresponding diradical. In order to control localization of the spin/charge density, we design diradical anion  $4^{2,1-}$  (Figure 2). The carbanion stabilizing 4-biphenyl, in the place of 4-*tert*-butylphenyl, substituent at the center site should localize the negative charge at the center

**Scheme 2**



site and the spin density at the terminal (nonadjacent) sites.<sup>16</sup> As illustrated in the Figure 1, such a spin localization at the nonadjacent (terminal) sites should lead to antiferromagnetic coupling between the two "unpaired" electrons. First, the corresponding triradical  $4^{3\bullet}$  and trianion  $4^{3-}$  are prepared and studied.

**A. Triradical  $4^{3\bullet}$  and Trianion  $4^{3-}$ .** Both  $4^{3\bullet}$  and  $4^{3-}$  are obtained by adaptation of the previously reported methods (Scheme 2, Experimental Section).

The  $\Delta m_s = 1, 2, 3$  regions of the ESR spectrum for triradical  $4^{3\bullet}$  in THF/2-MeTHF are characteristic of an  $S = 3/2$  state and are similar to the related triradicals (Figure 9).<sup>7</sup> Computer simulation of the  $\Delta m_s = 1$  region for the  $S = 3/2$  state adequately reproduces the experimental spectrum, except for the small discrepancy in the relative intensities of the center and side lines (Figure 9);<sup>17</sup> the slightly larger than expected intensity of the center line may be caused by a small amount of an  $S = 1/2$  impurity. The zfs parameters,  $|D/hc| = 0.0067 \text{ cm}^{-1}$  and  $|E/hc| = 0.00015 \text{ cm}^{-1}$ , are similar to those for the previously studied triradical  $1^{3\bullet}$  ( $|D/hc| = 0.0069 \text{ cm}^{-1}$  and  $|E/hc| = 0 \text{ cm}^{-1}$ ).<sup>7</sup> Detection of a transition in the  $\Delta m_s = 3$  region at 4 K unequivocally confirms the  $S = 3/2$  state. Furthermore, four symmetrical broad lines in the  $\Delta m_s = 2$  region are assigned to the  $S = 3/2$  state and the narrow center line corresponds to an  $S = 1$  impurity. In most samples of  $4^{3\bullet}$ , an  $S = 1$  impurity is also detected in the  $\Delta m_s = 1$  region.

The <sup>1</sup>H NMR (500 MHz) spectrum of  $4^{3\bullet}$  in toluene-*d*<sub>8</sub> reveals relatively broad ( $\Delta\nu_{1/2} \approx 6.5 \text{ kHz}$ ) resonance at 10 ppm and a group of relatively narrow ( $\Delta\nu_{1/2} < 50 \text{ Hz}$ ) resonances around 1 ppm;<sup>18a</sup> their relative integration is  $\sim 16/1$ . These resonances are assigned to *t*-Bu groups in 4-*tert*-butylphenyls adjacent to the sites with and without an "unpaired" electron, respectively; the downfield (paramagnetic) shift is compatible with negative spin density at the hydrogens of the *t*-Bu groups.<sup>18b</sup>

Magnetization ( $M$ ) of  $\sim 4 \times 10^{-3} \text{ M}$   $4^{3\bullet}$  in 2-MeTHF is measured as a function of magnetic field ( $H = 0-5.5 \text{ T}$ ) and temperature ( $T = 2, 5, 10 \text{ K}$ );  $S = 1.4$  is obtained from the two-parameter ( $S$  and magnetization at saturation,  $M_{\text{sat}}$ ) fit of  $M$  vs  $H/T$  to the Brillouin function.<sup>19,20</sup> The presence of the  $S < 3/2$  impurities accounts for the lower than expected value of  $S$  from magnetometry.<sup>20</sup> Therefore, the  $S = 3/2$  ground state for  $4^{3\bullet}$  is established.

Cyclic voltammetry of trianion  $4^{3-}$  in THF/TBAP at 200 K reveals two reversible oxidation waves at  $E_p = -1.42$  and  $-1.18 \text{ V}$  (relative  $i_p$ 's, 2:1). The UV-vis spectrum for trianion  $4^{3-}$

(16)  $pK_a$  of biphenyldiphenylmethane is lower by  $> 1$   $pK_a$  unit compared to that of triphenylmethane: Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. Kaufman, M. J.; Gronert, S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2829.

