15 min the mixture was concentrated under vacuum at 0 °C and the residue dissolved in 4 mL of dry methanol. Addition of 0.105 g (2.78 mmol) of sodium borohydride, at room temperature, resulted in decolorization. The mixture was partitioned between 20 mL of 10% ammonium hydroxide in saturated brine and 3 × 50 mL of dichloromethane. The extracts were concentrated under vacuum and the residue was subjected to centrifugal chromatography on a 1-mm silica gel plate. Elution with 10% methanol in dichloromethane provided the product, which was purified by preparative HPLC on silica gel, eluting with 10% methanol in dichloromethane, to give 3.7 mg (3.6%) of vinblastine, which matched (MS, HPLC, and TLC) authentic natural and synthetic samples.[18]

Method B.[25] To 0.100 g (0.126 mmol) of the enamine **37** in 100 mL of dry methanol was added, in one portion, 0.0409 g (0.252 mmol) of ferric chloride. The solution was cooled to 0 °C and, with stirring, air was bubbled through for 1 h and then 0.105 g (1.26 mmol) of sodium borohydride was added. The reaction mixture was then worked up as in method A to provide 0.0318 g (31%) of purified vinblastine (**13**).

Acknowledgment. This work was supported by the Cancer Institute of the National Institutes of Health by Grant R01 CA12010. Vindoline was generously supplied by Dr. A. J. Hannart of Omnichem. We are indebted to Dr. L. J. Sears of Montana State University for high-resolution mass spectra and to Scott Cowen and Rodney Parsons of our group for low-resolution mass spectra. A copy of the MACROMODEL computer program was generously given by Dr. Clark Still of Columbia University. We are indebted to Tim Wilson for repeating the reduction experiments with the enamine **22** for clarification of data.

Supplementary Material Available: Compound characterization data (including full IR and EIMS data) and a ^{13}C NMR spectrum for each new compound (43 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

π-Conjugated Systems with Unique Electronic Structure: A Case of "Planarized" 1,3-Connected Polyarylmethyl Carbodianion and Stable Triplet Hydrocarbon Diradical

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The effect of "planarization" on π-conjugated 1,3-connected polyarylmethyls in connection with the electronic structure and magnetic properties is examined. The synthesis, ESR and UV–vis spectroscopy, voltammetry, and magnetic studies of triplet diradical $6^{2\bullet}$ are reported. The corresponding dianion 6^{2-}, $2M^+$ (M = Li, K) is studied using NMR and UV–vis spectroscopy.

Introduction

The understanding of the electronic structure associated with the high spin molecules is related to the problem of magnetism.[1,2] Polyradicals, polycarbenes, and polynitrenes based upon 1,3-connected polyarylmethyl (methylene) π-conjugated systems are promising candidates for very high spin organic molecules.[3-5] For example, pentacarbene **1** (Chart I) is the highest spin, $S = 5$, organic molecule and tetraradical **2** is one of the highest spin, $S = 2$, polyradicals.[3d,4a] Polyanions and radical anions related to **2**, e.g., 1,3-connected polyarylmethyl decaanion **3** and radical anion **4**, possess an unusual uniform charge density distribution and localized spin density, respectively.[6] Such π-conjugated systems have been considered as ensembles of weakly coupled arylmethyl units via 1,3-phenylene bridges. In the related work, 1,3-connected polyarylmethyl diradical **5b** has been found to interact ferromagnetically in the solid state.[7] Because of the steric interactions, the above 1,3-connected polyarylmethyls are forced to be nonplanar. Out-of-plane twisting would hamper π-conjugation and might contribute to the weakness of the interactions between the arylmethyl units and influence magnetic interactions.

In order to examine if the unusual properties represented by decaanion **3** and diradicals **5a–c** are intrinsic to their electronic structure or caused by the out-of-plane twisting, we prepare a model system where the out-of-plane

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(6) (a) Utamapanya, S.; Rajca, A. *J. Am. Chem. Soc.* **1991**, *113*, 9242. Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5889. (b) Rajca, A. *J. Org. Chem.* **1991**, *56*, 2557.

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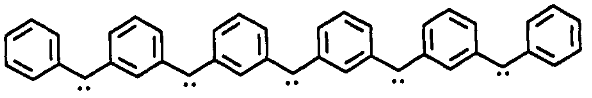
Chart I



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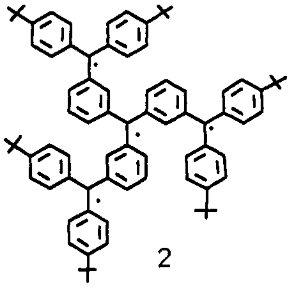

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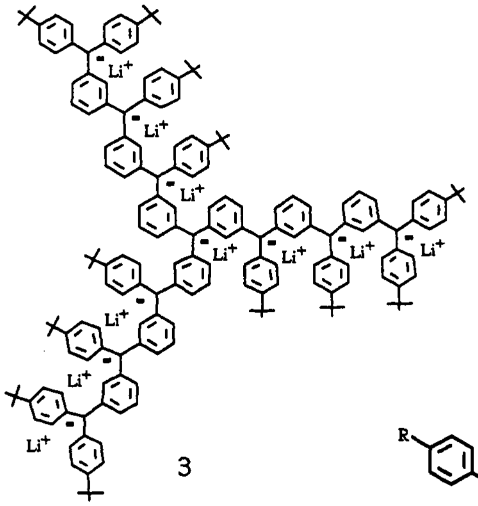

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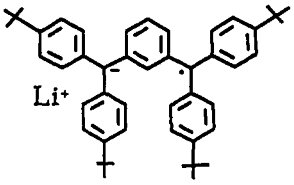

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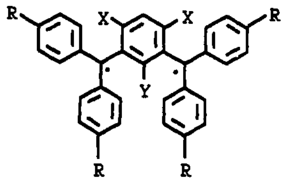
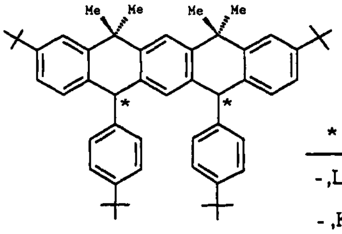


	X	Y	R
5a	Me	H	t-Bu
5b	i-Pr	H	t-Bu
5c	Me	Me	t-Bu
5d	H	H	H

twisting is restricted. For example, diradical $6^{2\cdot}$ can be considered as a "planarized" version of diradical **5b** or Schlenk hydrocarbon **5d**.[8]



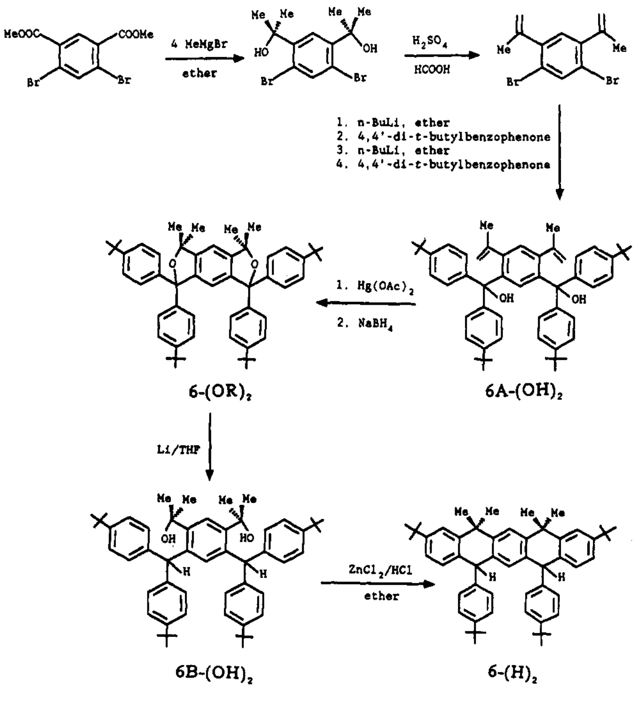
*	
-,Li⁺	6^{2-},2Li⁺
-,K⁺	6^{2-},2K⁺
·	$6^{2\cdot}$

We describe the synthesis and characterization of diradical $6^{2\cdot}$ (ESR, UV–vis, voltammetry, SQUID) and dianions 6^{2-},2Li⁺ and 6^{2-},2K⁺ (NMR, UV–vis).

