High-Spin Organic Polyradicals as Simple Spin Clusters

Andrzej Rajca [a]

[a] Department of Chemistry and Center for Materials Research and Analysis, University of Nebraska, Lincoln, NE, 68588-0304, U.S.A.

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ANDRZEJ RAJCA, Department of Chemistry and Center for Materials Research and Analysis, University of Nebraska, Lincoln, NE 68588-0304, U.S.A.

Abstract   Design of high-spin polyarylmethyl polyradicals as simple spin clusters is outlined. For selected spin clusters, connectivity dependent scaling of the spin coupling constants (J) and equations for magnetization vs. magnetic field and temperature are shown.

DESIGN OF HIGH-SPIN POLYRADICALS

In the past several years, progress has been made in synthesis of high-spin organic polyradicals. Such molecules may be viewed as ensembles of large number of interacting sites with "unpaired" electrons.[1-3] Currently, the most important technique for study of these molecules relies on fitting magnetic field dependence of magnetization to a Brillouin function in order to determine spin value S.[4,5] Analysis of temperature dependence of magnetization for such complex system would greatly improve their characterization.

Because the effects originating from magnetic anisotropy are negligible in most purely organic systems, isotropic Heisenberg

Hamiltonian (eq. 1) can be employed to describe exchange interaction between the sites with "unpaired" electrons.[6-9]

$$\text{Hamiltonian} = -2J_{ij}S_iS_j \qquad\qquad (1)$$

Application of eq. 1 to analyze magnetization for systems with large number of spins involves repeated numerical diagonalizations of huge matrices. However, eq. 1 can be solved exactly for numerous simple symmetrical clusters.[10] Therefore, design of multispin polyradical as an exactly solvable spin cluster would greatly aid its characterization.

Tetraradical 1,[11] a spin tetramer, and octaradical 2,[12] a spin octamer, with "identical" ferromagnetic J-couplings across each 1,3-phenylene moiety, provide examples of increasing complexity encountered in organic polyradicals (Figure 1); for 1, eq. 1 is exactly solvable by vector decoupling techniques but it is not solvable for 2. If outer ferromagnetic J-couplings in 2 could be made much smaller compared to the inner ones, then the octaradical could be approximated as a spin pentamer (one $S = 2$ plus four $S = 1/2$), for which eq. 1 can be solved exactly.[10] Such an example may be provided by octaradical 3, where J-couplings across biphenylene moiety are expected to be much smaller than those for 1,3-phenylene moiety (Figure 1). Importantly, the smaller J-couplings may provide sufficient thermal population of the low-spin excited states for a reliable fit of magnetization vs. temperature, even at low temperatures, which are required for study of thermally unstable polyradicals.

Biphenyl moieties offer a significant simplification in organic synthesis of hydrocarbon framework of polyradical. Efficient nonsymmetrical C(aryl)C(aryl)-bond forming reactions provide a concise synthetic route to 3 based upon attachment of four arms to the central core

