acid residue is present as its 2-deoxy-2-fluoroglucosyl ester since this would not extract well into the organic solvent. This sequence aligns perfectly with residues 355–361 of the previously published[20] sequence of *Agrobacterium* β-glucosidase, thus identifying glutamic acid residue 358 as the nucleophilic residue. Experiments are currently underway to further probe the function of this and nearby amino acid residues by mutagenesis analyses.

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A Polyarylmethyl Carbotetraanion

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π-Conjugated polyradicals such as meta-connected triarylmethyls have been proposed as candidates for ferromagnetic polymers (Figure 1).[1] Such molecules and polymers possess unique half-filled, multifold near-degenerate, nonbonding, and nondisjoint HOMOs.[2] These MO theory properties are associated with high-spin π-conjugated molecules.[2,3] Furthermore, calculations suggest uniform charge delocalization over the molecular fragments for such systems.[4] For typical π-conjugated systems such as polyenes and quinone-type structures, an excess of negative charge is localized in one part of the molecule.[5]

In the case of odd-alternant π-conjugated polyradicals, the related polyanions, which possess fully occupied HOMOs, should have similar electron distributions. Therefore, such diamagnetic polyanions can be used to probe the electron distribution in the corresponding polyradicals. We report preparation of the carbotetraanion $\mathbf{1}^{4-},\mathbf{4Li}^{+}$ and the reference carbodianion $\mathbf{2}^{2-},\mathbf{2Li}^{+}$ and carbanion $\mathbf{3}^{-},\mathbf{Li}^{+}$ (Figure 2). The synthesis of the precursor $\mathbf{1\text{-}(OEt)_4}$ for the tetraanion is outlined in Scheme I.[6]

The carbanions are generated from the ether precursors by using lithium metal in tetrahydrofuran-d_8 (THF-d_8).[7] Solutions of carbanions in THF-d_8, which also contain equivalent amounts of EtOLi, are examined by ^{1}H, ^{13}C, ^{13}C DEPT, and ^{7}Li NMR.[8] At a typical concentration of 0.04 M, there are less than 5% impurities and all spectral data corroborate the structures of carbanions.

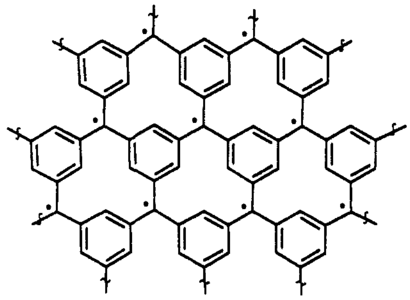

Figure 1.

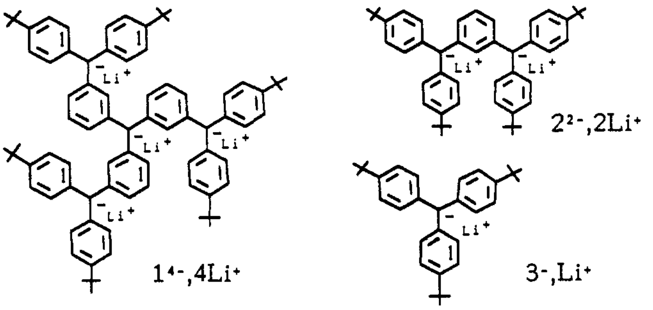

Figure 2. Carbanions $\mathbf{1}^{4-},\mathbf{4Li}^{+}$, $\mathbf{2}^{2-},\mathbf{2Li}^{+}$, and $\mathbf{3}^{-},\mathbf{Li}^{+}$.

