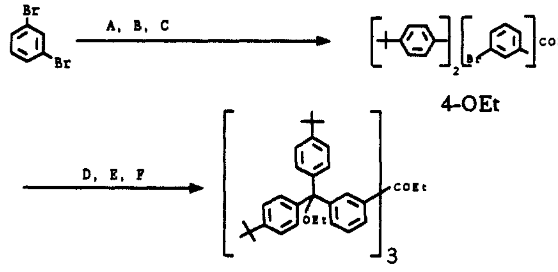
5890 *J. Am. Chem. Soc.* **1990**, *112*, 5890-5892

Scheme I. Synthesis of $\mathbf{1}$-(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)$_2$CO; (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 $\mathbf{1}$-$\mathbf{H_4}$, $\mathbf{1}$-$\mathbf{D_4}$, $\mathbf{2}$-$\mathbf{H_2}$, and $\mathbf{2}$-$\mathbf{D_2}$ 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 $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$ 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 $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$ 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, $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$ 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 $\mathbf{2}^{2-}$,$\mathbf{2Li}^+$ 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, $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$ and $\mathbf{2}^{2-}$,$\mathbf{2Li}^+$ (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 $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$, $\mathbf{2}^{2-}$,$\mathbf{2Li}^+$, and $\mathbf{3}^{-}$,$\mathbf{Li}^+$, 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, $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$ 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$_2$O 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) $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$: ^{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) $\mathbf{2}^{2-}$,$\mathbf{2Li}^+$: ^{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) $\mathbf{3}^{-}$,$\mathbf{Li}^+$: ^{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 $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$ (eq 1).[8]

Treatment of a 0.05 M solution of $\mathbf{1}^{4-}$,$\mathbf{4Li}^+$ 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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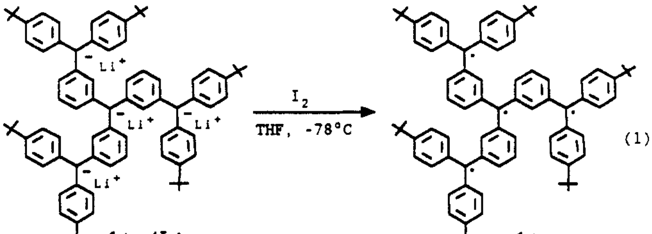


(1)

$1^{4-},4Li^+$ $1^{4\cdot}$

are assigned to a quintet (Figure 1); the center peak corresponds to a doublet impurity.[9] A half-field $\Delta m_s = 2$ resonance is also observed that further corroborates the presence of a high-spin species (Figure 1).[10]

Fitting of the four outer peaks in the quintet $\Delta m_s = 1$ spectrum to the perturbational solution of the quintet Hamiltonian yields the following approximate zero-field parameters: $|D/hc| = 0.00283$ cm^{-1} and $|E/hc| = 0.000022$ cm^{-1}.[11] When these values for the zero-field parameters are used as input to a quintet simulation program,[12] the peak positions (not intensities) in the $\Delta m_s = 1$ EPR spectrum for $1^{4\cdot}$ are reproduced to within 3 G. In particular, because of the very low value for the $|E/hc|$, the $H//x,y$ transitions are found coincident in pairs to within 3 G. Even better agreement with the experimental spectrum (within 2 G) is obtained with $|D/hc| = 0.00283$ cm^{-1} and $|E/hc| = 0$ (Figure 1). Such small values for $|E/hc|$ suggest *3-fold symmetry* for $1^{4\cdot}$. The $|D/hc|$ is below the values for the related triplet diradicals $2^{2\cdot}$ (0.0064 cm^{-1}) and $3^{2\cdot}$ (0.0079 cm^{-1}) (Figure 2).[13,14]

When the oxidation is carried out at a lower temperature such as 160 K and in Me_2O, the EPR spectra, which are taken at boiling liquid nitrogen temperature and 100 K, are similar to the spectrum in Figure 1. For such solutions the NMR measurement of the magnetic moment $\mu_{eff} = 4.3\ \mu_B$,[15] which is close to the theoretical spin-only value of 4.90 μ_B, is obtained in the range 133–163 K.