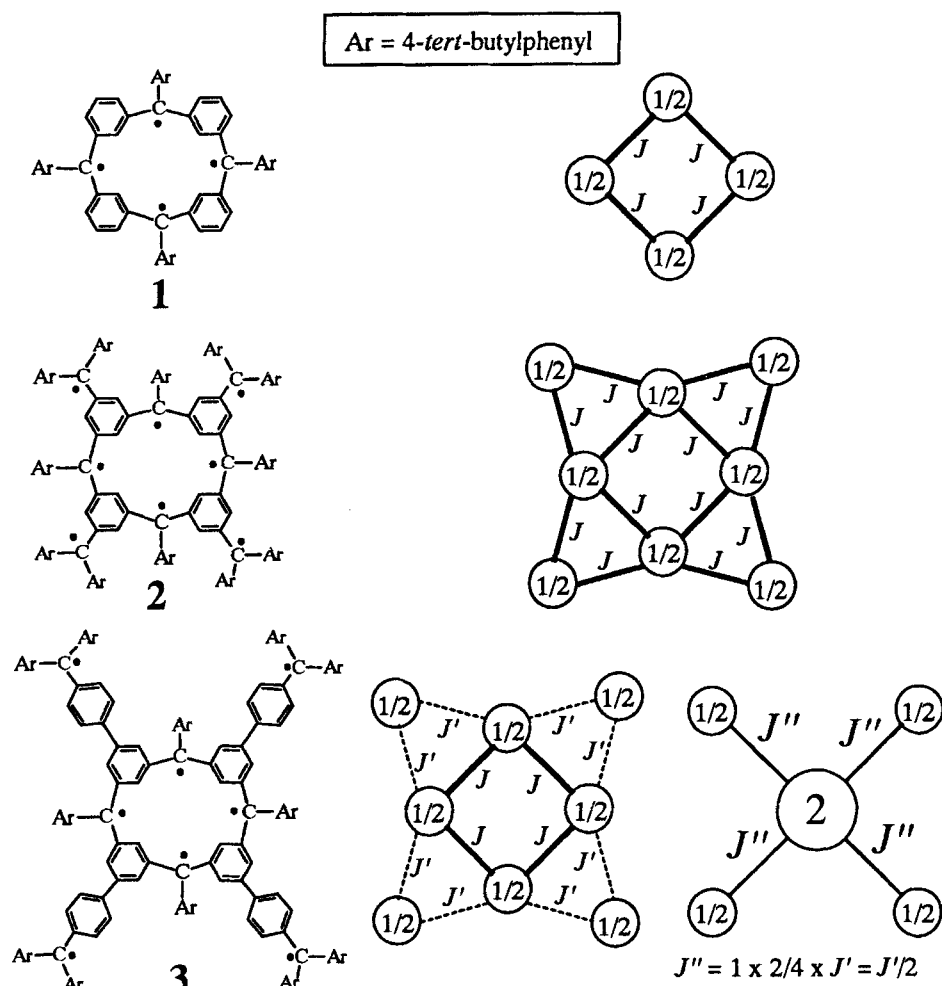Ar = 4-*tert*-butylphenyl

$J'' = 1 \times 2/4 \times J' = J'/2$

FIGURE 1. Polyradicals 1 - 3 and the corresponding spin clusters.

of calix[4]arene ring.[13] This modular approach to synthesis may allow for the straightforward extension to polyradicals with much greater number of spin sites than **3**.

SCALING OF J

When octaradical **3** is considered as a spin pentamer, for each pair of spins ($S = 2$ and $S = 1/2$) there are two pathways through biphenylene moiety, as opposed to a single pathway in the corresponding triradical **4** (Figures 1 and 2). Consequently, each pairwise J-coupling between $S = 2$ and $S = 1/2$ involves only 2 (out of 4) spin sites of the center $S = 2$ spin. Following, the analogous example, elucidated by Dougherty and coworkers,[9] the pairwise J-coupling in the pentamer should be scaled by a factor of $2/4 = 1/2$. Scaling of J in other high-spin polyradicals studied in our laboratory is shown in Figure 2. For polyradicals **4** and **5**, eq. 1 is exactly solvable and the corresponding clusters do not require scaling of J-coupling.

ANALYSIS OF MAGNETIC DATA

In order to minimize complications with intermolecular antiferromagnetic interactions, high-spin polyradicals are typically studied in dilute frozen solutions (matrices). Even with the best commercial SQUID magnetometers, significant magnetic fields (e.g., $H = 0.5$ Tesla) has to be applied for adequate signal-to-noise ratio. In conjunction with large values of S, significant saturation of magnetization at low temperatures is found; thus, such M vs. T data should be fit to exact equations for M as a function of H and T, without the usual $H/T \ll 1$ approximation,