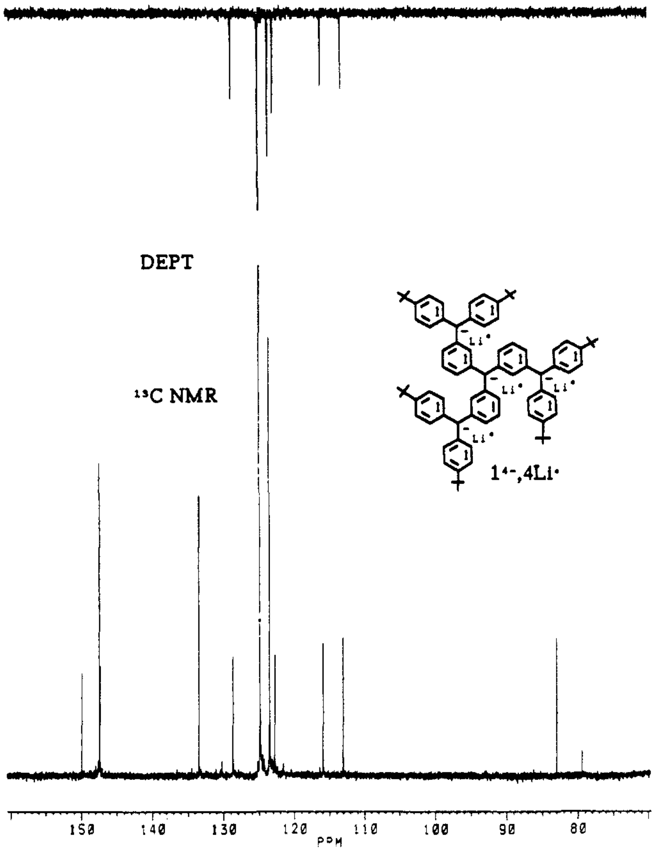

Figure 3. ^{13}C NMR spectra of $\mathbf{1}^{4-},\mathbf{4Li}^{+}$ in THF-d_8 at 303 K. The apparent single resonance at 147 ppm consists of two well-resolved resonances at 147.3 and 147.2 ppm.

Table I. Selected ^{13}C and ^{7}Li Chemical Shifts for Carbanions[a]

	peripheral[a]	central[a]	^{7}Li
$\mathbf{1}^{4-},\mathbf{4Li}^{+}$	82.9	79.3	−1.31
$\mathbf{2}^{2-},\mathbf{2Li}^{+}$	83.0		−1.08
$\mathbf{3}^{-},\mathbf{Li}^{+}$	87.2		−0.85

[a] The corresponding chemical shifts for $\mathbf{1\text{-}(OEt)_4}$ and $\mathbf{2\text{-}(OEt)_2}$ are 86.2–86.6 ppm and for $\mathbf{1\text{-}H_4}$ and $\mathbf{2\text{-}H_2}$ 56.0–56.5 ppm.

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[6] (a) For a comparable synthesis, see: Hellwinkel, D.; Stahl, H.; Gaa, H. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 794. (b) $\mathbf{1\text{-}(OEt)_4}$: FABMS, $M^+ - OEt + H = 1210$. Anal. Calcd for $C_{90}H_{110}O_4$: C, 86.08; H, 8.83. Found: C, 86.29; H, 8.74. (c) The synthesis of $\mathbf{2\text{-}(OEt)_2}$ required a simple modification in Scheme I; that is, dimethyl carbonate was replaced with 4,4′-di-*tert*-butylbenzophenone. **3-OEt** was similarly prepared by using (4-*tert*-butylphenyl)lithium; (d) **4-OEt**: Anal. Calcd for $C_{29}H_{35}BrO$: C, 72.64; H, 7.36. Found: C, 72.68; H, 7.18.

[7] Lithium (98+%, high in sodium, Aldrich) that was freshly cut under argon was used.

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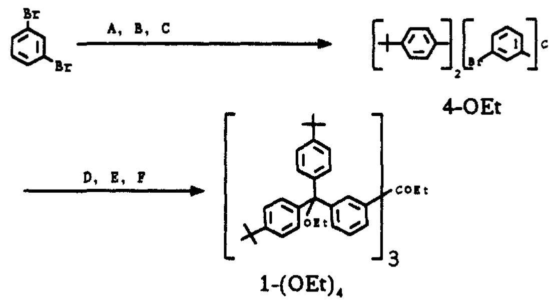
Scheme I. Synthesis of $\mathbf{1\text{-}(OEt)_4}$^{a}



^{a}(A) *n*-BuLi, ether, −30 °C 10 min; (B) 4,4′-di-*tert*-butylbenzophenone; (C) EtOCOCl; (D) *n*-BuLi, ether, −25 °C, 3 h; (E) $(MeO)_2CO$; (F) EtOCOCl.