Results and Discussion

Synthesis of the Hydrocarbon Precursor. Treatment of 4,6-dibromoisophthalate with 4 equiv of MeMgBr

Scheme I



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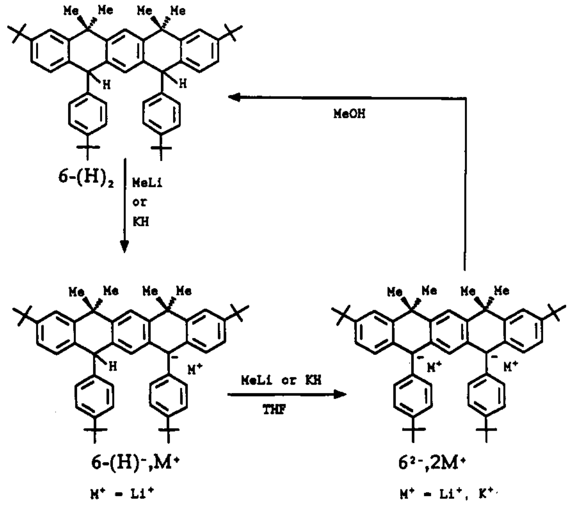
Scheme II



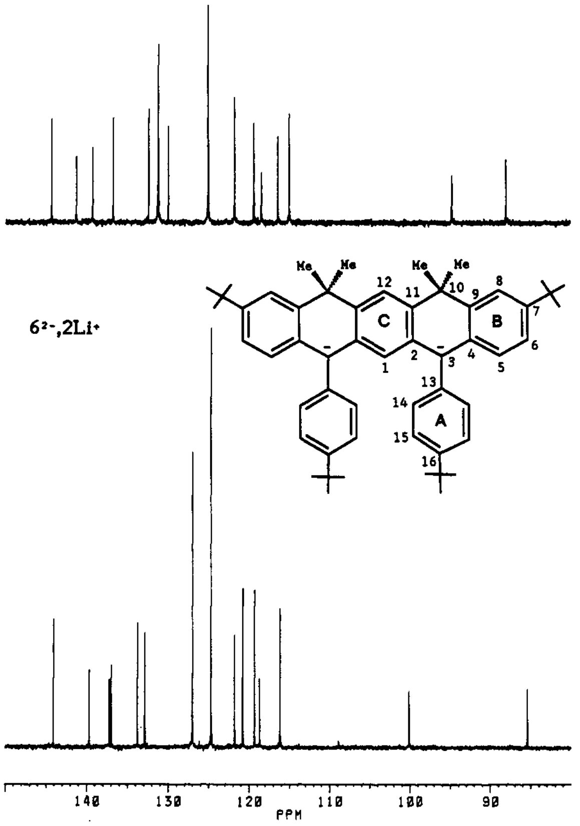


Figure 1. Partial ^{13}C NMR spectra for 6^{2-},2Li^+ and 6^{2-},2K^+ in THF-d_8.

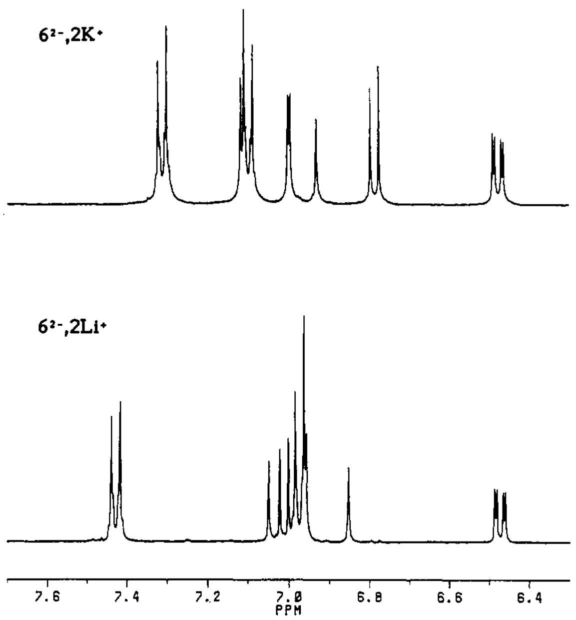


Figure 2. Partial ^1H NMR spectra for 6^{2-},2Li^+ and 6^{2-},2K^+ in THF-d_8.

Table I. 2D NMR Spectral Assignments of Cross Peaks for Aromatic Regions of ^1H and ^{13}C NMR Spectra for Dianions

assignment	6^{2-},2Li^+ cross peak	6^{2-},2K^+ cross peak
	2D ^1H–^1H COSY	
H15/H14[g]	7.428/6.972	
H1/none	7.048	
H5/H6	7.010/6.474[a]	
H8/H6	6.959/6.474	
H12/none	6.851[b]	
	2D ^1H–^{13}C HETCOR	
C15/H15[g]	126.97/7.428	125.02/7.099
C14/H14[g]	124.65/6.972	131.19/7.312
C6/H6	120.73/6.474	121.74/6.477
C8/H8	119.25/6.959	119.36/6.998
C12/H12	118.64/6.851	118.42/6.931
C5/H5	116.12/7.010	114.96/6.786
C1/H1	100.04/7.048	94.72/7.118
	Long Range 2D ^1H–^{13}C HETCOR (Only Quaternary Carbons Are Shown)	
C13/H15	144.04/7.428	144.26/7.099
C4/H8	139.65/6.959[b]	139.22/6.988
C16/*t*-Bu/H14	137.21/1.298/6.972[c]	141.23/1.334/7.312
C2	136.95[c]	136.70/6.931[d]
C9/br-Me	133.74/1.364	129.94/1.385
C7/*t*-Bu	132.86/1.213	132.37/1.212
C11/H1	121.75/7.0478	116.39/7.118[e]
C3/H1	85.39/7.048	88.00[f]

[a] Low intensity H5/H8 cross peak is also observed. [b] 1,2-CH cross peak, C4/H5, 139.65/7.010, is also observed. [c] C16, 137.21 ppm and C2, 136.95 ppm are indistinguishable because of insufficient digital resolution. [d] C2/H12 cross peak. [e] 1,3-CH cross peak, C11/br-Me, 116.39/1.385, is also observed. [f] No cross peak is observed. [g] H14 vs H15 and C14 vs C15 assignments are tentative.