$J'' = J'$

$J'' = 2/2 \times 1 \times J' = J'$

$J'' = 1/5 \times 2/2 \times J' = J'/5$

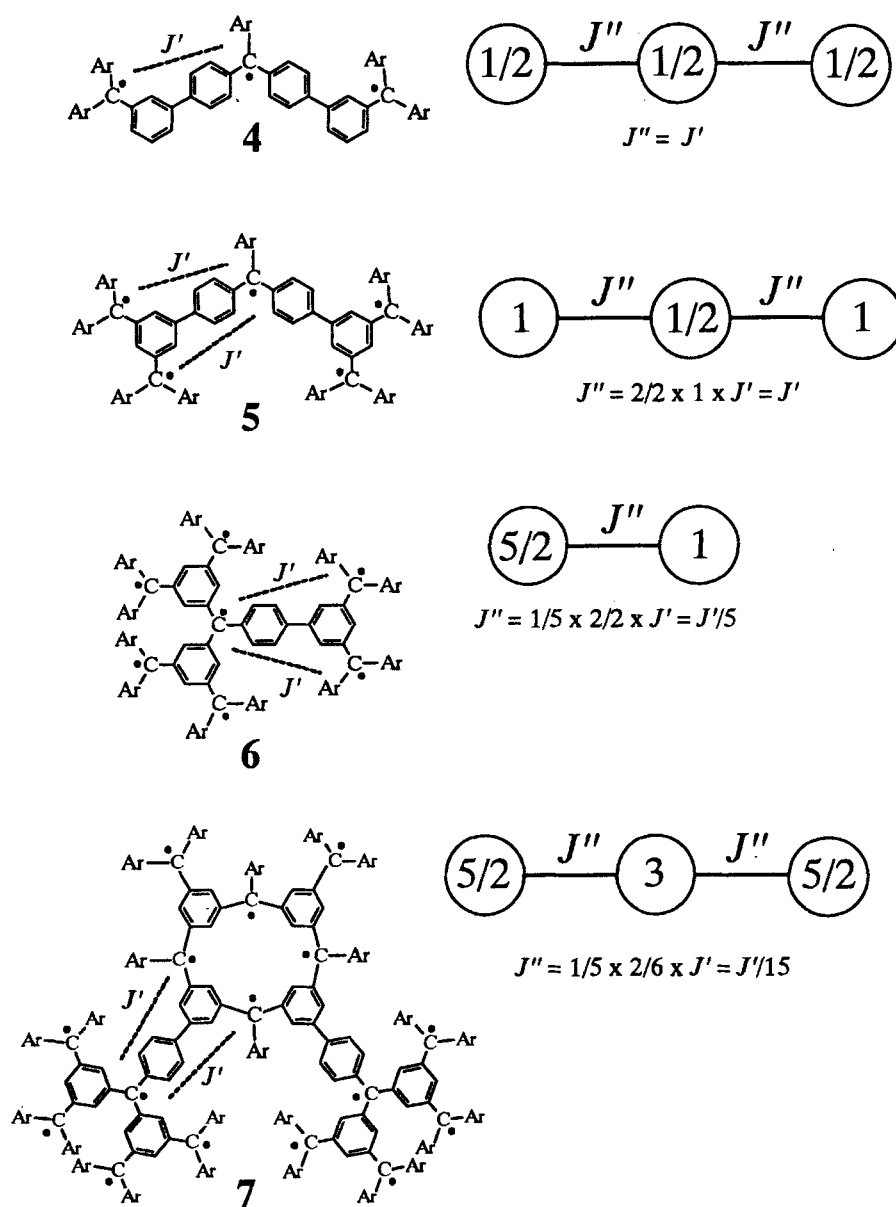$J'' = 1/5 \times 2/6 \times J' = J'/15$

FIGURE 2.   Polyradicals **4 - 7** and the corresponding spin clusters.

in order to adequately reflect the downward curvature in the MT vs. T plots at low temperatures.   One of the approaches for derivation of such equations, $M(H,T)$, is briefly reviewed below.

Eigenvalues, which are elucidated using exact vector decoupling technique applied to eq. 1 for each spin cluster,[10] are shown in Table 1.

TABLE 1.   Eigenvalues for spin clusters **3 - 7** described by Heisenberg Hamiltonian (eq. 1).   For each cluster total spin (S_t) and the corresponding energies (E) in the units of J/k are listed.

3		**4**		**5**		**6**		**7**	
S_t	E	S_t	E	S_t	E	S_t	E	S_t	E
4	0	3/2	0	5/2	0	7/2	0	8	0
3	8,4,4,4	1/2	1	3/2	1	5/2	7	7	16,6
2	14,10,10,	1/2	3	1/2	2	3/2	12	6	30,20,12
	10,8,8			1/2	4			5	42,32,24,18
1	18,14,14,14			3/2	5			4	52,42,34,28,24
0	20							3	60,50,42,
									36,32,30
								2	66,56,48,42,38
								1	60,52,46
								0	54

Starting with partition function (Z), $M(H,T)$ is obtained, based on eq. 2.[6]

$$M = NkT(\delta \ln Z/\delta H)_T \qquad (2)$$

An expedient way to write down an equation for $M(H,T)$ for each spin cluster is as follows:

1) in the nominator, each i-th eigenvalue with energy $b_i J$ (in units of temperature) and total spin S_i corresponds to term $[\exp(-b_i J/T)][1^*\sinh(1^*a) + 2^*\sinh(2^*a) + ... + S_i^*\sinh(S_i^*a)]$ for integer S_i or an analogous sum starting with $0.5^*\sinh(0.5^*a)$ replacing $1^*\sinh(1^*a)$ for half-integer S_i; "a" is defined as $1.345014^*H/(T - K)$, where H is in Tesla and K is a mean field parameter to account for small intermolecular interactions; all such terms are added over all eigenvalues,

2) in the denominator, each i-th eigenvalue with energy $b_i J$ and total spin S_i corresponds to analogous term as the nominator, except for sum of $S_i^*\sinh(S_i^*a)$ is replaced with sum of $2^*\cosh(S_i^*a)$; all such terms are added over all eigenvalues.