When the solutions of the tetraanion and dianion are quenched with MeOH and MeOD in the absence of lithium metal, the quenching products $\mathbf{1\text{-}H_4}$, $\mathbf{1\text{-}D_4}$, $\mathbf{2\text{-}H_2}$, and $\mathbf{2\text{-}D_2}$ are isolated in high chemical yields. The deuterated products have >90% D incorporation according to FABMS and NMR.

The ^{1}H and ^{13}C NMR spectra of $\mathbf{1^{4-},4Li^{+}}$ show a single resonance for the six equivalent *t*-Bu groups. In the aromatic region of the ^{13}C NMR spectrum, separate signals for four quaternary and six tertiary carbon resonances are observed (Figure 3). The aromatic region of the ^{1}H NMR spectrum of $\mathbf{1^{4-},4Li^{+}}$ shows two doublets for the six peripheral benzene rings and a triplet, two doublets, and a singlet absorption set for the three inner benzene rings. Thus, the equivalence of the six peripheral benzene rings and of the three inner benzene rings is established at 303 K. Consequently, $\mathbf{1^{4-},4Li^{+}}$ in THF-d_8 has 3-fold symmetry on the ^{1}H and ^{13}C NMR time scale at 303 K. Similar spectral analyses indicate 2-fold symmetry for $\mathbf{2^{2-},2Li^{+}}$ under identical conditions.

As expected, only one resonance is observed at 303 K for the Li^+ counterions associated with each carbanion; the ^{7}Li resonance is shifted upfield for the larger carbanions, $\mathbf{1^{4-},4Li^{+}}$ and $\mathbf{2^{2-},2Li^{+}}$ (Table I).[9]

Empirical relationships between ^{13}C chemical shifts and charge can be used to verify the molecular charges.[10] Charges for carbanions, which are calculated from the ^{13}C chemical shifts, are −3.48, −1.82, and −1.07 for $\mathbf{1^{4-},4Li^{+}}$, $\mathbf{2^{2-},2Li^{+}}$, and $\mathbf{3^{-},Li^{+}}$, respectively. The significant deviations from the integer values for the higher anions may be due to deshielding of the inner benzene ring carbons.

$\mathbf{1^{4-}}$ possesses one central and three peripheral triarylmethyl (anionic) carbons; the chemical shift difference between the peripheral and central carbons in tetraanion is only 3.6 ppm (Table I). Although the ^{13}C chemical shifts for the triarylmethyl (anionic) carbons appear more upfield for the monoanion than for the dianion and the tetraanion, the chemical shifts for these peripheral carbons level off at about 83 ppm. Because of the linear relationship between ^{13}C chemical shift and charge,[10] we conclude that extending the conjugation in meta-connected triarylmethyl anions does not perturb the electron density significantly in the separate triarylmethyl anion units. That is, $\mathbf{1^{4-},4Li^{+}}$ is an ensemble of four uniformly charged triarylmethyl anion fragments. Because these π-conjugated systems are odd-alternant, a similar conclusion is reached for both electron and spin density of the related radicals.

In summary, molecules that are topologically related to $\mathbf{1^{4-}}$ can be considered as ensembles of uniformly charged fragments.