is followed by dehydration of the intermediate diol under acidic conditions to give 4,6-dibromo-1,3-diisopropenylbenzene (Scheme I). Subsequently, the sequence of Br/Li exchange using n-BuLi and addition of the resultant aryllithium compound to 4,4′-di-*tert*-butylbenzophenone are applied twice in a one-pot preparation giving diol **6A**-$(OH)_2$. Reductions of diol **6A**-$(OH)_2$ to **6A**-$(H)_2$ have failed. An alternative route to **6**-$(H)_2$ via **6B**-$(OH)_2$ is based upon reductive transposition of hydroxyl groups in **6A**-$(OH)_2$. Oxymercuration–demercuration reaction produces diether **6**-$(OR)_2$, which upon reductive C–O bond cleavage using lithium metal gives diol **6B**-$(OH)_2$.[9] Friedel–Crafts cyclization of **6B**-$(OH)_2$ in $ZnCl_2$/HCl/ether affords hydrocarbon **6**-$(H)_2$ as, approximately, a 1:1 ratio of diastereomers (Scheme I).[10]

Carbodianion. Treatment of single diastereomer **6**-$(H)_2$ with either KH or MeLi in tetrahydrofuran-d_8 (THF-d_8) produces the corresponding carbodianions 6^{2-},2K^+ or 6^{2-},2Li^+. In the reaction of **6**-$(H)_2$ with MeLi, monoanion **6**-$(H)^-$,Li^+ is detected as an intermediate. Quenching the

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[9] Oxymercuration–demercuration reaction: Brown, H. C.; Lynch, G. J. *J. Org. Chem.* **1981**, *46*, 531.

[10] Bridged triarylmethanes from Friedel/Crafts reaction using $ZnCl_2$/HCl/ether: Hellwinkel, D.; Aulmich, G.; Melan, M. *Chem. Ber.* **1981**, *114*, 86. Hellwinkel, D.; Aulmich, G.; Warth, W. *Chem. Ber.* **1980**, *113*, 3275.

solution of dianion with MeOH gives a mixture of two diastereomers 6-$(H)_2$ (Scheme II).

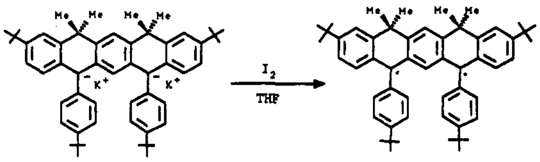
Solutions of carbodianions 6^{2-},$2Li^+$ and 6^{2-},$2K^+$ in THF-d_8 are examined by ^1H and ^{13}C NMR spectroscopy (Figures 1 and 2).[11] All proton and carbon resonances are assigned by ^1H–^1H COSY, ^1H–^{13}C HETCOR for one-bond and long-range couplings, and ^{13}C DEPT experiments (Table I).

The analysis of the NMR data is straightforward and we will only comment on its relationship to the molecular geometry for the dianion. The number of NMR resonances and their assignments indicate that on the NMR time scale, a C_{2v} symmetric structure for 6^{2-} and fast rotation of 4-*tert*-butylphenyl groups are observed. In particular, in ^1H and ^{13}C NMR spectra only one resonance corresponding to the methyl groups in the bridge is observed, e.g., for 6^{2-},$2K^+$, $\delta(^1H)$ 1.37 and $\delta(^{13}C)$ 28.6 at 303 K. Except for chemical shift changes, the NMR spectra are similar at lower temperatures; the number of resonances does not change except for spectral overlapping and only one resonance for the bridge methyl group is obtained at the lowest temperatures used, 153 K for ^1H and 168 K for ^{13}C.

Examination of Dreiding models for dianion 6^{2-} by selecting the "anionic" carbons, C3, as sp^2-hybridized reveals that two six-membered rings bearing the dimethylmethylene bridges are presumably in the boat conformations. Theoretically, two conformations for 6^{2-} are possible, i.e., two boats can be in either "parallel" (C_s) or "antiparallel" (C_2) orientations. Each conformation has two magnetically nonequivalent methyl groups in the bridges. The observation of a single NMR resonance for the bridge methyl groups may be explained by one of the following: (1) fast on the NMR time scale exchange between two C_s or two C_2 conformations or (2) a "planar" conformation (flattened boat with local C_{2v} symmetry).

^{13}C chemical shifts for para carbons in arylmethyl carbanions can be used to measure negative charge delocalization to the benzene ring.[12] In dianion 6^{2-}, quaternary carbons C7 and C16, which are expected to be minimally affected by the proximity of counterions, are particularly well suited as reporters of the negative charge distribution. In 6^{2-},$2K^+$, the ^{13}C chemical shifts for C7 (rings "A") a C16 (rings "B") are at 132.4 and 141.2 ppm, respectively; long-range HETCOR correlations with the *t*-Bu protons (1.21 and 1.34 ppm) and crosspeak C16/H14 support this assignment (Table I). Similar analysis for 6^{2-},$2Li^+$ is more difficult because of insufficient digital resolution for long-range HETCOR; the relevant ^{13}C chemical shift assignments are C16, 137.0 or 137.2 ppm and C7, 132.9 ppm (Table I). In the related alkyl-substituted, sterically-hindered nonplanar dianions without the bridges, the ^{13}C chemical shifts for the corresponding carbons are more upfield.[7] Using these ^{13}C NMR data, the following conclusions about the charge delocalization can be made: (1) more negative charge is delocalized to rings B compared to rings A and (2) the overall charge delocalization into the rings A and B is less than that for similar dianions without dimethylmethylene (DMM) bridges.[7] The relative amount of charge delocalization can be related to the degree of coplanarity in the π-conjugated carbanions. The DMM bridges constrain rings B, ring C, and the triarylmethyl "anionic" carbons to be approximately coplanar. Therefore, conclusion (1) is straightforward and in (2) ring C prevails in the competition for negative charge over rings B because two "anionic" carbons are adjacent to ring C as opposed to one "anionic" carbon for each ring B. Concentration of negative charge in the ring C is also confirmed by upfield shifts for carbons that are ortho and para in relation to the "anionic" carbons, i.e., C1 at 100.0 ppm and C11 at 121.8 ppm for 6^{2-},$2Li^+$. C1 and C11 are even more upfield (by about 5 ppm) for 6^{2-},$2K^+$ compared to 6^{2-},$2Li^+$.

Scheme III



6^{2-},$2K^+$

$6^{2\cdot}$

UV–vis spectra for carbodianion 6^{2-},$2Li^+$ in THF have broad bands with λ_{max} = 463 nm that are similar to the related "nonplanarized" 1,3-connected polyarylmethyl carbodianions.[6a,7]

The reaction of 6-$(H)_2$ with MeLi in THF-d_8 is followed with NMR spectroscopy. Both ^1H and ^{13}C NMR spectra of the monoanion 6-$(H)^-$,Li^+ (in the presence of dianion) are obtained at the intermediate stage of the reaction. Further reaction progress gives clean NMR spectra of dianion 6^{2-},$2Li^+$ (Figures 1 and 2). All expected ^{13}C resonances for 6-$(H)^-$,Li^+ are resolved in addition to the peaks corresponding to dianion 6^{2-},$2Li^+$. Interestingly, ^{13}C chemical shifts for the triarylmethyl "anionic" carbons (C3) in the monoanion and dianion are similar, i.e., 89.4 and 85.4 ppm, respectively. Using ^{13}C chemical shifts as a measure of negative charge at carbon, it appears that the negative charge distribution remains undisturbed upon the extension of conjugation from 6-$(H)^-$,Li^+ to 6^{2-},$2Li^+$; the second negative charge in 6^{2-},$2Li^+$ enters the triarylmethyl "anionic" carbon and the adjacent ring A, ring B, and ring C. This phenomenon is in agreement with the preceding conclusions about the relative charge distribution between ring "C" and rings "B" in the dianions.