$M(H,T)$, as a short program for fitting MT vs. T data, for cluster 7 is shown in the appendix; J, N, K, B are variable or fixed parameters corresponding to J/k, number of moles x 10^4, mean-field parameter for residual intermolecular interactions, correction for diamagnetism (if needed), respectively.

CONCLUSION

Design of high-spin organic polyradicals as symmetrical spin clusters should facilitate their synthesis and lead to an improvement in analysis of their magnetic data.

REFERENCES

1. A. Rajca, Chem. Rev., 94, 871 (1994).

2. D. A. Dougherty, Acc. Chem. Res., 24, 88 (1991).

3. H. Iwamura, Adv. Phys. Org. Chem., 26, 179 (1990).

4. N. Nakamura, K. Inoue, H. Iwamura, Angew. Chem., 105, 900 (1993).

5. A. Rajca, S. Utamapanya, J. Am.Chem. Soc., 115, 10688 (1993).

6. R. L. Carlin, Magnetochemistry, Springer-Verlag, 1986.

7. K. Itoh, Pure & Appl. Chem., 50, 1251 (1978).

8. H. Iwamura, N. Koga, Acc. Chem. Res., 26, 346 (1993).

9. S. J. Jacobs, D. A. Schultz, R. Jain, J. Novak, D. A. Dougherty, J. Am. Chem. Soc., 115, 1744 (1993).

10. E. Belorizky, P. H. Fries, J. Chim. Phys., 90, 1077 (1993).

11. A. Rajca, S. Rajca, S. R. Desai, J. Am.Chem. Soc., 117, 806 (1995).

12. A. Rajca, S. Rajca, R. Padmakumar, Angew. Chem., 106, 2193 (1994).

13. N. Miayura, A. Suzuki, Chem. Rev., 95, 2457 (1995).

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APPENDIX

Program, compatible with SigmaPlot software, for fitting MT vs T data for cluster **7**.

[Parameters]

J=10 ; *J/k* in K

N=0.005 ; number of moles of polyradical x 10000

[Variables]

H=col(21)*0.0001 ; H in Gauss

M=col(23) ; MT in emuK

T=col(20) ; T in K

[Equations]

K=0 ; mean-field parameter for intermolecular interactions

B=0 ; correction for diamagnetism

a=(1.345014*H)/(T-K)

c1=1+(2*cosh(a))

c2=c1+(2*cosh(2*a))

c3=c2+(2*cosh(3*a))

c4=c3+(2*cosh(4*a))

c5=c4+(2*cosh(5*a))

c6=c5+(2*cosh(6*a))

c7=c6+(2*cosh(7*a))

c8=c7+(2*cosh(8*a))

s1=sinh(a)

s2=s1+(2*sinh(2*a))

s3=s2+(3*sinh(3*a))

s4=s3+(4*sinh(4*a))

s5=s4+(5*sinh(5*a))

s6=s5+(6*sinh(6*a))

s7=s6+(7*sinh(7*a))

s8=s7+(8*sinh(8*a))

e6=1/exp((6*J)/T)

e12=1/exp((12*J)/T)

e16=1/exp((16*J)/T)

e18=1/exp((18*J)/T)

e20=1/exp((20*J)/T)

e24=1/exp((24*J)/T)

e28=1/exp((28*J)/T)

e30=1/exp((30*J)/T)

e32=1/exp((32*J)/T)

e34=1/exp((34*J)/T)

e36=1/exp((36*J)/T)

e38=1/exp((38*J)/T)

e42=1/exp((42*J)/T)

e46=1/exp((46*J)/T)

e48=1/exp((48*J)/T)

e50=1/exp((50*J)/T)

e52=1/exp((52*J)/T)

e54=1/exp((54*J)/T)

e56=1/exp((56*J)/T)

e60=1/exp((60*J)/T)

e66=1/exp((66*J)/T)

d81=c8+(c7*(e16+e6))+(c6*(e30+e20+e12))+(c5*(e42+e32+e24+e18))

d82=(c4*(e52+e42+e34+e28+e24))+(c3*(e60+e50+e42+e36+e32+e30))

d83=(c2*(e66+e56+e48+e42+e38))+(c1*(e60+e52+e46))+e54

n81=s8+(s7*(e16+e6))+(s6*(e30+e20+e12))+(s5*(e42+e32+e24+e18))

n82=(s4*(e52+e42+e34+e28+e24))+(s3*(e60+e50+e42+e36+e32+e30))

n83=(s2*(e66+e56+e48+e42+e38))+(s1*(e60+e52+e46))

```
f8=(n81+n82+n83)/(d81+d82+d83)
f=((f8*1.116*N)+B)*T
fit f to M
[Constraints]
J>0
;end of program
```