Third, solvent-mediated inversion (as opposed to a mere change[2,3]) of enantioselectivity via our model would not be expected for most enzymes. This prediction was verified by the ν_L/ν_D values in acetonitrile and toluene, respectively, for the transesterification of **1** catalyzed by six unrelated lipases:[5] 4.7 and 32 for porcine pancreatic, 5.1 and 1.7 for *Chromobacterium viscosum*, 13 and 4.5 for *Pseudomonas cepacia*, 20 and 74 for *Mucor meheii*, 16 and 4.7 for *Aspergillus niger*, and 10 and 3.8 for *Pseudomonas* sp. lipoprotein lipase. Thus while the dependence of the enantioselectivity on the solvent was different for all enzymes, its inversion was observed only for *A. oryzae* protease.

The data in Table I indicate that the stereochemical outcome of the protease-catalyzed transesterification can be fundamentally altered simply by replacing the solvent. Note that this phenomenon can be explained without invoking solvent-induced conformational changes of the enzyme (no evidence for those has been observed for other serine proteases in anhydrous media[6]). Therefore, enzyme enantioselectivity in such systems can be predicted solely on the basis of physicochemical properties of the solvent.

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(6) Burke, P. A.; Smith, S. O.; Bachovchin, W. W.; Klibanov, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 8290. Kanerva, L. T.; Klibanov, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 6864. Adams, K. A. H.; Chung, S.-H.; Klibanov, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 9418.

(7) This work was supported by NIH Grant GM 39794.

Poly(arylmethyl) Octet ($S = {}^7/_2$) Heptaradical and Undecet ($S = 5$) Decaradical

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The rational design of large molecules and clusters with a significant preference for high-spin ordering is important for a recent topic of organic magnetism.[1-5] Our previous studies suggested that, in the series of 1,3-connected poly(arylmethyls), extension of conjugation does not affect their electronic structure;[6] that is, the known large preference for a triplet ground state for 1,3-connected diradicals may translate into the significant stabilization of a high-spin ground state in polyradicals.[7,8]

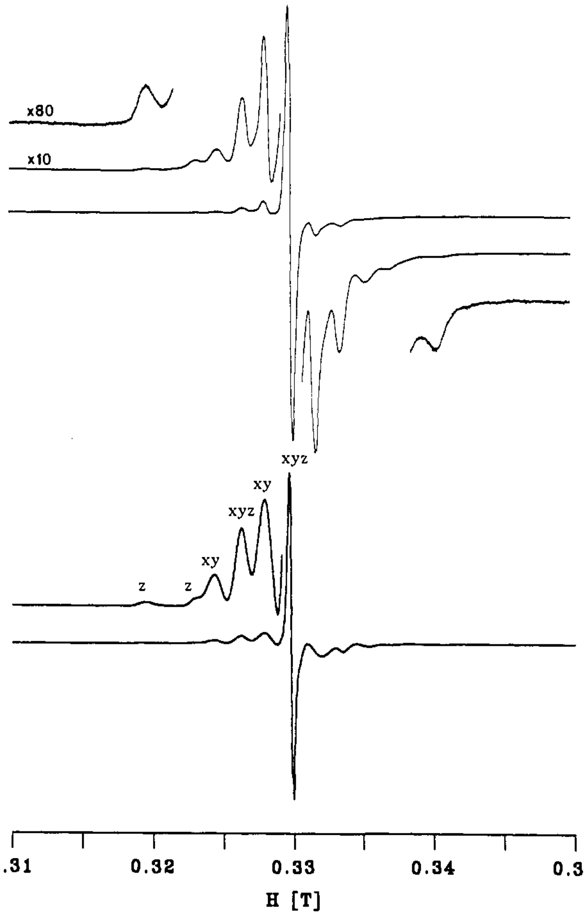
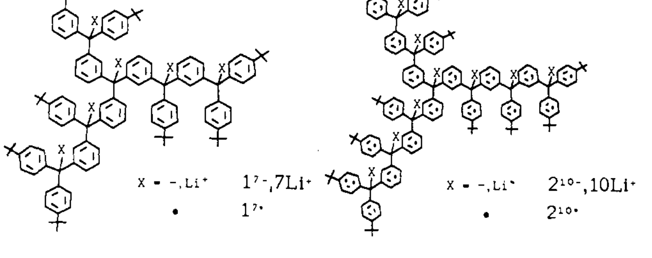


Figure 1. Top: X-band ESR spectrum for $\mathbf{1}^{7\bullet}$ in THF/2-MeTHF glass at 100 K. Bottom: Simulated $\Delta m_s = 1$ spectrum using m_s-dependent line widths and octet zfs, $|D/hc| = 0.001\,63$ cm^{-1} and $|E/hc| \approx 0$ cm^{-1}.