A typical low-temperature oxidation experiment is carried out as follows. A solution of tetraanion $1^{4-},4Li^+$ in THF that contains an equivalent amount of EtOLi byproduct is filtered, the THF is removed under vacuum, and the solid residue is dissolved in Me_2O (1 mL) at 160 K (EtOH/liquid nitrogen slush). The volume of the resulting red solution, which is 0.01–0.04 M in $1^{4-},4Li^+$, is measured at 160 K. A crystal of iodine (2 equiv) is added under the stream of argon, and after 10–30 min of vigorous stirring at 160 K, the reaction mixture becomes green. Subsequently, a portion of the reaction mixture is transferred at 160 K to an EPR tube. The tube is sealed under vacuum (all portions of the reaction mixture are kept at 160 K). For the NMR measurement, the sealed EPR tube (3.8-mm o.d.) is cleaned with Me_2O and mounted concentrically in a 5-mm NMR tube containing Me_2O. The tube assembly is cooled with liquid nitrogen and then quickly inserted into the NMR probe at 143 K. ^1H NMR spectra, which are acquired in the range 133–163 K, have two resonances corresponding to Me_2O in the inner (paramagnetic solution) and outer tube (pure Me_2O). The downfield resonance, which is more intense and broader, must arise from Me_2O in the paramagnetic solution (inner tube). For example, for a $1^{4\cdot}$ concentration of 0.024 M, the chemical shift difference ($\Delta\delta$) between the two resonances is 1.31 ppm at 143 K.

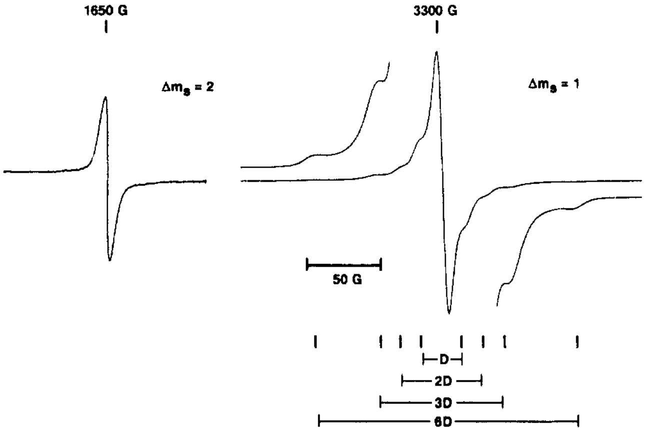
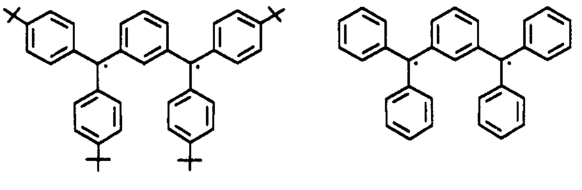


Figure 1. X-band EPR spectrum for $1^{4\cdot}$ in THF glass at 100 K; $\Delta m_s = 1$ transitions (Gauss): 3211, 3255, 3271, 3286, 3317, 3332, 3348, 3393 (the exact magnetic field values are obtained from a derivative spectrum). The bars indicate the simulated positions for the $\Delta m_s = 1$ turning points using $g = 2.0024$, microwave frequency 9.250 GHz, $|D/hc| = 0.00283$ cm^{-1}, and $|E/hc| = 0$ cm^{-1}: 3209 (z), 3255 (x, y), 3270 (z), 3285 (x, y), 3315 (x, y), 3331 (z), 3346 (x, y), 3391 (z). According to the numerical simulations, for $|E/hc| = 0$ cm^{-1} and $|D/hc| < 0.02$ cm^{-1} the line spacings can be expressed in terms of "D" as shown in the Figure. $\Delta m_s = 2$ transition (Gauss): 1652.