When the reaction of 6-$(H)_2$ with MeLi in THF is followed using UV–vis spectroscopy, a steady rise of the λ_{max} = 463 nm band is observed, which is similar to the band observed for dianion 6^{2-},$2Li^+$.

Comparison of the ^{13}C NMR and UV–vis data for the monoanion and dianions suggests that the dianion can be considered as a union of two weakly interacting triarylmethyl anions. To date such a conclusion is valid for all other investigated 1,3-connected polyarylmethyls. Therefore, a common feature, such as topology, must determine their electronic structure and overcome the different sterical conditions in the present systems and those previously examined.

Diradical. Treatment of a 0.1 M solution of carbodianion 6^{2-},$2K^+$ in THF with 1 molar equiv of iodine at 263 K for 30 min produces an inhomogeneous mixture of diradical $6^{2\cdot}$ and KI in THF (Scheme III). The solvent is removed on a vacuum line and KI is washed out with degassed MeOH. Solid diradical $6^{2\cdot}$ is stored under argon at ambient temperature.

Solutions, which are prepared by dissolving the solid $6^{2\cdot}$ in either THF or 2-methyltetrahydrofuran (2-MeTHF), are examined by ESR, UV–vis, and voltammetry. Solubility of $6^{2\cdot}$ in THF and 2-MeTHF is sufficient to obtain the spectra.

The Δm_s = 1 region of the ESR spectrum at 100 K for diradical $6^{2\cdot}$ in 2-MeTHF consists of three peaks (Figure 3). In the center part of the spectrum two overlapped first-derivative Gaussian peaks, one broad and one narrow,

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[11] Solution of 2^{2-},$2Li^+$ also contains excess of MeLi, CH_4, and presumably, undetected products of decomposition of deuterated THF by MeLi.

[12] O'Brien, D. H. In *Comprehensive Carbanion Chemistry*; Buncle, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980; Chapter 6.

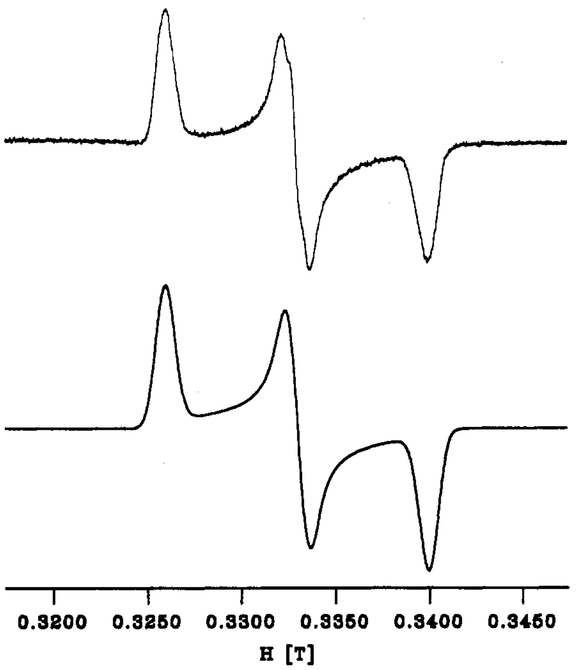

Figure 3. (Top) Experimental ESR spectrum for diradical $6^{2\bullet}$ in 2-MeTHF glass at 100 K. (Solid diradical $6^{2\bullet}$ is dissolved in 2-MeTHF). (Bottom) Simulated ESR spectrum for triplet state with zero-field splittings, $|D/hc| = 0.00655$ cm^{-1} and $|E/hc| = 0.00218$ cm^{-1}. Gaussian linewidth of 10 G is used.

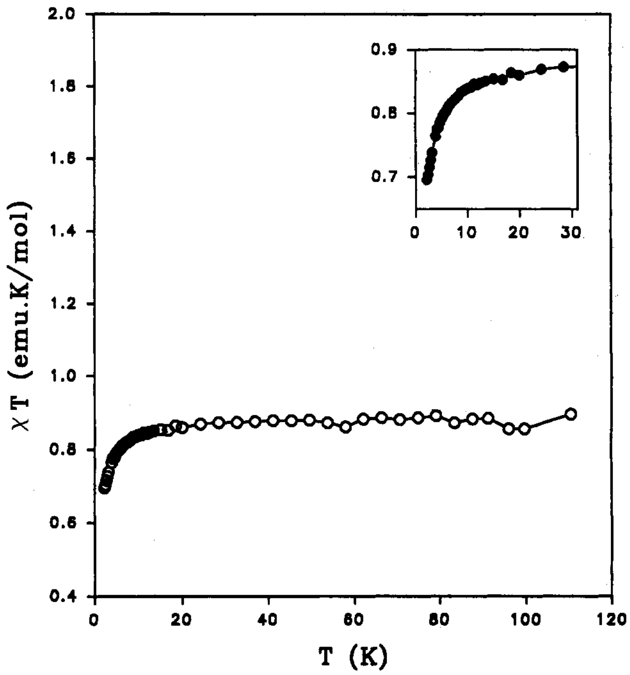

Figure 4. Plot of the product of magnetic susceptibility and temperature vs temperature for solid diradical $6^{2\bullet}$. SQUID data are obtained at $H = 500$ Oe.

can be seen. The broad center peak and two peaks on the sides are assigned to the triplet state with the zero-field splitting (zfs) parameters $|D/hc| = 3|E/hc|$.[13] The narrow center peak is a doublet impurity.[14]

The triplet spectrum is simulated using a computer program based upon second-order perturbation solution to the spin Hamiltonian.[15] The zfs parameters in the simulated spectrum are $|D/hc| = 0.00655$ cm^{-1} and $|Ehc| = 0.00218$ cm^{-1} and the derivative Gaussian linewidth is 10 G (Figure 3).

Because the diradicals and the dianions differ in the population of the two nonbonding MOs only, charge distribution in dianions may be similar to spin distribution in diradicals.[6a] According to the preceding NMR data, "planarization" of the Schlenk hydrocarbon dianion concentrates the negative charge density in the center part (ring C) of 6^{2-}; however, a significant portion of the negative charge density resides at the "anionic" carbons (C3). Therefore, a similar distribution of the spin density should be found in diradical $6^{2\bullet}$.