Now we report the preparation, magnetic resonance spectroscopy, and SQUID studies of the $S = {}^7/_2$ π-conjugated hydrocarbon heptaradical $\mathbf{1}^{7\bullet}$ and the homologous $S = 5$ decaradical $\mathbf{2}^{10\bullet}$. Both $\mathbf{1}^{7\bullet}$ and $\mathbf{2}^{10\bullet}$ are the highest spin π-conjugated polyradicals known to date,[6b,9] and the value $S = 5$ for $\mathbf{2}^{10\bullet}$ equals the S value of the highest spin organic molecule, the $S = 5$ pentacarbene.[4a]


X = –,Li⁺ 1^{7-},7Li⁺
• $1^{7\bullet}$

X = –,Li⁺ 2^{10-},10Li⁺
• $2^{10\bullet}$

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(1) Proceedings of the Symposium on Ferromagnetic and High Spin Molecular Based Materials; 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989. Miller, J. S.; Dougherty, D. A. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 1–562. Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

(2) Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, *253*, 301. Kinoshita, M.; Turek, P.; Tamura, M.; Nozawa, K.; Shiomi, D.; Nakazawa, Y.; Ishikawa, M.; Takahashi, M.; Awaga, K.; Inabe, T.; Maruyama, Y. *Chem. Lett.* **1991**, 1225. Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401.

(3) (a) Boyd, P. D. W.; Li, R.; Vincent, J. B.; Folting, K.; Chang, H. R.; Straib, W. E.; Huffmann, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8537. (b) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. *J. Am. Chem. Soc.* **1988**, *110*, 2795. (c) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. *J. Am. Chem. Soc.* **1991**, *113*, 5873. (d) McCusker, J. K.; Christmas, C. A.; Hagen, P. M.; Chadha, R. K.; Harvey, D. F.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 6114.

(4) (a) Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K.; Miko, F.; Sawaki, Y.; Iwamura, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1990**, *112*, 4074. (b) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. (c) Takui, T.; Itoh, K. *Chem. Phys. Lett.* **1973**, *19*, 120. (d) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(5) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. Tyutyulkov, N.; Polansky, O. E.; Schuster, P.; Karabunarliev, S.; Ivanov, C. I. *Theor. Chim. Acta* **1985**, *67*, 211.

(6) (a) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5889. (b) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5890. (c) Utamapanya, S.; Rajca, A. *J. Am. Chem. Soc.* **1991**, *113*, 9242.

(7) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791. Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 958.

(8) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991**, *113*, 9235. Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552.

(9) (a) Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5144, 5146. Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251. Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. II, Chapter 10. (b) Novak, J. A.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7618. Dougherty, D. A. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 25. (c) Kirste, B.; Grimm, M.; Kurreck, H. *J. Am. Chem. Soc.* **1989**, *111*, 108. (d) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5890.