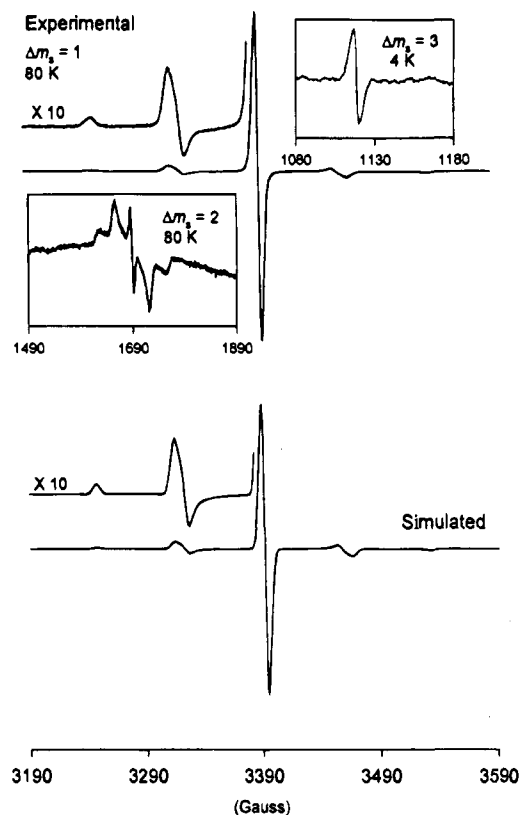
(17) Thayumanavan, S.; Rajca, A. Unpublished work. Rajca, A.; Utamapanya, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **1992**, *114*, 1884.

(18) (a)  $\sim 10^{-2} \text{ M}$   $4^{3\bullet}$  in toluene-*d*<sub>8</sub>. (b) LaMar, G. N.; Horrocks, D.; Holm, R. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(19) Henry, W. E. *Phys. Rev.* **1952**, *88*, 559.

(20) (a) For the fits at  $T = 2$  and 5 K, values for parameter dependence are 0.47 and 0.94, respectively. (b) Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 806.

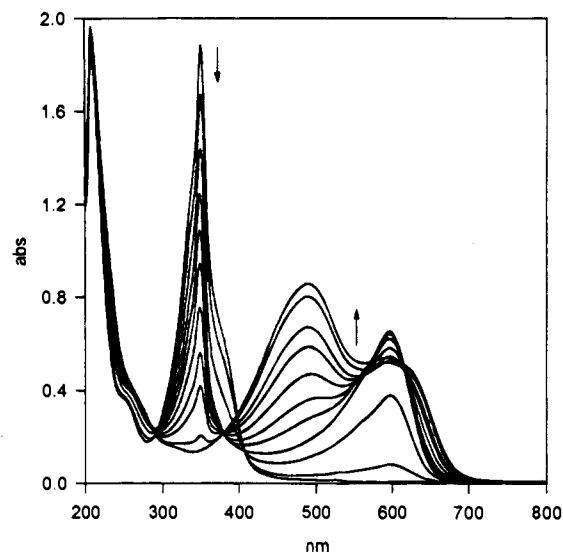
(15) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991**, *113*, 9235.



**Figure 9.** ESR spectroscopy of triradical  $4^{3\bullet}$ , which was obtained by oxidation of the corresponding trianion, using 1.5+ equiv of  $I_2$  at low temperature. Experimental:  $\Delta m_s = 1, 2,$  and  $3$  regions of the experimental spectrum in 2-MeTHF/THF glass at 80, 80, and 4 K, respectively; the  $\Delta m_s = 3$  region of the spectrum was obtained in a different cavity compared to the other regions. Simulated: simulation of the  $\Delta m_s = 1$  region using second-order perturbation theory solution to the spin-only dipolar Hamiltonian for the  $S = 3/2$  state with a Gaussian line width of 6 G, microwave frequency of 9.50 GHz, and the following zfs parameters:  $|D/hc| = 0.0067 \text{ cm}^{-1}$  and  $|E/hc| = 0.00015 \text{ cm}^{-1}$ .<sup>17</sup> The greater peak height of the center line (relative to the side lines) in the  $\Delta m_s = 1$  region in the experimental spectrum compared to the simulation may originate in a small admixture of  $S = 1/2$  impurities. Also, the center peak in the  $\Delta m_s = 2$  region indicates the presence of a small amount of  $S = 1$  impurities.