$|D/hc|$ can be related to the average distance between the unpaired electrons (centers of spin density distribution) in the triplet state; that is, the greater $|D/hc|$ corresponds to the smaller distance.[16] Although concentration of spin density in ring C should give a large $|D/hc|$, the value for diradical $6^{2\bullet}$ (0.00655 cm^{-1}) is less than those for **5a–c** (0.0087–0.0107 cm^{-1}). This result suggests that a significant part of the spin density resides in $2p_\pi$ orbitals at C3 and out-of-plane twist in **5a–c** may bring the $2p_\pi$ lobes closer to increase $|D/hc|$.[7]

A UV–vis spectrum for a solution of $6^{2\bullet}$ in THF shows a narrow band at $\lambda_{max} = 358$ nm. While the band shape is similar, the λ_{max} is red-shifted by several nm compared to the related "nonplanarized" 1,3-connected polyarylmethyl triplet diradicals.[7]

Diradical $6^{2\bullet}$ can be reduced to dianion 6^{2-} both chemically and electrochemically. When a solution of $6^{2\bullet}$ in THF is reduced with Li in the UV–vis cuvette, the $\lambda_{max} = 358$ nm band gradually disappears and the $\lambda_{max} = 463$ nm band forms. An isosbestic point is observed at $\lambda = 371$ nm.

Two cyclic voltammetric (CV) waves at −1.41 and −1.65 V vs SCE, which correspond to a reduction to radical anion and dianion, are observed for $6^{2\bullet}$ in THF/TBAP. Similarly, for oxidation of diradical to radical cation and dication, two waves are observed at 0.22 and 0.46 V, respectively. The waves for radical ions are reversible. The waves for dianion and dication are partially reversible at the CV scanning rates of <5 V. This is in accordance with the observation that a red solution of $6^{2-},2K^+$ is decolorized within minutes in THF/TBAP. (No electrochemical data for dianions could be obtained at ambient temperature.) The potential difference between the radical ion and dianion or dication waves, $\Delta E_p = 0.24$ V, indicates that the equilibrium for disproportionation of radical ion to diradical and dianion or dication favors significantly radical ion in THF/TBAP.[17] Thus, "planarization" does not alter significantly electrochemistry of $6^{2\bullet}$ compared to the related 1,3-connected polyarylmethyl diradicals **5a–c**.[7]

Solid-State Studies. Solid diradical $6^{2\bullet}$ is examined using a SQUID magnetometer. The product of magnetic susceptibility (χ) and temperature (T) is plotted versus temperature (T) at a constant applied magnetic field (H)

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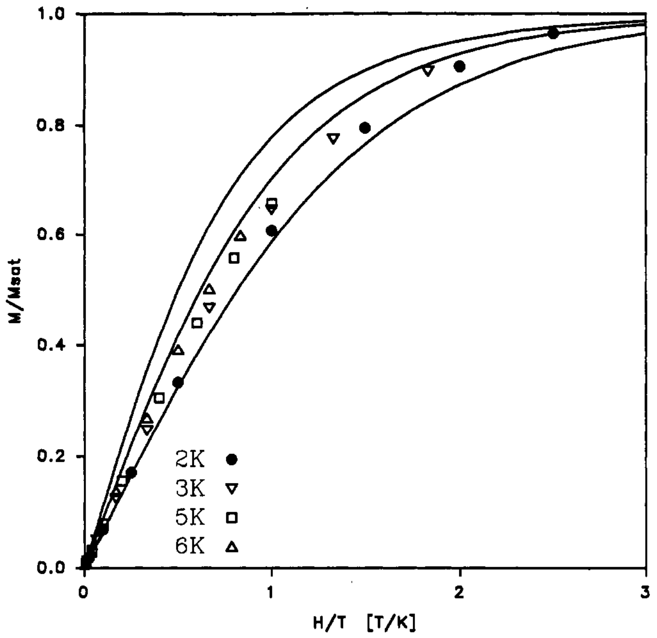

Figure 5. Normalized plots of magnetization vs the ratio of magnetic field and temperature for diradical $3^{2\bullet}$. SQUID data are obtained at $T = 2$ K, 3 K, 5 K, and 6 K. The Brilloun function plots (solid lines) correspond to $S = {}^1/_2$, 1, and ${}^3/_2$.

(Figure 4). At $T > 20$ K, the χT is approximately constant and can be fit to a Curie–Weiss law, $\chi = C/(T - \theta)$.[18] The Curie constant, $C = 0.89$ emu K mol^{-1}, corresponds to effective magnetic moment, $\mu_{\text{eff}} = 2.7\ \mu_B$; a calculated spin-only μ_{eff} for a paramagnet consisting of triplet molecules is 2.8 μ_B.[18] An inaccurate mass of solid diradical (±5%) and impurities may explain this small discrepancy in μ_{eff}. A small and negative Weiss constant, $\theta = -0.6$ K, suggests a weak antiferromagnetic (AFM) interaction. Furthermore, the downward turn in the χT vs T plot for $T < 20$ K supports the presence of a weak AFM interaction in solid $6^{2\bullet}$.

This weak AFM behavior at low temperatures is confirmed by magnetization studies; that is, the normalized plots of magnetization (M/M_{sat}) versus H/T indicate smaller spin (S) at 2 K compared to 3 K, 5 K, and 6 K.[18] The M/M_{sat} vs H/T plots correspond to theoretical Brillouin function plots for $S < 1$ that suggest the onset of the antiferromagnetic interactions at $T > 6$ K in agreement with the susceptibility studies (Figure 5).

Conclusion

Constraining the out-of-plane distortions of the π-conjugated system of 1,3-connected polyarylmethyl diradical and dianion preserves the unusual electronic structure associated with other 1,3-connected polyarylmethyl polyradicals and polyanions. However, magnetic properties in the solid state are sensitive to the steric hindrance; that is, solid diradicals $6^{2\bullet}$ and **5b** show antiferromagnetic and ferromagnetic interactions, respectively.

Experimental Section

Materials and Procedures. Air-sensitive dianions and diradicals were handled using either glovebox or vacuum line techniques. UV–vis and electrochemistry studies were carried out in a glovebox. Vacuum lines and the glovebox system were described previously.[6b]

For organic synthesis, diethyl ether (ether) and tetrahydrofuran (THF) were distilled from Ph_2CO/Na in an Ar or N_2 atmosphere immediately before use. All reagents were purchased from Aldrich except for n-BuLi (Alfa).

Dimethyl 4,6-dibromoisophthalate was prepared in a four-step synthesis according to modified literature procedures.[19] Conditions for the oxymercuration–demercuration reaction, which is used for the preparation of **6-(OR)$_2$**, were adopted from Brown and Lynch.[9] Hellwinkel and co-workers used $ZnCl_2/HCl$/ether for Friedel–Crafts cyclizations;[10] we employed similar reaction conditions to obtain bridged polyarylmethane **6-(H)$_2$**.

In addition to elemental analysis data for selected compounds, the purity of all synthetic intermediates is documented by the full ^1H and $^{13}C\{^1H\}$ NMR spectra, which are available as supplementary material.

4,6-Dibromo-α,α,α′,α′-tetramethyl-1,3-benzenedimethanol. MeMgBr (36.0 mL of a 3.0 M solution in ether, 108.0 mmol) was added to a solution of dimethyl 4,6-dibromoisophthalate (9.50 g, 27.0 mmol) in THF at 0 °C. The reaction mixture was slowly allowed to attain ambient temperature over 5 h. Subsequently, after cooling to 0 °C, water and dilute HCl were added. After extraction with ether and drying over $Na_2CO_3/MgSO_4$, concentration in vacuo gave the crude product as a solid (9.12 g). Crystallization from EtOAc/hexane gave colorless crystals 5.18 g (54%) mp 187.5–188.5 °C. ^1H NMR ($CDCl_3$): 8.095 (s, 1 H), 7.803 (s, 1 H), 2.1 (bs, 2 H), 1.741 (s, 12 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 145.56, 140.07, 125.91, 118.82, 73.56, 29.37.