0002-7863/92/1514-1884$03.00/0

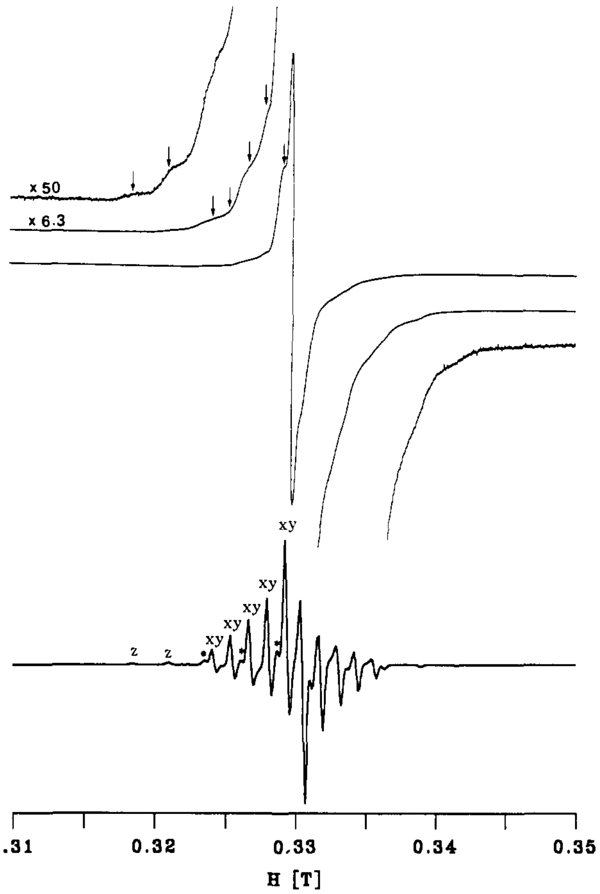

Figure 2. Top: X-band ESR spectrum for $\mathbf{2}^{10\bullet}$ in THF/2-MeTHF glass at 100 K. Bottom: Simulated spectrum ($\Delta m_s = 1$) using a Gaussian line width of 3 G and undecet zfs, $|D/hc| = 0.001\,20$ cm^{-1} and $|E/hc| \approx 0$ cm^{-1}. The peaks in the spectrum that are labeled "z" and "xy" correspond to the indicated coincidences of "x", "y", and "z" turning points. The label (*) is equivalent to "z".

Treatment of 7–9 × 10^{-3} M $\mathbf{1}^{7-}$,7Li$^+$ and $\mathbf{2}^{10-}$,10Li$^+$ in tetrahydrofuran (THF) with 4.0 and 5.7 equiv of I$_2$ at 180 K for 30 min produces solutions of $\mathbf{1}^{7\bullet}$ and $\mathbf{2}^{10\bullet}$, respectively.[6,10] After dilution at low temperature with 2-methyltetrahydrofuran (2-MeTHF), ESR spectra at 100 K are obtained for 1 × 10^{-3} M polyradicals.

The simulations of the ESR spectra ($\Delta m_s = 1$) suggest high-spin states for both polyradicals. The zero-field splittings (zfs) are as follows: $\mathbf{1}^{7\bullet}$, octet with $|D/hc| = 0.001\,63$ cm^{-1} and $|E/hc| \approx 0$ cm^{-1}; $\mathbf{2}^{10\bullet}$, undecet with $|D/hc| = 0.001\,20$ cm^{-1} and $|E/hc| \approx 0$ cm^{-1} (Figures 1 and 2).[11] For $\mathbf{1}^{7\bullet}$, the experimental spectrum is adequately simulated using m_s-transition-dependent Gaussian line widths; a small additional Gaussian contribution to the peak in the center is also added (Figure 1).[11] For $\mathbf{2}^{10\bullet}$, the low resolution of the experimental spectrum allows only for identification of the peaks that are either well-separated from other peaks or intense; e.g., in the left half of the spectrum, such peaks (shoulders) are marked with arrows, and in the high-resolution simulation, they are labeled with letters (Figure 2). The center peak in the spectrum corresponds to a half-integral spin impurity (Figure 2).

Magnetic moment (μ_{eff}) measurement for 2 × 10^{-3} M $\mathbf{2}^{10\bullet}$ in Me$_2$O using Evans's NMR method gives $\mu_{\mathrm{eff}} = 11\ \mu_B$ at 150 K, which is in agreement with the theoretical spin-only value of 11.0 μ_B for $S = 5$.[6b,12]

For SQUID measurements, ~5 × 10^{-3} M $\mathbf{1}^{7\bullet}$ in 2-MeTHF and $\mathbf{2}^{10\bullet}$ in THF are used.[17] A small volume of the solution is transferred at 130 or 160 K to an ESR quartz tube (4 mm o.d.) containing frozen THF (60-mm height) in order to form a sample band of 3-mm height.[13] Repetitive application of temperature gradients to the wall of the tube allows for complete transfer of the solution (from the wall of the tube) onto the frozen THF. (This process is very difficult because of the necessity of maintaining a low temperature to avoid decomposition of the polyradical.) Subsequently, the tube is immersed in liquid N$_2$ and filled with either 2-MeTHF or THF (60-mm height) above the frozen sample by vacuum transfer. The tube is flame sealed about 60 mm above the frozen solvent and, then, mounted to the SQUID sample holder using heat-shrink tubing. Under He atmosphere, the tube is cleaned and inserted to the SQUID chamber at 10 K; a symmetric SQUID signal, $M \approx +10^{-4}$ emu, is obtained ($H = 0.5$ T).