in THF has two broad bands at  $\lambda_{\text{max}} \approx 490$  and 593 nm, with a relative ratio of absorbances of  $\sim 2/1$  (Table 1). Analogously, triradical  $4^{3\bullet}$  in THF has  $\lambda_{\text{max}} \approx 350$  nm with a shoulder at  $\lambda_{\text{max}} \approx 370$  nm. Comparison between the above spectra and those for the previously discussed trianions and triradicals suggests that the longer  $\lambda_{\text{max}}$  band (or shoulder) should be associated with the presence of the 4-biphenyl substituent at the center site.<sup>21</sup>

**B. Diradical Anion  $4^{2\bullet 1-}$ .** When the reaction of triradical  $4^{3\bullet}$  with an excess of Li in THF is monitored by UV-vis spectroscopy, the bands corresponding to the radical sites ( $\lambda_{\text{max}} \approx 350$  nm, sh  $\approx 370$  nm) are being replaced with the bands corresponding to the anion sites ( $\lambda_{\text{max}} \approx 490$  and 593 nm) (Figure 10). Because  $4^{2\bullet 1-}$  is expected to be the first intermediate (product) of the reaction, the initial spectral changes, such as the disappearance of the band with shoulder at  $\lambda_{\text{max}} \approx 350$  nm (sh,  $\lambda_{\text{max}} \approx 370$  nm) and appearance of the band at  $\lambda_{\text{max}} \approx 597$  nm with the isosbestic point at  $\lambda \approx 409$  nm, should be relevant to the conversion of  $4^{3\bullet}$  to  $4^{2\bullet 1-}$ . The subsequent spectral changes are analogous to those observed for  $1^{3\bullet}$  (Figure



**Figure 10.** UV-vis spectra following the reaction of triradical  $4^{3\bullet}$  with Li in THF:  $4^{3\bullet} \rightarrow 4^{2\bullet 1-} \rightarrow 4^{1\bullet 2-} \rightarrow 4^{3-}$ . The first and the last spectra correspond to triradical  $4^{3\bullet}$  ( $\lambda_{\text{max}} \approx 350$  nm, sh,  $\sim 370$  nm) and trianion  $4^{3-}$  ( $\lambda_{\text{max}} \approx 490, 593$  nm), respectively. The isosbestic points, which are discussed in the text, are at  $\lambda \approx 380$  and 409 nm. The spectra are acquired with low resolution (bandwidth 4 nm) to allow for fast scanning without band distortion.

5). The band at  $\lambda_{\text{max}} \approx 350$  nm diminishes while the band at  $\lambda_{\text{max}} \approx 490$  nm appears and increases with the isosbestic point at  $\lambda \approx 380$  nm. Furthermore, the band at  $\lambda_{\text{max}} \approx 597$  nm broadens and shifts to  $\lambda_{\text{max}} \approx 593$  nm (Figure 10).