$2^{2\cdot}$ $3^{2\cdot}$

Figure 2. Diradicals $2^{2\cdot}$ and $3^{2\cdot}$.

Magnetic susceptibilities, which are used for calculation of μ_{eff}, are obtained by using Evans's formula with correction for the parallel orientation of the sample tube to the magnetic field.[15] The concentration of the paramagnetic species, the temperature, and $\Delta\delta$ enter the calculation. $\Delta\delta$ is corrected for the presence of the salts (LiI and EtOLi) by measuring $\Delta\delta$ after the sample is exposed to air; for example, for the 0.024 M solution at 143 K, the $\Delta\delta$ increases from 1.31 to 1.43 ppm after the correction. The temperature measurement should not significantly contribute to the error in μ_{eff}.[16] The inaccurate concentration of $1^{4\cdot}$ is probably the major source of error: (a) the filtration of $1^{4-},4Li^+$ in THF is not complete; (b) $1^{4-},4Li^+$ in THF is not pure (95+%), and the solvent change from THF to Me_2O may further deteriorate the purity; (c) thus, the amount of iodine, which is used for the calculation of the concentration of $1^{4\cdot}$, is not stoichiometric; (d) the volume measurement at 160 K is accurate to about ±0.05 mL (±5%); (e) the solution volume is equated to the solvent volume; and (f) the temperature dependence of the density of Me_2O is neglected in the range 133–163 K. The lack of stoichiometry (a, b, and c) is most likely to give a lower than expected μ_{eff}. Also, the concentration of $1^{4\cdot}$ should be kept low (e.g., 0.024, 0.015 M) to avoid precipitation at low temperatures and excessive NMR line broadening.

The EPR spectra and μ_{eff} measurements support the presence of a quintet $1^{4\cdot}$ as a *dominant* species at $T > 77$ K.[17]

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(9) (a) Only a fraction of the quintet tetraradical contributes to its signal intensity in a randomly oriented glass sample. (b) After the solution of $1^{4\cdot}$ is kept at ambient temperature for 1 h, the EPR spectrum at 100 K suggests a mixture of unidentified doublet and triplet species. Only the inner triplet resonances appear close to the quintet peaks.

(10) The instrument settings such as gain, modulation amplitude, and microwave power for the $\Delta m_s = 2$ transition are increased by a factor of 25, 40, and 16, respectively, compared to the settings for the $\Delta m_s = 1$ region.

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(17) The Curie plot is linear for both the EPR intensities in the range 90–120 K and the paramagnetic susceptibilities obtained from the NMR data in the range 140–160 K. These temperature ranges may not allow us to draw conclusions upon the nature of the ground state for $1^{4\cdot}$.

Our results show that oxidation of carbomultianions offers a valuable method for preparation and characterization of hydrocarbon multiradicals in solution. Even greater in size and higher spin multiplicity hydrocarbon multiradicals can be made more stable by introducing steric hindrance at all para sites. It remains to be seen if such ferromagnetic *microdomains* will lead to ferromagnetic order at $T \gg 4$ K.

Finally, the quintet state for $\mathbf{1}^{4\bullet}$ in conjunction with the uniformly charged triarylmethyl anion fragments in $\mathbf{1}^{4-},4Li^{+}$ suggests a relationship between spin multiplicity and electron density distribution.

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The Elusive Methyleneoxirane: Preparation and Characterization by Flash-Vacuum Pyrolysis and Neutralization-Reionization Mass Spectrometry

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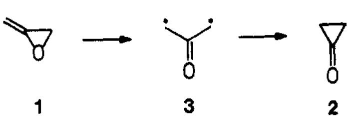
Typifying the interesting chemistry of strained small-ring compounds, e.g., methylenecyclopropane,[1] -cyclopropene,[2] -aziridine,[3] and -thiirane,[4] methyleneoxirane (allene oxide, **1**) was predicted by Hoffmann[5] to isomerize readily to cyclopropanone (**2**) via electrocyclic ring opening involving oxyallyl intermediate **3** (eq 1). While **1** has been studied intensively by theory,[6] it has



(1)

been elusive in experimental investigations, such as its role in the oxidation of allene[7] (although bulky substituents can make eq 1 observable).[8] Here we report on the first preparation and characterization of $\mathbf{1}^{\bullet+}$ and **1**.