4,6-Dibromo-1,3-diisopropenylbenzene. 4,6-Dibromo-α,α,α′,α′-tetramethyl-1,3-benzenedimethanol (5.25 g, 14.9 mmol) was stirred under reflux in a mixture of formic acid (120 mL) and sulfuric acid (3 mL). After being refluxed for 1 h, the reaction mixture was cooled in an ice bath and diluted with cold water. Extraction with chloroform, drying with $MgSO_4$, and concentration in vacuo gave the product as a colorless oil (4.40 g, 92%). The oil slowly changed to colorless crystals with mp close to ambient temperature. ^1H NMR ($CDCl_3$): 7.744 (s, 1 H), 7.021 (s, 1 H), 5.227 (m, 2 H), 4.950 (m, 2 H), 2.073 (m, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 144.61, 143.94, 135.96, 130.19, 120.19, 116.58, 23.32.

6A-(OH)$_2$. n-BuLi (4.65 mL of a 2.3 M solution in hexane, 10.7 mmol) was added to a solution of 4,6-dibromo-1,3-diisopropenylbenzene (3.378 g, 10.69 mmol) in ether (50 mL) at −15 °C. After stirring for 1 h at −15 to −12 °C), solid 4,4′-di-*tert*-butylbenzophenone (3.147 g, 10.69 mmol) was added to the homogeneous reaction mixture at −12 °C. The temperature in the cooling bath was allowed to raise to 10 °C over 5 h. Subsequently, a second portion of n-BuLi (4.70 mL of a 2.3 M solution in hexane, 10.8 mmol) was added at −15 °C and, after 1 h at −15 to −10 °C, a second portion of solid 4,4′-di-*tert*-butylbenzophenone (3.148 g, 10.70 mmol) followed. The reaction mixture was allowed to attain ambient temperature over a 12-h period and, then, cold water was added to the inhomogeneous reaction mixture at 0 °C. After extraction with ether and drying over $MgSO_4$, concentration in vacuo afforded 9.119 g of a light yellow solid. The crude product was stirred in boiling MeOH (70 mL) for 30 min. After filtration at ambient temperature, 5.288 g (66%) of white solid was obtained, mp 212–213.5 °C. Anal. Calcd for $C_{54}H_{66}O_2$: C, 86.81; H, 8.90. Found: C, 86.78; H, 9.03. FABMS (ONPOE), cluster: m/z (peak height) at $(M - H)^+$ 745 (49), 746 (32), 747 (25); $(M - OH)^+$ 728 (42), 729 (157), 730 (90), 731 (63). ^1H NMR ($CDCl_3$): 7.172 (d, $J = 8.5$ Hz, 8 H), 6.807 (d, $J = 8.5$ Hz, 8 H), 6.782 (s, 1 H), 5.868 (s, 1 H), 5.047 (bs, 2 H), 4.461 (bs, 2 H), 4.388 (s, 2 H), 2.046 (s, 6 H), 1.263 (s, 36 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 149.51, 148.45, 144.66, 141.31, 138.97, 136.16, 129.58, 127.32, 124.38, 116.18, 83.22, 34.33, 31.33, 25.90. ^{13}C DEPT (135 °C) CH, CH_3 136.16, 129.56, 127.31, 124.39, 31.33, 25.90; CH_2 116.19.

6-(OR)$_2$. THF (30 mL) was added to a freshly prepared stirred solution of $Hg(OAc)_2$ (10.0 g, 31.3 mmol) in water (30 mL) and immediately followed by solid **6A-(OH)$_2$** (5.32 g, 7.12 mmol). After the reaction mixture was stirred for 12 h, a 3 M solution of NaOH in water (100 mL) was added immediately followed by an instantly prepared cold solution of $NaBH_4$ (100 mL, 0.5 M in $NaBH_4$, 3 M in NaOH). A black precipitate of elemental mercury was

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formed. The reaction mixture was stirred for 30 min at ambient temperature. After extraction with ether, washing the ether layer with water, and drying over $MgSO_4$, concentration in vacuo afforded a crisp white foam. Crystallization from MeOH/acetone gave 4.15 g (78%) of a crude product as a white powder. A small sample was further purified by column chromatography (silica gel, 70–230 mesh; hexane/CH_2Cl_2, from 2.5/1 to 0.8/1) and treatment with boiling pentane. A white powder was obtained, mp 259–260 °C. Anal. Calcd for $C_{54}H_{66}O_2$: C, 86.81; H, 8.90. $C_{54}H_{66}O_2\cdot(H_2O)_{0.75}$: C, 85.27; H, 8.94. Found: C, 85.30; H, 8.86. ^{1}H NMR ($CDCl_3$): 7.236, 7.204 (AB, *J* = 8 Hz 16 H), 7.030 (s, 1 H), 6.806 (s, 1 H), 1.523 (s, 12 H), 1.274 (s, 36 H). ^{13}C{^{1}H} NMR ($CDCl_3$): 149.66, 147.46, 143.40 (spectral overlap), 126.95, 124.61, 120.22, 112.39, 90.84, 84.95, 34.36, 31.33, 29.93. ^{13}C DEPT (135 °C) CH, CH_3 126.95, 124.61, 120.22, 112.38, 31.33, 29.94.

6B-(OH)$_2$. Crude 6-(OR)$_2$ (2.6 g) was stirred vigorously with an excess amount of cut lithium wire (1.4 g) in THF (50 mL) for 6 days. Subsequently, water was added to the reaction mixture at 0 °C. After extraction with ether and drying over $MgSO_4$, concentration in vacuo gave a crude product (2.5 g). Treatment with boiling hexane (50 mL, 30 min) afforded 2.0 g (77%) of a white powder, mp 249.5–251.5 °C. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - H)^+$ 749 (37); $(M - H - H_2O)^+$ 731 (74), 732 (56), 733 (45). ^{1}H NMR ($CDCl_3$): 7.386 (s, 1 H), 7.162 (d, *J* = 8 Hz, 8 H), 6.924 (s, 1 H), 6.759 (d, *J* = 8 Hz, 8 H), 6.449 (s, 2 H), 1.676 (s, 12 H), 1.65 (bs, 2 H), 1.273 (s, 36 H). ^{13}C{^{1}H} NMR ($CDCl_3$): 148.37, 142.24, 141.97, 140.77, 139.90, 128.97, 124.80, 122.63, 74.02, 50.99, 34.29, 32.08, 31.42. ^{13}C DEPT (135 °C) CH, CH_3 139.90, 128.97, 124.80, 122.63, 50.99, 32.08, 31.42.