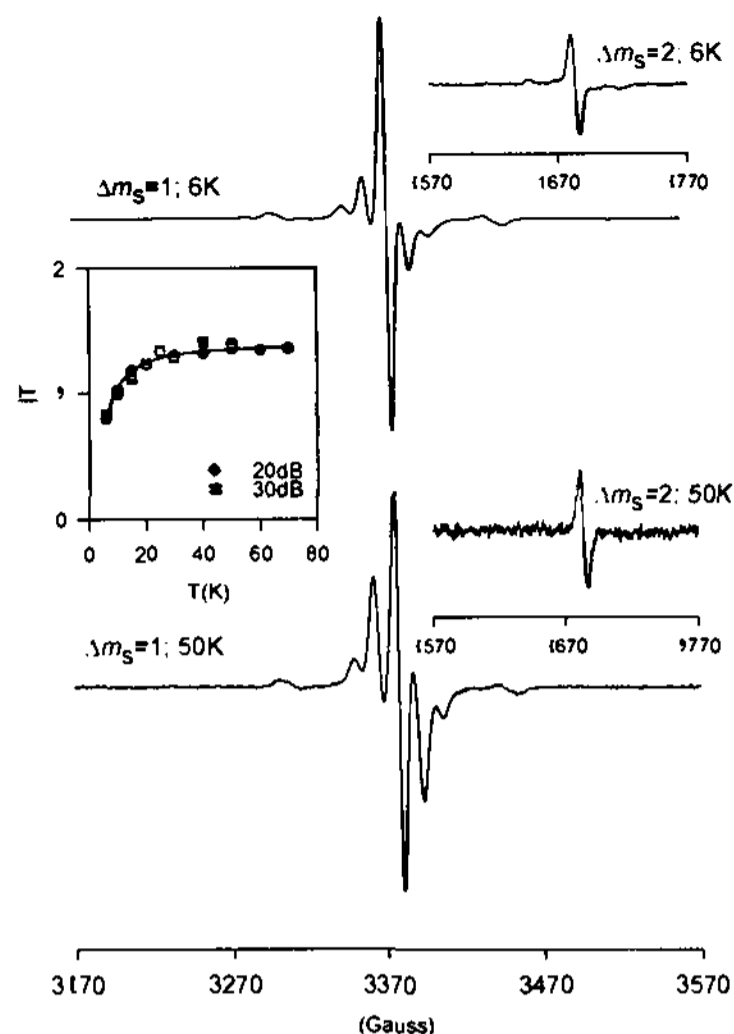
The initial ESR-active product of the reaction of triradical  $4^{3\bullet}$  in 2-MeTHF with an excess of Li gives an  $S = 1$  spectrum with a zfs parameter,  $|D/hc| = 0.0027 \text{ cm}^{-1}$ , which is much smaller than that for diradical anion  $1^{2\bullet 1-}$  (Figure 11). A similar ESR spectrum with small  $D$  is obtained when trianion  $4^{3-}$  is oxidized with 1 equiv of  $I_2$ . (Triradical  $4^{3\bullet}$  is obtained using 1.5+ equiv of iodine.)

These spectroscopic data suggest that diradical anion  $4^{2\bullet 1-}$  is the first product of the follow-up experiments. The appearance of the band at  $\lambda_{\text{max}} \approx 597$  nm in the early stage of the follow-up experiments and a relatively small value of  $|D/hc|$  imply that the negative charge is associated with the center site in  $4^{2\bullet 1-}$ .<sup>14b,21</sup>

The ESR spectra in the  $\Delta m_s = 1, 2$  regions ( $T = 6-70$  K) for a mixture of diradical anion  $4^{2\bullet 1-}$  and triradical  $4^{3\bullet}$  show the expected increase in intensity at low temperatures; however, this increase in intensity is relatively less for diradical anion  $4^{2\bullet 1-}$  compared to triradical  $4^{3\bullet}$  (Figure 11). The [zfs parameter,  $|D/hc| = 0.0027 \text{ cm}^{-1}$ , for diradical anion  $4^{2\bullet 1-}$  remains unchanged in this temperature range.] In particular, the  $IT$  vs  $T$  plot for the  $\Delta m_s = 2$  region of the diradical anion  $4^{2\bullet 1-}$  is approximately constant in the  $T = 25-70$  K range, with downward turn at lower temperatures. These results suggest the presence of weak antiferromagnetic interactions associated with diradical anion  $4^{2\bullet 1-}$ . Intermolecular interactions cannot be rigorously excluded; however, interactions of this strength in a  $\sim 10^{-3}$  M solution of sterically hindered polyarylmethyl diradical anion are unlikely.<sup>22</sup> In the most probable case of intramolecular antiferromagnetic interactions, the fit of the  $IT$  vs  $T$  data for the  $\Delta m_s = 2$  region to the Bleaney-Bowers

(21) For a review of spectrophotometric studies of arylmethyl anions, see: Buncel, E.; Menon, B. *Comprehensive Carbanion Chemistry, Part A*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980; Chapter 3.

(22) Formation of an ion quartet (a dimer) for  $\sim 10^{-3}$  M  $4^{2\bullet 1-}$  in 2-MeTHF/THF (with possible antiferromagnetic intermolecular interaction) is unlikely in the sterically hindered lithium salt of triarylmethyl carbanion; i.e., alkali metal salts of triarylmethyl carbanions are monomeric (typically, ion pairs) in ethereal solvents; refs 16 and 21, also: Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1965**, *87*, 669.