The plots of the product of magnetic susceptibility (χ) and T versus T (χT vs T) are flat between 5 and 80 K ($\mathbf{1}^{7\bullet}$) and 20 and 100 K ($\mathbf{2}^{10\bullet}$).[17] Therefore, the ESR spectra at 100 K and magnetic studies at low temperature pertain to the same spin species.

At $T < 5$ K ($\mathbf{1}^{7\bullet}$) and $T < 20$ K ($\mathbf{2}^{10\bullet}$), the χT vs T plots turn downward, indicating antiferromagnetic (AFM) interactions. Similar AFM behavior is observed in the normalized plots of magnetization (M/M_{satd}) vs H/T when the experimental points for T = 2, 5, 10, and 20 K ($\mathbf{1}^{7\bullet}$) and T = 2, 3, 5, and 10 K ($\mathbf{2}^{10\bullet}$) are compared to the Brillouin curves.[14,17] The onset of AFM interactions for $\mathbf{2}^{10\bullet}$ is solvent dependent; $T < 10$ K in 2-MeTHF and 20 K in THF.[15] The AFM interactions are observed for solutions of various high-spin polyradicals;[16] their origin is likely to be intermolecular.

The magnetization data correspond to $^7/_2 > S > {}^5/_2$ ($\mathbf{1}^{7\bullet}$ in 2-MeTHF at $T \geq 5$ K) and $S = 4$ ($\mathbf{2}^{10\bullet}$ in THF at $T = 10$ K).[17] These data may be affected by the AFM interactions; also, the complexity of the SQUID sample preparation and extreme instability of polyradicals may increase the amount of low-spin contaminants to give the low S. For example, the ESR spectrum of $\mathbf{1}^{7\bullet}$ *after* the SQUID measurements is similar to the spectrum in Figure 1; however, the spectrum is less resolved and a small extraneous peak is observed.[17]

We conclude that heptaradical $\mathbf{1}^{7\bullet}$ and decaradical $\mathbf{2}^{10\bullet}$ possess a ground-state octet ($S = {}^7/_2$) and undecet ($S = 5$), respectively.

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Note Added in Proof. The work on the $S = 6$ hexacarbene, the highest spin ever reported for a purely organic molecule, has been submitted for publication in this journal by Iwamura and co-workers (private communication from Professor H. Iwamura).

Supplementary Material Available: SQUID data for $\mathbf{1}^{7\bullet}$ in 2-MeTHF and $\mathbf{2}^{10\bullet}$ in THF and ESR spectrum of $\mathbf{1}^{7\bullet}$ after SQUID measurement (3 pages). Ordering information is given on any current masthead page.

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(10) Rajca, A. *J. Org. Chem.* **1991**, *56*, 2557.

(11) Thayumanavan, S.; Rajca, A. Unpublished work. Teki, Y.; Takui, T.; Itoh, K. *J. Chem. Phys.* **1988**, *88*, 6134. Teki, Y.; Takui, T.; Yagi, H.; Itoh, K. *J. Chem. Phys.* **1985**, *83*, 539. Iwasaki, M. *J. Magn. Reson.* **1974**, *16*, 417.

(12) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.

(13) Attempts to form a narrow sample band above frozen 2-MeTHF are defeated by diffussive spreading of the sample and, consequently, distortion of the SQUID signal.

(14) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986. Henry, W. E. *Phys. Rev.* **1952**, *88*, 559.

(15) Although 2-MeTHF is preferred over THF as a solvent because of less interference from antiferromagnetic interactions, we find the preparation of the sample band of $\mathbf{2}^{10\bullet}$ in 2-MeTHF unsatisfactory. The application of temperature gradients during sample-band formation is far more effective for THF solution. Therefore, overheating (and decomposition of polyradical) can be more easily avoided.

(16) Rajca, A.; Utamapanya, S. Unpublished data.

(17) Supplementary material.