6-(H)$_2$. Anhydrous HCl gas was passed through a stirred mixture of **6B**-(OH)$_2$ (2.130 g, 2.843 mmol) and anhydrous $ZnCl_2$ (4.4 g, 32 mmol) in ether (150 mL) for 5 h. After an additional 22 h of stirring, a yellow reaction mixture was poured onto ice/water (200 mL). After extraction with ether, several washings of the ether layers with water and a saturated solution of $NaHCO_3$, and drying over $MgSO_4$, concentration in vacuo afforded 2.127 g of a white solid. Column chromatography at elevated pressure (20 psi, silica gel, 230–400 mesh, CH_2Cl_2/hexane, 7/40) gave 3 fractions of the product as white solids: crude diastereomer I (more polar, 485.9 mg), crude diastereomer II (less polar, 531.7 mg), and the mixture I/II (100.3 mg). The overall yield was 55%. Recrystallization of diastereomer I from acetone gave 207.7 mg of a white powder, mp 248–249 °C. Anal. Calcd for $C_{54}H_{66}$: C, 90.70; H, 9.30. Found: C, 90.52; H, 9.40. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - H)^+$ 713 (16), 714 (12), 715 (6); $(M - CH_3)^+$ 699 (15), 700 (9). HR-FABMS, calcd for $C_{54}H_{65}$ $(M - H)^+$: 713.5086; found 713.5085, 713.5069. ^{1}H NMR ($CDCl_3$): 7.730 (s, 1 H), 7.594 (d, *J* = 2 Hz, 2 H), 7.167 (d, *J* = 8 Hz, 4 H), 7.138 (dd, *J* = 8, 2 Hz, 2 H), 6.959 (d, *J* = 8 Hz, 2 H), 6.852 (d, *J* = 8 Hz, 4 H), 6.828 (s, 1 H), 5.127 (s, 2 H), 1.713 (s, 6 H), 1.689 (s, 6 H), 1.329 (s, 18 H), 1.296 (s, 18 H). ^{13}C{^{1}H} NMR ($CDCl_3$): 148.98, 148.49, 143.58, 143.02, 141.91, 135.36, 134.75, 130.09, 128.90, 128.82, 124.98, 122.89, 121.99, 48.14, 38.70, 34.64, 34.32, 32.61, 31.73, 31.51, 31.45 ^{13}C DEPT (135 °C) CH, CH_3 130.08, 128.90, 128.82, 124.98, 122.89, 121.98, 48.13, 32.60, 31.73, 31.51, 31.45. Note: one aromatic ^{13}C resonance (CH) was not resolved. Spectral data for a crude diastereomer II. ^{1}H NMR ($CDCl_3$): 7.746 (s, 1 H), 7.575 (d, *J* = 2 Hz, 2 H), 7.195 (d, *J* = 8 Hz, 4 H), 7.150 (dd, *J* = 8, 2 Hz, 2 H), 7.063 (d, *J* = 8 Hz, 2 H), 6.972 (d, *J* = 8 Hz, 4 H), 6.860 (s, 1 H), 5.154 (s, 2 H), 1.755 (s, 6 H), 1.649 (s, 6 H), 1.328 (s, 18 H), 1.263 (s, 18 H).

Preparation of Carbodianions. Dianions were prepared by treatment of the hydrocarbon precursor with MeLi in THF-*d*$_8$ or stirring the hydrocarbon precursor with KH (multimolar excess) in THF (or THF-*d*$_8$) for several days. THF-*d*$_8$ (99% D, Cambridge Isotopes) was vacuum transferred from Ph_2CO/Na. For glovebox experiments (UV–vis and electrochemistry), THF was purified by distillation from Ph_2CO/Na and high-vacuum transfer from Ph_2CO/K (excess K).

NMR Spectroscopy. Samples for NMR studies of carbanions were flame-sealed under vacuum in 5-mm NMR tubes. Chemical shifts are reported relative to TMS (0.00 ppm) using THF-*d*$_8$ (^{1}H, 3.580 ppm and ^{13}C, 67.45 ppm) as an internal standard. All spectra were obtained using a Bruker WM 400 spectrometer (400.1 MHz for ^{1}H; 100.6 MHz for ^{13}C). In the summaries of ^{1}H NMR spectra, only first-order couplings are shown, e.g., doublets of triplets, which are usually observed for the aromatic protons associated with the *tert*-butylphenyls, are reported as doublets. Methanol was used as a standard for the low temperature calibration.[20]

2D NMR spectra were acquired in the absolute magnitude mode with the quadrature detection in both dimensions; 256 increments of 1 K with either 16 scans (COSY) or 64 scans (HETCOR) were accumulated. Zero-filling, multiplication by the sine window function, Fourier transform, and, for COSY spectrum, symmetrization were applied. All ^{1}H–^{13}C HETCOR experiments were ^{1}H-decoupled in both dimensions. For partial correlation of the ^{1}H and ^{13}C aromatic regions, HETCOR pulse sequences were optimized for ^{1}J(CH) = 151.5 and doublet multiplets. For full correlation of quaternary carbons with protons, HETCORs were optimized for *J* = 10 and all multiplets.

6^{2-},2Li^{+}. ^{1}H NMR (THF-*d*$_8$): 303 K 7.428 (d, *J* = 8.6 Hz, 4 H), 7.048 (s, 1 H), 7.010 (d, *J* = 8.5 Hz, 2 H), 6.972 (d, *J* = 8.6 Hz, 4 H), 6.959 (d, *J* = 2.3 Hz, 2 H), 6.851 (s, 1 H), 6.474 (dd, *J* = 8.5 Hz, 2.3, 2 H), 1.364 (s, 12 H), 1.298 (s, 18 H), 1.213 (s, 18 H); 223 K 7.43 (d, *J* = 8 Hz, 4 H), 7.35 (s, 1 H), 7.15 (d, *J* = 8 Hz, 2 H), 6.86, 6.84, 6.82 (m, 6 H), 6.72 (s, 1 H), 6.37 (d, *J* = 8 Hz, 2 H), 1.33 (s, 12 H), 1.28 (s, 18 H), 1.20 (s, 18 H); 193 K 7.41 (s, 4 H), 7.35 (s, 1 H), 7.14 (s, 2 H), 6.81 (s, 6 H), 6.70 (s, 1 H), 6.35 (s, 2 H), 1.28 (s, 30 H), 1.20 (s, 18 H). ^{13}C{^{1}H} NMR (THF-*d*$_8$): 303 K 144.04, 139.65, 137.21, 136.95, 133.74, 132.86, 126.97, 124.65, 121.75, 120.73, 119.25, 118.64, 116.12, 100.04, 85.39, 39.09, 34.41, 32.51, 32.36, 29.01; ^{13}C DEPT (135 °C), CH, CH_3 126.95, 124.65, 120.73, 119.25, 118.63, 116.12, 100.08, 32.51, 32.36, 29.01. ^{13}C{^{1}H} NMR (THF-*d*$_8$): 223 K 143.2, 139.9, 136.7, 133.2, 133.1, 130.8, 124.5, 124.2, 123.1, 120.1, 119.0, 116.9, 115.4, 106.5, 88.4, 39.0, 34.4, 34.3, 32.6, 32.4, 29.1; 193 K 143.0, 139.8, 136.6, 133.1, 132.7, 130.6, 124.2 (overlap), 123.2, 120.1, 119.0, 116.4, 115.3, 107.0, 88.7, 38.9, 34.4, 34.3, 32.6, 32.5, 29.0.