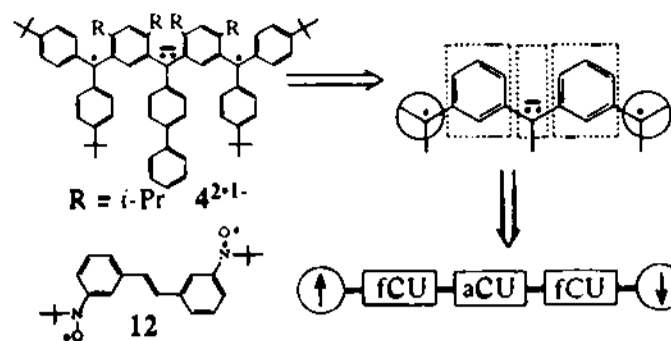
**Figure 11.** ESR spectroscopy of diradical anion  $4^{2-1-}$ , which was obtained by oxidation of the corresponding trianion, using 1+ equiv of  $I_2$  at low temperature. Top spectrum with insert:  $\Delta m_s = 1$  and 2 regions of the ESR spectrum in 2-MeTHF/THF glass at 6 K. Bottom spectrum with insert: as above but at 50 K. Four symmetrical lines (adjacent to the center line) in the  $\Delta m_s = 1$  region and the center line in the  $\Delta m_s = 2$  region are assigned to the thermally populated  $S = 1$  state of diradical anion  $4^{2-1-}$  ( $|D/hc| = 0.0027 \text{ cm}^{-1}$  and  $|E/hc| \approx 0 \text{ cm}^{-1}$ ). The remaining lines are assigned to triradical  $4^{3-}$ . Box: plot of the product ( $IT$ ) of the intensity ( $I$ ) for the  $\Delta m_s = 2$  signal of diradical anion  $4^{2-1-}$  and temperature ( $T$ ) versus  $T$ ; circles and squares correspond to experimental points at microwave power attenuation of 20 and 30 dB, respectively. The solid curve is obtained by a two-parameter fit of the experimental data (attenuation of 20 dB) to the modified Bleaney–Bowers equation ( $IT$  vs  $T$ ); fitting parameters,  $J/k = -4.4 \text{ K}$  (equivalent to  $\Delta E_{ST} \approx -18 \text{ cal/mol}^{-1}$ ) and normalization factor, are obtained with parameter dependence of 0.4, indicating a reliable fit.

equation indicates that the singlet ground state ( $S = 0$ ) for diradical anion  $4^{2-1-}$  is separated from the lowest triplet excited state ( $S = 1$ ) by an energy gap,  $\Delta E_{ST} \approx -18 \text{ cal/mol}^{-1}$  ( $J/k \approx -4.4 \text{ K}$ ).<sup>23</sup>

As far as spin coupling is concerned, diradical anion  $4^{2-1-}$  can be considered as two spin sites (terminal arylmethyls), sequentially connected two ferromagnetic (1,3-phenylenes) and one antiferromagnetic (central arylmethyl anion) coupling units (two fCU's and one aCU).<sup>24</sup> A analogous spin coupling path, with 1,2-connected ethylene replacing carbanion, is found in dinitroxide **12**, which is the ground state singlet with  $\Delta E_{ST} \approx -30 \text{ cal/mol}^{-1}$ .<sup>24</sup>

## Conclusion

Polyradical polyanions, which are derived from the corresponding high-spin polyradicals, have their charge and spin localized at the separate triarylmethyl sites. Modification of the aryl substituents at the triarylmethyl sites allows for control



of charge/spin localization at the specific sites, with the following important consequences for spin coupling: (1) when spin sites are adjacent, spin coupling between the “unpaired” electrons is ferromagnetic, analogous to that in the parent polyradicals, (2) when spin sites are not adjacent, because the pathway between them includes a site with negative charge (electron pair), spin coupling between the “unpaired” electrons is antiferromagnetic (Figure 1). The present results conform to the most simple theoretical models; most likely, they should be applicable to not only sterically hindered polyarylmethyls but also other ferromagnetically coupled chains as well.

Design of new structures for electron transfer (and electrical conductivity) via control of spin coupling, based upon previous findings in two-site chains<sup>5</sup> and the present results on multi-site chains, is in progress in our laboratory.