Table I. Collisionally Activated Dissociation (O_2, 50% T^a) and $^{+}NR^{+}$ (Hg, 70% T/O_2, 50% T) Mass Spectra[b,c]

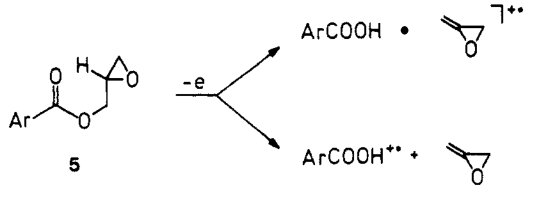
	CAD				$^{+}NR^{+}$			
m/z	$\mathbf{1}^{\bullet+}$	$\mathbf{6}^{\bullet+}$	$\mathbf{7}^{\bullet+}$	$\mathbf{8}^{\bullet+}$	$\mathbf{1}^{\bullet+}$	$\mathbf{6}^{\bullet+}$	$\mathbf{7}^{\bullet+}$	$\mathbf{8}^{\bullet+}$
56					69	100	3	63
55	(11)	(22)	(20)	(233)	3.5	7.5	0.8	100
54	15	12	3	18	4	3	0.2	13
53	15	14	11	15	11	3.5	0.3	12
42	100	3	24	<0.5	22	0.5	4.5	1
41	17	24	11	4	8	8	2.5	6.5
39	22	5.5	4	9.5	5.5	2.5	1.5	15
30	11	<0.5	<0.5	<0.5	5.5	<0.5	<0.5	1.5
29	40	5.5	6	44	23	3	<0.5	57
28	(122)	(87)	(181)	(76)	100	40	100	79
27	69	100	100	100	44	32	24	90
15	<0.5	1.5	<0.5	<0.5	<0.5	0.8	0.6	0.5
14	6.5	2	3.5	1.5	8	1	3	7
$\sum_{\text{ions}}$	560	455	500	625	420	275	235	635

[a] Transmittance. [b] Integrated peak areas. Intensities in parentheses include dissociations of metastable ions. [c] From ionization of the following: $\mathbf{6}^{\bullet+}$, 2,2,5-trimethyl-1,3-dioxane-4,6-dione; $\mathbf{7}^{\bullet+}$, succinnic anhydride; and $\mathbf{8}^{\bullet+}$, acrolein.

In unsuccessful attempts to generate $\mathbf{1}^{\bullet+}$, ionized spiro[norborn-2-ene-5,2'-oxirane][9] (**4**), 1-(phenylsulfinyl)-2,3-epoxypropane, and 5,6-epoxyhexan-2-one[10] yield only $C_5H_6^{\bullet+}$, $PhSOH^{\bullet+}$, and $CH_3C(OH){=}CH_2^{\bullet+}$, respectively. However, the γ-hydrogen

4

rearrangement (eq 2) of ionized glycidol benzoates (**5**) produces $C_3H_4O^{\bullet+}$ (17% abundance for Ar = 4-$NO_2C_6H_4$); its collisionally activated dissociation (CAD) spectrum[11] is strikingly different from those of the isomers $CH_3CH{=}C{=}O^{\bullet+}$ (**6**),[12] $^{\bullet}CH_2CH_2CO^{+}$ (**7**),[13] and $CH_2{=}CHCH{=}O^{\bullet+}$ (**8**)[13] (Table I). Structure $\mathbf{1}^{\bullet+}$



(2)

is supported by the favored formation of its structural subunits $C_2H_2O^{\bullet+}$ (m/z 42), $CH_2O^{\bullet+}$ (m/z 30), and $CH_2^{\bullet+}$ (m/z 14). Its isomerization to $CH_2{=}C^{+}OCH_2^{\bullet}$ should be quite endothermic,[14]

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