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(8) Downfield resonance from THF-d_8 was used as a 0.0 ppm reference for ^{1}H (3.580 ppm) and ^{13}C (67.5 ppm) spectra. A 1.0 M solution of LiCl in D_2O at 303 K was used as a 0.0 ppm reference for ^{7}Li and ^{6}Li NMR spectra. *J* values are in hertz. (a) $\mathbf{1^{4-},4Li^{+}}$: ^{1}H NMR 7.225 (d, $J = 8.8$, 12 H), 7.21 (br s, 3 H), 6.574 (d, $J = 8.8$, 12 H), 6.455 (t, $J = 7.7$, 3 H), 6.38 (br d, $J = 8$, 3 H), 6.25 (br d, $J = 8$, 3 H), 1.183 (s, 54 H); ^{1}H COSY (cross peaks) 7.225/6.574, 7.21/6.38/6.25, 6.455/6.38/6.25 [EtOLi, 3.734 (br q, 8 H), CH_3 is overlapped by the tetraanion *t*-Bu]; ^{13}C NMR 149.8, 147.3, 147.2, 133.4, 128.6, 124.8, 123.4, 122.6, 115.8, 113.0, 82.9, 79.3, 34.2, 32.4 [EtOLi, 59.5 (w), 59.2, 23.5 (w), 23.4]; ^{13}C DEPT (135°) CH, CH_3, 128.5, 124.7, 123.3, 122.6, 115.8, 112.9, 32.3 [EtOLi, CH_2, 59.4, 59.1; CH_3, 23.3]; ^{7}Li NMR −1.31 [EtOLi, 0.12]. (b) $\mathbf{2^{2-},2Li^{+}}$: ^{1}H NMR 7.265 (d, $J = 8$, 9 H), 6.593 (d, $J = 8$, 8 H), 6.494 (d, $J = 8$, 2 H), 6.290 (t, $J = 8$, 1 H), 1.178 (s, 36 H) [EtOLi, 3.730 (q, $J = 7$, 4 H), 1.149 (t, $J = 7$, 6 H)]; ^{13}C NMR 149.0, 147.6, 133.5, 130.2, 128.3, 124.7, 123.4, 116.2, 83.0, 34.2, 32.4 [EtOLi, 59.6 (vw), 59.4 (w), 59.2, 23.3 (not resolved)]; ^{13}C DEPT (135°) CH, CH_3, 130.1, 128.3, 124.7, 123.4, 116.2, 32.4 [EtOLi, CH_2, 59.2; CH_3, 23.3]; ^{7}Li NMR −1.08 [EtOLi, 0.09, 0.75 (w)]. (c) $\mathbf{3^{-},Li^{+}}$: ^{1}H NMR 7.240 (d, $J = 9$, 6 H), 6.564 (d, $J = 9$, 6 H), 1.177 (s, 27 H) [EtOLi, 3.75–3.65 (m, 2 H), CH_3 (3 H) is hidden under the *t*-Bu resonance]; ^{13}C NMR 147.7, 134.2, 124.7, 123.6, 87.2, 34.2, 32.3 [EtOLi, 59.7 (vw), 59.4 (w), 59.1, 23.4 (w), 23.3]; ^{13}C DEPT (135°) CH, CH_3, 124.7, 123.6, 32.3 [EtOLi, CH_2, 59.4 (w), 59.1; CH_3, 23.4 (w), 23.3]; ^{7}Li NMR −0.85 [EtOLi, 0.07, 0.10, 0.75 (br, w)]; ^{6}Li NMR −0.86 [EtOLi, 0.10].

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A Polyarylmethyl Quintet Tetraradical

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Ferromagnetism without transition metals is a contemporary challenge for chemistry and physics.[1-4] Ferromagnetic polymers comprise one of the postulated routes toward this goal;[5] a similar strategy may rely on molecules approaching the size of ferromagnetic domains. Thus, high-spin, large, and stable organic molecules may be prerequisites.[6] The first molecular ferromagnets and ferrimagnets have been reported recently.[1,7]

Now we report preparation of the hydrocarbon tetraradical $\mathbf{1^{4\bullet}}$ by oxidation of the related carbotetraanion $\mathbf{1^{4-},4Li^{+}}$ (eq 1).[8]

Treatment of a 0.05 M solution of $\mathbf{1^{4-},4Li^{+}}$ in tetrahydrofuran (THF) that contains an equivalent amount of EtOLi byproduct with 2 molar equiv of iodine at 195 K for 0.5 h produces a solution of $\mathbf{1^{4\bullet}}$. The $\Delta m_s = 1$ region of the EPR spectrum at 100 K for the same sample of $\mathbf{1^{4\bullet}}$ consists of eight symmetrical peaks, which

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