## Experimental Section

**Materials.** Ether and tetrahydrofuran (THF) for use in synthesis were distilled from sodium/benzophenone in a nitrogen atmosphere. THF for use in the glovebox was transferred twice under high vacuum (from purple sodium/benzophenone and potassium/benzophenone). 2-Methyltetrahydrofuran (2-MeTHF) was distilled from  $\text{CaH}_2$ , then distilled from sodium/benzophenone, and finally transferred from purple sodium/benzophenone under vacuum directly to the reaction mixture. Major chemicals are obtained from Aldrich. Preparation of the key starting materials for the present synthesis is described elsewhere.<sup>25</sup>

**Special Procedures.** Solutions of carbopolyanions in THF were prepared in a glovebox; outside the glovebox, carbopolyanions were handled on a  $10^{-3}/10^{-5}$  Torr vacuum line.

**NMR Spectroscopy and Other Analyses.** NMR spectra were obtained using Omega spectrometers ( $^1\text{H}$ , 500 and 300 MHz) and a Bruker spectrometer ( $^1\text{H}$ , 400 MHz) in  $\text{CDCl}_3$  or  $\text{THF}-d_6$ . The chemical shift references were as follows:  $^1\text{H}$ , TMS, 0.0 ppm ( $\text{CDCl}_3$ ),  $\text{THF}-d_6$ , 3.58 ppm ( $\text{THF}-d_6$ ), and toluene- $d_8$ , 2.09 ppm (toluene- $d_8$ );  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 77.0 ppm and  $\text{THF}-d_6$ , 67.45 ppm. Paramagnetic  $^1\text{H}$  NMR spectra employed the spectral width of 40 kHz; standard baseline corrections were applied. SQUID magnetometry was carried out, as described previously for other polyradicals.<sup>21b</sup>

Voltammetry data were obtained, in a glovebox, at 200 K, as previously described for a triradical.<sup>7</sup> Because of the high basicity of polyanions, solutions of polyanions with supporting electrolyte (TBAP/THF) were prepared at  $T < 240 \text{ K}$  and, then, rapidly cooled to  $\sim 200 \text{ K}$ .

Elemental analyses were completed by Dr. G. M. Dabkowski, Director-Microlytics, P.O. Box 199, South Deerfield, MA 01373.

**ESR Spectroscopy.** X-band ESR spectra were acquired with 200D SRC and Bruker 200D instruments, equipped with an Oxford Instruments ESR900 liquid helium cryostat (4–80 K), liquid nitrogen insert dewar (80 K or ambient), or Varian nitrogen flow system (100–300 K), as described elsewhere.<sup>7</sup>

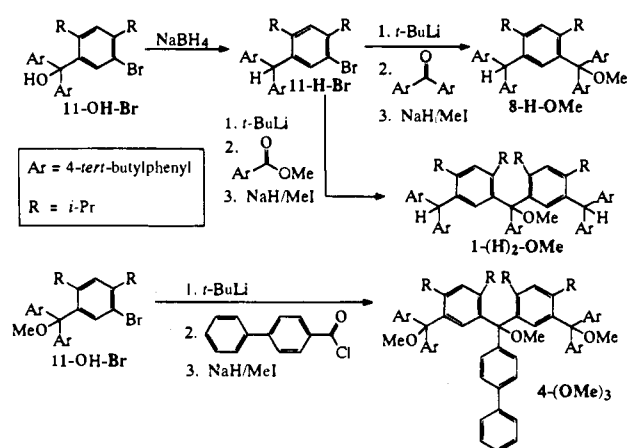
**UV–Vis Spectroscopy.** UV–vis absorption spectra were recorded at ambient temperature in a 2-mm pathlength quartz cell using a Perkin-Elmer Lambda 6 spectrometer attached to the glovebox, as described elsewhere.<sup>5</sup> The glassware (quartzware) was dried in an oven ( $> 110 \text{ }^\circ\text{C}$ , 24 h), evacuated in the antechamber overnight, and then pretreated with the corresponding carbopolyanion solution immediately prior to use.

(23) Bleaney–Bowers equation: Bleaney, B.; Bowers, H. D. *Proc. R. Soc. London A* **1952**, 214.

(24) Yoshinka, N.; Lahti, P. M.; Kaneko, T.; Kuzumaki, Y.; Tsushida, E.; Nishide, H. *J. Org. Chem.* **1994**, 59, 4272.

(25) Rajca, A.; Janicki, S. *J. Org. Chem.* **1994**, 59, 7099.