6^{2-},2K^{+}. ^{1}H NMR (THF-*d*$_8$): 303 K 7.312 (d, *J* = 8.6 Hz, 4 H), 7.118 (s, 1 H), 7.099 (d, *J* = 8.6 Hz, 4 H), 6.998 (d, *J* = 2.3 Hz, 2 H), 6.931 (s, 1 H), 6.786 (d, *J* = 8.5 Hz, 2 H), 6.477 (dd, *J* = 8.5, 2.3 Hz, 2 H), 1.385 (s, 12 H), 1.344 (s, 18 H), 1.212 (s, 18 H); 243 K 7.35 (d, *J* = 8.5 Hz, 4 H), 7.25 (s, 1 H), 7.09 (d, *J* = 8.5 Hz, 4 H), 6.98 (d, *J* = 2.2 Hz, 2 H), 6.89 (s, 1 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 6.47 (dd, *J* = 8.5, 2.2 Hz, 2H), 1.37 (s, 12 H), 1.35 (s, 18 H), 1.33 (s, 18 H); 203 K 7.36 (d, *J* = 8 Hz, 4 H), 7.31 (s, 1 H), 7.08 (d, *J* = 8 Hz, 4 H), 6.96 (s, 2 H), 6.90, 6.88, 6.87 (m, 3 H), 6.46 (d, *J* = 8 Hz, 2 H), 1.35 (s, 30 H), 1.21 (s, 18 H); 168 K 7.36 (s, 5 H), 7.06 (s, 4 H), 6.92, 6.90, 6.84 (m, 5 H), 6.42 (s, 2 H), 1.35 (s, 30 H), 1.21 (s, 18 H); 153 K 7.36 (s), 7.06 (s), 6.90 (s), 6.41 (s), 1.35 (s), 1.21 (s). ^{13}C{^{1}H} NMR (THF-*d*$_8$): 303 K 144.26, 141.23, 139.22, 136.70, 132.37, 131.19, 129.94, 125.02, 121.74, 119.36, 118.43, 116.39, 114.98, 94.72, 88.00, 38.78, 34.69, 34.43, 32.53, 32.31, 28.62. ^{13}C DEPT (135 °C) CH, CH_3 131.19, 125.02, 121.74, 119.35, 118.42, 114.97, 94.72, 32.53, 32.31, 28.62. ^{13}C{^{1}H} NMR (THF-*d*$_8$): 168 K 143.9, 139.9, 138.4, 135.8, 131.0, 130.8, 128.9, 124.7, 121.2, 118.9, 117.0, 116.6, 113.3, 95.3, 88.6, 38.4, 34.7, 34.4, 32.6, 32.3, 27.7.

6-(H)$^{-}$,Li^{+} (the spectra are obtained from a mixture containing the dianion 2^{2-},2Li^{+}). ^{13}C{^{1}H} NMR (THF-*d*$_8$): 148.15, 147.84, 147.54, 146.57, 145.05, 140.79, 138.72, 138.07, 137.38, 131.98, 131.63, 131.51, 130.04, 129.62, 129.49, 129.37, 124.91, 124.69, 124.31, 123.15, 122.46, 120.96, 119.72, 119.43, 113.80, 113.04, 89.35, 49.97, 39.37, 38.62, 35.53, 35.13, 34.78, 34.60, 34.34, 32.83, 32.58, 32.26, 31.99, 31.94, 29.20.

MeOH Quenching of Dianions. MeOH (excess amount) was added to a solution of dianion at 0 °C under argon. Usual aqueous workup followed. ^{1}H NMR analysis indicated a mixture of diastereomers 6-(H)$_2$.

Diradical 6$^{2\bullet}$. A filtered and centrifuged solution of dianion 6^{2-},2K^{+} (0.1175 mmol) in THF (1.5 mL) was placed in a double tube recrystallizer (ultrafine glass frit, 4–8 μm) on the vacuum line. After I_2 (29.7 mg, 0.1170 mmol) was added under a stream of argon at −10 °C and mixture stirred for 30 min at −10 °C, THF was removed under vacuum. The remaining solid residue was thoroughly washed with deoxygenated MeOH. The light yellow solid was dried under vacuum overnight (5×10^{-4} Torr) to give 70.6 mg (84%) of the solid diradical. The solid diradical can be stored in the glovebox at ambient temperature for several days.

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J. Org. Chem. **1992**, *57*, 1767–1772 **1767**

ESR Spectroscopy. A Bruker 200D SRC instrument was used to obtain X-band ESR spectra. Temperatures in the range of 300 to 100 K were controlled by a nitrogen flow system equipped with heat exchanger, Pt-resistance thermometer, and heater (Varian); temperatures were measured using a thermocouple. Half-field, $\Delta m_s = 2$, transition was detected.

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 spectrophotometer. The spectrometer sample chamber was accessible from a glovebox. Preparations of all solutions were carried out in a glovebox under an argon atmosphere.

A solution of 2^{2-},2Li$^+$ in THF was obtained under similar conditions as in the preparation of the NMR sample of 2^{2-},2Li$^+$ in THF-d_8. Small aliquots from the reaction mixture were taken and diluted with 7×10^{-4} M MeLi/THF before recording the spectrum. For a reaction mixture, which was 0.7 M in MeLi and 0.1 M in **2**-(H)$_2$, UV–vis spectra recorded after both 16 and 22 h at ambient temperature showed $\lambda_{max} = 463$ nm.

The reaction of **2**-(H)$_2$ (3×10^{-5} M) with MeLi (0.02 M) in THF was also followed directly with UV–vis spectroscopy. The spectra were acquired at 10-min intervals and, after several hours, at 1-h intervals. A steady rise of the $\lambda_{max} = 463$ nm band was observed.

Reaction of $\mathbf{6}^{2\bullet}$ with Li in THF was followed with UV–vis spectroscopy as already described for similar systems.[6a]

Electrochemistry. All electrochemical measurements were carried out in a glovebox using a PARC Model 270 electrochemistry system as described previously.[7] THF was used as solvent. The concentration of the electroactive solute was 0.001–0.003 M and of supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was 0.1–0.2 M. Three-electrode home-made voltammetric cells were used: silver wire quasi-reference electrode, Pt foil counter electrode, and a Pt disk working microelectrode (dia. 100 μm, BAS). The solution volume was 2 mL. Ferrocene (0.510 V vs SCE) was used as a reference.[21] Separation between potential at the peaks of the oxidation and reduction CV waves was about 100 mV for ferrocene and diradical.

SQUID. Magnetic measurements were carried out on two SQUID magnetometers (MPMS, Quantum Design) at the University of Nebraska—Lincoln and at NIST in Boulder, CO. The technical details of measurements and sample preparation were described previously. The measurements at NIST were carried out by Robert Loughran.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for 24 closed-shell molecules and NMR spectra for carbodianions (25 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Polydiscamide A: A New Bioactive Depsipeptide from the Marine Sponge *Discodermia* sp.

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A depsipeptide, polydiscamide A (**1**), composed of 13 amino acids including a novel amino acid 3-methylisoleucine, was isolated from a Caribbean sponge, *Discodermia* sp. Its structure was elucidated by means of spectroscopic, chemical degradation, and derivatization techniques. Polydiscamide A inhibits the in vitro proliferation of the cultured human lung cancer A549 cell line.

Marine sponges are a well-established source of unique and of biologically active peptides. Discodermins A–D[1–3] from *Discodermia kiiensis*, theonellapeptolide F[4] from *Theonella* sp., jaspamide[5,6] from *Jaspis* sp., fenistins[7] from *Leucophloeus fenestrata*, and geodiamalide[8] from *Pseudaxinyssa* sp. are recent examples. The occurrence of biologically active novel structural types calyculins,[9] discodermolide,[10] and discodermide[11] in several *Discodermia* spp. led us to extend our research on a related undescribed species of deep-water sponge of the genus *Discodermia*.

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