Scheme 3



Synthesis of 11-H-Br, 8-H-OMe, 1-(H)<sub>2</sub>-OMe, and 4-(OMe)<sub>3</sub>. Previously described synthetic methods are employed.<sup>25</sup> Experimental details for the above compounds are found in the supporting information.

**Polyanions 1<sup>3-</sup>, 2<sup>3-</sup>, 3<sup>3-</sup>, 4<sup>3-</sup>, 5<sup>4-</sup>, 6<sup>4-</sup>, 7<sup>4-</sup>.** Treatment of the corresponding polyethers with excess Li in THF for 2–7 days in a glovebox at ambient temperature gave polyanions, as described previously. For biphenyl-substituted trianion, 4<sup>3-</sup>, stirring of 4-(OMe)<sub>3</sub> (71.2 mg) with Li in THF (1.0 mL) was limited to 4 days.

**Triradical 4<sup>3•</sup>.** Solid triradical 4<sup>3•</sup> is prepared by the methods reported previously for analogous stable diradicals and triradicals.<sup>7</sup> <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>) and ESR (2-MeTHF) spectra of 4<sup>3•</sup> indicated that a typical sample had purity in the 80–95% range.

**Preparation of Polyradical Polyanions and Follow-Up Studies.**  
**Method 1:** 1<sup>2•1-</sup>, 2<sup>2•1-</sup>, 3<sup>2•1-</sup>, 4<sup>2•1-</sup>, 5<sup>2•2-</sup>, 6<sup>2•2-</sup>, 7<sup>2•2-</sup>. The experimental procedures and the glassware are analogous to those for the preparation of the corresponding tri- and tetradicals, as described previously.<sup>7</sup> Iodine (1 equiv) was added under a stream of argon to a stirred solution of polyanion in THF at <195 K on a vacuum line; after 30–60 min, the solution of polyradical polyanion is diluted several-fold with 2-MeTHF. Similarly, 1.5 equiv of I<sub>2</sub> was used to partially oxidize tetraanions in the attempted preparations of triradical anions. **Method 2:** solids 1<sup>1•2-</sup>, 1<sup>2•1-</sup>, 4<sup>2•1-</sup>, 8<sup>1•1-</sup>. In a glovebox, stoichiometric amounts

of triradicals (or diradicals) and trianions (or dianions) in THF were mixed, followed by evaporation of THF under vacuum, using a vacuum line in the glovebox, to give red or red-brown solids. ESR spectra for polyradical polyanions in 2-MeTHF are similar to those obtained by other methods. No disproportionation is detected for radical dianion 1<sup>1•2-</sup> in 2-MeTHF; however, diradical anions 1<sup>2•1-</sup> and 4<sup>2•1-</sup> in 2-MeTHF show partial disproportionation to the corresponding triradicals and radical dianions (ESR spectroscopy).

Characterization of diradical anions in the solid state was complicated by the unknown degree of disproportionation and possible dimerization (oligomerization) in the solid state. For example, magnetizations for radical dianion 1<sup>1•2-</sup> and radical anion 8<sup>1•1-</sup> at *T* = 2, 5, 10 K (*H* = 0–5.5 T) follow the expected *S* = 1/2 Brillouin function (*M* vs *H/T*) but the values of *M*<sub>sat</sub> are only about one-half of the theoretical values. **Method 3:** 1<sup>2•1-</sup>, 4<sup>2•1-</sup>, 8<sup>1•1-</sup> and **Method 4:** 1<sup>1•2-</sup>, 8<sup>1•1-</sup>. A solution of polyradical or polyether in 2-MeTHF (or THF) was stirred with Li, as described in ref 5; ESR spectra were recorded at time intervals, until the desired product was obtained. For selected runs, the sample was placed in a glovebox and diluted with THF (or 2-MeTHF) and UV–vis spectra were recorded.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We acknowledge partial support by the National Science Foundation (CHE-9203918). Mass spectral determinations were performed by the Midwest Center for Mass Spectrometry with partial support by the National Science Foundation, Biology Division (DIR-9017262). We thank M. Zhong and Dr. S. R. Desai for their help with the synthesis.

**Supporting Information Available:** Experimental details for the synthesis of 11-H-Br, 8-H-OMe, 1-(H)<sub>2</sub>-OMe, and 4-(OMe)<sub>3</sub>, as depicted in Scheme 3 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951523N